Ultrafast intersystem crossing in benzene: Towards coherent control

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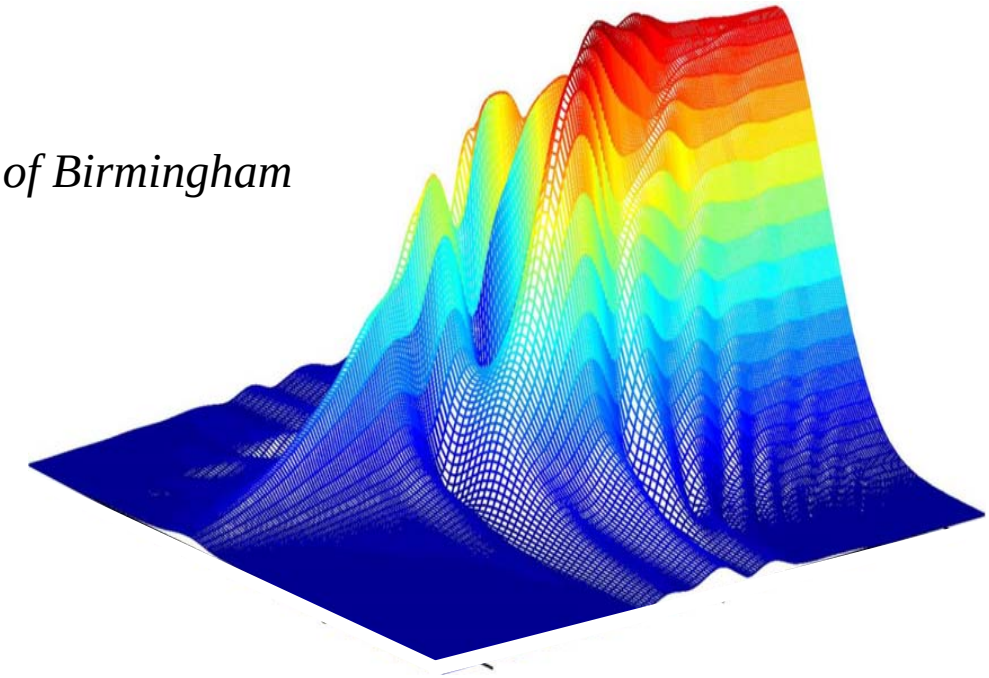
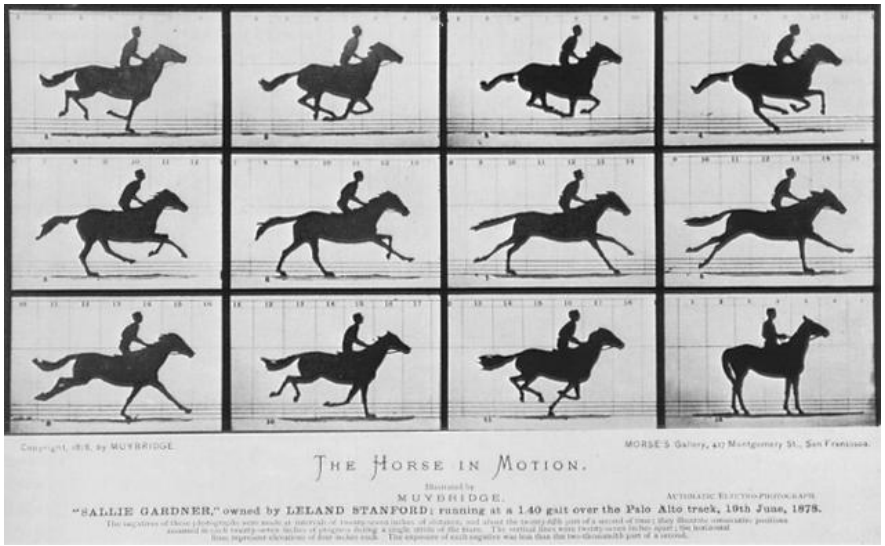


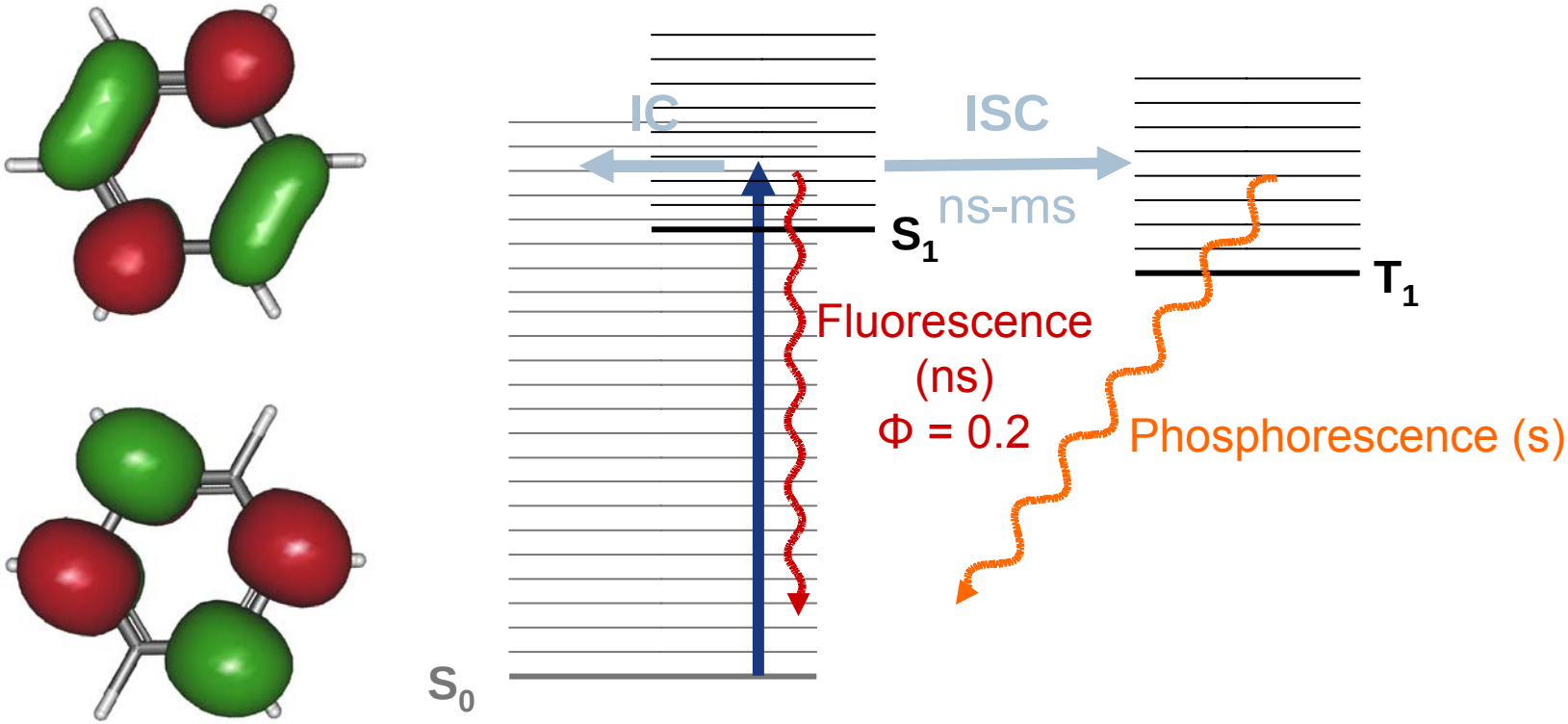
Femtosecond molecular dynamics



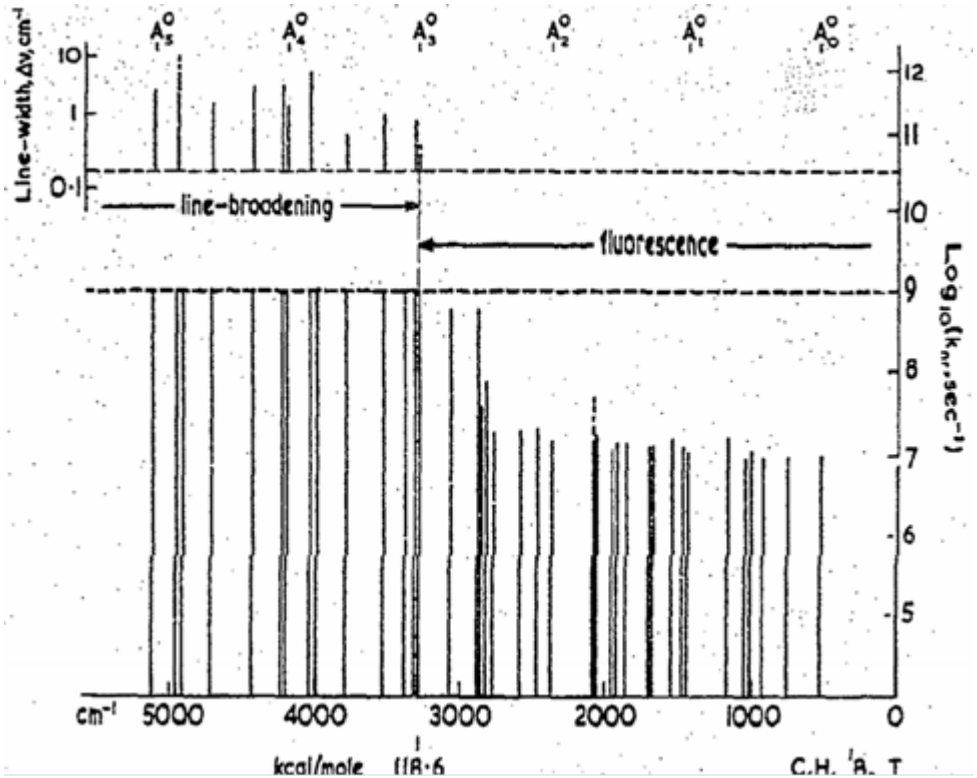
- Typical vibration period for covalent bond is ~10 fs.
- Applications of femtosecond lasers to probe dynamics on this timescale – Ahmed Zewail 1999 Chemistry Nobel Prize.
- 21st century challenge is to obtain **detailed** understanding of dynamics at level of quantum mechanics and to **control** molecular dynamics.

Ultrafast intersystem crossing in benzene

Russell Minns and Dorian Parker



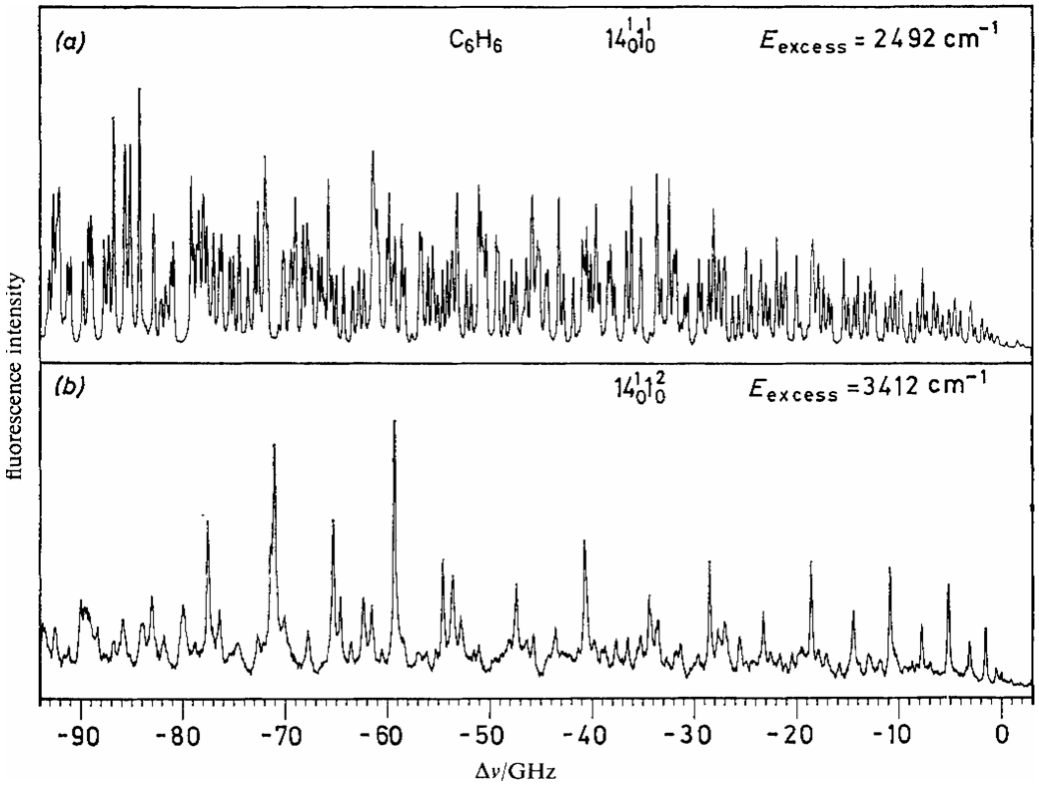
Benzene “channel 3”



non-radiative
decay rate

J.H.Callomon *et al*. Chem. Phys. Lett. **13** 125 (1972)

Benzene “channel 3”

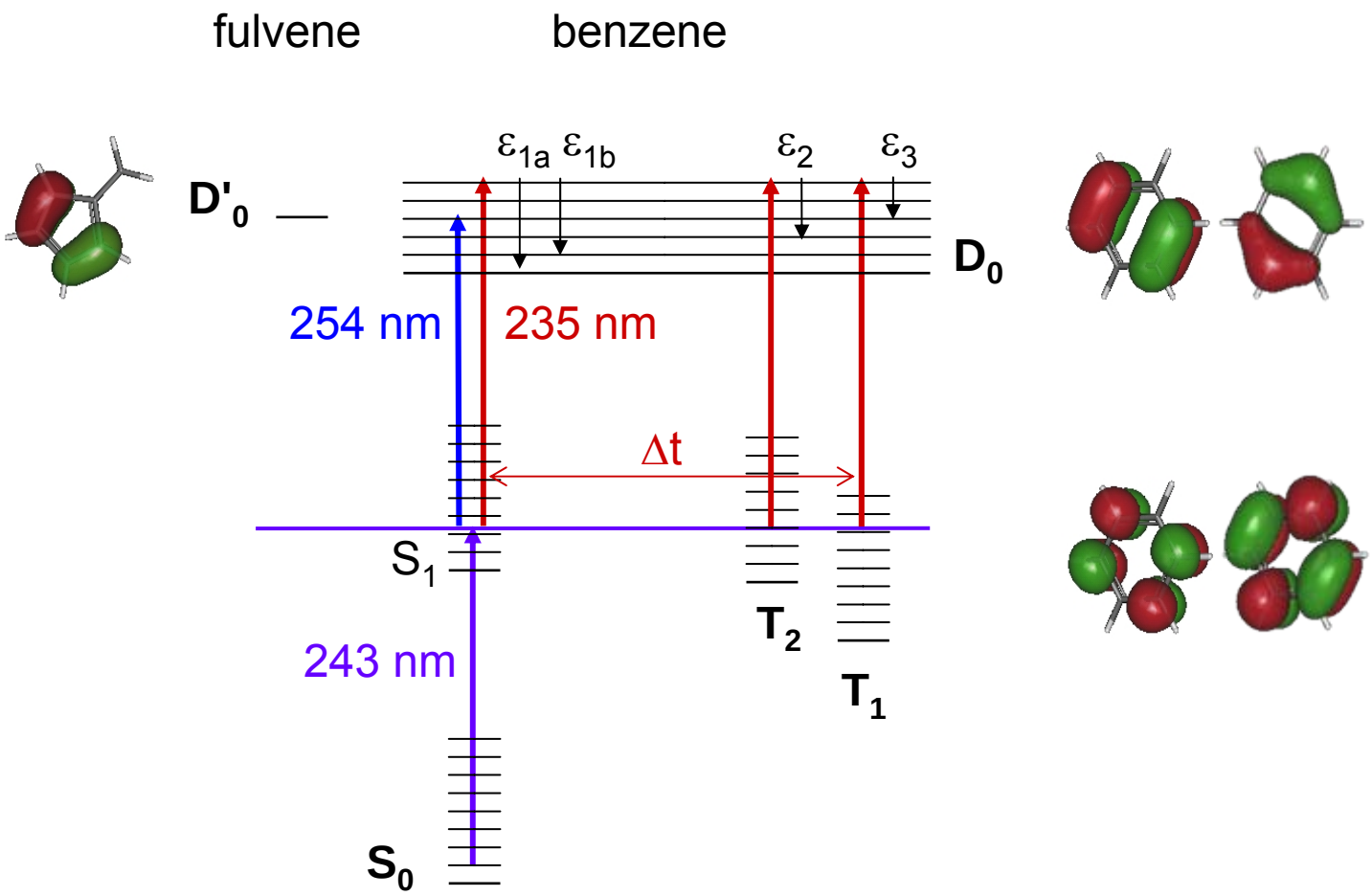


below “channel 3”

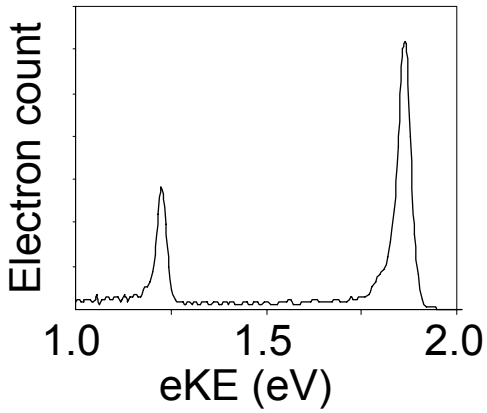
above “channel 3”

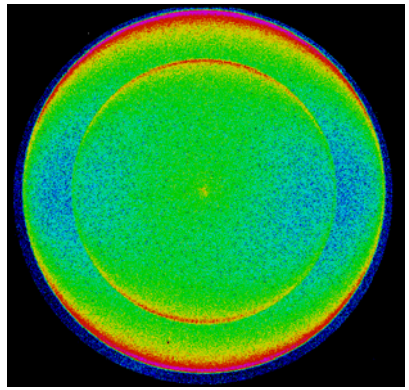
E. Riedle et al. Faraday. Discuss. Chem. Soc. **75**, 387. (1983)

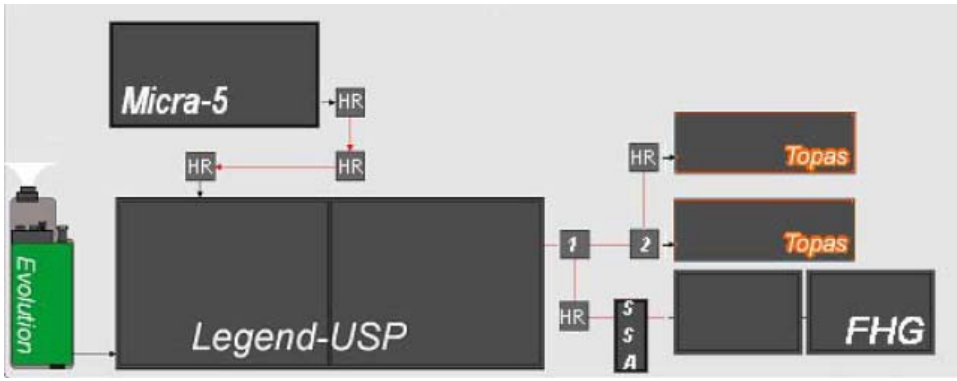
Experiment

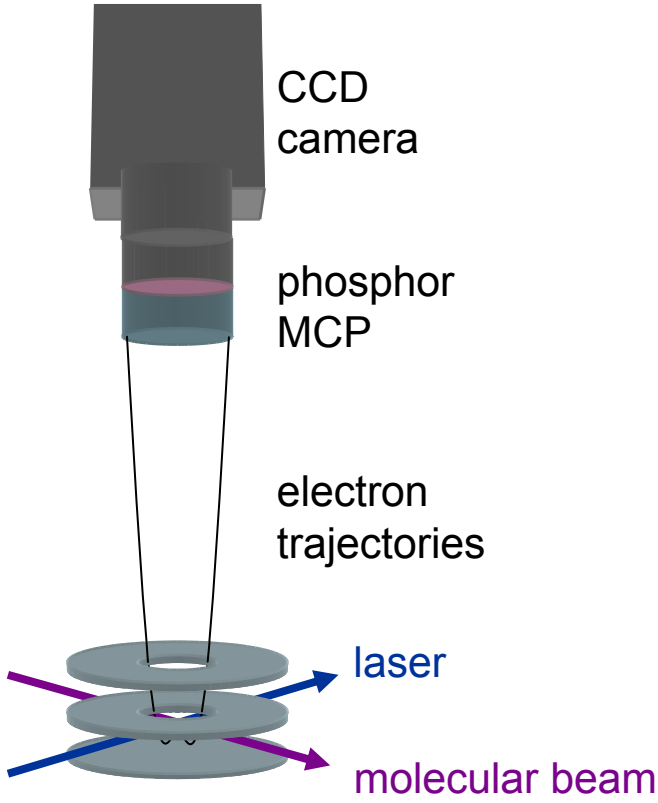

fulvene
benzene
ε_{1a} ε_{1b}
ε_2
ε_3
D'0
D0
254 nm
235 nm
Δt
S1
T2
T1
243 nm
S0

Time-resolved photoelectron imaging



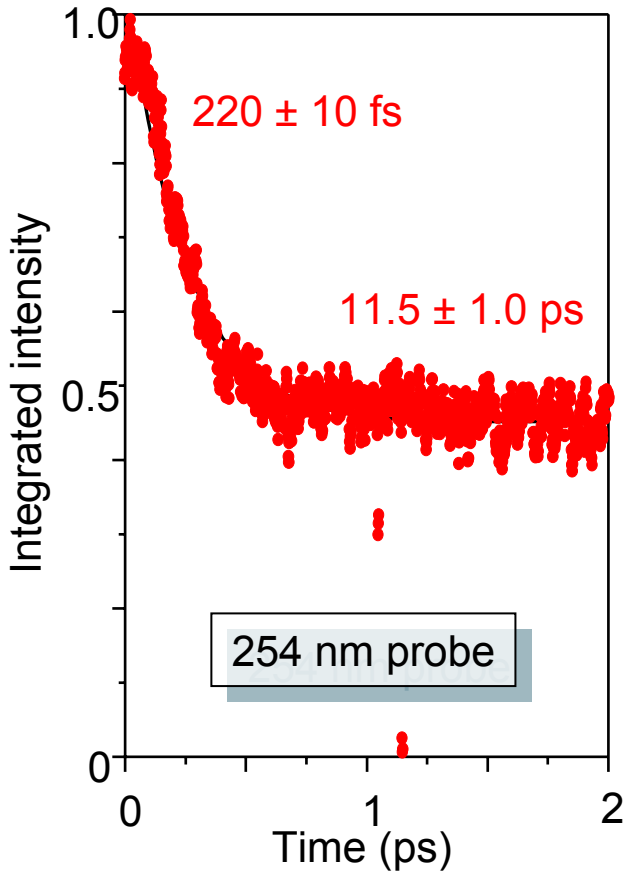


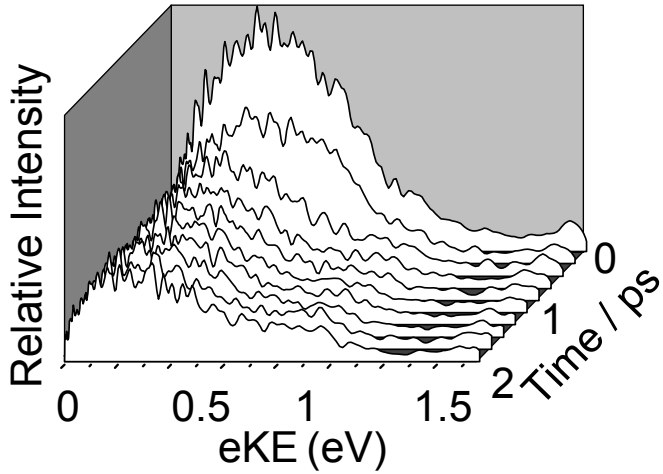


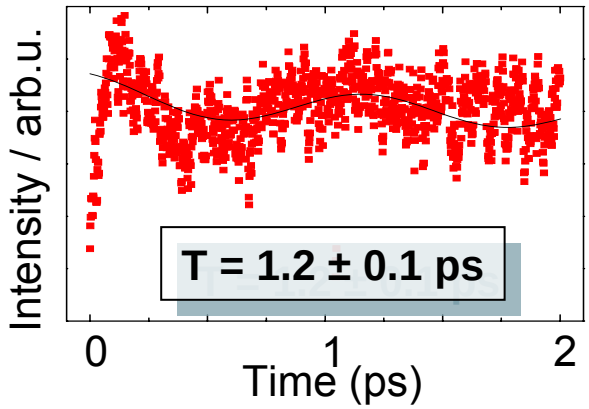


Eppink and Parker, Rev. Sci. Instrum. **68** 3477 (1997)

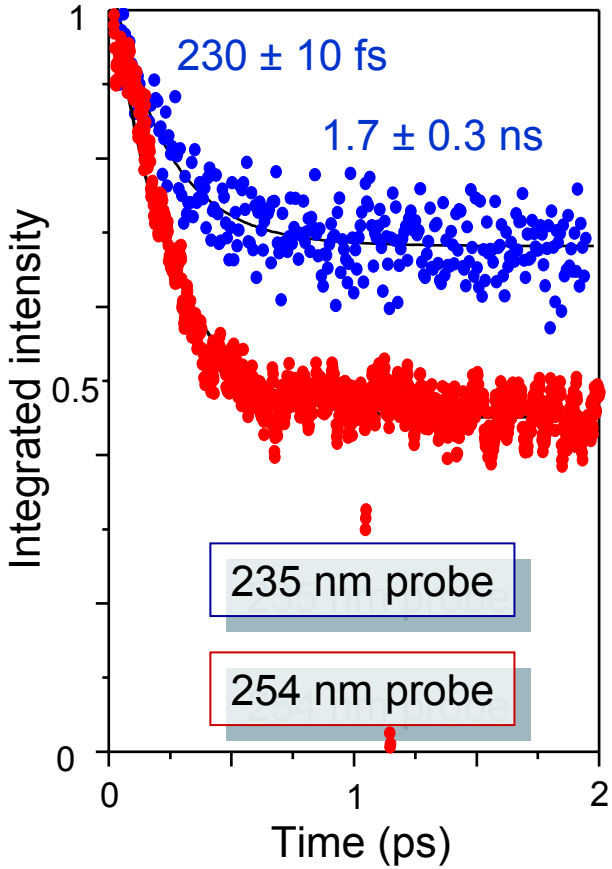
Benzene S_1 decay dynamics



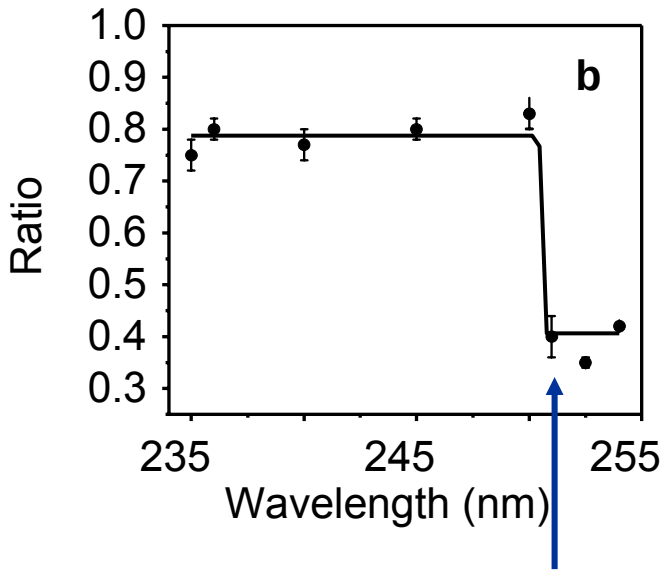




Benzene S_1 decay dynamics

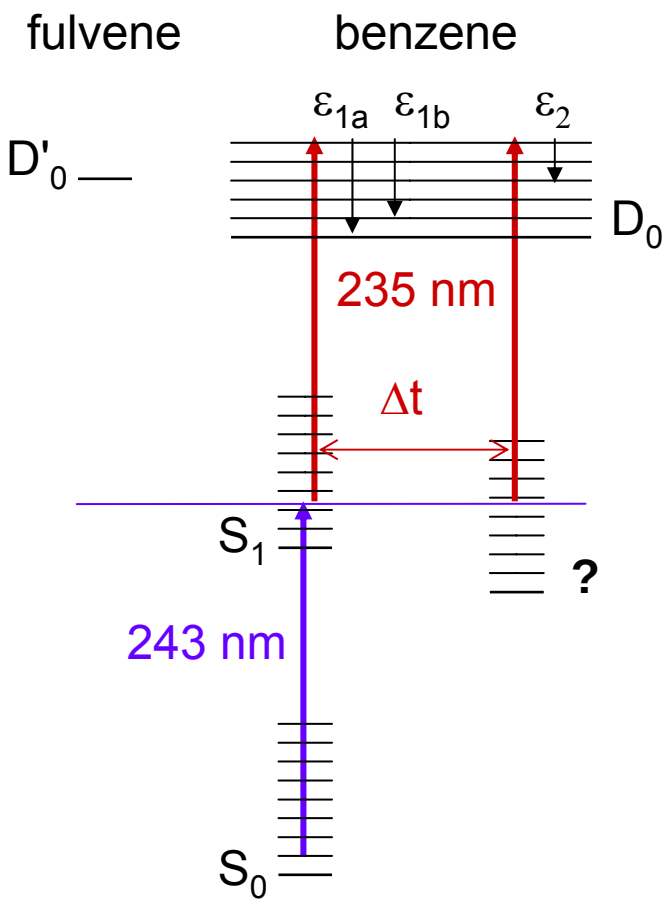


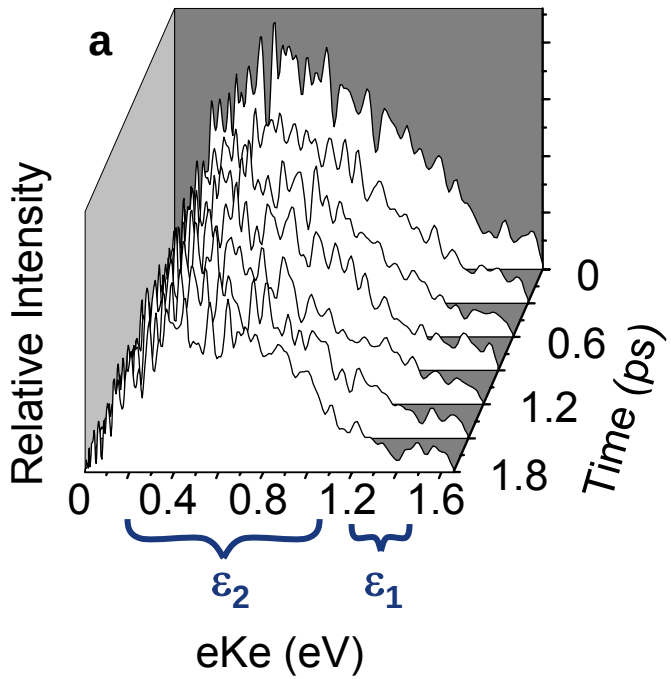
Slow decay / fast decay



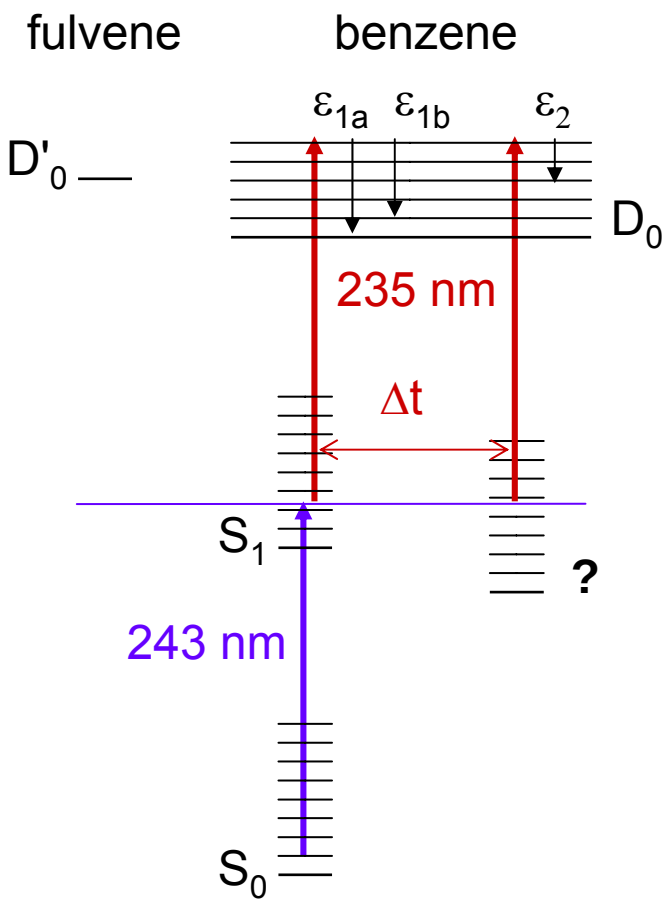
new ionisation pathway suggests change in electronic character

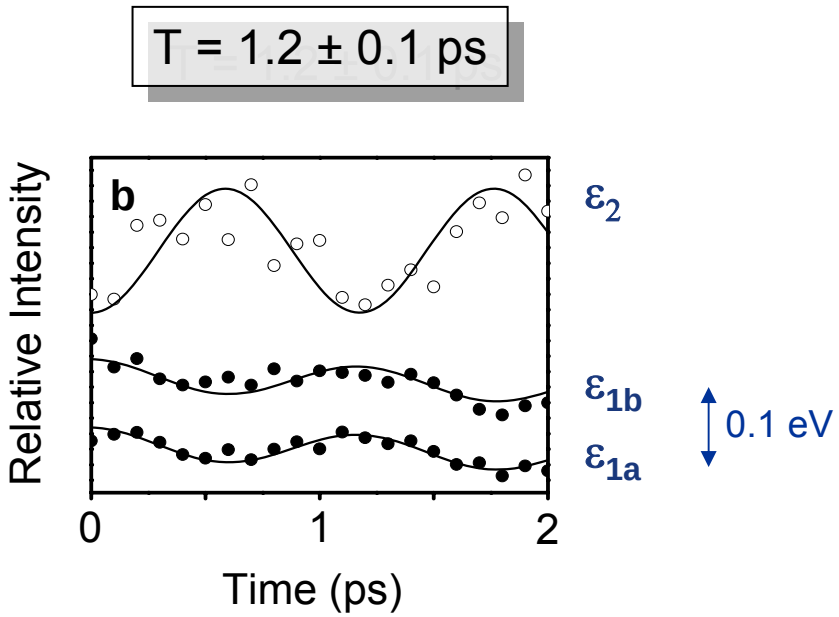
Photoelectron images



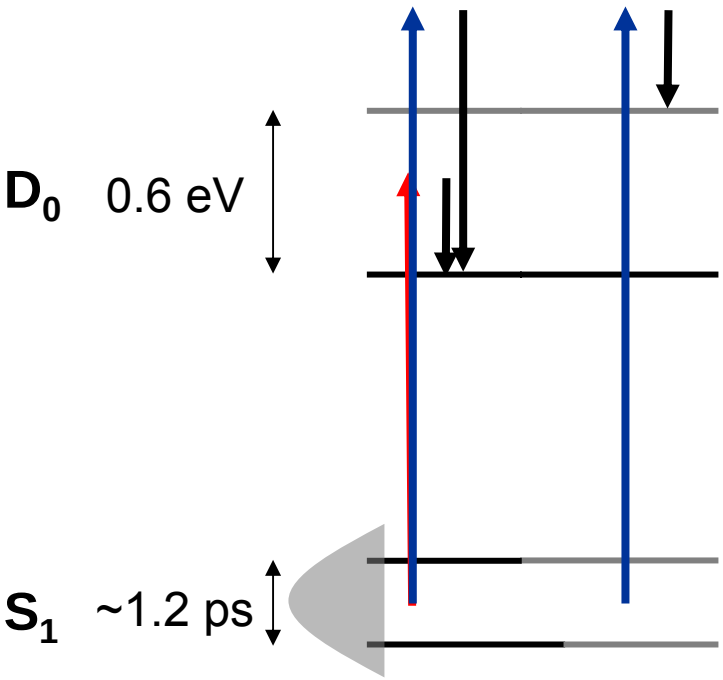


Wave packet motion





Wave packet motion



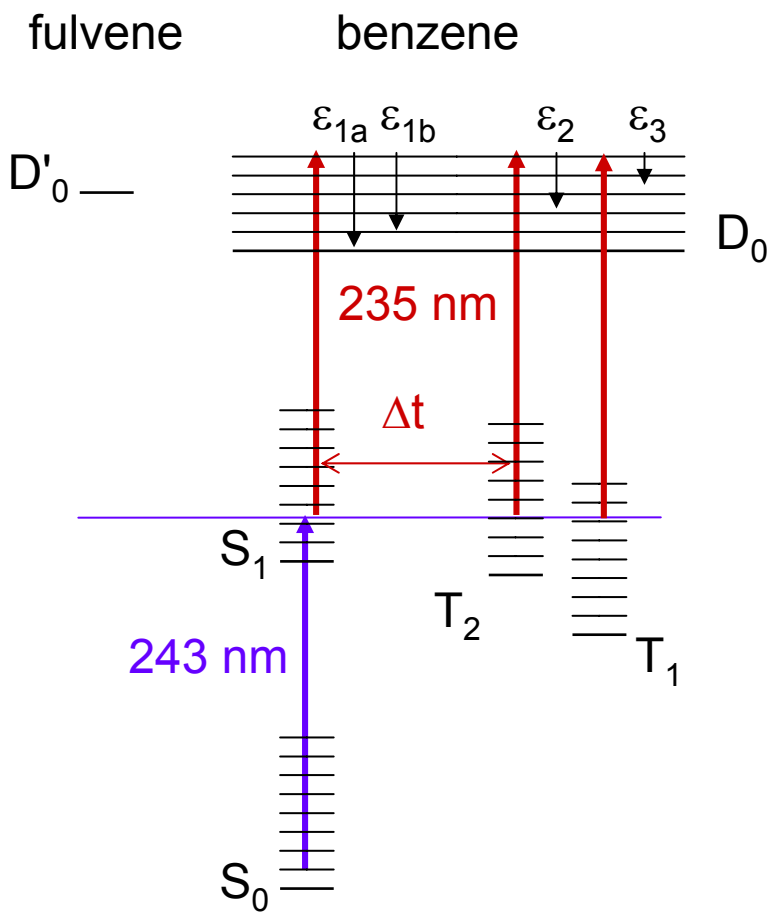
High energy energy probe (235 nm)

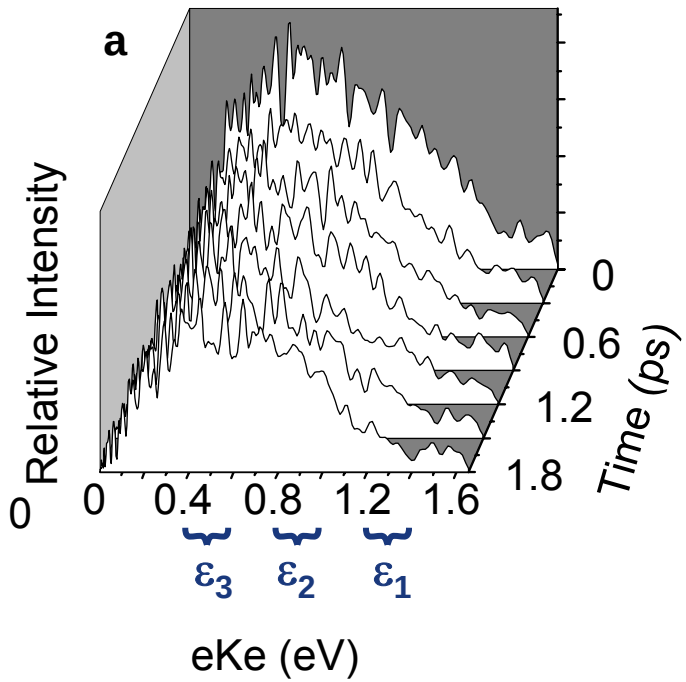
Low energy probe (254 nm)

$$\Psi_2 = a_2|bright\rangle + b_2|dark\rangle$$

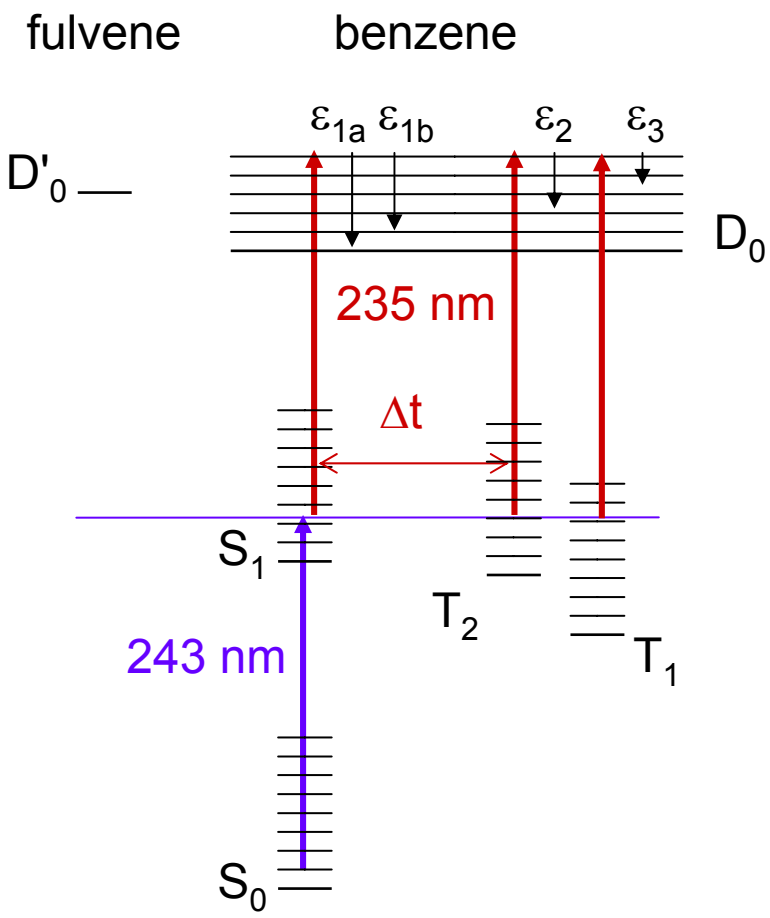
$$\Psi_1 = a_1|bright\rangle + b_1|dark\rangle$$

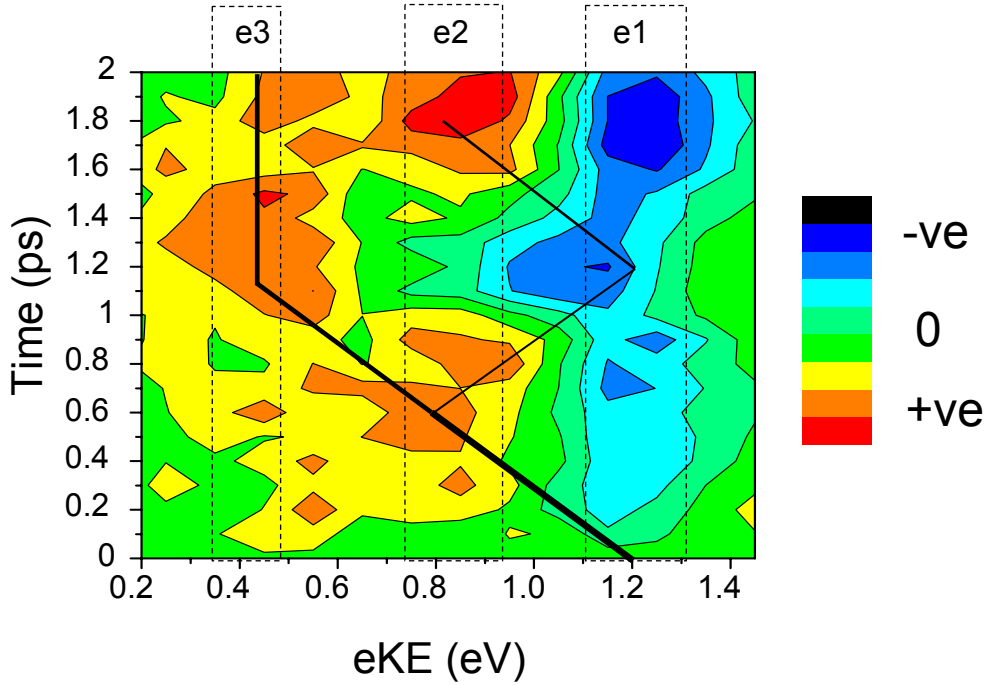
Photoelectron images



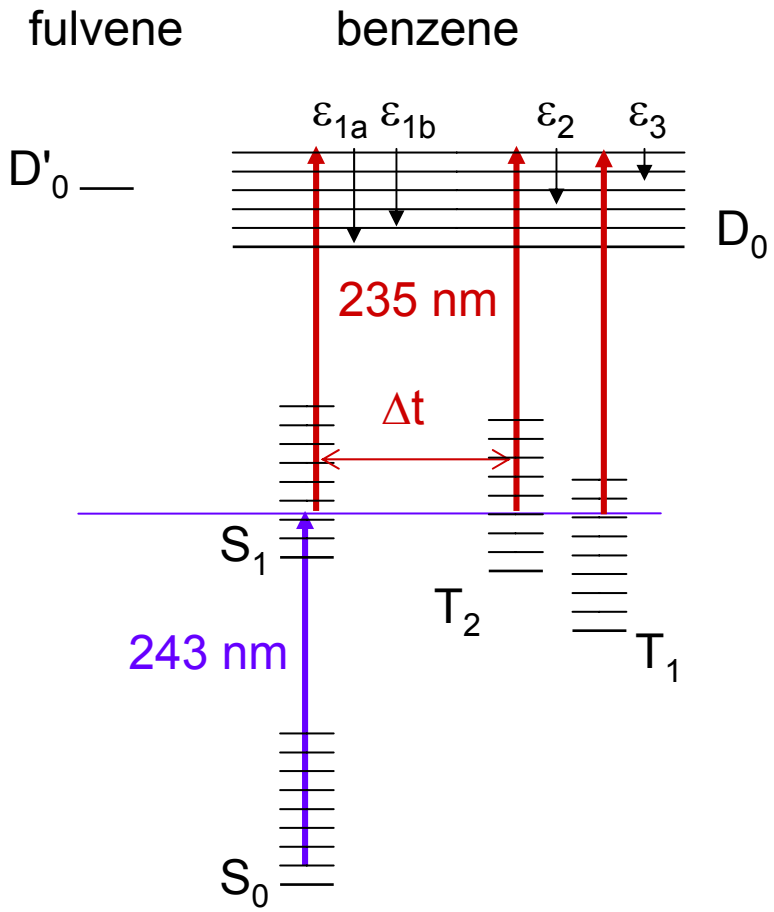


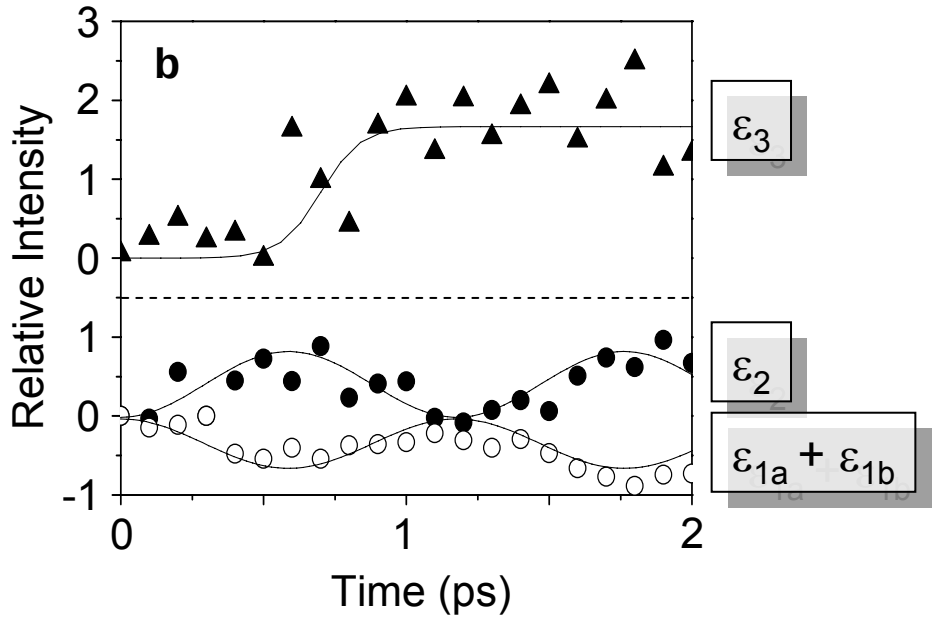
Doorway state





Doorway state

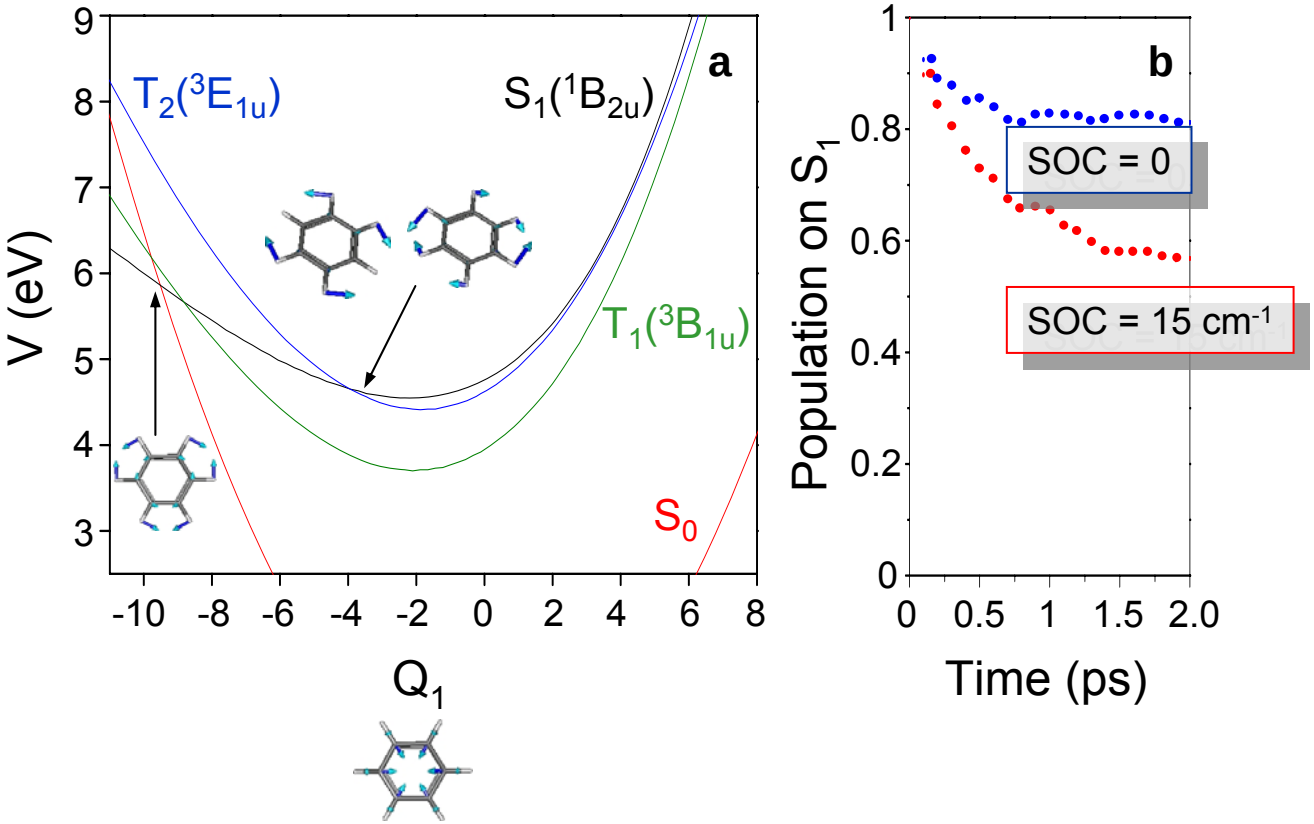




To be submitted to J. Chem. Phys.

Quantum dynamics simulations

Tom Penfold and Graham Worth, Birmingham



Spin-orbit coupling

S_1/T_1 = 1.5 cm^{-1}

S_1/T_2 = 0

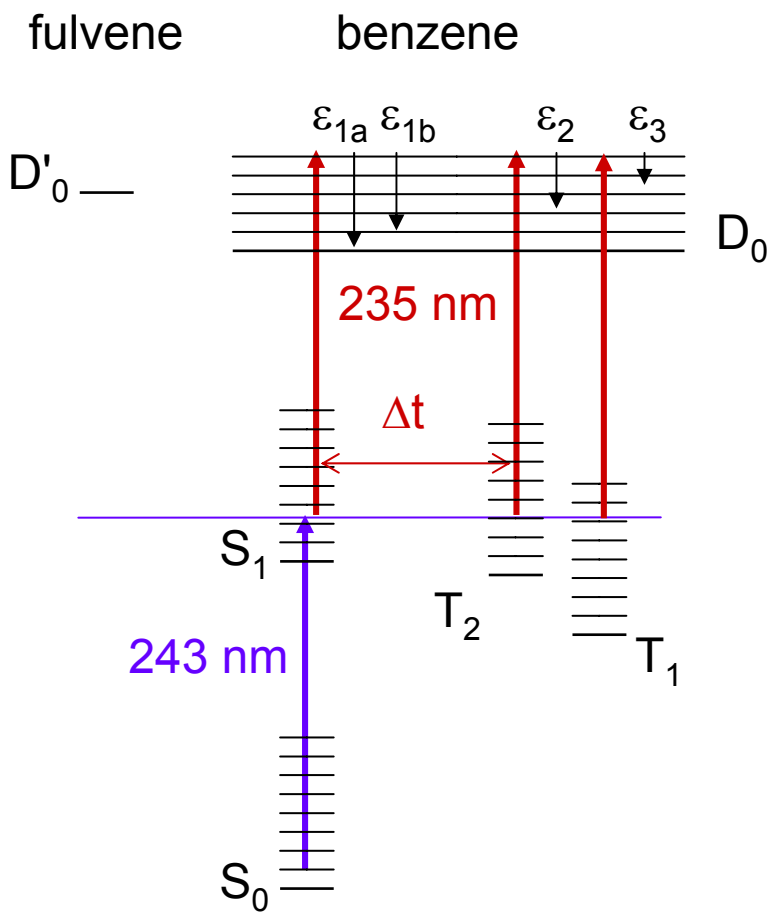
Rises along e_{2g} modes due to T_2/T_1 mixing

Significant gradient along prefulvene mode

MOLPRO program at CASPT2 level

Heidelberg MCTDH package

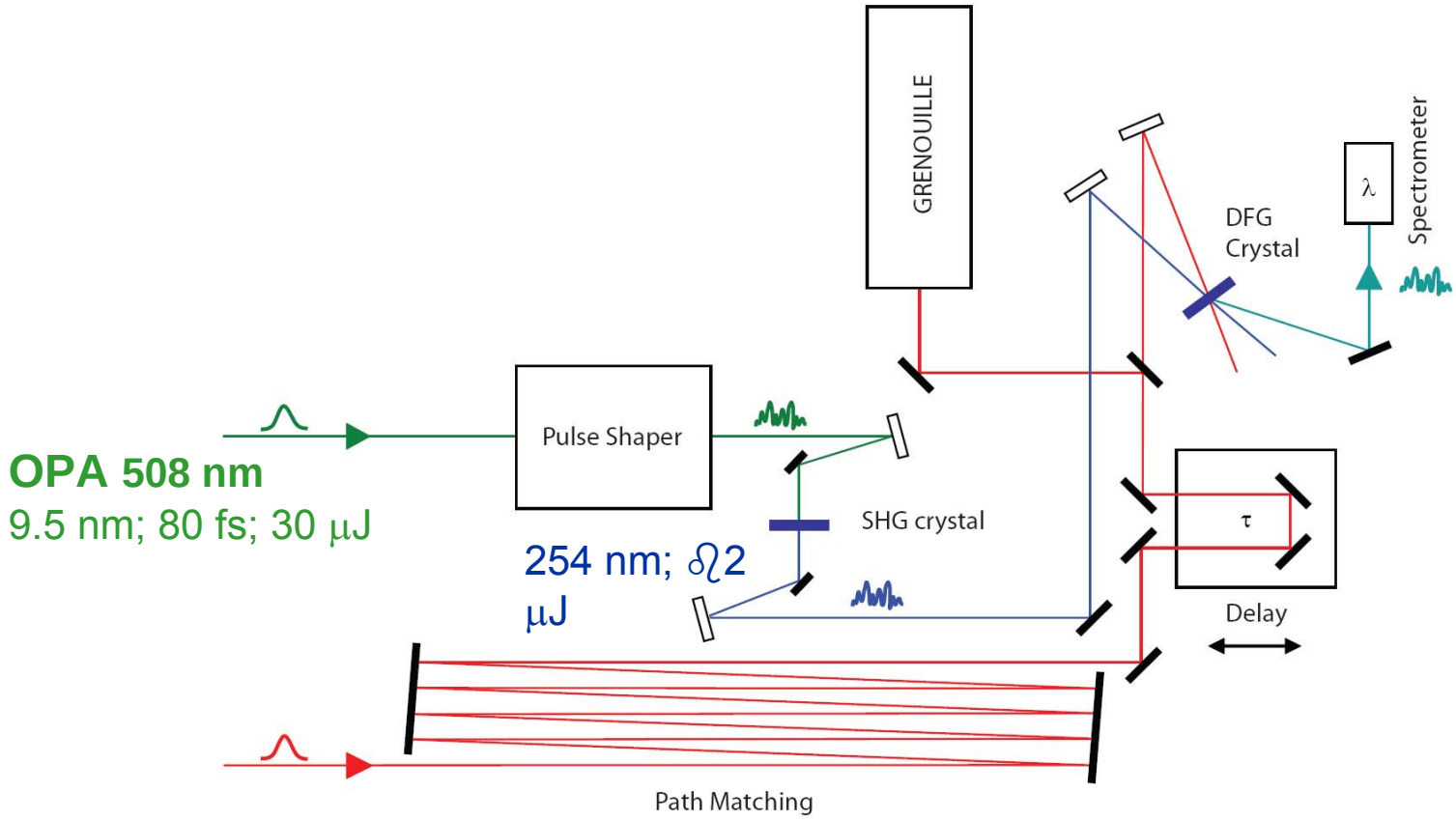
Coherent control



- Exploit the simple oscillation and use pulse sequences to control the composition of the wave packet
- Use shaped wave packets to manipulate the lifetime
- What is the route to the fulvene isomer?

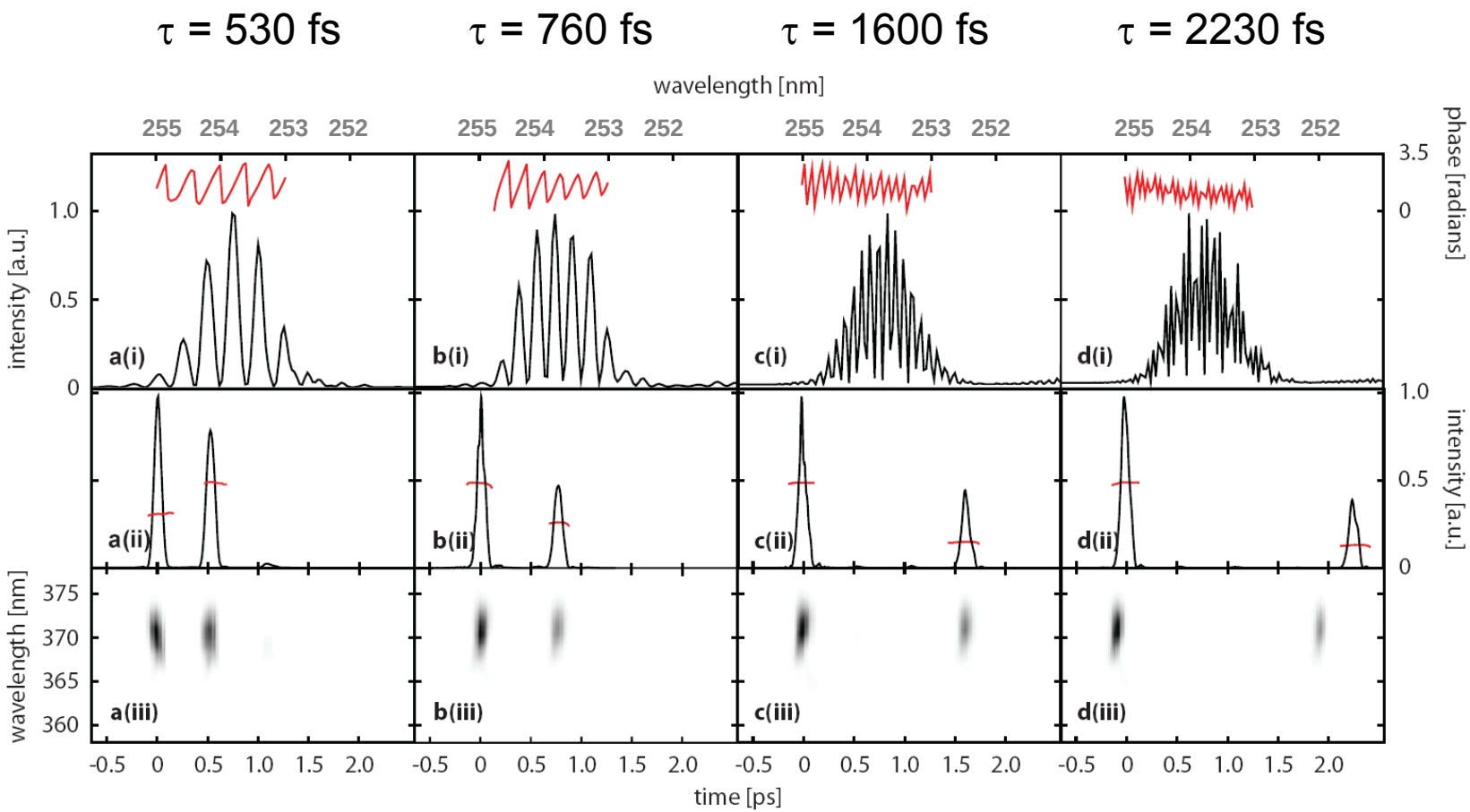
Pulse shaping in the UV

Dorian Parker, Abigail Nunn and Russell Minns



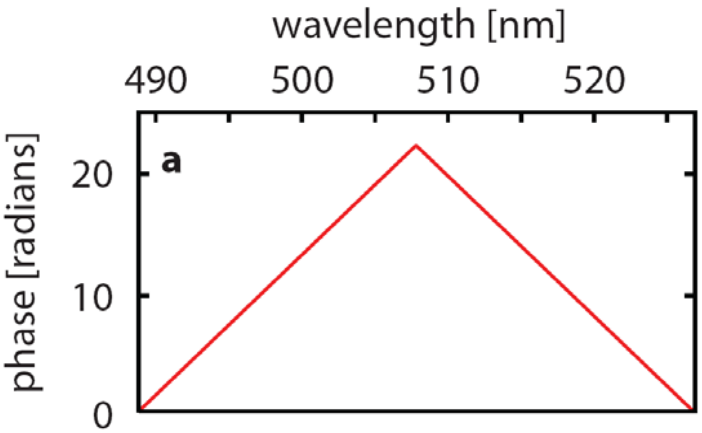
Sauerbrey et al. Appl. Phys. B **73** 272 (2001): Shaped 400 nm light using type I SHG

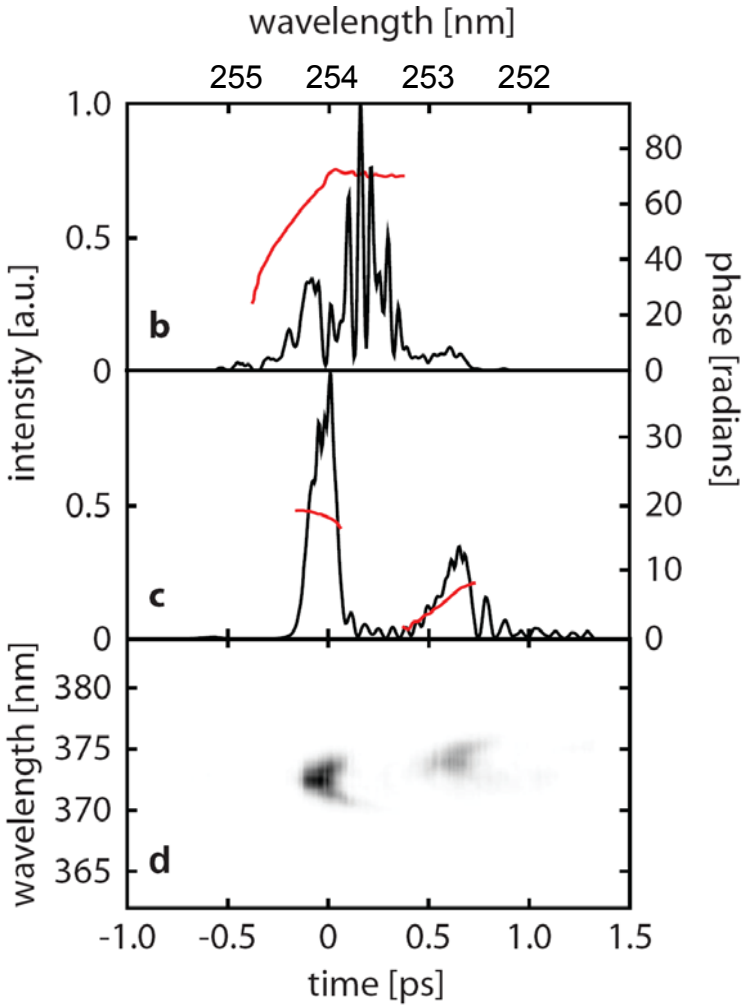
Pairs of pulses at 254 nm



Submitted to Appl. Phys. B

Pair of pulses at 253.6 and 254.6 nm (τ = 650 fs)





Summary and outlook

- Observation of ultrafast ISC in a hydrocarbon, which is without precedent.
  - Singlet-triplet coupling usually weak.
- Increase the energy of the probe photon in TRPES experiments to access the entire reaction coordinate.
- Coherent control (pulse sequences and shaping)
  - Control ISC
  - Detect the fulvene isomer and improve its yield

Acknowledgements

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Beatrice Chatel

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