Durham University

IN SILICO PHOTOCHEMISTRY GROUP

In silico determination of photolysis properties for atmospheric volatile organic compounds

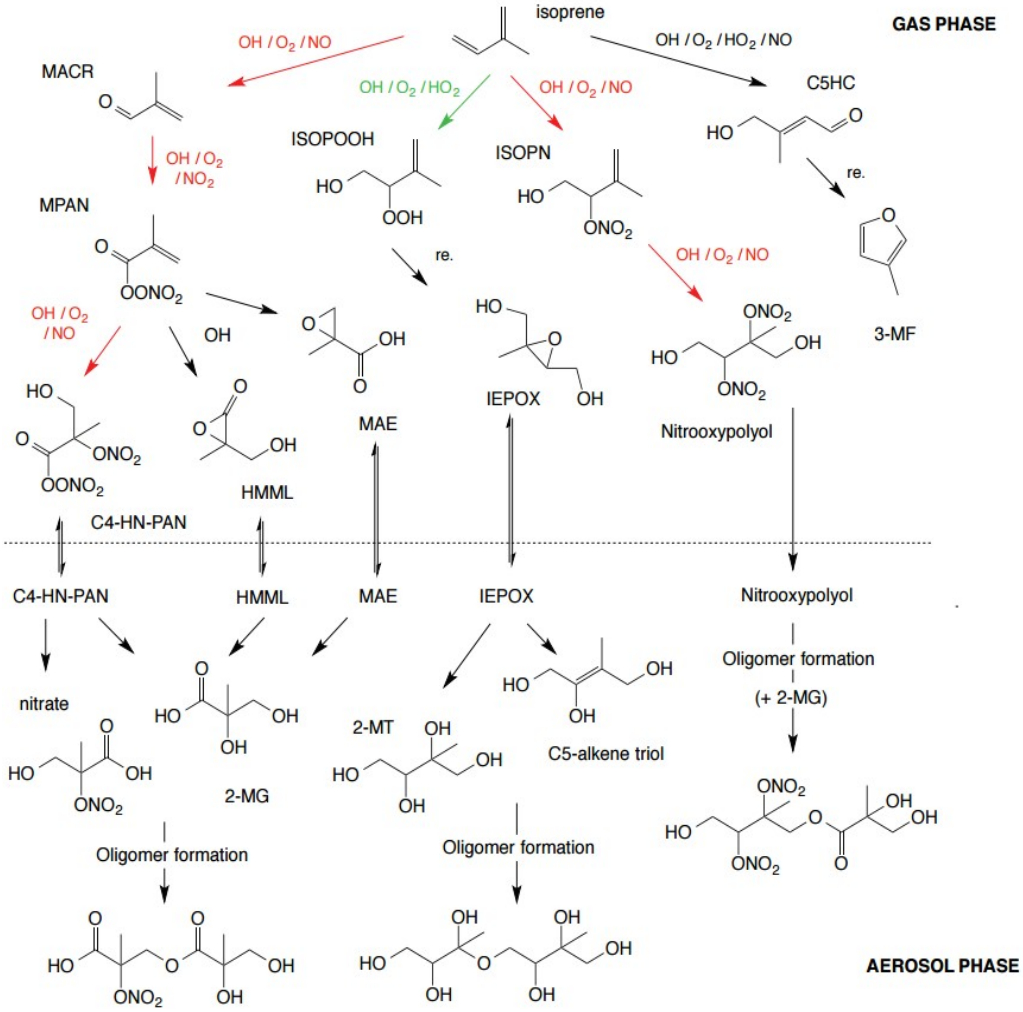
Antonio Prlj

March 17, 2021

VISTA

Volatile Organic Compounds (VOC)

- Contribute to air polution and atmospheric heat balance
- Short lifetime, leading to a complex network of chemical reactions in the troposphere
- Coupled kinetic networks of thousands of chemical reactions, *e.g.* Master Chemical Mechanism
- Many data are missing, while experiments are challenging to conduct *e.g.* photolysis rate constants
- Urgent need to develop reliable "i*n silico*" atmospheric chemistry protocols



Environ. Sci. Technol. 2007, **41**, 1514-1521

Photolysis Rate Constant

$$A + h\nu \rightarrow \text{products}$$

$$J = \int \Phi(\lambda)\ \sigma(\lambda)\ F(\lambda)\, d\lambda$$

Wavelength dependent quantum yield

Absorption cross section

Actinic flux *i.e.* solar irradiance

Photolysis Rate Constant

$$A + h\nu \rightarrow \text{products}$$

$$J = \int \Phi(\lambda)\ \sigma(\lambda)\ F(\lambda)\, d\lambda$$

Wavelength dependent quantum yield

Absorption cross section

Actinic flux *i.e.* solar irradiance

Calculate ***ab initio***

Peroxide as a Test Case

M. Baasandorj e*t al. Phys. Chem. Chem. Phys.,* 2010, **12**, 12101-12111.

$$(CH_3)_3COOH + h\nu \rightarrow OH + (CH_3)_3CO^{\bullet}$$

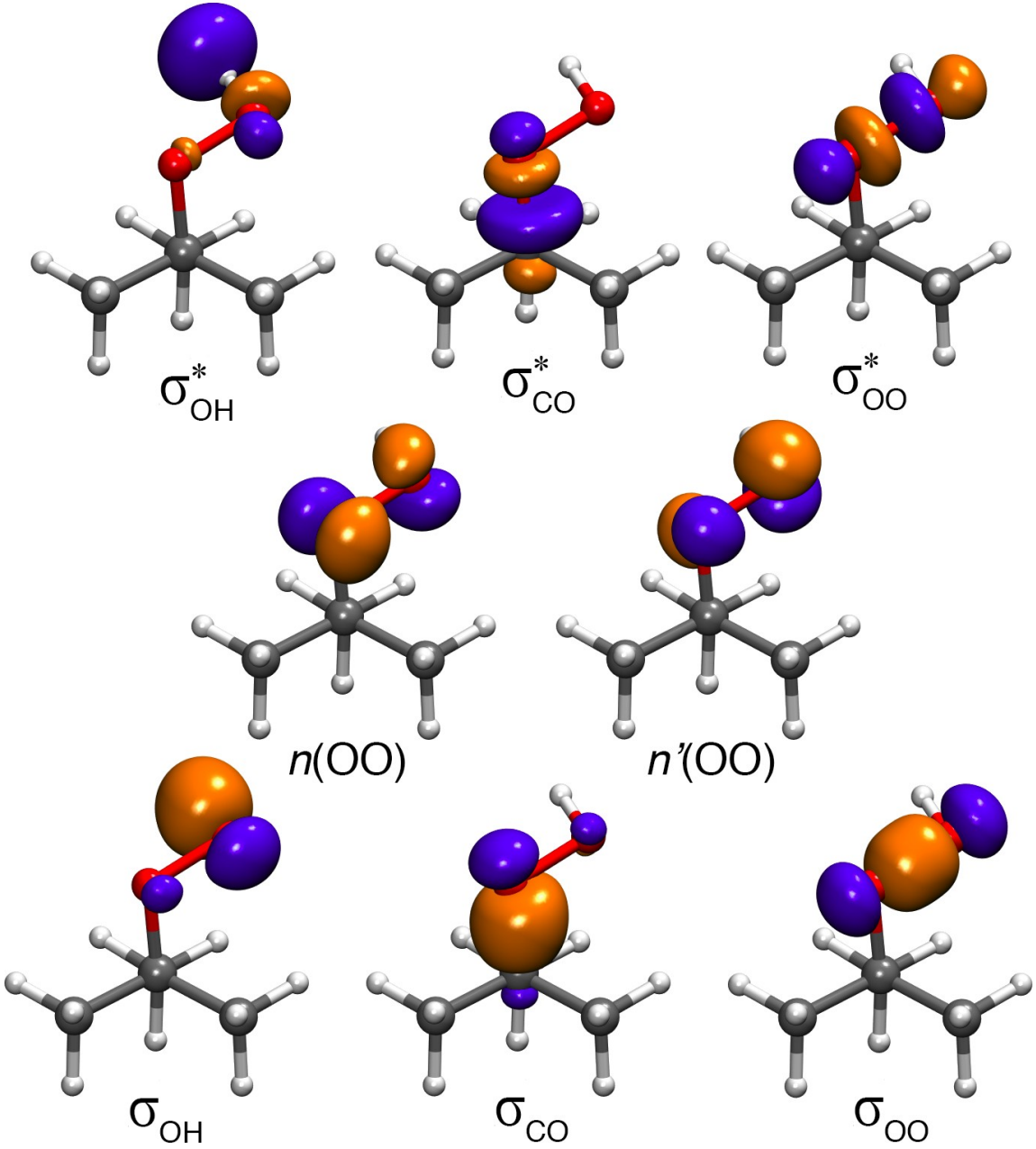
$$\rightarrow H + (CH_3)_3COO^{\bullet}$$

$$\rightarrow HO_2 + (CH_3)_3C^{\bullet}$$

- Tert-butyl peroxide is relatively stable compared to other peroxides / VOCs
- experimentally available absorption cross section & quantum yield
- Near unity OH quantum yield measured at 248 nm, Φ = 1.04 ± 0.07

Which Electronic Structure?

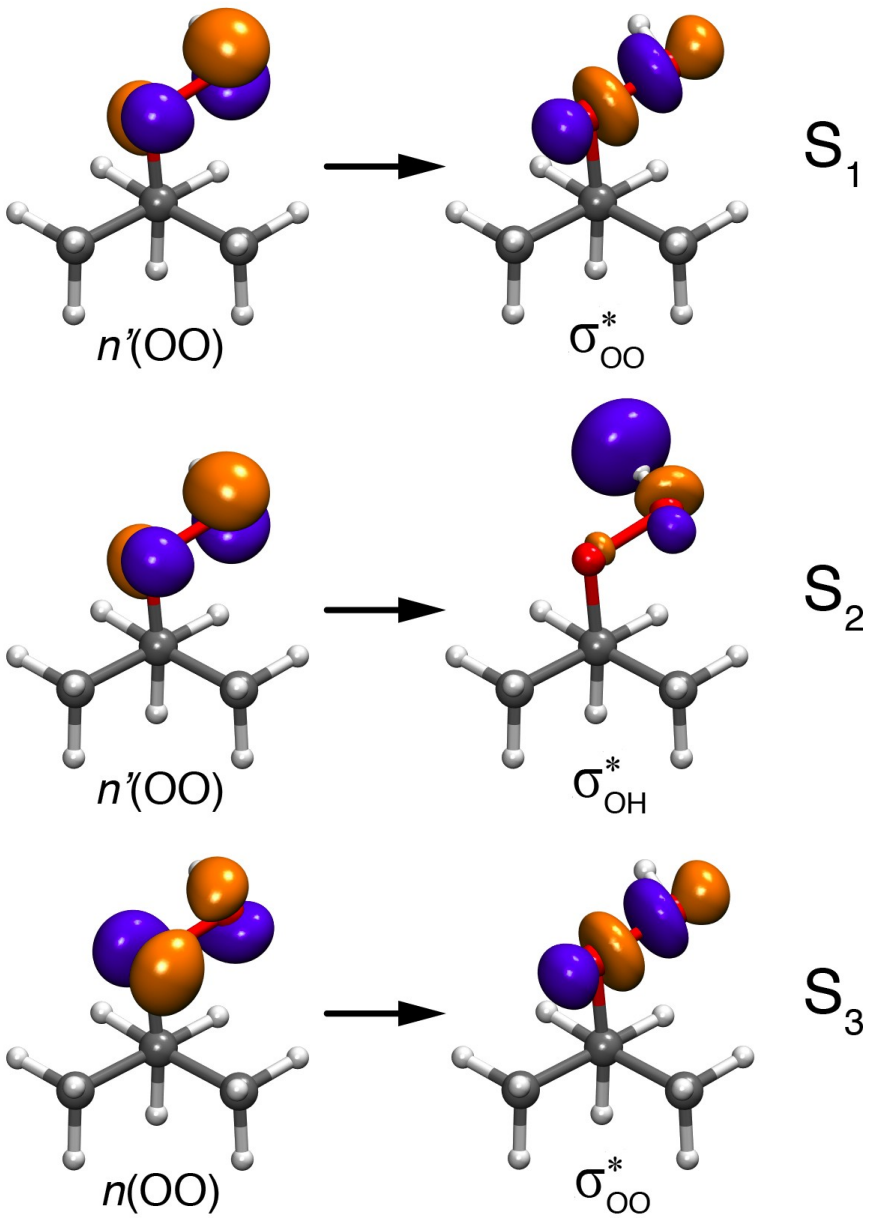
Electronic Wavefunction



- **XMS-CASPT2(10,8)/ def2-SVPD** based on SA4-CASSCF(10,8)/ def2-SVPD orbitals
- Validation along “dissociation” coordinates – single reference methods not adequate!
- Diffuse excited state character

A. Prlj, L. M. Ibele, E. Marsili & B. F. E. Curchod *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.

Excited States

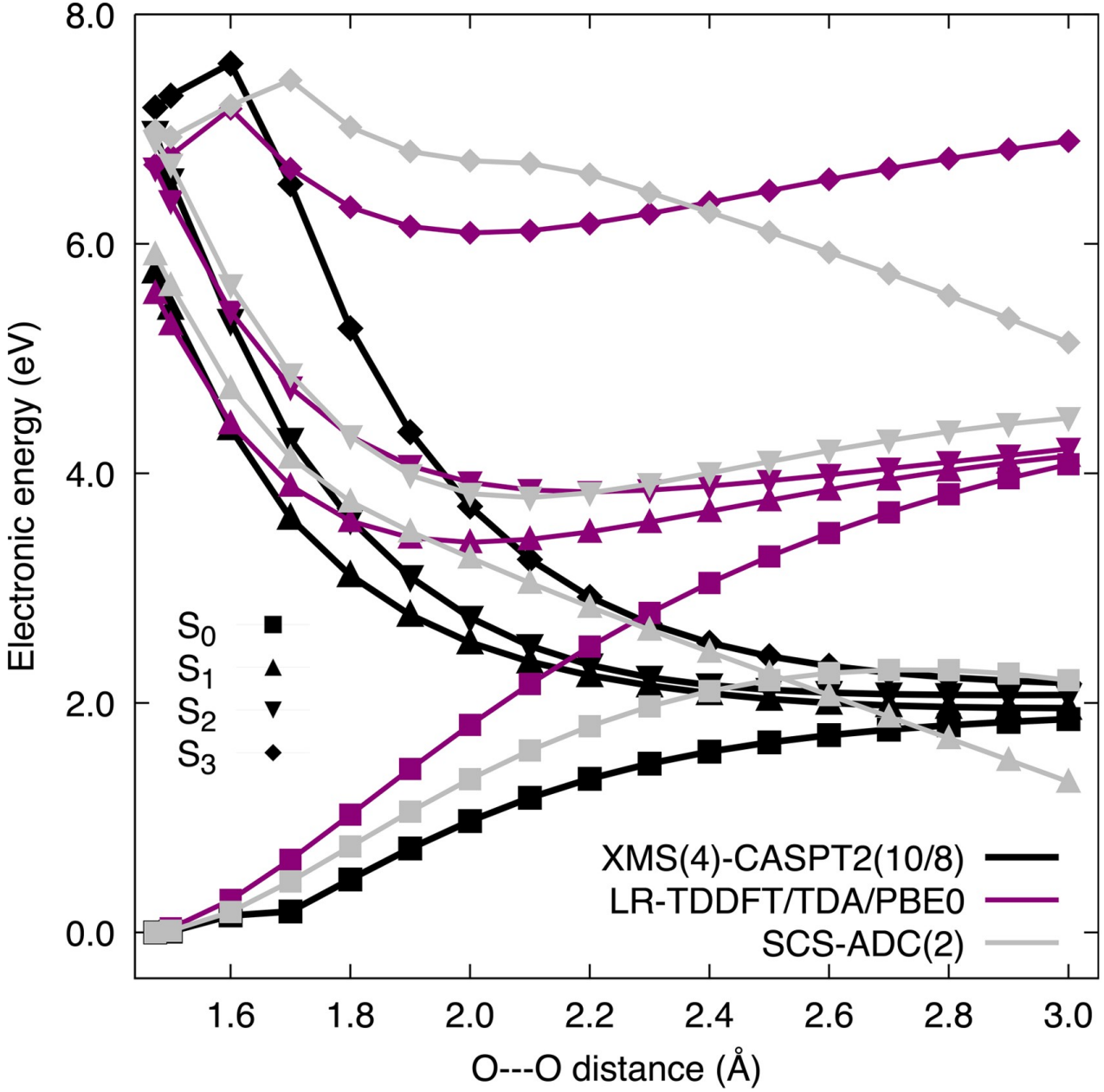


Valence-Rydberg mixing

Mulliken, *Acc. Chem. Res.* 1976, **9**, 7.

A. Prlj, L. M. Ibele, E. Marsili & B. F. E. Curchod *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.

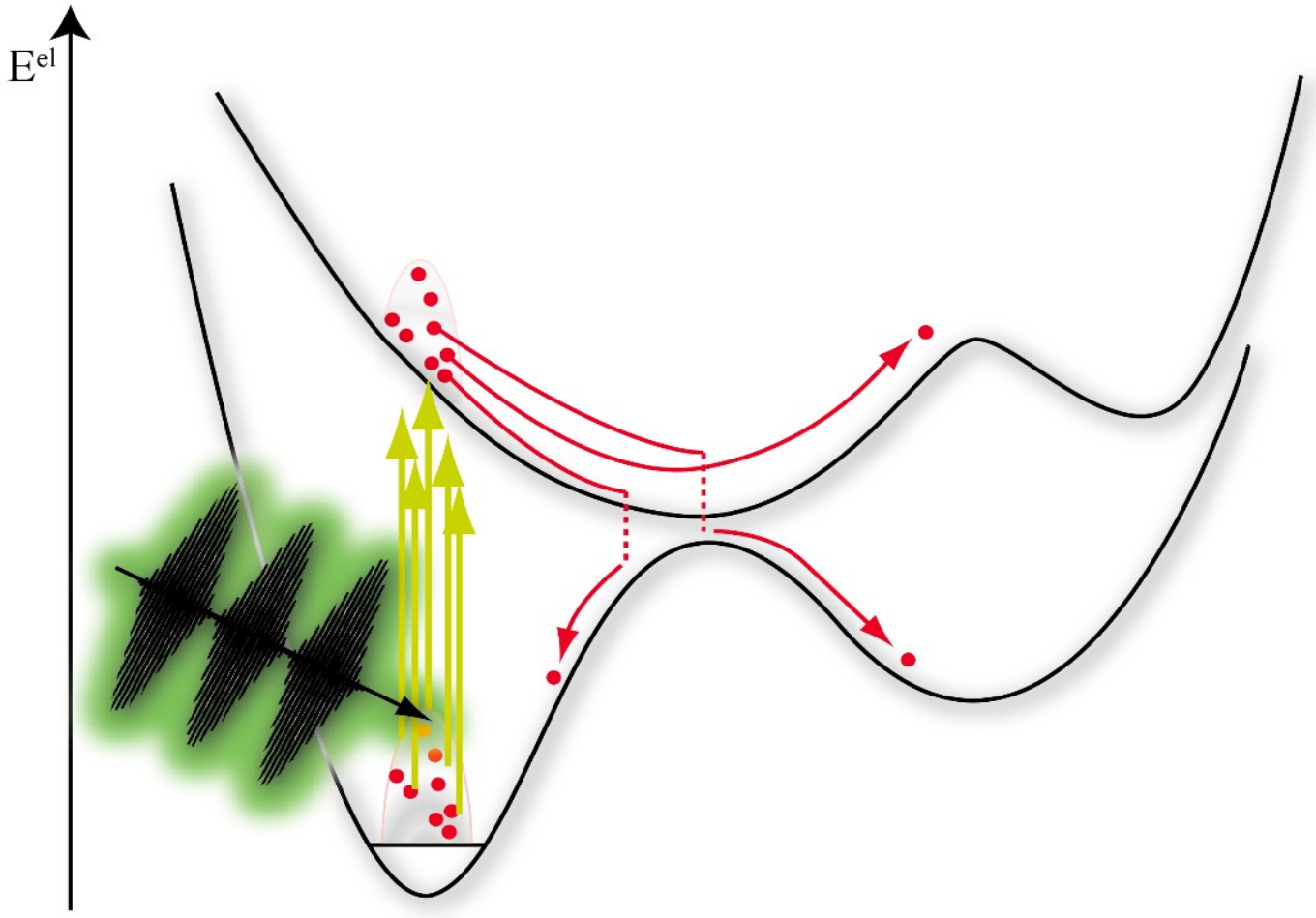
Excited States



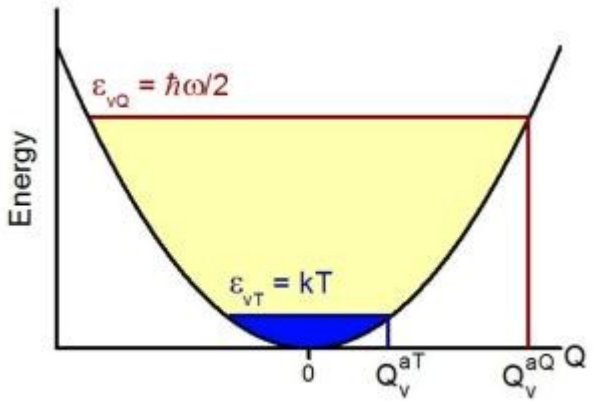
A. Prlj, L. M. Ibele, E. Marsili & B. F. E. Curchod *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.

Initial Conditions and Dynamics

- excited state dynamics – **surface hopping,** multiple spawning
- **Wigner distribution** – convenient way to sample ground state phase space



Initial Conditions



- Ground state phase space of a molecule is typically sampled by harmonic oscillator Wigner distribution
- **Thermal sampling** does not provide sufficient kinetic energy to account for zero-point vibrations

M. Barbatti and K. Sen, *Int. J. Quantum Chem.*, 2016, **116**, 762-771.

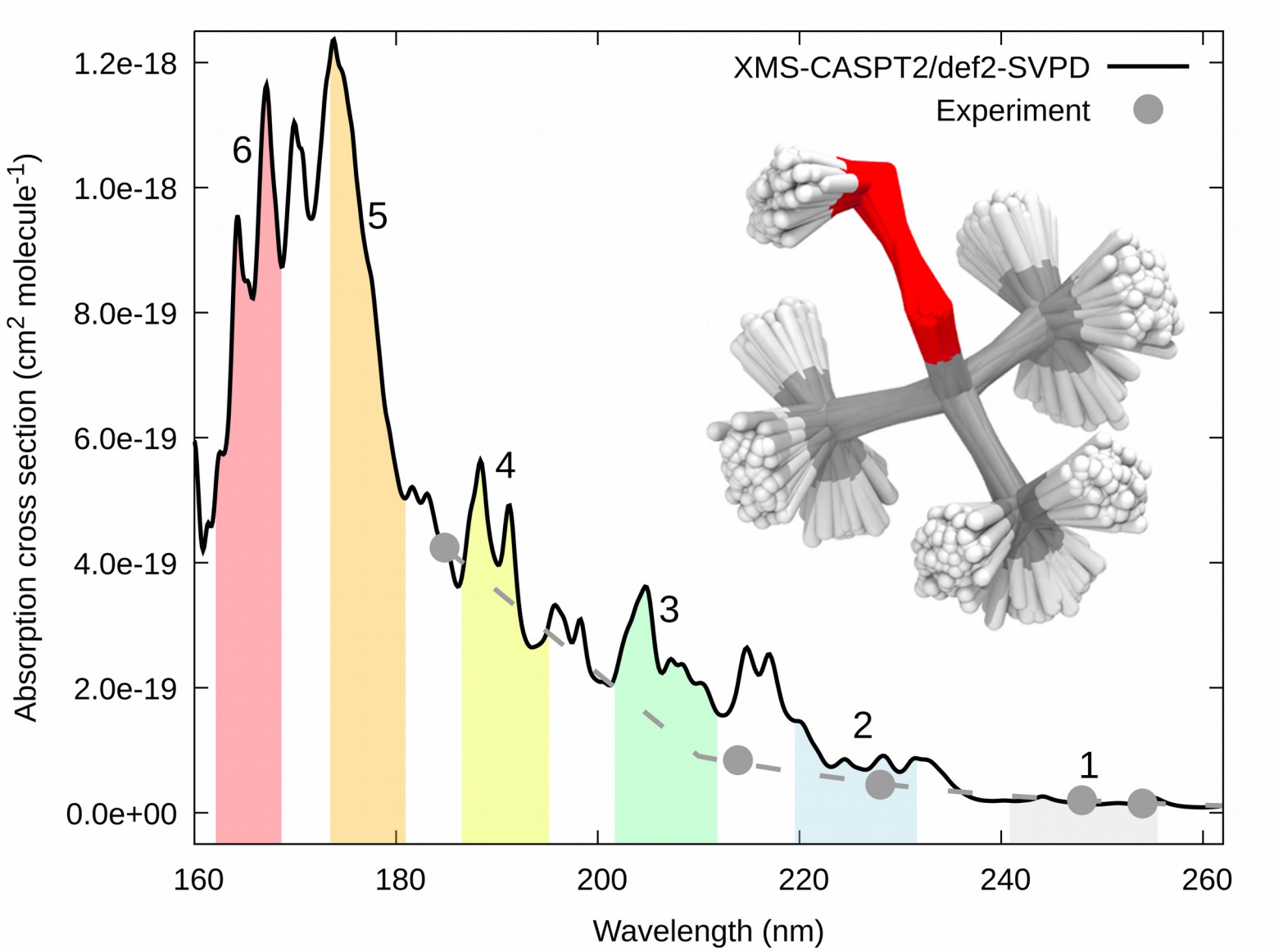
- **Wigner sampling** is not convenient for large and anharmonic systems
- **Quantum thermostat** based on generalized Langevin equation – different temperatures for different normal modes

M. Ceriotti, G. Bussi and M. Parrinello, *Phys. Rev. Lett.*, 2009, **103**, 030603.

Absorption Cross Section

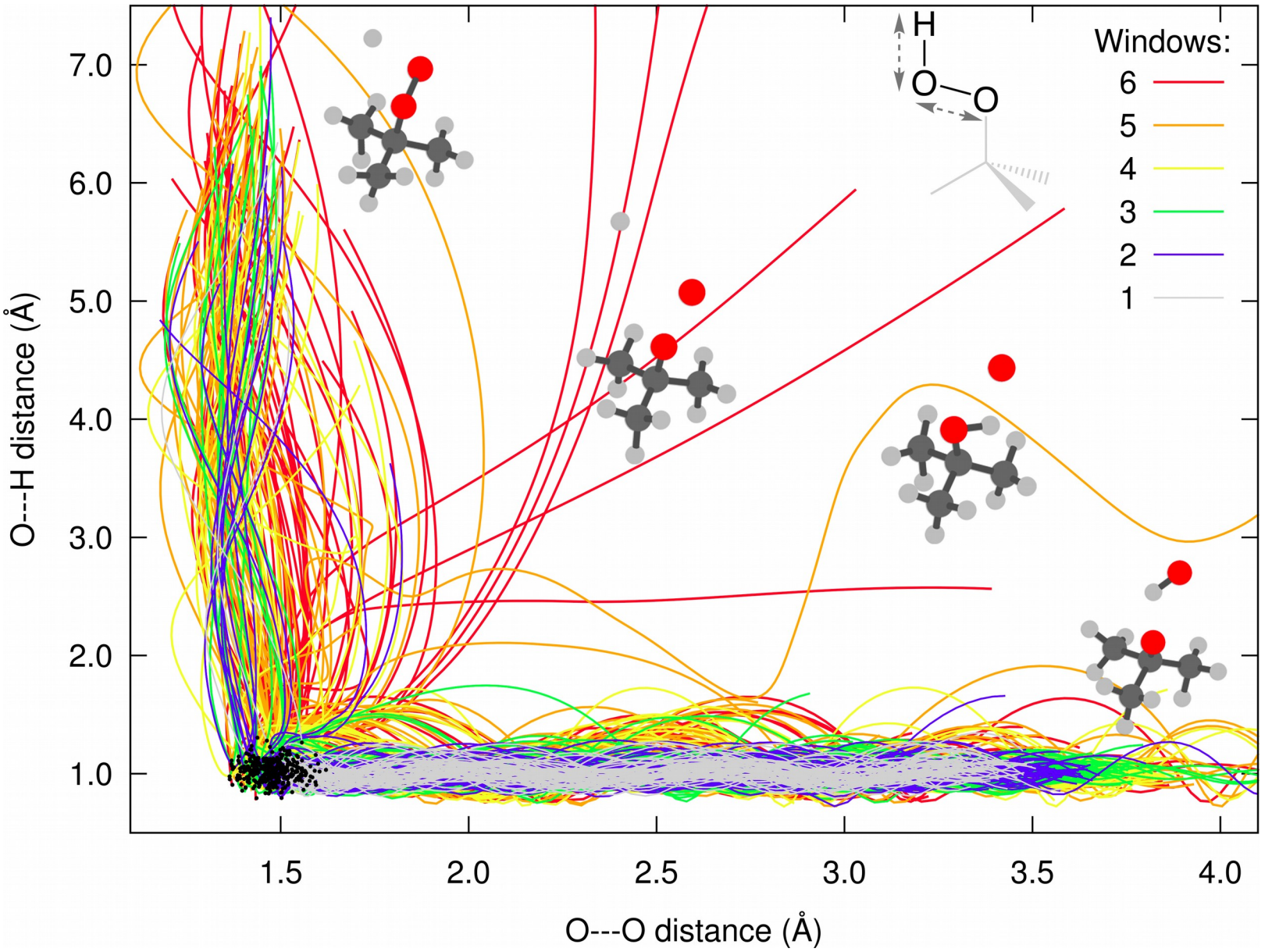
Absorption Cross Section

- Nuclear ensemble approach (Barbatti *et al.*, *Theor. Chem. Acc.*, 2012, **131**, 1237.)



A. Prlj, L. M. Ibele, E. Marsili & B. F. E. Curchod *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.

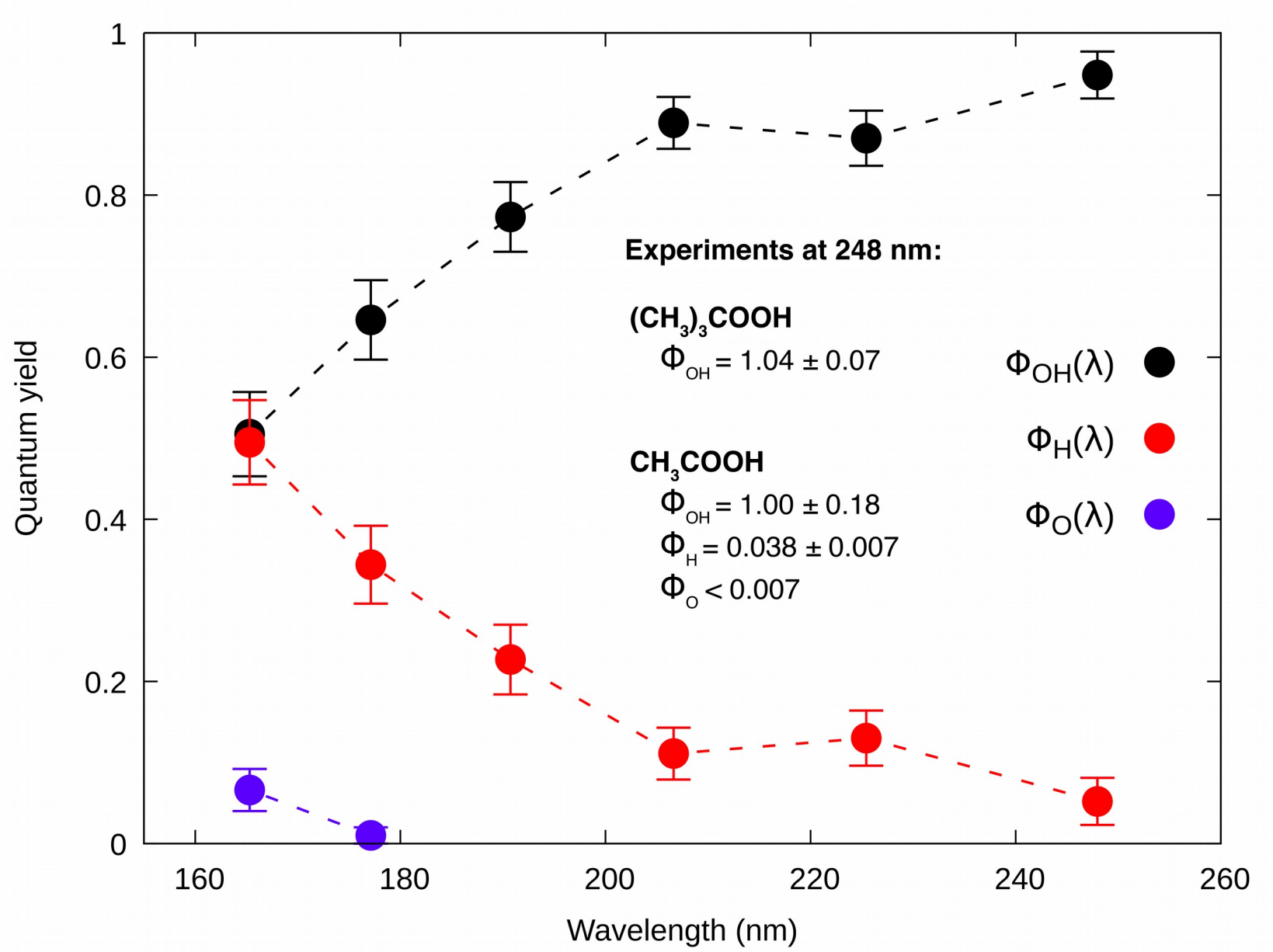
Analysis of Trajectory Swarms



A. Prlj, L. M. Ibele, E. Marsili & B. F. E. Curchod *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.

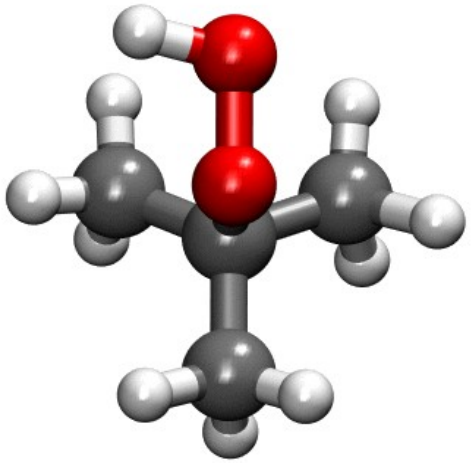
Photolysis Quantum Yields

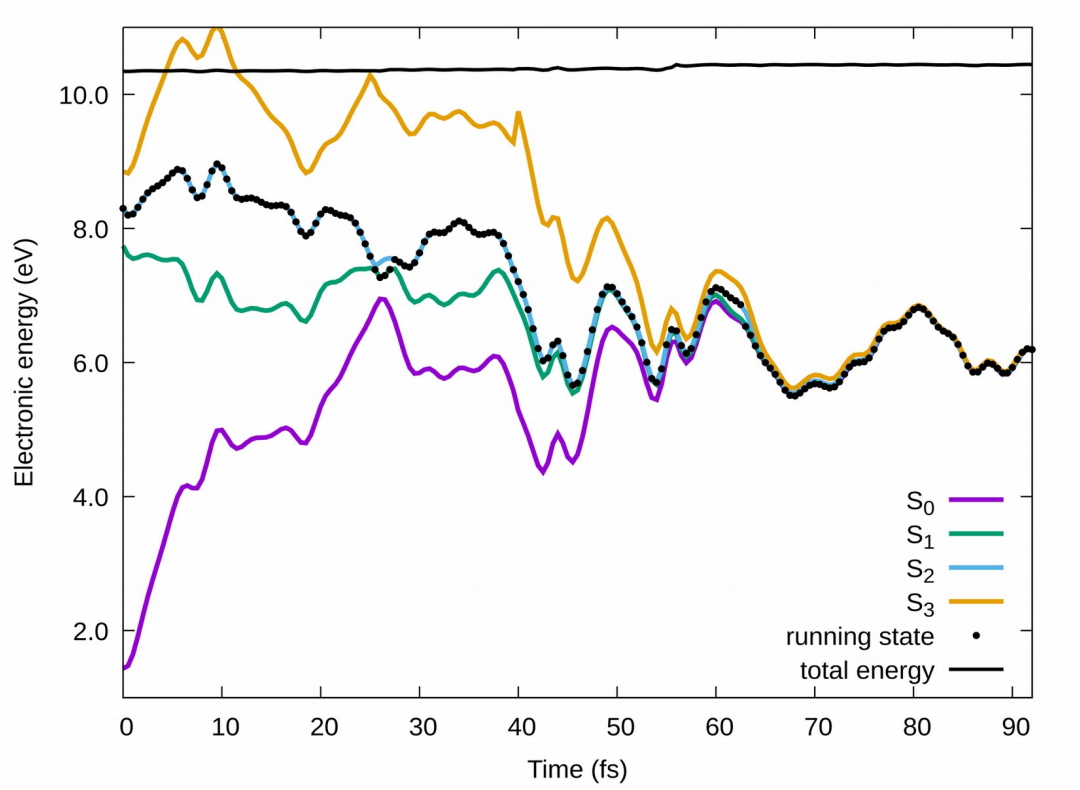
Wavelength dependent quantum yield



A. Prlj, L. M. Ibele, E. Marsili & B. F. E. Curchod *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.

H “roaming” and O dissociation





Conclusion

Can we predict *in silico* photolysis rate constants?

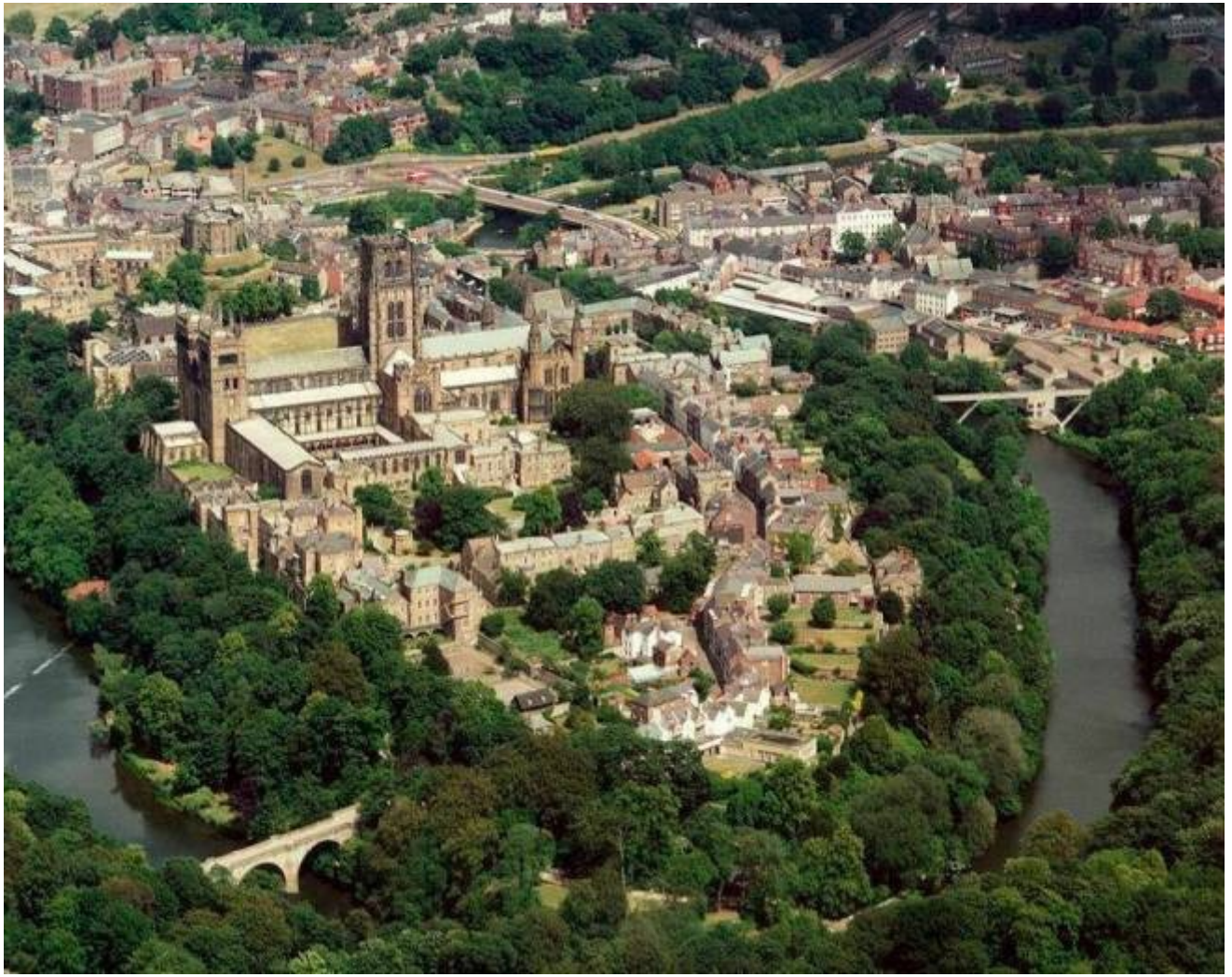
- Absorption cross sections – nuclear ensemble approach
- Quantum yields – surface hopping dynamics

We need to be careful about:

1. Electronic structure
2. Sampling of initial conditions

- Applying protocol on other VOCs

Durham University



Acknowledgements

Prof. Basile Curchod, Durham

Lea-Maria Ibele, Durham

Emanuele Marsili, Durham

European Research Council
Established by the European Commission