Reaction Dynamics – Relaxation Pathways

Andrew Orr-Ewing

School of Chemistry
University of Bristol, UK

www.bristoldynamics.com

Outline

1. Intramolecular and intermolecular relaxation pathways

2. Gas-phase molecules

   - Dynamics at conical intersections

   - Experimental studies

3. Molecules in solution

   - Effects of a surrounding medium

   - Experimental studies using ultrafast spectroscopy

1.0 Intramolecular and intermolecular relaxation pathways

Molecular collisions, exothermic chemical reactions or absorption of light (IR, visible or UV) can produce molecules with internal energies higher than at thermal equilibrium. This energy can randomize quickly throughout the molecule by internal conversion and intramolecular vibrational energy redistribution (IVR).

Molecules that are surrounded by a medium such as a gas or liquid (the "bath") can lose excess energy and re-establish thermal equilibrium through collisions or other intermolecular interactions.

On timescales faster than intermolecular interactions quench excess energy, or for isolated molecules, other chemical pathways can also open. Examples are:

- **Bond dissociation** (unimolecular reaction or photodissociation)
- **Internal conversion (IC)** to another electronic state of the same spin
- **Intersystem crossing (ISC)** to another electronic state of different spin
- **Isomerization**
- **Radiative decay** (chemiluminescence, fluorescence, phosphorescence)

These, and quenching processes following photoexcitation are illustrated in a Jablonski diagram.

Jablonski diagram:
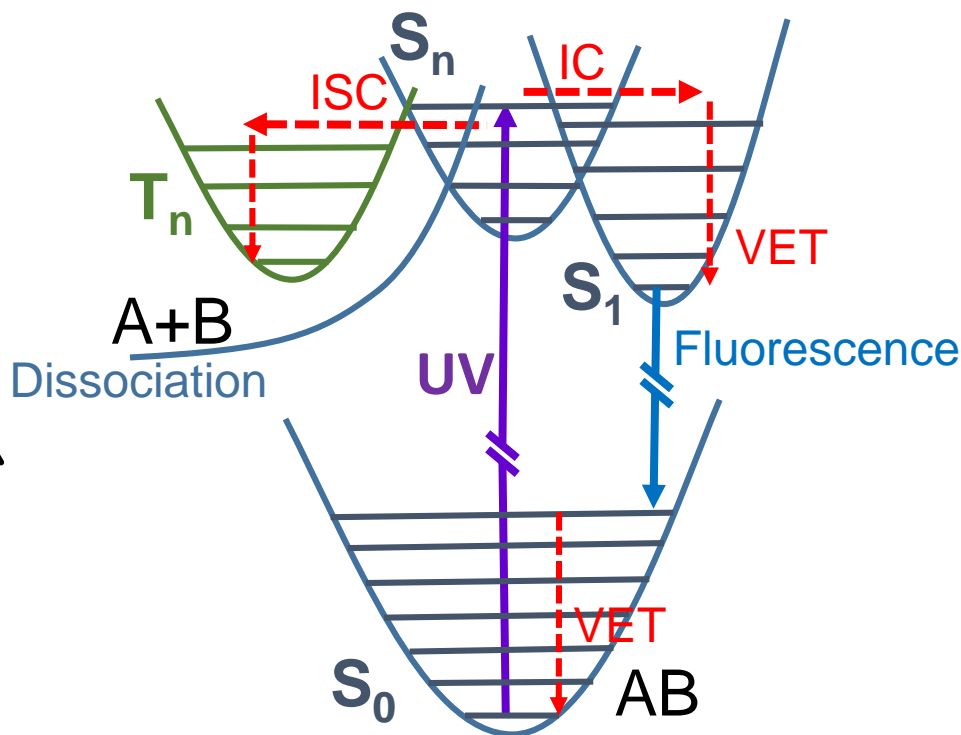
Typical timescales:

IC – ultrafast (sub-picosecond)
ISC – ultrafast to nanosecond
VET – few picosecond in solution
Dissociation – ultrafast
Fluorescence – nanosecond

VET / quenching occurs through interactions with a bath gas or liquid.

Internal conversion and intersystem crossing require non-adiabatic transitions between adiabatic electronic states.

Conical intersections connect electronic states.

1.1 Intramolecular relaxation: conical intersections

If we solve the Schrödinger equation for coupled electronic states of a molecule with inclusion of electrostatic terms but neglect of coupling interactions between states, and within the Born-Oppenheimer approximation, we obtain diabatic potential energy surfaces (PESs) which describe the dependence of the potential energy on nuclear coordinates.

The diabatic PESs vary smoothly with nuclear coordinates, and are coupled by matrix elements of the coupling terms in the Hamiltonian (e.g. spin-orbit interactions).
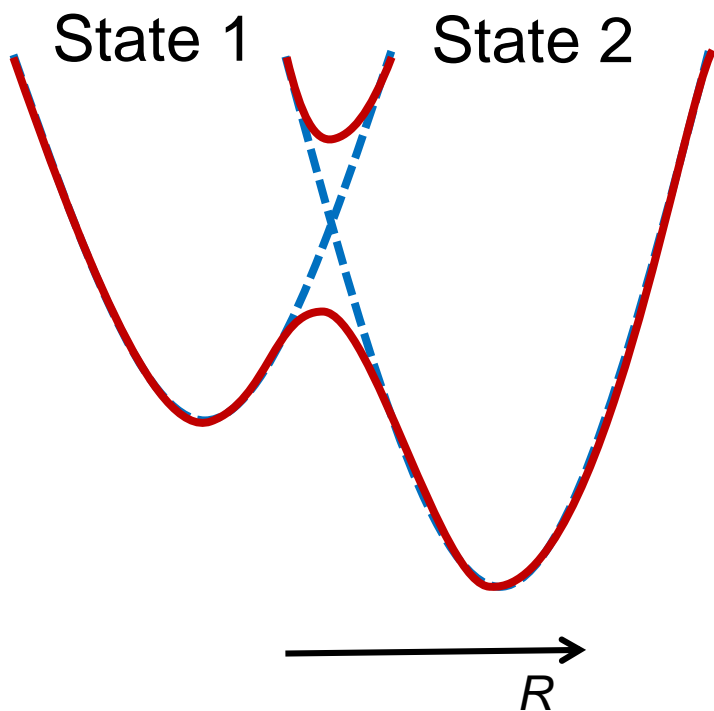
Inclusion of the coupling interactions in the solution of the Schrodinger equation gives adiabatic PESs which can show a change in overall electronic character at regions of near-degeneracy or transition states.

The adiabatic PESs are coupled by the nuclear kinetic energy operator: the "*derivative coupling*" terms are largest in regions where the electronic character changes rapidly with nuclear coordinates.[#]

Non-adiabatic transitions between adiabatic states correspond to a breakdown of the Born-Oppenheimer approximation.

[#] See, for example, Ch. 4 of Brouard & Vallance, *Tutorials in Molecular Reaction Dynamics* (RSC, 2010); Worth & Cederbaum, Annu. Rev. Phys. Chem. **55**, 127 (2004).

# Diabatic and adiabatic representations

State 1   State 2

R

$$\begin{pmatrix} H_{11}(R) & V_{12}(R) \\ V_{12}(R) & H_{22}(R) \end{pmatrix} \underline{c}(R) = E(R)\underline{c}(R)$$

Diagonalization of a matrix of diabatic states $H_{ii}(R)$ and couplings $V_{ij}(R)$ gives the adiabatic PESs $E(R)$.

The eigenvectors give the weightings of the diabatic PESs contributing to the adiabatic PESs.

Diabatic and adiabatic representations of the ground state for the Cl + CH$_4$ → HCl + CH$_3$ reaction.
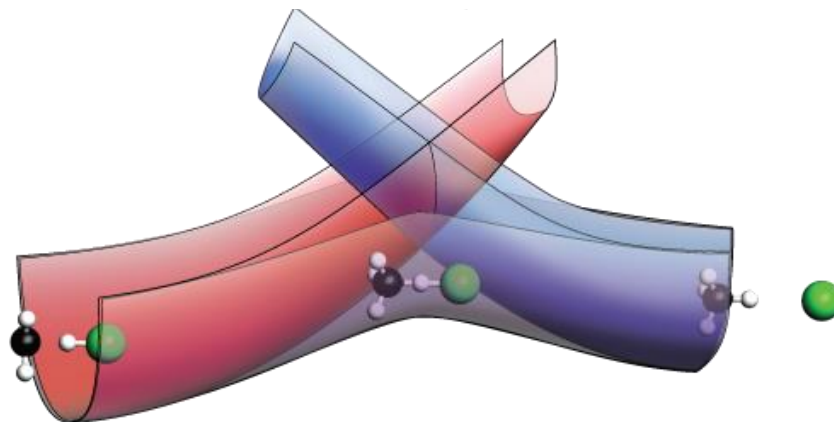
Electronic state crossings and conical intersections

In a diatomic molecule, adiabatic PE curves of the same symmetry cannot cross.

For polyatomic molecules, multi-dimensional seams of conical intersections occur between adiabatic PESs and act as funnels through which molecules change electronic state.
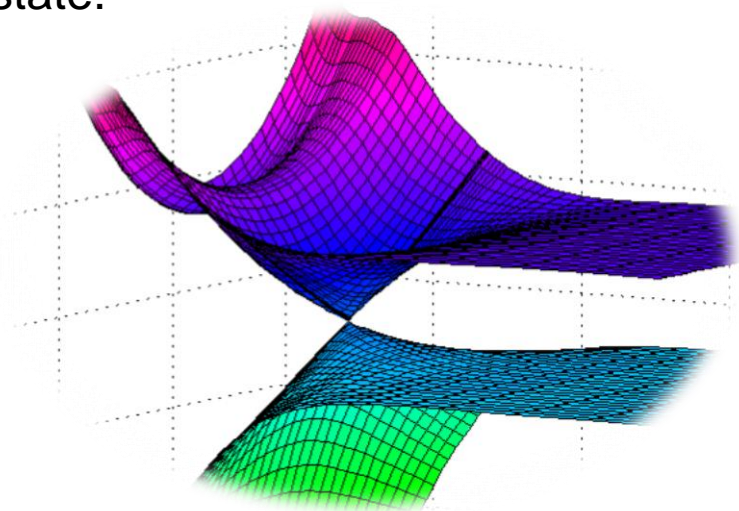
A conical intersection arises when two adiabatic states have a point of degeneracy. Two coordinates are sufficient to describe the region of the conical intersection. They define the **branching space** (or **g-h plane**).[#]

 # D.R. Yarkony, *Rev. Mod. Phys.* **68**, 985 (1996)
   Worth & Cederbaum, Annu. Rev. Phys. Chem. **55**, 127 (2004)

For a symmetry-derived conical intersection (connecting states of different symmetry):

The tuning coordinate: the direction along which the nuclei move to bring the two electronic states close enough in energy to reach a point of degeneracy, while maintaining the molecular symmetry.

The coupling coordinate: a direction of motion away from the intersection which distorts the molecule and lowers its symmetry, inducing a coupling between the two states which pushes them apart.

There is a multidimensional seam of intersections along the remaining degrees of vibrational freedom.

Energy

2D branching space

Tuning coordinate

Coupling coordinate

Examples of non-adiabatic dynamics at conical intersections arise in the photochemistry of most molecules: they control internal conversion between electronic states. See **Sections 2** and **3**. They also introduce non-adiabatic pathways in bimolecular chemical reactions.
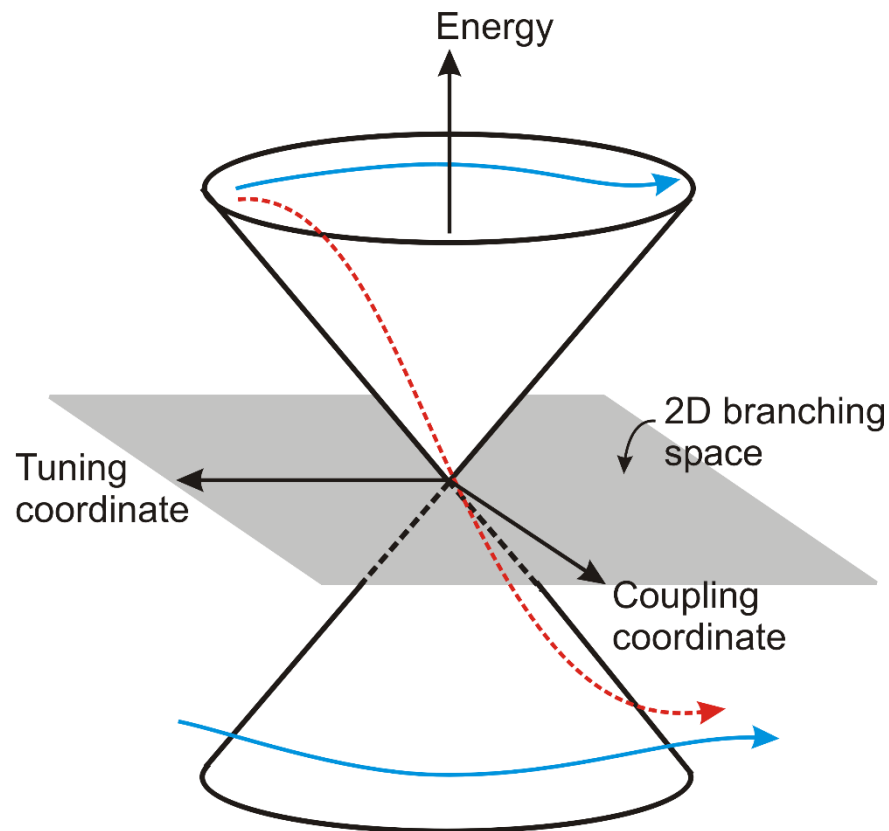
1.2 Intermolecular energy transfer in the gas-phase: inelastic collisions

Non-reactive collisions between molecules that exchange internal and translational energy are called inelastic collisions. The energy transfer might be:

- Electronic to translational (E – T) (or *vice versa*)
- Vibrational to translational (V – T) (or *vice versa*)
- Rotational to translational (R – T) (or *vice versa*)

Laboratory studies of rates and dynamics of energy transfer provide information on the intermolecular potential energy surface that governs the collisions.

Angular scattering distributions (the ***differential cross sections***), and their dependence on changes in quantum state (and hence internal energy) can be studied in detail using crossed molecular beam and velocity map imaging methods.

Comparisons with quantum scattering calculations (e.g. using the HIBRIDON code[#]) provide rigorous tests of intermolecular potential energy functions.

HIBRIDON is a package of programs for time-independent quantum treatment of inelastic collisions, written by M.H. Alexander (University of Maryland) *et al.*

Example: inelastic scattering of CD$_3$ radicals with He atoms

Tkáč *et al.*, Chem. Sci. **4**, 4199 (2013)
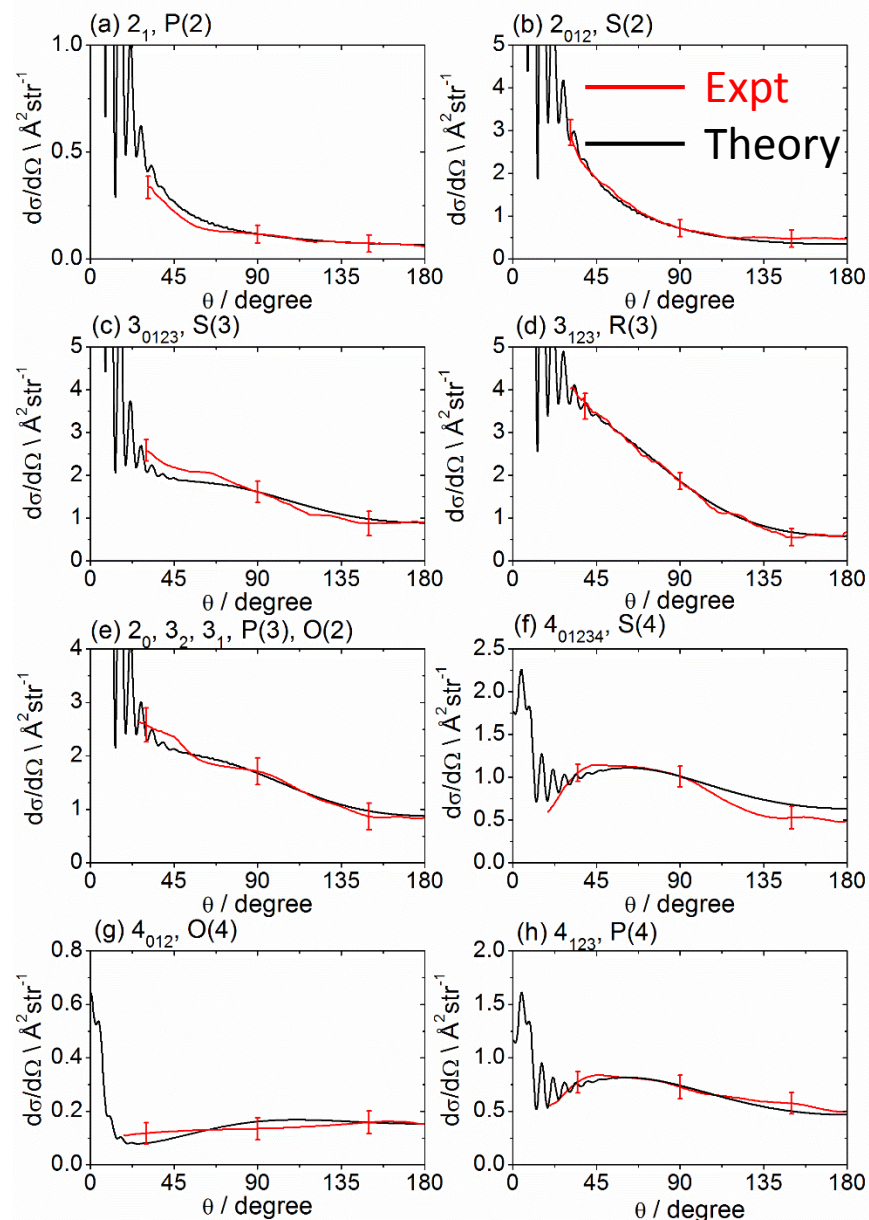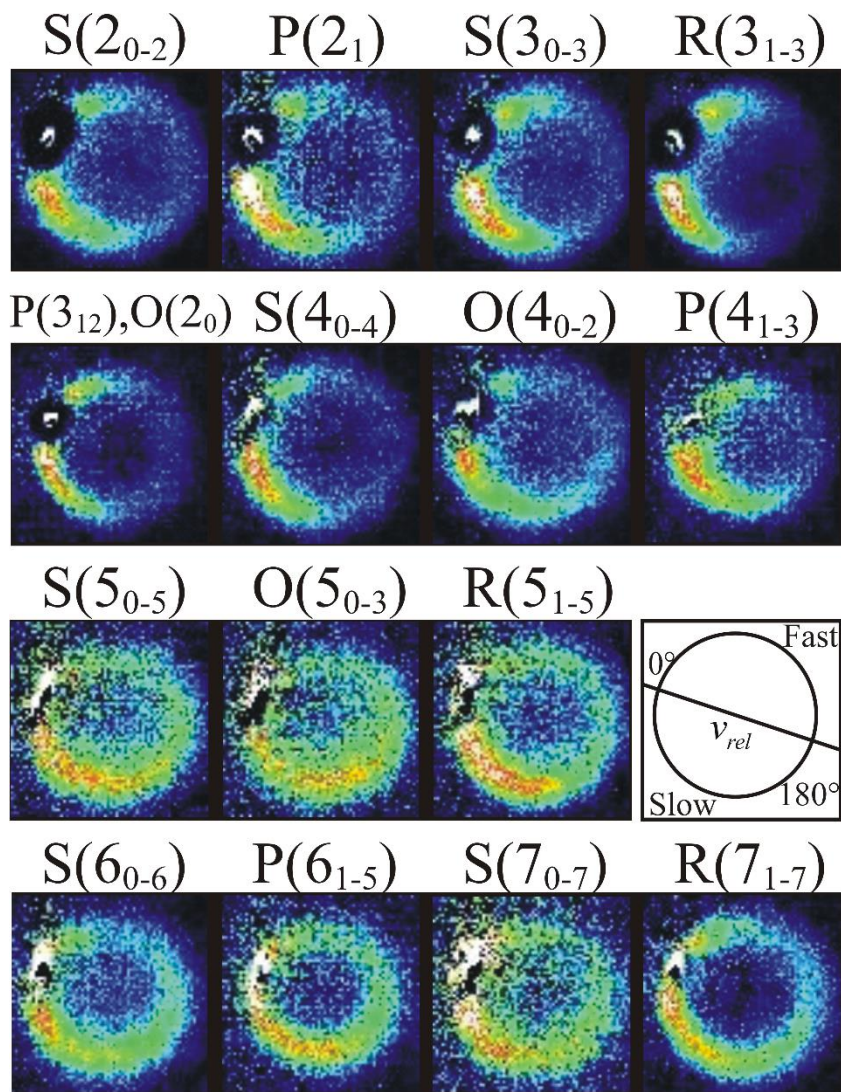
2.0 Relaxation dynamics in isolated gas-phase molecules

Consider a molecule which has absorbed a UV photon and is in an excited electronic state. If the molecule is isolated, it cannot lose the excess energy of the absorbed photon through collisions with surrounding molecules.

It can lose excess energy by:

- Radiative decay back to the ground state by emission of a photon.

- Dissociation (or predissociation) into photofragments on a dissociative excited state: $ABC \rightarrow AB + C$

- Autoionization (if the internal energy is high enough): $ABC \rightarrow ABC^+ + e^-$

Or it can undergo processes which retain its internal energy:

- Internal conversion (IC to the ground state can be followed by unimolecular dissociation)

- Intersystem crossing (El Sayed rules: ISC is faster if there is a change of orbital type, e.g.: $^1n\pi^* \rightarrow {}^3\pi\pi^*$ but $^1\pi\pi^* \nleftrightarrow {}^3\pi\pi^*$; $^1n\pi^* \nleftrightarrow {}^3n\pi^*$)

- Isomerization

Many of these processes involve passage through a conical intersection.

2.1 Non-adiabatic dynamics at conical intersections

The role of conical intersections in mediating relaxation pathways in photoexcited gas-phase molecules can be studied by:

Theoretical / computational methods, using *ab initio* computation of coupled PESs and propagation of nuclear dynamics by:

- Classical trajectories with surface hopping (Tully, Truhlar, …)

- Time-dependent wavepacket propagation (Balint-Kurti, Schinke …)

- Ab initio multiple spawning (AIMS, Martinez)

- Multi-configuration time-dependent Hartree (MCTDH, Meyer, Worth, …)

S_1

S_0

Time $\rightarrow$

T.J. Martinez, Acc. Chem. Res. **39**, 119 (2006)
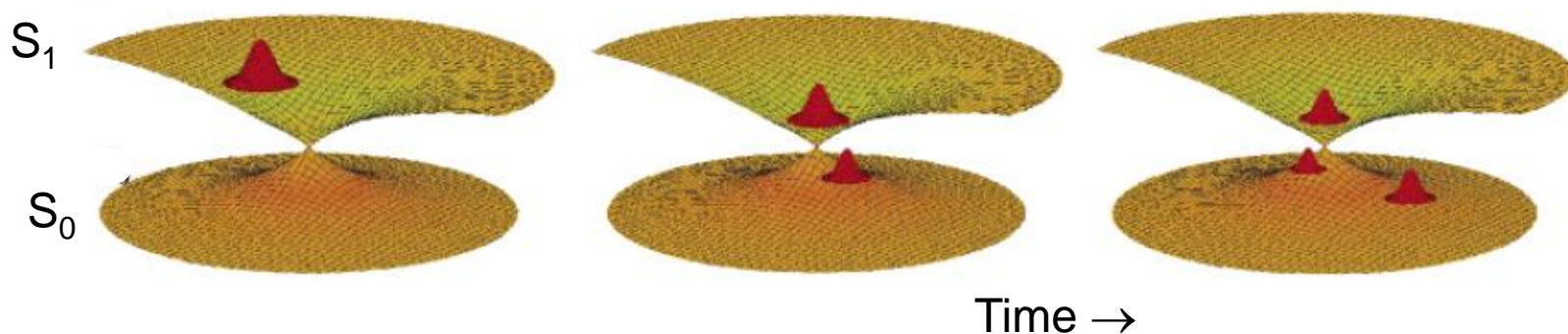
Experimental methods, e.g.

- **Photofragment translational spectroscopy (PTS)**

$$ABC \xrightarrow{h\nu} A + BC$$
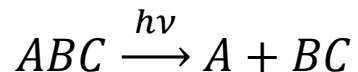
Measure speed of A (e.g. by VMI, or H-atom PTS) and use momentum conservation to deduce total kinetic energy release (TKER) of photofragments.

Deduce internal energies of photofragment BC using energy conservation:

$$E_{ph} + E_{int}(ABC) = D_0(A - BC) + E_{int}(A) + E_{int}(BC) + TKER$$

- **Ultrafast photofragment spectroscopy**

Observe time-dependent build-up of photofragments on fsec – psec timescale, e.g. by combining ultrafast pump-probe spectroscopy with VMI.

- **Time-resolved photoelectron spectroscopy**

Use the time-evolution of the photoelectron spectrum to map transitions between excited states and internal conversion to the ground state. See Lecture 1.

Example of PTS: photodissociation of phenol

Importance of conical intersections between excited $\pi\pi^*$ and repulsive $\pi\sigma^*$ proposed by Sobolewski and Domcke.[#]
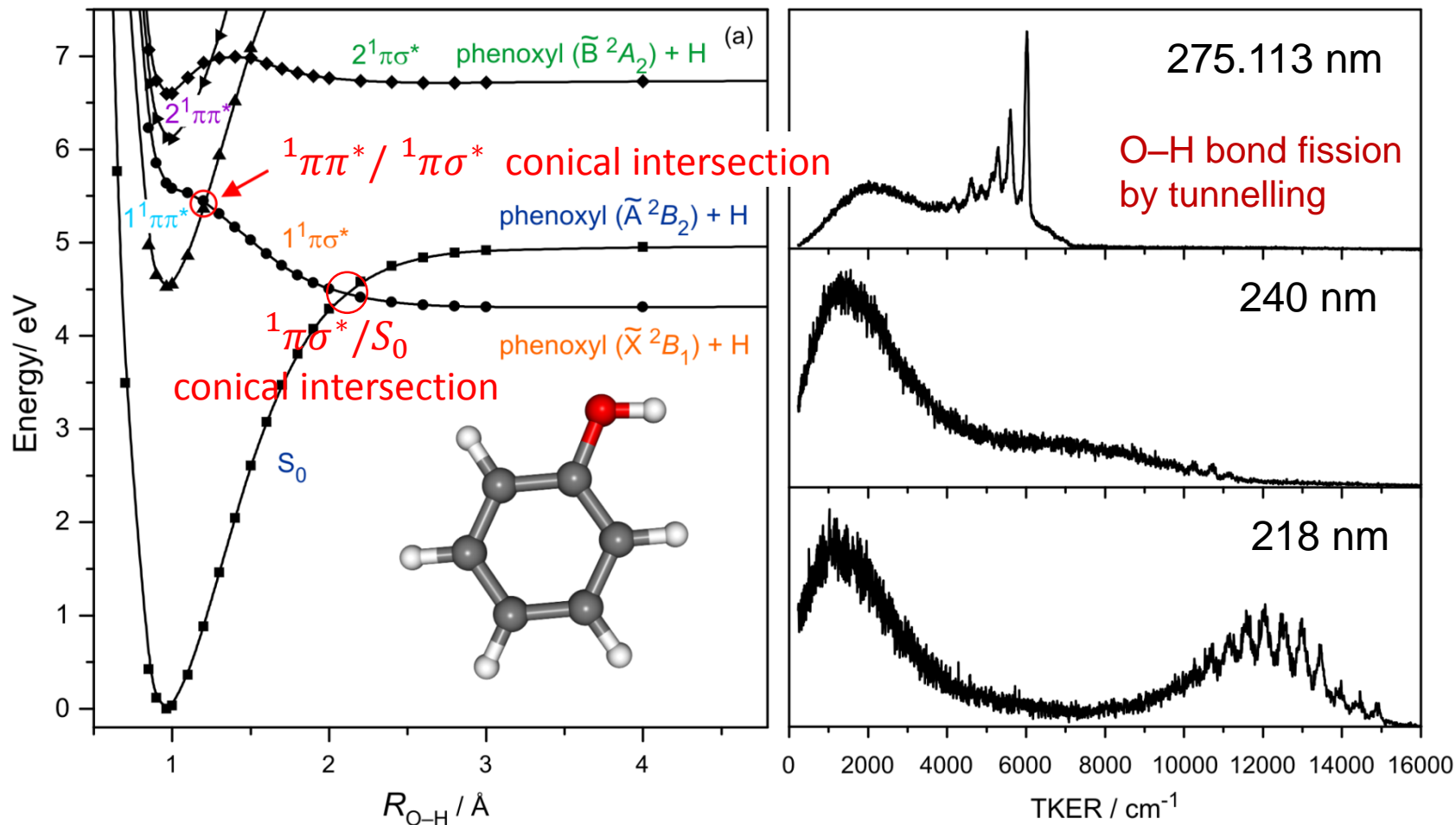
Sobolewski and Domcke, Chem. Phys. 259, 181 (2000)
  Nix *et al.*, J. Chem. Phys. **125**, 133318 (2006)

Example of PTS: photodissociation of phenol

- Longer wavelength UV excitation results in O–H bond fission by tunnelling under the $1^1\pi\pi^*/1^1\pi\sigma^*$ conical intersection
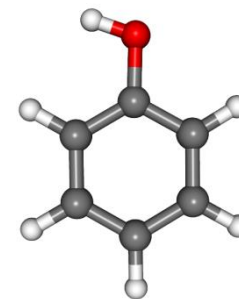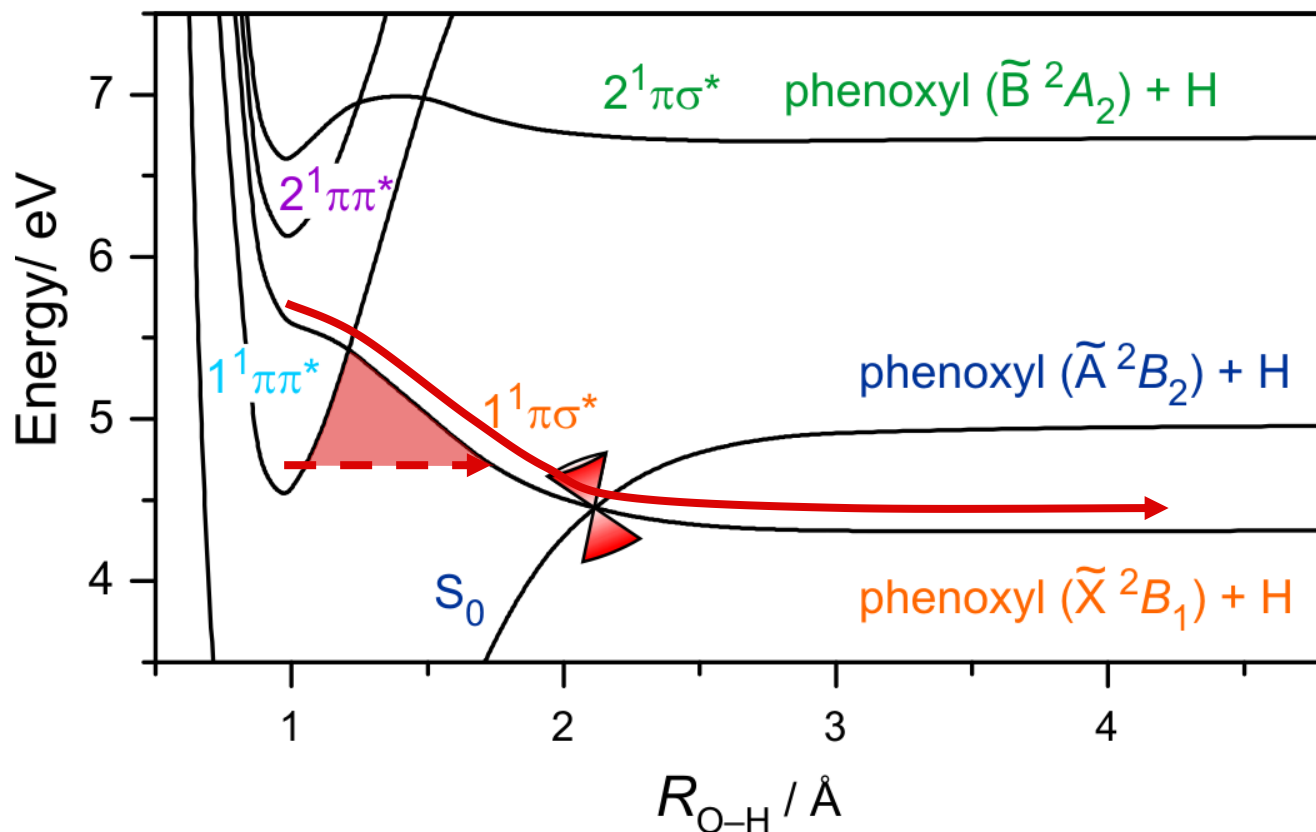

phenol

- Franck-Condon and symmetry constraints lead to population of a limited sub-set of product vibrational modes

Pino *et al. JCP* 2010 **133** 124313; Dixon *et al. JCP* 2011 **134** 194303.

Example of PTS: photodissociation of thiophenol
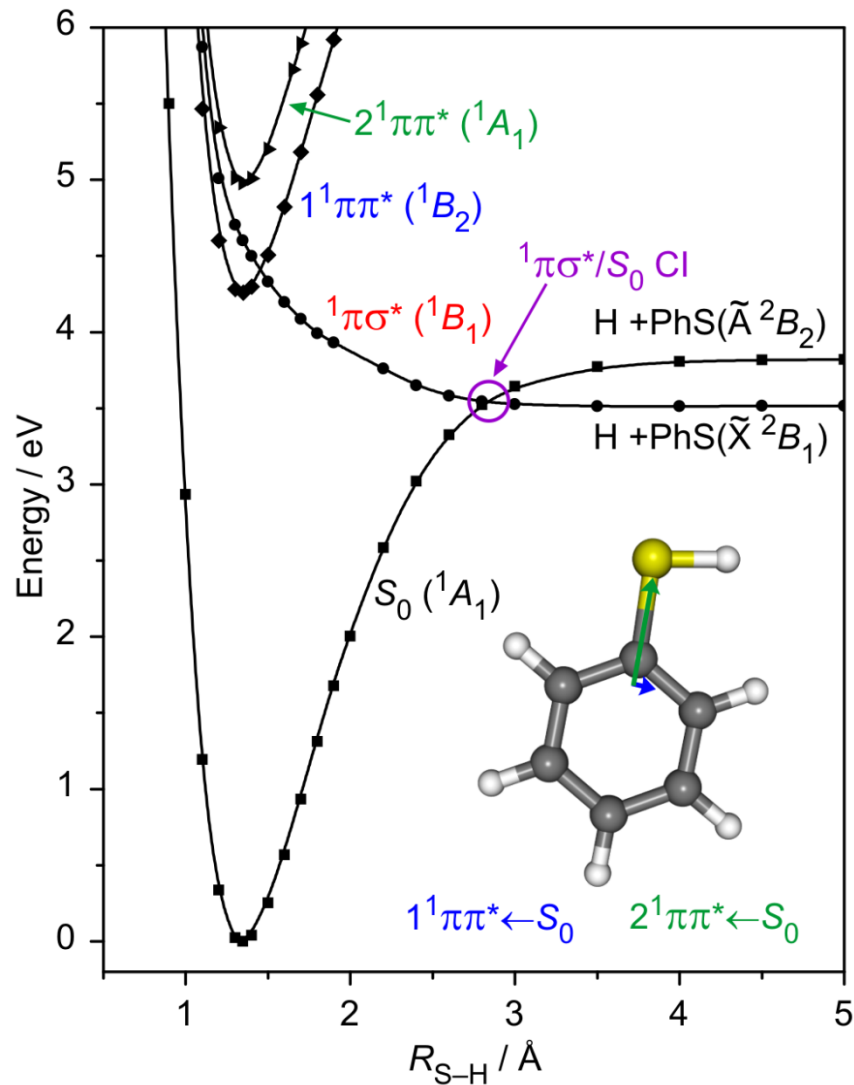
Two dissociation mechanisms:

- Longer wavelengths: tunnelling under $1^1\pi\pi^*$/$1^1\pi\sigma^*$ conical intersection.
- Shorter wavelengths: prompt dissociation on $1^1\pi\sigma^*$ PES.
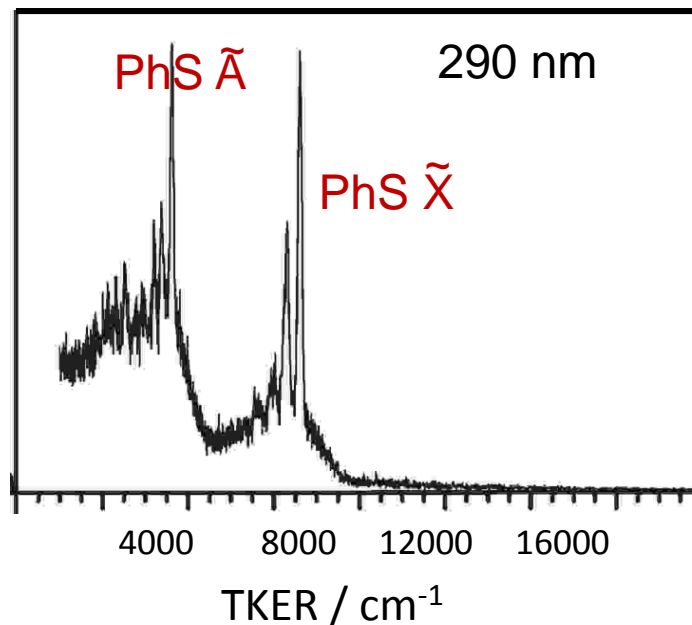
Branching between the PhS $\tilde{A}$ and $\tilde{X}$ states determined at the **second** conical intersection ($^1\pi\sigma^*/S_0$).

Example of time-resolved photoelectron and photoionization spectroscopy: dynamics that follow $\pi \rightarrow \pi^*$ excitation in ethene (a model system for light-induced cis-trans isomerization in larger chromophores).
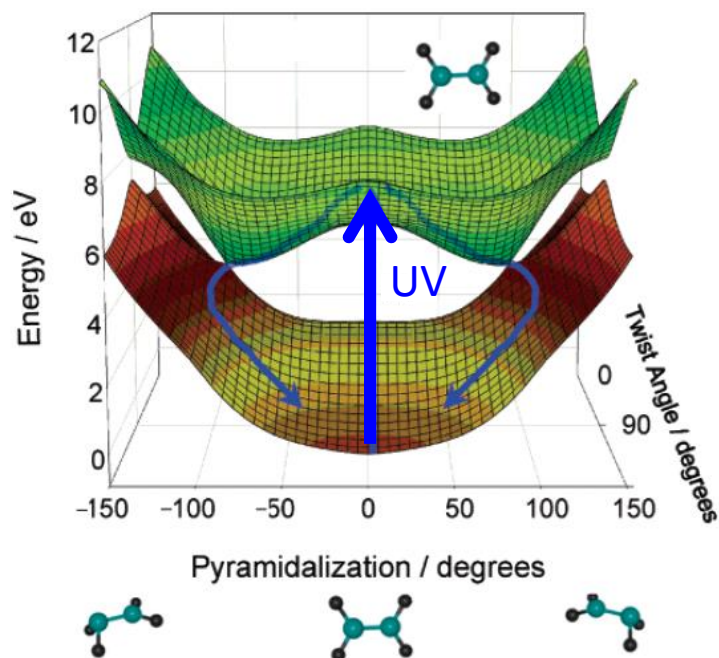
TR-PES and AIMS explore excited state dynamics of ethene. Need a ~9.3 eV probe pulse to ionize ethene across full excited state excursion to measure its lifetime.

Ultrafast XUV ionization of 161-nm excited ethene accesses dissociative cation states. Yields of cation fragments track the dynamics on the excited state (via CH_2^+) and ethylidene formation (via CH_3^+).

Martinez, Acc. Chem. Res. **39**, 119 (2006)
Allison *et al.*, JCP **134**, 244306 (2011); JCP **136**, 124317 (2012)

3.0 Relaxation dynamics for molecules in solution

The short intervals (~100 fs) between solvent-solute interactions make energy transfer to the solvent bath competitive with the intramolecular relaxation pathways (IC, ISC, dissociation,…).
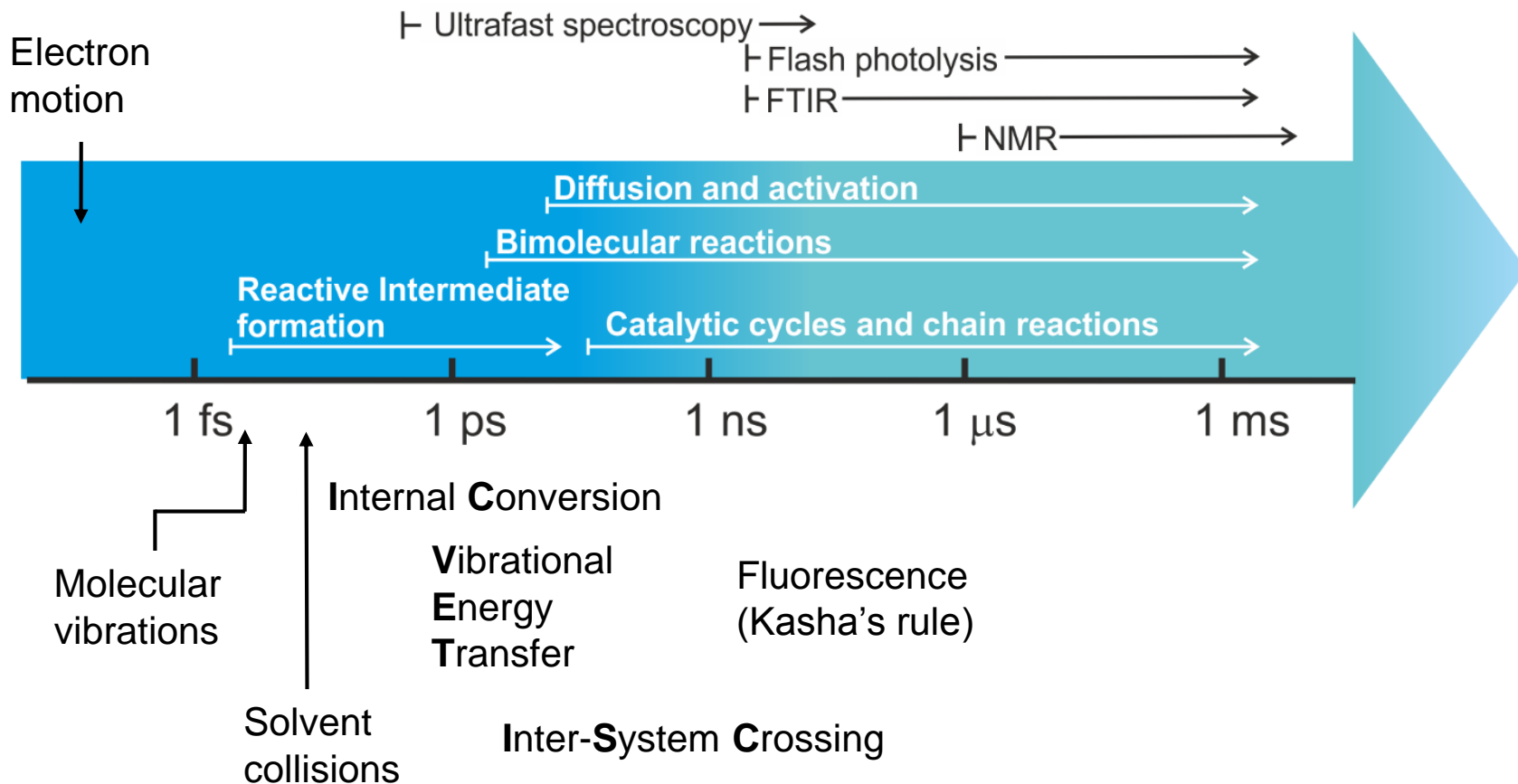
Vibrational energy transfer (VET) to the solvent is difficult to model theoretically.

For a quantized harmonic oscillator in a liquid bath, the rate coefficient for relaxation from level $|n\rangle$ to level $|n-1\rangle$ is:[#]

$$k_{n,n-1} = \frac{n}{\mu\hbar\omega}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle F_i(t)F_i(0)\rangle$$

$|n\rangle$ ———————

$k_{n,n-1}$

$|n-1\rangle$ ———————
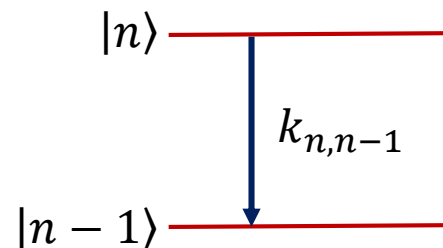
Here, $F_i(t)$ is the force exerted by the bath on the ith vibrational mode with reduced mass μ, and the average is over the bath modes.

The force correlation function can be related to a frequency-dependent solvent friction $\xi(\omega)$ by Fourier transform, and the relaxation rate coefficient becomes:

$$k_{n,n-1} = \frac{2n\,\xi(\omega)k_B T}{\mu\hbar\omega\{1 + e^{-\hbar\omega/k_B T}\}}$$

Note the linear dependence on n and the inverse dependence on ω.

Owrutsky, Raftery and Hochstrasser, Annu. Rev. Phys. Chem. **45**, 519 (1994).

However, this model of vibrational relaxation in a classical bath neglects:

- Resonant V-V energy transfer (e.g. Förster coupling)
- Anharmonic coupling of vibrational modes of the solvent and solute, e.g. through complex formation.

In many common solvents (e.g. acetonitrile, chloroform, hexane) VET to the solvent occurs on picosecond timescales. Energy release in exothermic reactions can therefore be to the reaction products before dissipation into the solvent bath.[#]
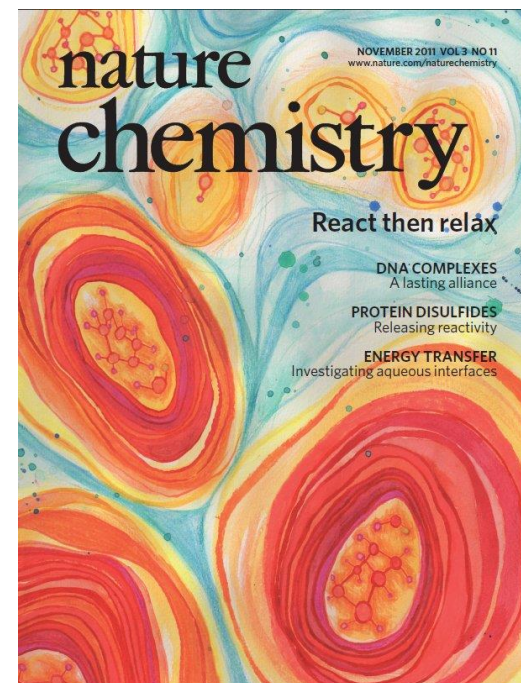
Other relaxation pathways in solution include:

Charge-transfer pathways (e.g. metal-to-ligand or solute-to-solvent).

Geminate recombination of photofragments before they diffuse apart, and VET.
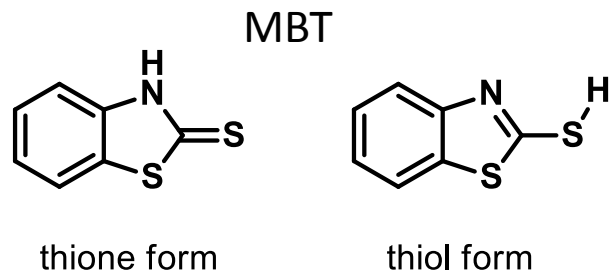
Isomerization pathways (e.g. ring-opening of heterocyclic compounds), which can be studied in solution by transient absorption spectroscopy.

[#] Greaves *et al*. Science, **331**, 1423 (2011); Glowacki *et al*. Nature Chem. **3**, 850 (2011). Orr-Ewing, J. Chem. Phys. **140**, 090901 (2014); Ann. Rev. Phys. Chem. **66**, 119 (2015)
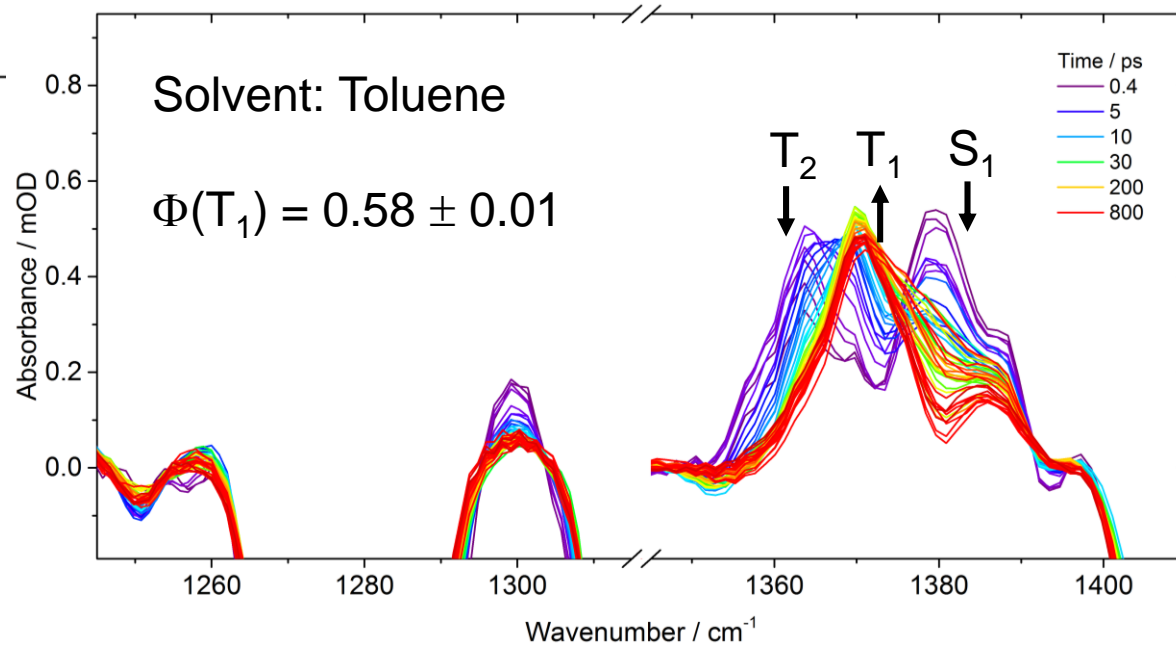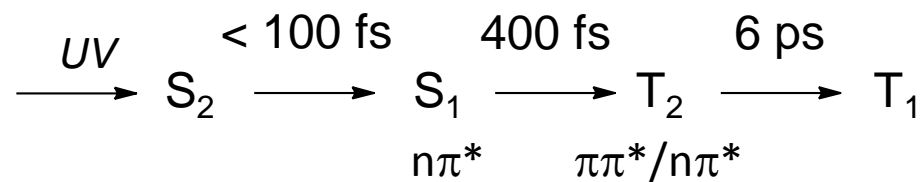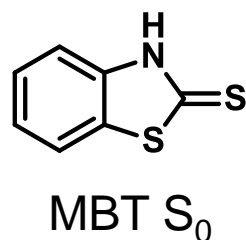
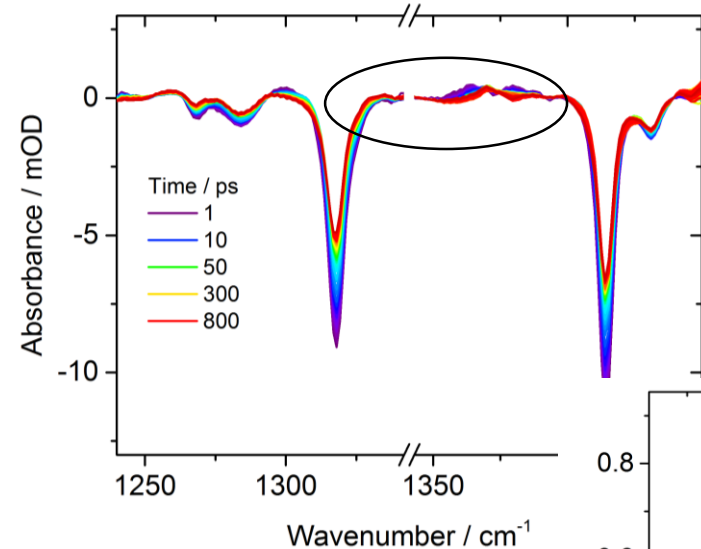# 3.1 Internal conversion and intersystem crossing in solution

Photochemistry of a thione compound MBT

MBT

thione form   thiol form

Solvent: Methanol

$S_2\,(\pi\pi^*) \leftarrow S_0$

Transient electronic absorption spectroscopy

Time / ps
1
10
50
200
500

T_1 T_2

$S_1(n\pi^*)$

T_1

T_2

S_1

D. Koyama *et al.*, PCCP **18**, 26224 (2016).

MBT

thione form   thiol form

Solvent: Methanol

$S_2\,(\pi\pi^*) \leftarrow S_0$

Transient electronic absorption spectroscopy

Time / ps
-0.2
-0.1
0.0
0.1
0.2

T_2

$S_1(n\pi^*)$

T_1

T_2

S_1

D. Koyama *et al.*, PCCP **18**, 26224 (2016).

Transient vibrational absorption spectroscopy

MBT S_0

$UV \longrightarrow S_2 \xrightarrow{< 100 \text{ fs}} S_1 \xrightarrow{400 \text{ fs}} T_2 \xrightarrow{6 \text{ ps}} T_1$

$n\pi^*$ $\pi\pi^*/n\pi^*$

Solvent: Toluene

$\Phi(T_1) = 0.58 \pm 0.01$
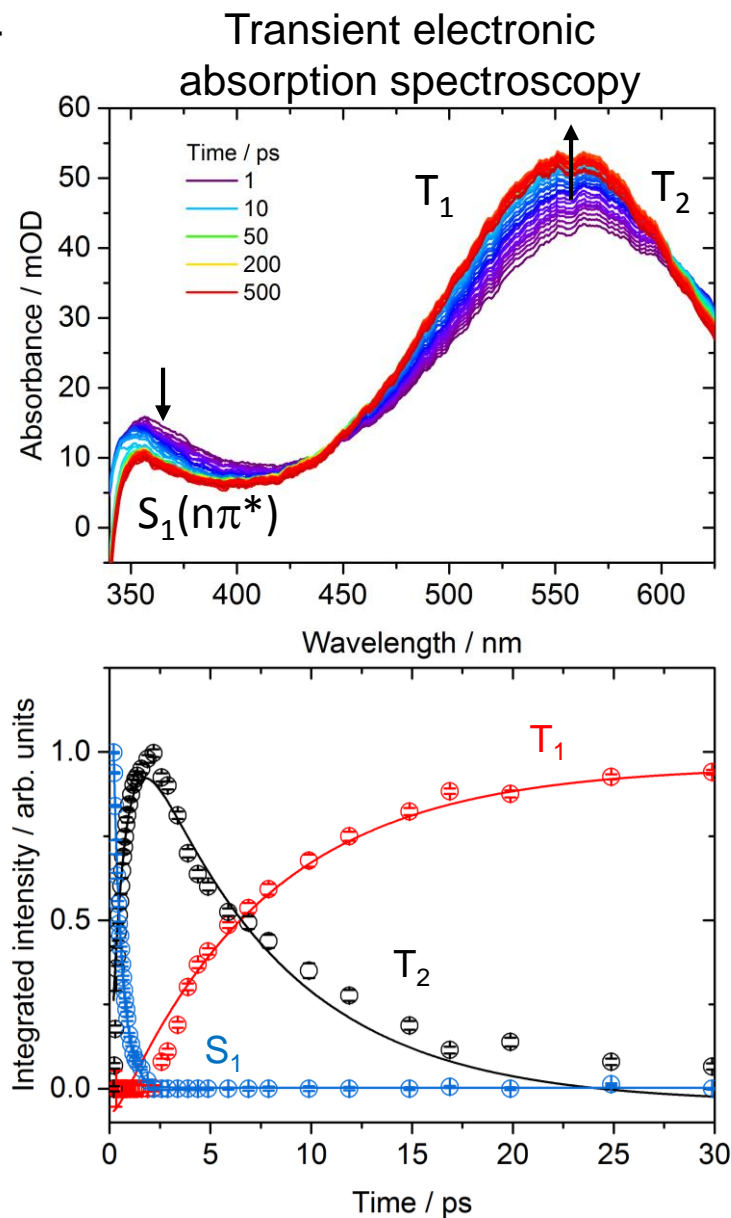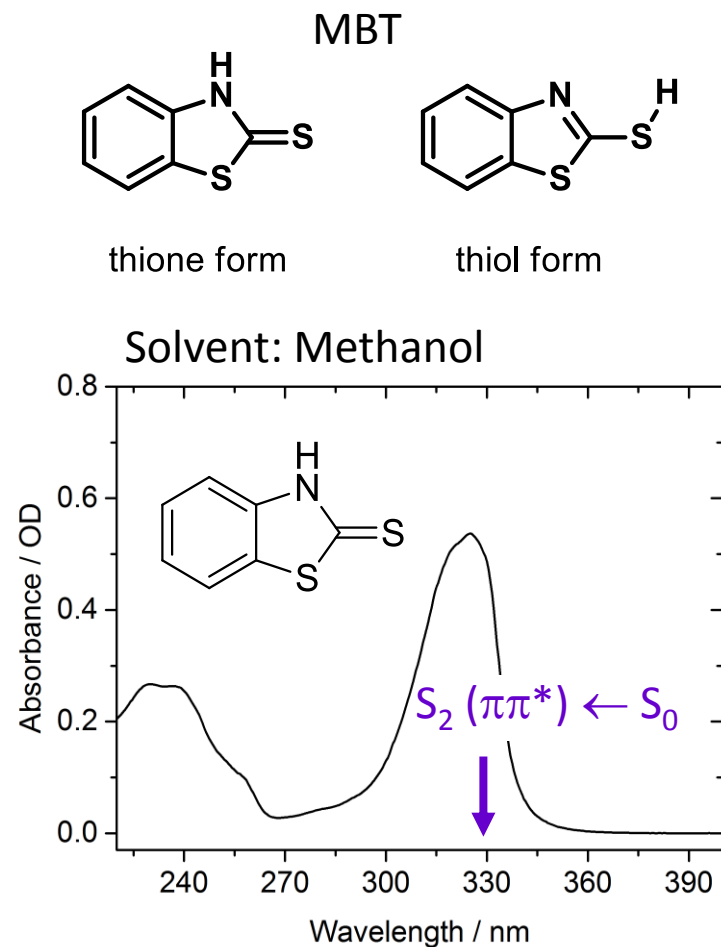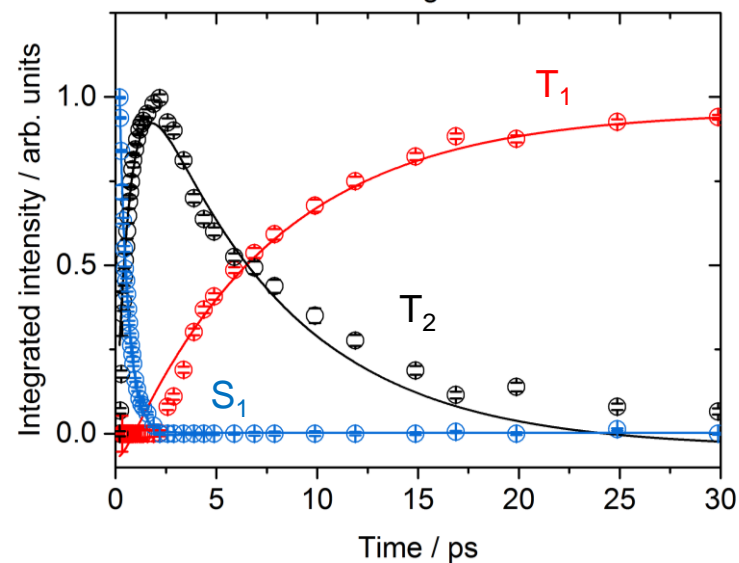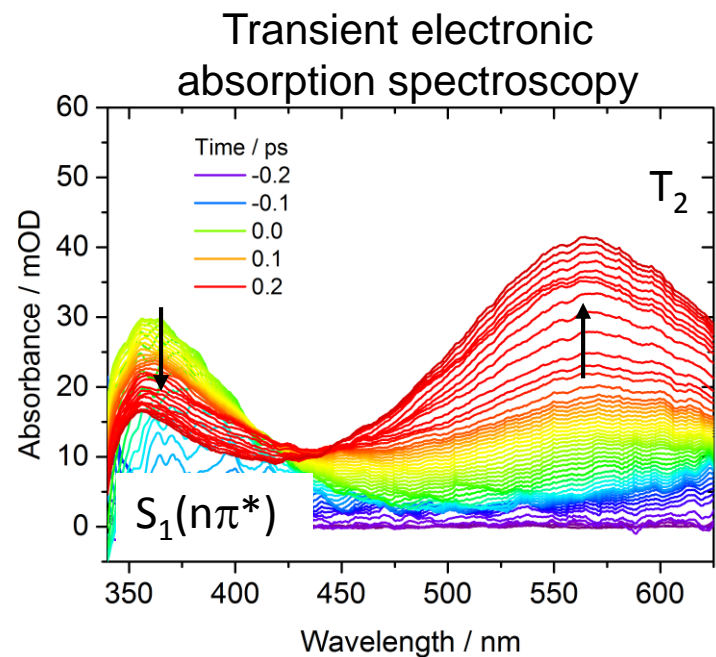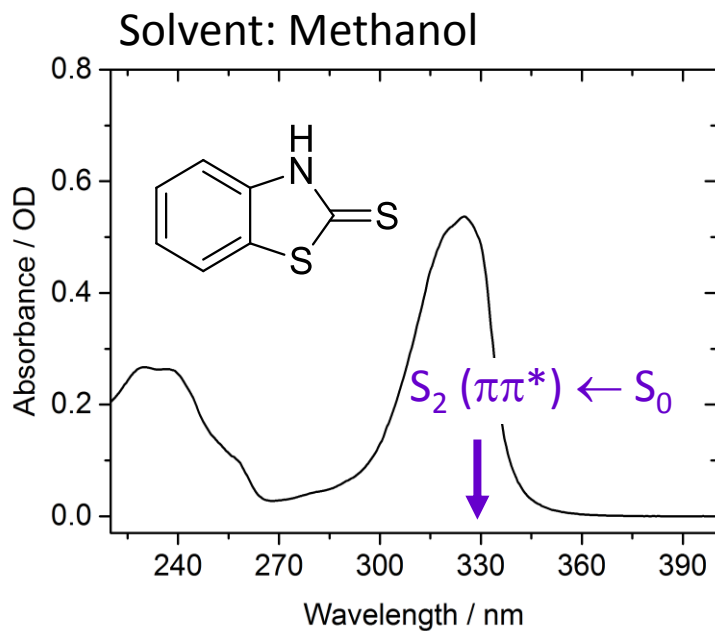
Similar photochemistry occurs in the thio-versions of the nucleobases, e.g. thiouracil.

3.2 Photochemical ring-opening as an example of isomerization dynamics
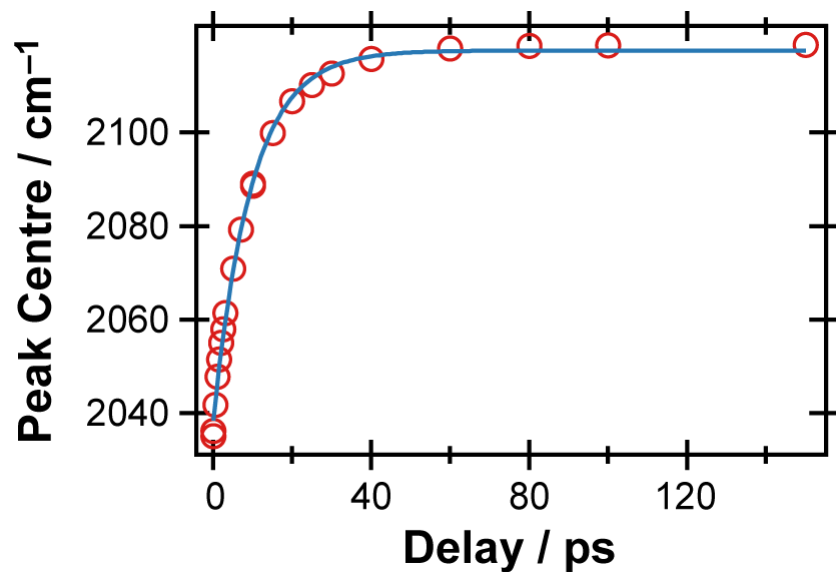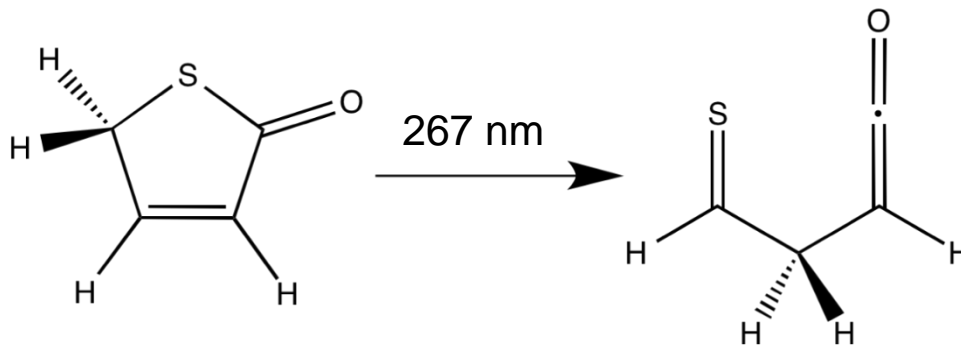

2(5*H*)-thiophenone → (267 nm) → thioaldehyde-ketene
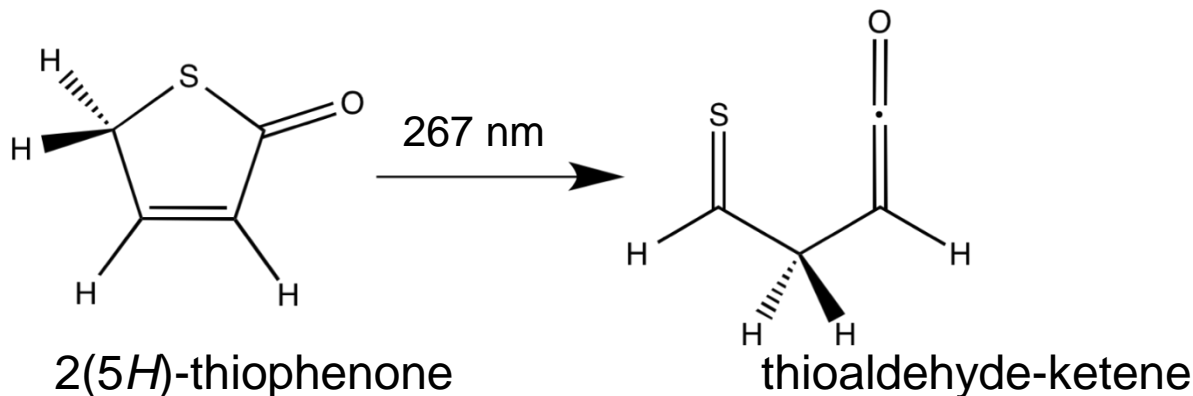
## Transient vibrational absorption spectroscopy
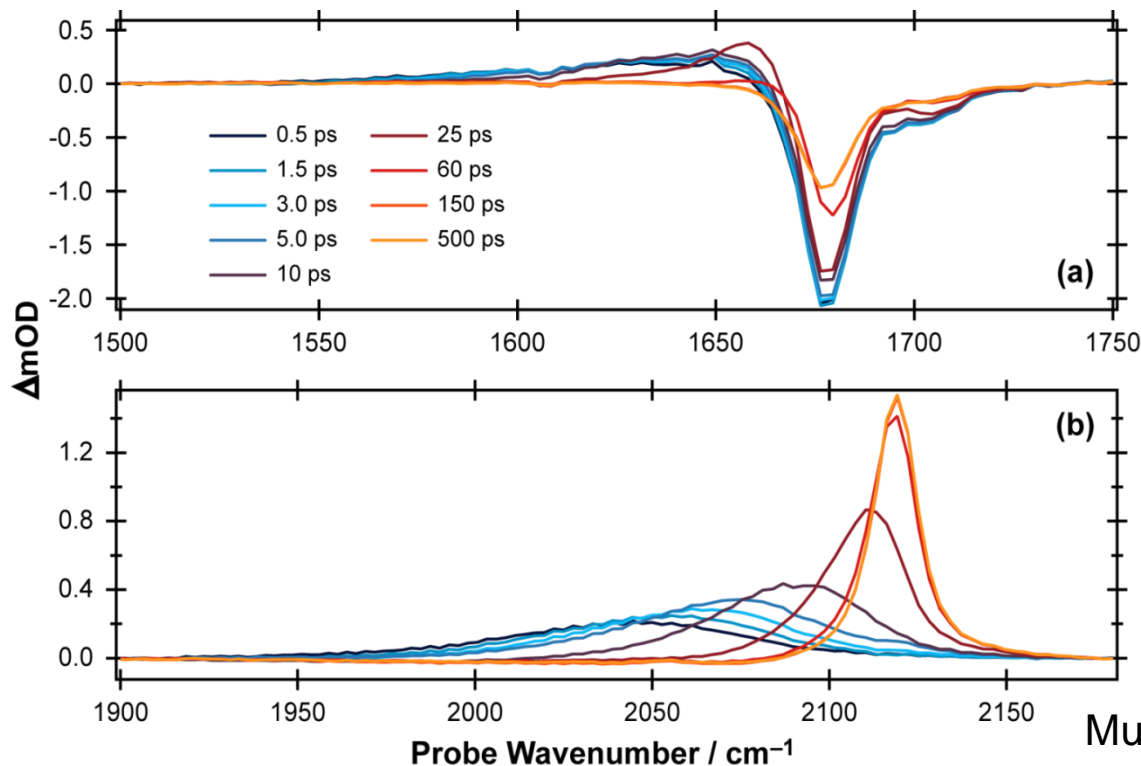
Partial recovery of parent S_0 bleach at longer delay times indicates re-formation of parent molecule.

Formation and vibrational cooling of ring opened (thioaldehyde ketene) product.

Murdock *et al*. PCCP **16**, 21271 (2014)

Sample kinetics: Shift of product peak centre because of vibrational relaxation of ring-opened thioaldehyde ketene product.
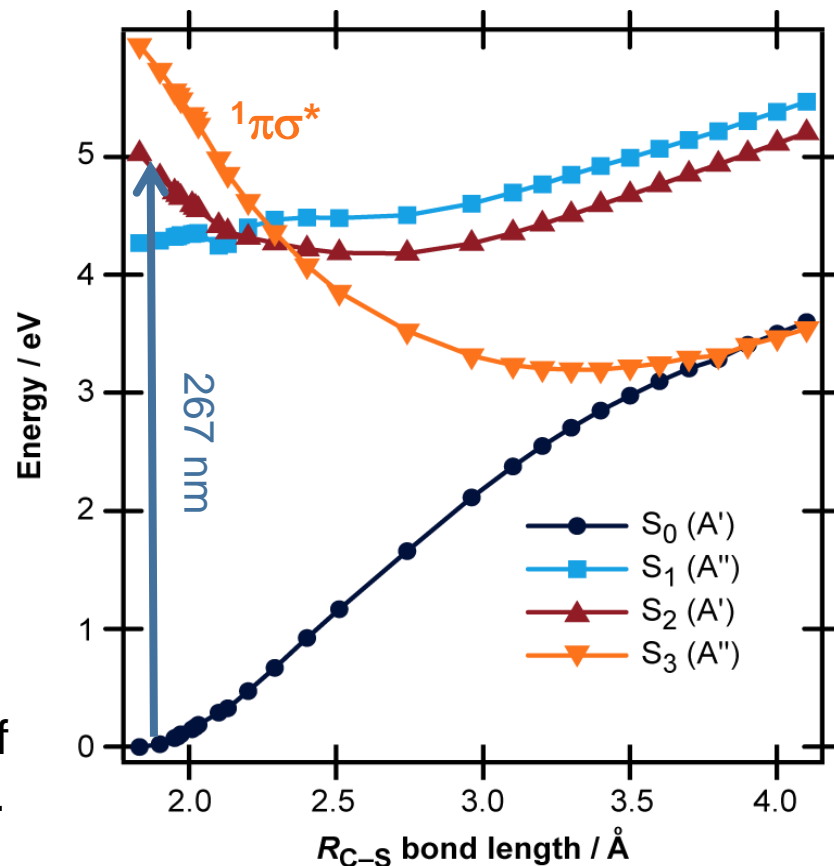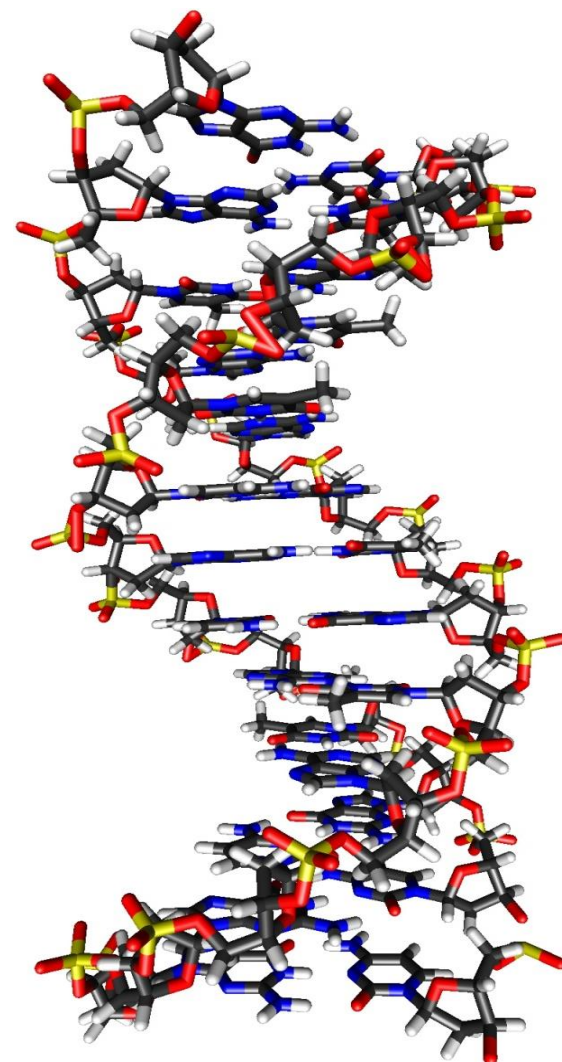
$\pi\sigma^*$ **potential** enables coupling to S_0 PES and isomerization

3.3 Internal conversion to the ground state – resistance to photodamage in DNA nucleobases

- $\pi^{*} \leftarrow \pi$ bands in DNA nucleobases span $\lambda = 200 - 300$ nm

- UV radiation may cause photo-damage
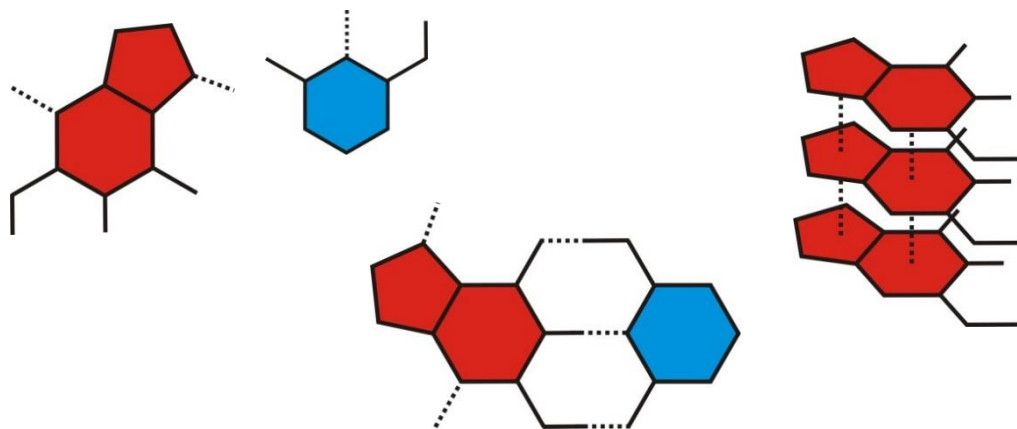
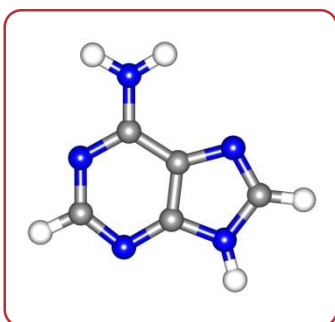- Efficient electronic deactivation reduces quantum yields of photo-lesions
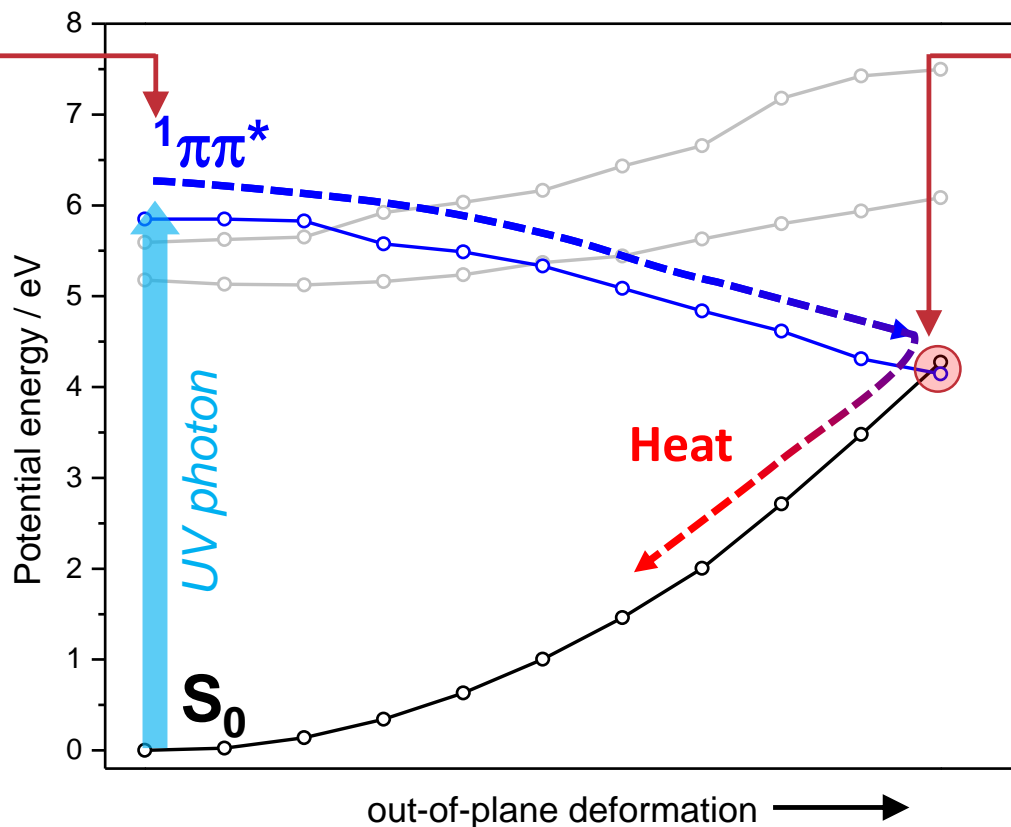
R. Improta, Chem. Rev. **16**, 3540 (2016)
K. Röttger *et al.*, Angew. Chem. Int. Ed. **54**, 14719 (2015)

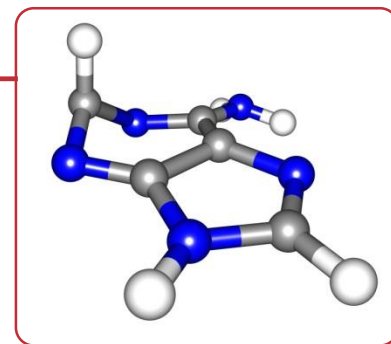**Example:** Ultrafast relaxation in UV excited adenine

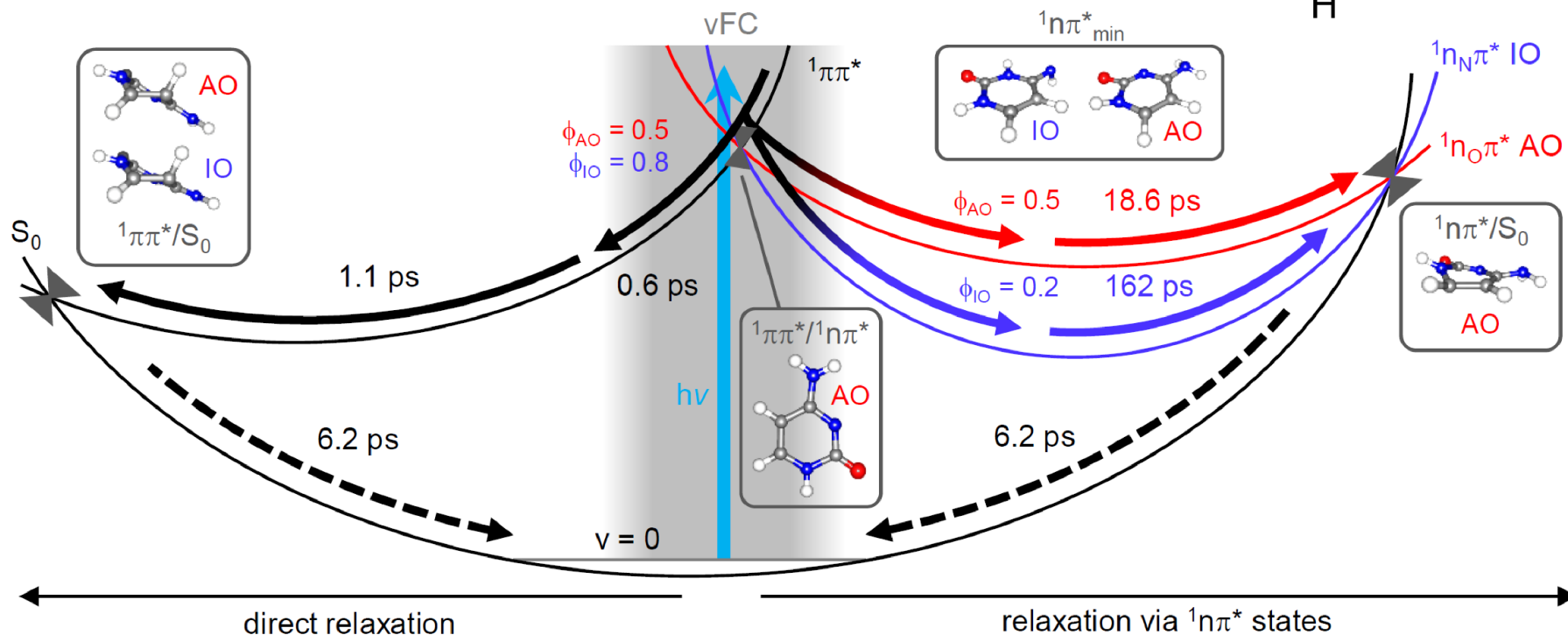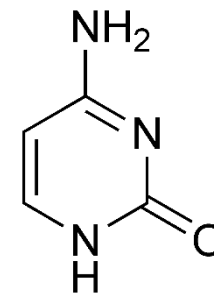Main deactivation pathway by barrierless ring deformation

Planar

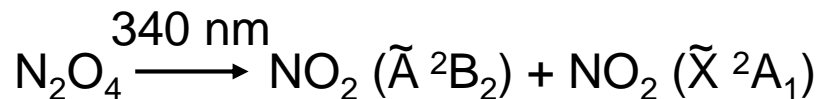Ring distortion

Conical Intersection

Yield > 90%

Kleinermanns *et al.*, Int. Rev. Phys. Chem. **32**, 308 (2013)
Barbatti *et al.*, PNAS **107**, 21453 (2010)

Example: Ultrafast relaxation pathways in cytosine deduced by transient absorption spectroscopy
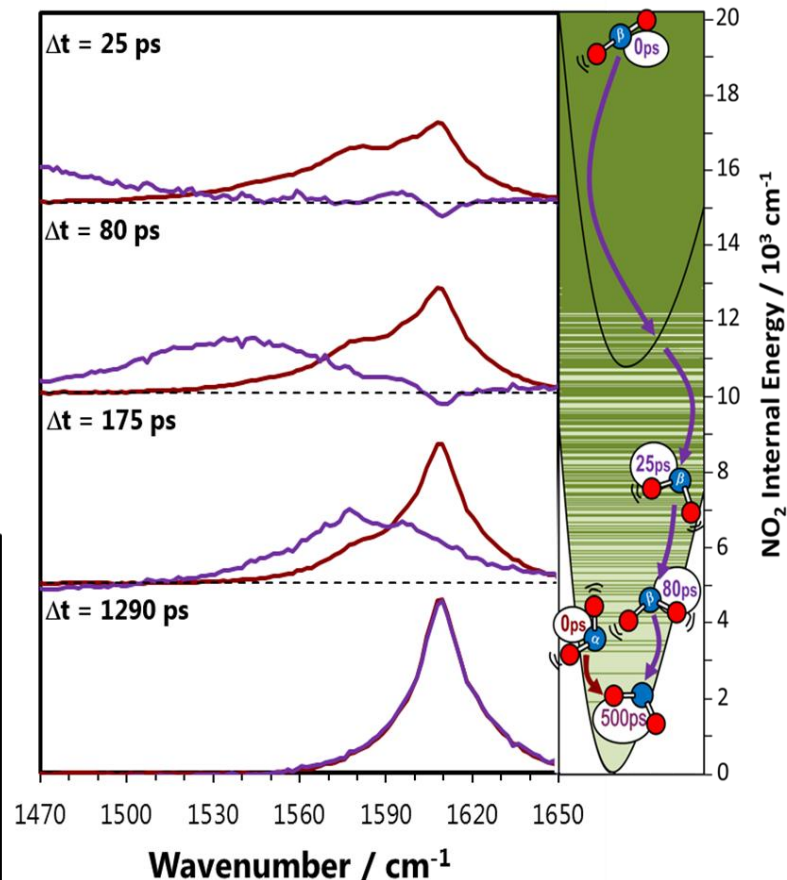

Röttger *et al.*, Faraday Discuss. **194**, 683 (2016)

3.4 Vibrational relaxation in solution

$$N_2O_4 \xrightarrow{\text{340 nm}} NO_2 \, (\tilde{A} \, ^2B_2) + NO_2 \, (\tilde{X} \, ^2A_1)$$

$$E_{int} \sim 22000 \text{ cm}^{-1}$$
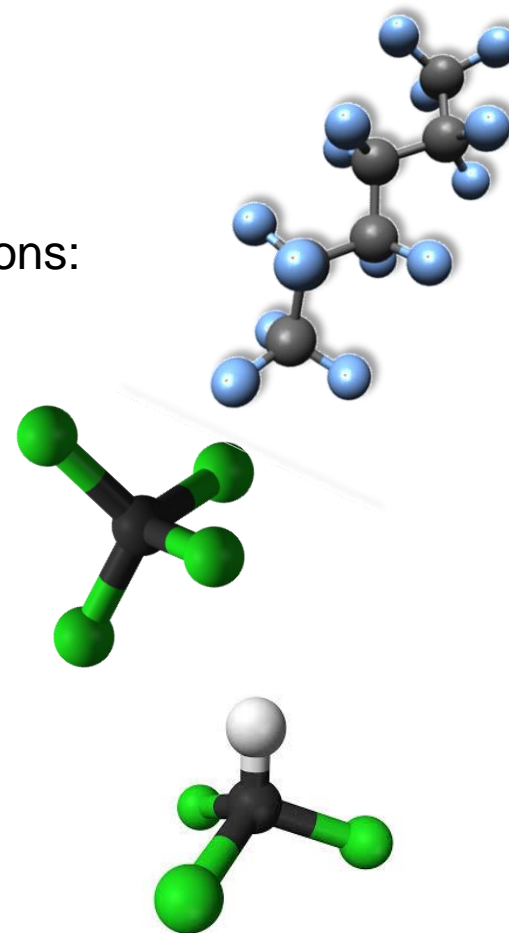
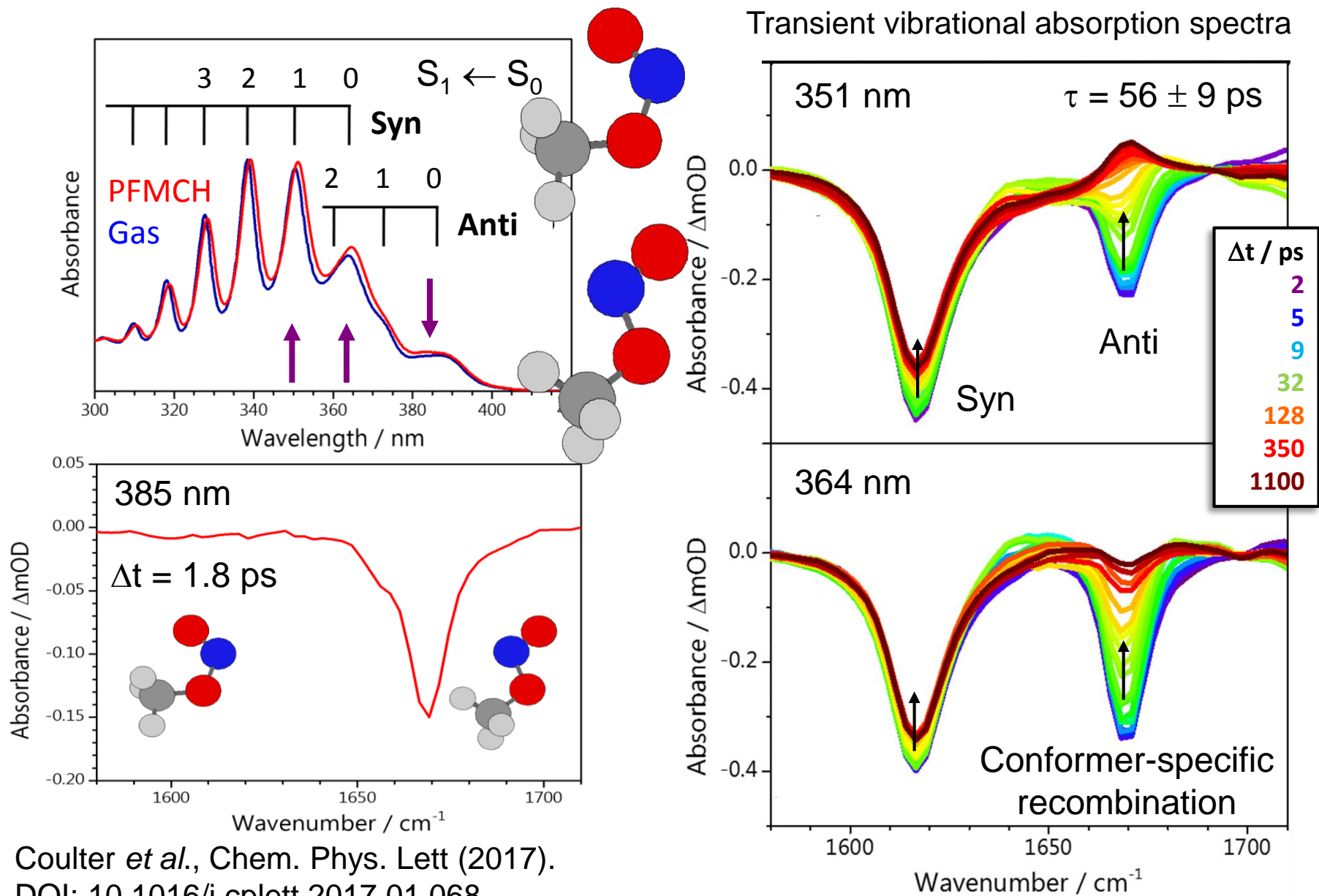Vibrational cooling of NO_2 in various solvents
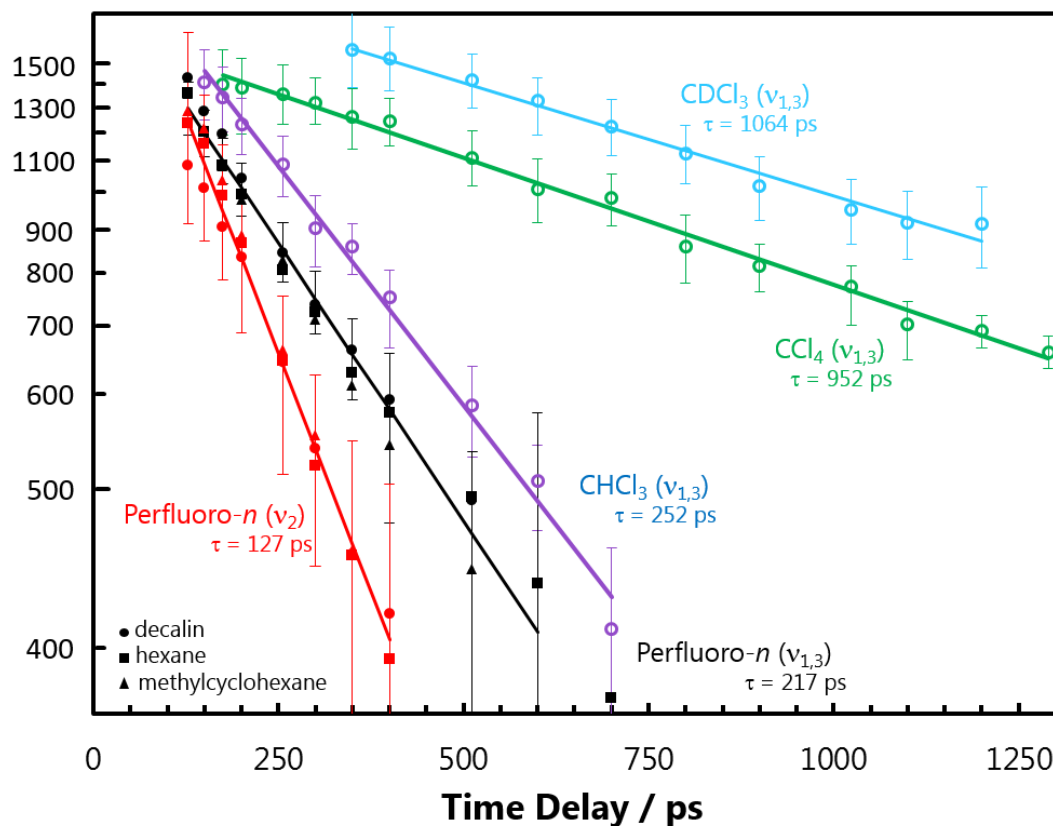
Transient vibrational absorption spectra

Rates of vibrational cooling of NO_2 are governed by:
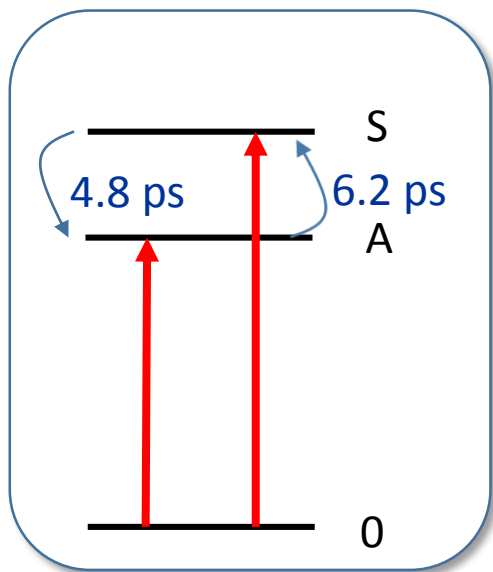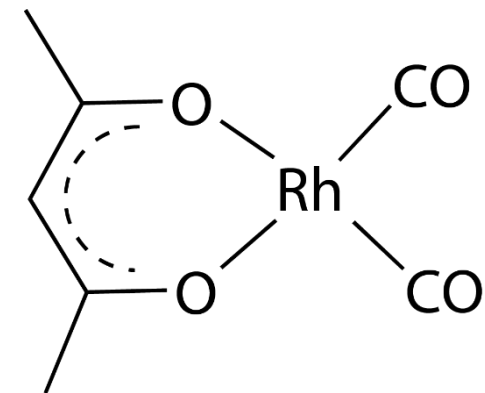
- Short-range repulsive interactions in perfluorocarbons:
  Impulsive coupling (**V – V** & **V – T**)

- Short-range attractive interactions in CCl_4:
  Anharmonic coupling (**V – V**)

- Longer-range Förster coupling (**V – V**)

3.5 Geminate recombination and relaxation in solution: CH₃ONO photolysis

Transient vibrational absorption spectra

$S_1 \leftarrow S_0$

3 2 1 0
Syn

2 1 0
Anti

PFMCH
Gas

Absorbance

300 320 340 360 380 400
Wavelength / nm

351 nm $\tau = 56 \pm 9$ ps

Absorbance / ΔmOD

0.00
-0.2
-0.4

Anti

Syn

Δt / ps
2
5
9
32
128
350
1100

385 nm

Δt = 1.8 ps

Absorbance / ΔmOD

0.05
0.00
-0.05
-0.10
-0.15
-0.20

1600 1650 1700
Wavenumber / cm⁻¹

364 nm

Absorbance / ΔmOD

0.0
-0.2
-0.4

Conformer-specific recombination

1600 1650 1700
Wavenumber / cm⁻¹

3.6 Intramolecular vibrational energy redistribution and relaxation from 2DIR

2DIR spectrum of coupled carbonyl symmetric (S) and anti-symmetric (A) stretching modes of a rhodium dicarbonyl complex

H.J.B. Marroux *et al.*, Phys. Chem. B **120**, 4125 (2016)
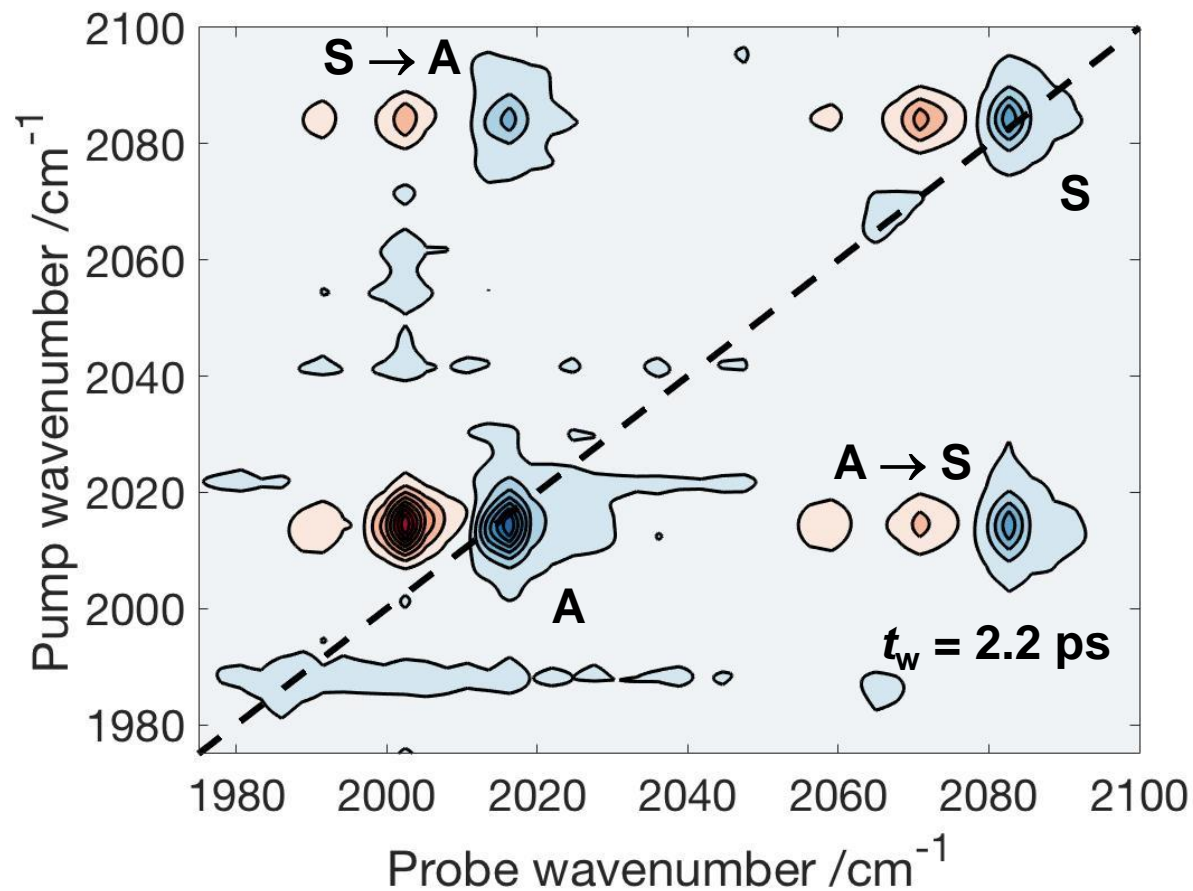
3.7 Relaxation of electronic states observed by 2D electronic spectroscopy

Example: tryptophan to heme electron transfer in myoglobin (MbCN)

- Excited Trp[7] relaxes by energy transfer to the heme;
- Trp[14] relaxes by electron transfer to the heme in < 40 ps
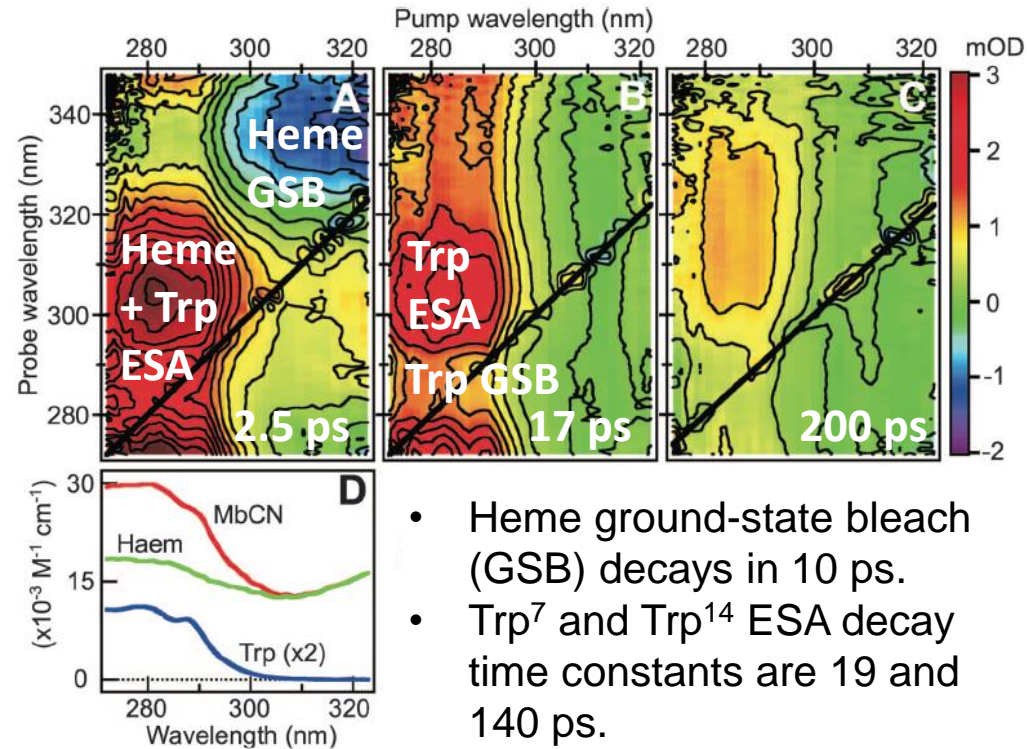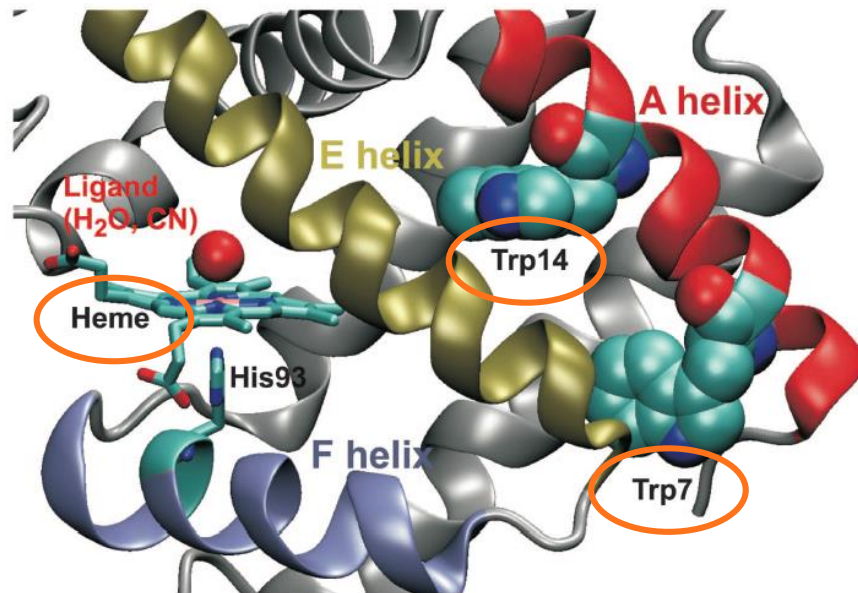
- Heme ground-state bleach (GSB) decays in 10 ps.
- Trp[7] and Trp[14] ESA decay time constants are 19 and 140 ps.
- >2.5 ns lifetime feature evident in panel C results from Trp[14] electron transfer to heme.

C. Consani *et al.*, Science **339**, 1586 (2013)

4.0 Conclusions

A variety of experimental techniques allow us to study mechanisms of molecular relaxation in the gas phase and in solution.

In general, there is competition between relaxation pathways on ultrafast timescales.

We now have experimental tools to identify non-adiabatic dynamics at **conical intersections**, and to observe energy flow within molecules and from molecules to the surrounding medium.

QM techniques are being developed to model accurately the non-adiabatic chemical dynamics.

Transient absorption spectroscopy measurements in weakly interacting solvents can probe processes which are difficult to observe using established gas-phase techniques.

5.0 Current and future challenges

Observation of isomerization (e.g. ring-opening) pathways in the gas phase.

- Ultrafast photoionization and photoelectron spectroscopies
- Coulomb explosion techniques

Direct observation of dynamics at conical intersections.

- Ultrafast XUV and X-ray spectroscopy methods
- Coherent spectroscopy techniques

Observation of solvent response to reaction and photoexcitation in solution.

- THz spectroscopy
- Ultrafast X-ray scattering

Time-resolved diffraction to image evolving molecular structures during reactions – "*molecular movies*".

6.0 Acknowledgements

Philip Coulter

Michael Grubb

Daisuke Koyama

Hugo Marroux

Dan Murdock

Gareth Roberts

Katharina Röttger

Mike Ashfold