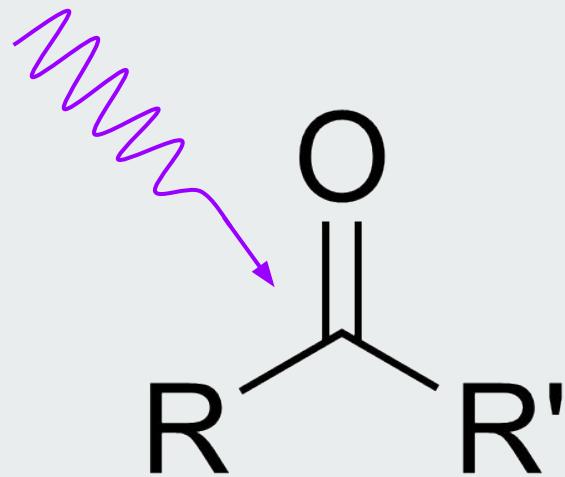

Rationalising carbonyl photochemistry through theory and structure

Keiran Rowell - 7th Feb 2019

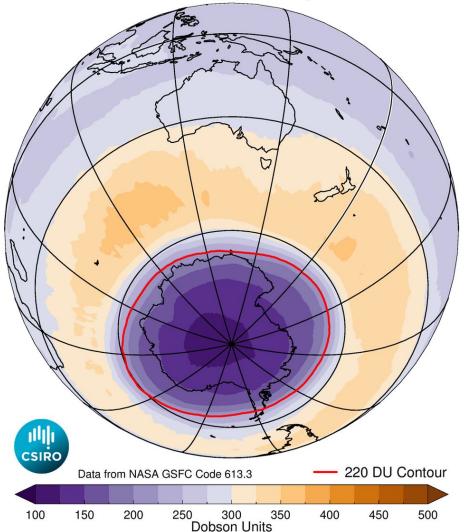
Supervisors: Prof. Scott Kable, A/Prof. Meredith Jordan



Atmospheric chemistry & its challenges

Ozone hole

OMI Ozone Oct 1-15 average, 2015



Kyoto protocol

London 1952 smog



Clean Air Act

Photochemical smog



Environmental Protection Agency

Largely photochemically driven.

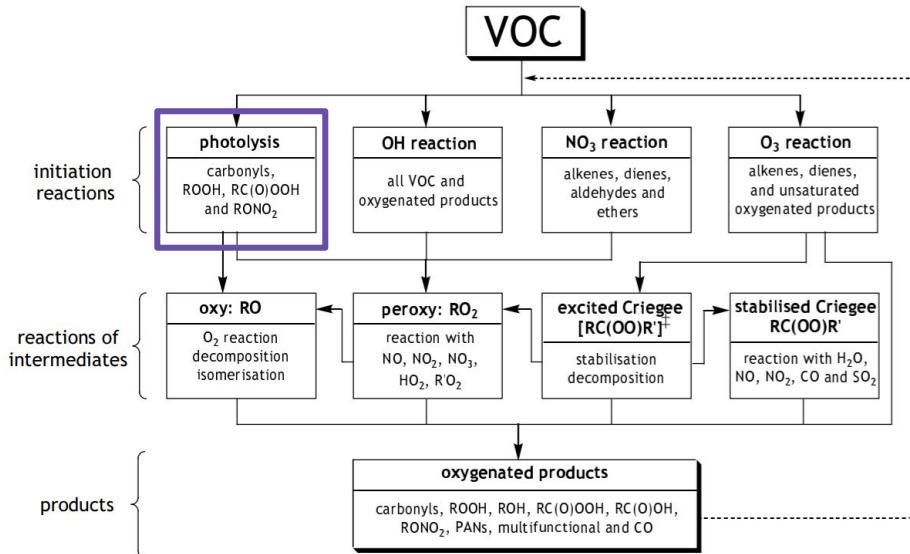
Predictive modelling could have prevented disaster!

Modelling atmospheric chemistry

Field measurements



Computer modelling



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Carbonyls in the Atmosphere

Jenkin M., Saunders S., Pilling M., Atmospheric Environment, 1997, 31, 81-104

The atmosphere is highly oxidising

- ▶ Volatile organic compounds (VOCs) emitted by industrial & biogenic
- ▶ Carbonyls produced on all VOC degradation pathways to CO₂
- ▶ 100s of different carbonyls
- ▶ Larger biogenic carbonyls can have complex structures

Models approximate w/ generic rules!

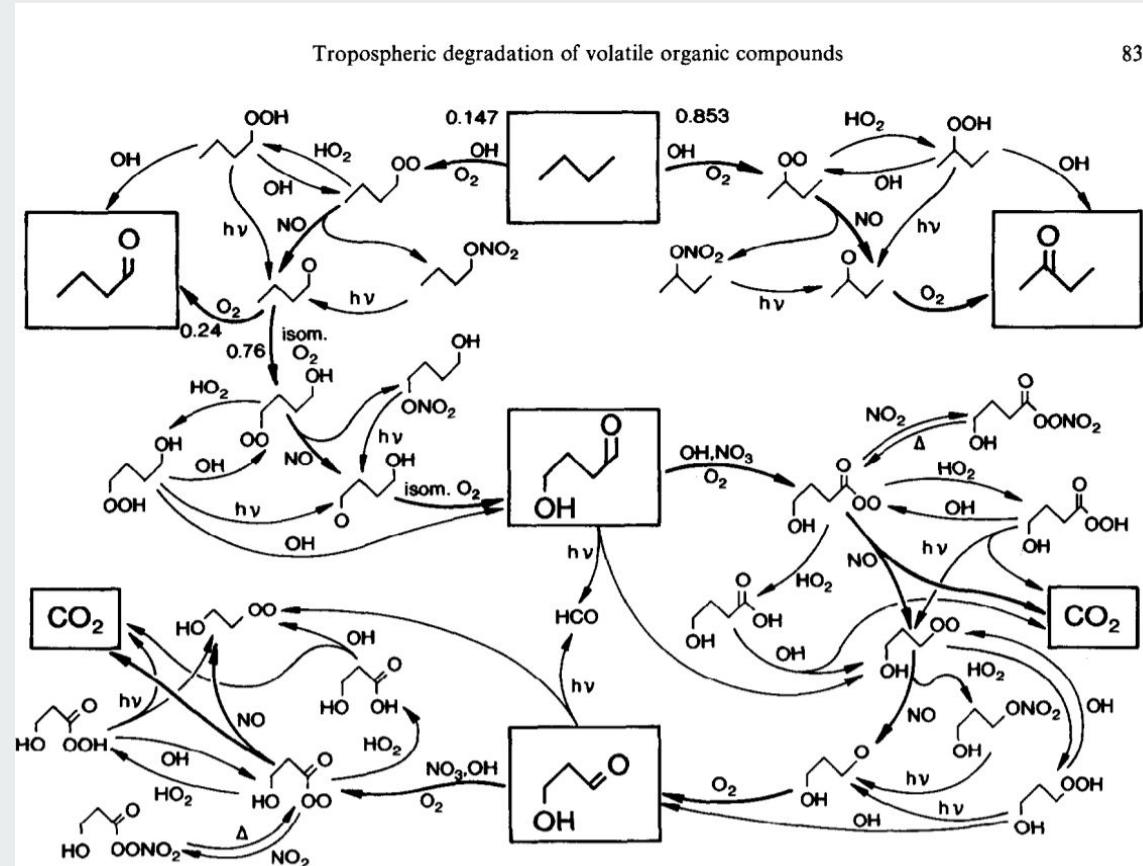
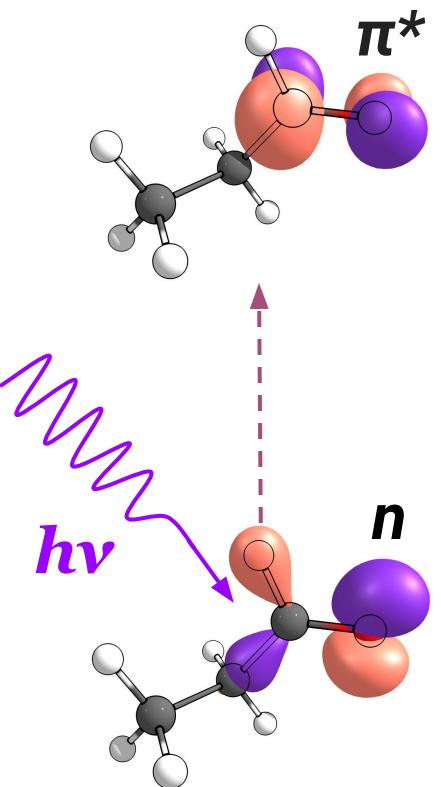


Fig. 1. Schematic representation of the degradation of butane, showing most of the chemistry which makes up the mechanism for this compound.

Known photochemistry: Norrish reactions (Types I & II)

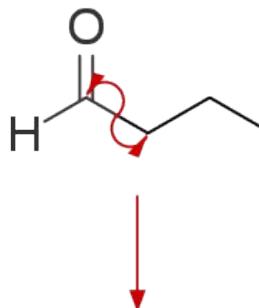


Electronically excited reactions

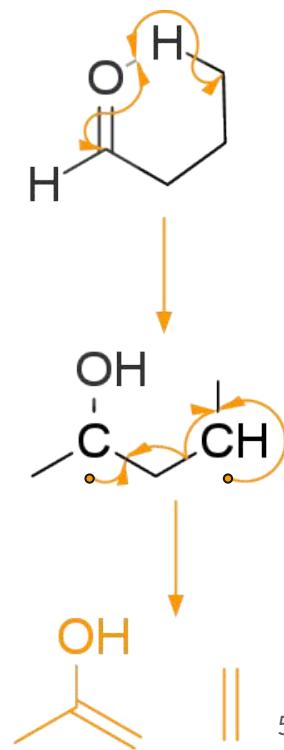
- $n \rightarrow \pi^*$ HOMO-LUMO gap small enough for UV excitation (330-300nm)
- Discovered by Norrish *et al.* in 1930s
- Norrish I (NTI) produces radicals
- NTII produces an enol, which are implicated in organic acid formation

Quantum yields (QY) known for prototypical carbonyls

Norrish I



Norrish II



Photolysis rate coverage in models is limited

Carbonyls	Photoproducts	ID	Rate
HCHO	→ HCO + H	(J ₁₁)	4.642×10^{-5}
	→ CO + H ₂	(J ₁₂)	6.853×10^{-5}
CH ₃ CHO	→ HCO + CH ₃	(J ₁₃)	7.344×10^{-6}
C ₂ H ₅ CHO	→ HCO + C ₂ H ₅	(J ₁₄)	2.879×10^{-5}
n-C ₃ H ₇ CHO	→ HCO + n-C ₃ H ₇	(J ₁₅) ^b	2.792×10^{-5}
	→ CH ₃ CHO + C ₂ H ₄	(J ₁₆)	1.675×10^{-5}
i-C ₃ H ₇ CHO	→ HCO + i-C ₃ H ₇	(J ₁₇) ^b	7.914×10^{-5}
CH ₂ =C(CH ₃)CHO	→ CH ₃ C=CH ₂ + HCO	(J ₁₈) ^b	1.140×10^{-5}
	→ CH ₂ =C(CH ₃)CO + H	(J ₁₉) ^b	1.140×10^{-5}
CH ₃ C(O)CH ₃	→ CH ₃ CO + CH ₃	(J ₂₁)	7.992×10^{-7}
CH ₃ C(O)C ₂ H ₅	→ CH ₃ CO + C ₂ H ₅	(J ₂₂) ^b	5.804×10^{-6}
CH ₃ C(O)CH=CH ₂	→ CH ₃ CH=CH ₂ + CO	(J ₂₃)	1.836×10^{-5}
	→ CH ₃ CO + CH=CH ₂	(J ₂₄) ^b	1.836×10^{-5}
α-Dicarbonyls			
(CHO) ₂	→ CO + CO + H ₂	(J ₃₁)	6.845×10^{-5}
	→ CO + HCHO	(J ₃₂)	1.032×10^{-5}
	→ HCO + HCO	(J ₃₃)	3.802×10^{-5}
CH ₃ C(O)CHO	→ CH ₃ CO + HCO	(J ₃₄) ^b	1.537×10^{-4}
CH ₃ C(O)C(O)CH ₃	→ CH ₃ CO + CH ₃ CO	(J ₃₅) ^b	3.326×10^{-4}

Norrish I

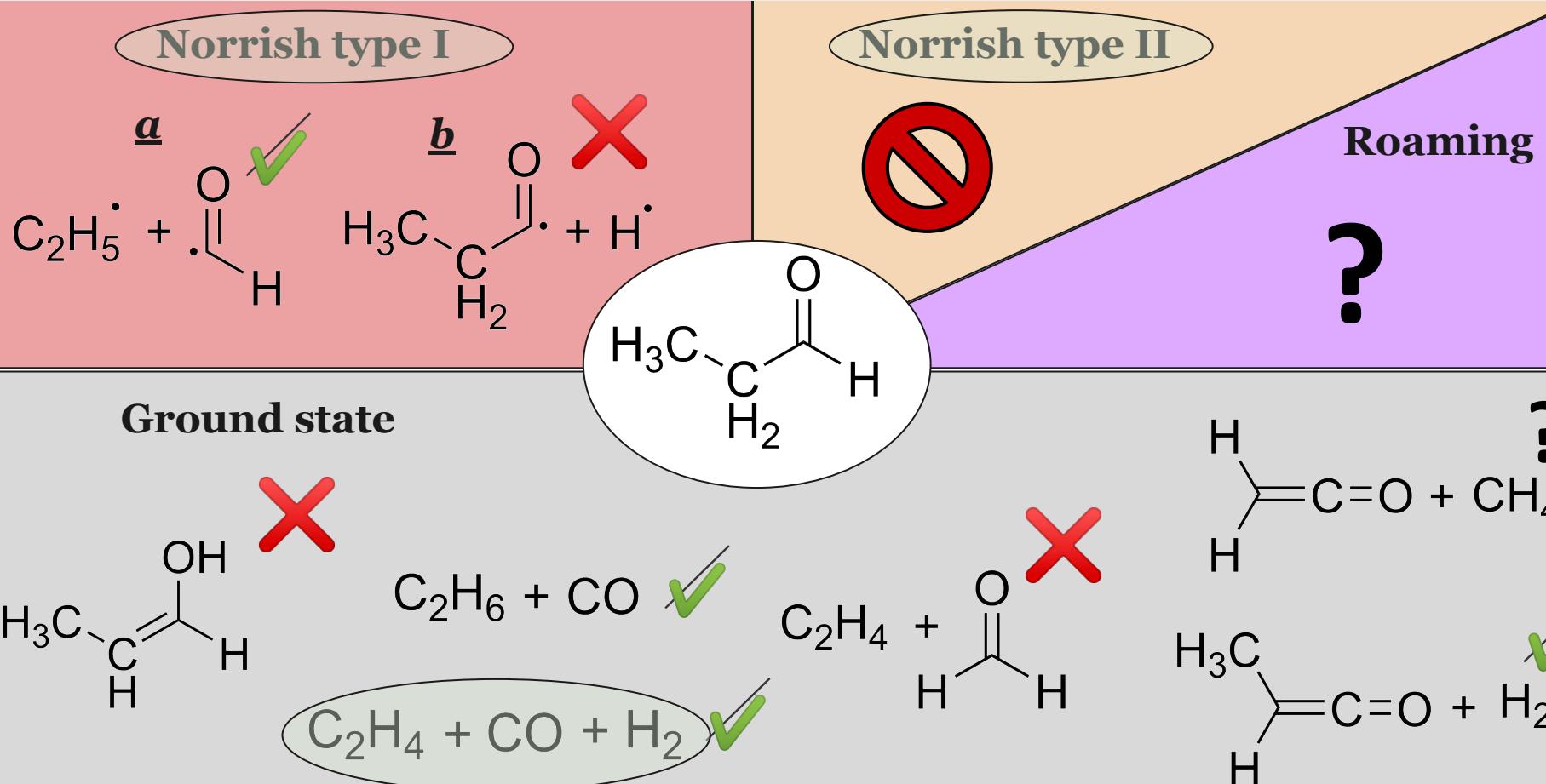
Norrish II

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Approximate hierarchy of information sources

- 1) Experimental data (evaluated)
- 2) Experimental data (direct)
- 3) SARs (published)
- 4) SARs/analogy assumptions
- 5) Theoretical studies

The past 10 years: photochemistry beyond NTI & NTII

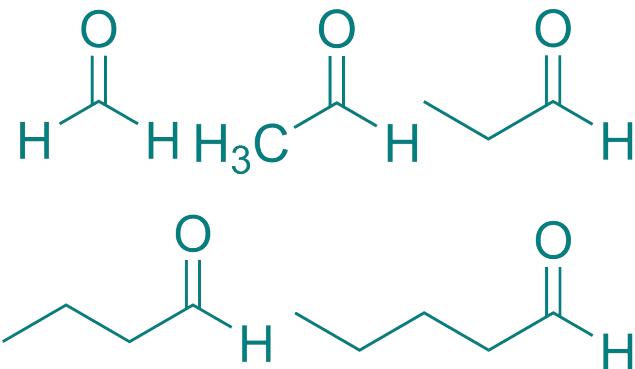


Aims

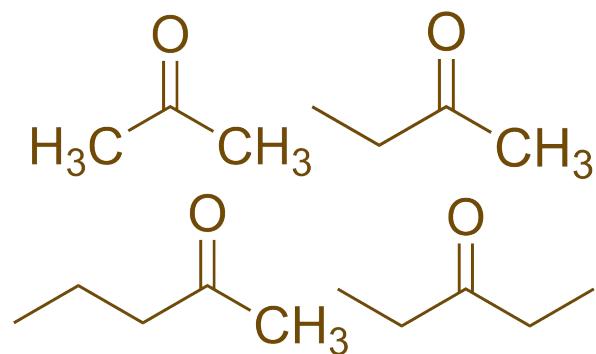
- **SARs for carbonyl photochemistry**
 - Improve **MCM** rates — **NTI** & **NTII** need to account for structure
 - Expand **ground state photochemistry** — currently ignored in MCM!
 - Complete photochemistry of **20 carbonyls** to generalise to **100s of structures**
- **Guide discovery & interpretation of photolysis channels**
 - Reaction thresholds, distinguish mechanisms, kinetics & dynamics
 - Explain and predict the results from FT-IR & VMI experiments
- **Develop inexpensive & reliable computational scheme for photochemistry**
 - Electronic structure problems **more difficult with photolysis**
 - Traditional approaches use **very expensive** and cumbersome ***ab initio*** methods
 - Need validated, efficient scheme to predict photochemistry in a consistent way

My carbonyl data set

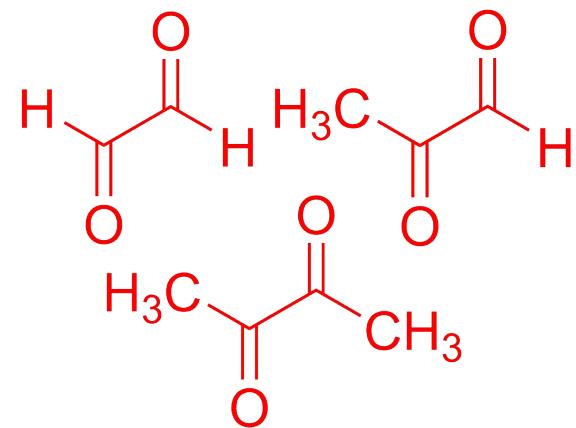
Linear aldehydes



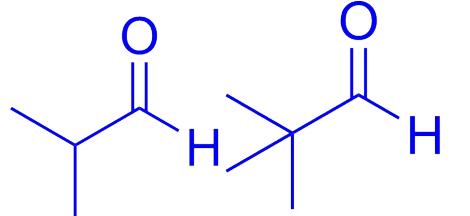
Ketones



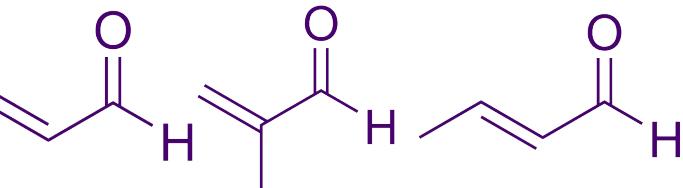
Dicarbonyls



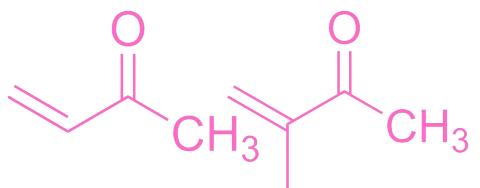
Branched aldehydes



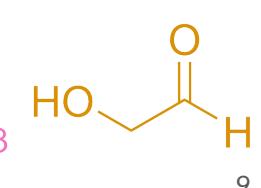
Enals



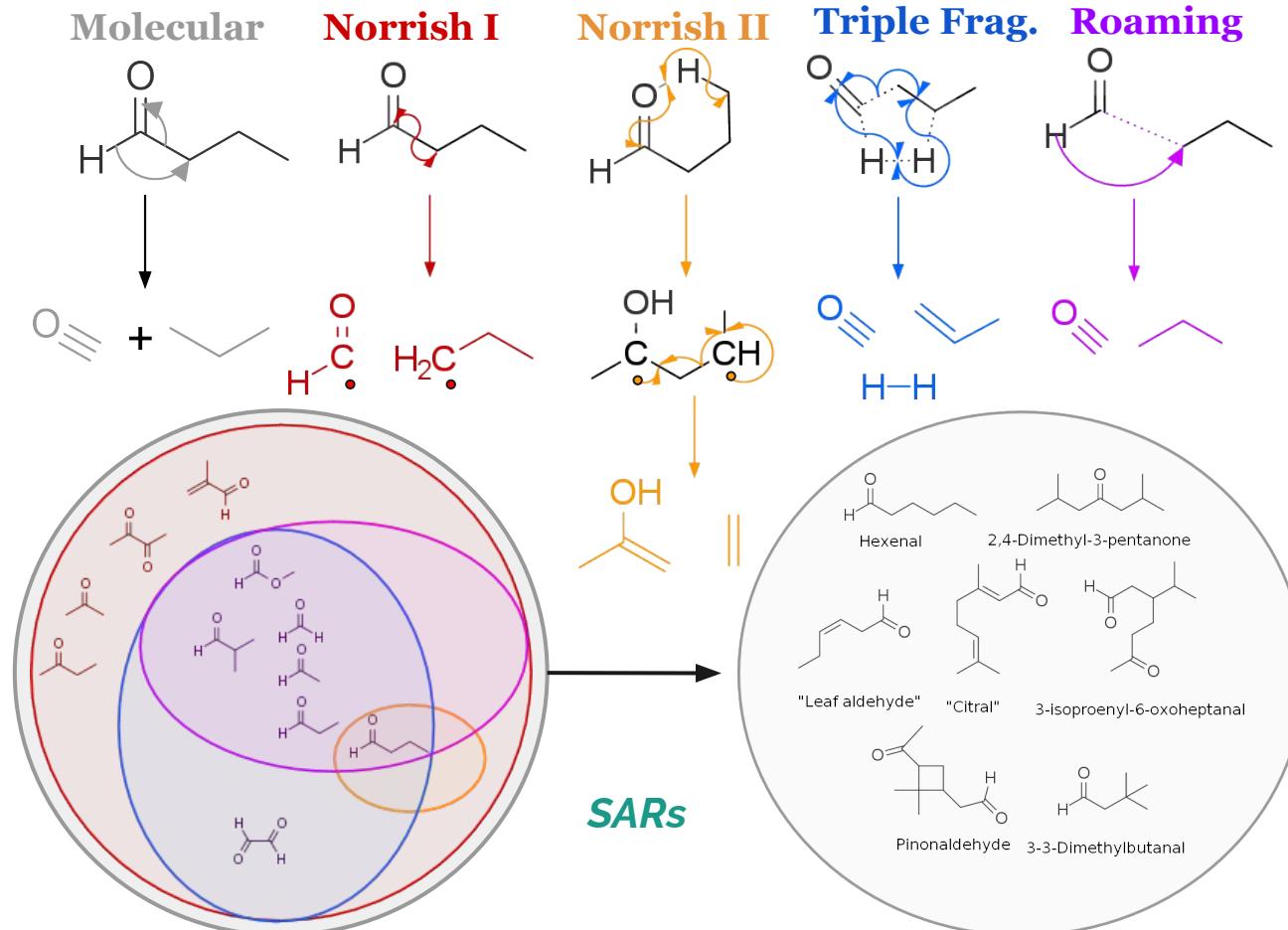
Enones



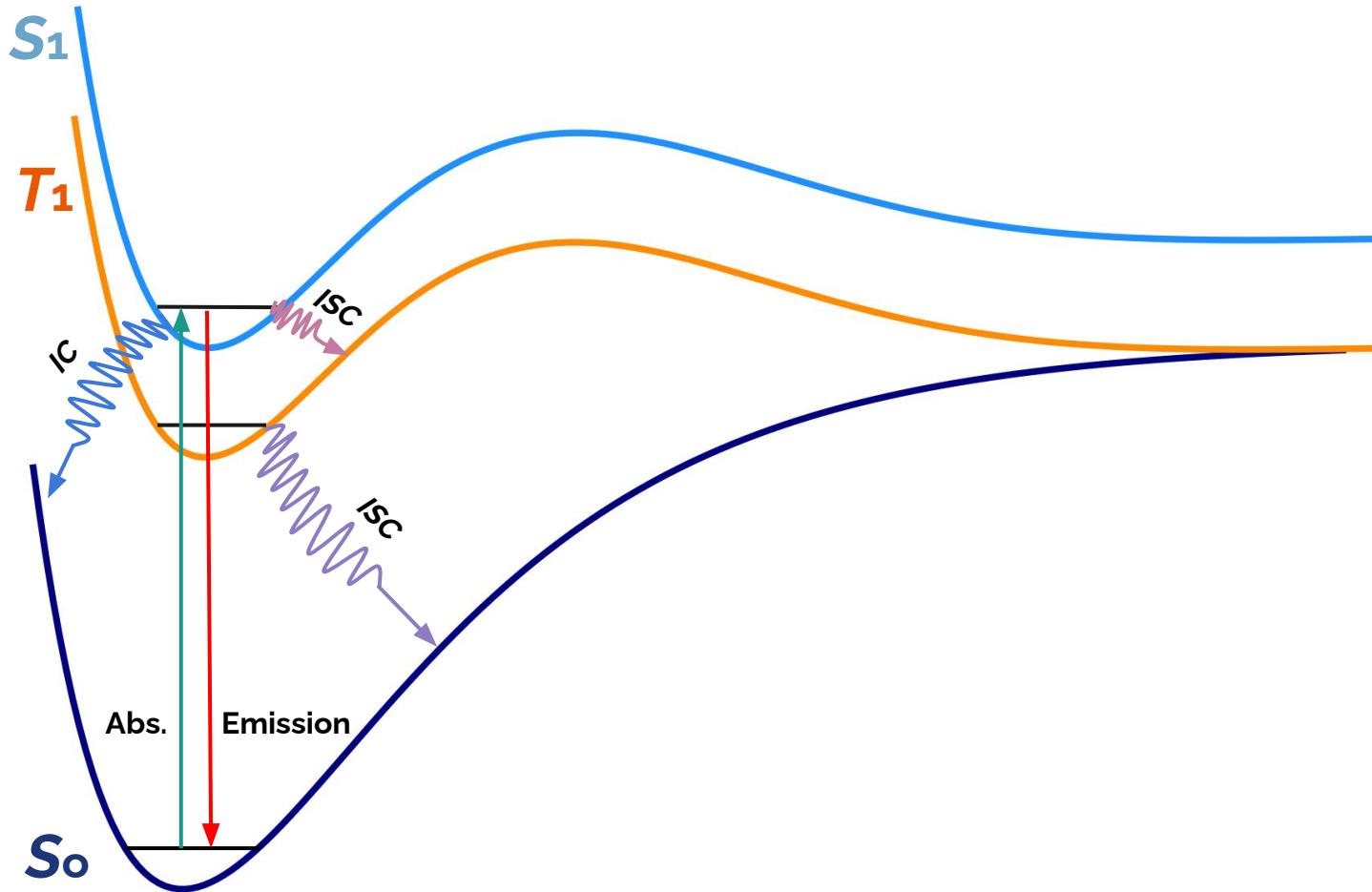
Carbohydrate

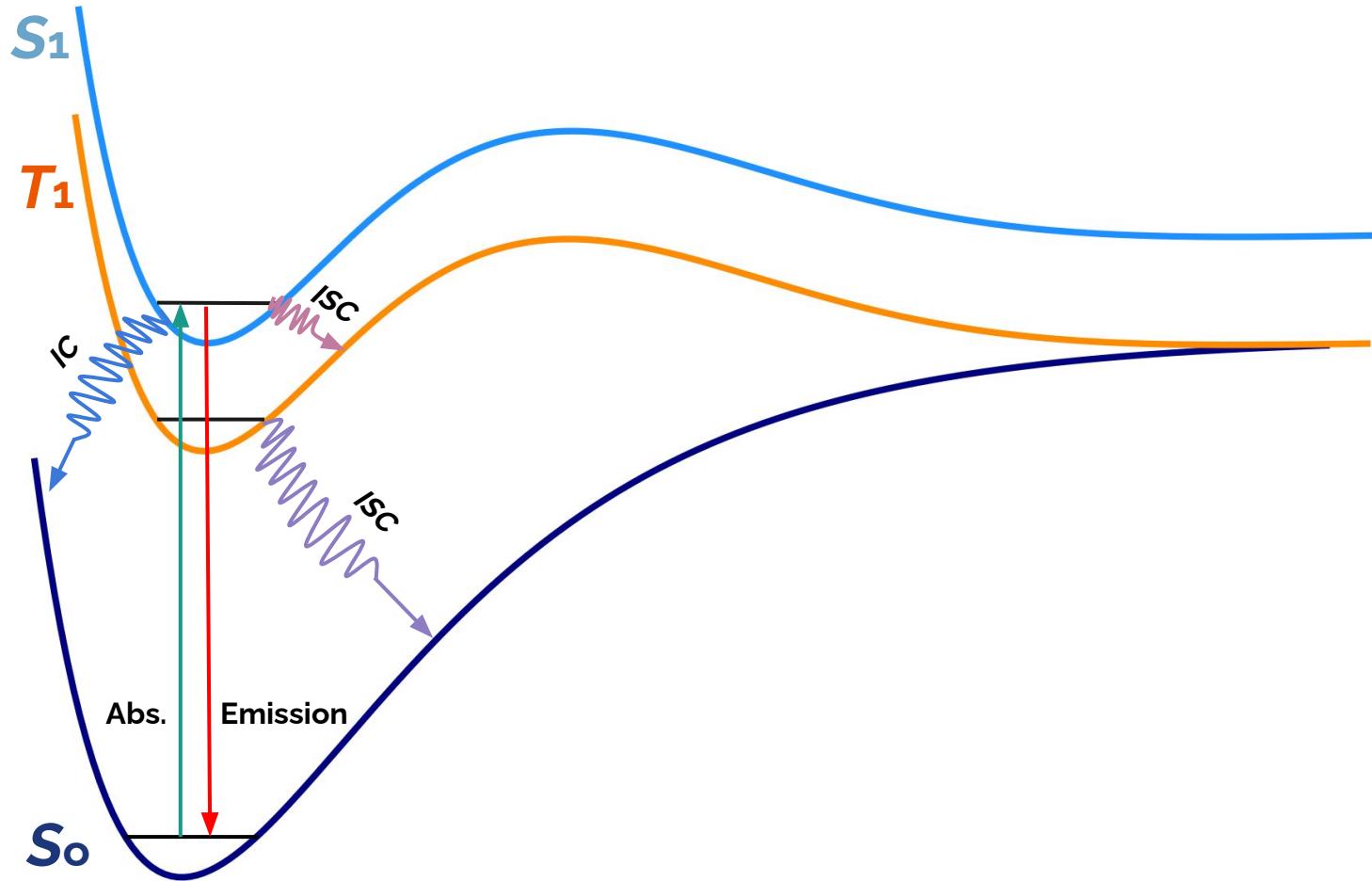


SARs for photochemistry by carbonyl classes

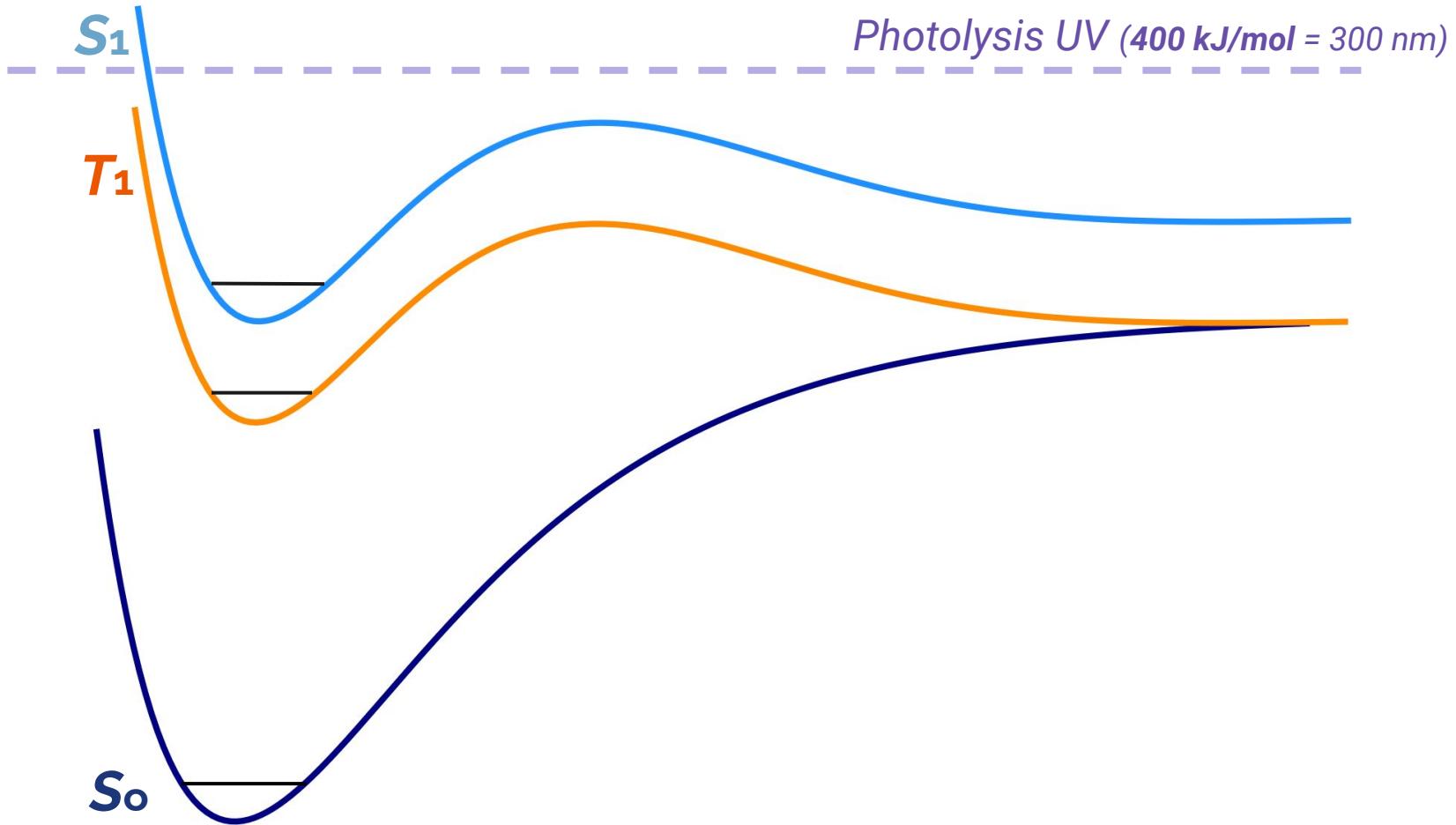


Theory & Electronic Surfaces

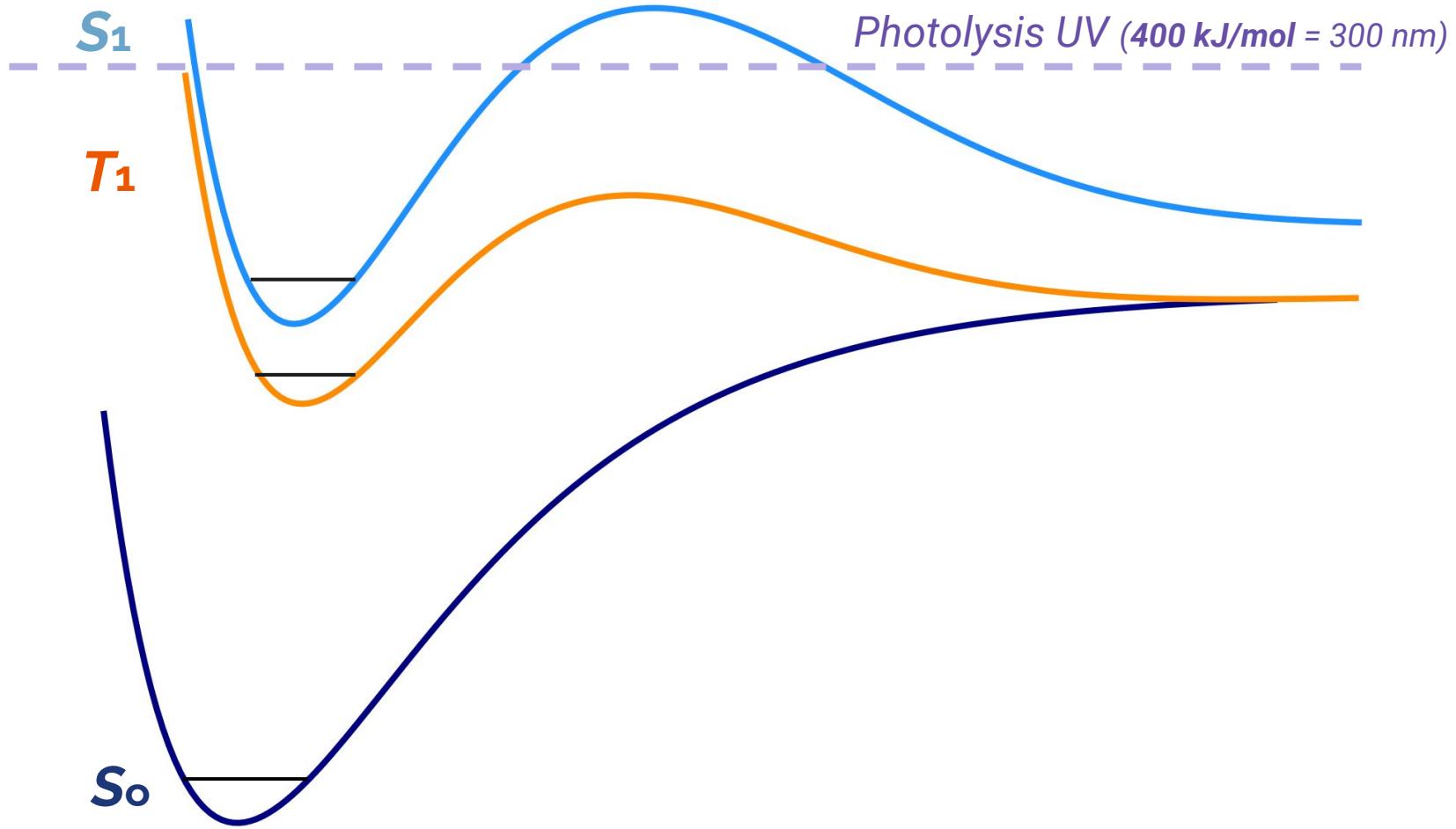




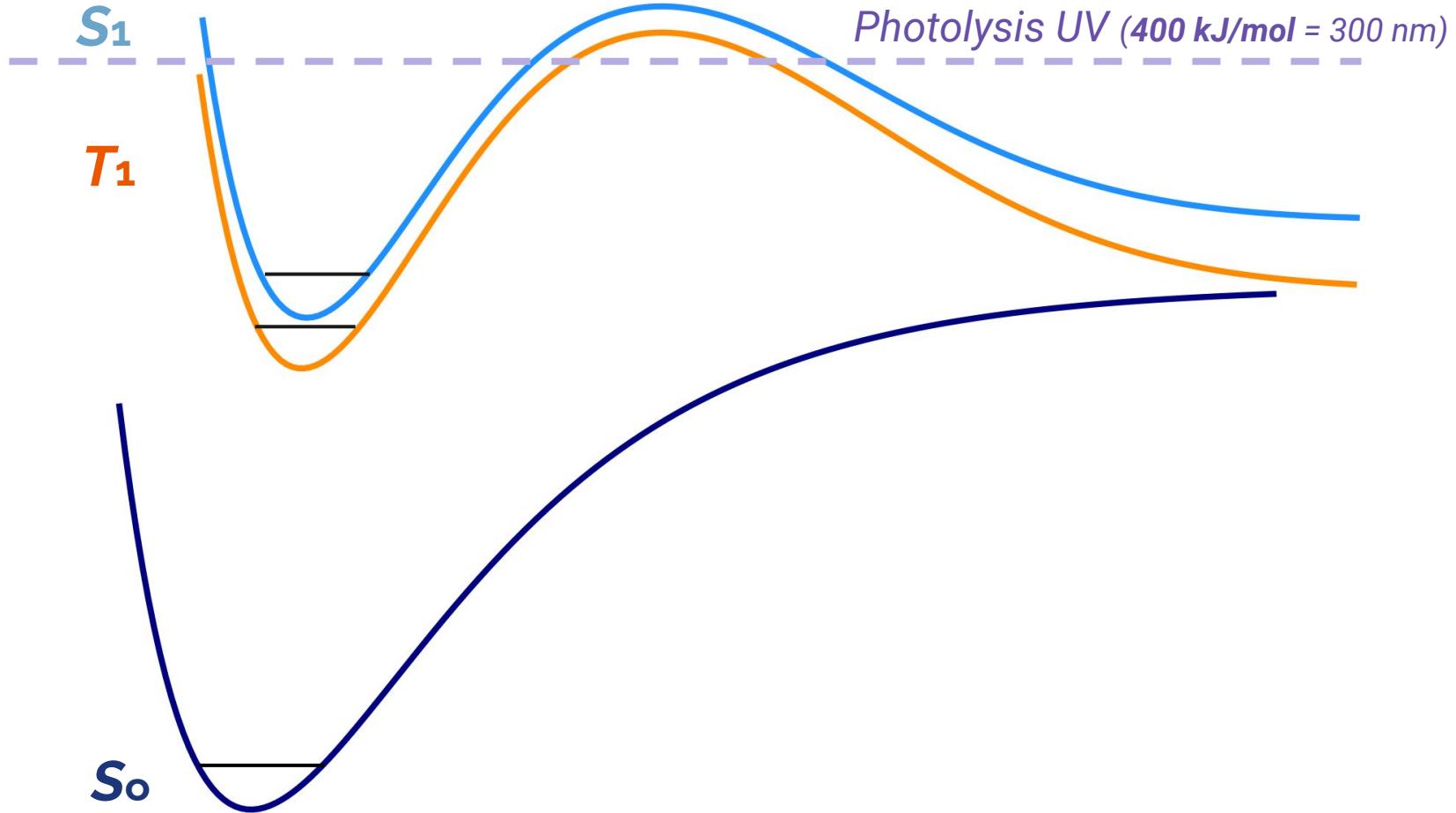
Theory & Electronic Surfaces



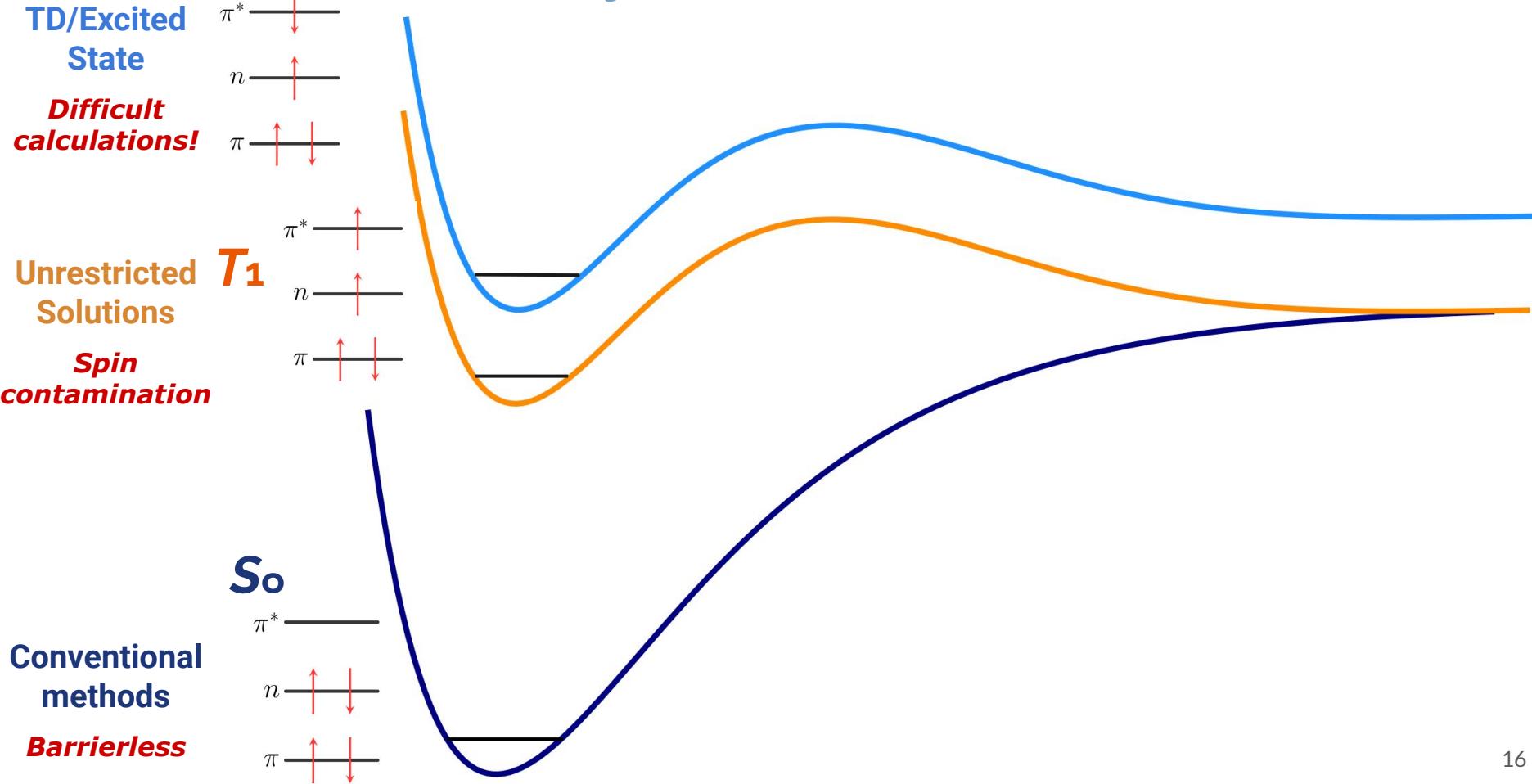
Theory & Electronic Surfaces



Theory & Electronic Surfaces



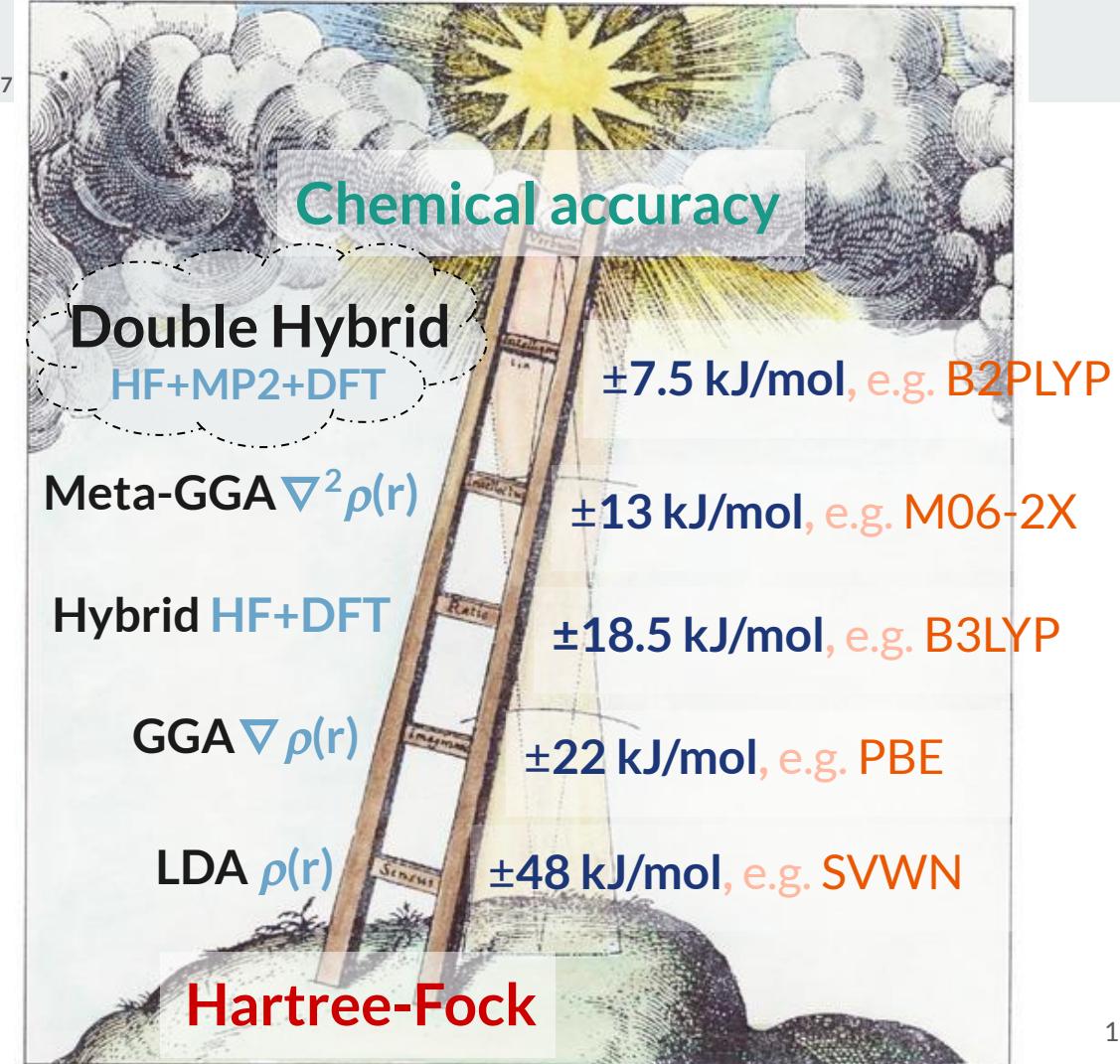
Theory & Electronic Surfaces



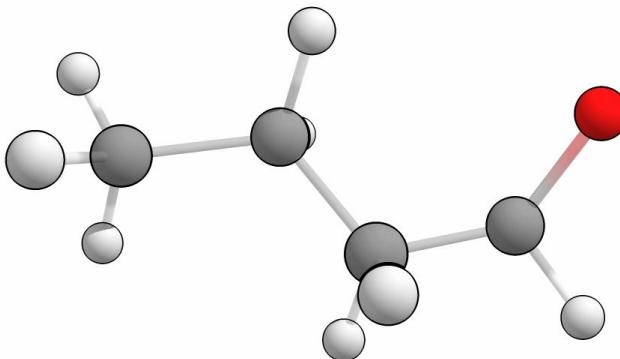
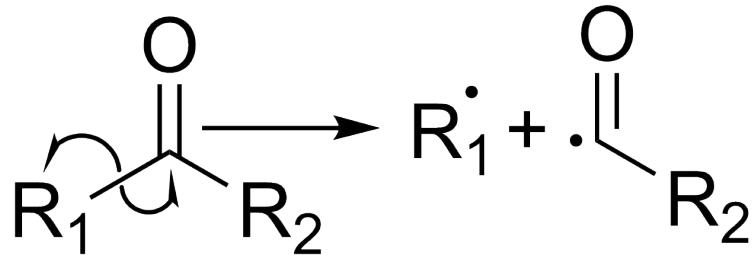
My Methods

- ▶ Photochemical barriers predicted must be accurate ($\pm 10 \text{ kJ/mol}$)
- ▶ Wavefunction methods *too expensive*
- ▶ Excited states greatly complicate theoretical approaches

Photochemical calculations are
more arduous

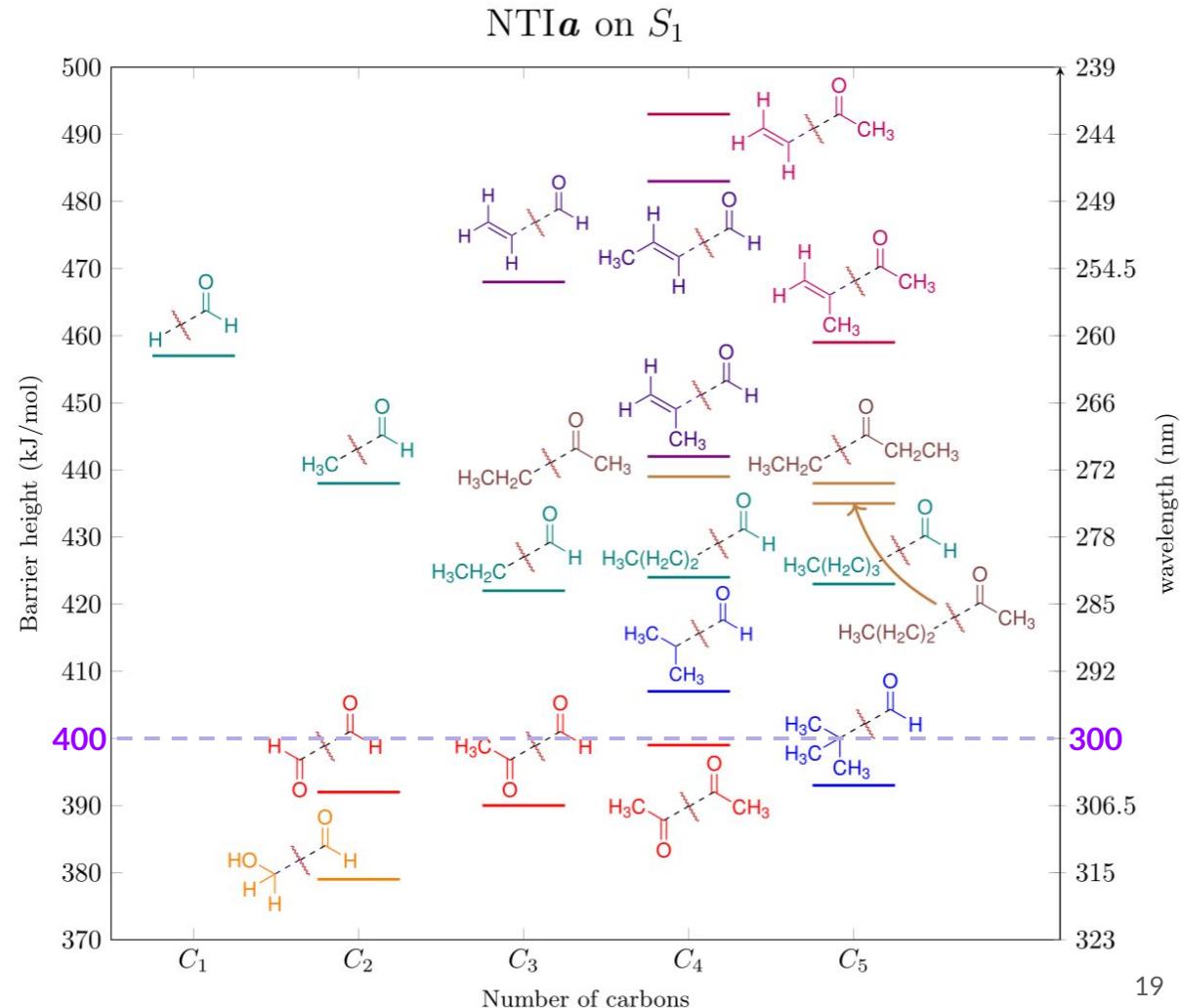


Norrish Type I (NTI)



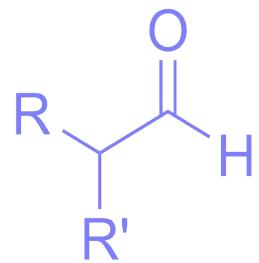
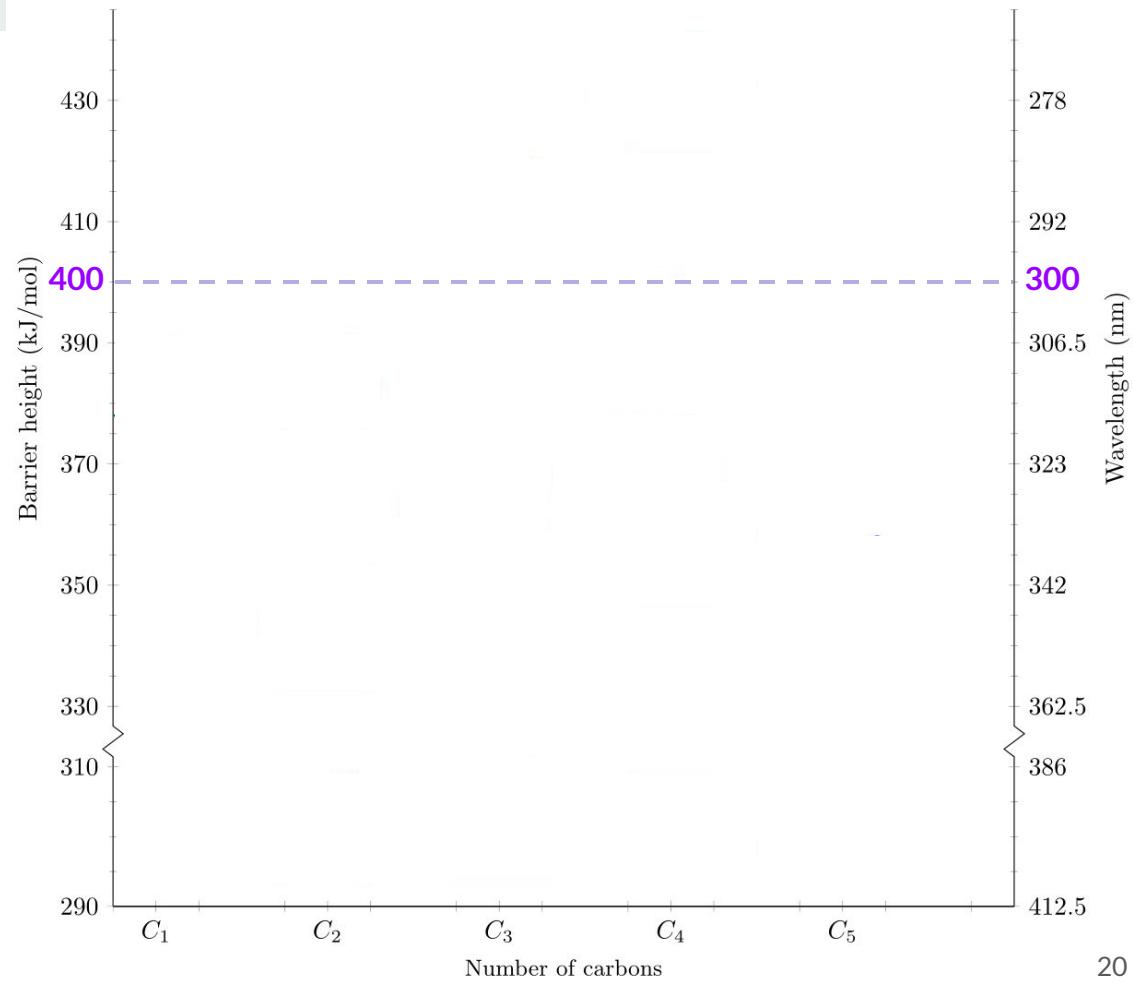
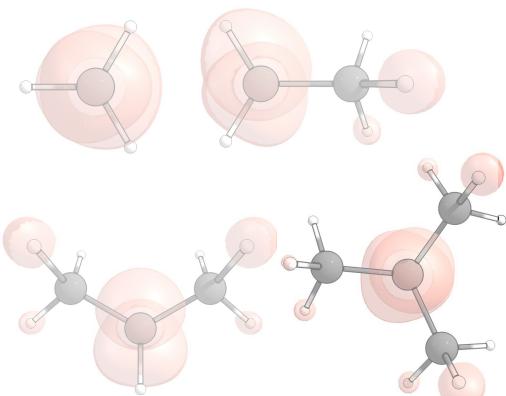
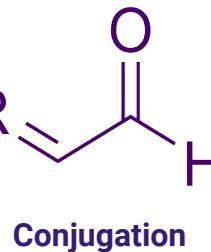
NTI*a* S_1 barriers

- Linear aldehydes & ketones:
- ◆ S_1 barriers inaccessible (>400 kJ/mol)
- ◆ Singlet invoked for unquenchable rxn
- S_1 can be ignored in atmosphere
- ◆ Experiment actually seeing T_1 & S_0
- Barrier height explained by SARS
- ◆ Particularly important for T_1 rxns



NTI*a* on T_1

NTI*a* T_1 barriers

**vs.**

NTI α T_1 accuracy



Experimental: ●

- Chaung M-C., Foltz M., Moore B., *J. Chem. Phys.*, **1987**, 87, 3855
 Huber J., *Chem. Phys. Lett.*, **2003**, 377, 481
 Metha G., Terentis A., Kable S., *J. Phys. Chem. A*, **2002**, 106, 5817
 Zuckermann H., Schmitz B., Haas Y., *J. Phys. Chem.*, **1988**, 92, 4835
 Chen M-W., Lee S., Chen I-C., *J. Chem. Phys.*, **2003**, 119, 8347

CCSD(T): ▲

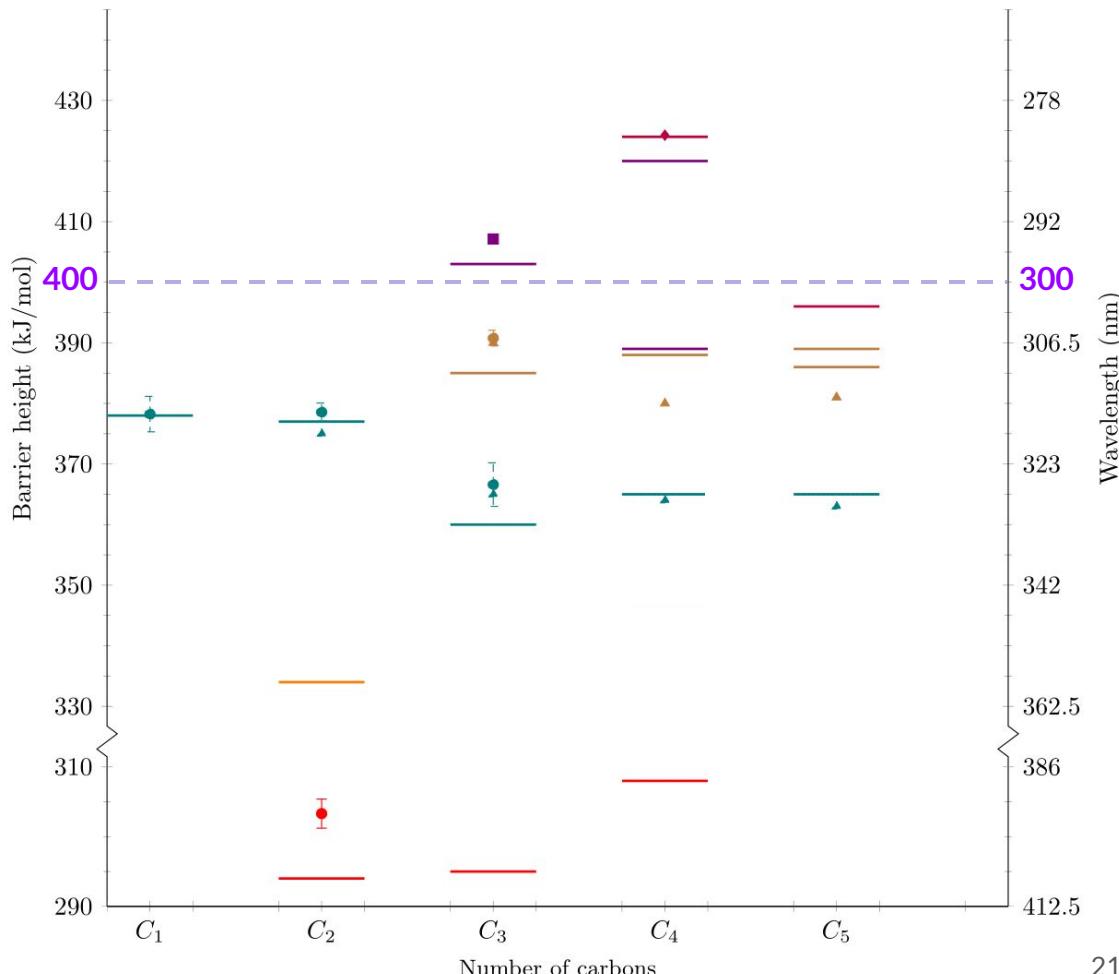
- Harrison A., Kable S., *J. Chem. Phys.*, **2018**, 148, 164308
 Shaw M., *Photochemical formation of enols from carbonyls*, [PhD thesis], USYD, Dec. 2017

CASPT2: ■

- Fang W., *JACS*, **1999**, 121, 8376

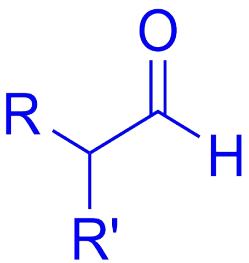
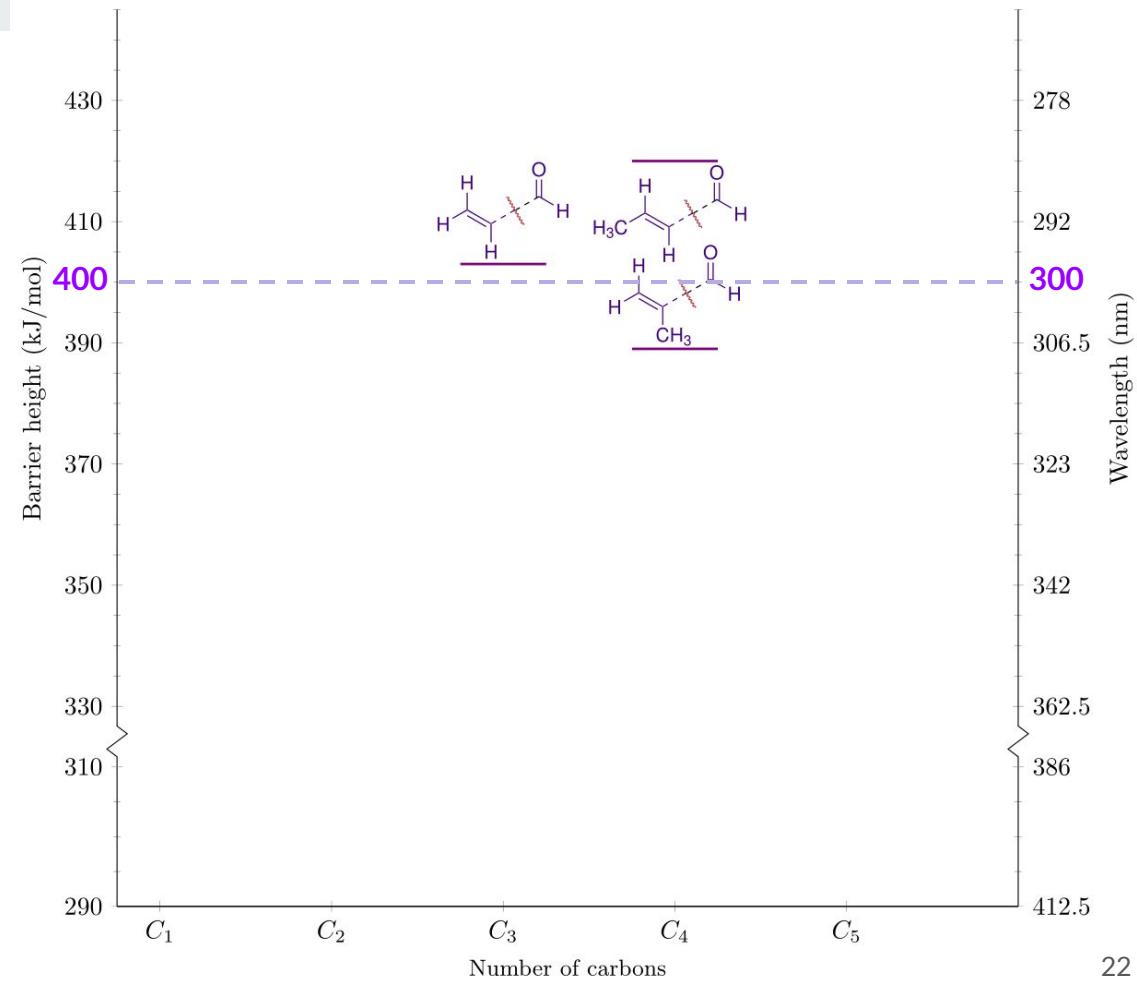
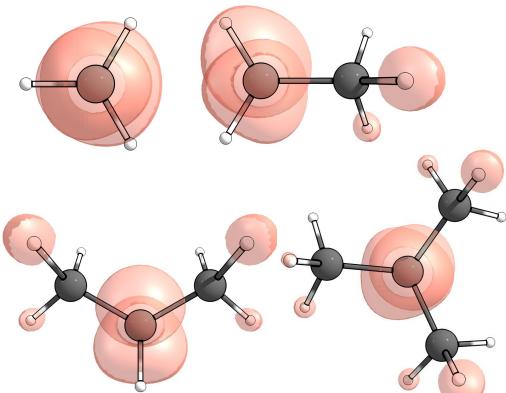
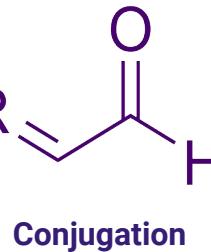
G3X-K: ♦

- Sui S., Uta W., da Silva G., *ACS Earth Space Chem.*, **2018**, 2, 753



NTI*a* on T_1

NTI*a* T_1 barriers

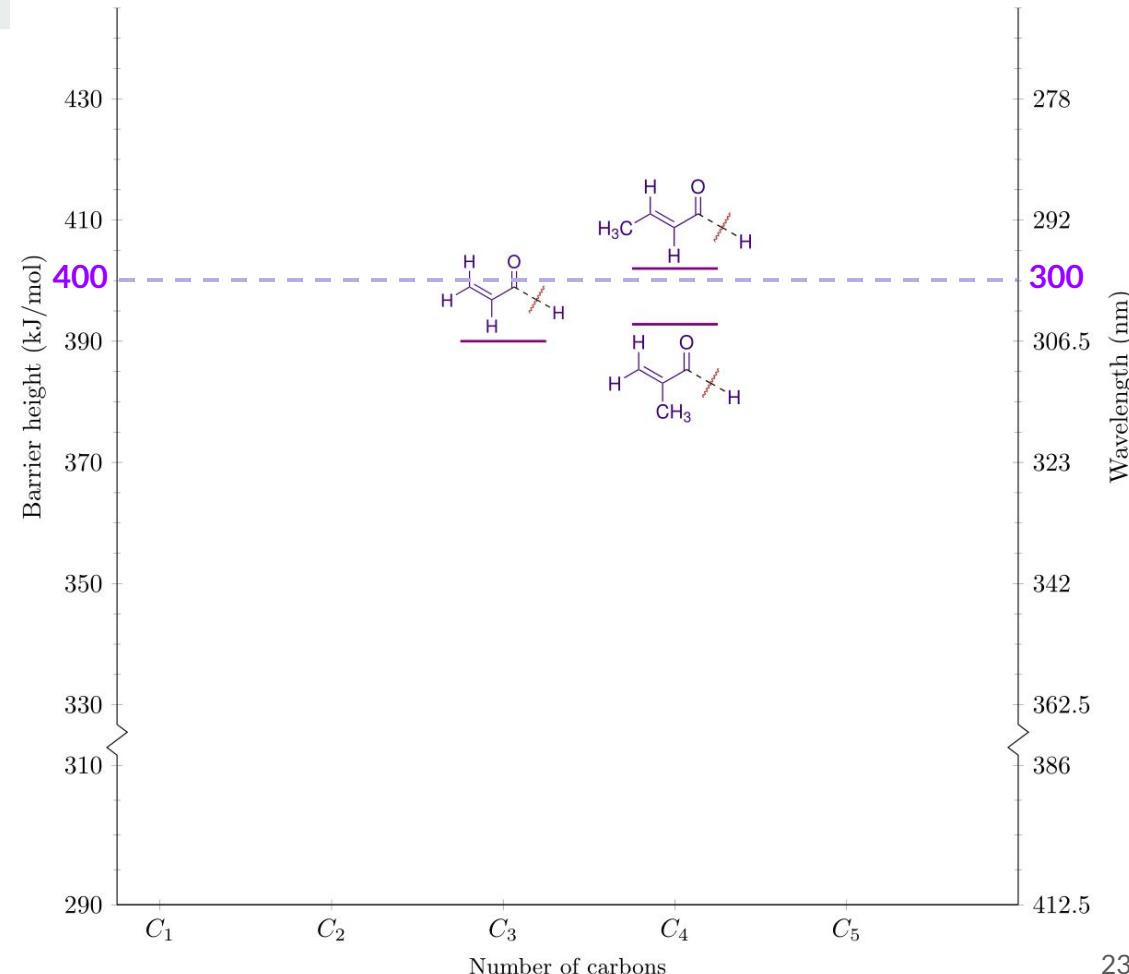
**vs.**

NTI*b* on T_1

NTI*b* T_1 barriers

- If α,β -conjugated: cleave other bond

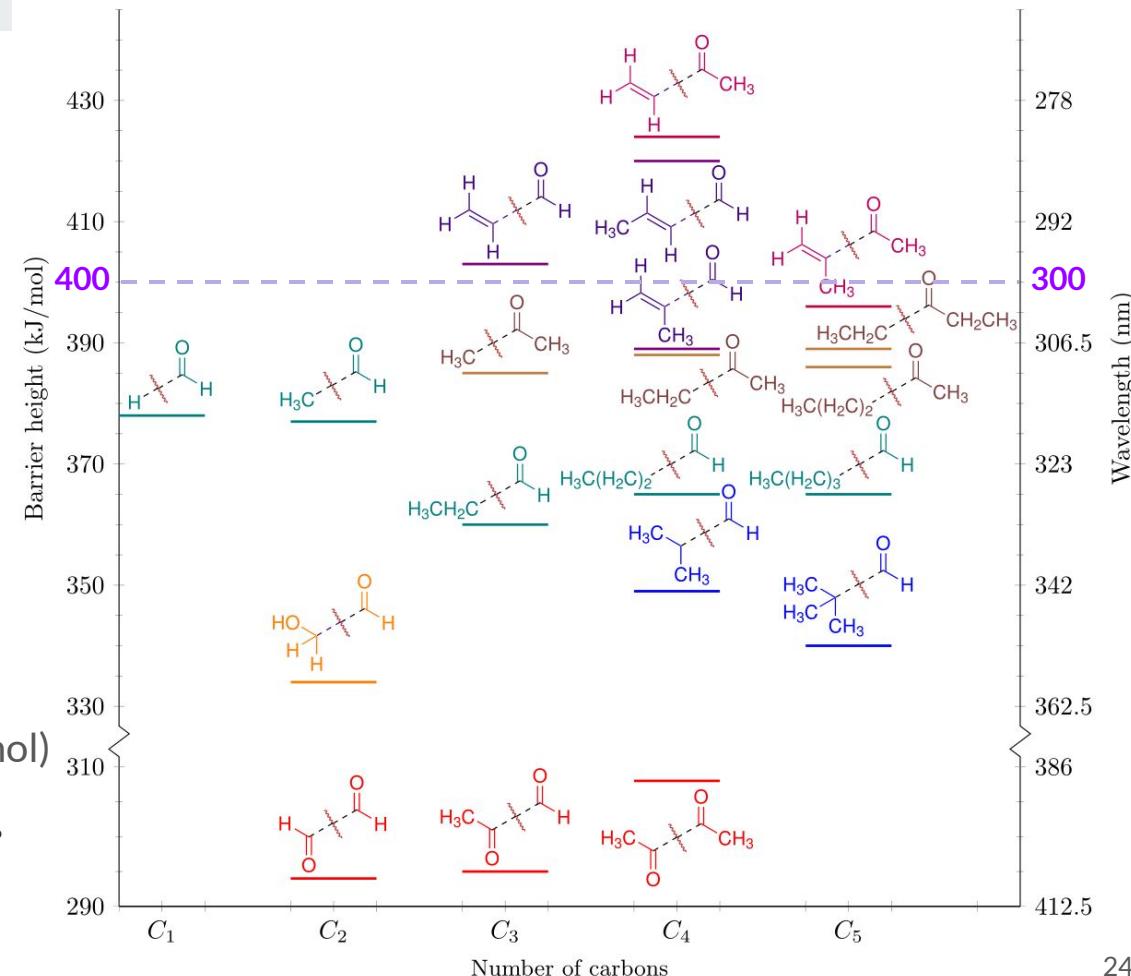
- Supported by FT-IR
 - ◆ H^\bullet source needed in acrolein expt.
 - ◆ Most enals negligible QYs



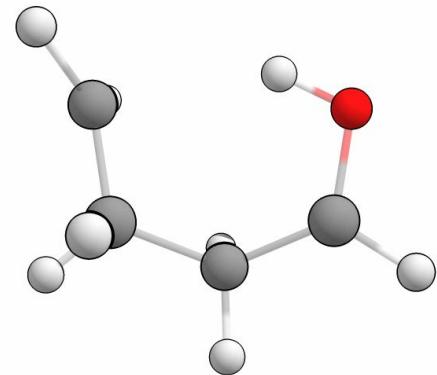
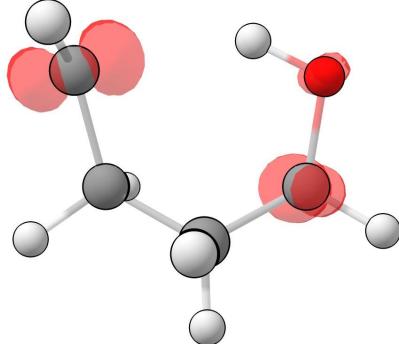
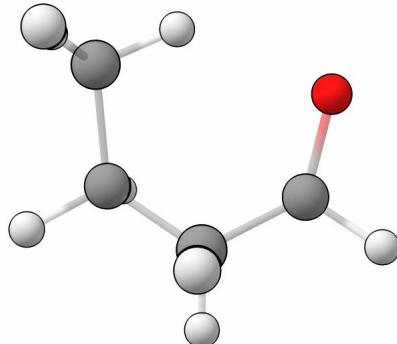
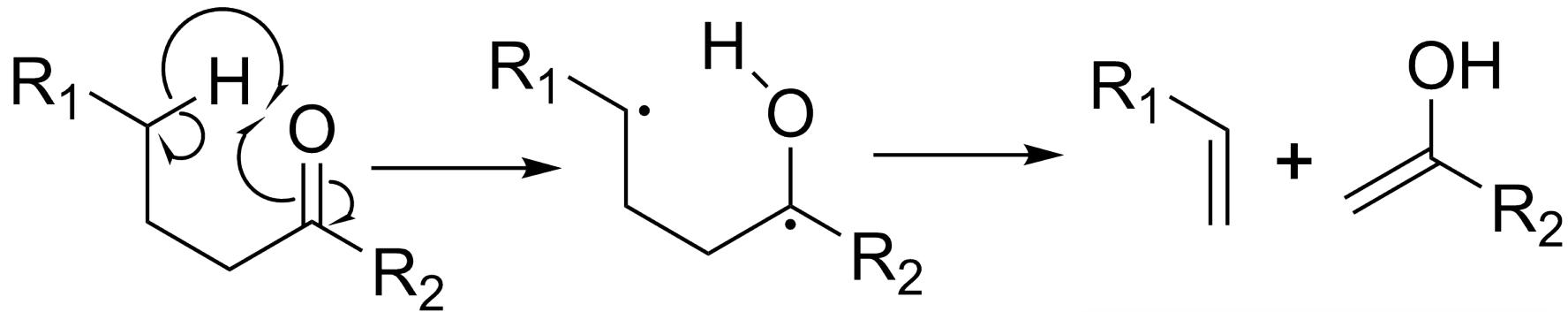
NTI*a* on T_1

NTI*b* T_1 barriers

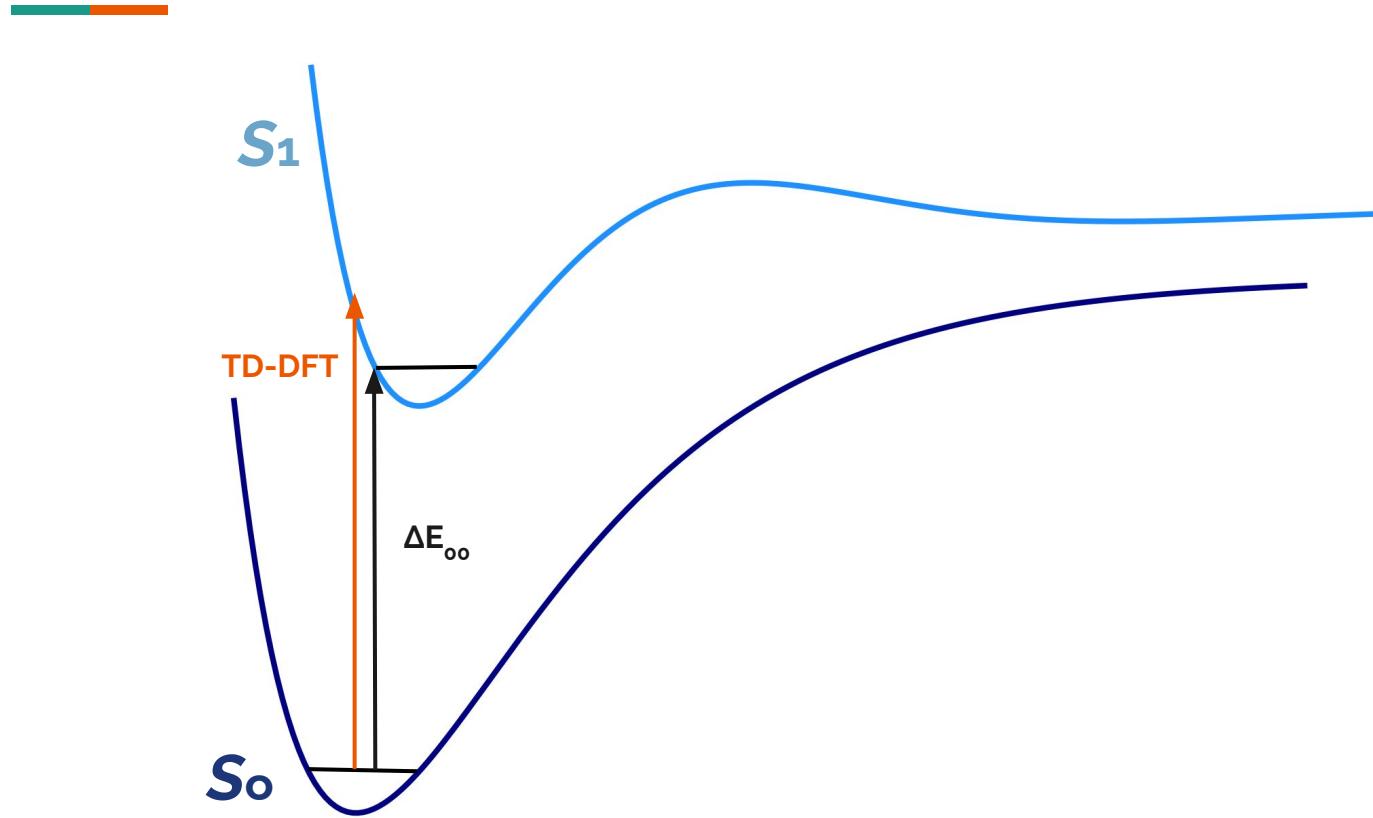
- If α,β -conjugated: cleave other bond
- Supported by FT-IR
 - ◆ H^\bullet source needed in acrolein expt.
 - ◆ Most enals negligible QYs
- NTI*b* has close barrier heights (± 10 kJ/mol)
 - ◆ Same intrinsic barrier to forming H^\bullet



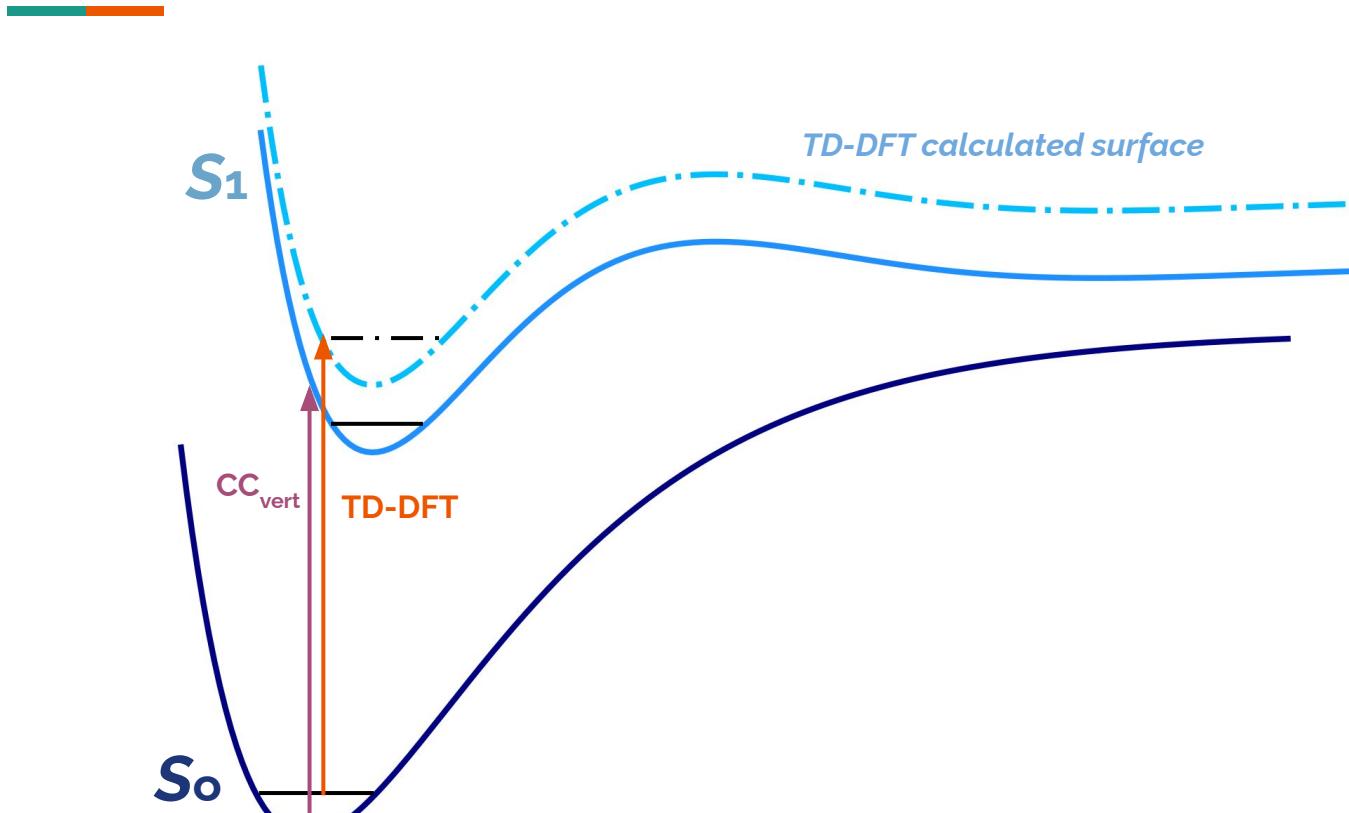
Norrish Type II (NTII)



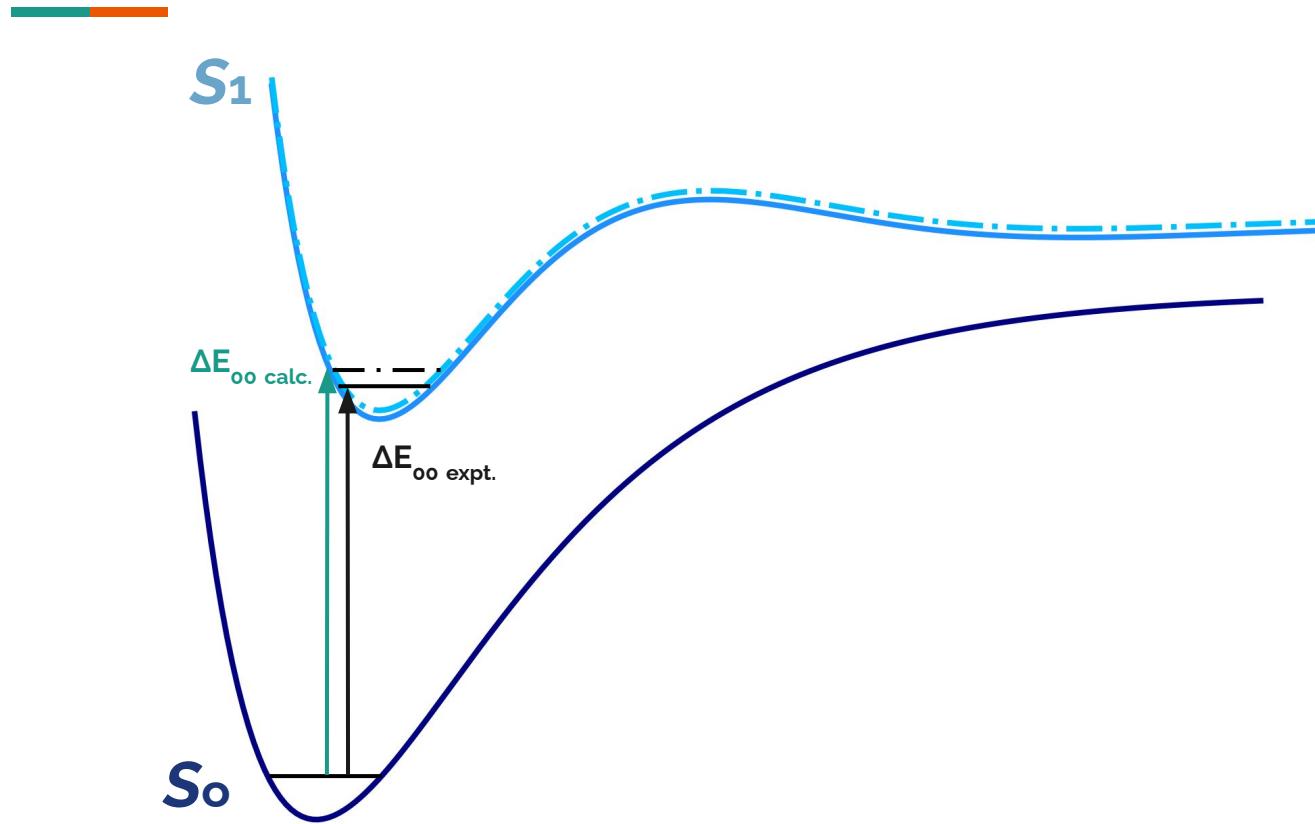
Energies on the S_1 surface?



TD-DFT calculations?



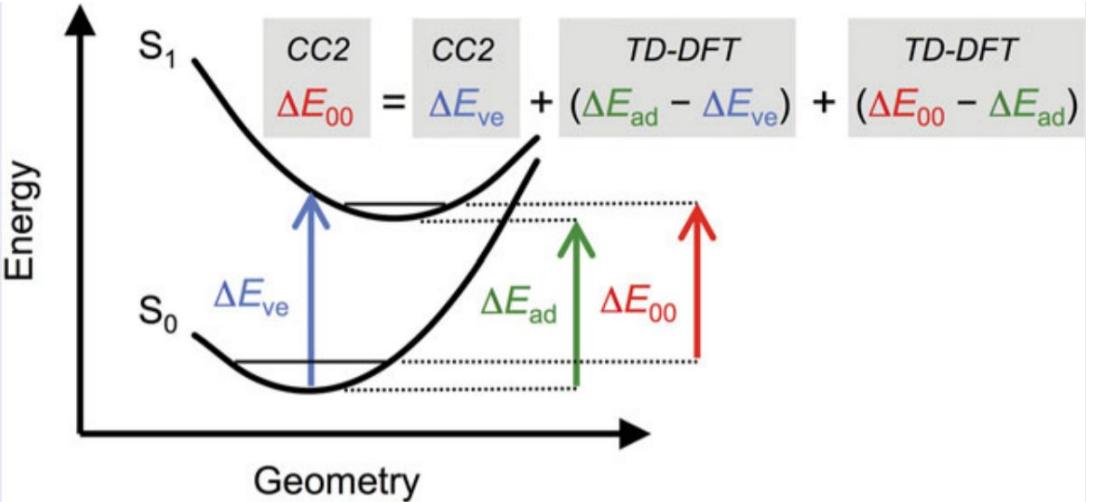
Coupled cluster corrections.



a) Godunov I., Yakovlev N., *Journal of Structural Chemistry*, 1995, 36, 238-253, & ref's therein. b) bt-PNO-STEOM-CCSD/cc-pVQZ (vert.) + RI-TD-B3LYP/def2-TZVP (adiab.)

Composite $S_0 \rightarrow S_1$ energies

TD-DFT is **inaccurate** (10s of kJ/mol) — use **composite procedure**



Costly: 100+ hrs on 12 CPUs

Molecule	$S_0 \rightarrow S_1$ exp. ^a	$S_0 \rightarrow S_1$ theory ^b
<i>Aldehydes</i>		
Formaldehyde	337	355
Acetaldehyde	356	365
Propanal	350	363
Butanal	N/A	363
Pentanal	N/A	364
2-Methylpropanal	349	362
Pivaldehyde	349	359
Glyoxal	262	265
Methylglyoxal	265	263
<i>Ketones</i>		
Acetone	364	367
Butanone	359	366
Pentan-2-one	N/A	361
Pentan-3-one	N/A	369
Diacetyl	265	259
<i>α,β-Unsaturated carbonyls</i>		
Acrolein	310	310
Crotonaldehyde	317	329
Methacrolein	317	315
Methyl vinyl ketone	313	310
Methyl isopropenyl ketone	N/A	315
<i>Carbohydrates</i>		
Glycolaldehyde	N/A	339

MAD: ±7 kJ/mol

NTII S_1 barrier

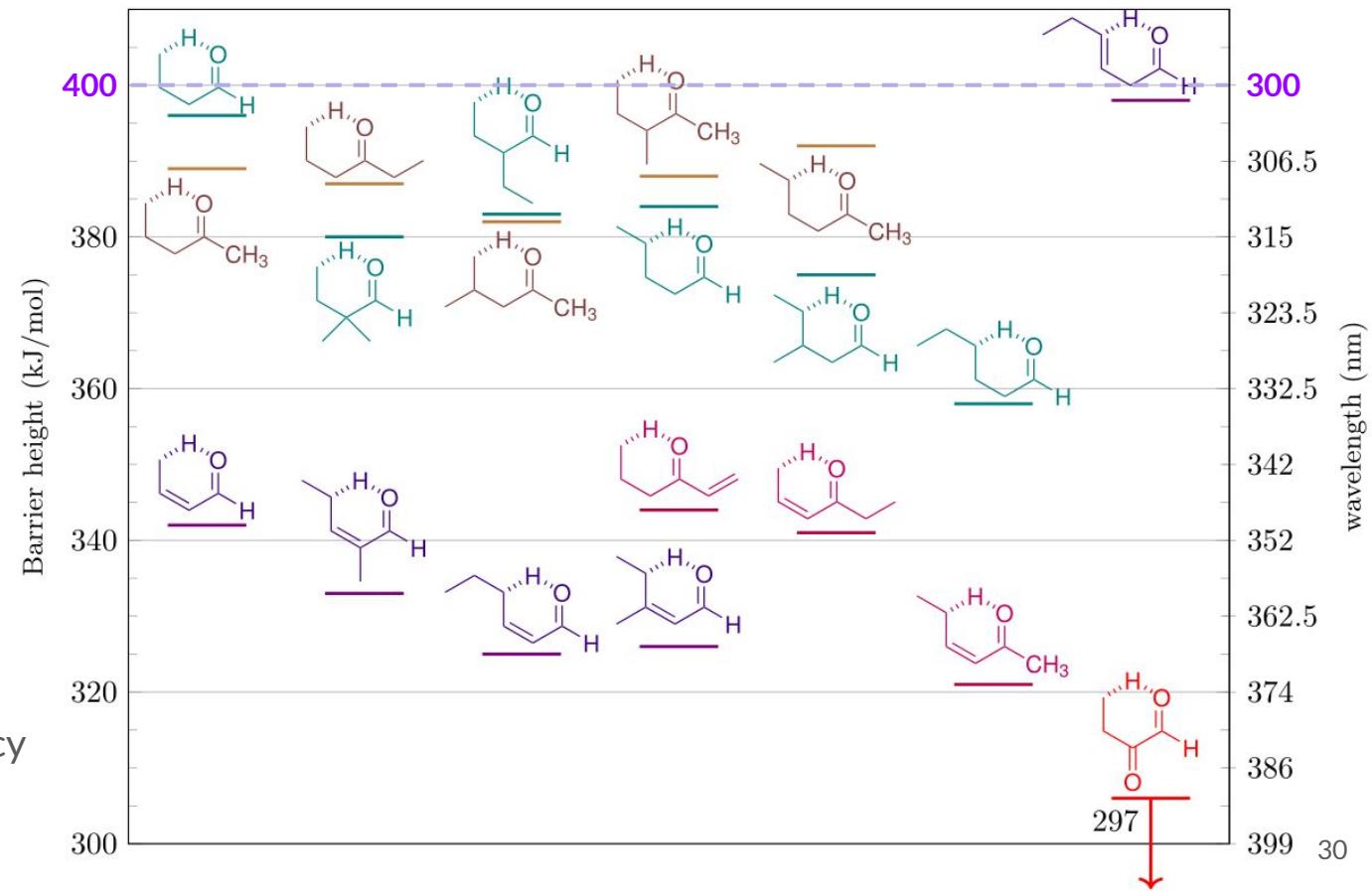
S_1 NTII on borderline:

- ▷ Upper end of actinic UV
- ▷ Reaction competes w/ ISC

ISC rate unchanging:

- ▷ λ above barrier important
- ▷ limitation of method accuracy

NTII on S_1



NTII T_1 barrier

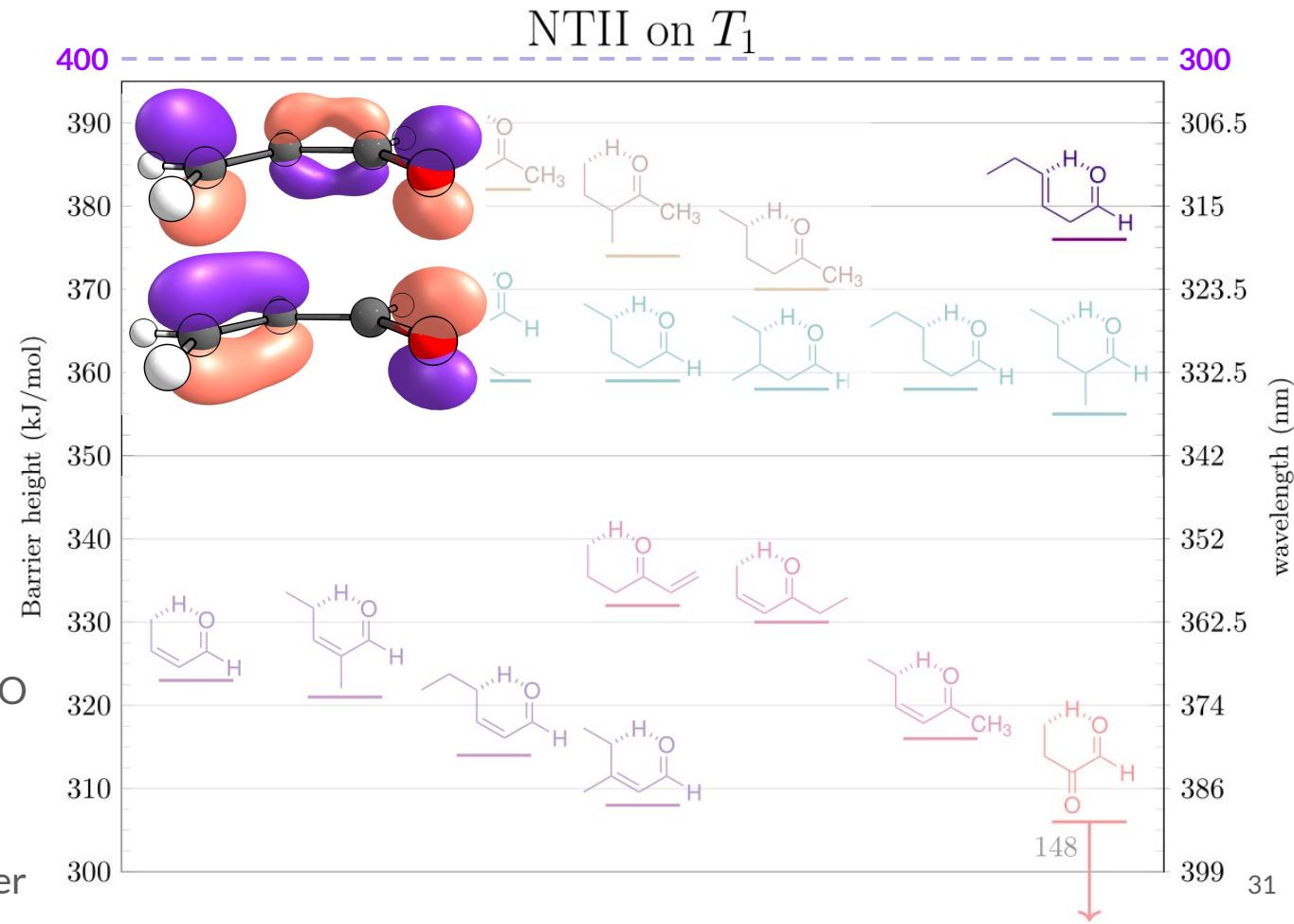


Biradical formation:

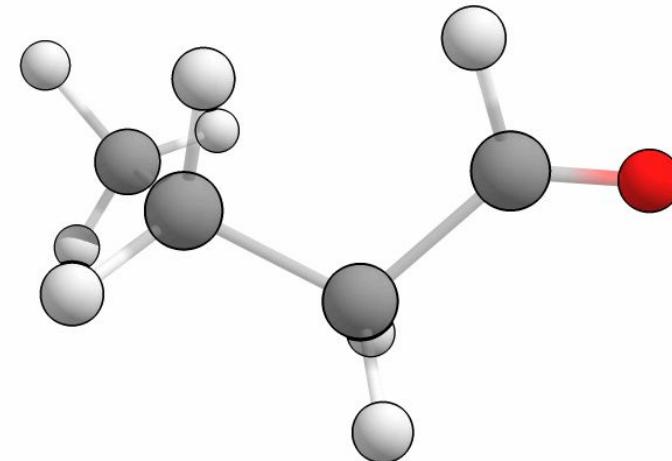
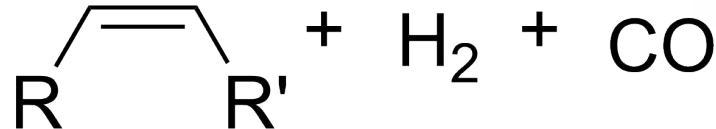
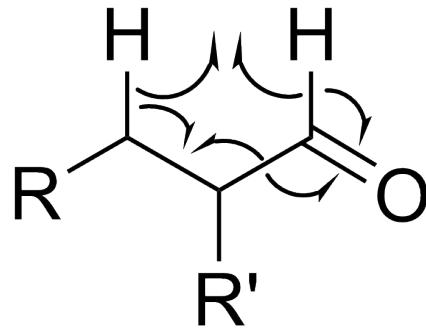
- ▷ 2 hyperconjugation sites
- ▷ α -branching: C \cdot -O radical
- ▷ γ -substitution: C \cdot alkyl

Conjugated carbonyls:

- ▷ Low NTII from HOMO/LUMO
- ▷ Dicarbonyls low barriers
- ▷ β/γ unsaturation raises barrier



Triple Fragmentation (3F)

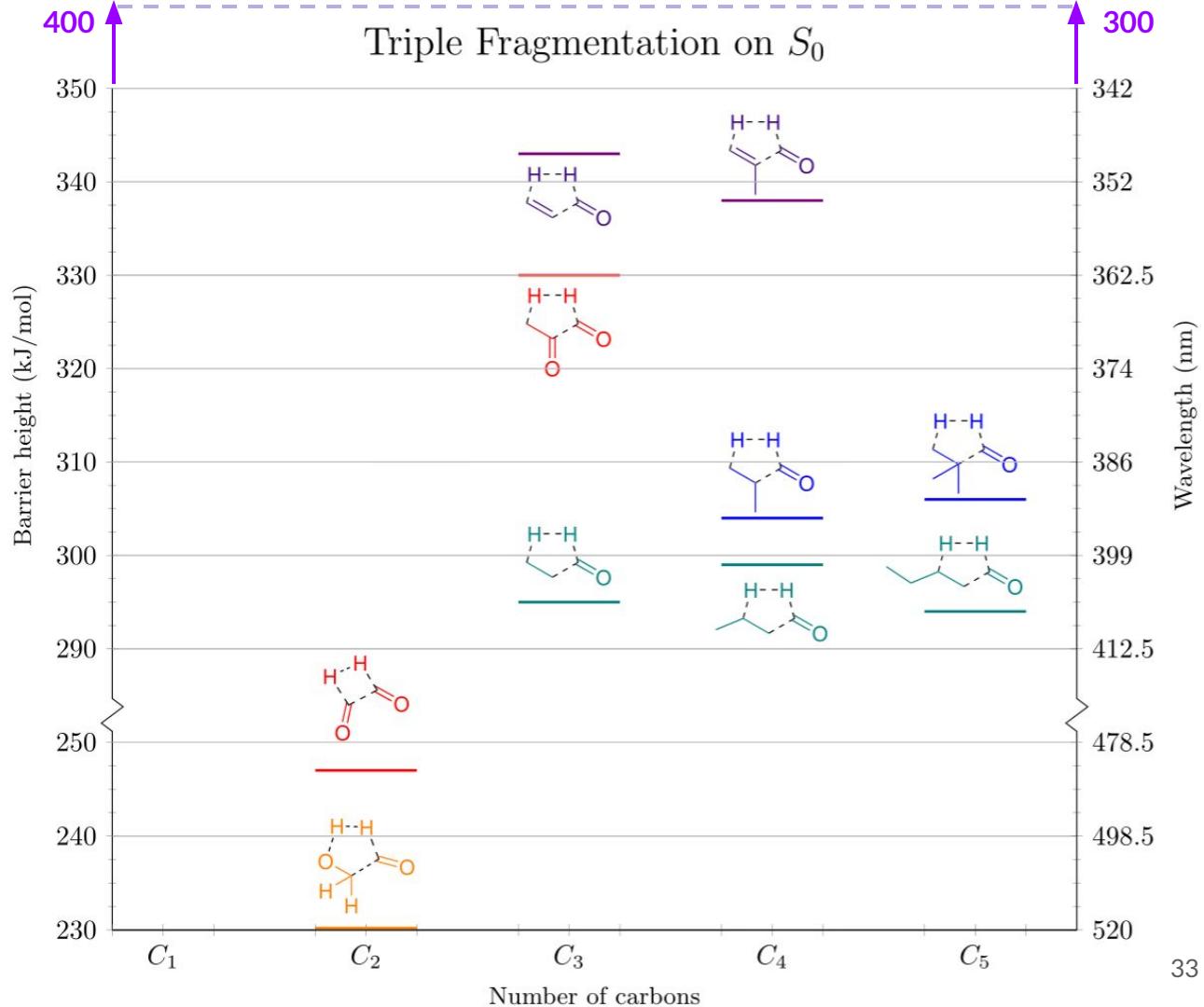


3F S_0 barrier



- ▶ Very low barriers
- ▽ If S_0 is reached then reactions
- ▽ 3F eng. favoured, conf. limited

9 ground state reactions studied



Conclusions — carbonyl photochemistry rationalised

Elucidated structural effects:

- Hyperconjugation ↓ conjugation ↑ barriers
 - ▷ NTI α -branching: -10 kJ/mol
 - ▷ NTI α,β -unsaturation: +40 kJ/mol
 - ▷ NTIb beats NTIa in enals & enones
- NTII γ & C=O substitution stabilise biradical
 - ▷ Pentanal + longer have low S_1 barrier
 - ▷ If S_1 barrier high: T_1 , NTI, & S_o compete
- S_o reactions occur due to fast ISC rates
 - ▷ Many competing reactions
 - ▷ Balance of barrier height & conformation

Explained experimental data:

- Enal's low photoactivity due to NTIa barrier
- Acrolein FT-IR explained by NTIb
- Ground state channels predicted (3F, ketene)

Developed reliable scheme for photochemistry:

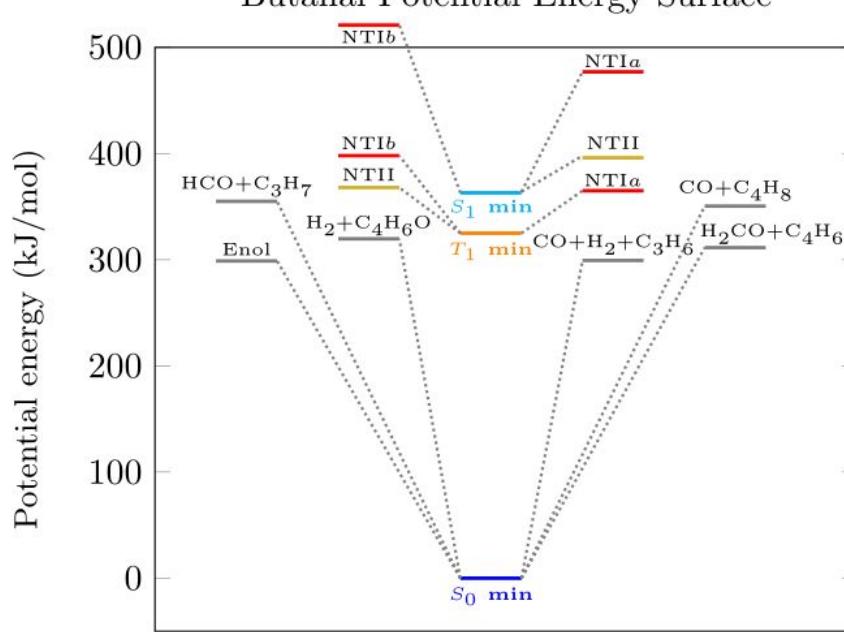
- Photochemical accuracy, @ fraction of CPU cost
- ± 4.5 kJ/mol for T_1 & S_1 barrier heights
- S_1 calculations feasible by composite methods

Further Work – SARs for quantum yields

All **100s** of electronic structure calculations are finished!

Master Equation

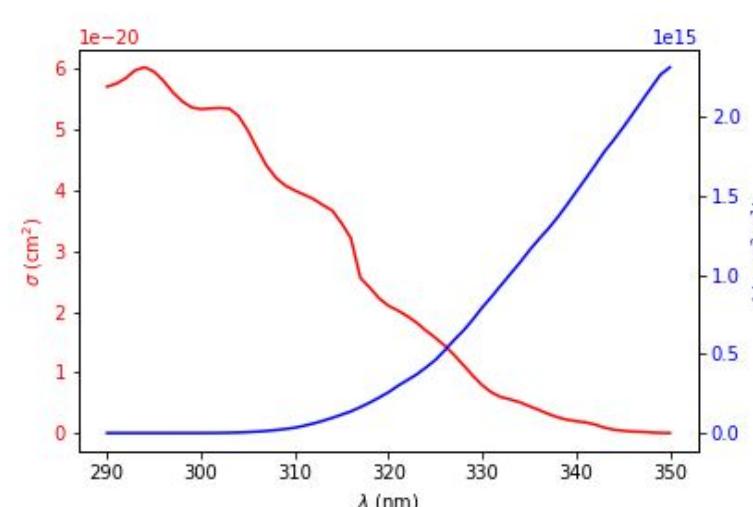
Butanal Potential Energy Surface



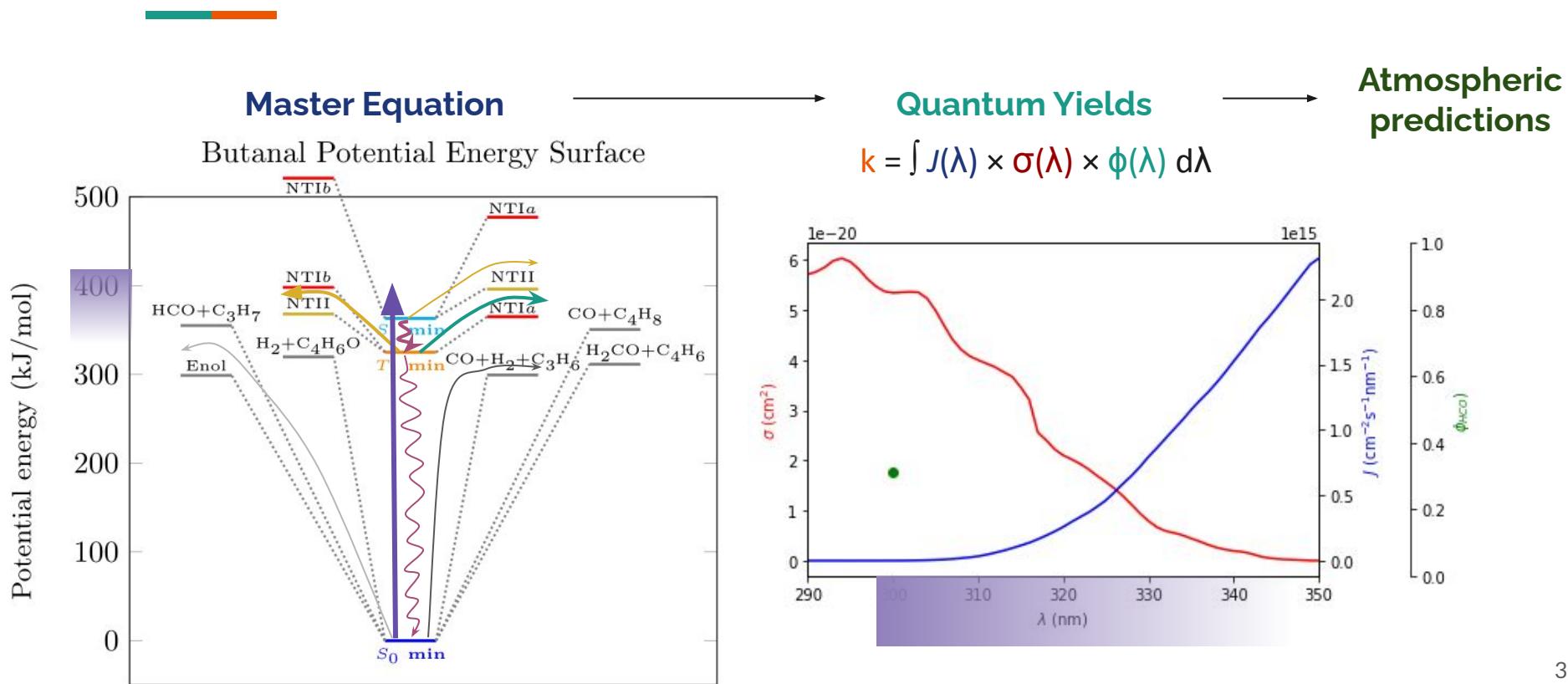
Quantum Yields

$$k = \int J(\lambda) \times \sigma(\lambda) \times \phi(\lambda) d\lambda$$

Atmospheric predictions



Further Work – SARs for quantum yields



Further Work – SARs for quantum yields



Master Equation

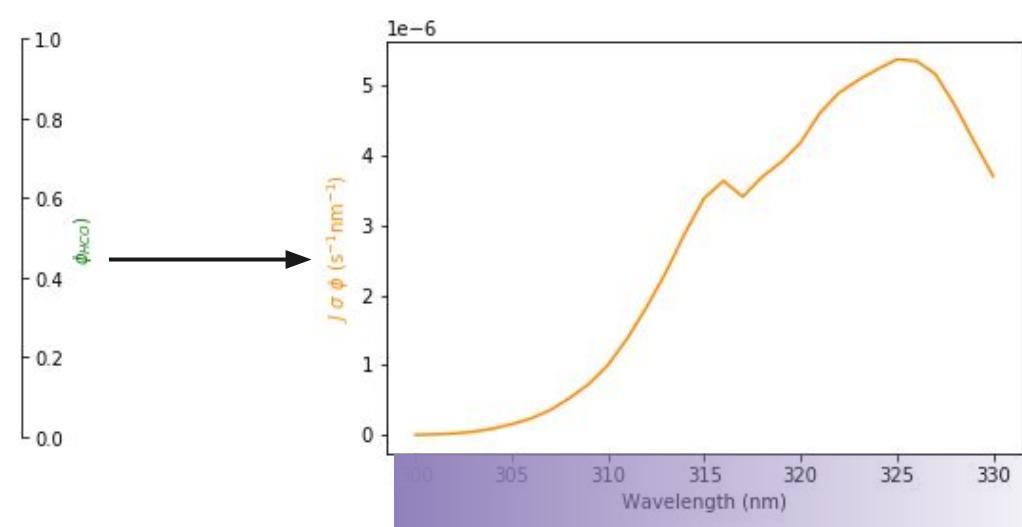
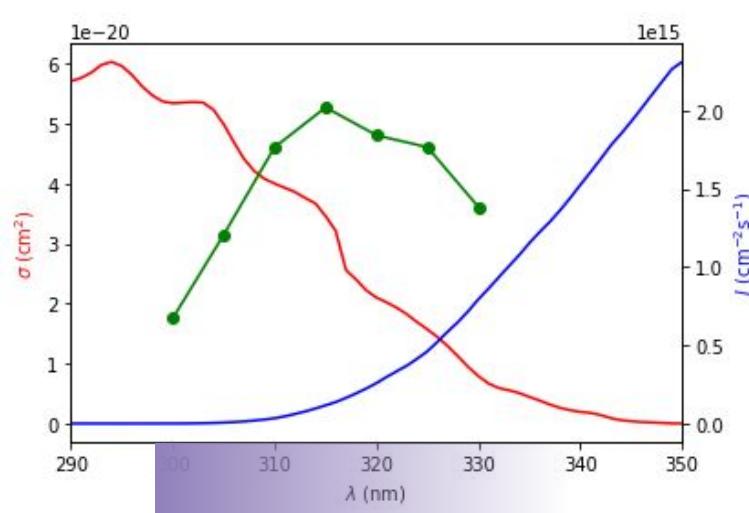


Quantum Yields



Atmospheric predictions

$$k = \int J(\lambda) \times \sigma(\lambda) \times \phi(\lambda) d\lambda$$

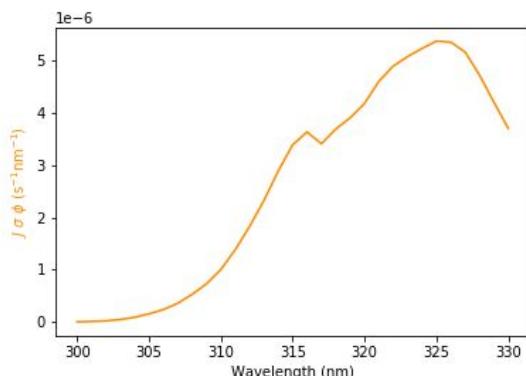


Further Work – SARs for quantum yields



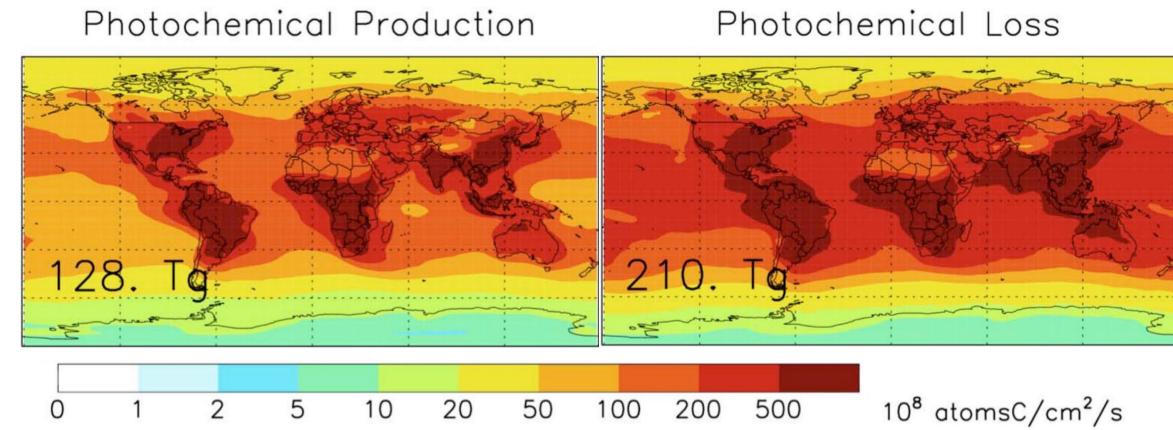
Quantum Yields

$$k = \int J(\lambda) \times \sigma(\lambda) \times \phi(\lambda) d\lambda$$



Atmospheric predictions

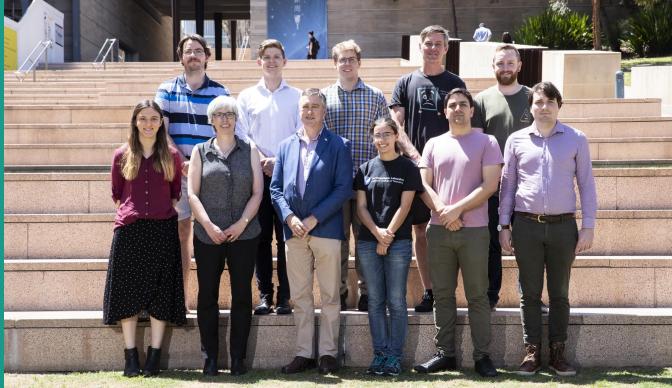
CH_3CHO photolysis



Acknowledgements

Supervisors: Prof. Scott Kable & A/Prof. Meredith Jordan

Gas-phase/reaction dynamics group:



The wider Molecular Photonics group:



Resources:

ORCA – *ab initio* quantum chemistry package



Katana – UNSW Science HPC cluster



Raijin – NCI supercomputer

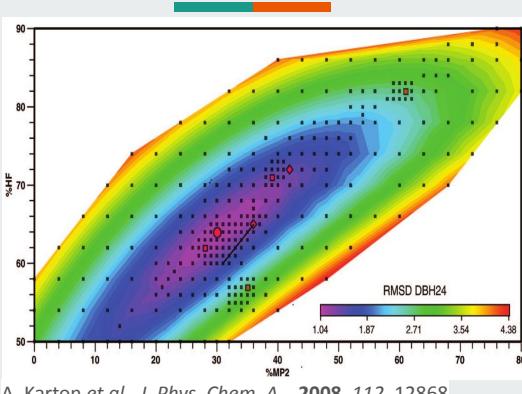


NCI & UNSW HPC support

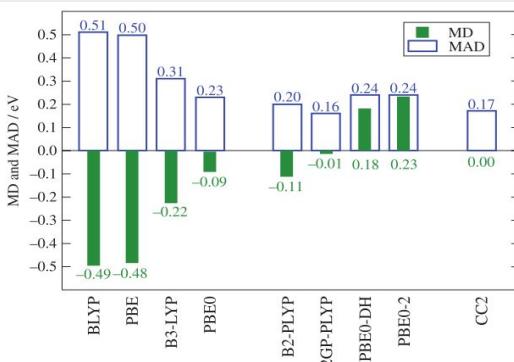
UNSW & the Australian Government
for the RTP Scholarship

Double-Hybrids for Photochemistry?

Why B2-GP-PLYP?



A. Karton et al., J. Phys. Chem. A., 2008, 112, 12868



Benefits:

General Purpose:

- in the basin of various reference data sets
- RMSD < 2 kcal/mol comparable : G3
- Implementable in Gaussian, ORCA
- Inherits all the benefits of MP2
- RI-MP2 speedup!
- Superior performance for excited states

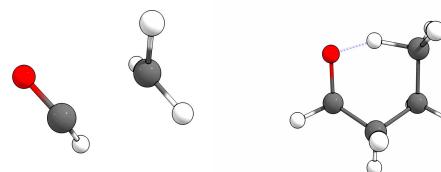
L. Goerigk, S. Grimme, WIRES Comp. Mol. Sci., 2014, 4, 576

Disadvantages:

- Inherits basis-set dependence of MP2 (should use triple- ζ^+)
- Analytical frequencies lacking, even gradients for excited state
- Not on the post-HF ladder of systematic improvement

Results:

- Quick structural comparison:
Opt w/ RIJK: virtually the same. RMSD, $\Delta r < 0.001 \text{ \AA}$
B3LYP -> B2-GP-PLYP biggest change c.f. D3, $1\zeta/3\zeta$.
However diff. w/ benchmark small regardless ($\sim 0.004 \text{ \AA}$)
- Obtained S_0 min, T_1 min, NTI T_1 T.S.s for C1-4 carbonyls
Largest opt+freq calcs. < 4 hrs w/ 4 CPUs on ORCA
Some spurious low imag-freqs, solved: smaller increment



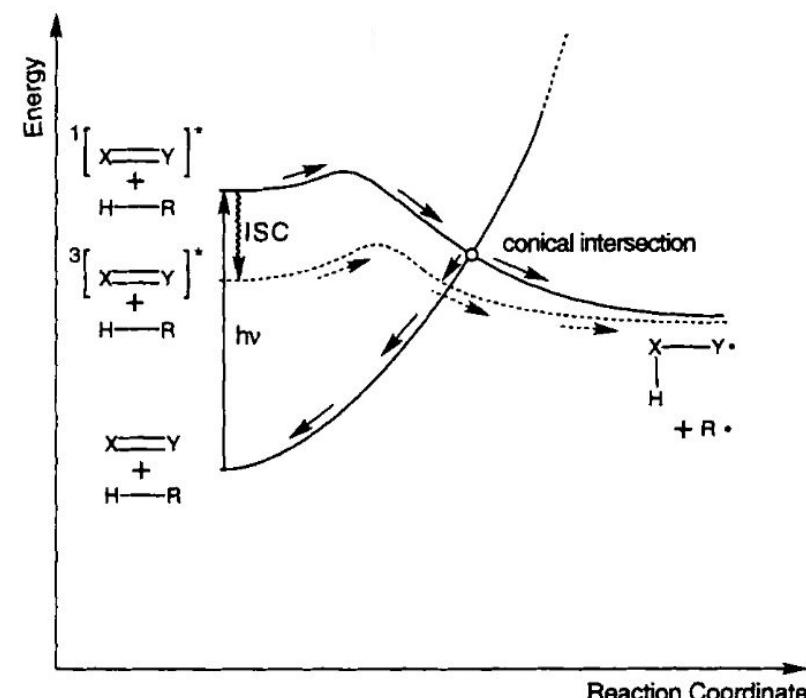
Next:

- S_1 structures
- EP3(cc) CBS energies

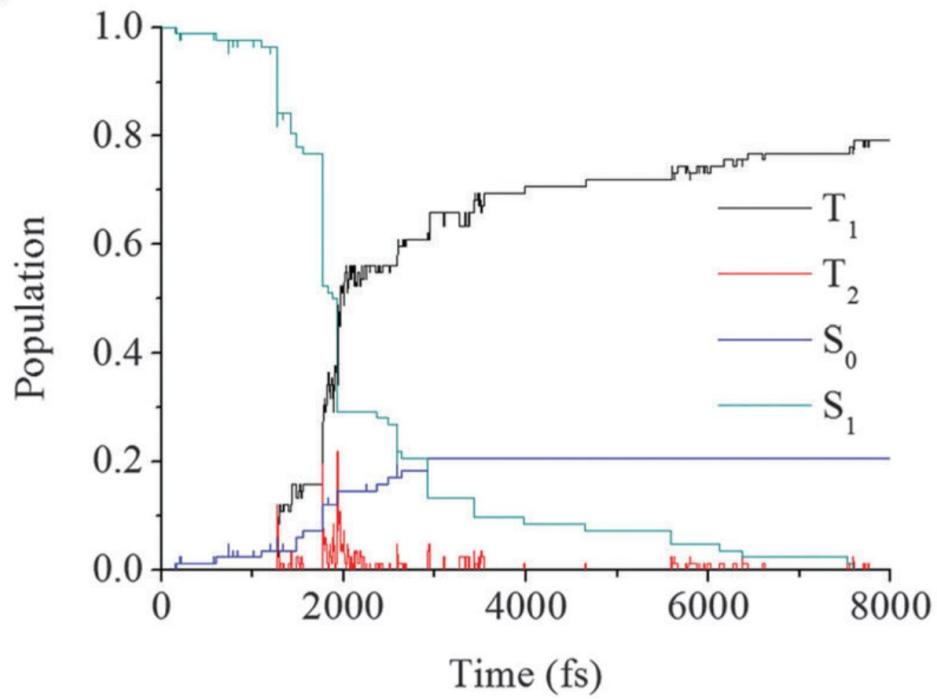
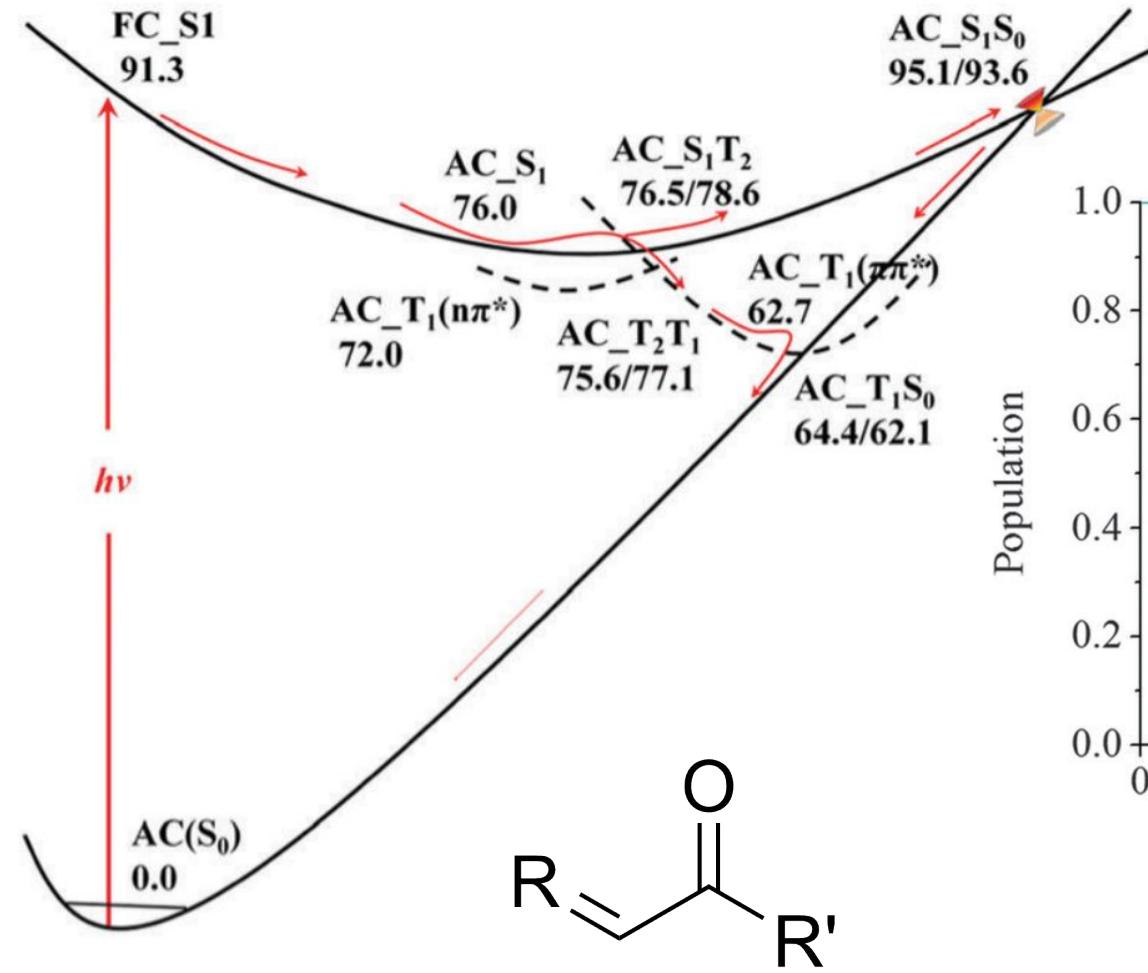
Surface(s) of NTII?

- Quenching distinguishes between S_1 & T_1 reactivity
 - ▷ Experiments conducted at 380-385 kJ/mol
- Different species showed different quenching sensitivity:
 - ▷ Molecule dependent preference
 - ▷ Hexan-2-one: S_1 , pentan-2-one: T_1 , butanal: S_1 & T_1
 - ▷ Further studies implicate both states
 - ▷ Wavelength (λ) dependent
- The triplet biradical has a μ s lifetime and can be trapped.

The NTII conical intersection



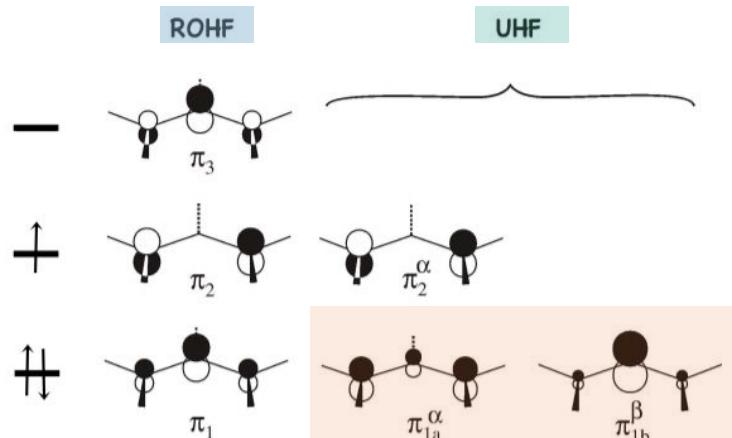
- S_1/S_0 surfaces intersect: ~80% deactivation
- DFT fails entirely. Need multireference calc₄₁



Restricted vs. Unrestricted calculations. Spin-contamination

Restricted calculations restrict α & β electrons to the **same** spatial orbital.

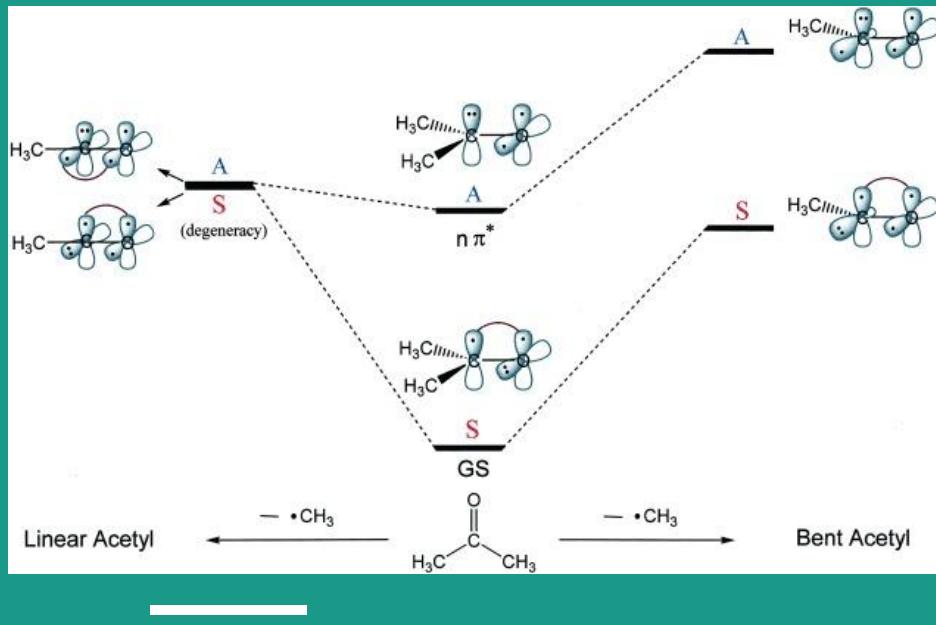
Unrestricted calculations solve the α & β electrons **separately** leading to **different** spatial orbitals.



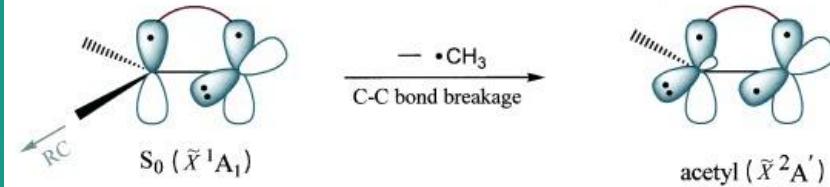
Higher states contaminate; **no longer spin eigenfunctions!**

We **expect** $\langle S^2 \rangle = s(s+1)$ [0.75: triplet – 2: singlet]

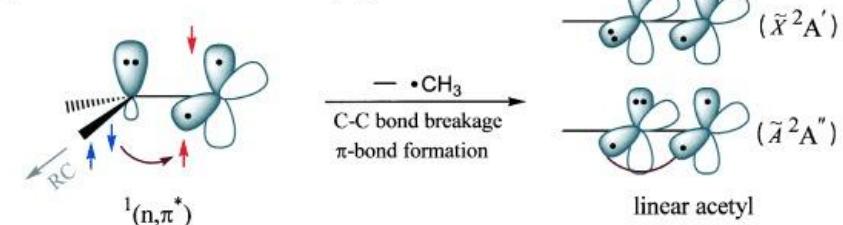
State correlation diagrams



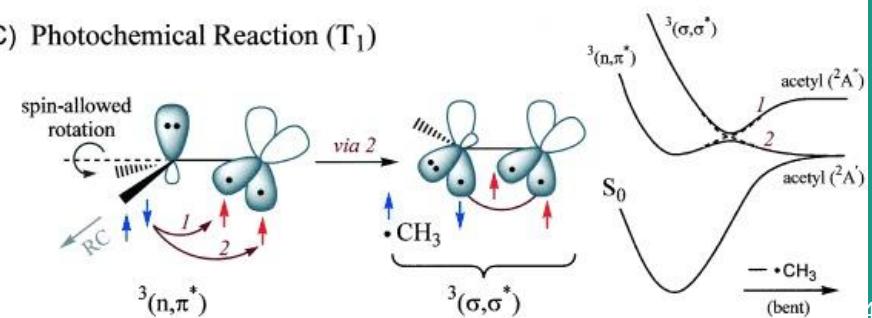
A) Thermal Reaction (S_0)



B) Photochemical Reaction (S_1)



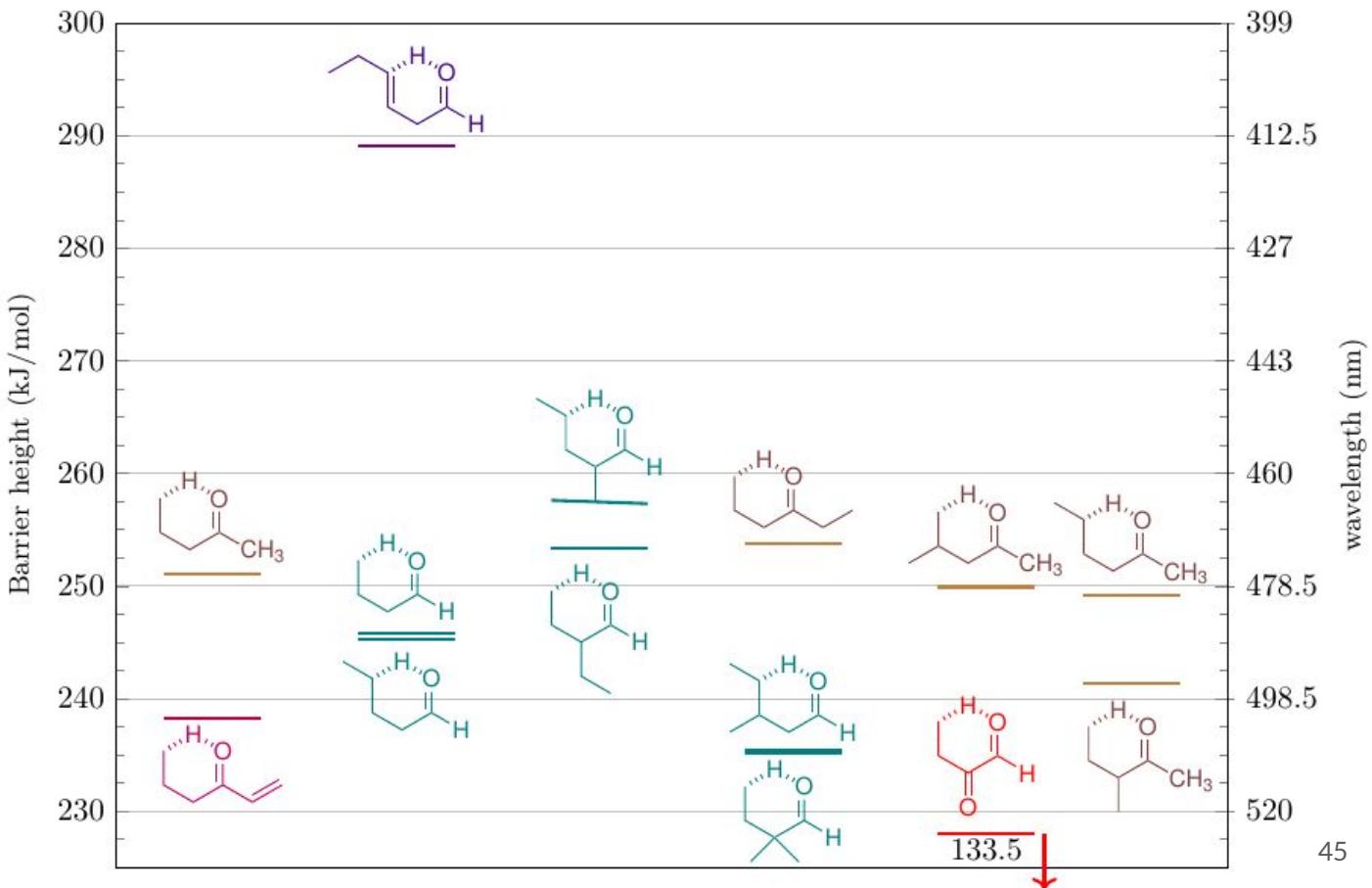
C) Photochemical Reaction (T_1)



S_0 reaction?

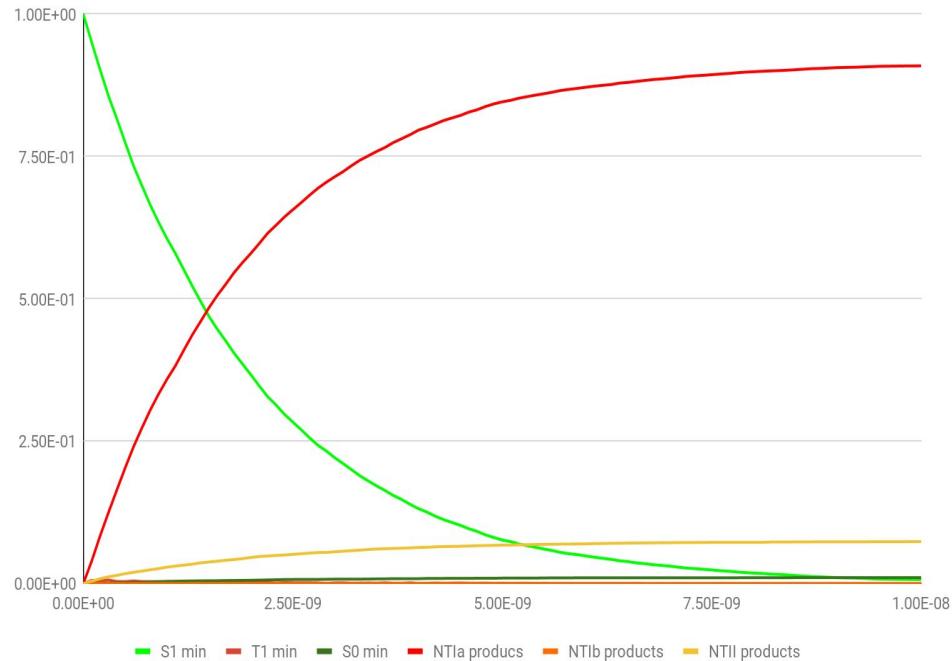
A horizontal bar consisting of two colored segments: teal on the left and orange on the right.

Concerted NTII on S_0

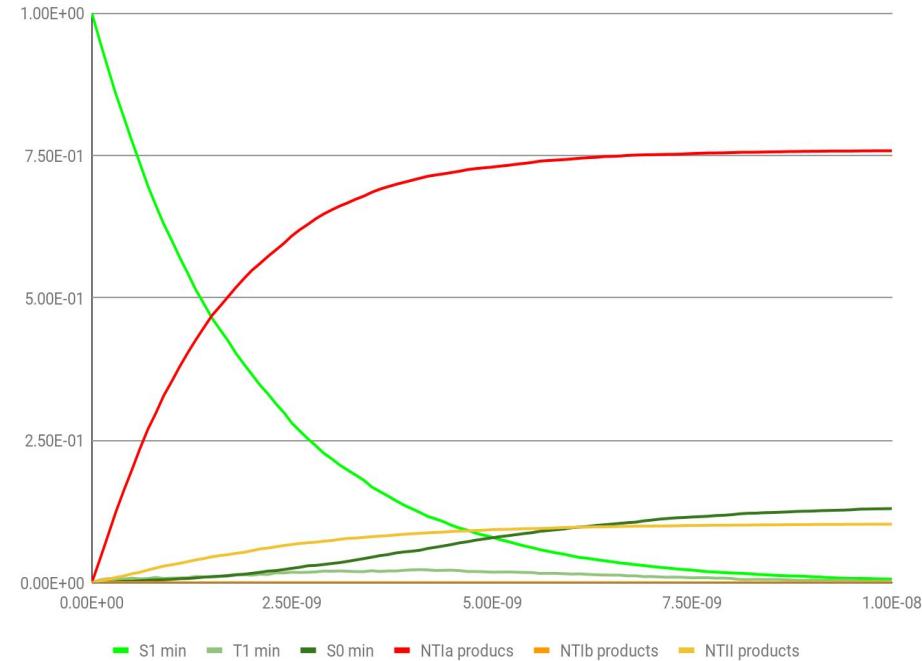


Early testing results (ISC rates, no isomers, no S₁ react., no TF) Qualitative!!

Butanal reaction pathways, 300 nm, 0 atm

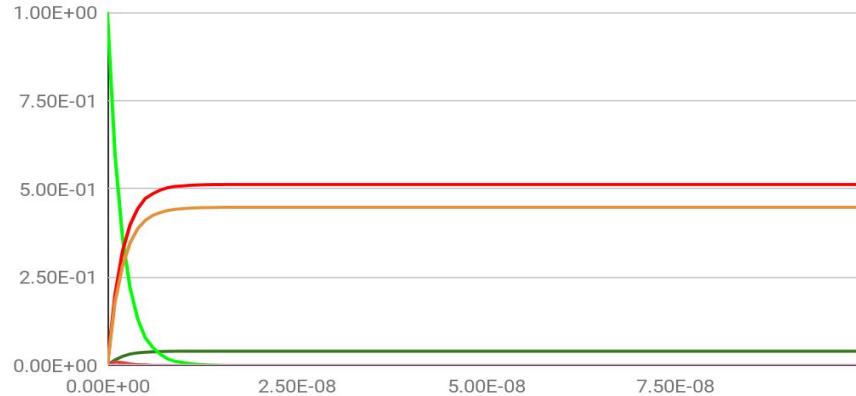


Butanal reaction pathways, 300 nm, 1 atm



NTII predominant in longer carbonyls (pentanal etc.)

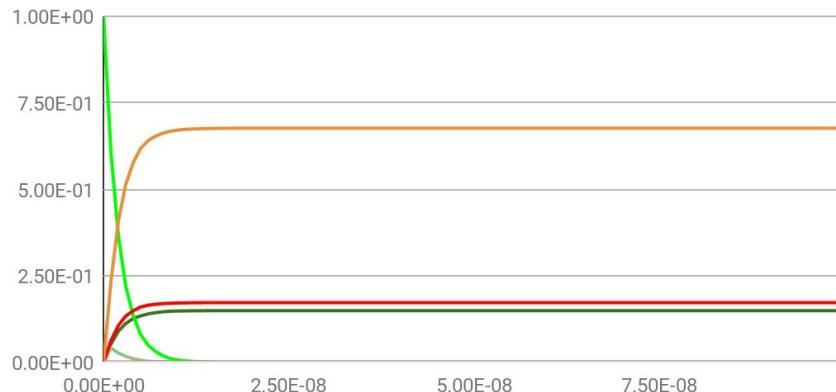
pentanal 300 nm, 0 atm



pentanal 300 nm, 1 atm



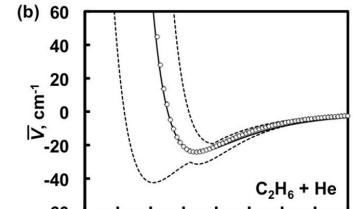
pentanal 315 nm, 0 atm



pentanal 315 m, 1 atm

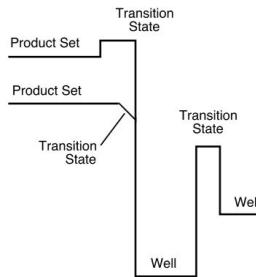


Creating a photolysis parameter set

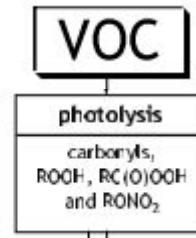


P -dependence (CET)

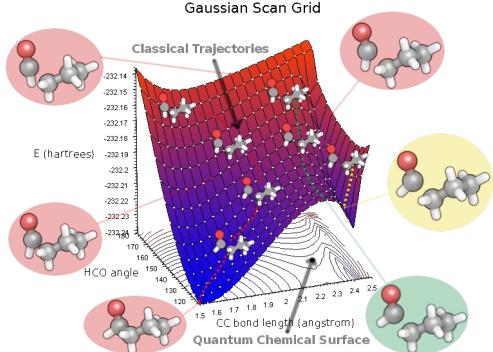
ME/MultiWell



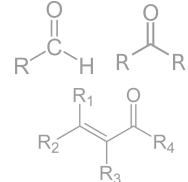
MCM



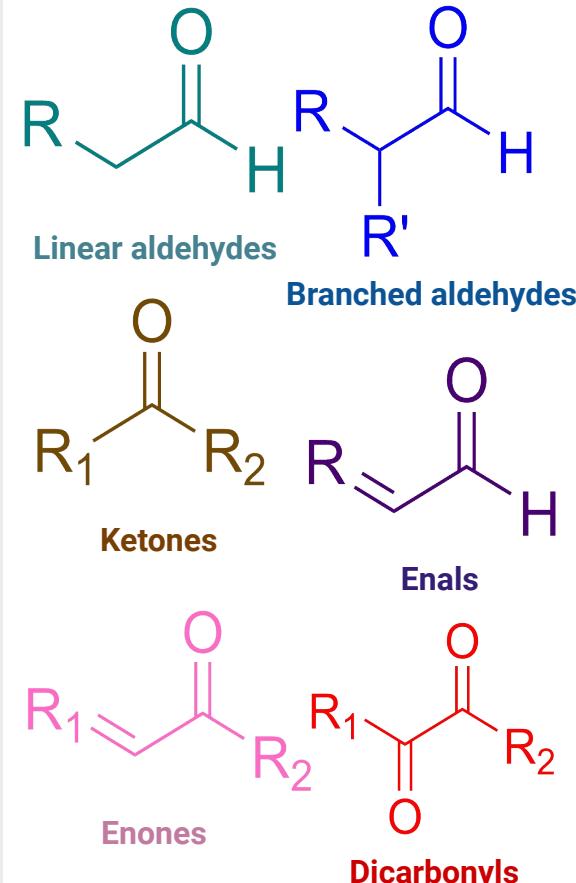
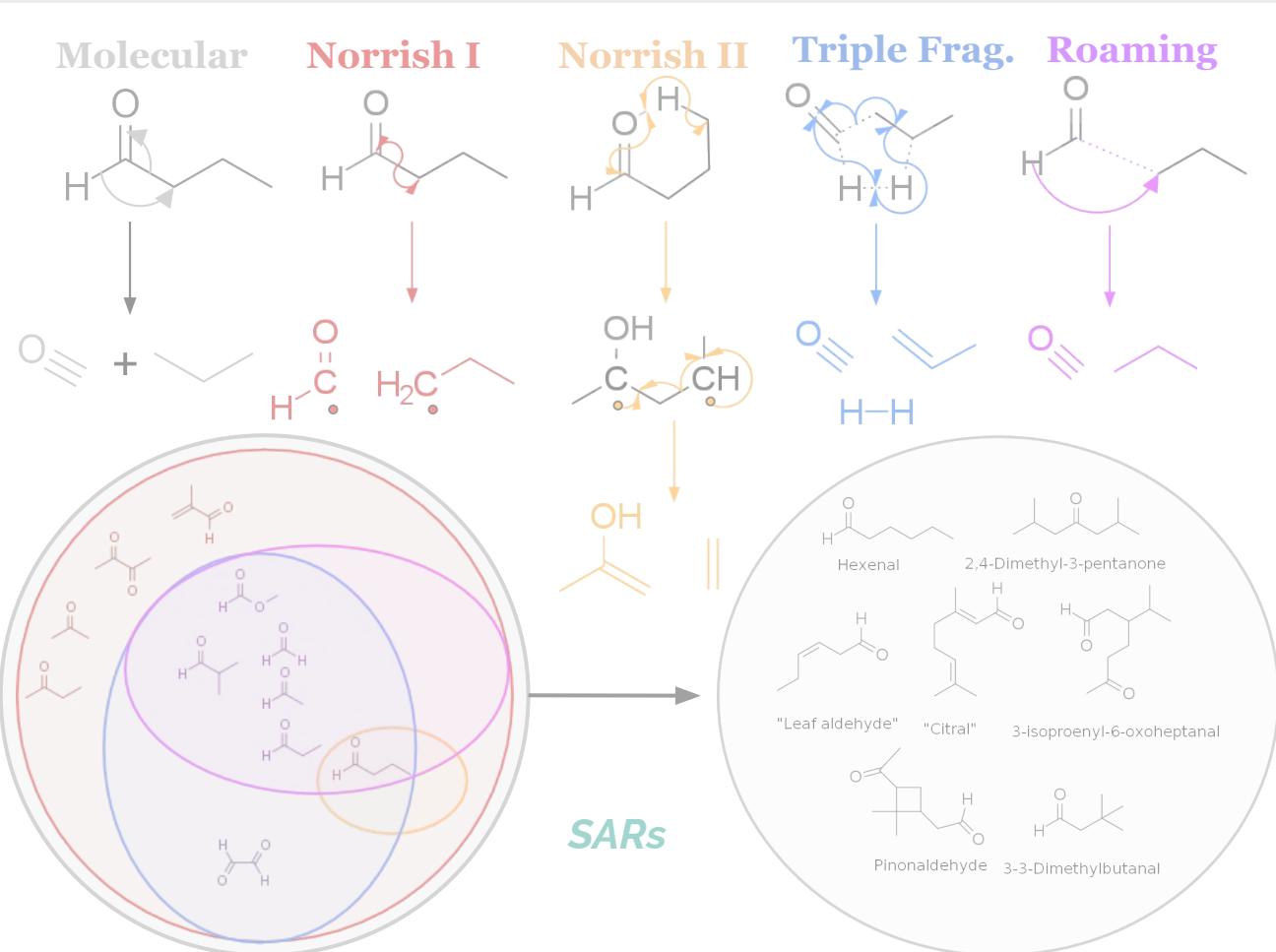
λ -dependence (QCTs)



SARs



SARs for photochemistry by carbonyl classes



Further Work & Conclusions

- Master Equation (ME) modelling for competing photolysis pathways
 - Vibrational frequencies from barrier calculations for the basis for ME calculations
 - Unimolecular reactions – RRKM: $k(E) \propto N^\ddagger(E-E_0) / \rho(E)$
 - Collisionally cooling models in ME
- Photolysis rates to compare with MCM values
 - Sensitivity analysis – sources of error
 - Test impact – trials propagating MCM with modified rates
- Developed a computational scheme for photochemistry
 - ± 4 kJ/mol small carbonyls – within 10 kJ/mol for kinetics – best frequencies
- Rationalised experimental photolysis data
 - Enal non-reactivity due to large NTI a barrier, acrolein explained by NTI b
- Elucidated simple structure-activity relationships for photolysis barriers
 - General barrier height rules from hyperconjugation, conjugation, & excitation energies