



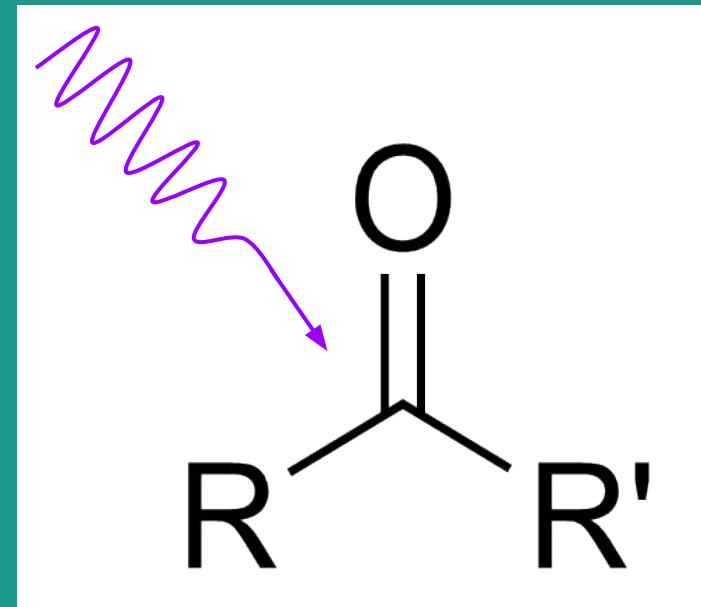
PhD recap

Structure–Activity Relationships for Carbonyl Photolysis

Keiran Rowell - Feb 14, 2020

Chapter 1

Introduction to Carbonyl Photolysis



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!

Tropospheric degradation of volatile organic compound

83

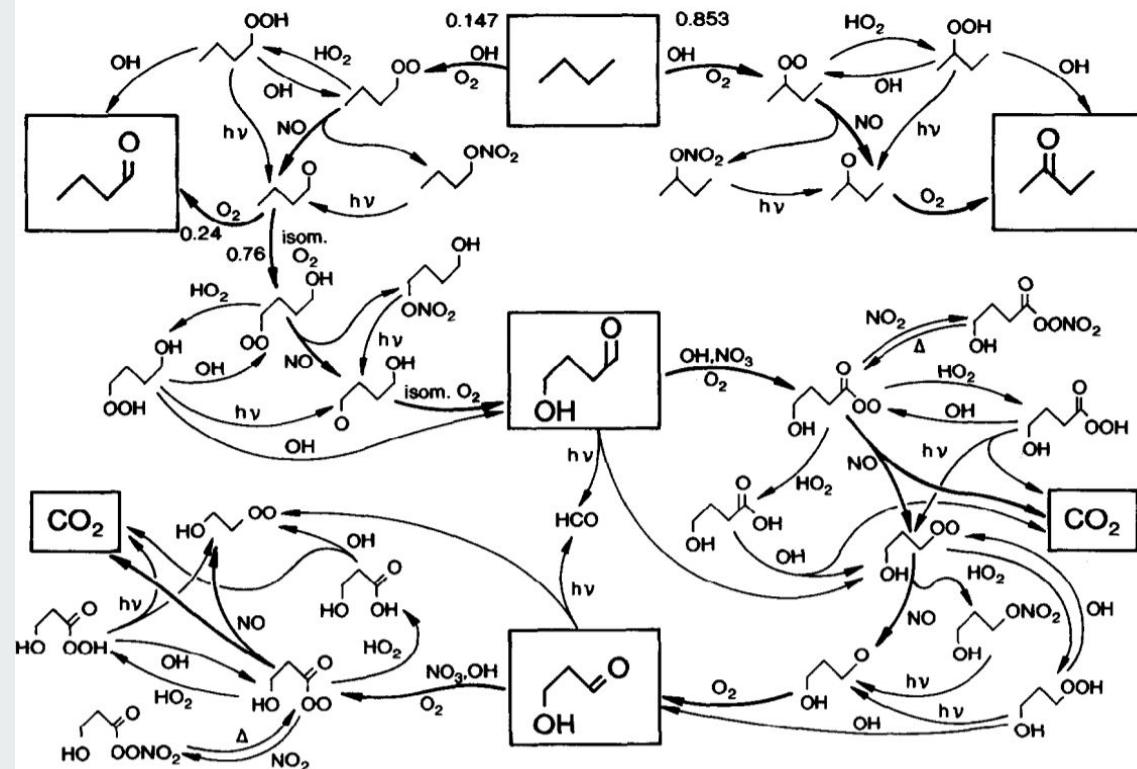


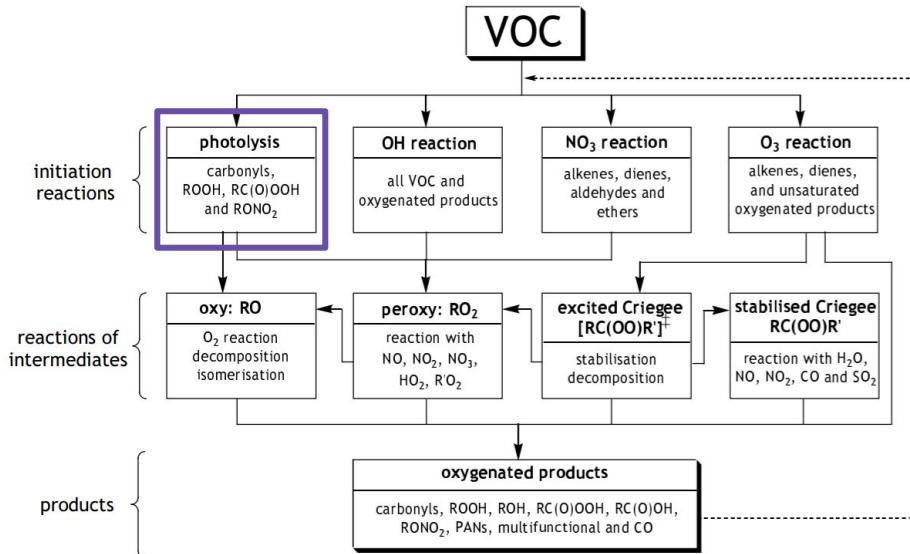
Fig. 1. Schematic representation of the degradation of butane, showing most of the chemistry which makes up the mechanism for this compound.

Modelling atmospheric chemistry

Field measurements



Computer modelling



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of York

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}
	→ 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

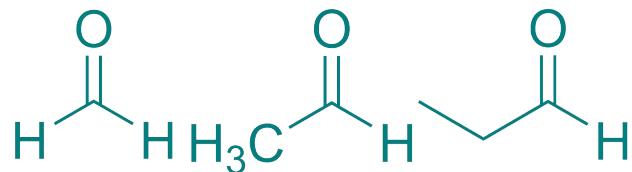
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Approximate hierarchy of information sources

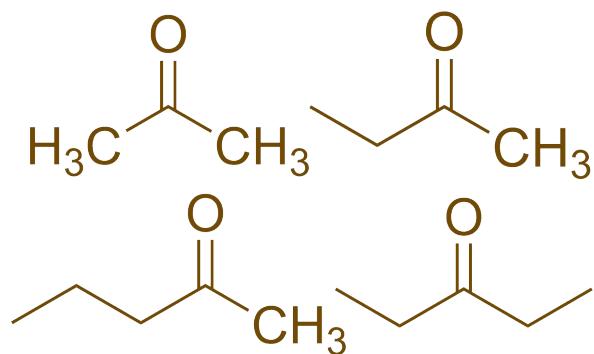
- 1) Experimental data (evaluated)
- 2) Experimental data (direct)
- 3) SARs (published)
- 4) SARs/analogy assumptions
- 5) Theoretical studies

My carbonyl data set

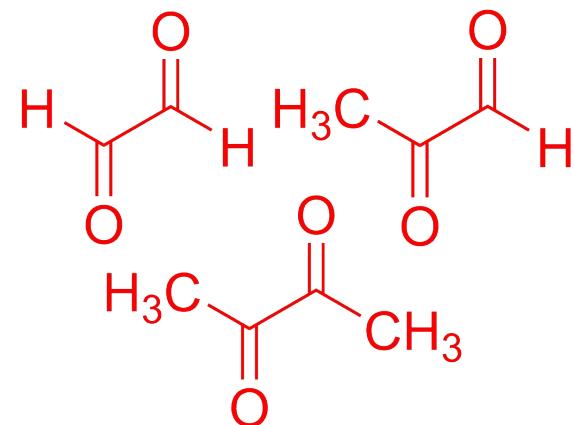
Linear aldehydes



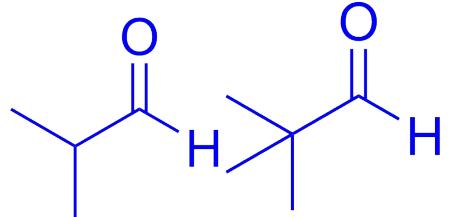
Ketones



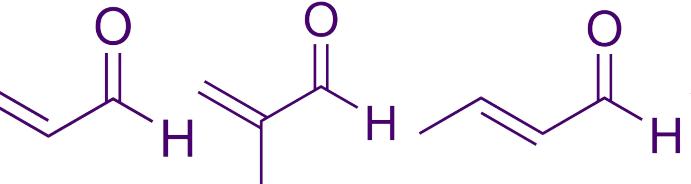
Dicarbonyls



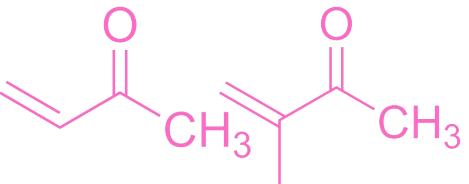
Branched aldehydes



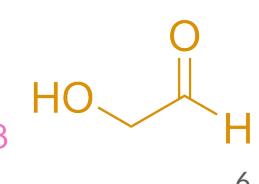
Enals



Enones



Carbohydrate



Photoexcitation of carbonyls

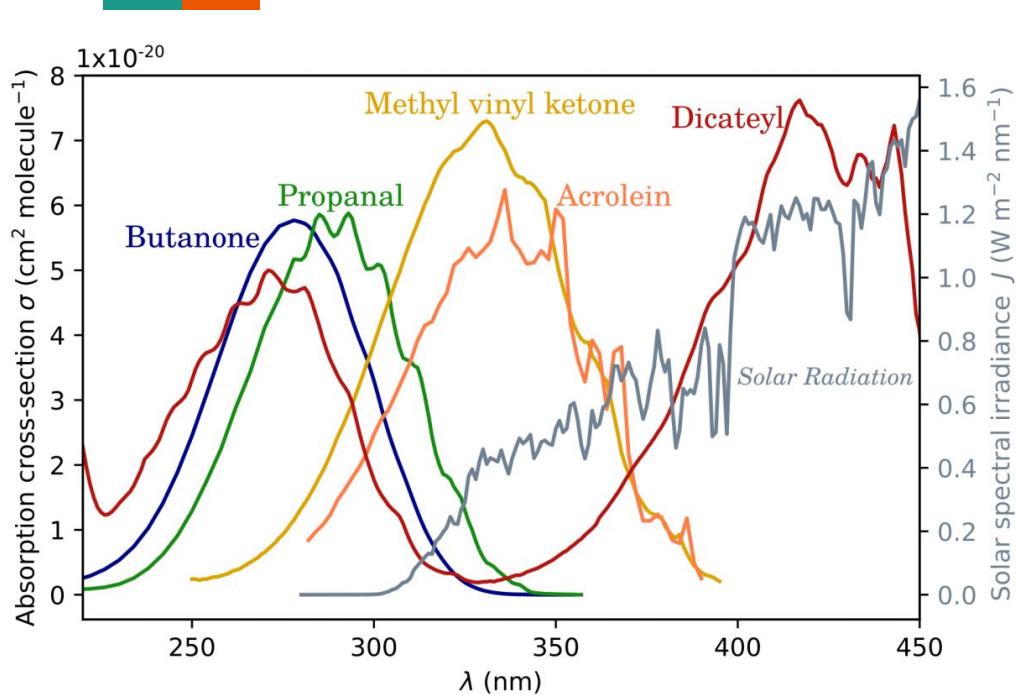


Figure 1.1: UV absorption spectra of butanone, propanal, methyl vinyl ketone (MVK), acrolein, and diacetyl, compared to solar radiation in the troposphere.

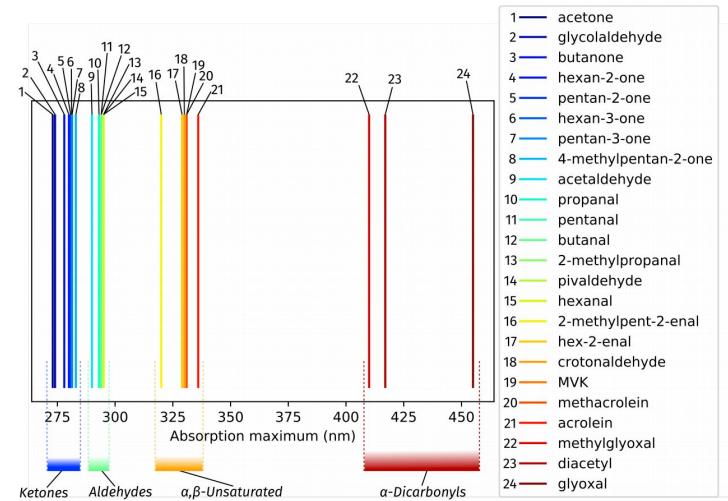


Figure 1.2: ‘Bar code’ plot of the λ_{\max} values from Table 1.1. The λ_{\max} values are separated into distinct regions by the type of carbonyl.

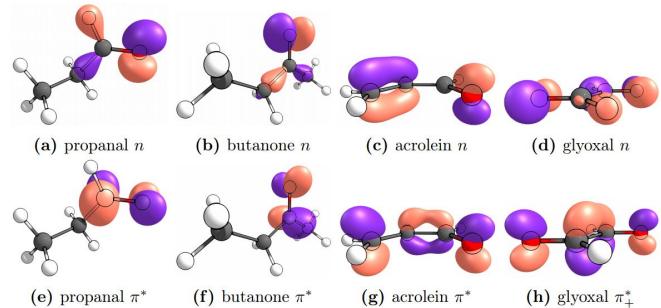
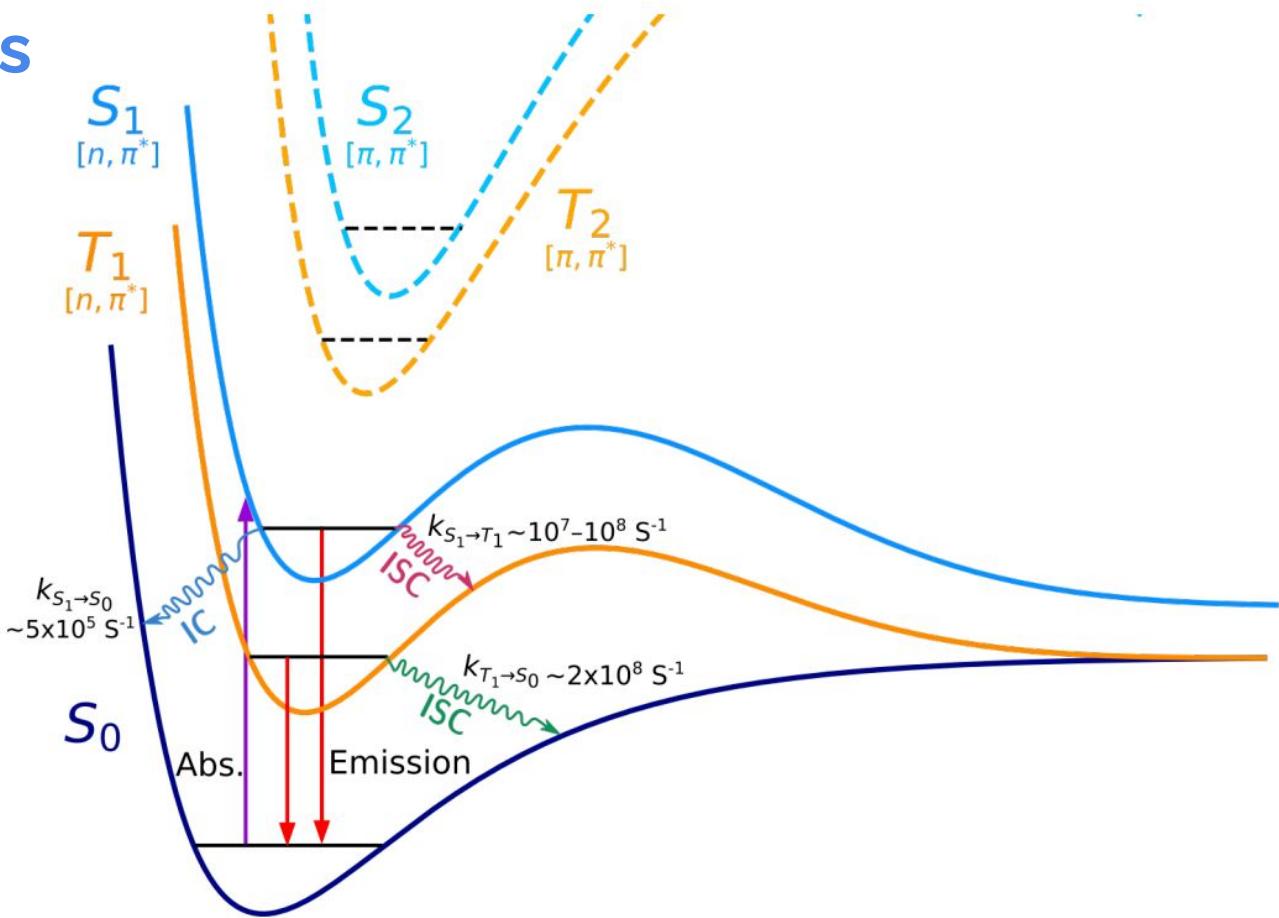
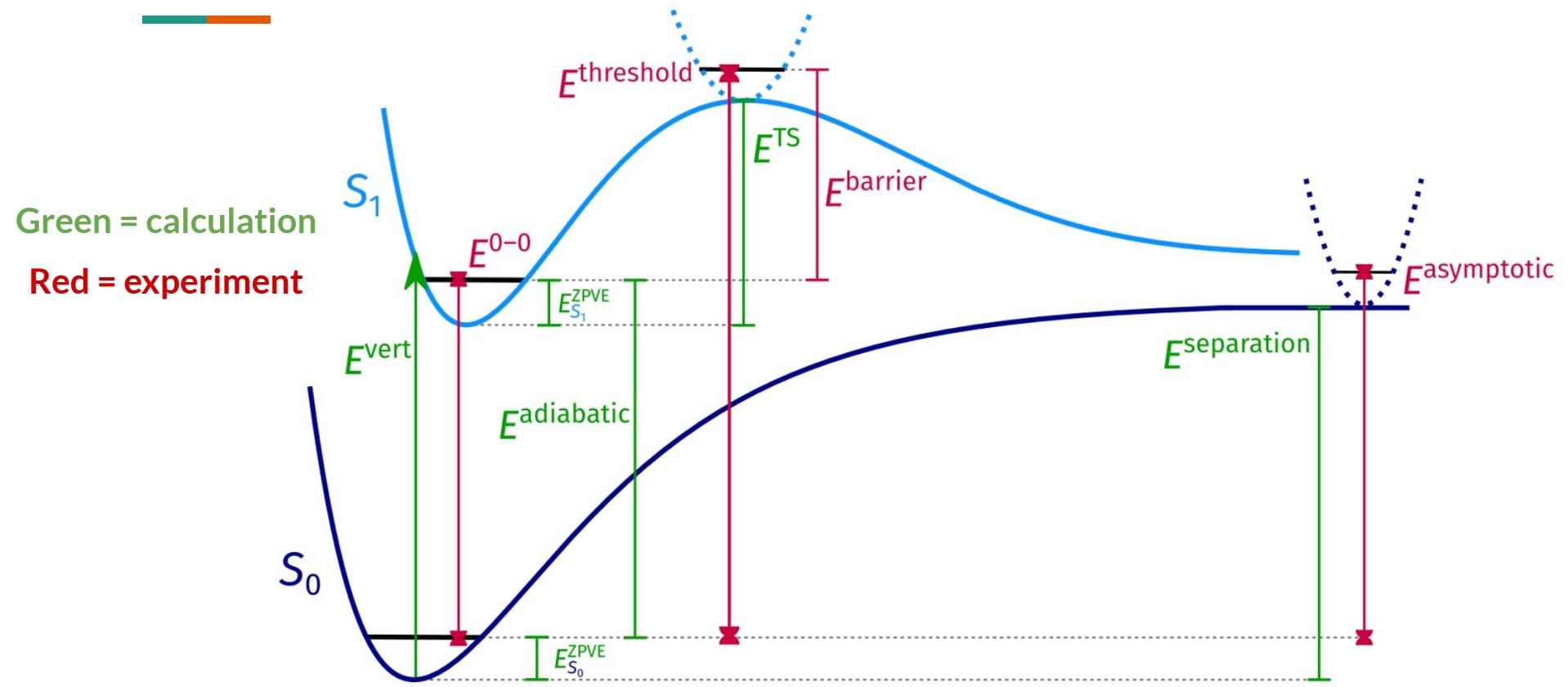


Figure 1.3: Natural transition orbital⁴⁹ representations of the computed n (top) and π^* (bottom) orbitals for select carbonyls from the dataset in this thesis.

Electronic states

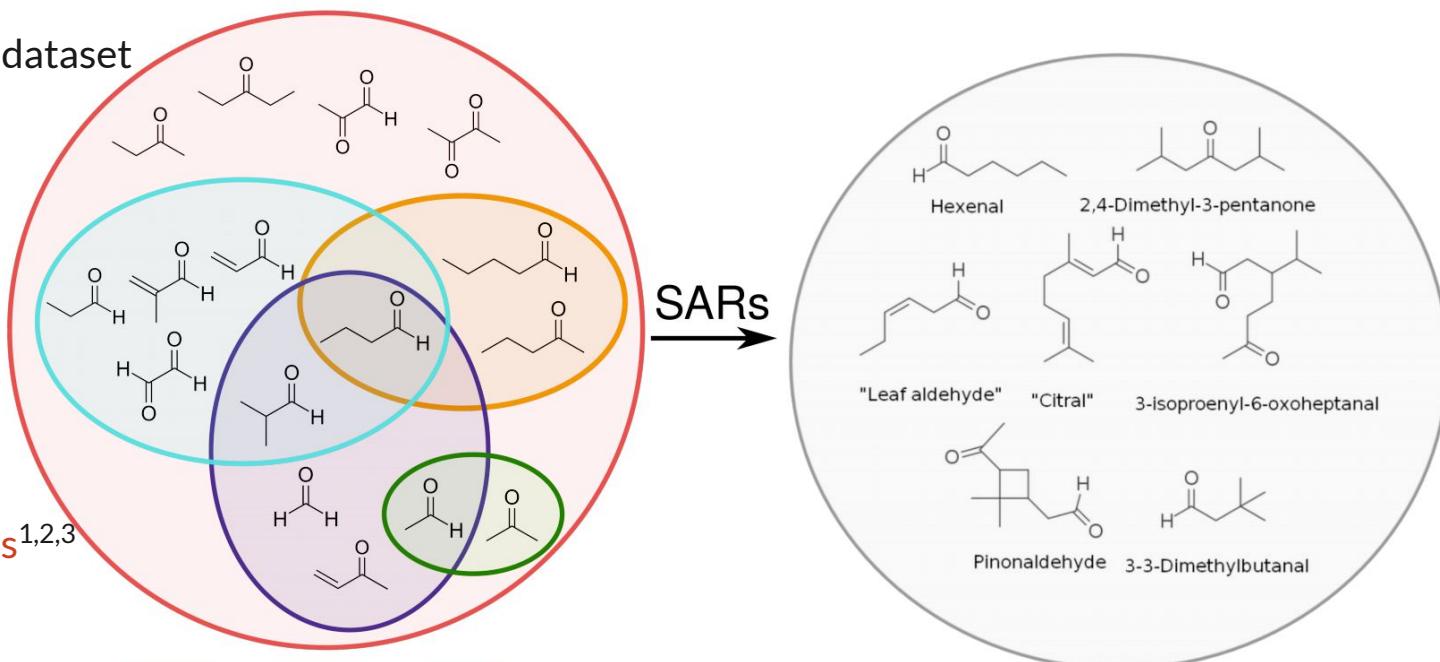


Calculating photolysis



Aim: structure-activity relationships for photolysis

- 38 (20+18) carbonyls in dataset
- 3 states (S_0 , T_1 , S_1)
- 10 types of reaction
- Method benchmarks
- Summary SARs
- No contemporary SARs^{1,2,3}



Future: apply SARs to other atmospheric carbonyls

- NTI
- NTII
- TF
- Decarbonylation
- Ketene production

Parameterise atmospheric carbonyls

Chapter 2

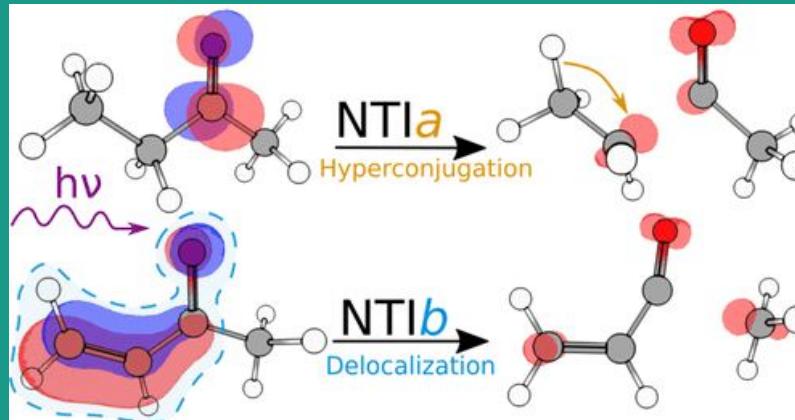
The Norrish Type I Reaction

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PHYSICAL CHEMISTRY A
 Cite This: *J. Phys. Chem. A* 2019, 123, 10381–10396
Article
pubs.acs.org/JPCA

Structural Effects on the Norrish Type I α -Bond Cleavage of Tropospherically Important Carbonyls

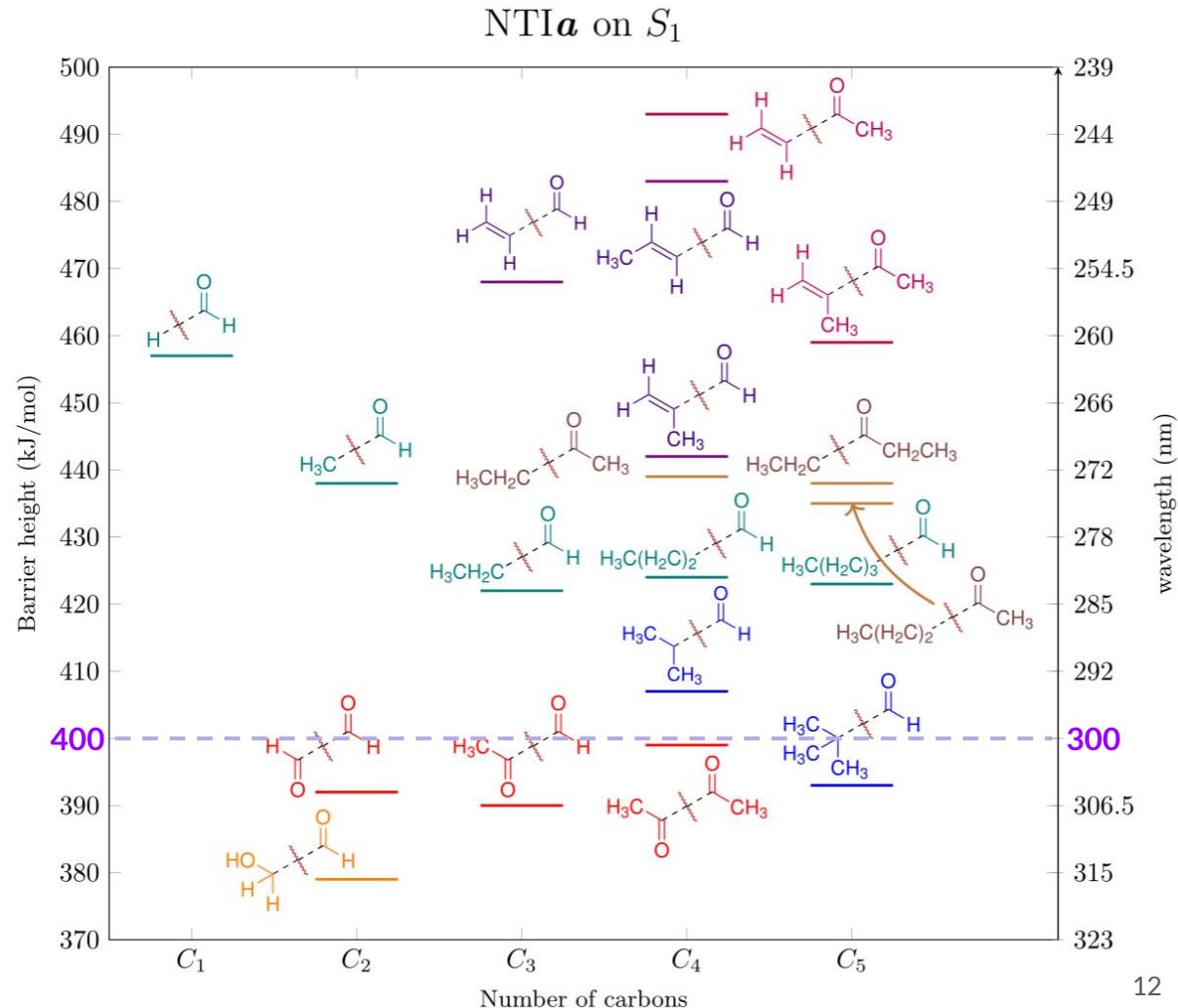
Published as part of *The Journal of Physical Chemistry* virtual special issue "Leo Radom Festschrift".

Keiran N. Rowell,[†] Scott H. Kable,^{†,‡} and Meredith J. T. Jordan^{*,‡,§}



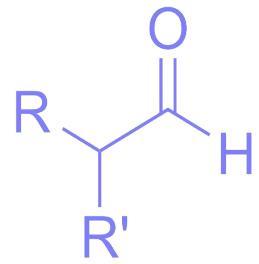
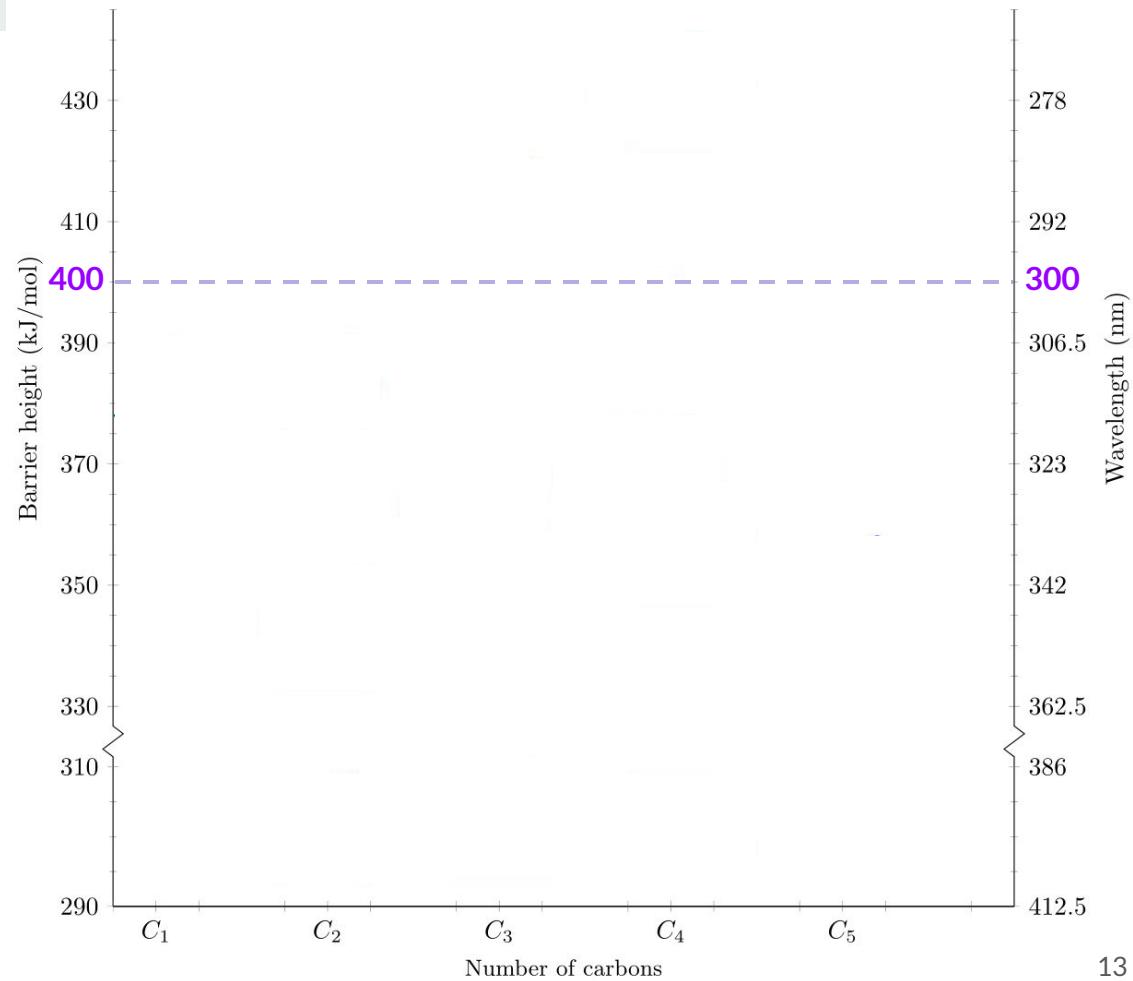
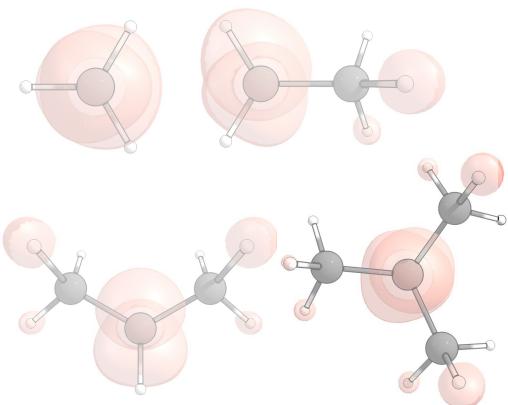
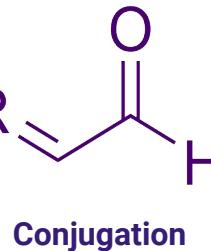
NTI*a* S_1 barriers

- 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



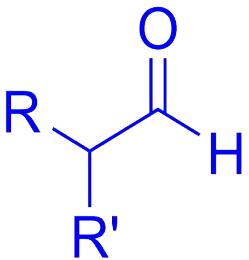
NTI*a* on T_1

NTI*a* T_1 barriers

**vs.**

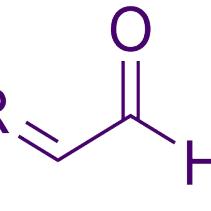
NTI*a* on T_1

NTI*a* T_1 barriers

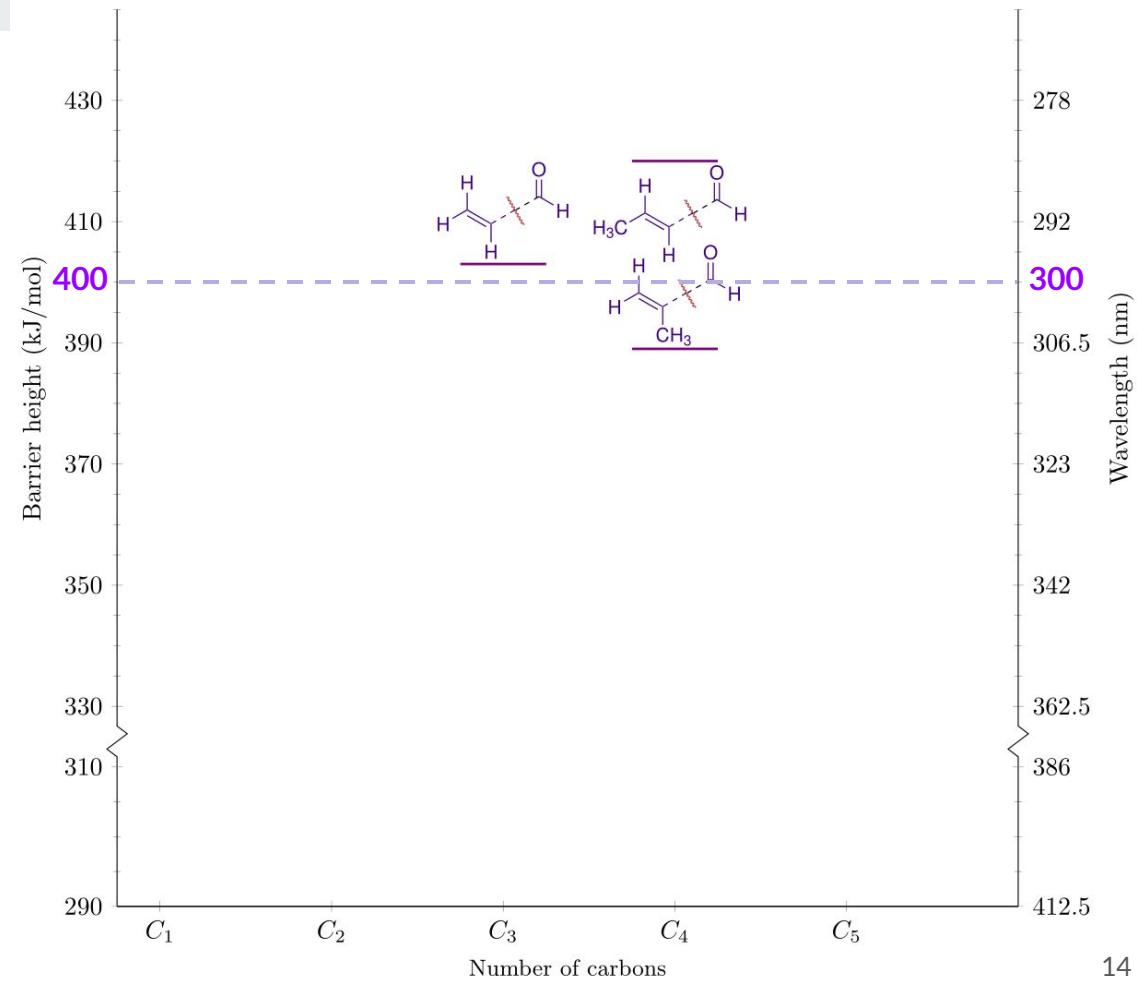
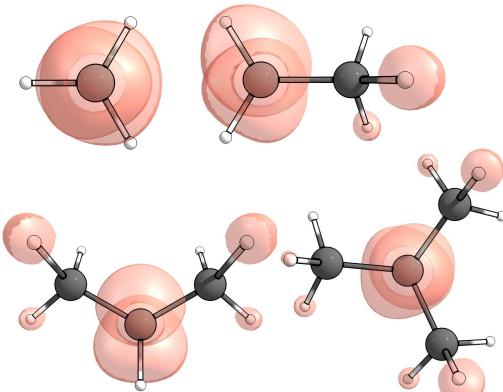


Branching

vs.



Conjugation

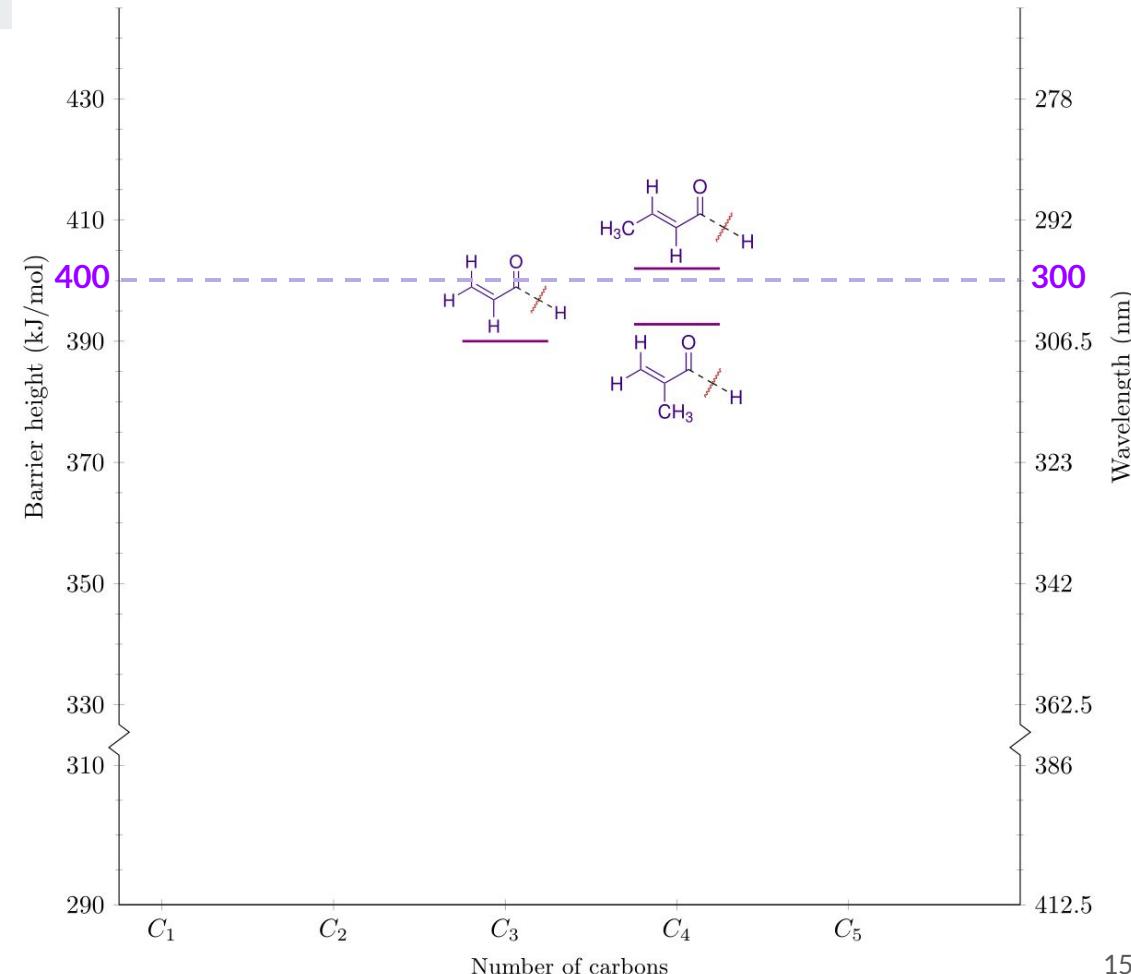


NTI*b* on T_1

NTI*b* T_1 barriers

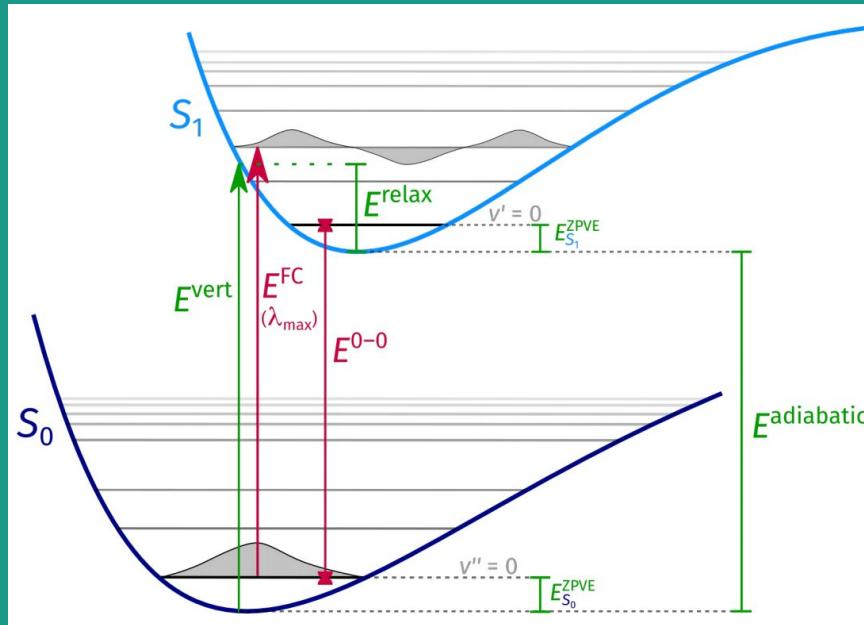
- If α,β -conjugated: cleave other bond

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

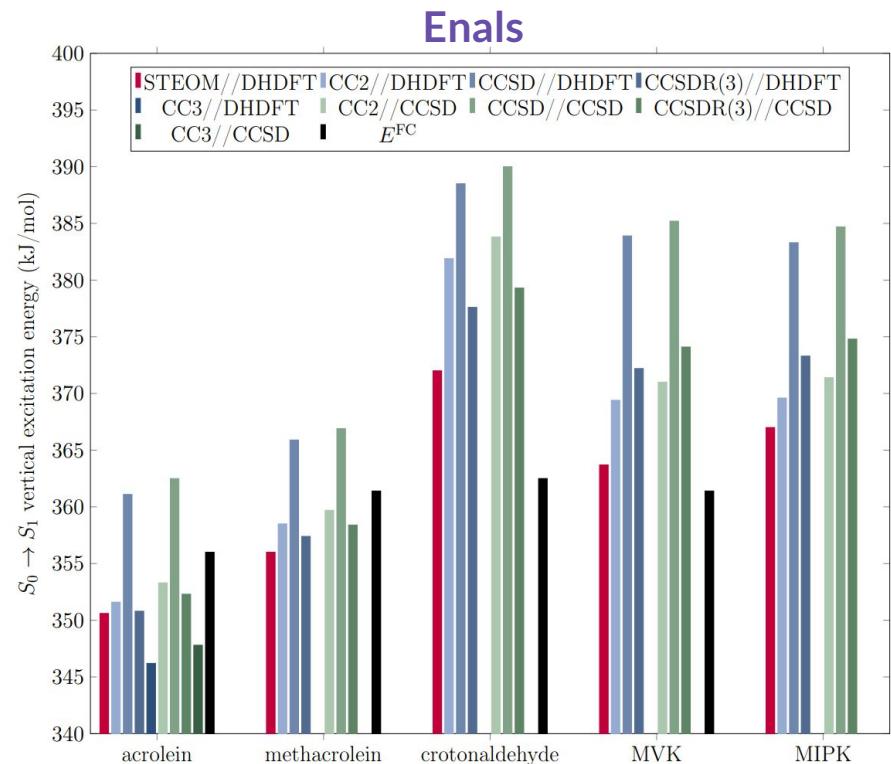
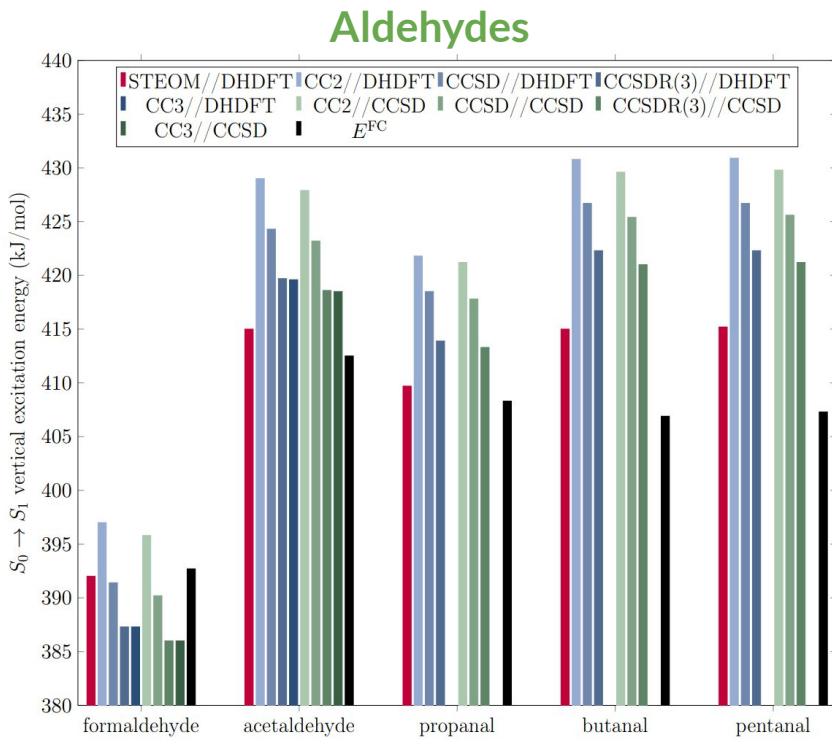


Chapter 3

Vertical, Adiabatic, and o-o Excitation Energies



Vertical excitation energy calculations



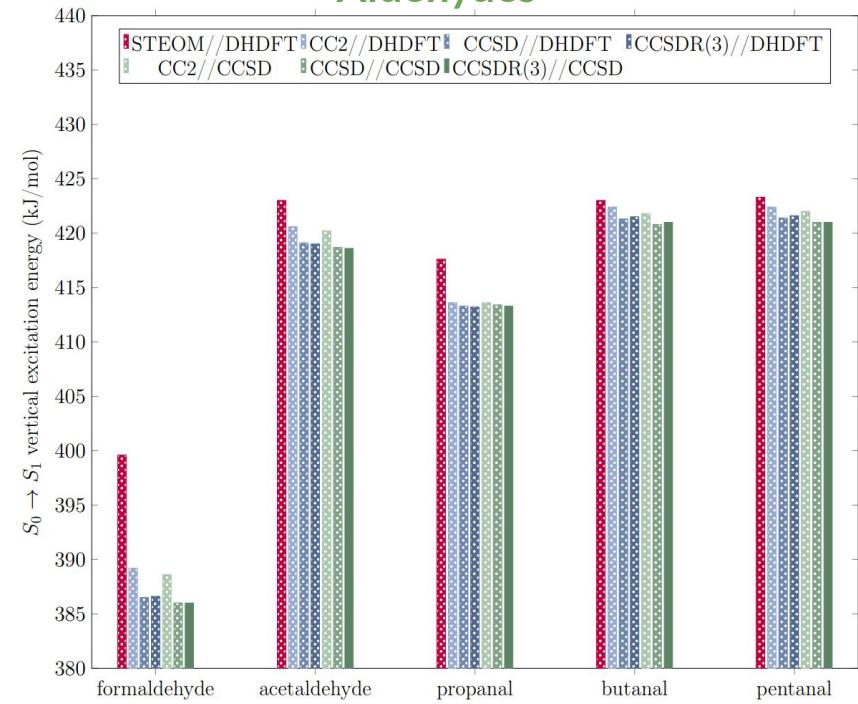
E^{vert} scaling factors

	B2GP-PLYP geometries				CCSD geometries	
	STEOM-CCSD	CC2	CCSD	CCSDR(3)	CC2	CCSD
Total	1.0190	0.9879	0.9837	0.9997	0.9880	0.9840
Standard Error	0.0035	0.0030	0.0014	0.0010	0.0026	0.0018
Saturated	1.0194	0.9804	0.9876	0.9983	0.9819	0.9893
Standard Error	0.0051	0.0014	0.0003	0.0005	0.0010	0.0002
Unsaturated	1.0182	1.0062	0.9749	1.0029	1.0027	0.9723
Standard Error	0.0035	0.0033	0.0013	0.0007	0.0035	0.0009

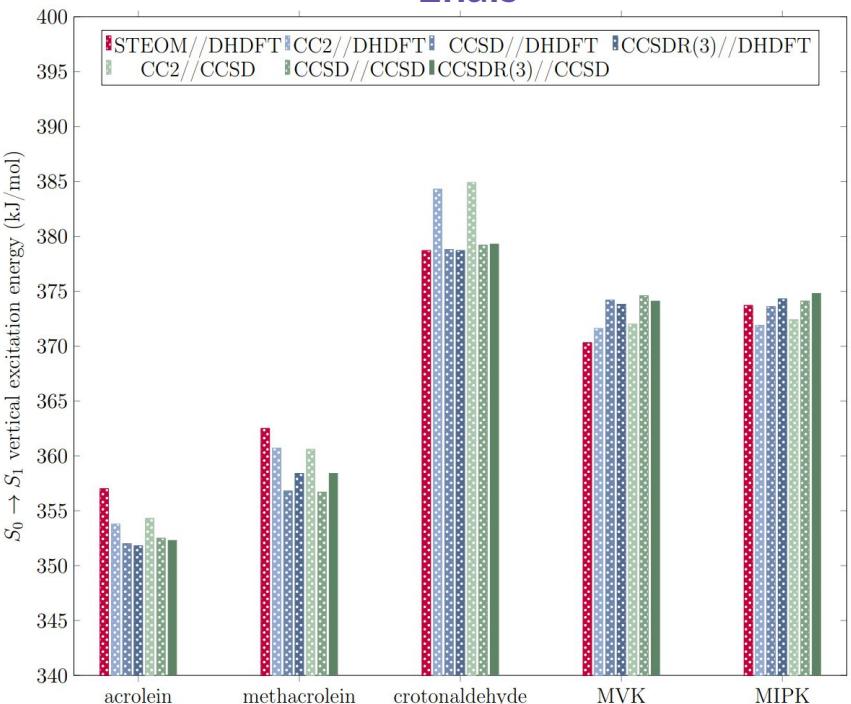
Scaled vertical excitation



Aldehydes



Enals

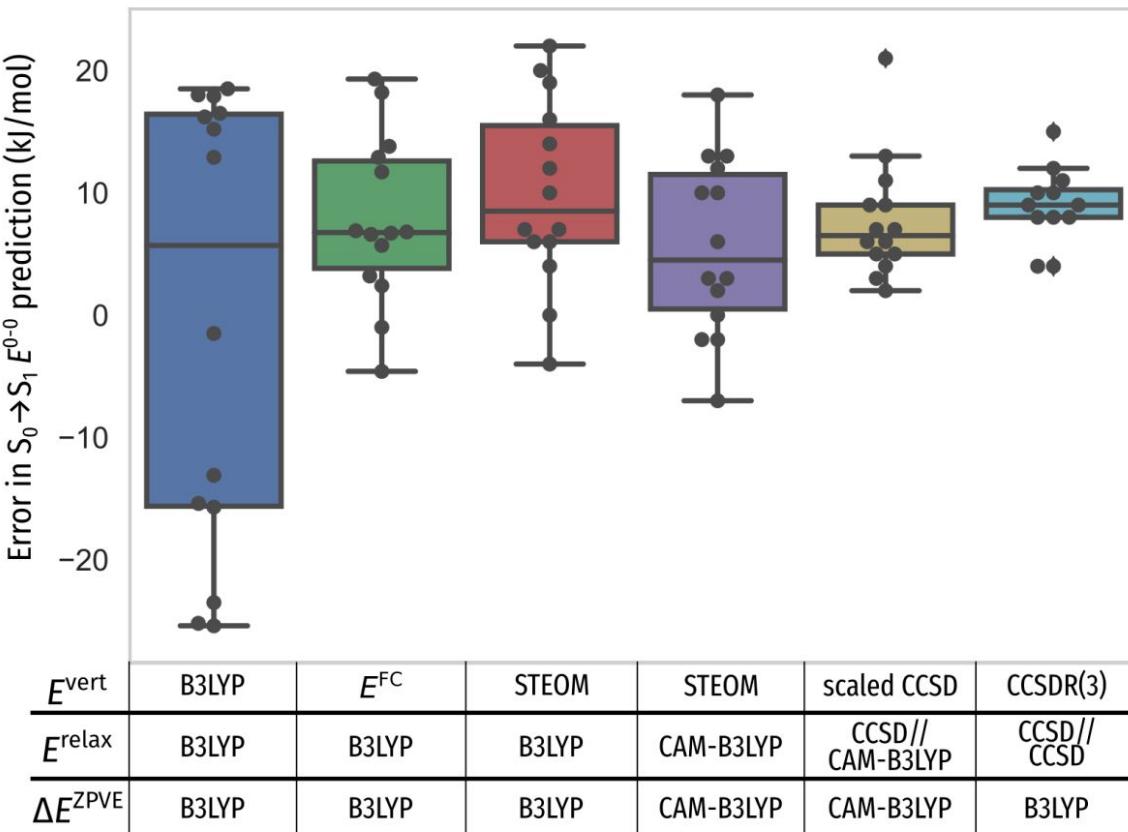


E^{0-0} protocols

Table 3.1: Experimental E^{0-0} energies. (kJ/mol)

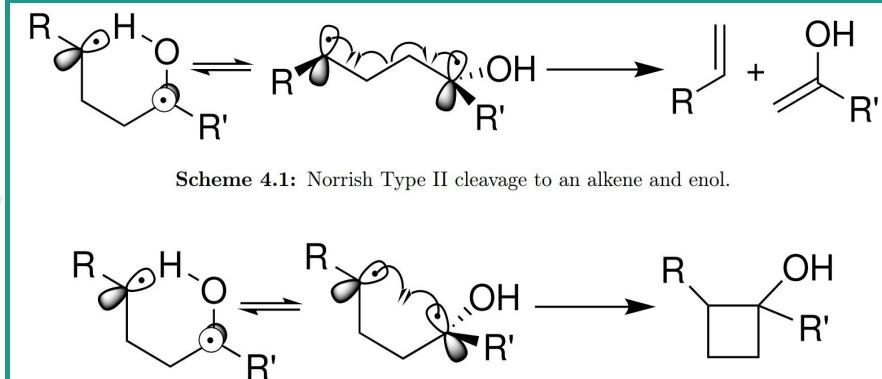
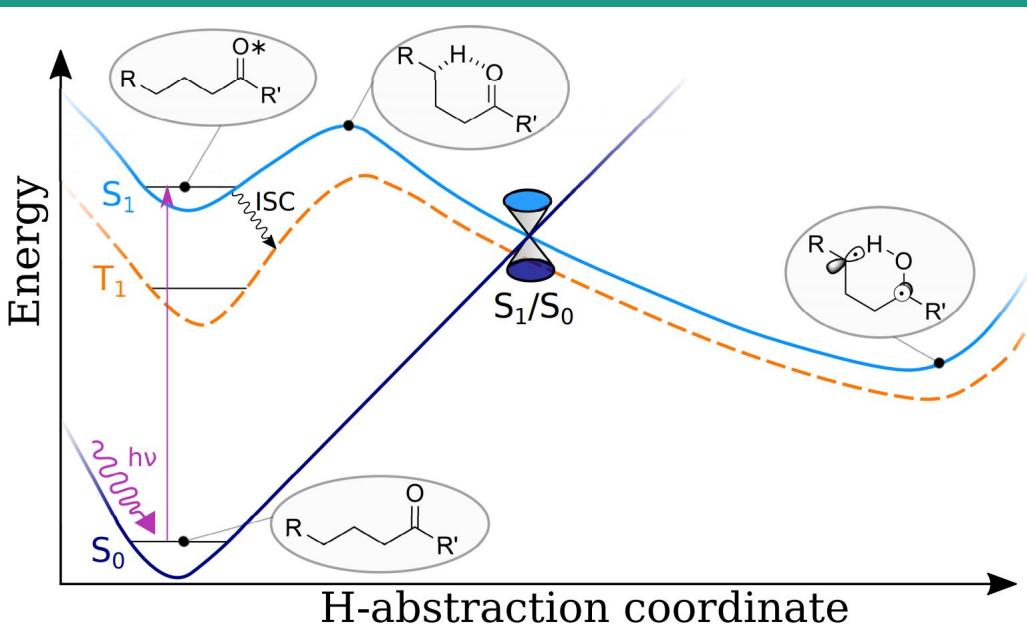
Molecule	$S_0 \rightarrow S_1 E^{0-0}$	$S_0 \rightarrow T_1 E^{0-0}$
<i>Aldehydes</i>		
Formaldehyde	337 ⁶	301 ⁶
Acetaldehyde	356 ⁷	326 ⁷
Propanal	350 ^{8†}	—
Butanal	—	—
Pentanal	—	—
2-Methylpropanal	349 ^{9†}	—
Pivaldehyde	349 ^{10†}	—
<i>Ketones</i>		
Acetone	364 ^{11†}	—
Butanone	359 ^{12†}	—
Pentan-2-one	—	—
Pentan-3-one	—	—
<i>α,β-Unsaturated carbonyls</i>		
Acrolein	310 ¹³	277 ¹³
Crotonaldehyde	317 ¹⁴	298 ¹⁵
Methacrolein	317 ¹⁴	297 ¹⁵
Methyl vinyl ketone	313 ¹⁴	—
Methyl isopropenyl ketone	—	—
<i>α-Dicarbonyls</i>		
Glyoxal	262 ¹⁶	230 ¹⁶
Methylglyoxal	265 ¹⁷	233 ¹⁸
Diacetyl	265 ¹⁹	—
<i>Carbohydrates</i>		
Glycolaldehyde	—	—

† Source publication/spectra could not be obtained.

Figure 3.16: Box and scatter plots of errors in $S_0 \rightarrow S_1 E^{0-0}$ predictions using different protocols. The method used for each component in E^{0-0} is shown below each column.

Chapter 4

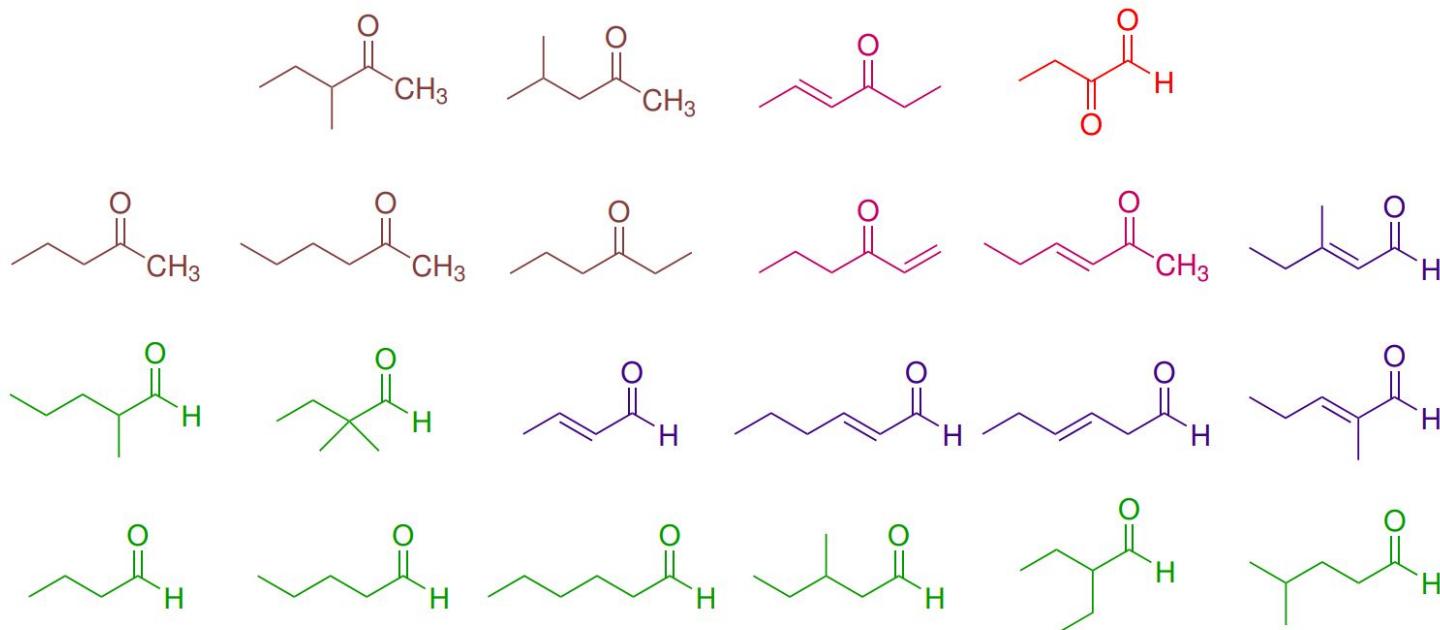
The Norrish Type II Reaction



Scheme 4.1: Norrish Type II cleavage to an alkene and enol.

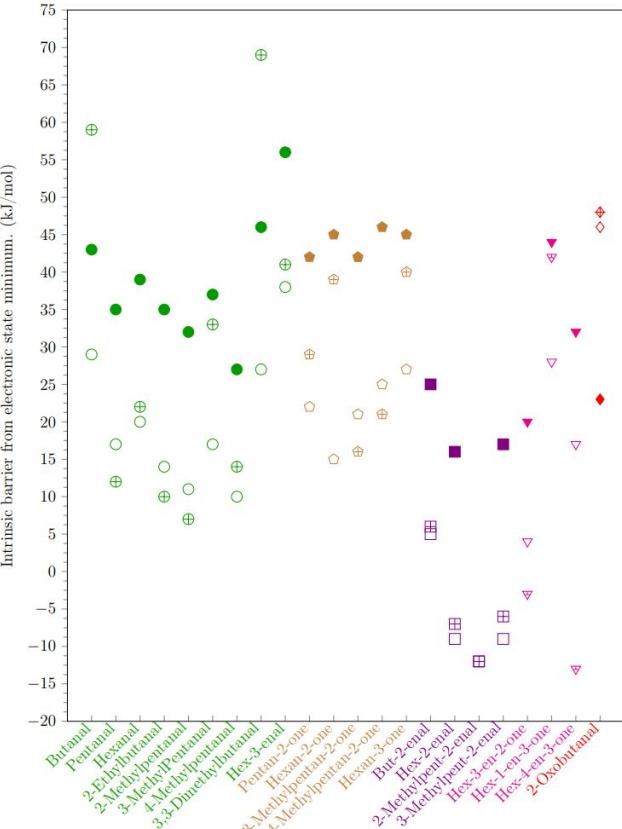
Scheme 4.2: Norrish Yang cyclisation to a substituted cyclobutanol.

NTII larger carbonyl dataset



Scheme 4.3: “Large” carbonyl dataset of species for which Norrish Type II reaction thresholds are calculated.

T_1 (filled) and S_1 (open) NTII intrinsic reaction barriers



	<i>S</i> ₁ NTII intrinsic barrier					ΔE_{ZPVE}
Single point energy:	CAM-B3LYP	M06-2X ^a	B2GP-PLYP	EOM-CCSD	Literature	CAM-B3LYP
<i>Aldehydes:</i>						
Butanal	10	57	29	59	34 ^b , 13 ^c , 15 ^d	-6
Pentanal	2	62	17	12	16 ^b , 6 ^c	-6
Hexanal	5	17	20	22		-5
2-Ethylbutanal	-2	9	14	10		-7
2-Methylpentanal	-2	7	11	7		-7
3-Methylpentanal	4	16	17	22		-6
4-Methylpentanal	-2	9	10	14		-4
3,3-Dimethylbutanal	12	70	26	69		-7
Hex-3-enal	21	27	38	41		-10
<i>Ketones:</i>						
Pentan-2-one	8	20	28	29	23 ^b , 14 ^c	-9
Hexan-2-one	2	36	15	39	16 ^b	-8
3-Methylpentan-2-one	7	17	21	16		-9
4-Methylpentan-2-one	10	11	25	21		-8
Hexan-3-one	11	22	26	40		-9
<i>Enals:</i>						
But-2-enal	-9	4	5	6	-8 ^c	-6
Hex-2-enal	-19	-5	-9	-7		-4
2-Methylpent-2-enal	-18	-8	-12	-12		-4
3-Methylpent-2-enal	-16	-2	-9	-6		-4
<i>Enones:</i>						
Hex-3-en-2-one	-6	-3	4	-3		-6
Hex-1-en-3-one	15	14	28	42		-9
Hex-4-en-3-one	2	-13	17	-13		-8
<i>Dicarbonyls:</i>						
2-Oxobutanal	21	30	46	48		-7

^a GD3 dispersion parameters used since GD3BJ dispersion parameters are not available for M06-2X functional in Gaussian 16.

^b TD-M06-2X/6-31++G(3df,2p)//TD-M06-2X/6-31++G(d,p) from Shaw.²⁶

^a XMCQDPT2/6-31+G(d) // SA-CASSCF/6-31+G(d) from Kletskii *et al.*⁴

^d CIS(D)/cc-pVTZ from Tadić *et al.*⁵

CASSCF calculations & S_1 / S_0 conical intersection

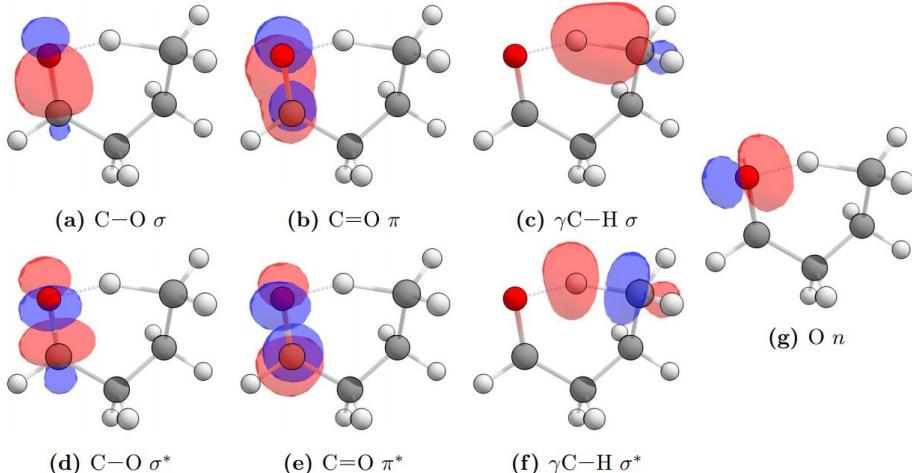
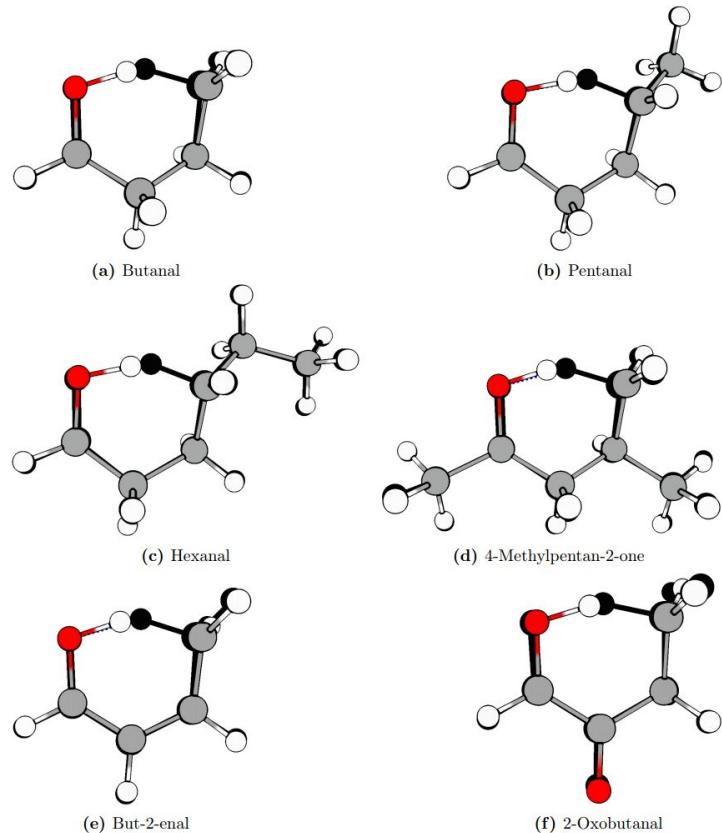
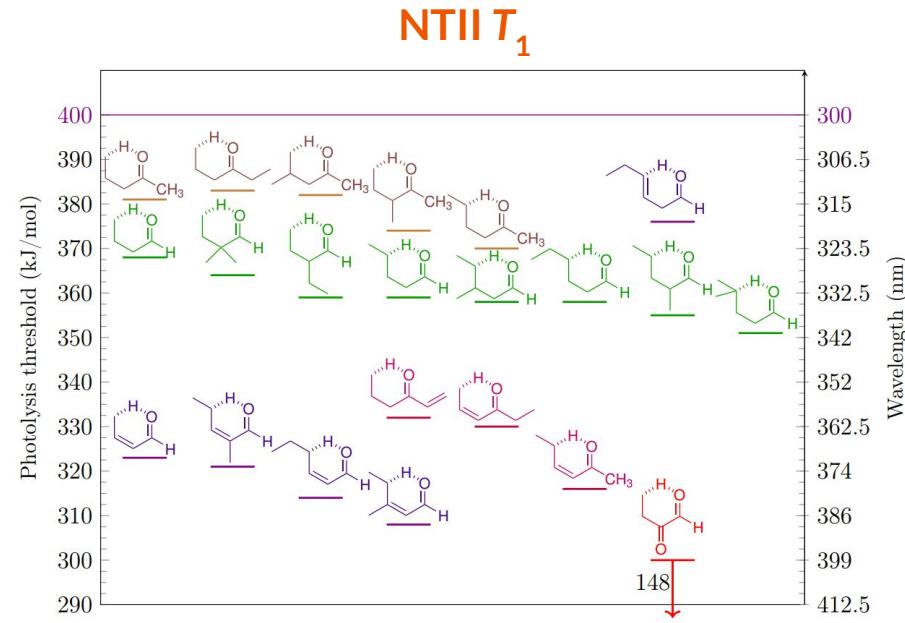
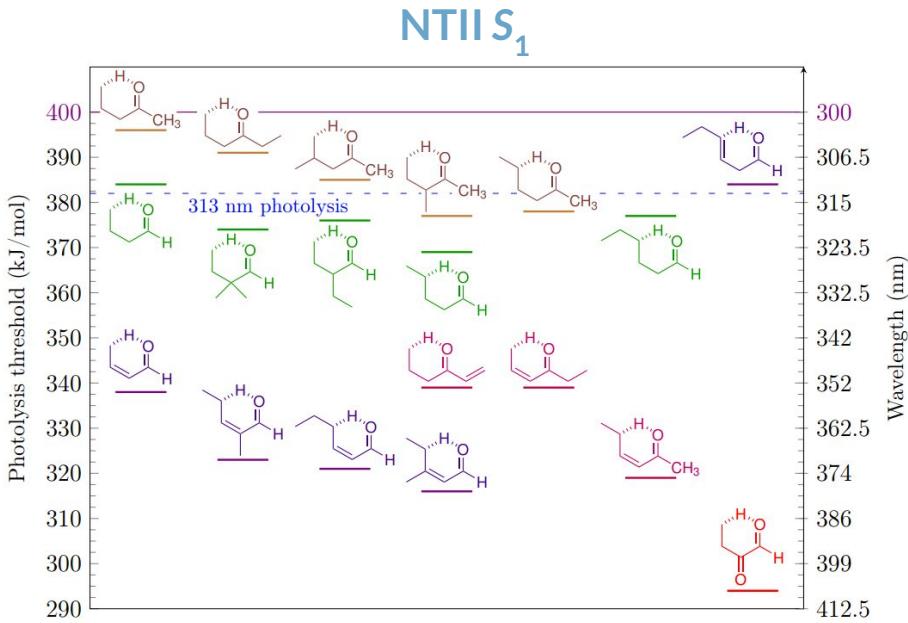


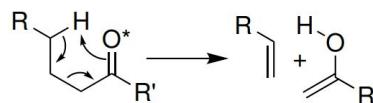
Figure D.1: Natural bond orbitals for butanal, showing those typical for the active space of a CAS(8,7) calculation on a saturated carbonyl. CAS(10,8) active spaces include the other oxygen-centred NBO.



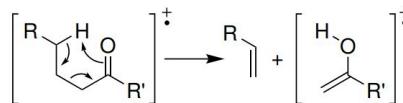
NTII S_1 and T_1 photolysis thresholds



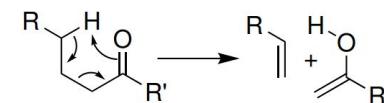
Reaction on S_o ?



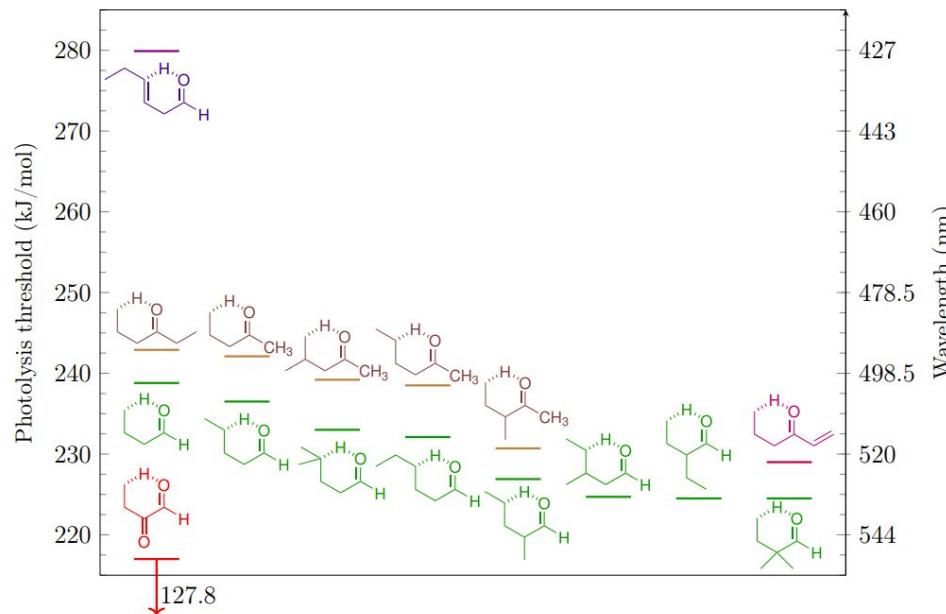
(a) Concerted NTII



(b) McLafferty



(c) Retro-ene



Chapter 5

Ground State Reactions

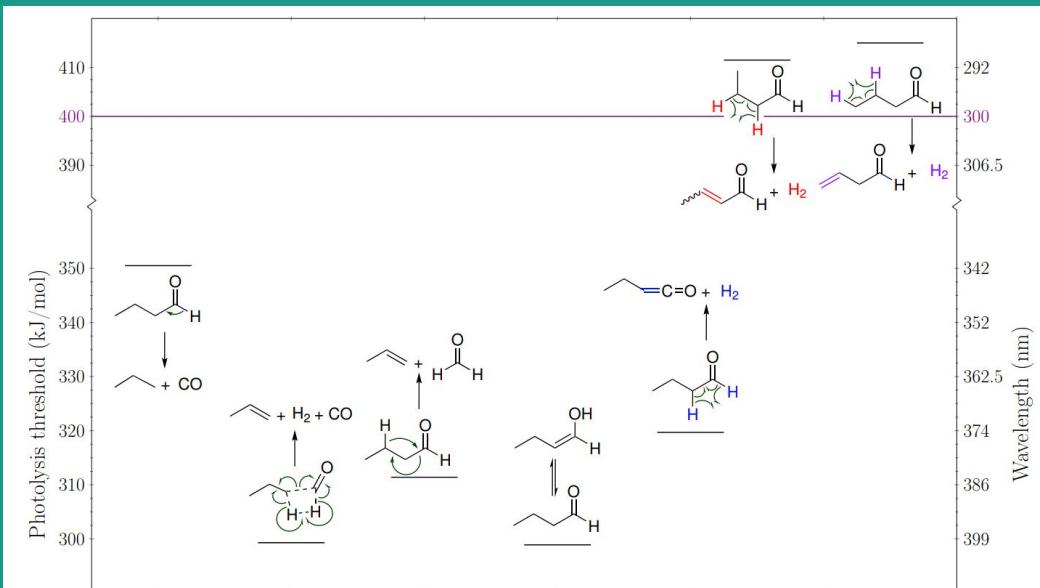
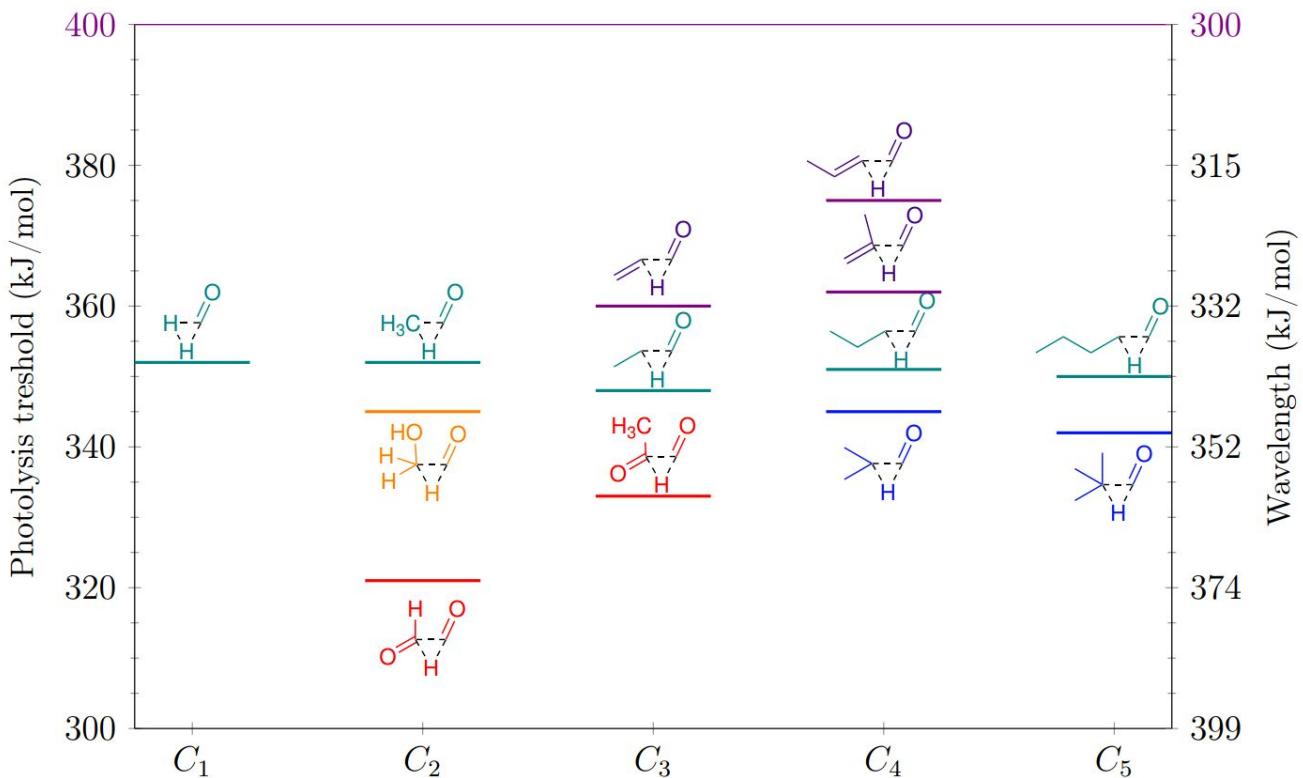
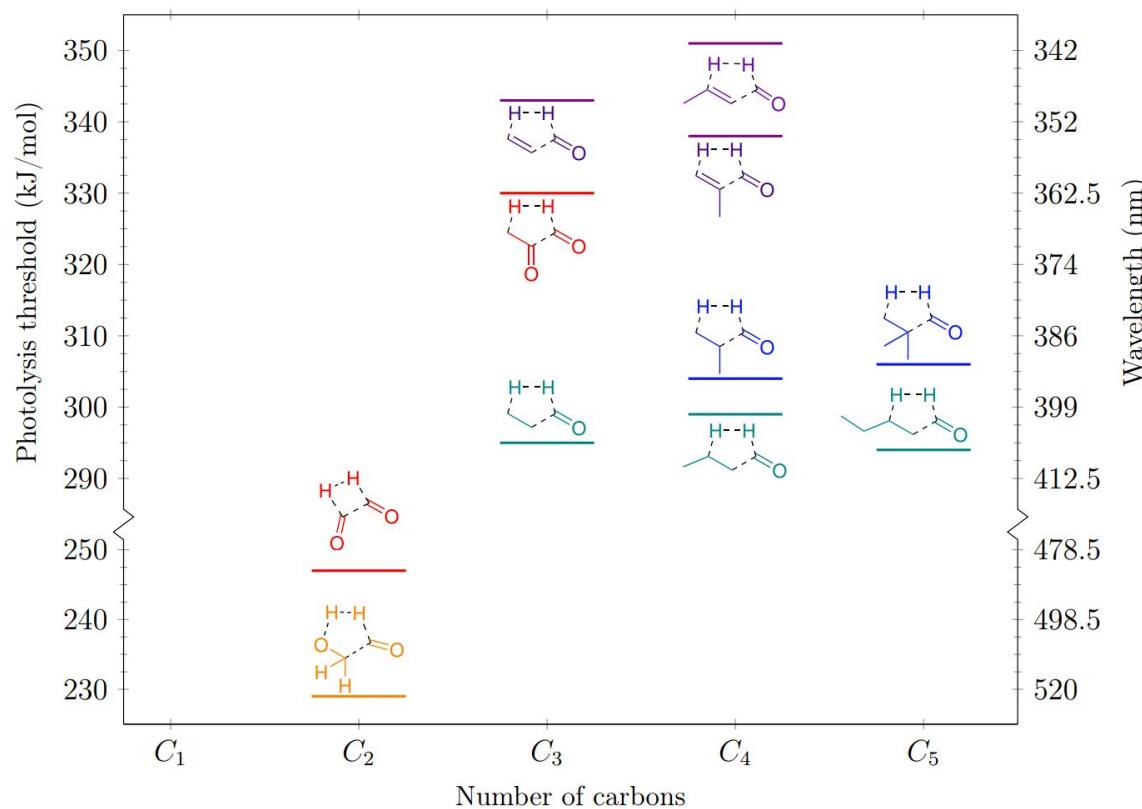


Figure 5.1: Possible S_0 reaction channels in butanal. Seven of the eight S_0 reaction classes studied in this chapter are illustrated.

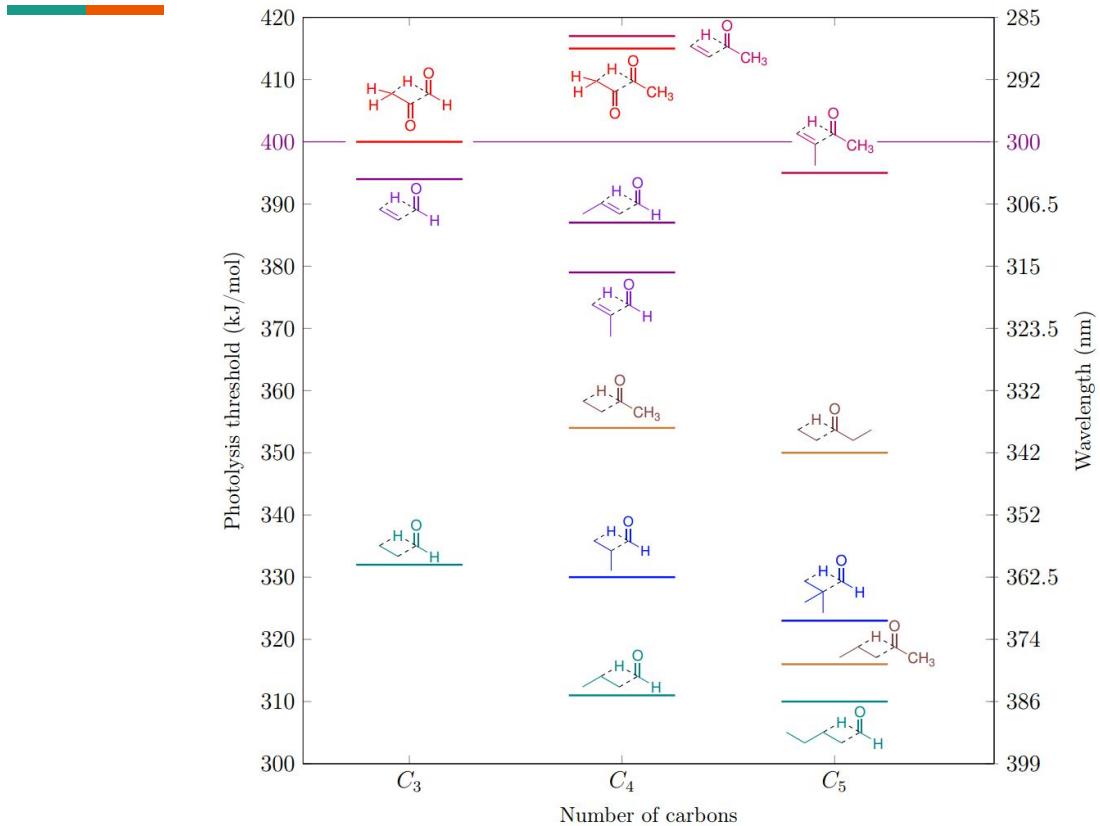
Decarbonylation



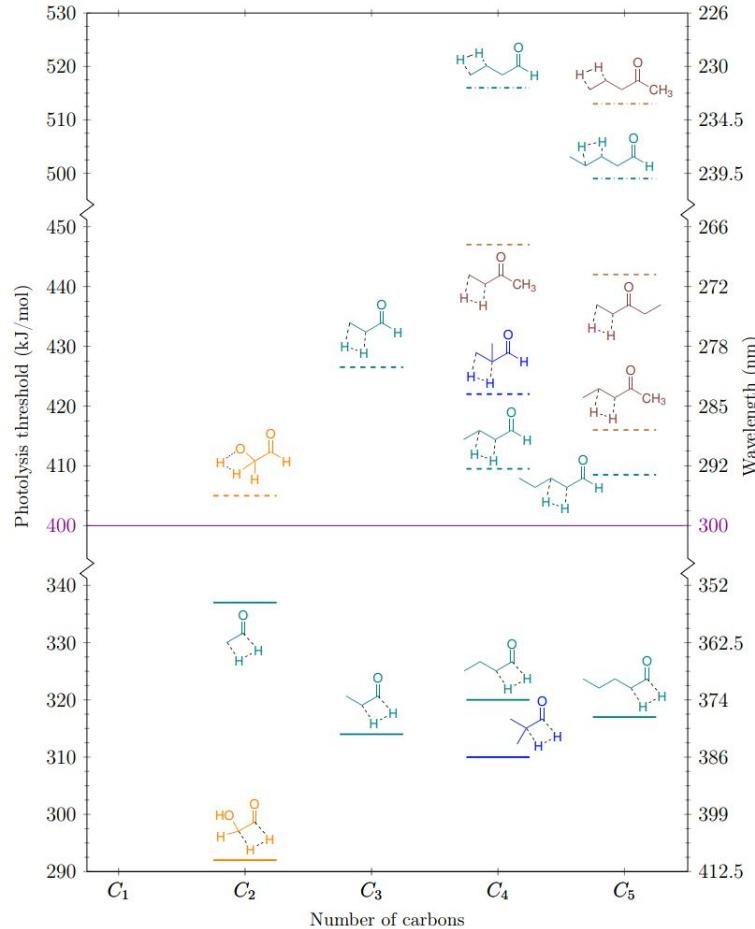
Triple Fragmentation



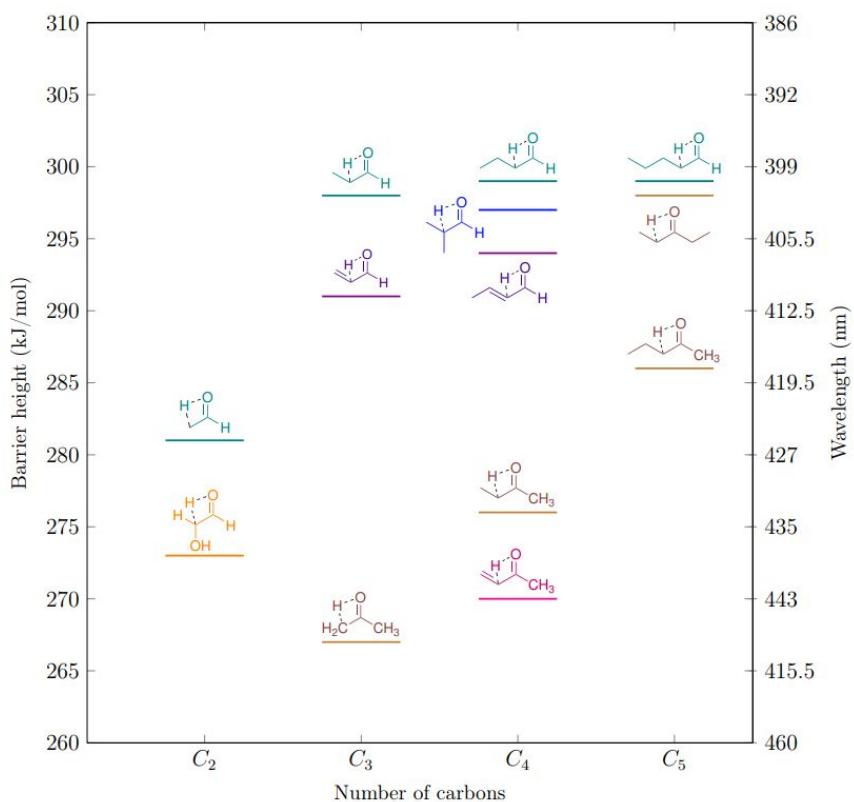
Norrish Type III (α -H transfer)



H₂ loss reactions



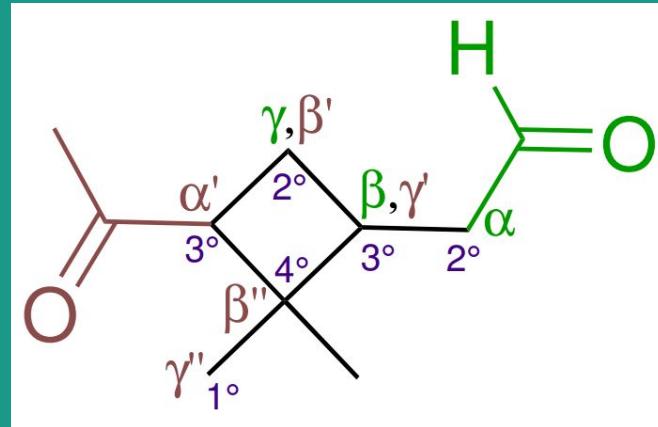
Keto-enol tautomerisation



Chapter 6

Application of SARs to Carbonyl Photolysis

Pinonaldehyde



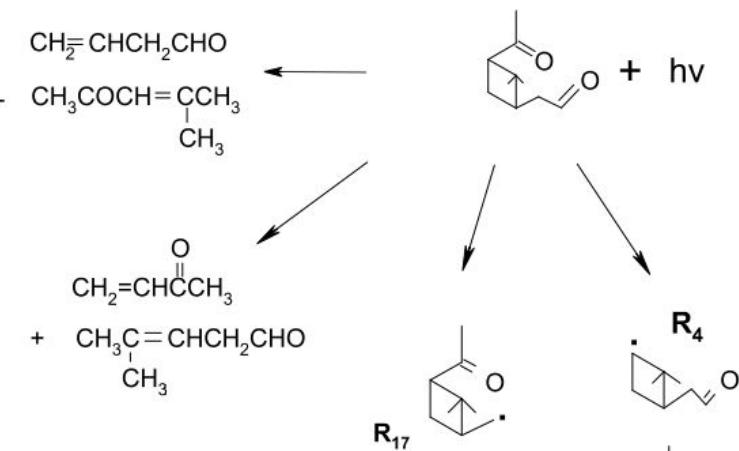
Previous photolysis schemes

Atmos. Chem. Phys., 4, 2285–2311, 2004
www.atmos-chem-phys.org/acp/4/2285/
SRef-ID: 1680-7324/acp/2004-4-2285
European Geosciences Union



Alpha-pinene oxidation by OH: simulations of laboratory experiments

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Uses “surrogates”
(no experimental data)

- Both “NTII” reactions same QY, hexanal
- **Aldehyde NTIa** QY from hexanal
- **Ketone NTIa'** QY from butanone
- **Poor surrogates:** even though butanone's NTIa threshold is higher, will have lower apparent QY than hexanal due to NTII
- **Degree of substitution doesn't match.**

NTII is not ‘molecular’ channel:
Doesn't cleave two bonds rules!

Pinonaldehyde smog chamber data



PERGAMON

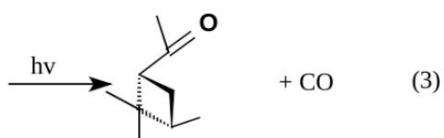
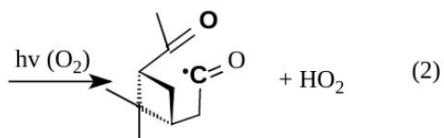
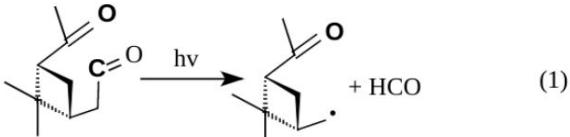
Atmospheric Environment 37 (2003) 1835–1851

ATMOSPHERIC
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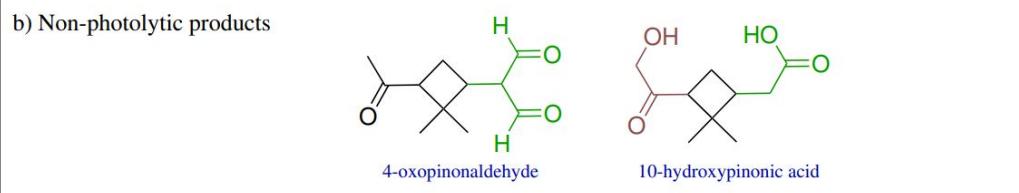
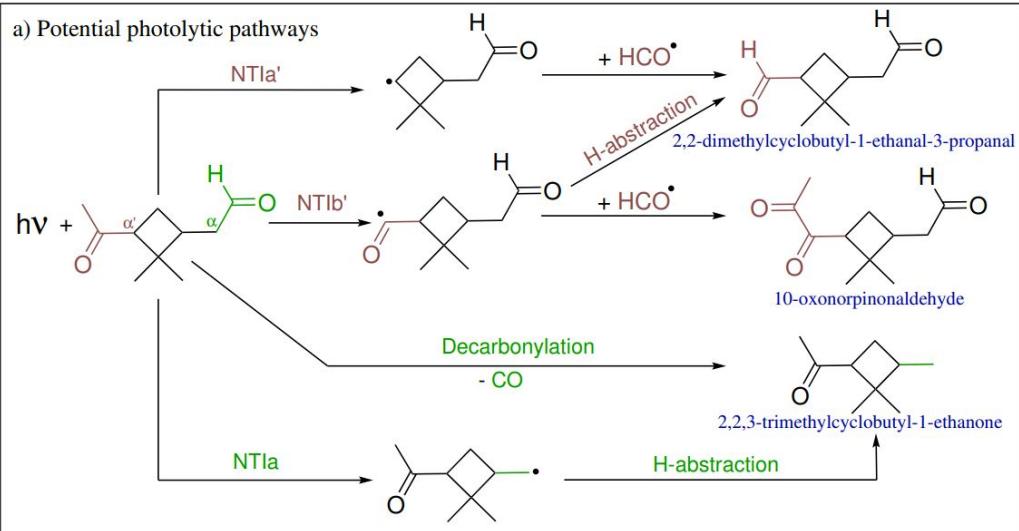
www.elsevier.com/locate/atmosenv

Gas phase photolysis of pinonaldehyde in the presence of sunlight

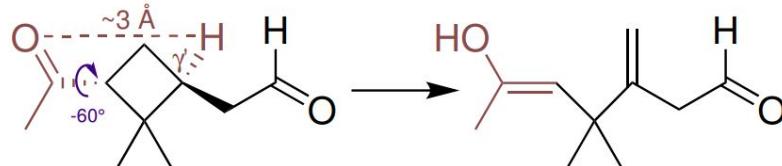
M. Jaoui*, R.M. Kamens



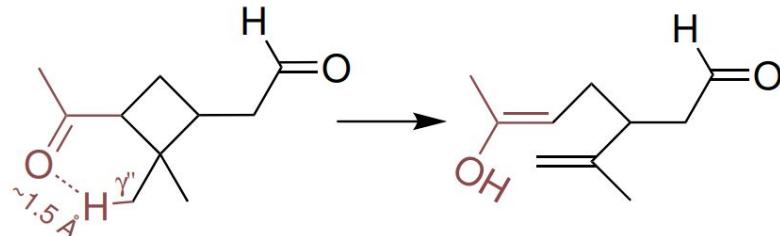
Scheme 2.



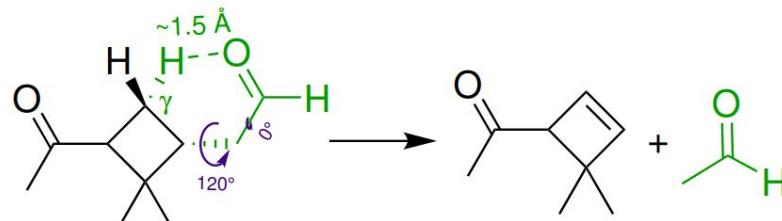
Applying SARs: what about pinonaldehyde NTII?



(a) The γ' -H is too distant from the ketone moiety in pinonaldehyde for NTII abstraction.



(b) The γ'' -H is more readily accessible for abstraction by the ketone moiety in pinonaldehyde.

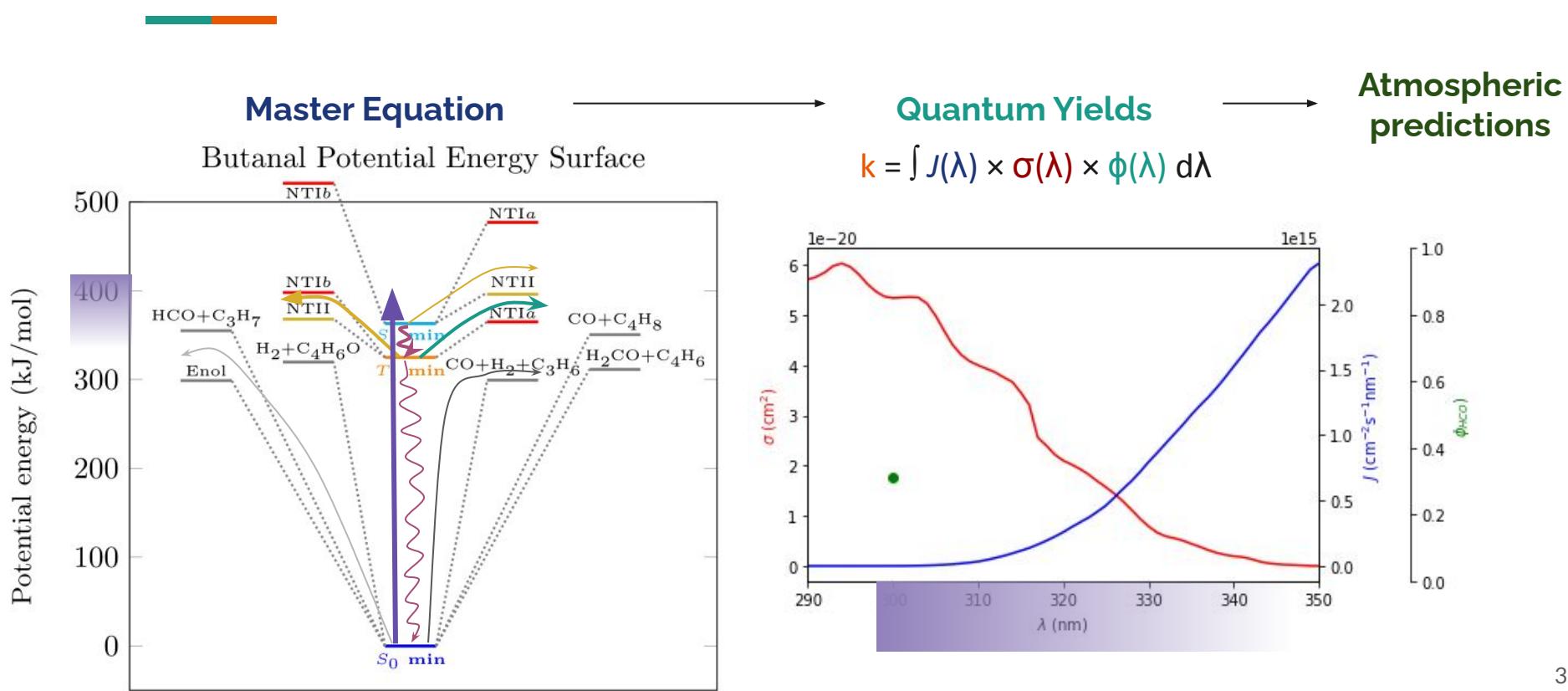


(c) Abstraction of the γ -H by the aldehyde moiety in pinonaldehyde is conformationally plausible, but requires some disfavoured dihedral angles and likely involves significant ring-strain of the cyclobutene moiety.

Chapter 7

Conclusions and Future Work

Future Work — SARs for quantum yields



Future Work — SARs for quantum yields



Master Equation

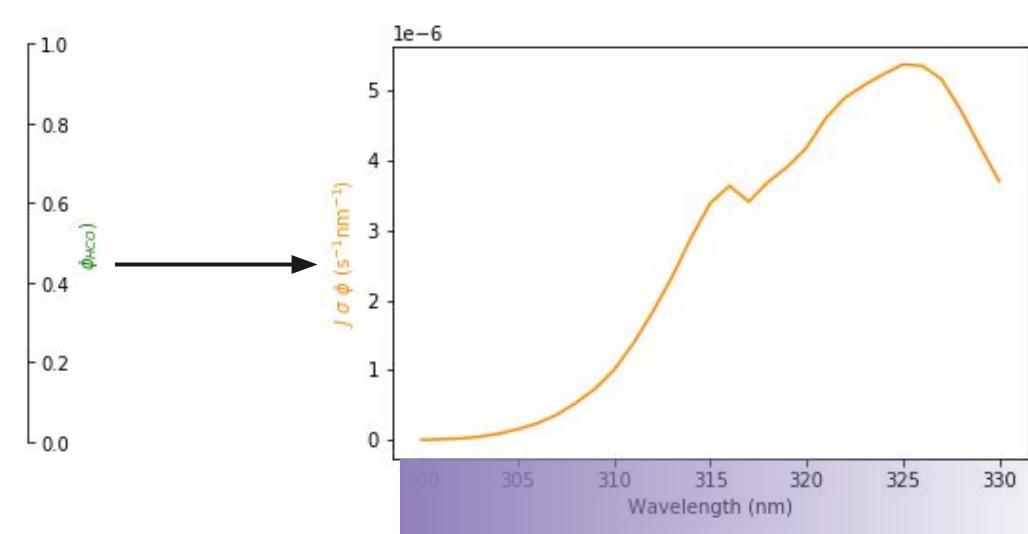
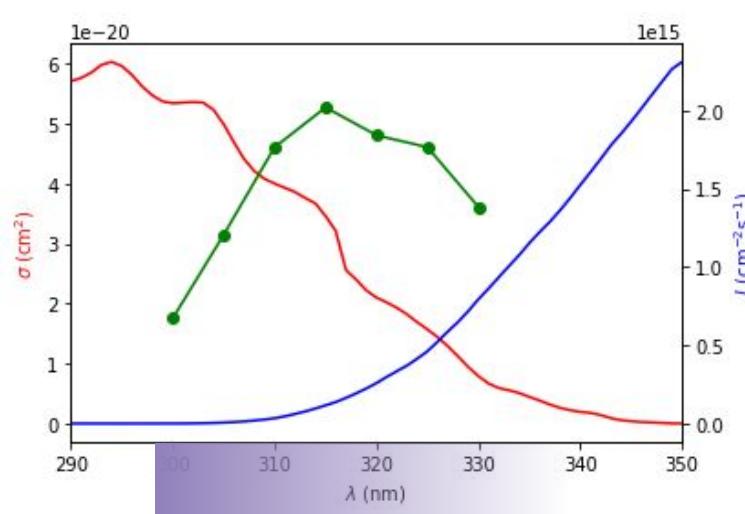


Quantum Yields



Atmospheric predictions

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

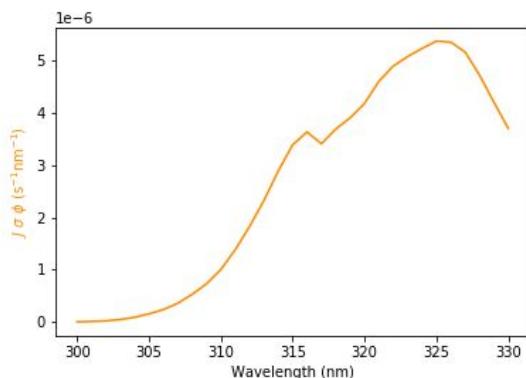


Future Work — SARs for quantum yields



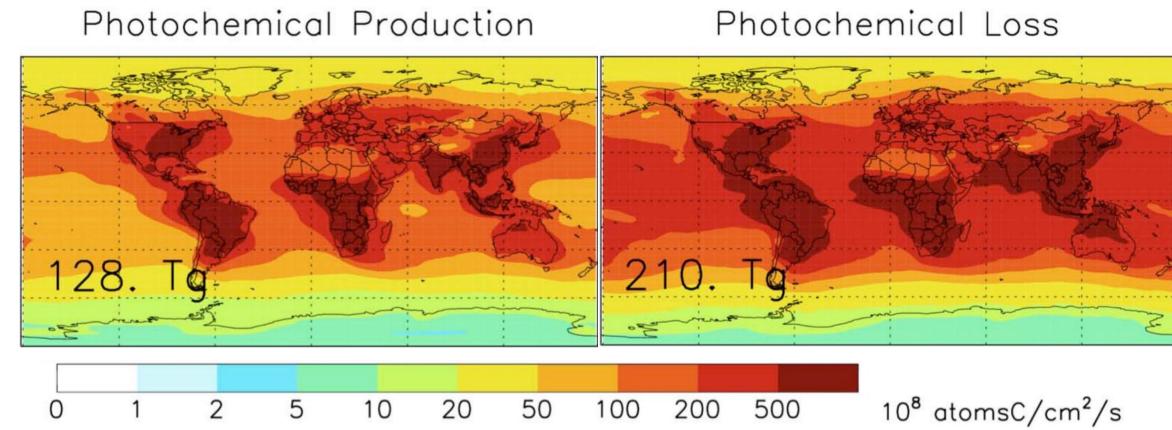
Quantum Yields

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



Atmospheric predictions

CH3CHO photolysis

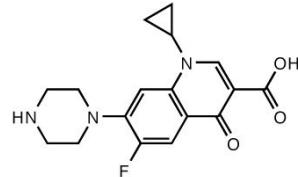


Structure search: <http://www.chemspider.com/StructureSearch.aspx>

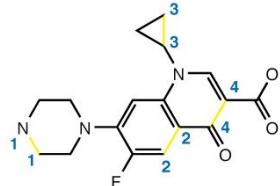
Future Work – SARs via SMILES



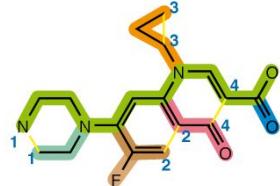
A



B



C



D

N1CCN(CC1)C(C(F)=C2)=CC(=C2C4=O)N(C3CC3)C=C4C(=O)O

Structure search

Draw structure Convert structure Load structure

Use our editor to draw your structure

Ketcher Elemental

pysmiles 1.0.0

`pip install pysmiles`

A lightweight SMILES reader and writer

Navigation

Project description

Release history

Download files

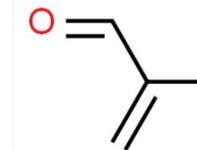
Project description

build passing coverage 98%

pysmiles: The lightweight and pure-python SMILES reader and writer

Found 1 result

Search term: Structure Search - Exact



Methylpropenal

Molecular Formula	C ₄ H ₆ O
Average mass	70.090 Da
Monoisotopic mass	70.041862 Da
ChemSpider ID	6314

More details:

Systematic name	Methacrylaldehyde
SMILES	<chem>CC(=C)C=O</chem>
Std. InChI	<chem>InChI=1S/C4H6O/c1-4(2)3-5/h3H,1H2.2H3</chem>
Std. InChIKey	<chem>STNJBCKSHOAVAJ-UHFFFAOYSA-N</chem>

Thank you!

