

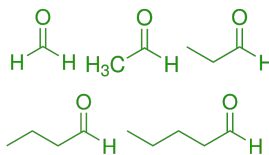


Carbonyl photochemistry on the ground state

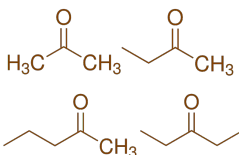
Group Meeting - Feb 5th 2021 - Keiran Rowell

Absorption spectra of carbonyl classes

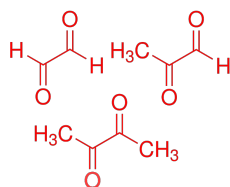
Linear Aldehydes



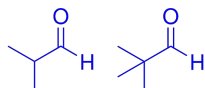
Ketones



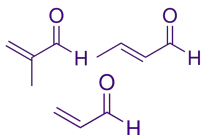
Dicarbonyls



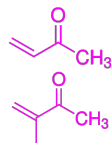
Branched Aldehydes



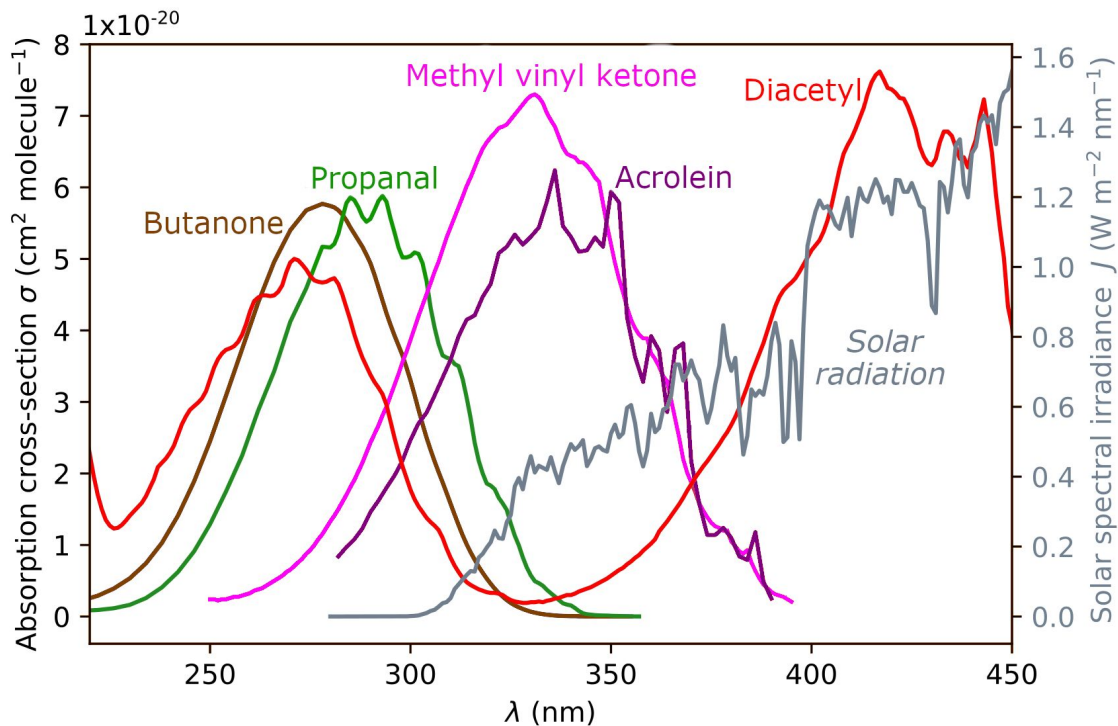
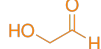
Enals

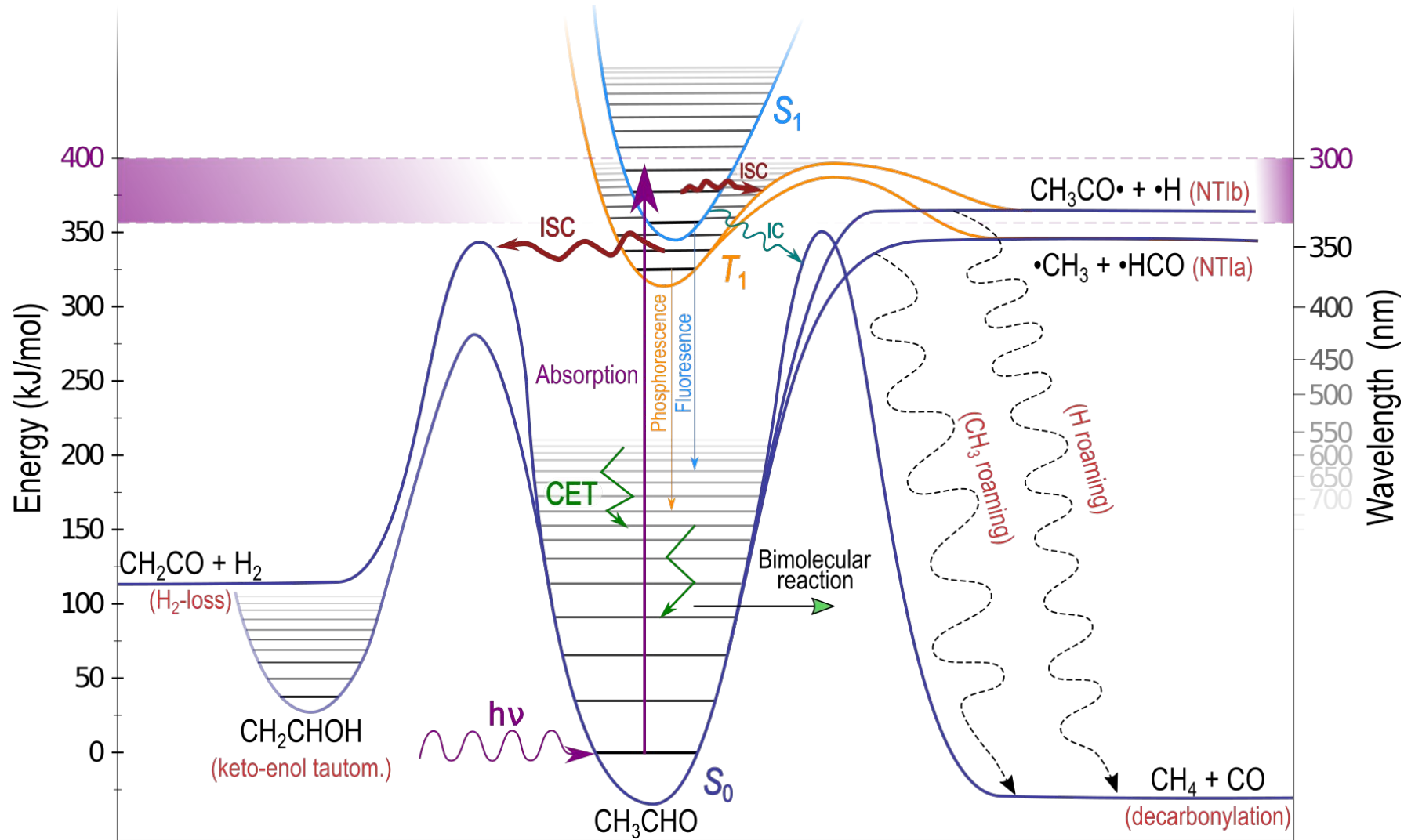


Enones

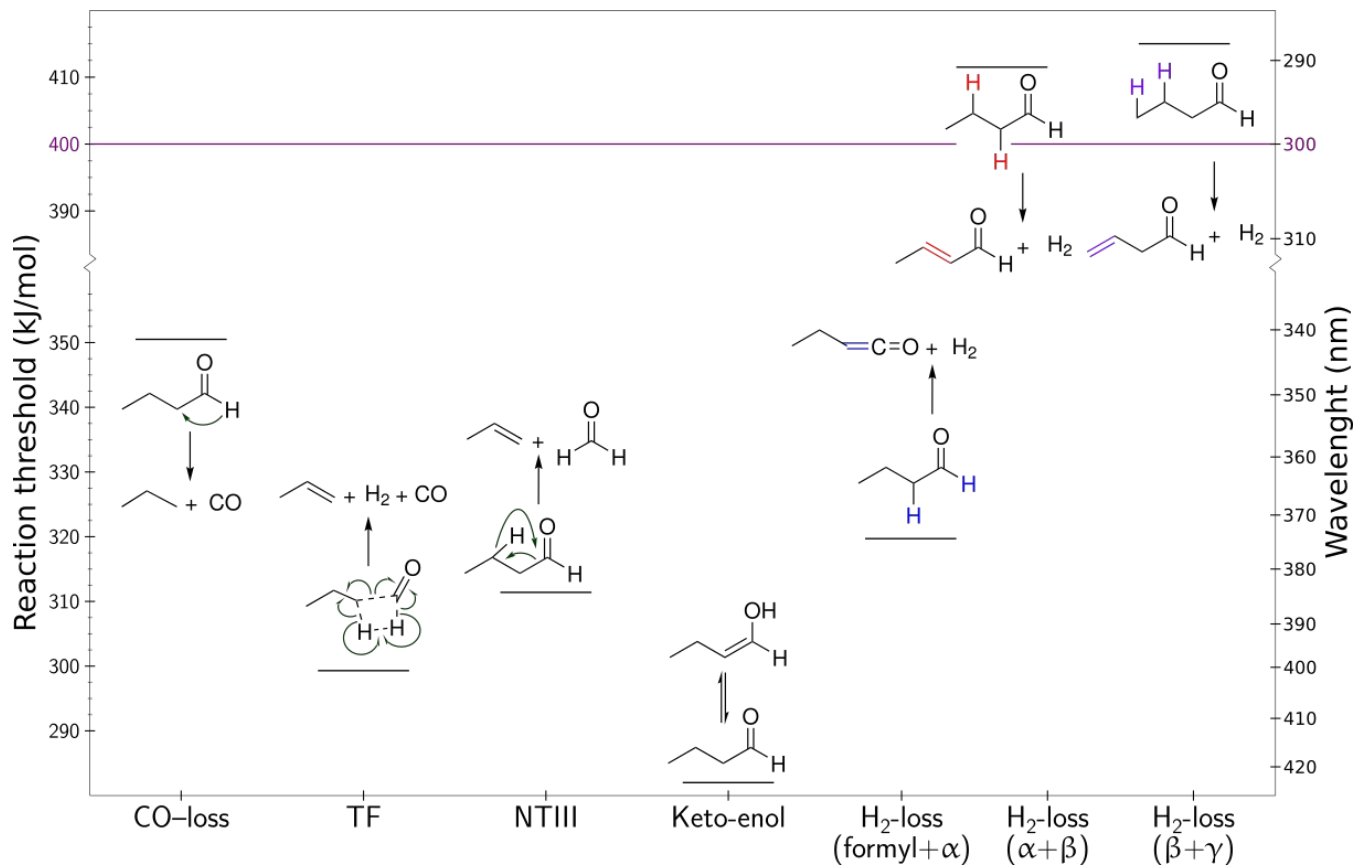


Carbohydrate





Possible S_0 reactions in butanal



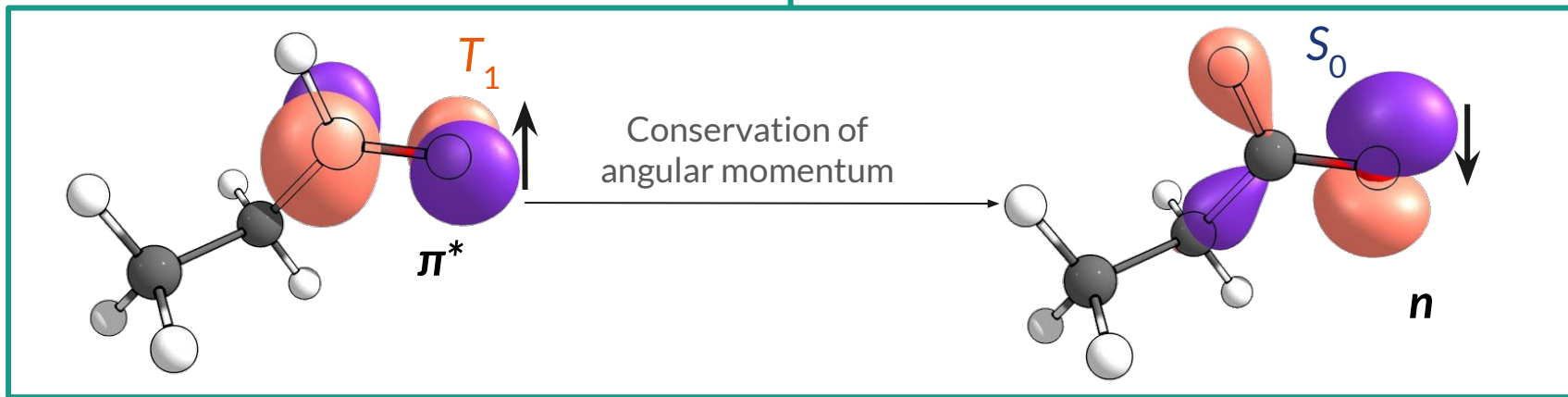
Electronic crossing to S_0

$$k_{NR} = \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \rho(E_f)$$

Wavefunction overlap (FC)

Density of states

Coupling magnitudes – $T_1 \rightarrow S_0$ Spin-orbit coupling (SOC)



Acetaldehyde PES

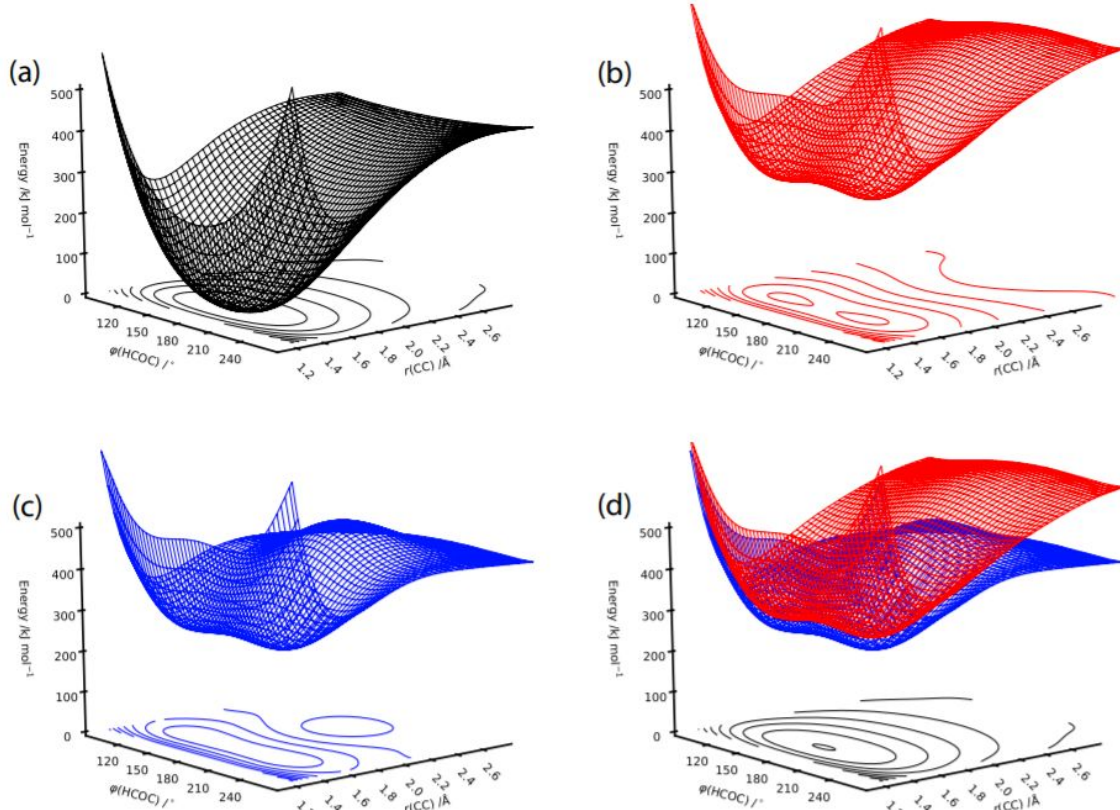
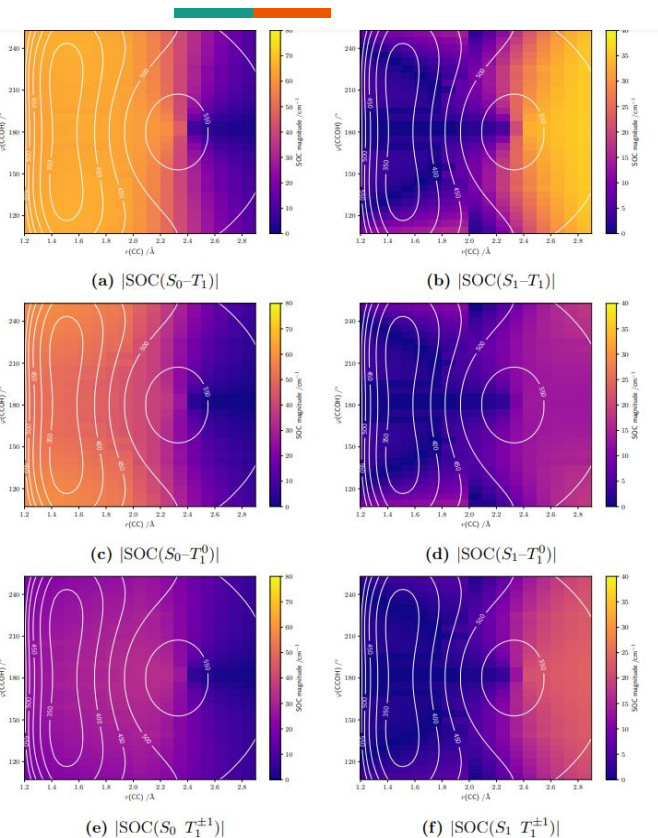


Figure 2.4: CH_3CHO PESs fitted to MRCI(CASSCF(6,6))/aug-cc-pVTZ electronic energies, for (a) S_0 (black), (b) S_1 (red), (c) T_1 (blue) and (d) S_1 and T_1 surfaces, superimposed, with S_0 contours on base of plot. Contour spacing is 50 kJ mol^{-1} , from zero as the minimum electronic energy on the S_0 surface.

Acetone PES

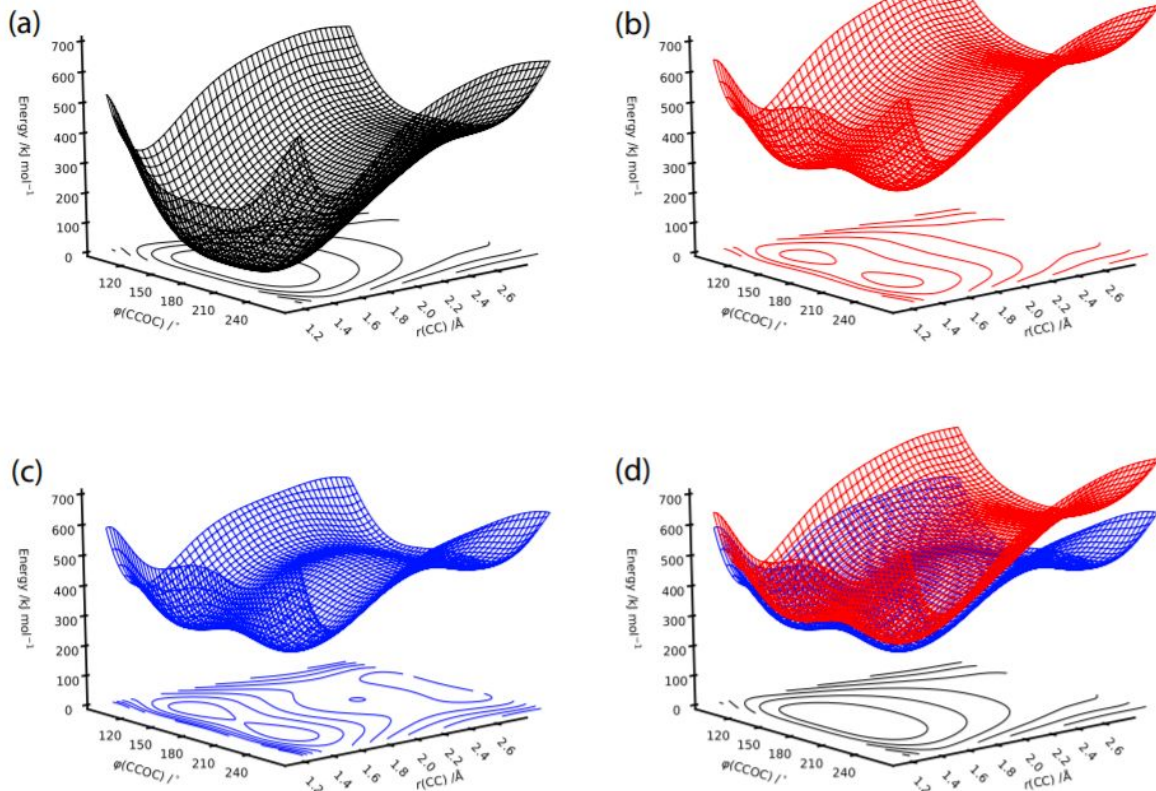
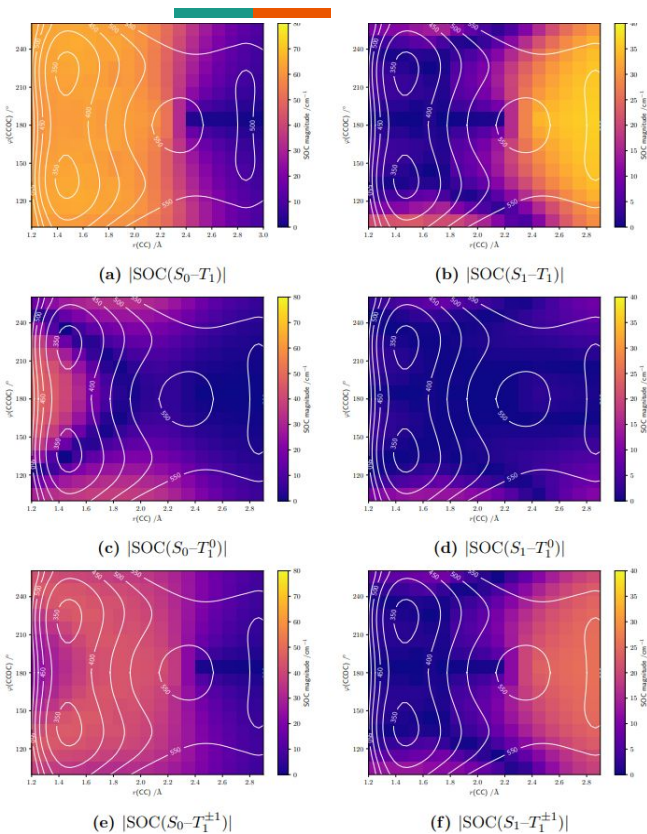


Figure 2.5: $(\text{CH}_3)_2\text{CO}$ PESs fitted to MRCI(CASSCF(6,6))/aug-cc-pVTZ electronic energies, for (a) S_0 (black), (b) S_1 (red), (c) T_1 (blue) and (d) S_1 and T_1 surfaces, superimposed, with S_0 contours on base of plot. Contour spacing is 50 kJ mol^{-1} , from zero as the minimum electronic energy on the S_0 surface.

Electronic surface crossing rates

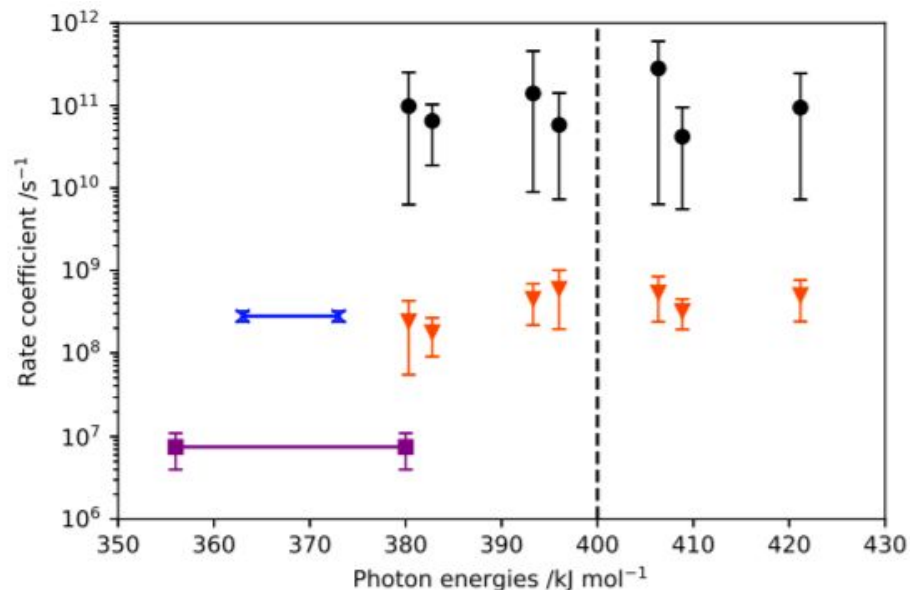
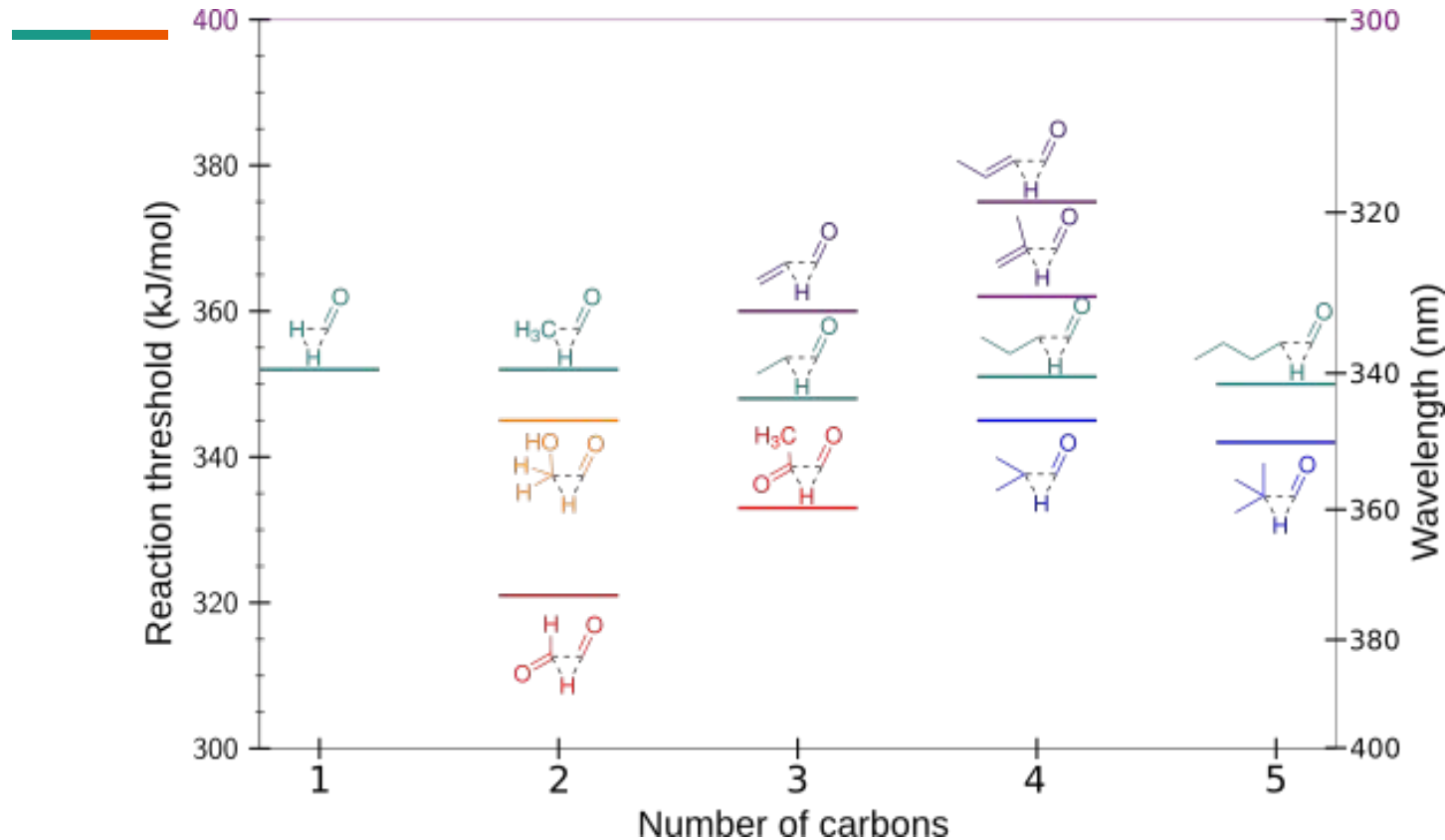


Figure 2.10: Rate coefficients for ISC in CH_3CHO as a function of energy; red triangles $S_1 \rightarrow T_1$, black circles $T_1 \rightarrow S_0$. Blue data is literature $k_{ISC}(S_1 \rightarrow T_1)$ ⁴⁷ and purple data is literature $k_{IC}(S_1 \rightarrow S_0)$ ⁴⁸ (see text). Uncertainties as described in Section 2.2.3.

Decarbonylation



Roaming as dominant mechanism

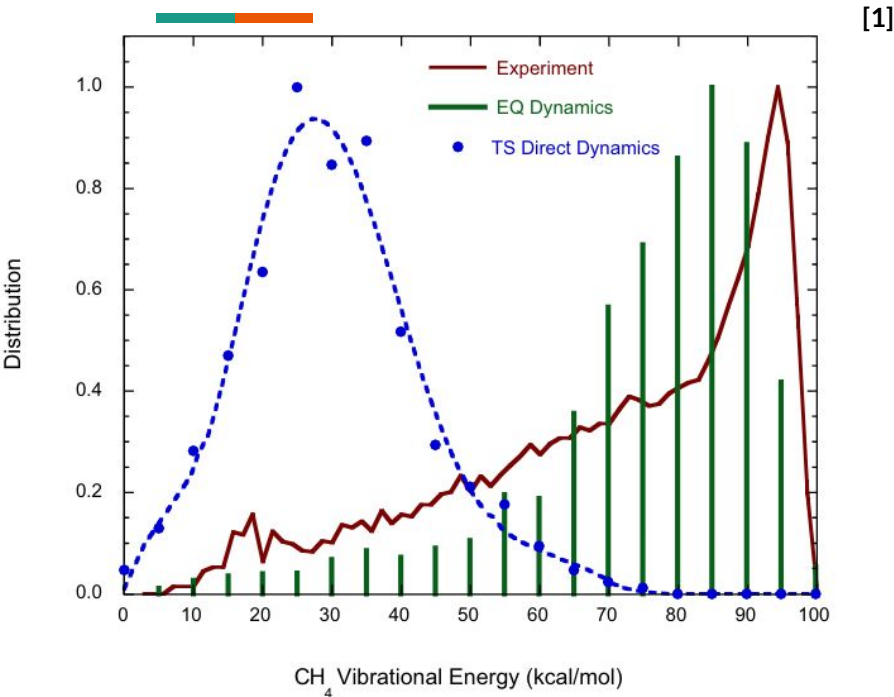


Fig. 3. Vibrational energy distributions of CH₄ from experiment and two sets of QCT calculations described in the text. A dashed blue line is drawn through the direct dynamics points as a guide.

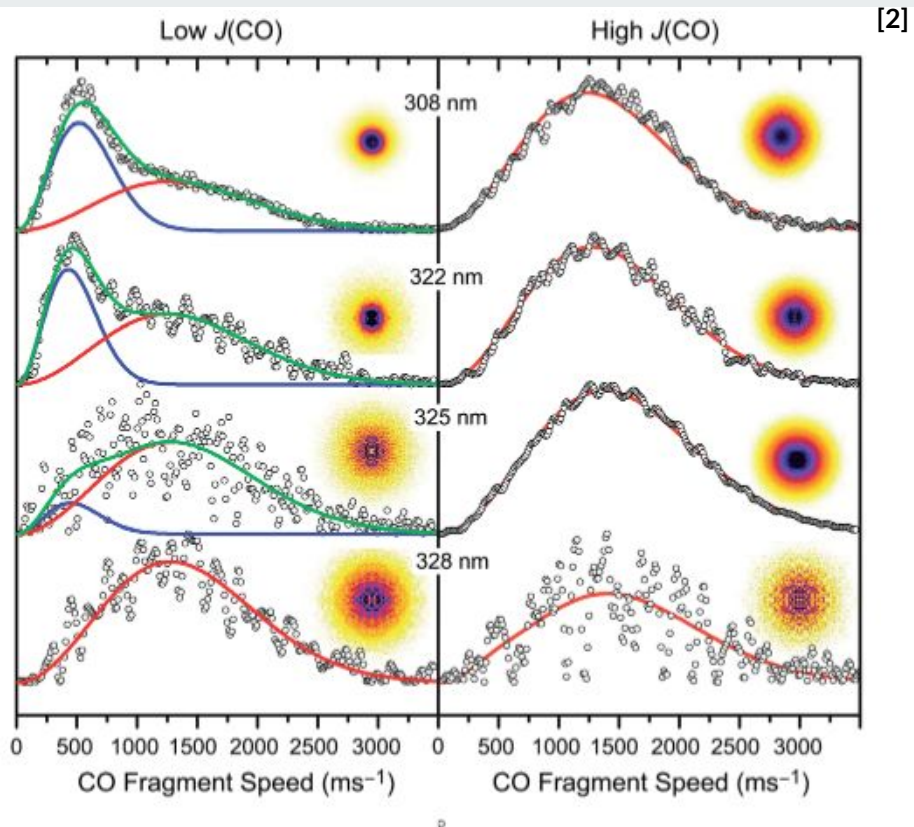
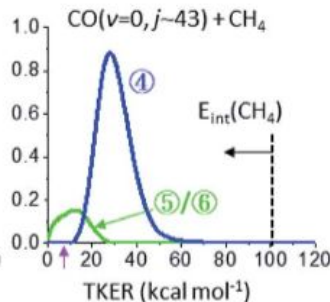
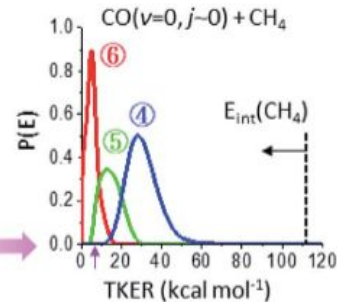
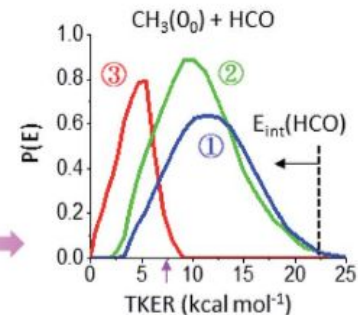
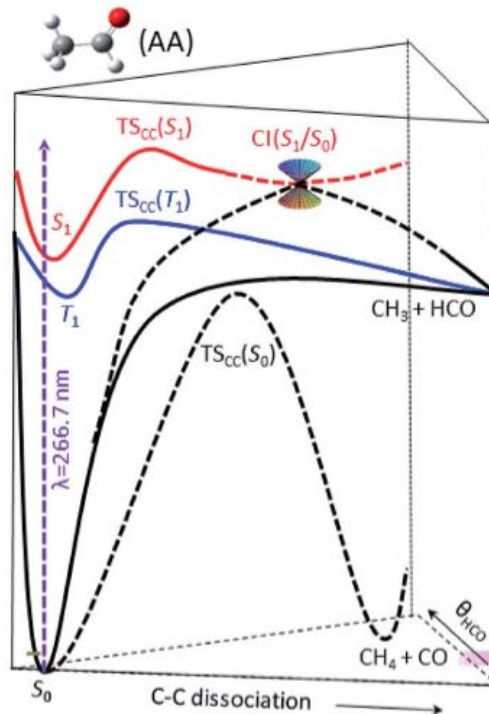


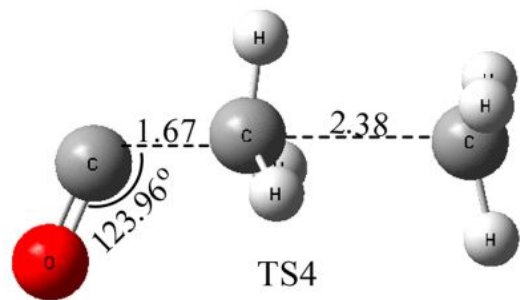
Fig. 3 CO speed distributions and two Boltzmann fits to the data (see Table 1). The cold component in the low-*J* data disappears for photolysis between 325 and 328 nm.

Some disagreement



Probed product	Component ^a	τ (ps) ^b	Branching ^c	$\langle f_{\text{TKER}} \rangle$	Assigned pathway
CH ₃ (0 ₀)	Blue	190 ± 10	36%	0.51	① TS _{cc} (T ₁)
	Green	1750 ± 150	45%	0.45	② Isom.(S ₀ , T ₁)
	Red	800 ± 50	19%	0.18	③ CI(S ₁ /S ₀)
CO($v=0, j \sim 0$)	Blue	300 ± 15	46%	0.28	④ TS _{cc} (S ₀)
	Green	290 ± 15	24%	0.13	⑤ Non-TS _{cc} (S ₀)
	Red	480 ± 30	30%	0.05	⑥ CI(S ₁ /S ₀)
CO($v=0, j \sim 43$)	Blue	300 ± 20	86%	0.31	④ TS _{cc} (S ₀)
	Green	310 ± 20	14%	0.12	⑤/⑥ Non-TS _{cc} (S ₀)

Proposed CO-loss in ketones



Only “Roaming” TS found^[1]

NEW MECHANISM OF PHOTODISSOCIATION OF GASEOUS ACETONE^[2]

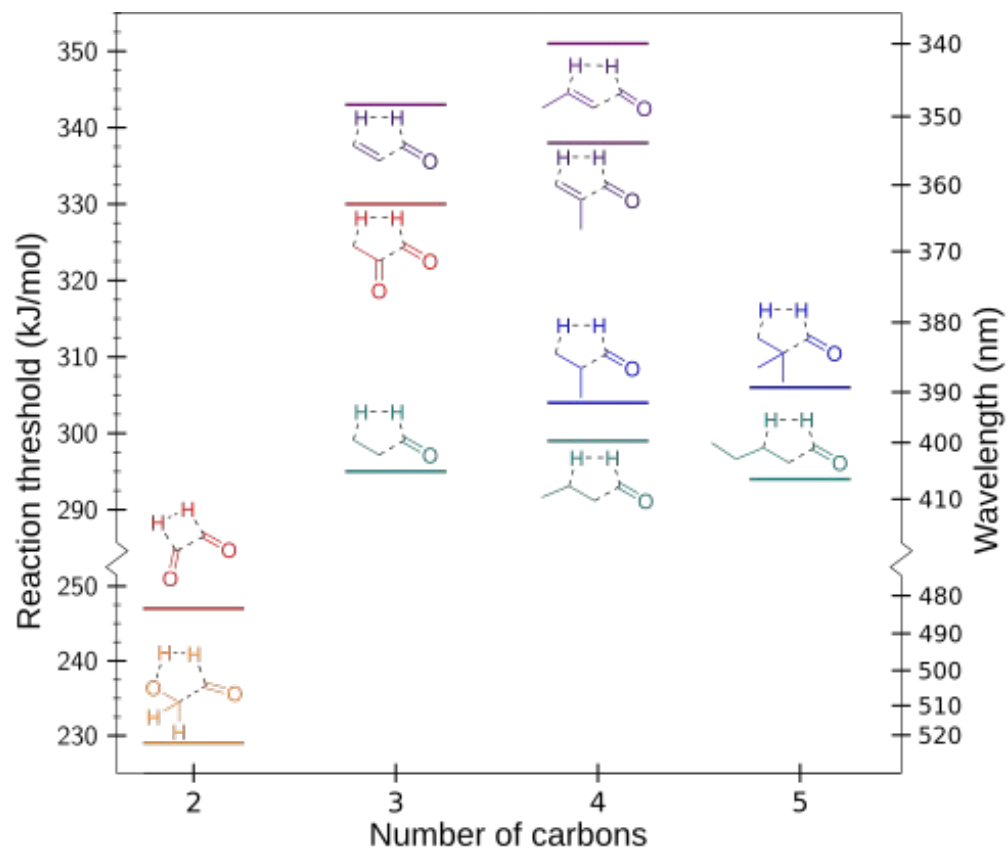
1273

Table 1. Calculation of the fraction of the ethane formed by induced predissociation of photolyzed acetone (9)

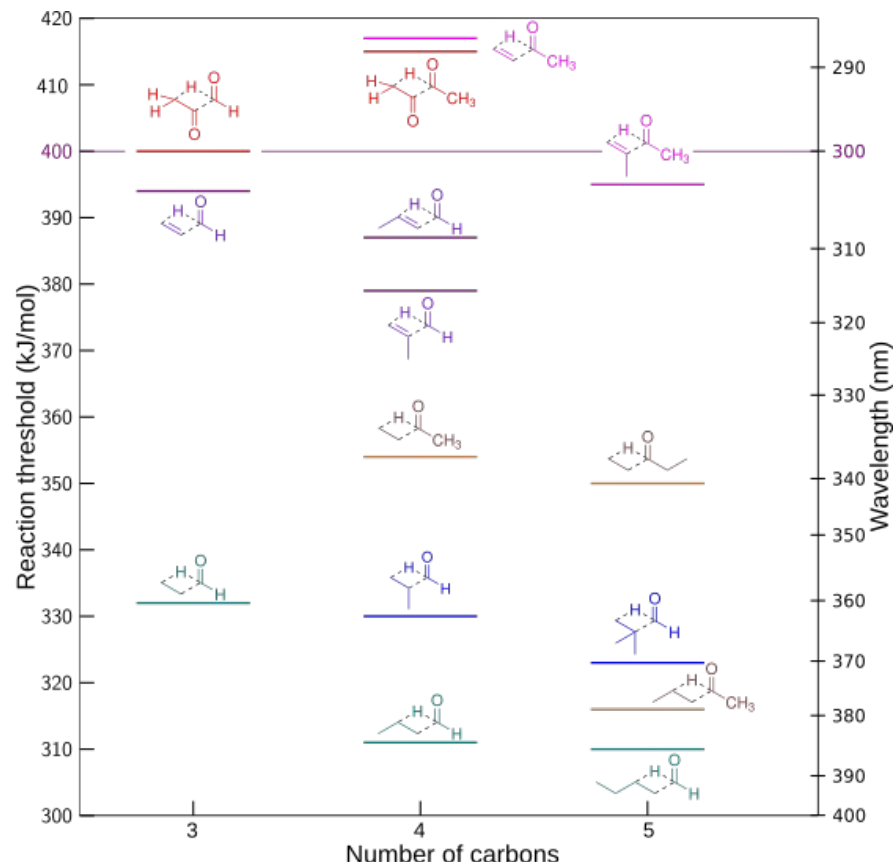
[Acetone] ₀ , ^b molecules/cm ³	Isotopic molecule	Measured isotopic composition of ethane, molar fraction	Calculated of recombination of CH ₃ and CD ₃ , molar fraction ^a	Contribution predissociation (9), molar fraction	Ethane formed intramolecularly, %
9.7 × 10 ¹⁷ ^b	CH ₃ CH ₃	0.477 ± 0.001	0.3065	0.170 ± 0.002	} 26.3 ± 0.4
	CH ₃ CD ₃	0.337 ± 0.001	0.3373	0	
	CD ₃ CD ₃	0.186 ± 0.001	0.0928	0.093 ± 0.002	
3.9 × 10 ¹⁸ ^b	CH ₃ CH ₃	0.487 ± 0.009	0.3265	0.161 ± 0.015	} 24.5 ± 2.4
	CH ₃ CD ₃	0.340 ± 0.008	0.3402	0	
	CD ₃ CD ₃	0.173 ± 0.008	0.0886	0.084 ± 0.009	
3.9 × 10 ¹⁸ ^c	CH ₃ CH ₃	0.360 ± 0.001	0.2088	0.151 ± 0.002	} 28.1 ± 0.4
	CH ₃ CD ₃	0.357 ± 0.001	0.3573	0	
	CD ₃ CD ₃	0.283 ± 0.001	0.1528	0.130 ± 0.002	

^a Calculated by combinatorial formulas [6] without account for isotopic effects. ^b Temperature of photolyzed gas 340 K. ^c Photolysis temperature 418–438 K.

Concerted Triple Fragmentation



Norrish Type III - beta-H transfer

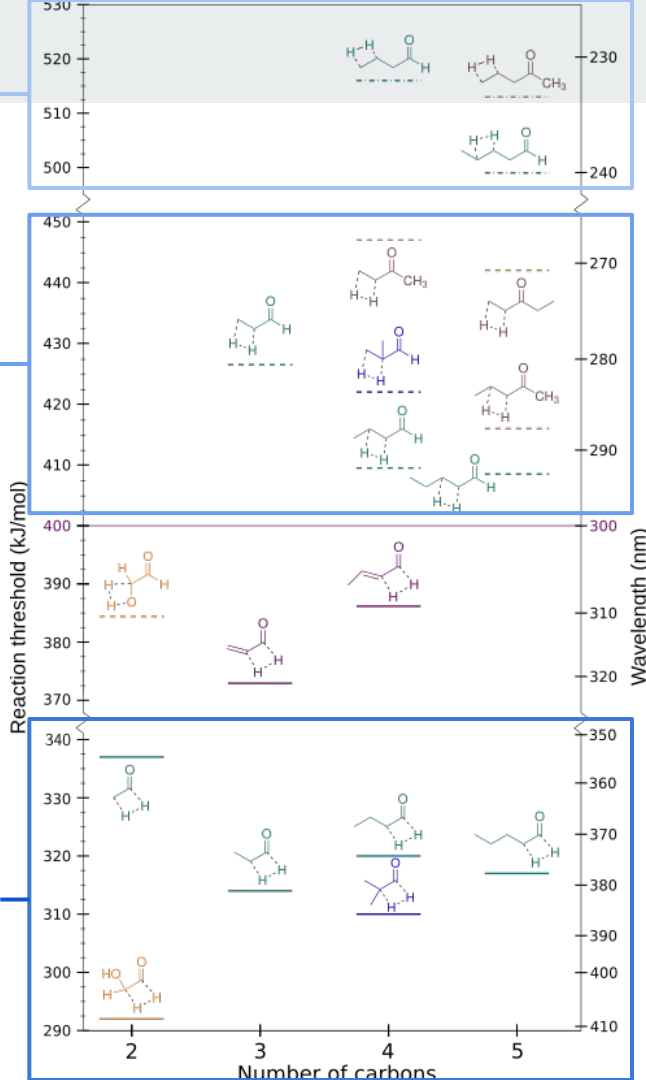


$\beta\text{-H} + \gamma\text{-H}$

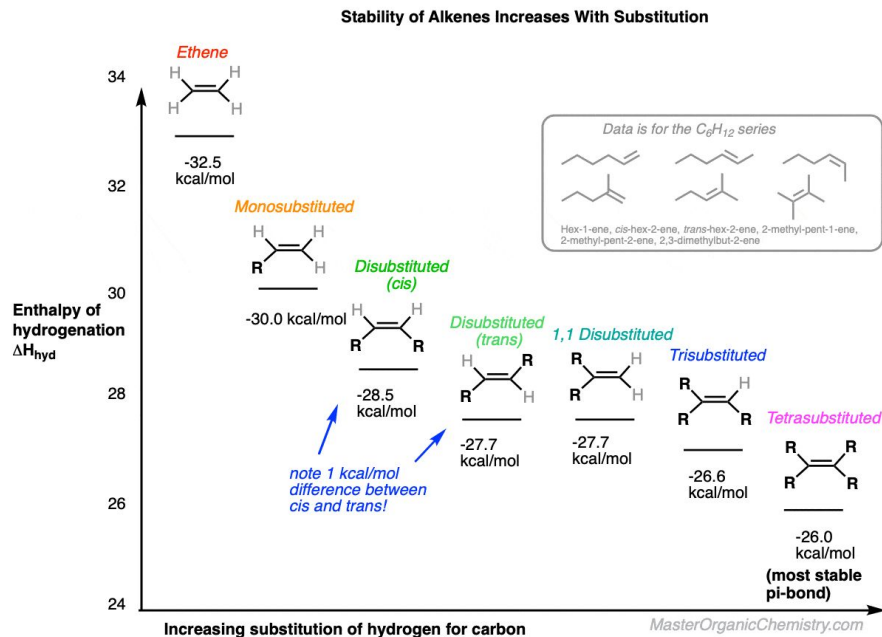
H₂-loss

$\alpha\text{-H} + \beta\text{-H}$

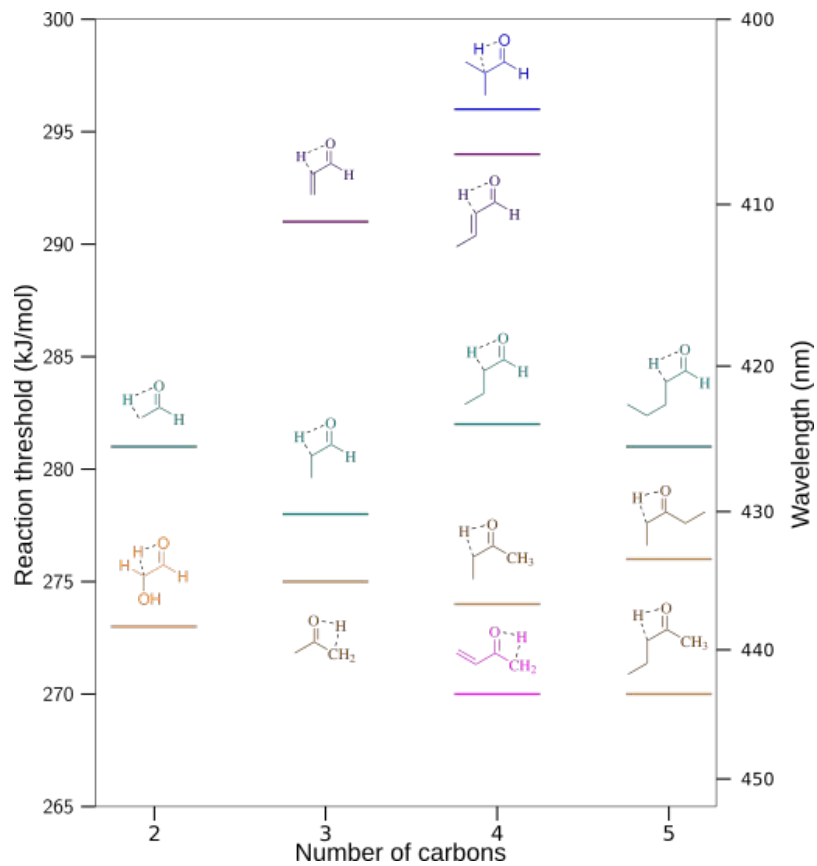
Formyl-H + $\alpha\text{-H}$



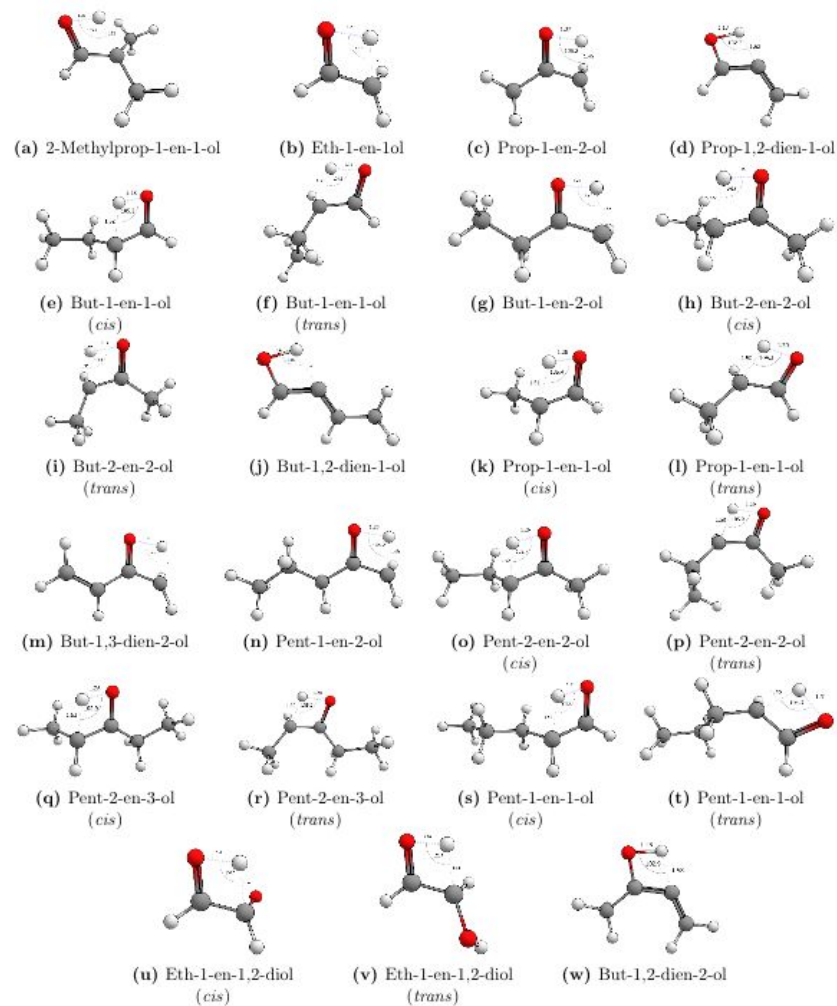
1 "Alkene Stability Increases with Substitution", Master Organic Chemistry, <https://www.masterorganicchemistry.com/2020/04/09/alkene-stability/>, Last update April 30th, 2020



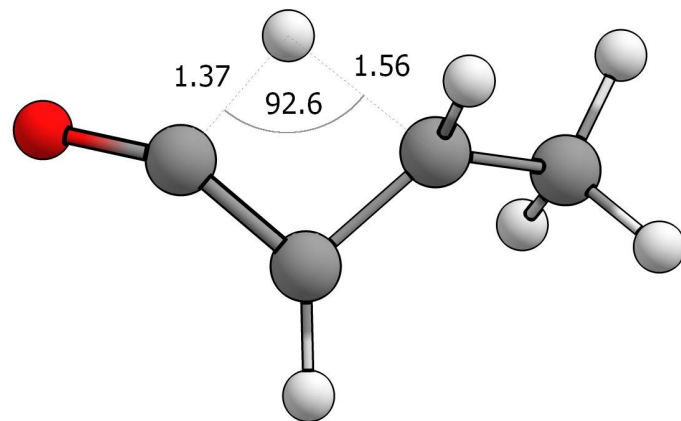
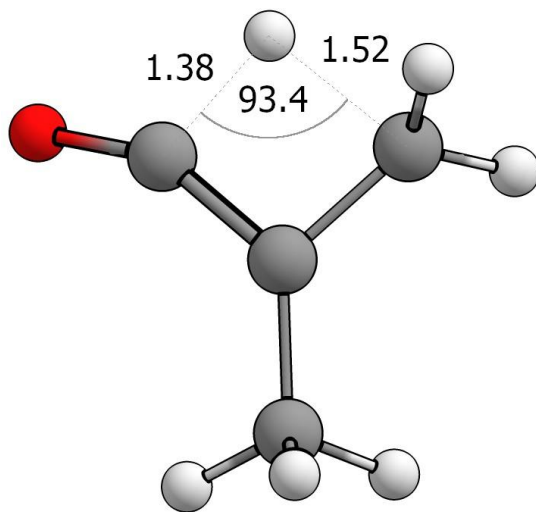
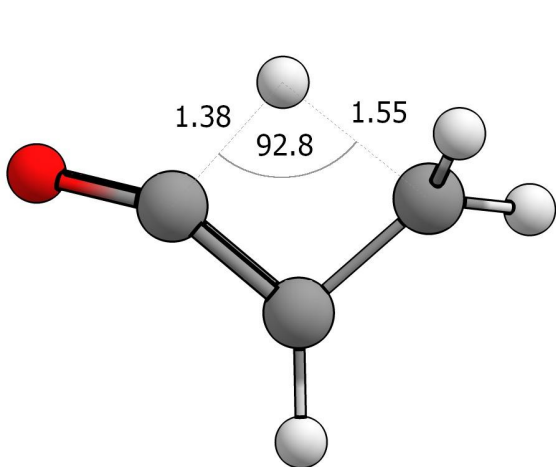
Keto-enol tautomerisation



S4. Keto-enol tautomerisation transition state geometries



Enal-Ketene tautomerisation



Potential atmospheric implications

Enols → organic acids^[1]

- Organic acids under-modelled factor of ~ 2 ^[2]
 $\text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CHOH}$ alone not enough.

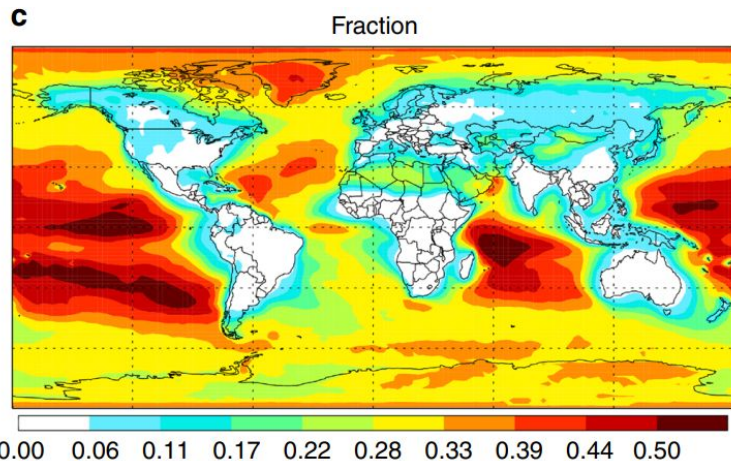


Fig. 5. c Fraction of total FA produced via photo-tautomerization

Missing photolytic H_2

- $\sim 60\%$ in H_2 is photolytic with $\frac{1}{2}$ from H_2CO ^[3]
- Irradiation of CDOM produces H_2 ^[4]
- H_2 above marine CDOM undermodelled^[5] — known to be photolytic from isotopic data^[6]





Thank you!