COMBUSTION RESEARCH FACILITY

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New Mechanistic Insights into the Non-adiabatic Dynamics of the O(^{3}P) + Propene Reaction

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$O(^3P)$ + alkene reactions

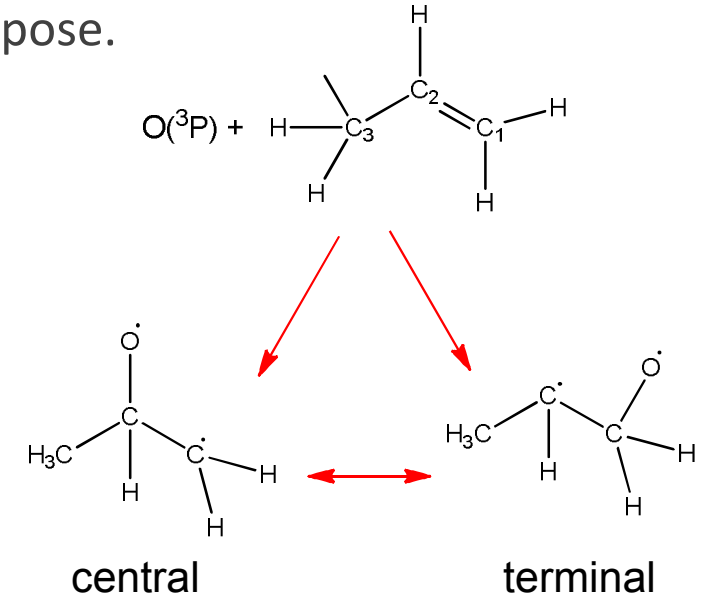
- $O(^3P)$ is a key oxidant in combustion chemistry above 1100 K.
  - $O(^3P) + HCCH \rightarrow {}^3CH_2 + CO$
    $\rightarrow HCCO + H$

    } Triplet surface only
- Reactions begin on the triplet surface, but may end on the singlet
  - Multi-surface, multi-channel reaction dynamics

- Previous Studies
  - R. J. Cvetanovic & co-workers (Rev. Chem. Intermed. **5**, 183 (1985))
  - I. R. Sims, I. W. M. Smith, S. J. Klippenstein (Science **317**, 102 (2007))
  - J. M. Bowman, P. Casavecchia, et al. (JCP **137**, 22A532 (2012))
  - W. L. Hase, T. L. Windus, et al. (JPCA **113**, 12663 (2009))
  - …many others on $O + C_2H_4$

$O(^3P)$ + C3 and larger alkenes

- Cvetanovich Rules:
  - $O(^3P)$ electrophilic addition to least-substituted carbon in C=C bond, forming a triplet biradical
  - Triplet biradicals decompose via H or CH_2 loss
  - Intersystem Crossing (ISC) leads to singlet surface, on which hot epoxides or hot carbonyl compounds decompose.
- Open Questions:
  - Central vs. terminal addition of O(3P).
  - Time-resolved product branching ratios.
  - Where is triplet-singlet crossing seam?
  - Multiple triplet surfaces needed?
  - Are multi-dimensional non-adiabatic calculations needed to predict observables?



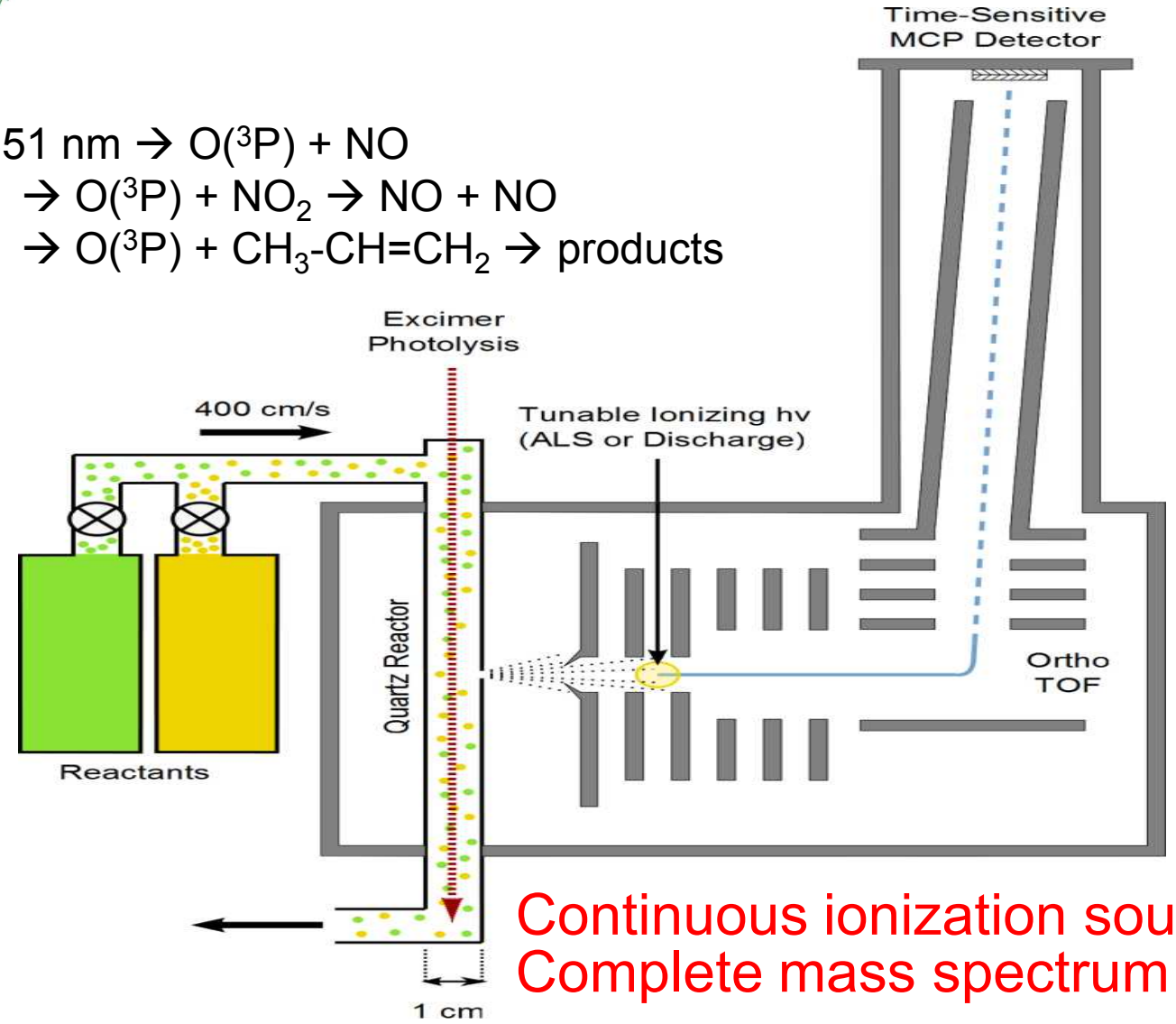
Previous experimental approaches

- Two traditional categories
  - Non-time-resolved, end product analysis of many species (Cvetanovich)
  - Time-resolved monitoring of 1 or 2 species

- Our approach
  - Time-resolved detection of many species, collisional environment
    - Global view of reaction
    - Discriminate primary from secondary chemistry (time-resolution)
    - Distinguish product isomers (tunable photoionization)
    - Sensitive to stabilization dynamics via collisions
  - P. Casavecchia: many species, single-collision environment ($O + C_2H_4$)
    - Translational energy and angular distributions!

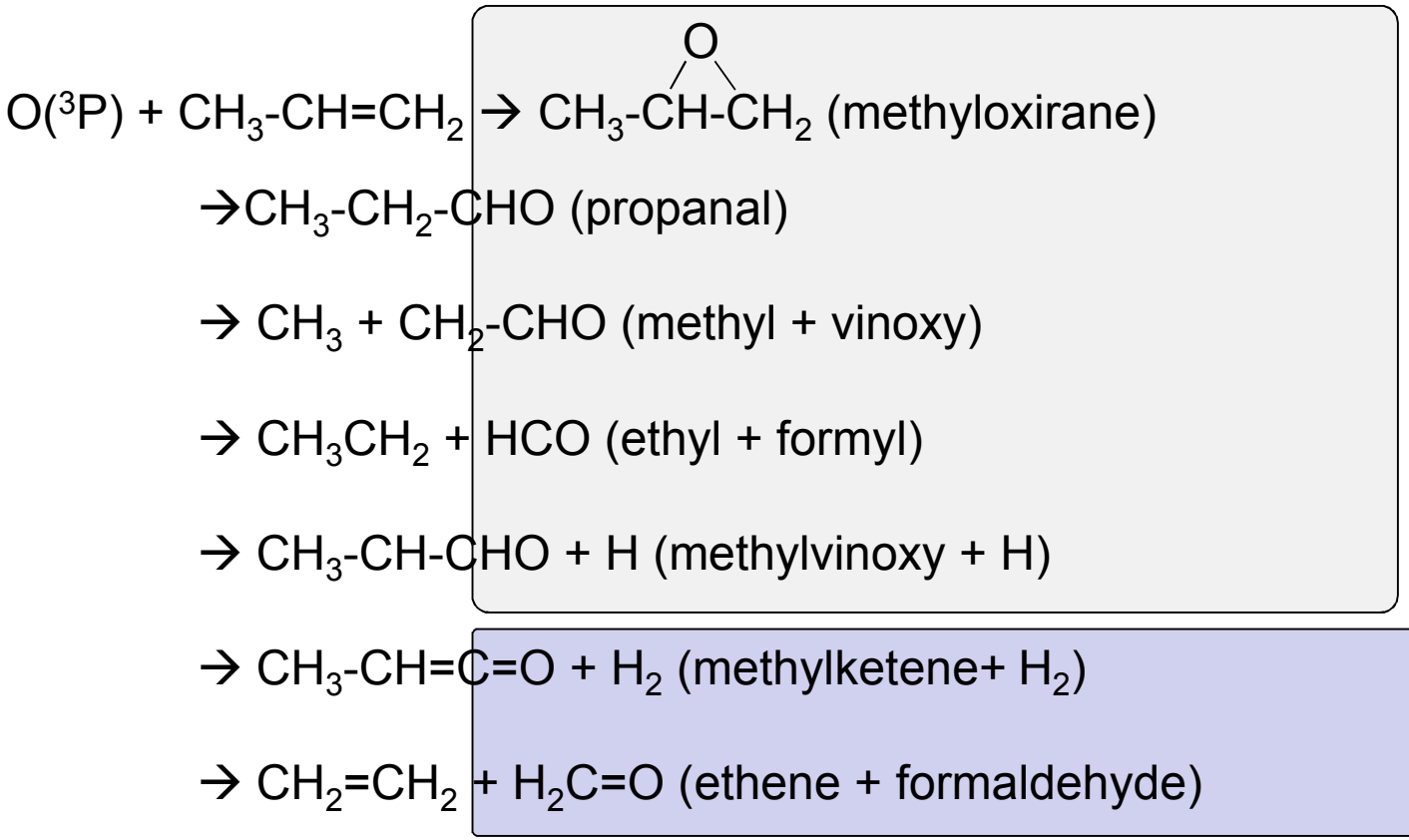
Multiplexed Photoionization Mass Spectrometer

NO_2 + 351 nm → $O(^3P)$ + NO
→ $O(^3P)$ + NO_2 → NO + NO
→ $O(^3P)$ + CH_3-CH=CH_2 → products

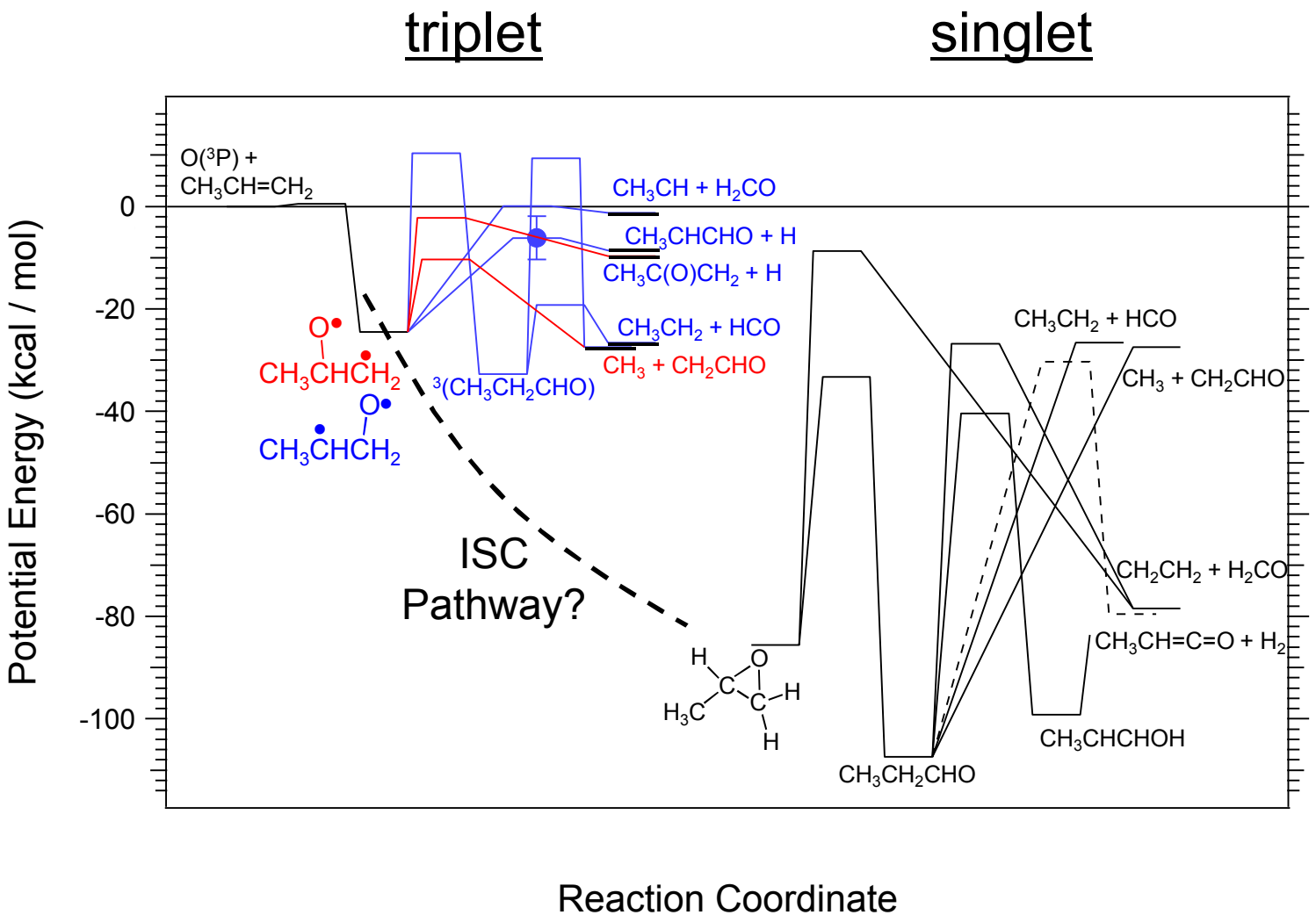


Continuous ionization source
Complete mass spectrum every 20 μs

Open product channels



Potential Surfaces Preview



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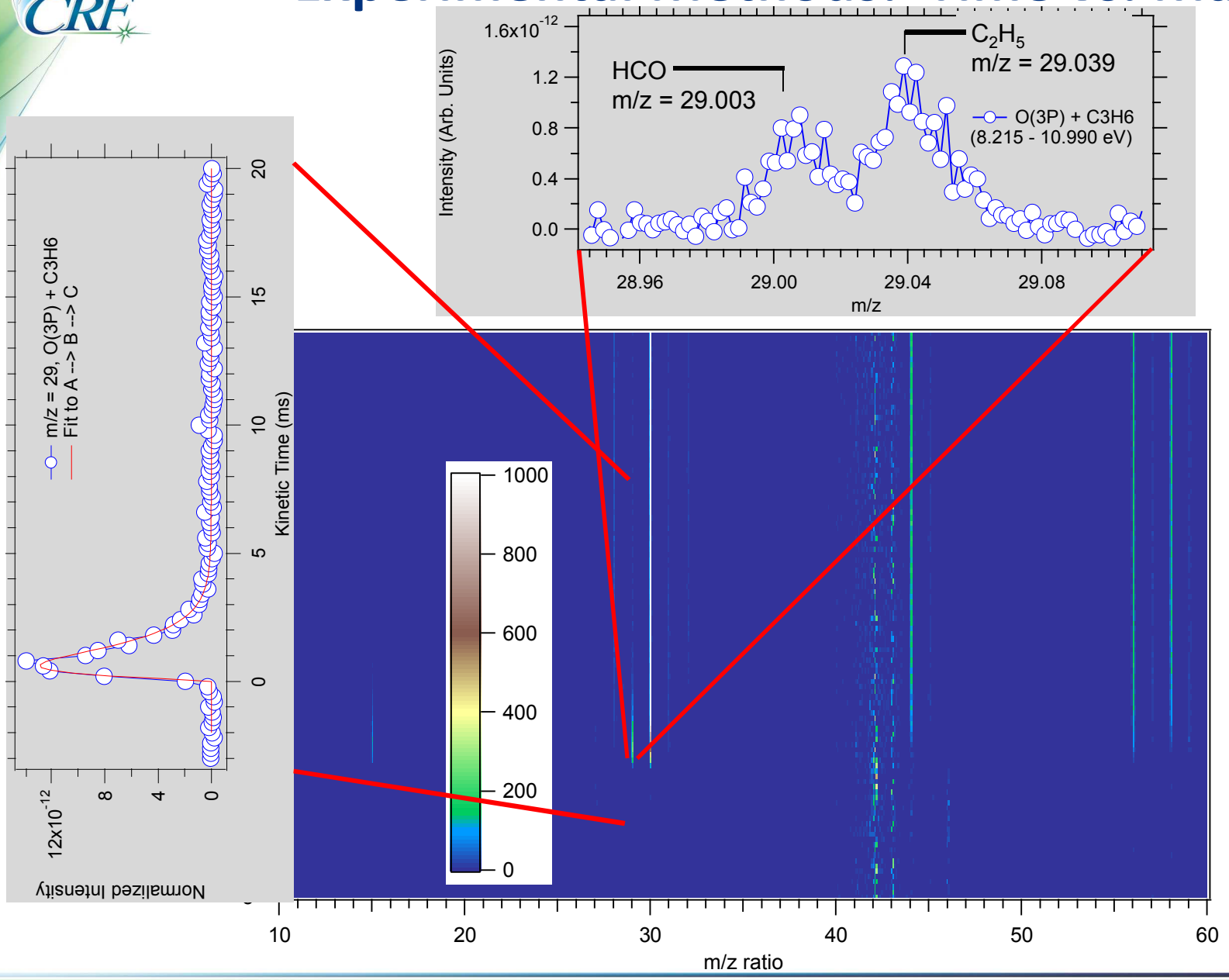
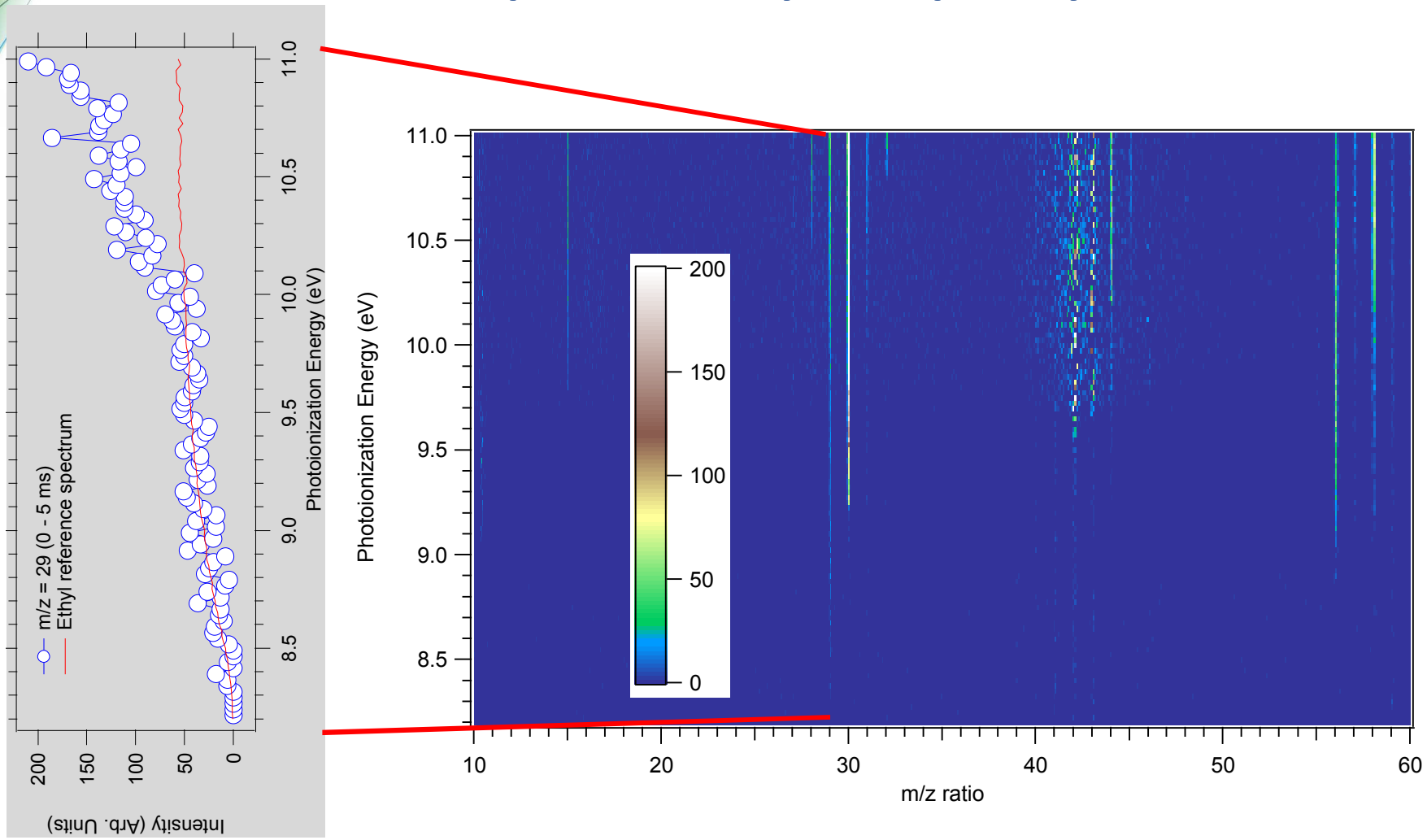
Experimental Methods: Time vs. Mass



Experimental Methods: Photon Energy vs. Mass
S(m/z, t, hν) → S(t, hν)



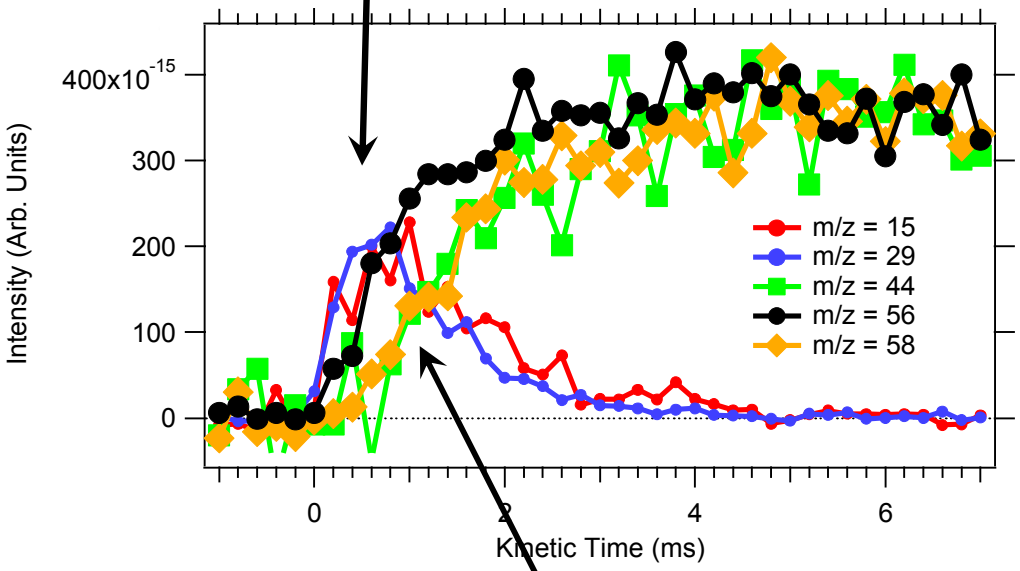
Primary vs. Secondary Products

Primary

CH_3 + CH_2-CHO (methyl + vinoxy) [15 + 43]

CH_3CH_2 + HCO (ethyl + formyl) [29 + 29]

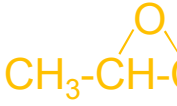
$CH_3CH=C=O$ + H_2 (methylketene + H_2) [56 + 2]



Secondary

CH_3 CHO (acetaldehyde) [44]

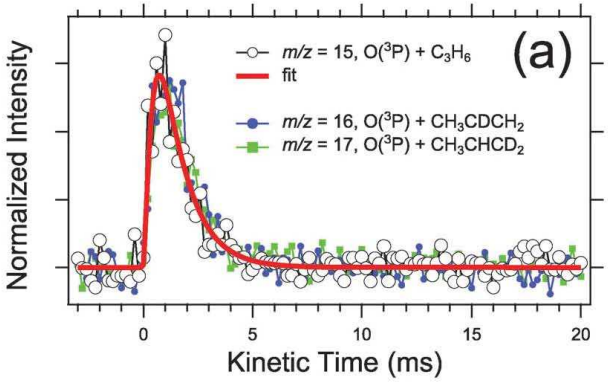
CH_3CH_2 CHO (propanal) [58]

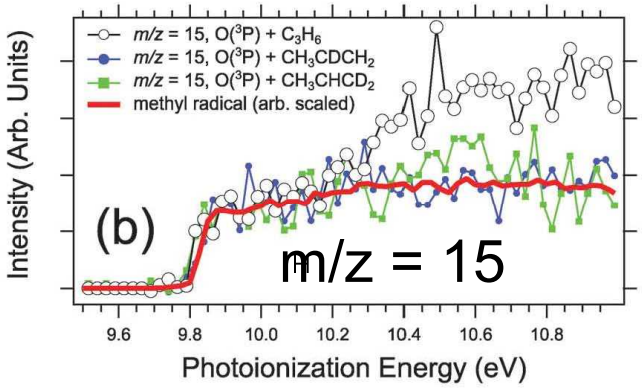


(methyloxirane) [58]

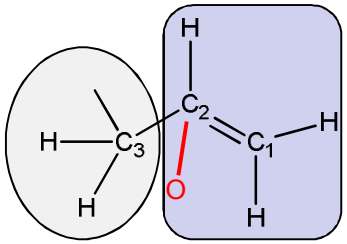
m/z = 15 (methyl and daughter ions)

- Use isotopic labeling to explore pathways:
  - CH_3-CH=CH_2 ; CH_3-CD=CH_2 ; CH_3-CH=CD_2
- CH_3-CH=CH_2 ⇒ m/z = 15 ⇒ methyl + daughter ions
- CH_3-CD=CH_2 ⇒ m/z = 15 ⇒ methyl only
  m/z=16 ⇒ mostly daughter ions
- CH_3-CH=CD_2 ⇒ m/z = 15 ⇒ methyl only
  m/z=17 ⇒ mostly daughter ions

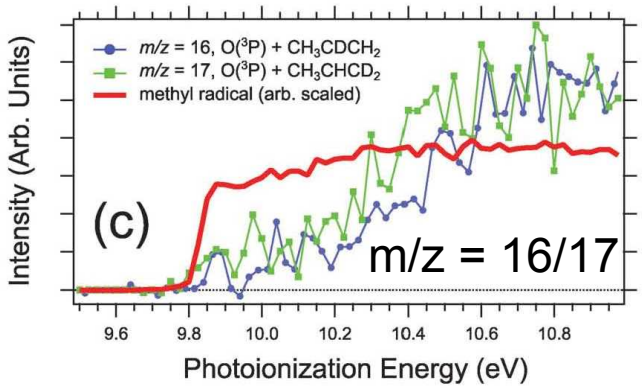




Conclusion 1: Almost all methyl radicals come from methyl group of propene

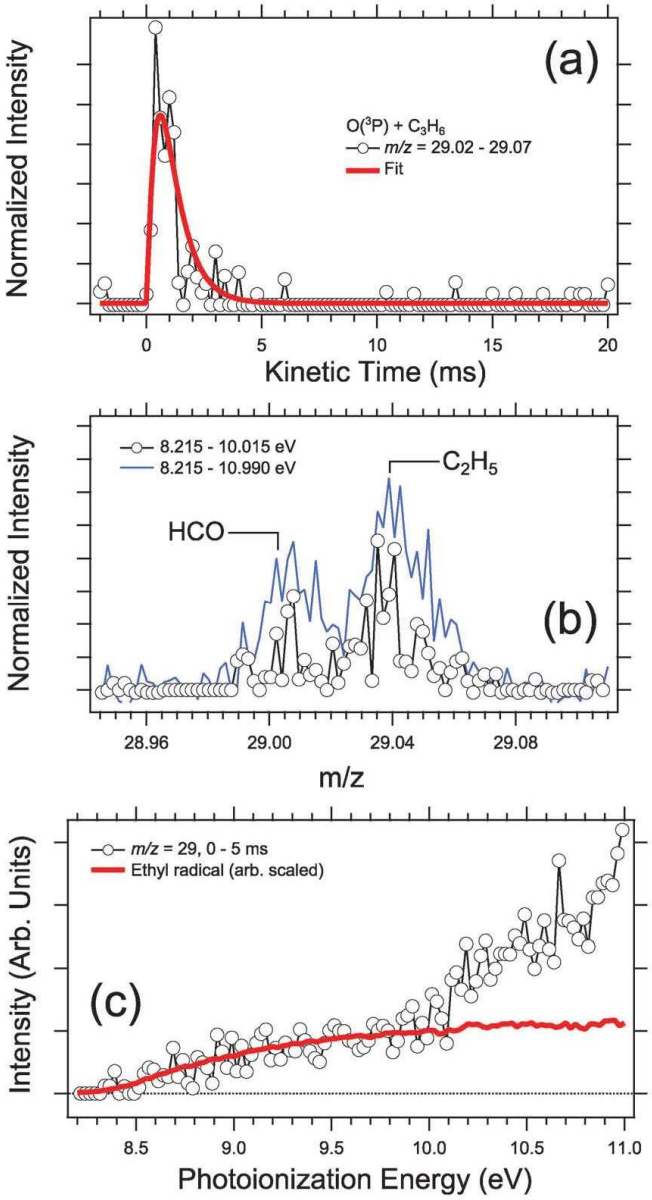


Vinoxy fragmentation to CH_3^+ daughter ion



C_2H_5 + HCO channel (m/z ~ 29)

- Both ethyl and formyl detected
- Daughter ion from something at 10.1 eV
- Branching ratio from ethyl fragment

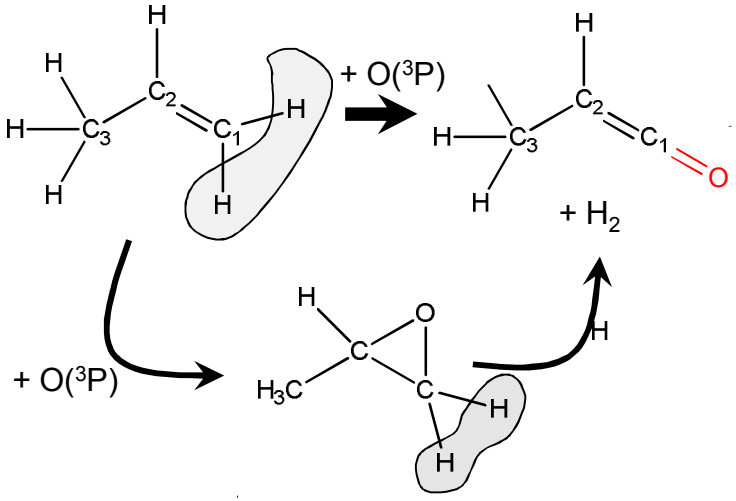


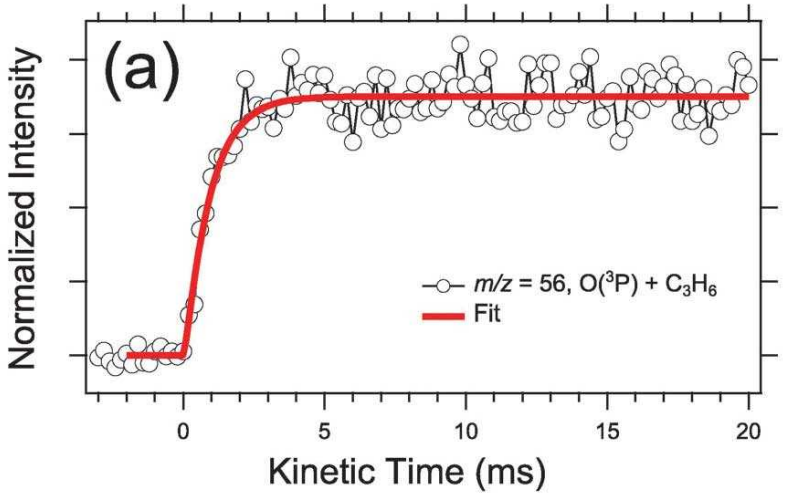
Conclusion 2:

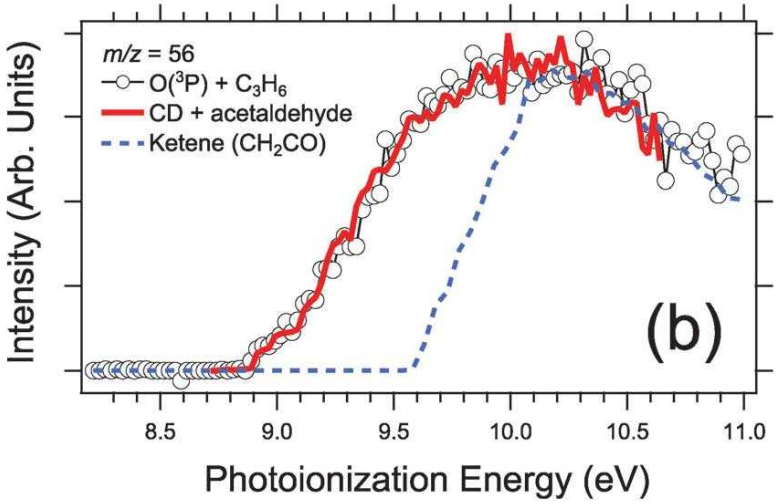
$$\frac{C_2H_5 + HCO}{CH_3 + CH_2CHO} = \frac{0.91 \pm 0.30}{1}$$

Methylketene chanel (m/z = 56)

- m/z = 56 is perfect fit to known methylketene spectrum
- $CH_3CH=C=O + H_2$ must arise from singlet PES
- Deuterated propenes show that:







Conclusion 3: methylketene channel is 5% (± 4) of methyl channel

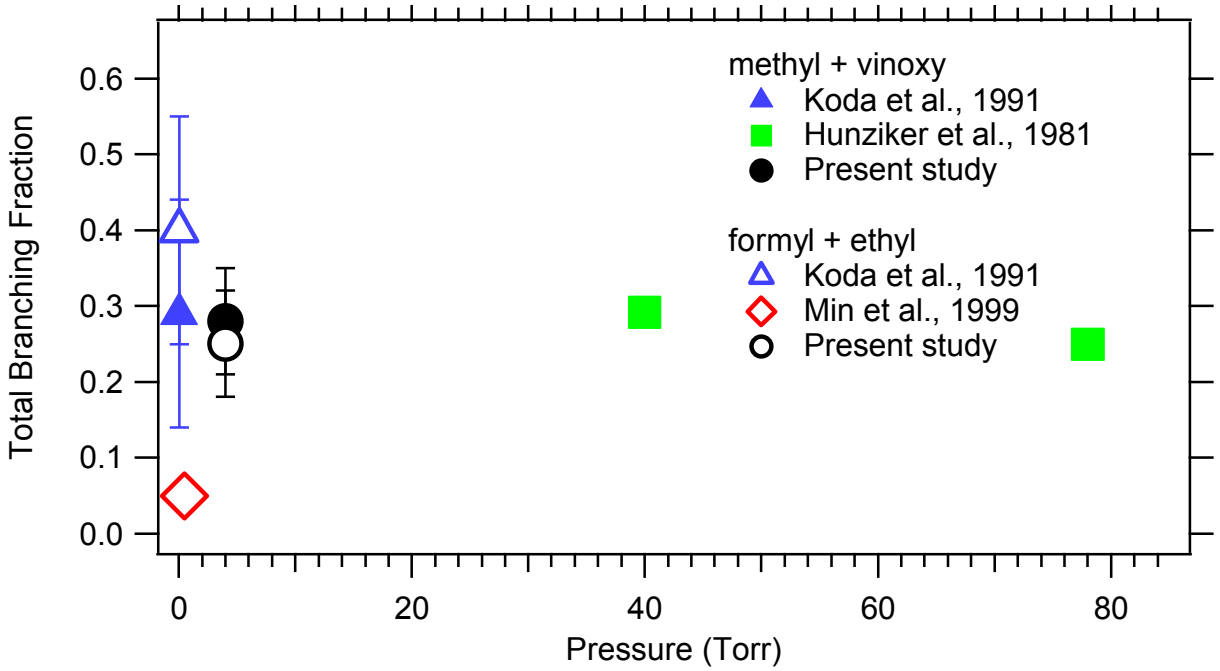
H + CH_3CHCHO (methylvinoxy)

- Both vinoxy (CH_2CHO) and methylvinoxy show no signals at parent masses (m/z = 43 and m/z = 57)
- Poor Franck Condon factors and unstable cations
- Vadim Kynazev measured $O(^3P)$ + propene → H + products
  - V. D. Kynazev et al., Int. J. Chem. Kinet. **24**, 545 (1992).
  - Measured absolute branching fraction 0.46 ± 0.11

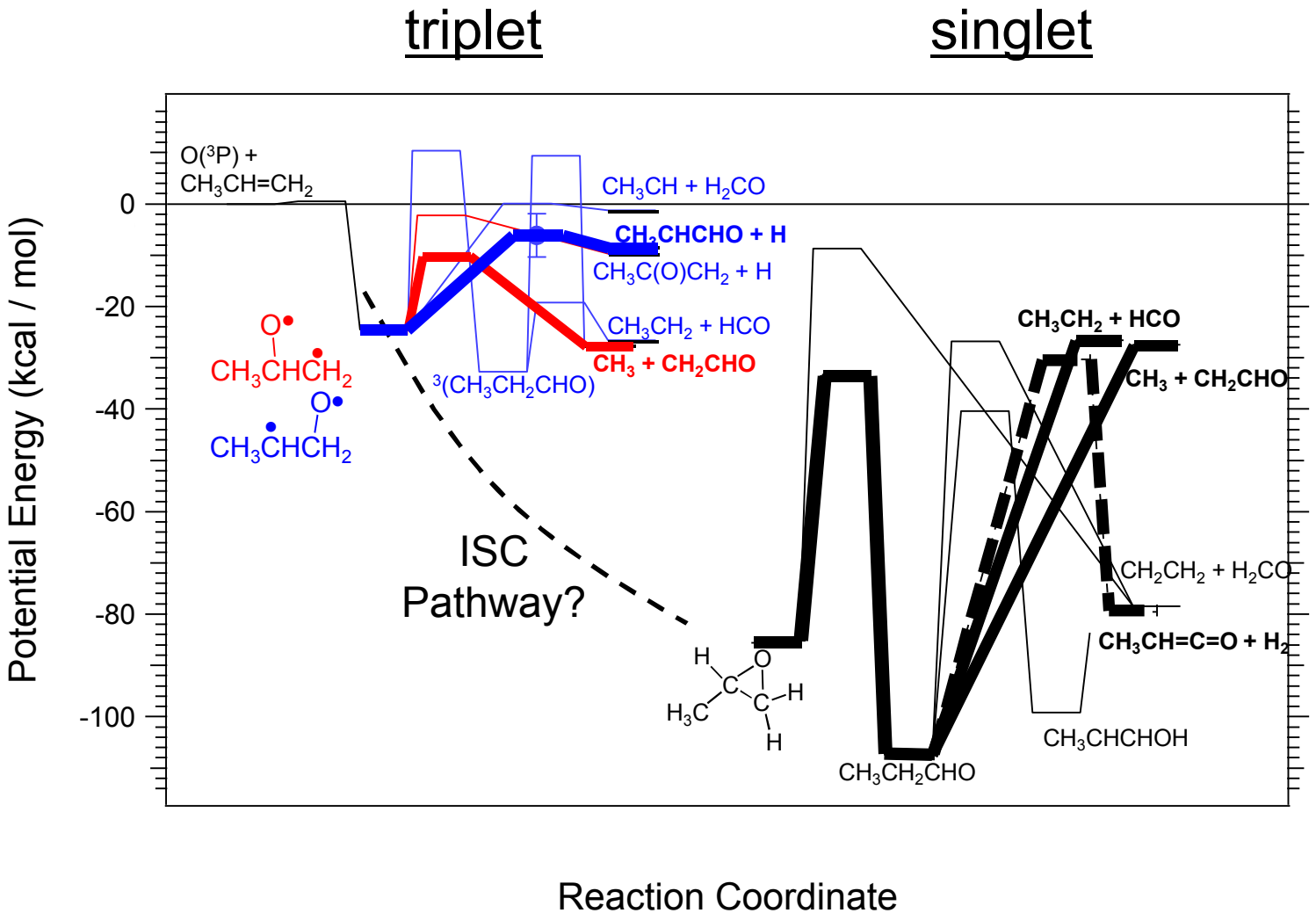
Conclusion 4: H + methylvinoxy is a major channel and the only channel we cannot observe

Experimental product branching ratios

Product channel	Branching ratio relative to CH_3 + CH_2CHO	Total branching fraction[b]
(CH_3) + CH_2CHO – **R1c**	1.00	0.28 ± 0.07
(C_2H_5) + HCO – **R1d**	0.91 ± 0.30	0.25 ± 0.07
H_2 + (CH_3CHCO) – **R1f**	0.05 ± 0.04	0.014 ± 0.011
H + CH_3CHCHO – **R1e**	Not observed	0.46 ± 0.11



Potential Energy Surfaces



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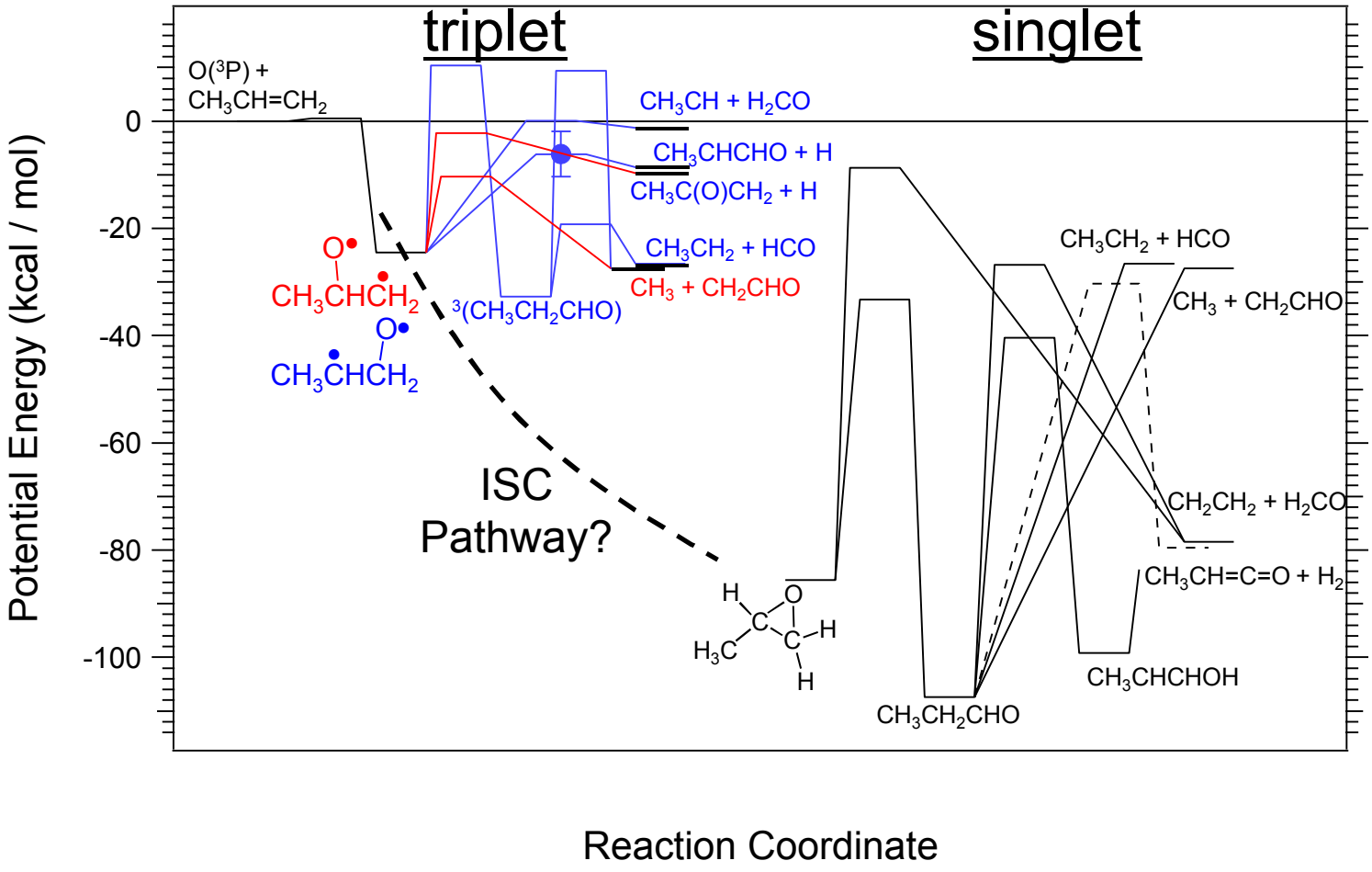
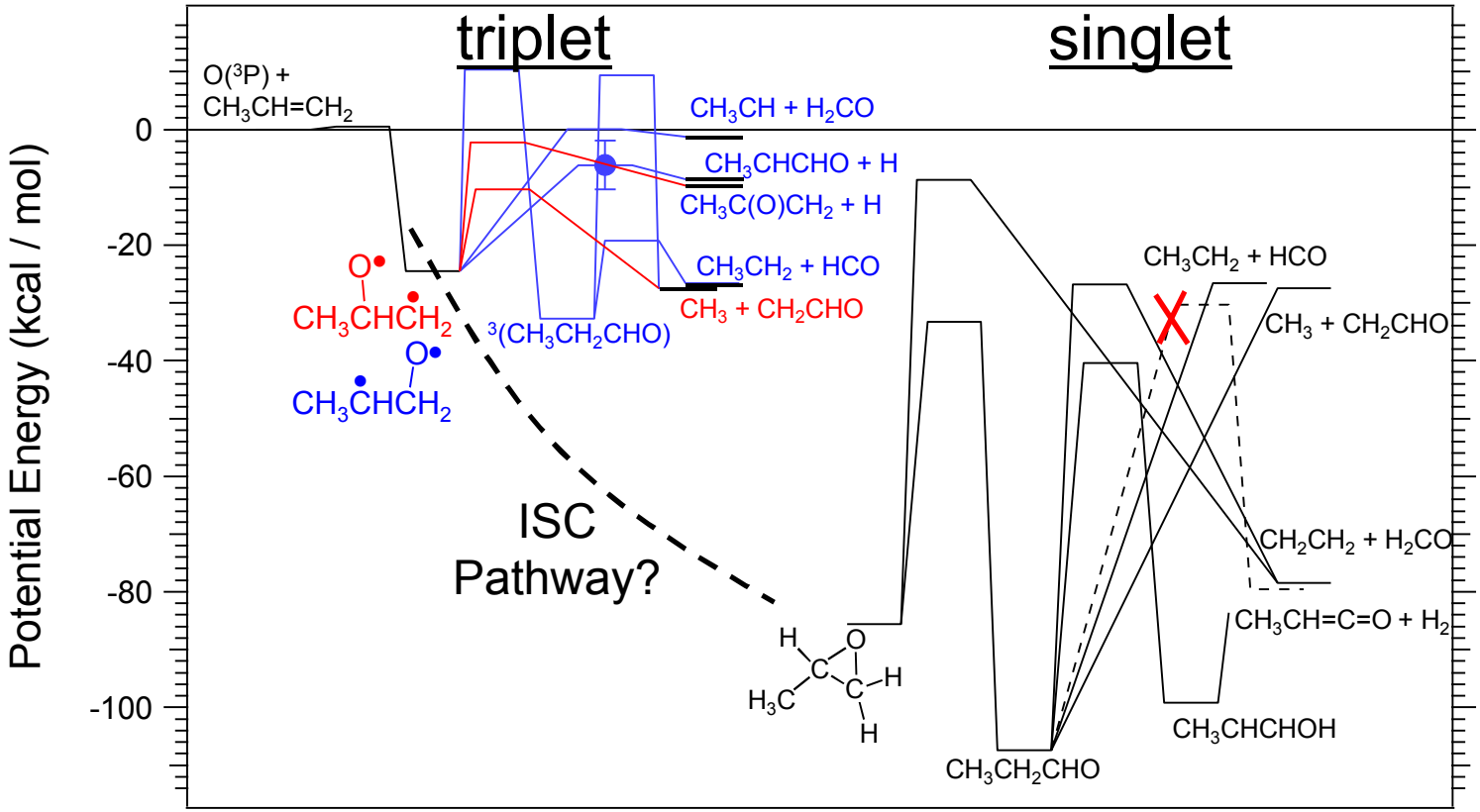
Conclusions



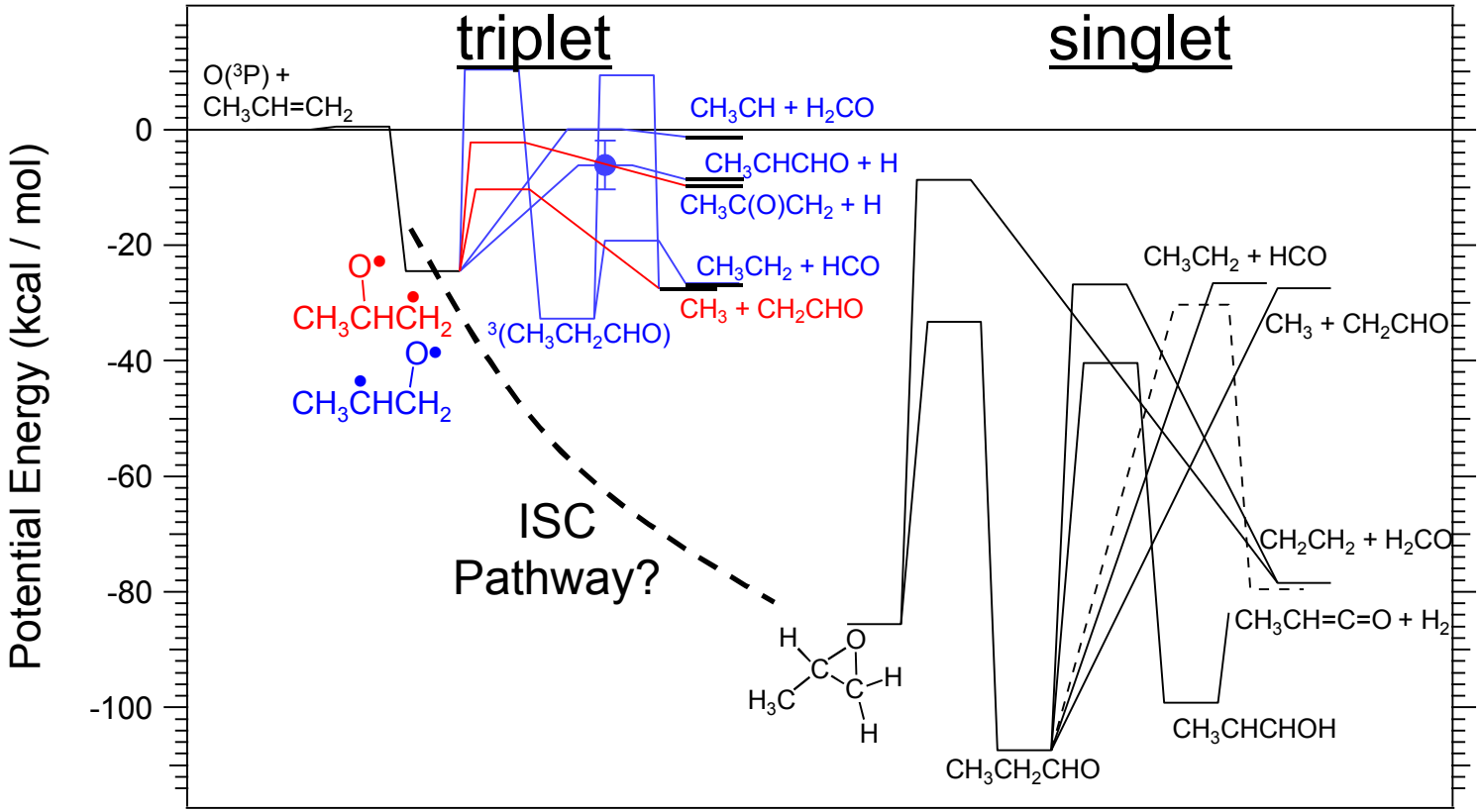
- No evidence for deuterium scrambling
  - CH_3 + CH_2CHO (vinoxy) arises from simple bond fission

Conclusions



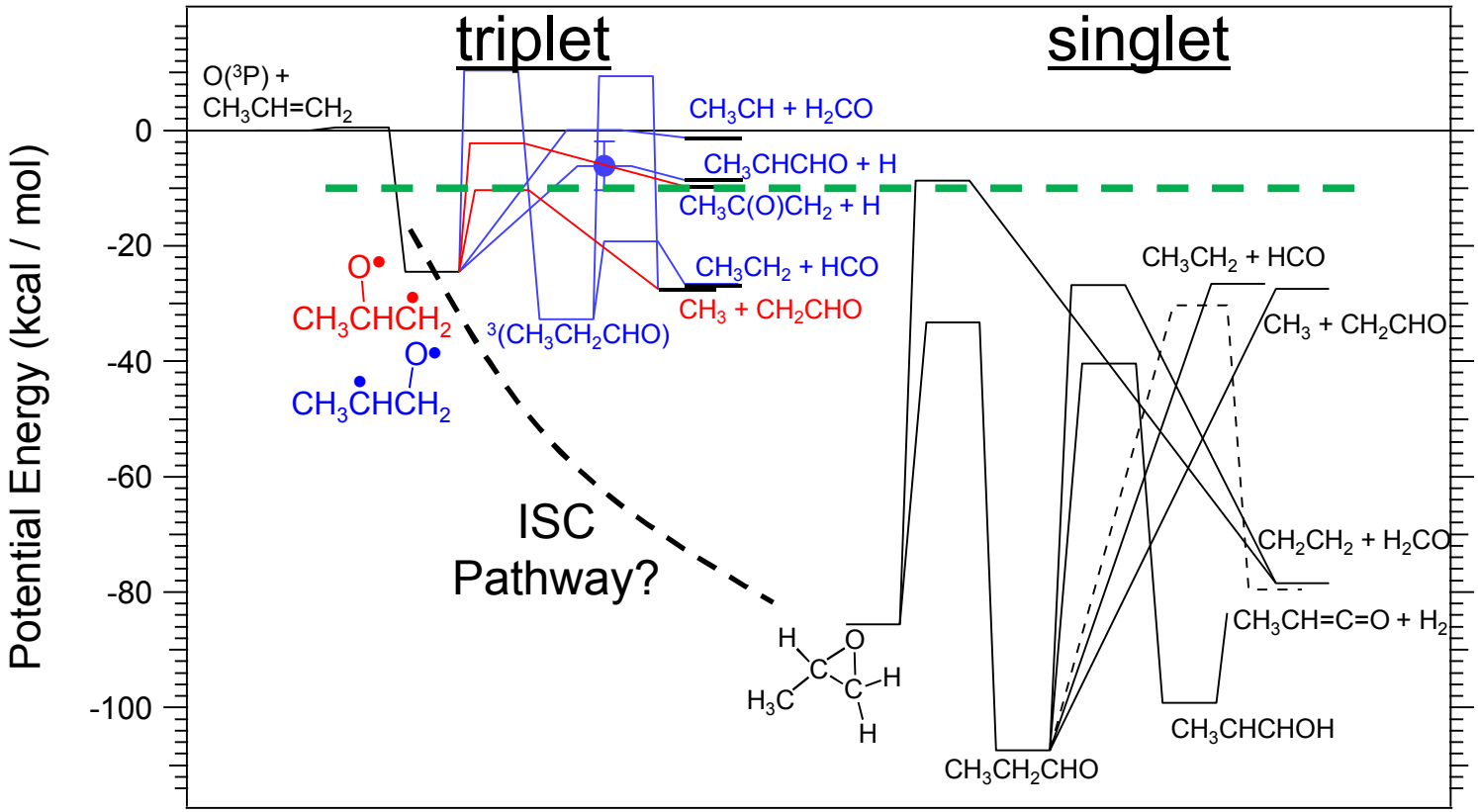
- **H_2 + $CH_3CH=C=O$ pathway (singlet surface) does NOT go through propanal—must happen via methyloxirane**
  - Intersystem crossing leads directly to methyloxirane, not to propanal or other species.
  - Barrier for this tight elimination from methyl similar to isomerization to propanal.

Conclusions



- CH_3CH_2 + HCO is also created on the singlet surface
  - (barrier too high on the triplet).

Conclusions

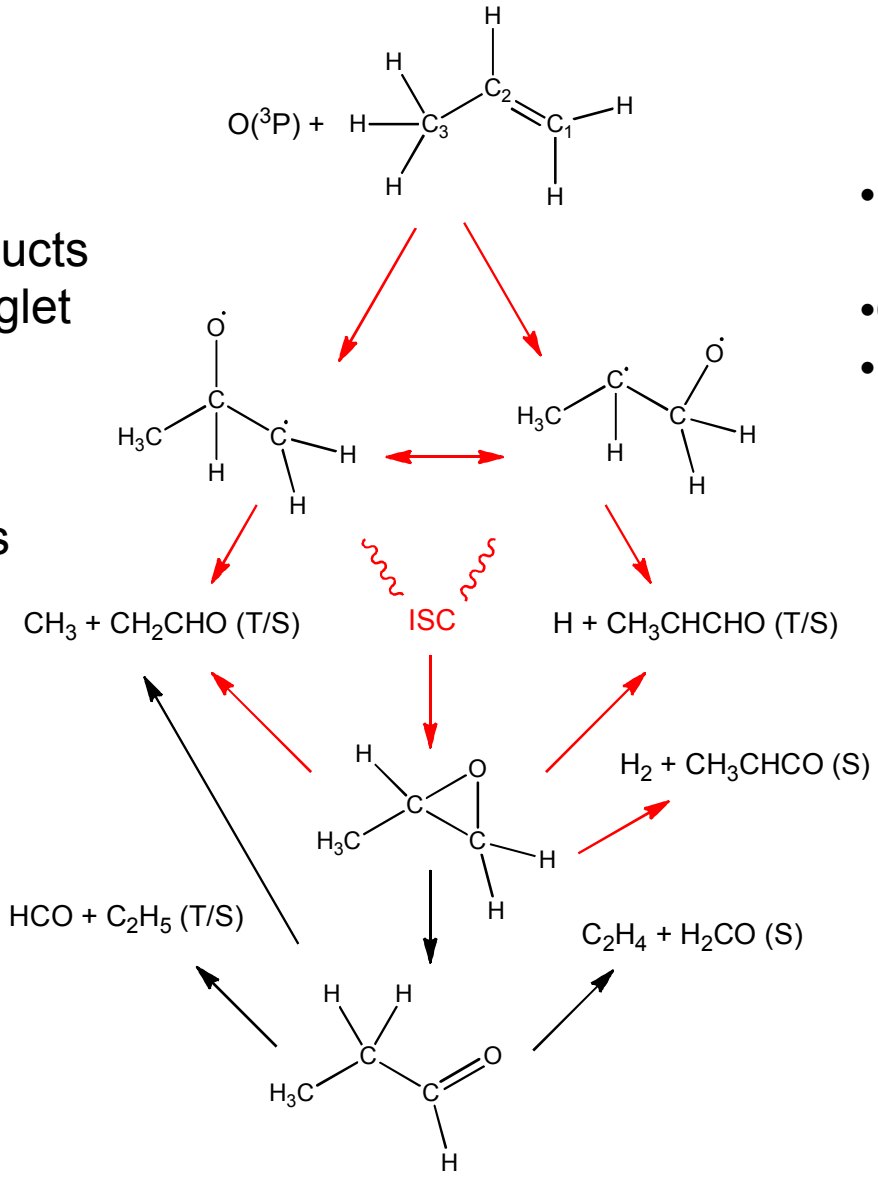


- Rate of intersystem crossing must be similar to rate of CH_3 + CH_2CHO on triplet surface

Pathway summary

Conclusions

- ~40% of total products are born on the singlet surface
- No stabilization to C_3H_6O at 4 torr
- ISC crossing leads directly to methyloxirane



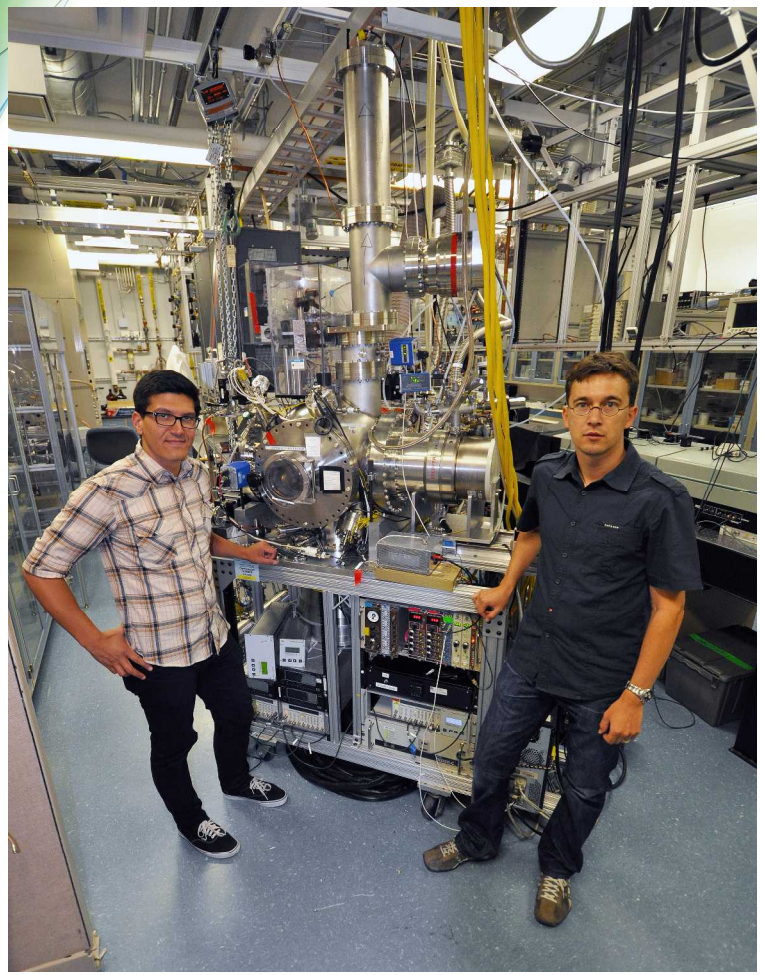
Our Needs

- Improved PESs
  - (Red arrows)
- QCT calculations?
- Non-adiabatic TST

Future of theoretical calculations

- 1)Quantum studies the gold standard – too hard for > 4 atoms
- 2) Quasi-classical trajectories (analytic or on-the-fly) the silver standard
  - Hase & Windus → Multireference wavefunctions needed.
  - Bowman & Casavecchia → analytic surface w/MRCI → QCT
- 3) Robust statistical methods needed for larger systems
  - Morokuma / Klippenstein / Harvey
- 4) Will multidimensional treatments be needed to reproduce rates, branching ratios, and product state distributions?
  - Spin-orbit coupling depends on more than just reaction coordinate
  - Non-adiabatic transition itself depends on more than reaction coord.

Acknowledgements



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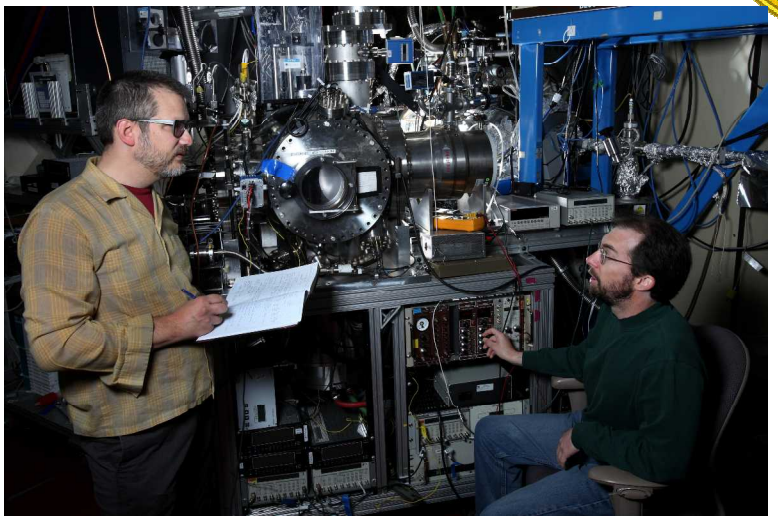

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Secondary chemistry

- H atoms from H + CH_3CHCHO
- H + NO_2 → OH + NO
- OH + propene → H2CO, Acetone, propanal, methyloxirane