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Multiplexed Photoionization Mass Spectrometry Studies of $O(^3P)$ + Cyclopentene Reveal Unexpected Pathways

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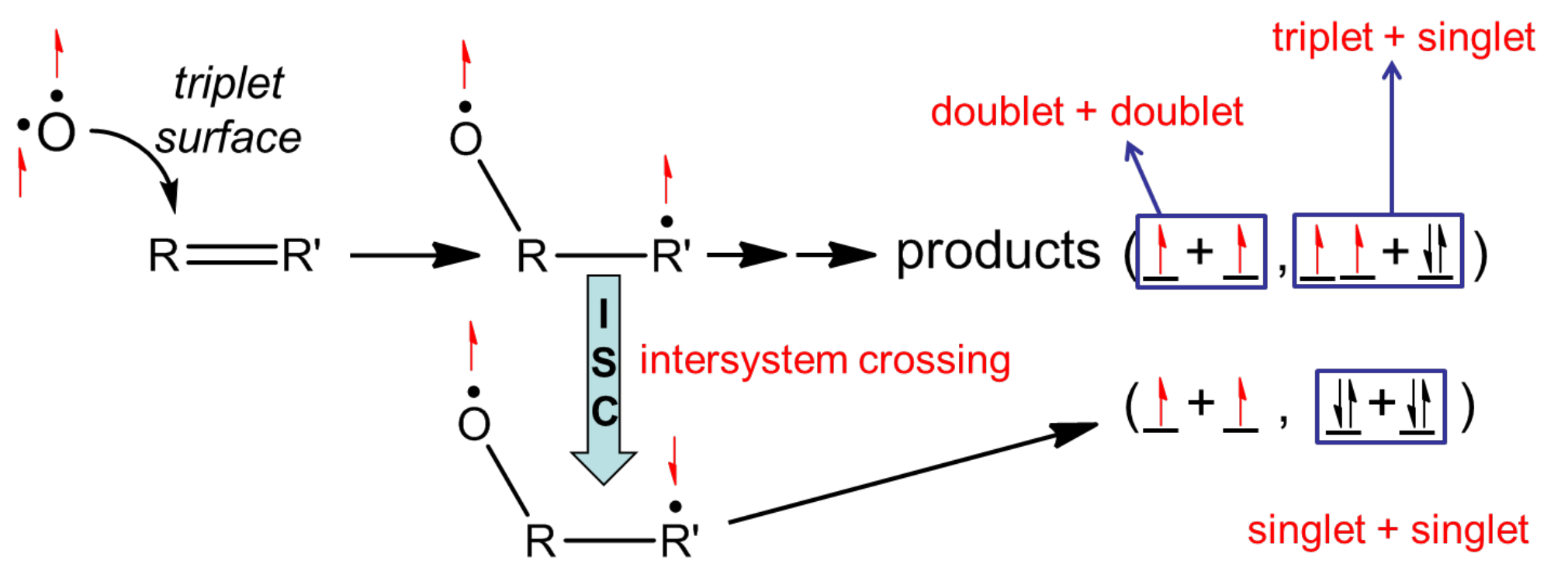
Introduction

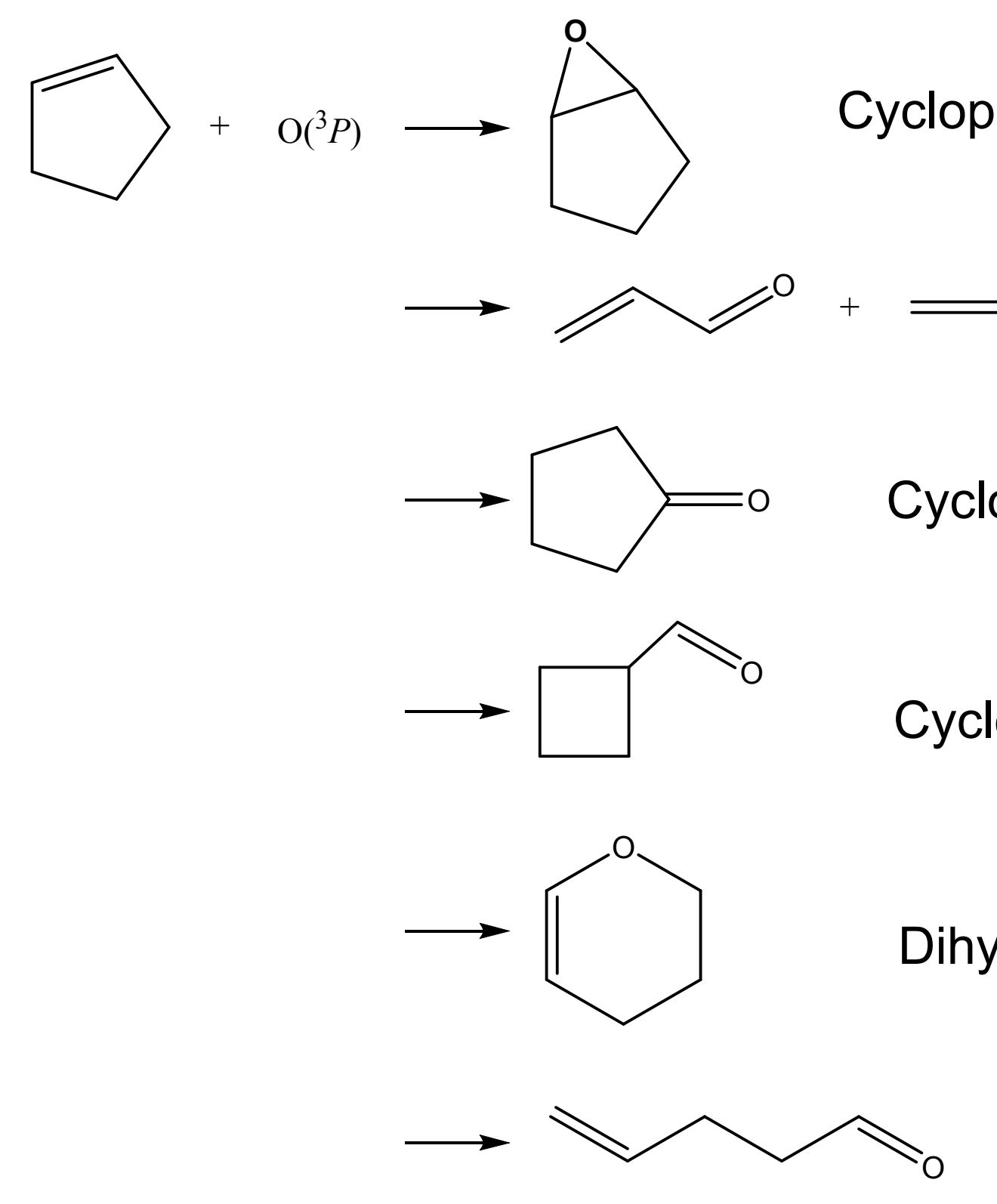
In combustion environments, $O(^3P)$ and OH radical are generated from the $H+O_2$ elementary reaction. Reaction of $O(^3P)$ with unsaturated hydrocarbons is dominated by the addition of O atom to the unsaturated bond, yielding a triplet biradical and leading to a competition between reactive pathways on singlet and triplet potential energy surfaces (PES).



Earlier work on reactions with acyclic unsaturated hydrocarbons[1-4] suggested formation of bimolecular products with varying contributions from pathways on triplet and singlet PES.

Does $O(^3P)$ reaction with cyclic unsaturated hydrocarbons restrict available pathways? Do unimolecular isomerization pathways become feasible?

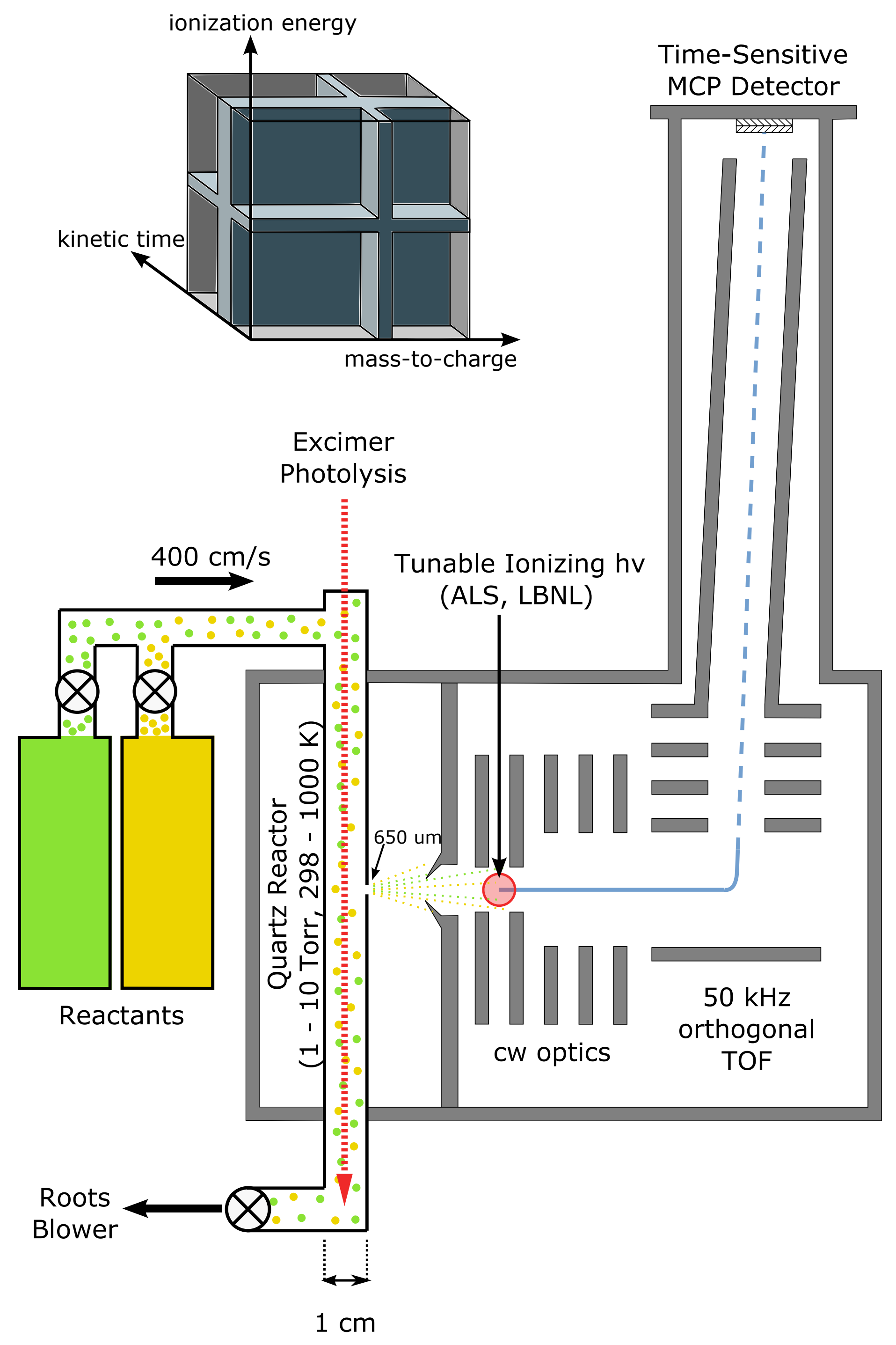
Cvetanovic[5] reported a rate coefficient of the reaction of O(3P) with cyclopentene to be $k = 2.11 \times 10^{-11}$ cm^3s^{-1}. Previous works[6,7], in which products were detected using gas chromatography and time-resolved Fourier transform infrared spectroscopy, indicated the following pathways:



Cyclopentene oxide (CPO)
Acrolein and ethene
Cyclopentanone (CPN)
Cyclobutylcarboxaldehyde (CBA)
Dihydropyran (DHP)
4-pentenal (4-PA)

Theoretical work[8] using CCSD(T)//MP2/6-311G(d,p) level suggested these pathways to exist on the singlet PES, and that a new product, 2-cyclopentenol, to be formed.

Time-resolved Multiplexed Photoionization Mass Spectrometry[9]



Excimer laser at 351 nm photolyses NO_2 to produce $O(^3P)$

Mix of NO_2 and $c\text{-}C_5H_8$ in He sent into a quartz reactor tube whose temperature and pressure are maintained at 298 K and 4 Torr.

Products side-sampled from quartz reactor flow tube through a pinhole, and skimmed prior to ionization

Tunable synchrotron VUV radiation photionizes products

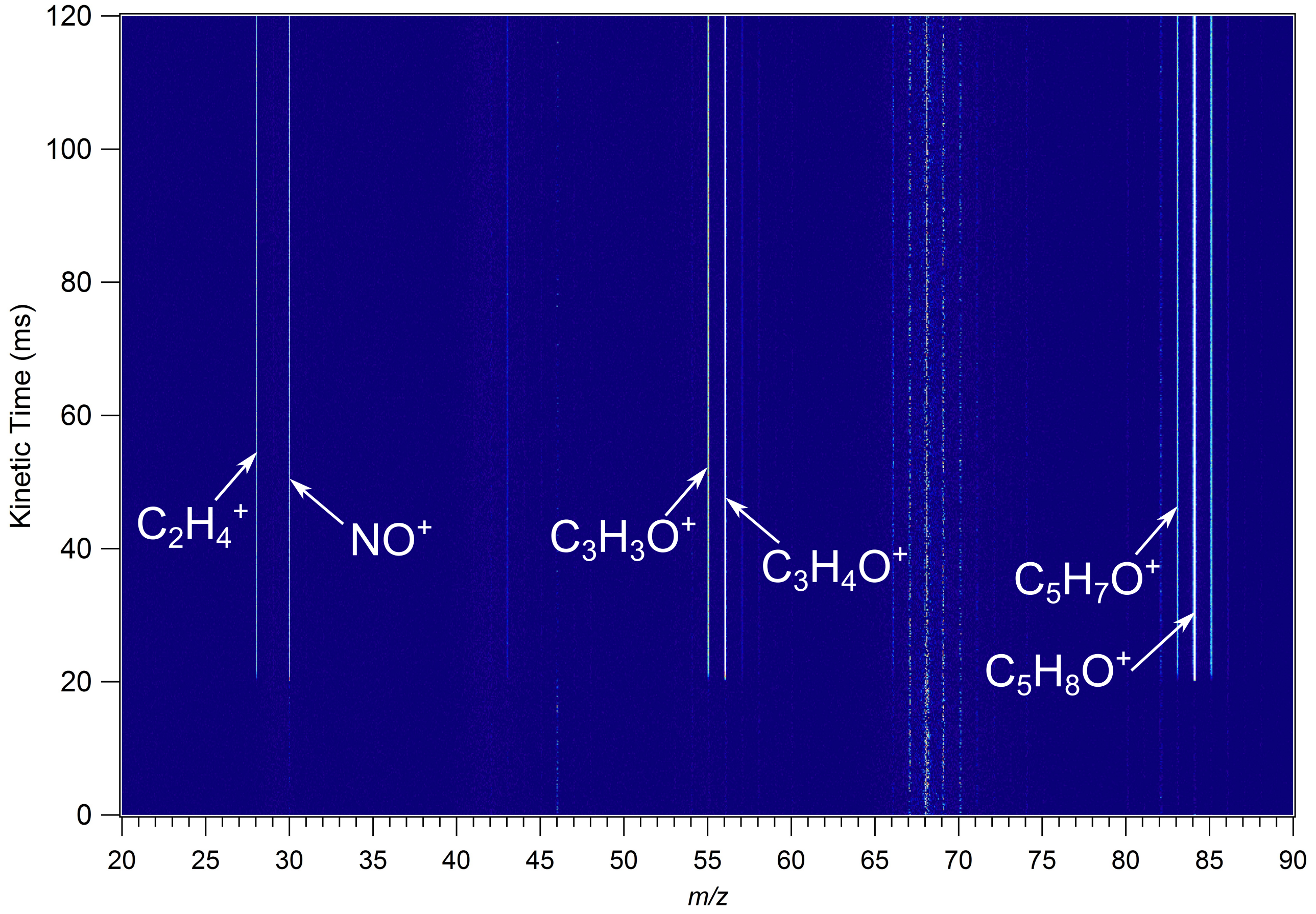
Orthogonal acceleration TOF equipped with a time-sensitive MCP detector measures mass spectrum every 20 ms

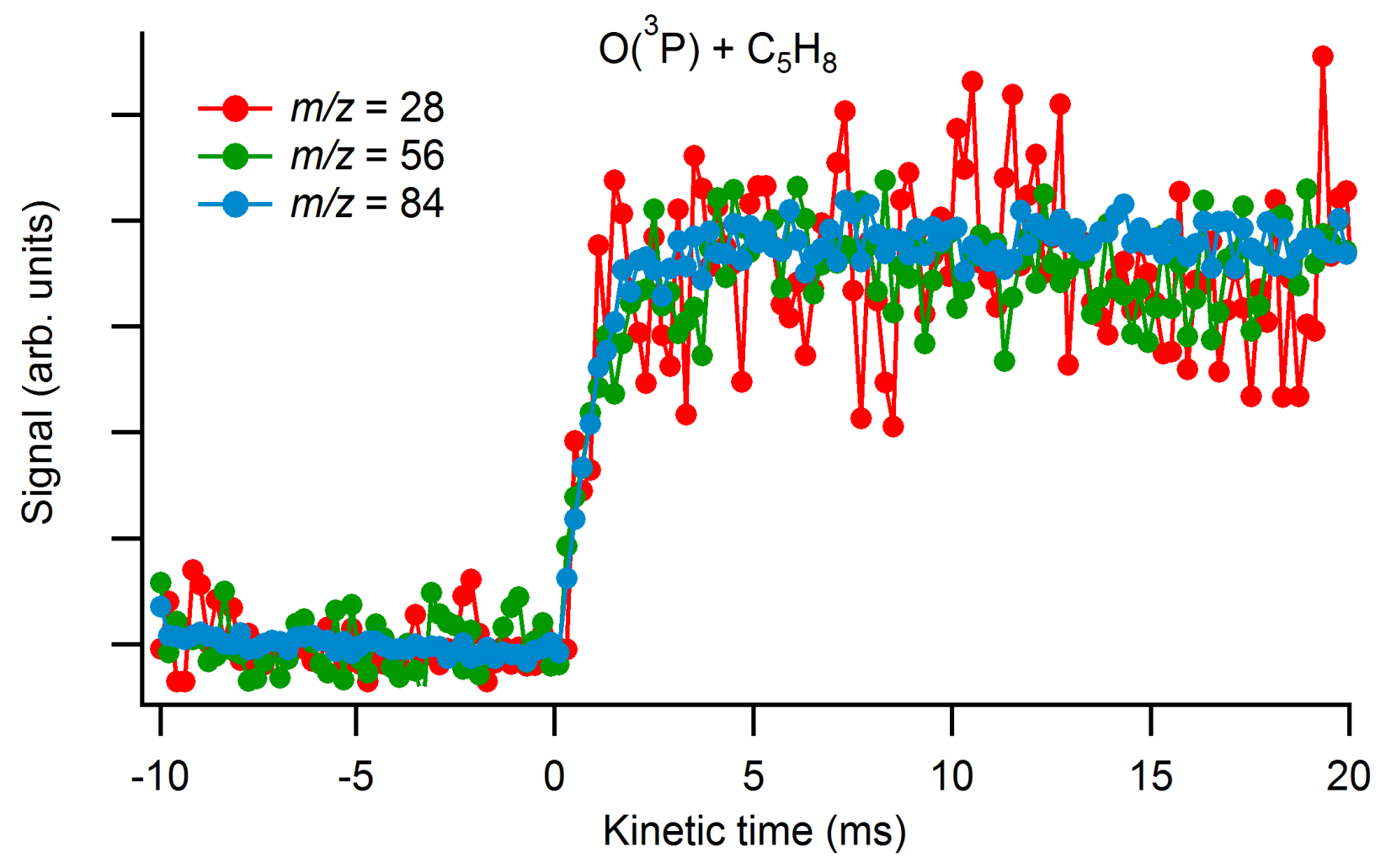
Mass-resolution ~1600

Three-dimensional data set, $I(m/z, t, E)$, as a function of time after photolysis (t), photoionization energy (E), and mass-to-charge (m/z).

Results

4 Torr, 298 K, 8.2 - 11 eV



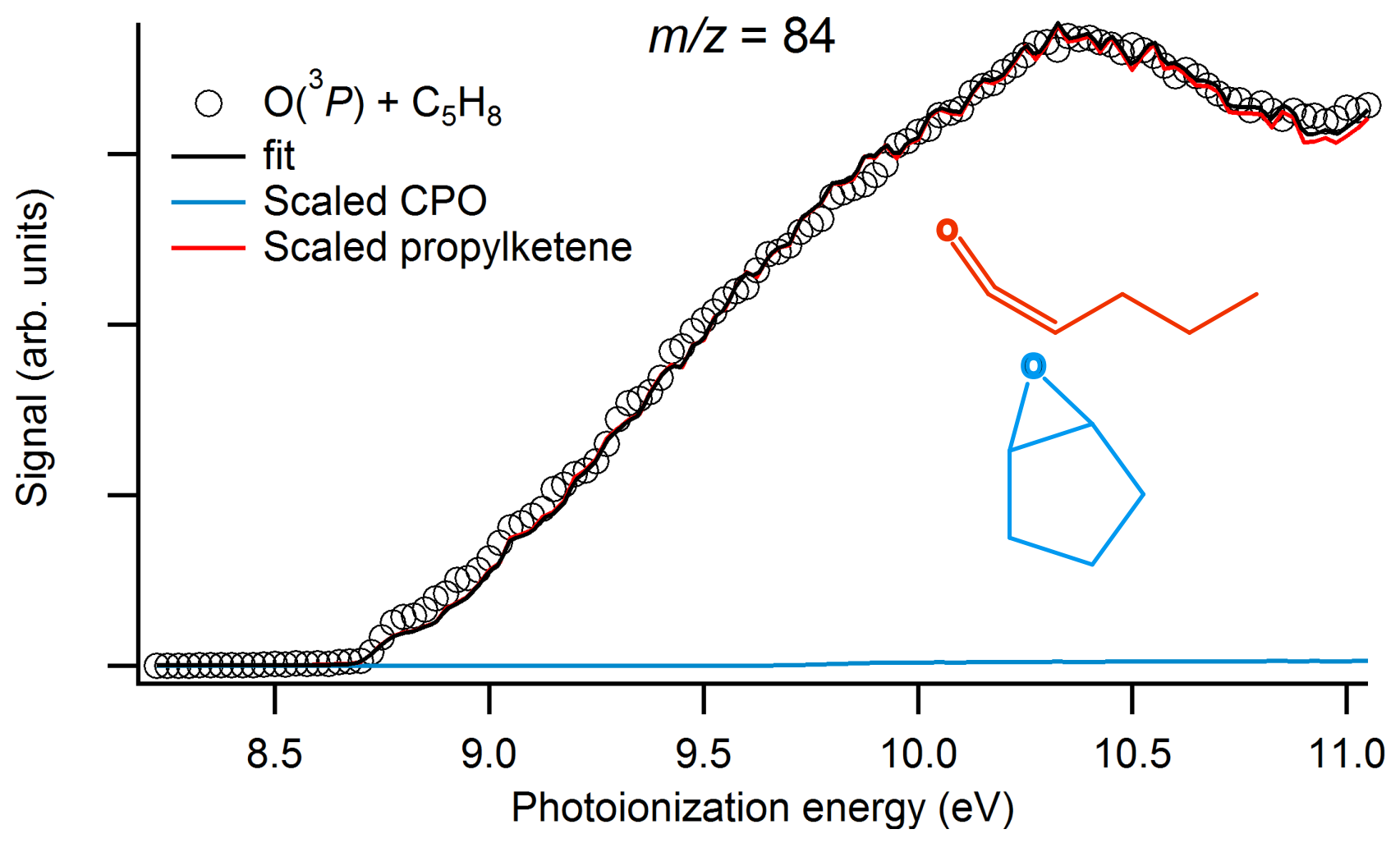


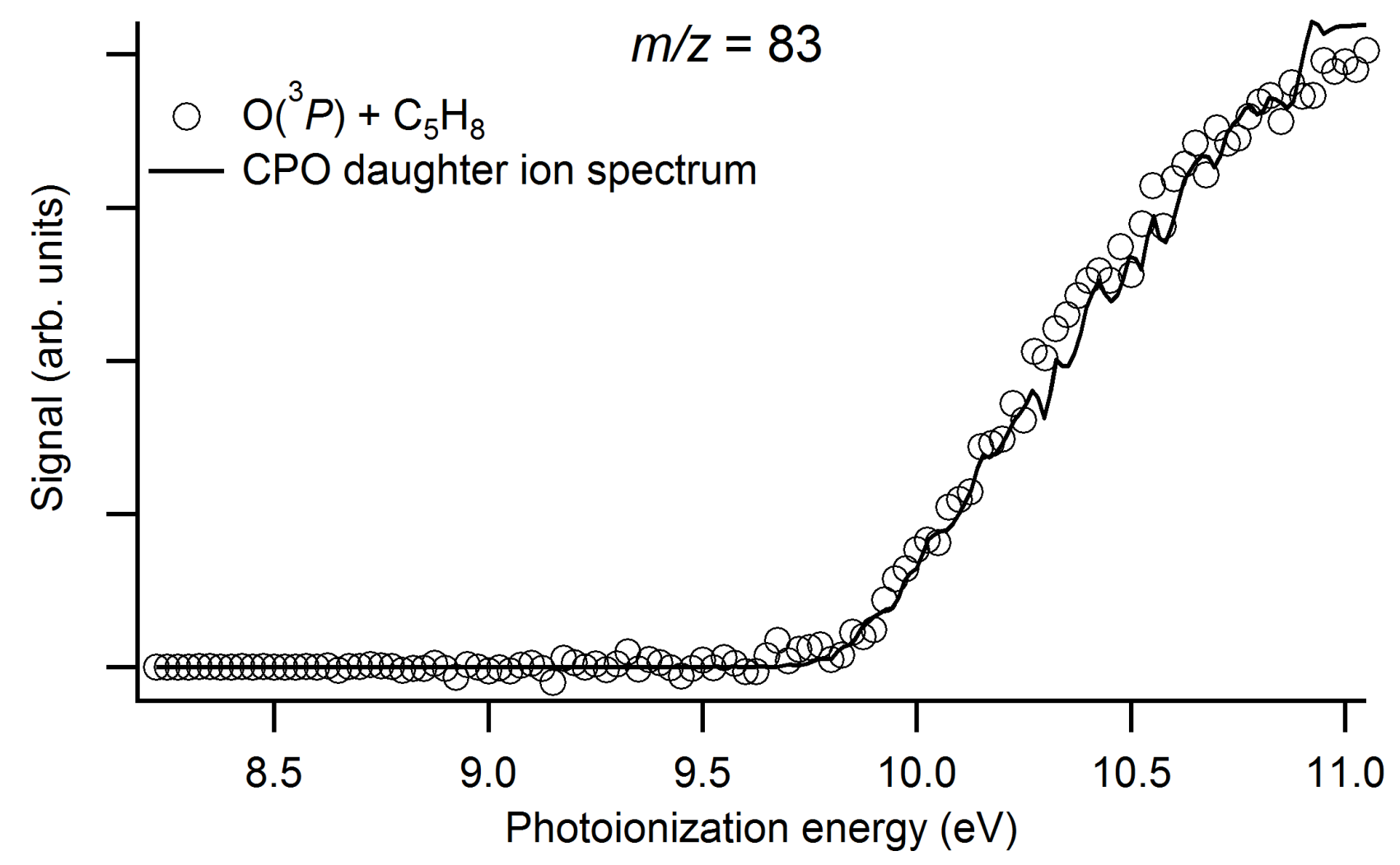
$[c\text{-}C_5H_8]_0 = 7.8 \times 10^{13}$ cm^{-3}
$[NO_2]_0 = 7.6 \times 10^{12}$ cm^{-3}
$[O(^3P)]_0 = 1.5 \times 10^{11}$ cm^{-3}

Predicted pseudo-first order rate = 1720 s^{-1}
Rise time extracted from fits to first-order rate law accounting for instrument response ~1200 s^{-1}

All products are primary products

Isomerization channels





Photoionization spectrum at *m/z* 84 dominated by shape resonance feature, and closely matches the absolute cross-section of propylketene.

m/z 83 daughter ion spectrum resembles CPO daughter ion cross-section

m/z 84 spectral fit to linear combination of cross sections of propylketene and CPO yield branching of ~94%:6%

Ionization energies of previously reported isomerization products inconsistent with *m/z* 84 spectrum:
CPN ~9.25 eV, CBA 9.65 eV (CBS-QB3), 4-PA 9.54 eV (CBS-QB3), 2-cyclopentenol 9.26 eV (CBS-QB3), DHP 8.3 eV

However, large propylketene cross-section can overshadow contribution of isomers whose ionization onsets are higher than that of propylketene. This rules out only DHP from the products observed in this experiment

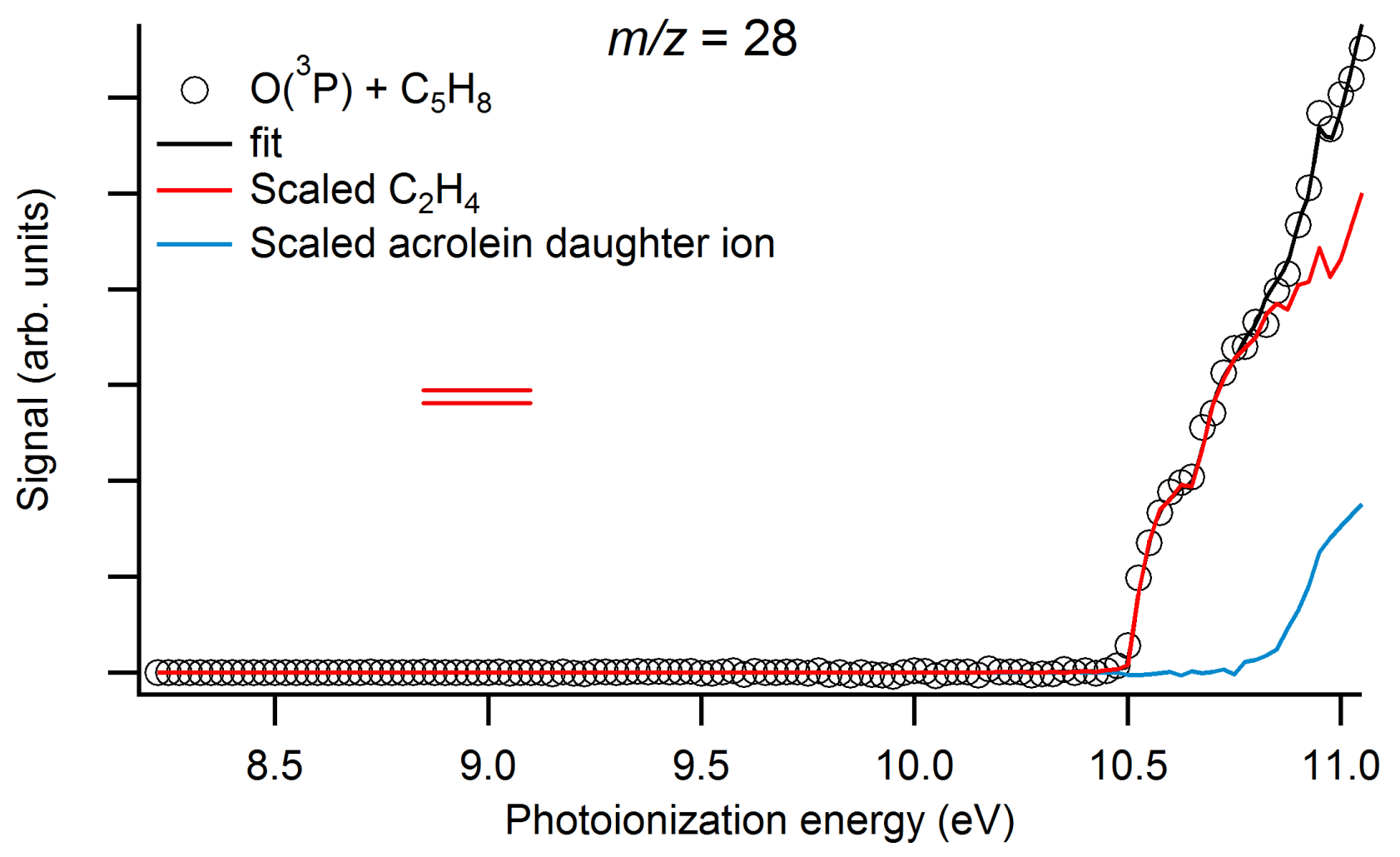
Bimolecular channels

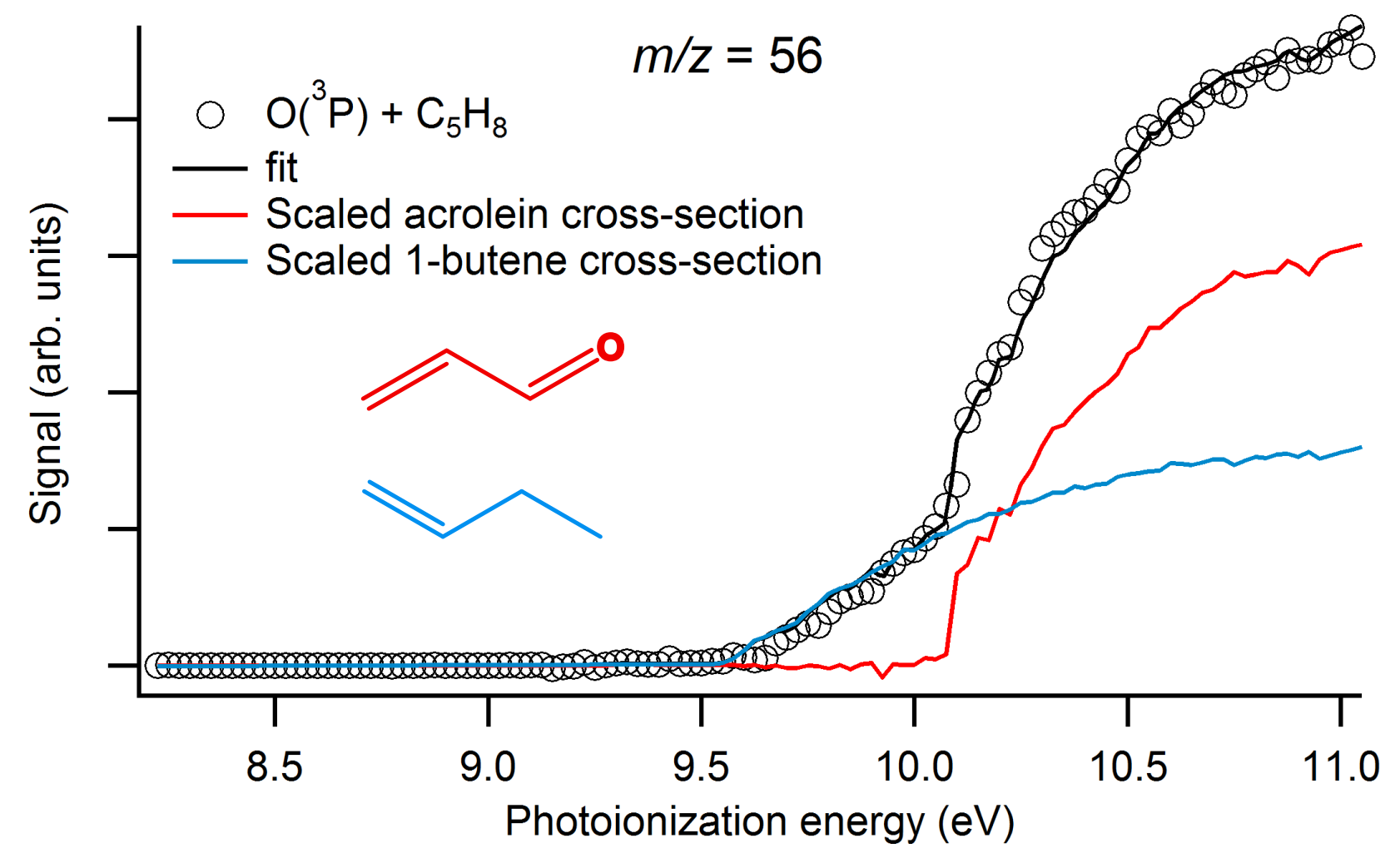
m/z 28 photoionization spectrum shows formation of ethene

m/z 56 spectrum shows clear signatures for the presence of acrolein and 1-butene, with branching of ~65%:35% at this mass.

Two bimolecular pathways:
1) Acrolein + Ethene
2) 1-butene + CO (previously unobserved)

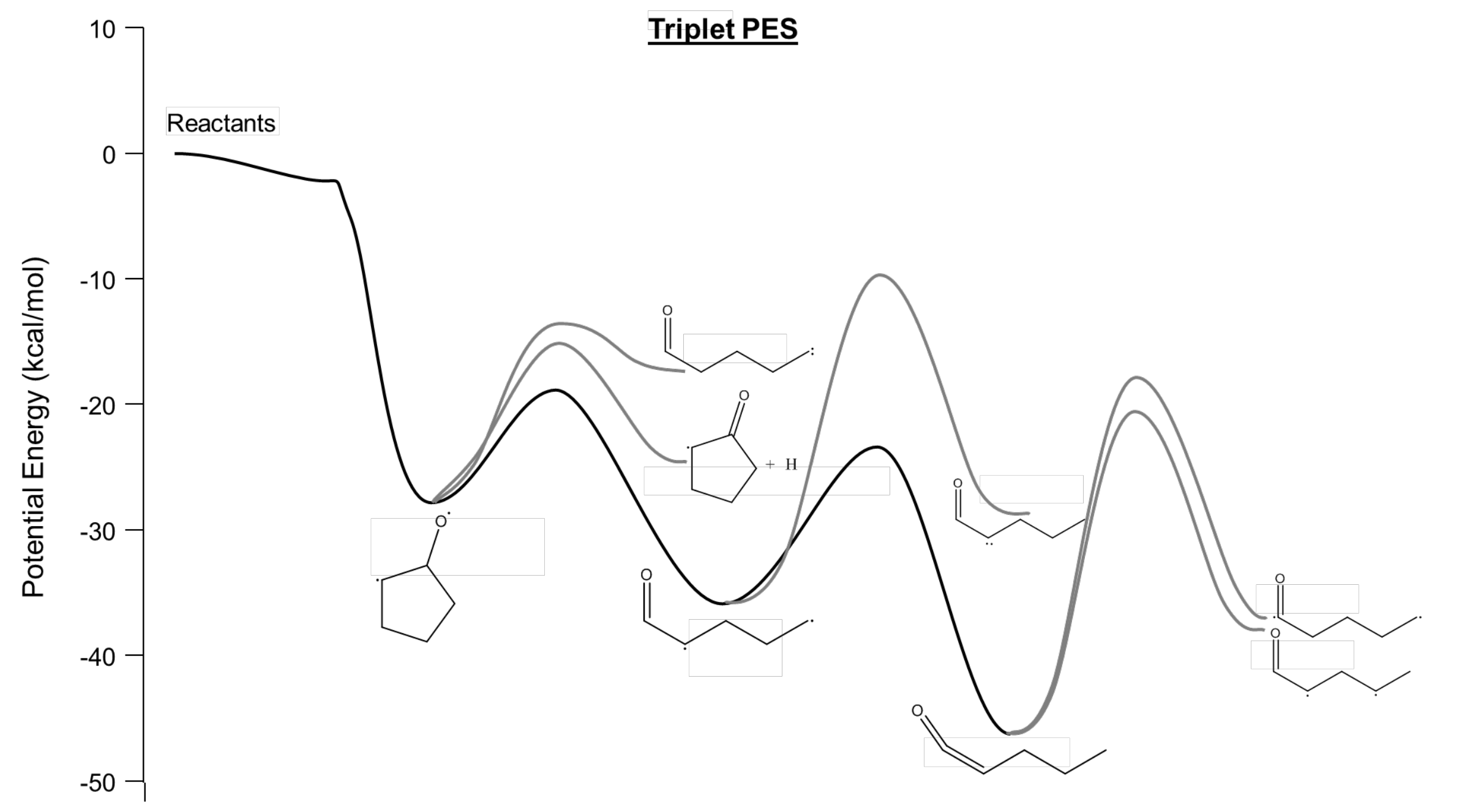
Product Branching:
Propylketene ~40%
Acrolein + Ethene ~37%
1-butene + CO ~20%
CPO ~3%

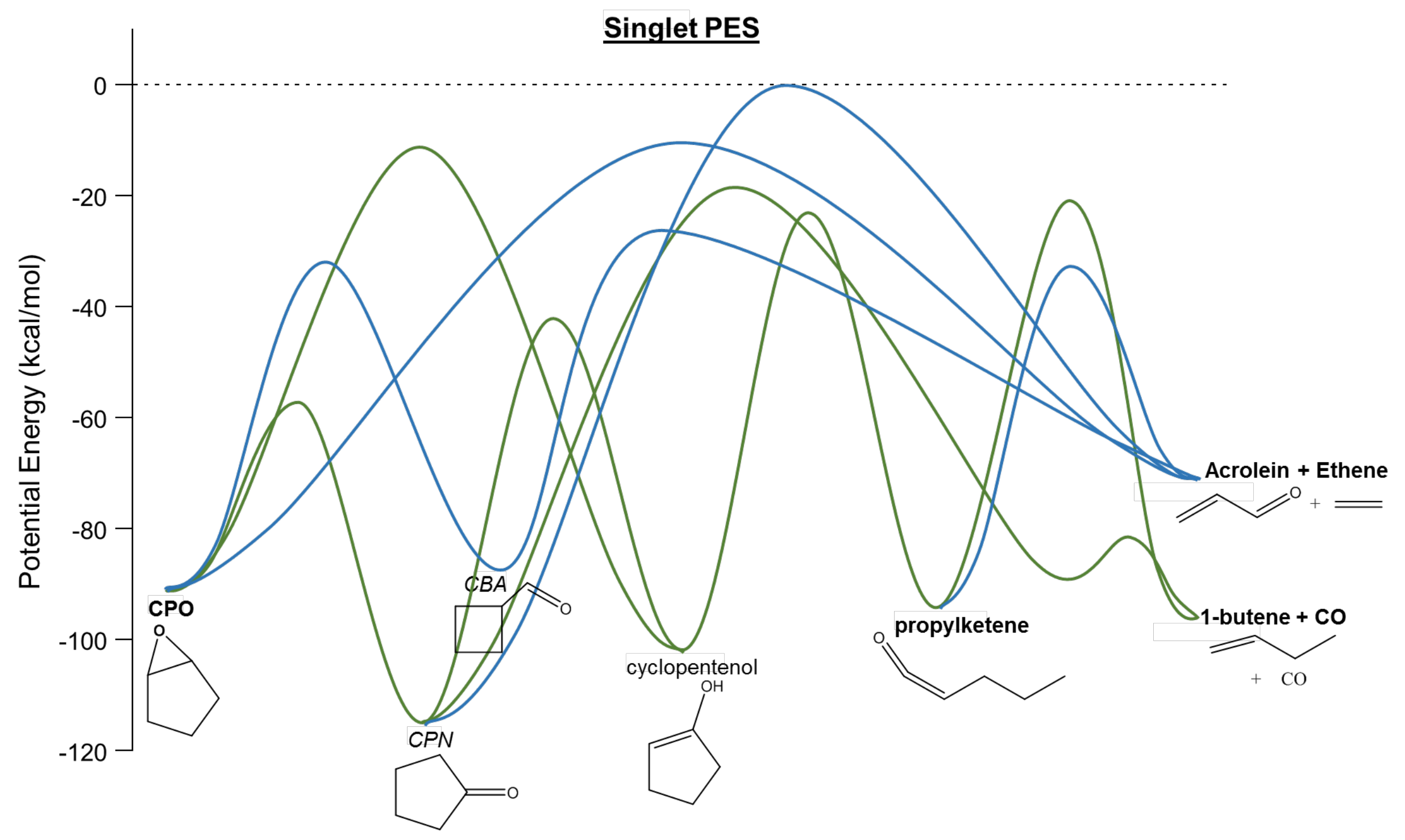




Interpretation

Automatic exploration of PES by KinBot[10] in conjunction with CBS-QB3 electronic structure calculations within Gaussian09 provided stationary point and transition state energies of possible pathways to product formation on triplet and singlet PES.

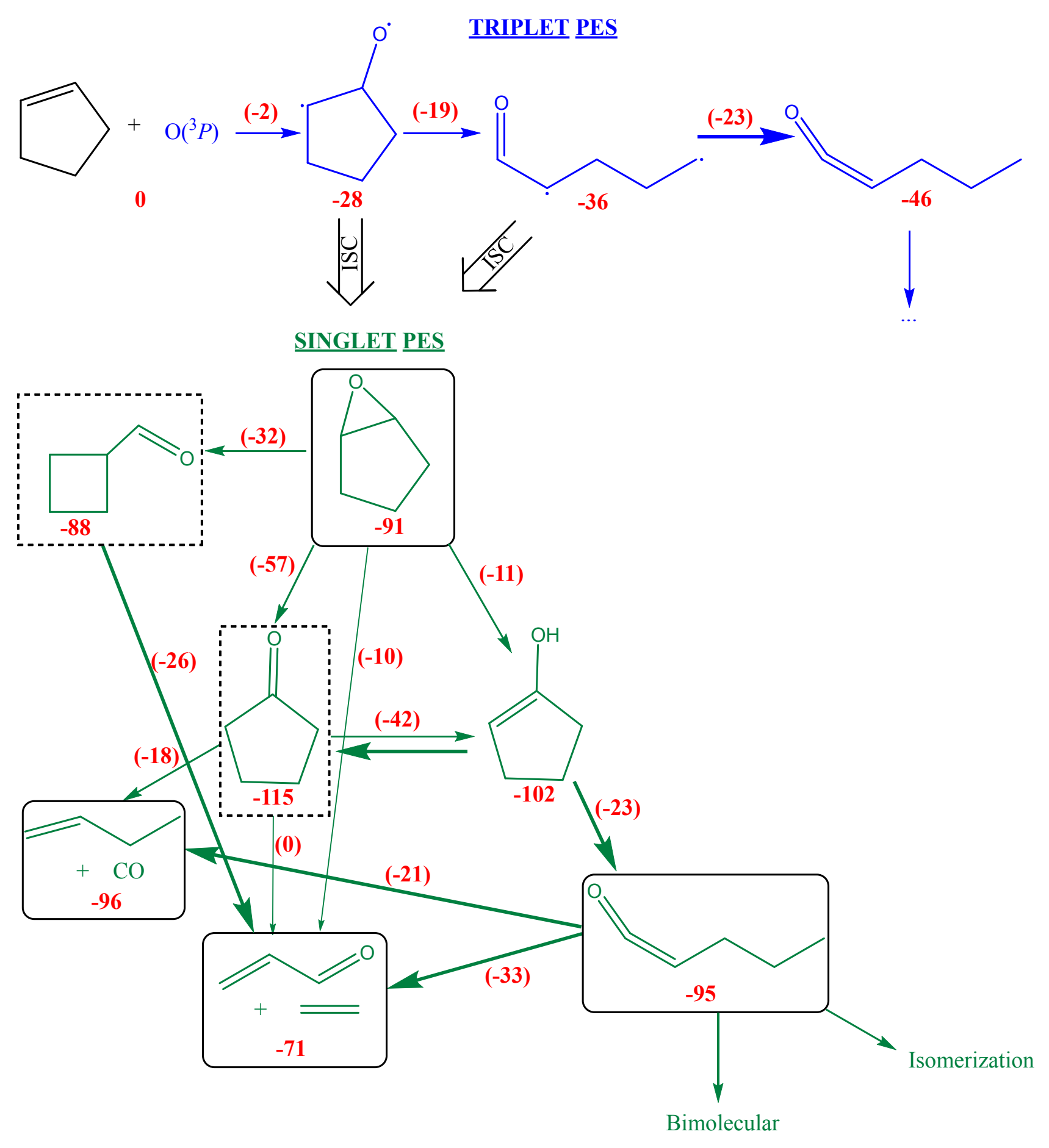




Triplet PES:
- Low barrier pathway, relative to entrance channel, to propylketene formation
- Propylketene occupies the lowest energy well on the triplet surface

Singlet PES:
- Crucial role ot 1-cyclopentene in formation of propylketene. Ionization energy of 1-cyclopentenol from CBS-QB3 is 8.3 eV, and there is no experimental evidence for its formation. Expect negligible concentrations of 1-cyclopentenol for two reasons:
    a) Master equation calculations reveal propylketene formation is ~50-60 times faster, at energies close to the entrance channel, than the backward reaction involving ring closure.
    b) The equilibrium between 1-cyclopentenol and CPN is skewed towards CPN due to its deeper well
- More energetically feasible pathways for the formation of bimolecular products, including those via propylketene, previously not identifed.

Summary and outstanding questions



1. Clear experimental evidence for the formation of propylketene, CPO, acrolein + ethene and 1-butene + CO.

2. DHP and 1-cyclopentenol not observed, while other isomerization products maybe present but overshadowed by propylketene signal at adduct mass.

3. Electronic structure calculations suggest that propylketene is formed both on the singlet and triplet PES. How does triplet propylketene quench to the singlet state?

4. Other products formed on the singlet PES.

5. Why do we see isomerization products at such low pressures? Perhaps due to the large number of vibrational modes, the system approaches the high pressure limit already at 4 Torr, 298 K

References and Acknowledgements

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