Is the ground electronic state of 1-alkenylperoxy cations a triplet or a singlet?

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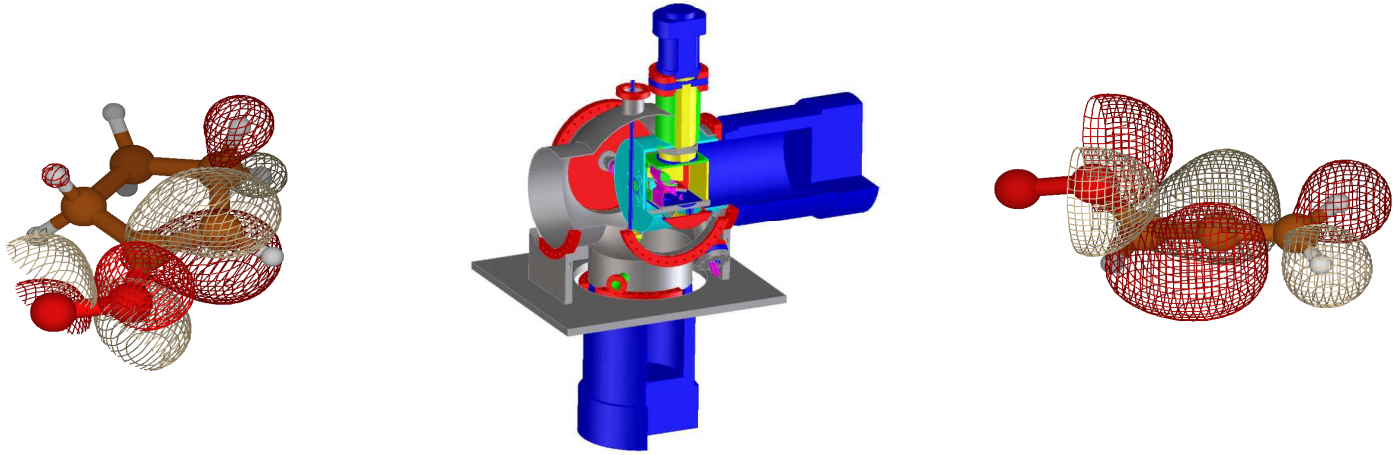

20th International Conference on Molecular Energy Transfer
June 7, 2007

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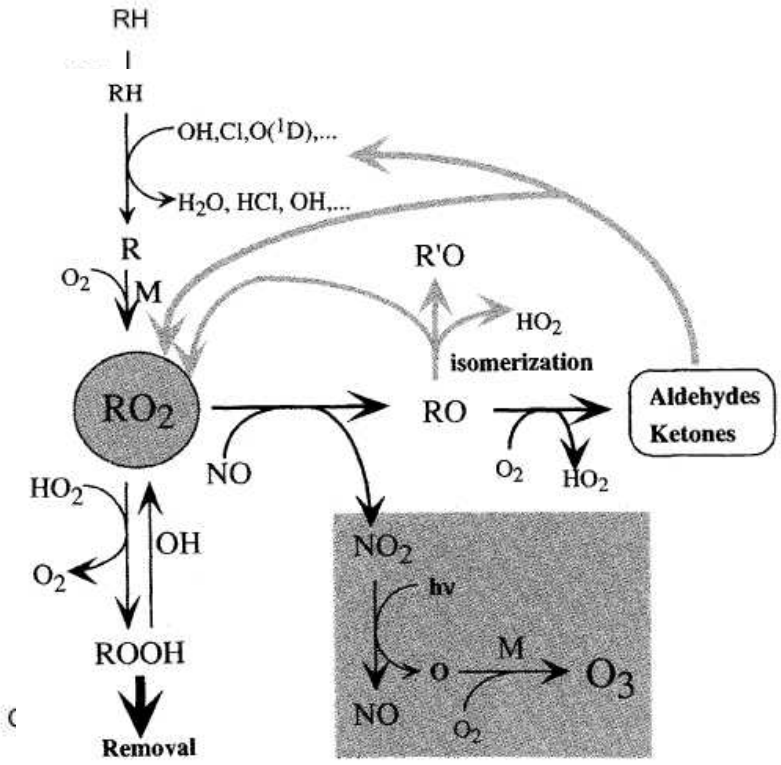
Why Study Alkenylperoxy?

- Pivotal role as reaction intermediates in the low temperature oxidation of organic compounds.
- Alkenylpe ıe oxidation of alkenes.



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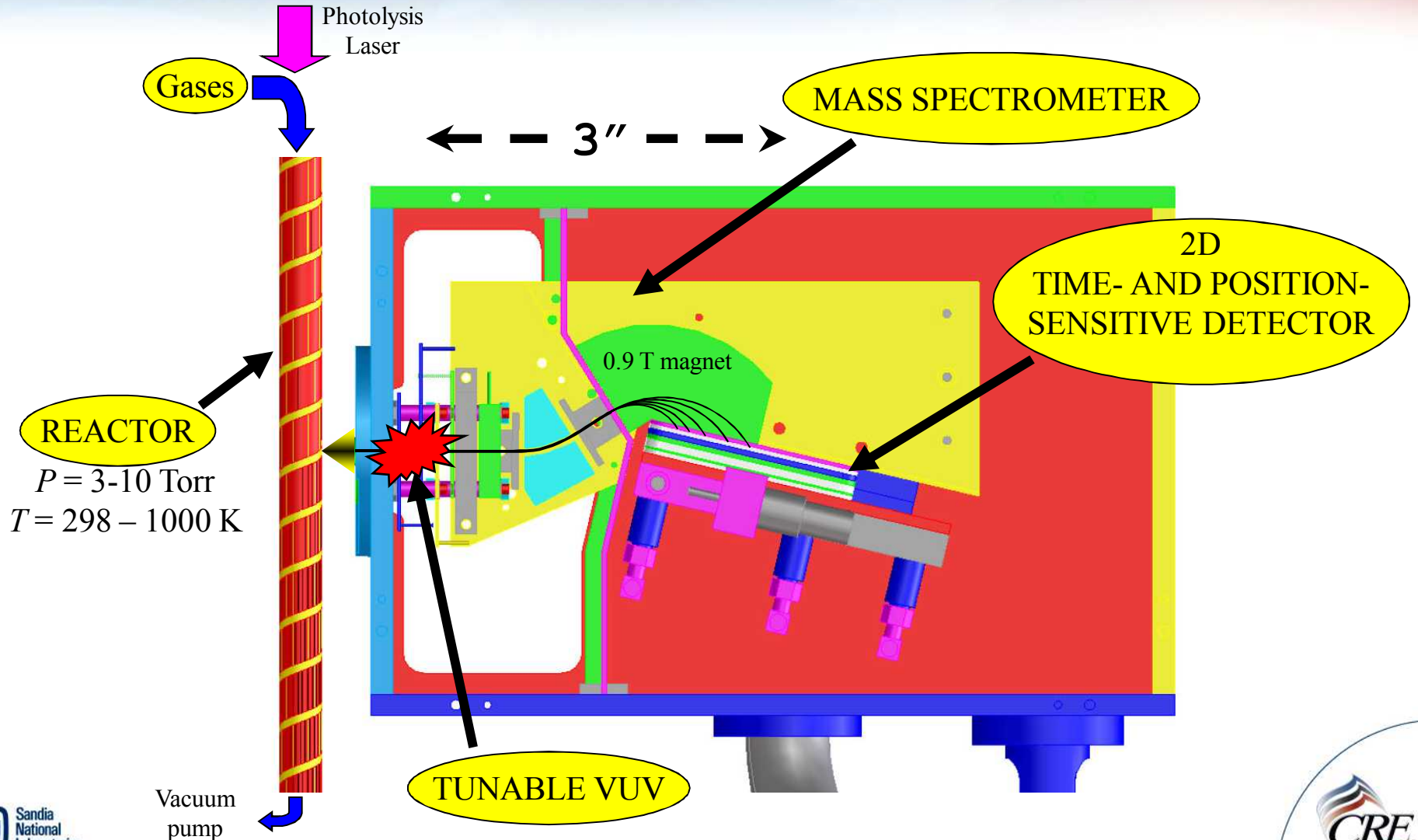
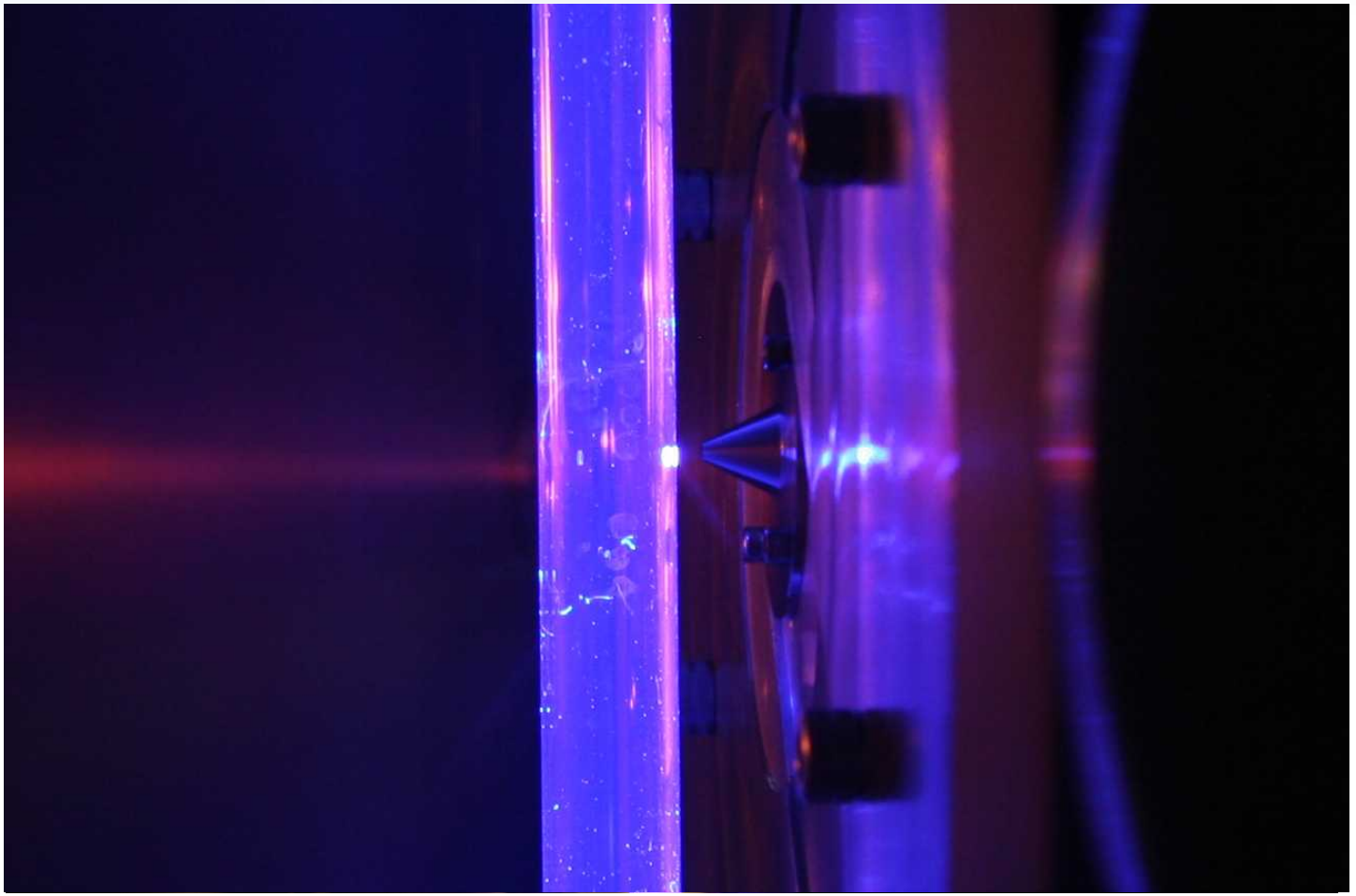
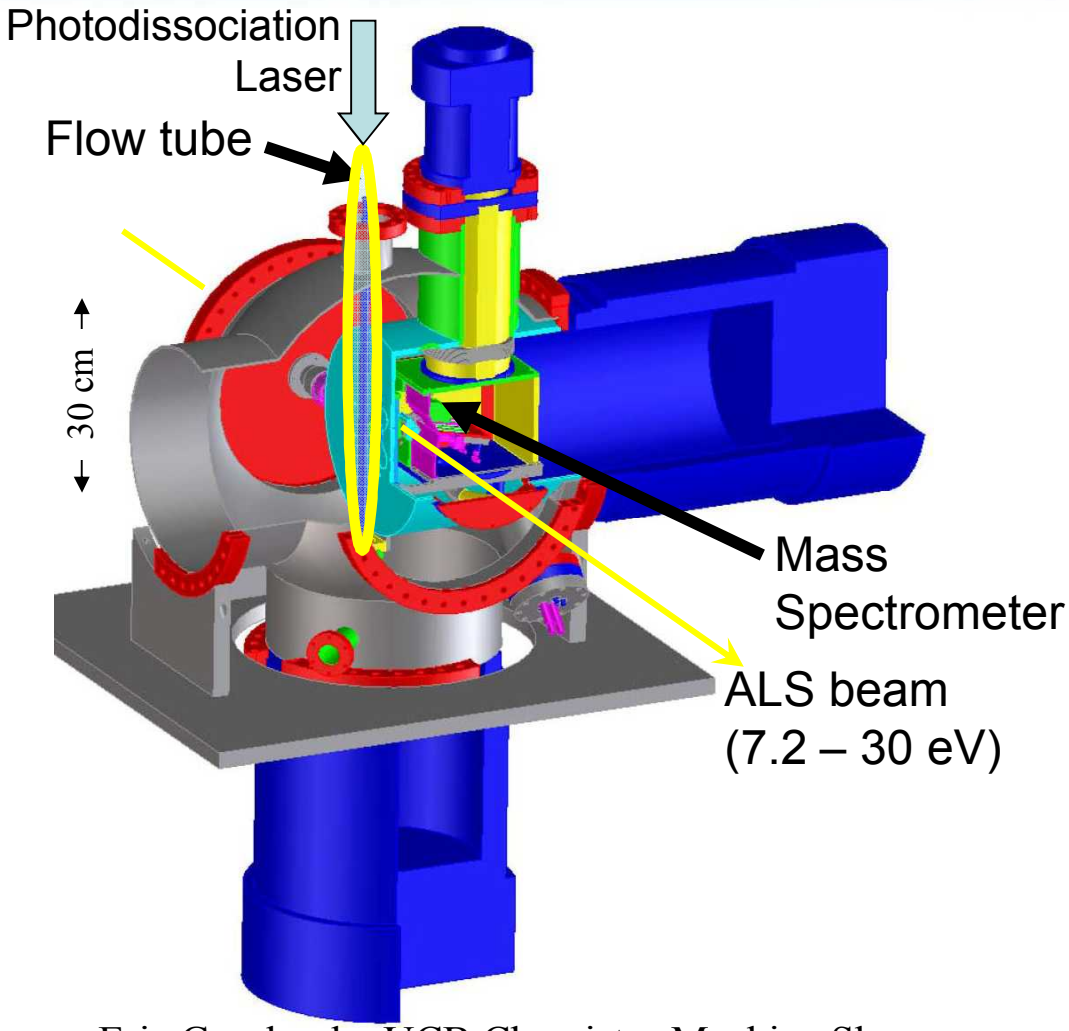
Mass Spectrometer & Detector



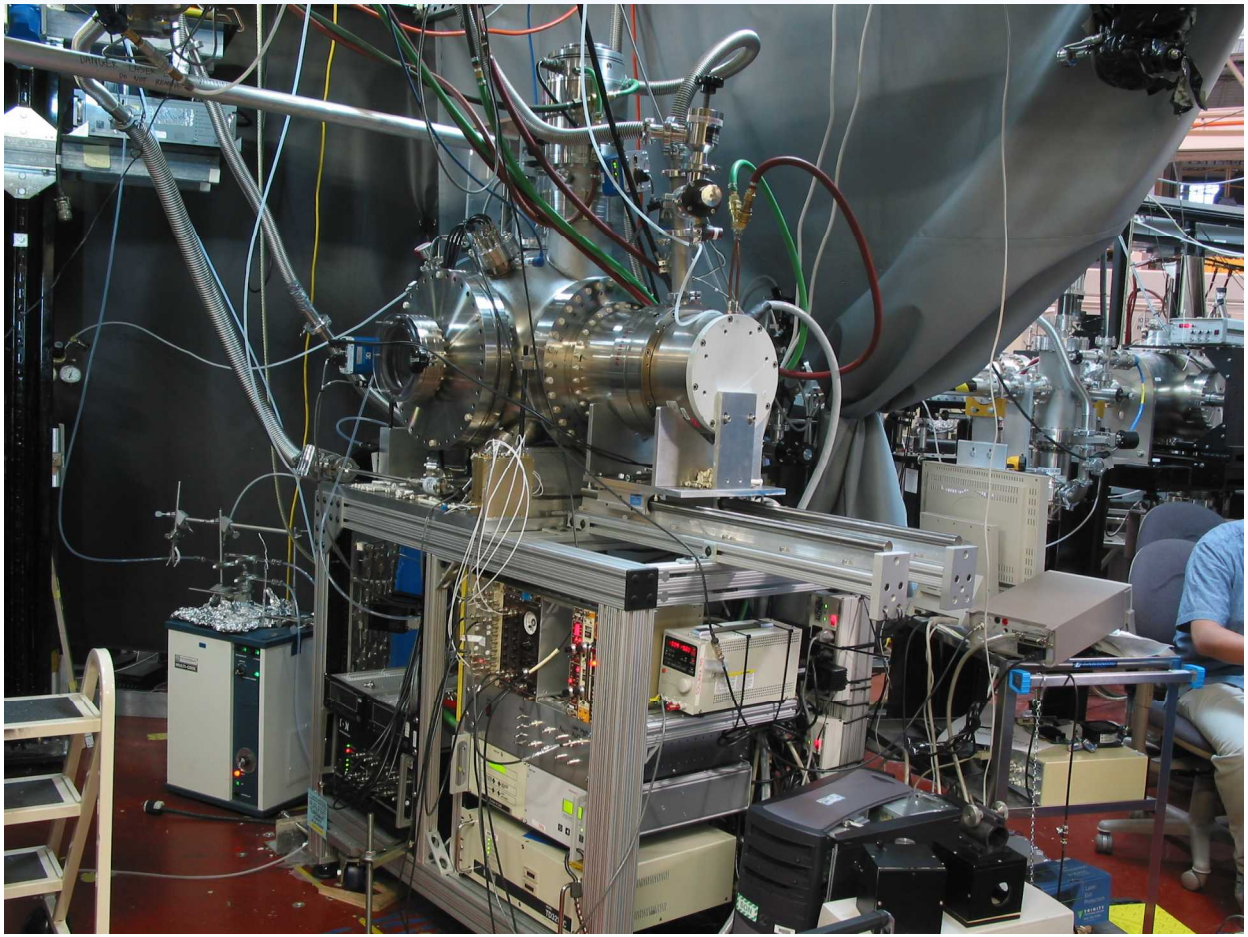
Reactor, Pinhole, and Skimmer



Apparatus Design



Multiplexed Kinetics Mass Spectrometer



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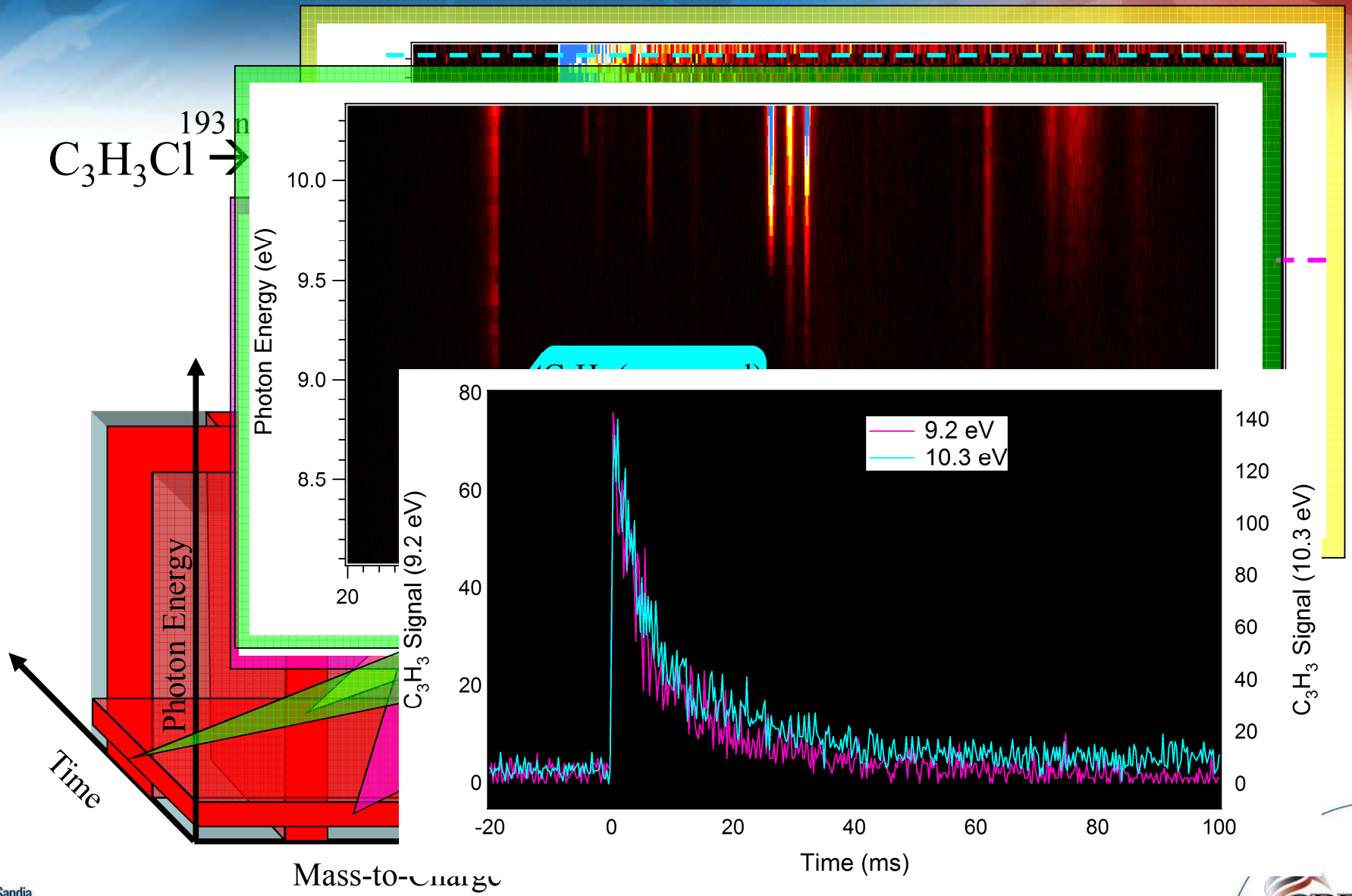
Multiplexed Photoionization Mass Spectrometer

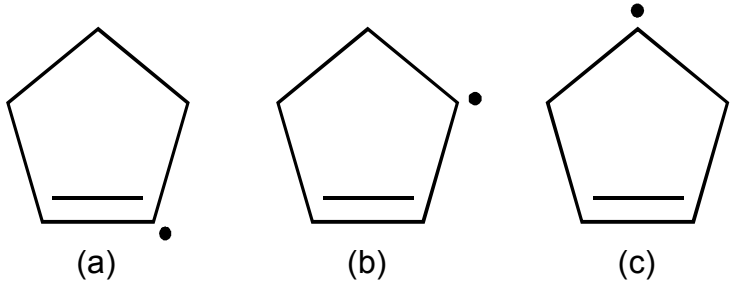
- Universal detection of all species ← Mass spectrometery
- Simultaneous detection of all species ← Multiplexed mass spectrometer
- Isomer-resolved detection ← Tunable VUV photoionization
- High sensitivity ← Single-ion counting MCP detector
- Variable temperature & pressure

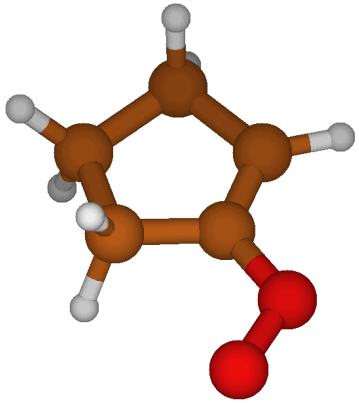
Three-Dimensional Data: $S(m, t, h\nu)$



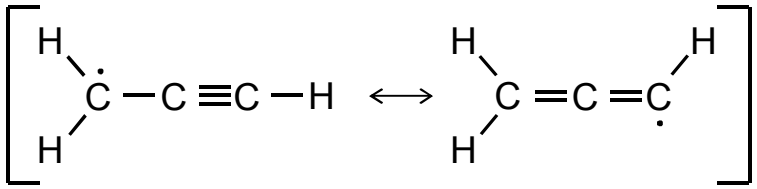
Systems

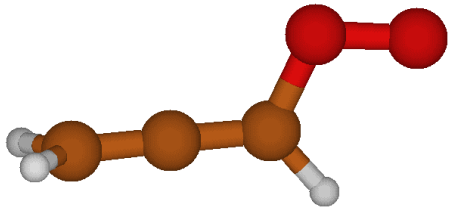
- 1-cyclopentenylperoxy (1-*c*-C_5H_7OO)





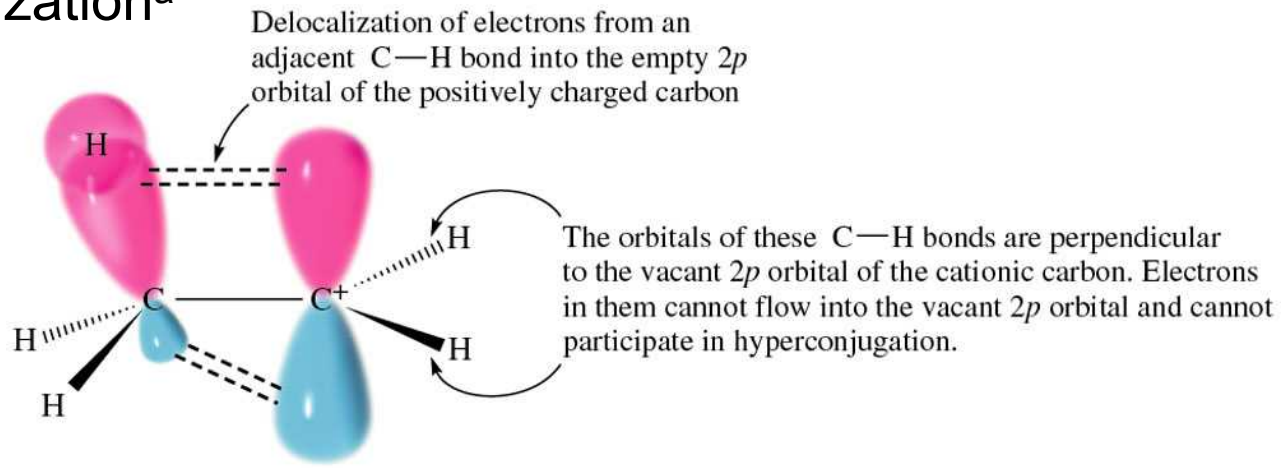
- Propargylperoxy (C_3H_3OO)





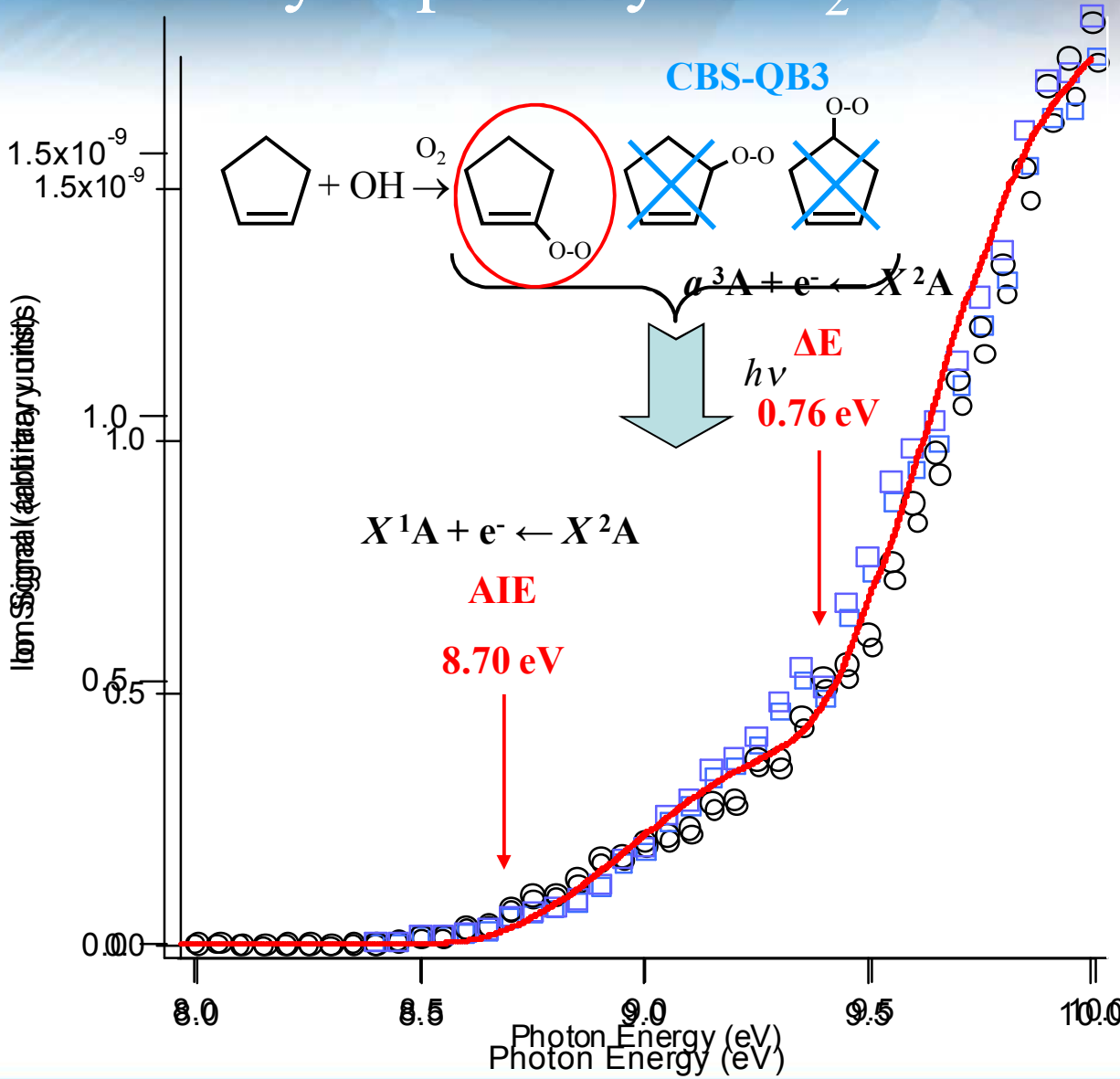
Background

- Only previously experimentally studied peroxy cations: CH_3OO^+,[a] $C_2H_5OO^+$,[a,b] and $C_3H_7OO^+$ [a,b]
- Only CH_3OO^+ shows thermodynamic stability[a]
- Larger alkylperoxy cation triplet ground states are unbound[a,b]
- Increasing relative stability of alkyl cation fragments with respect to the parent ion as result of hyperconjugation stabilization[a]



[a]Meloni *et al.*, J. Am. Chem. Soc. **2006**, *128*, 13559-13567.
[b]Fu *et al.*, J. Chem. Phys. **2006**, *125*, 014310.

Cyclopentenyl + O_2 reaction



$P = 4$ Torr

$T = 298$ K

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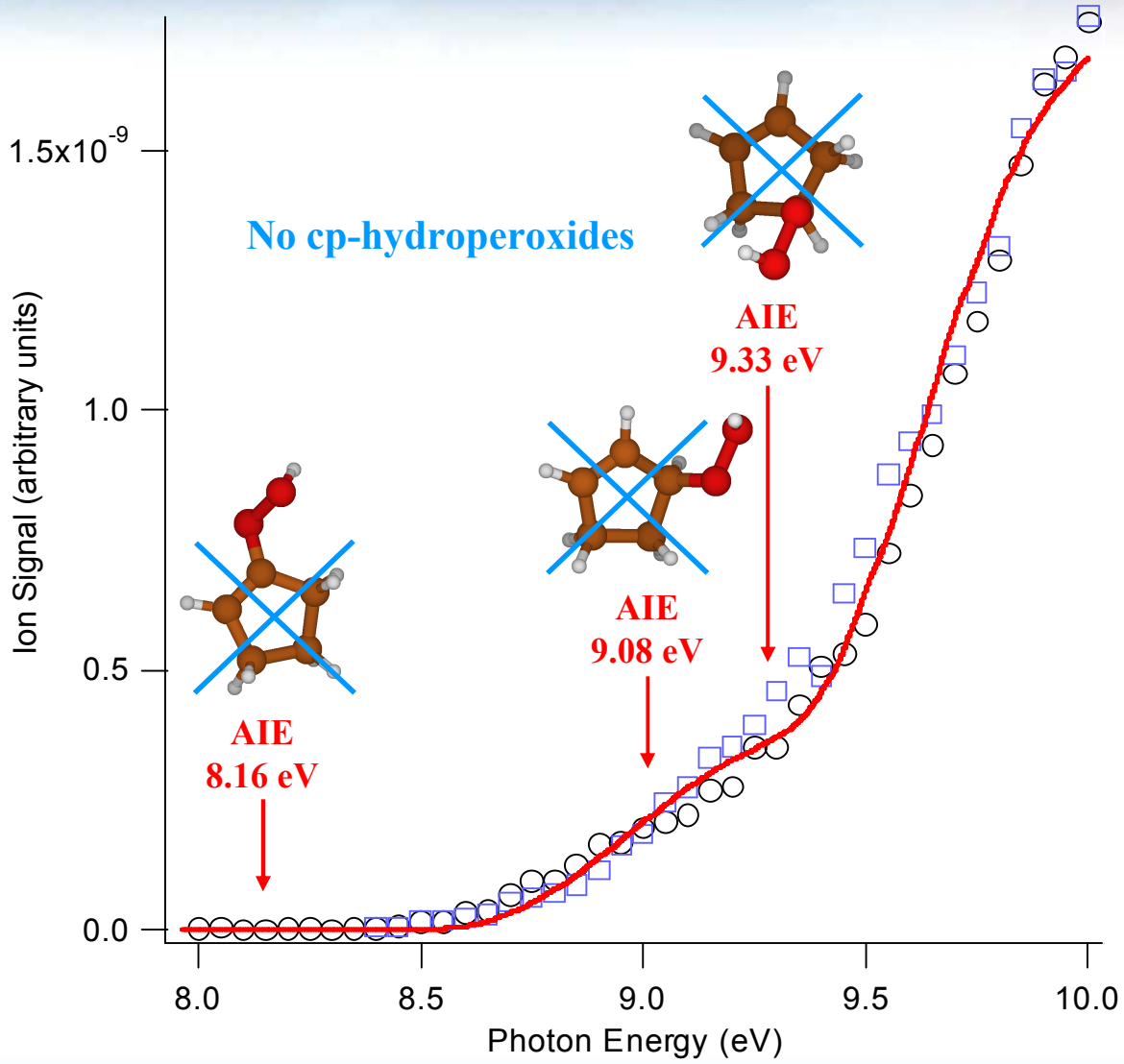
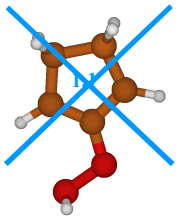
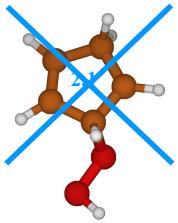
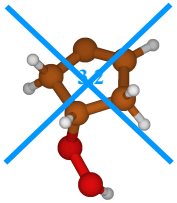
Cyclopentenyl + O_2 reaction

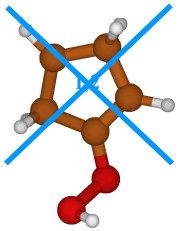


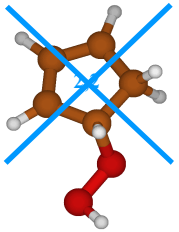
Cyclopentenyl + O_2 reaction

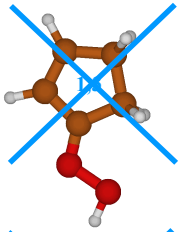

AIE
7.04 eV

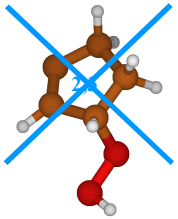

AIE
5.53 eV

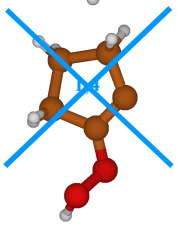

AIE
7.93 eV

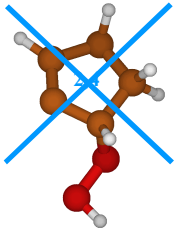

AIE
5.56 eV

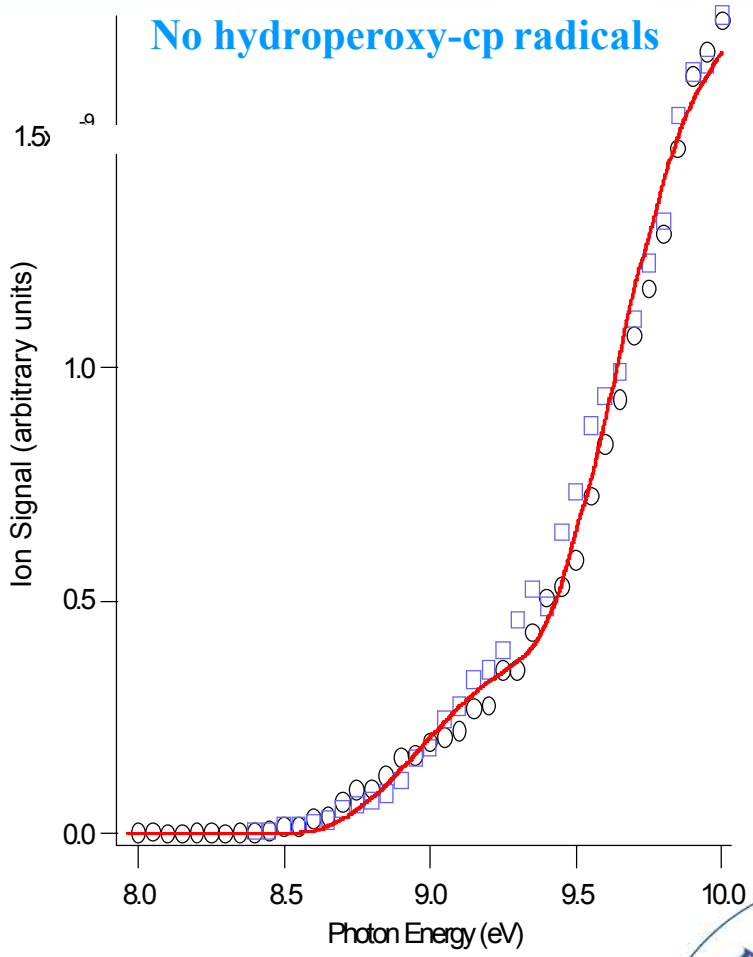

AIE
7.41 eV


AIE
7.57 eV


Diss. Ion.


AIE
7.94 eV


Diss. Ion.



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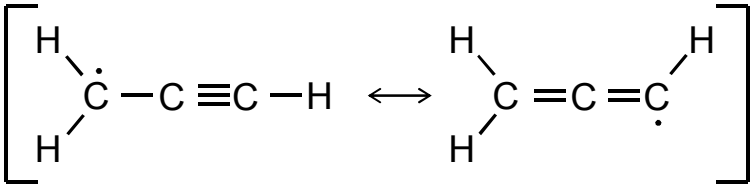
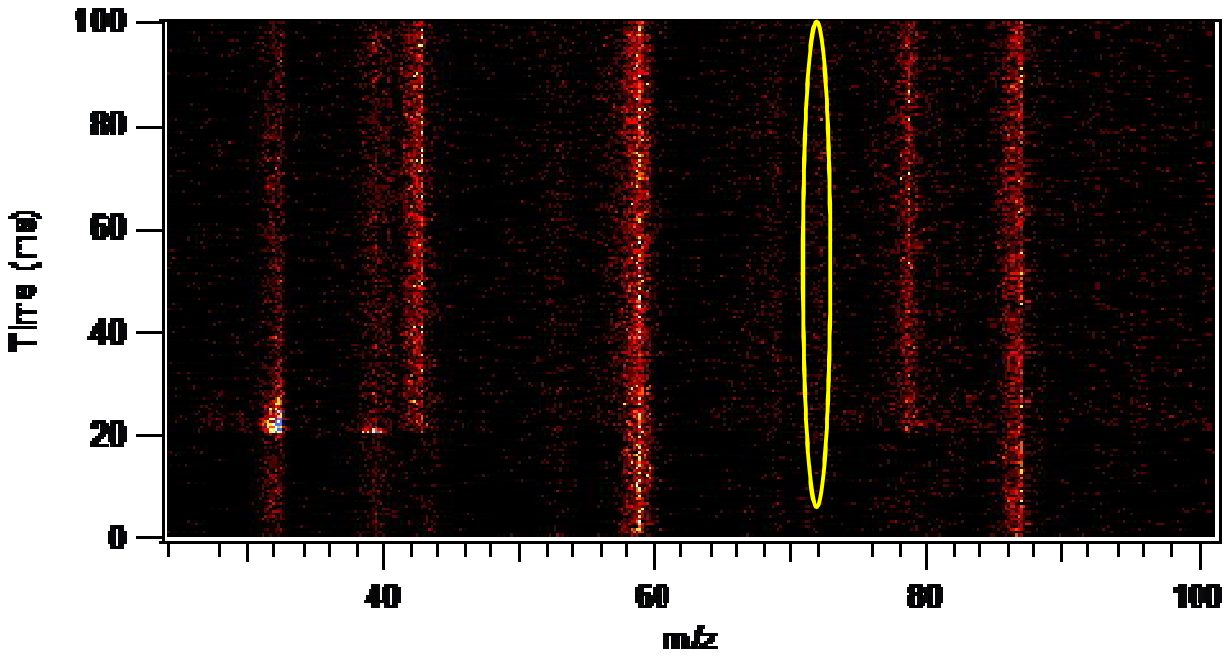
Propargyl + O_2 reaction

$C_3H_3Br \xrightarrow{h\nu}$ propargyl





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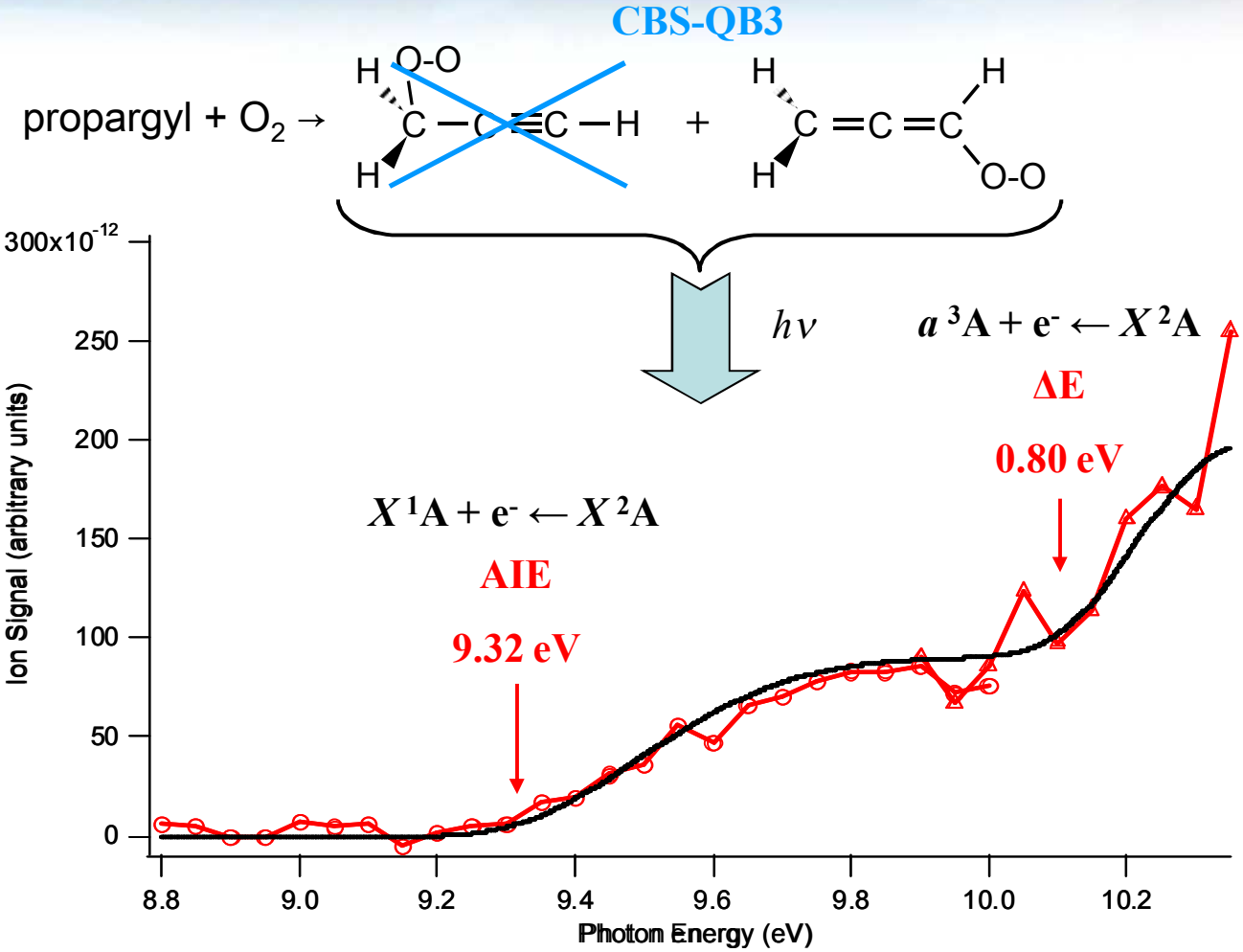
Propargyl + O_2 reaction



$P = 6$ Torr

$T = 298$ K

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Propargyl + O_2 reaction

Thermodynamics

$D_0^o(CH_2=C=CH\text{-}OO) = 81 \pm 6 \text{ kJ mol}^{-1}$

CBS-QB3 $D_0^o(CH_2=C=CH\text{-}OO) = 83 \text{ kJ mol}^{-1}$

$\Delta_f H_0^o(C_3H_3) = 344 \pm 4 \text{ kJ mol}^{-1}$

$$\Delta_f H_0^o(CH_2=C=CHOO) = \Delta_f H_0^o(C_3H_3) - D_0^o(CH_2=C=CH\text{-}OO) = 263 \pm 7 \text{ kJ mol}^{-1}$$

CBS-QB3 $\Delta_f H_0^o(CH_2=C=CHOO) = 261 \text{ kJ mol}^{-1}$

AIE $(CH_2=C=CHOO) = 9.32 \pm 0.05$ eV

CBS-QB3 AIE$(CH_2=C=CHOO) = 9.36$ eV

$$\Delta_f H_0^o(CH_2=C=CHOO^+) = \Delta_f H_0^o(CH_2=C=CHOO) + \text{AIE}(CH_2=C=CHOO) = 1162 \pm 8 \text{ kJ mol}^{-1}$$

CBS-QB3 $\Delta_f H_0^o(CH_2=C=CHOO^+) = 1164 \text{ kJ mol}^{-1}$

$$D_0^o(CH_2=C=CH\text{-}OO^+) = \Delta_f H_0^o(C_3H_3^+) - \Delta_f H_0^o(CH_2=C=CH\text{-}OO^+) = 19 \pm 8 \text{ kJ mol}^{-1}$$

CBS-QB3 $D_0^o(CH_2=C=CH\text{-}OO^+) = 23 \text{ kJ mol}^{-1}$

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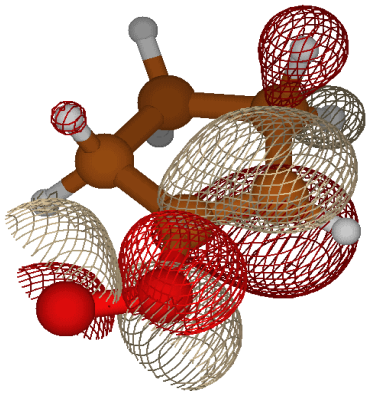
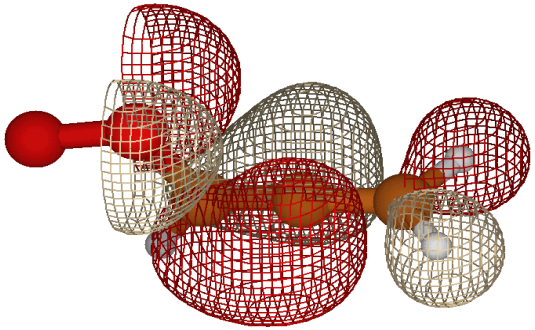
MOs character

- Different ground state multiplicity for 1-alkenylperoxy cations
- Alkylperoxy cations have a triplet ground state → only CH_3OO^+ has a bound ground state
- Alkylperoxy photoionization occurs by removal of an e^- from the doubly occupied σ_{C-O} MO → lowering total energy by further stabilization of the fragment (formation of additional bonds)
- Major difference for 1-alkenylperoxy is the antibonding nature of HOMO

Description of MOs



$\pi^*_{C_\alpha - O}$



Bond distances in angstrom and angles in degrees optimized at the B3LYP/6-311+G** level of theory.

Molecule	$r_{C_\alpha=C_\beta}$	$r_{C_\alpha-O}$	r_{O-O}	$\angle C_\alpha OO$	θ [a]
$X\,^2A$ **CH_2=C=CHOO**	1.31	1.40	1.32	112	180
$X\,^1A$ **CH_2=C=CHOO** $^+$	1.35	1.34	1.25	118	180
$X\,^2A$ **1-*c*-C_5H_7OO**	1.34	1.37	1.33	114	177
$X\,^1A$ **1-*c*-C_5H_7OO** $^+$	1.39	1.32	1.28	117	179

[a] θ is the dihedral angle formed by the $C_\beta = C_\alpha - O - O$ bonds.

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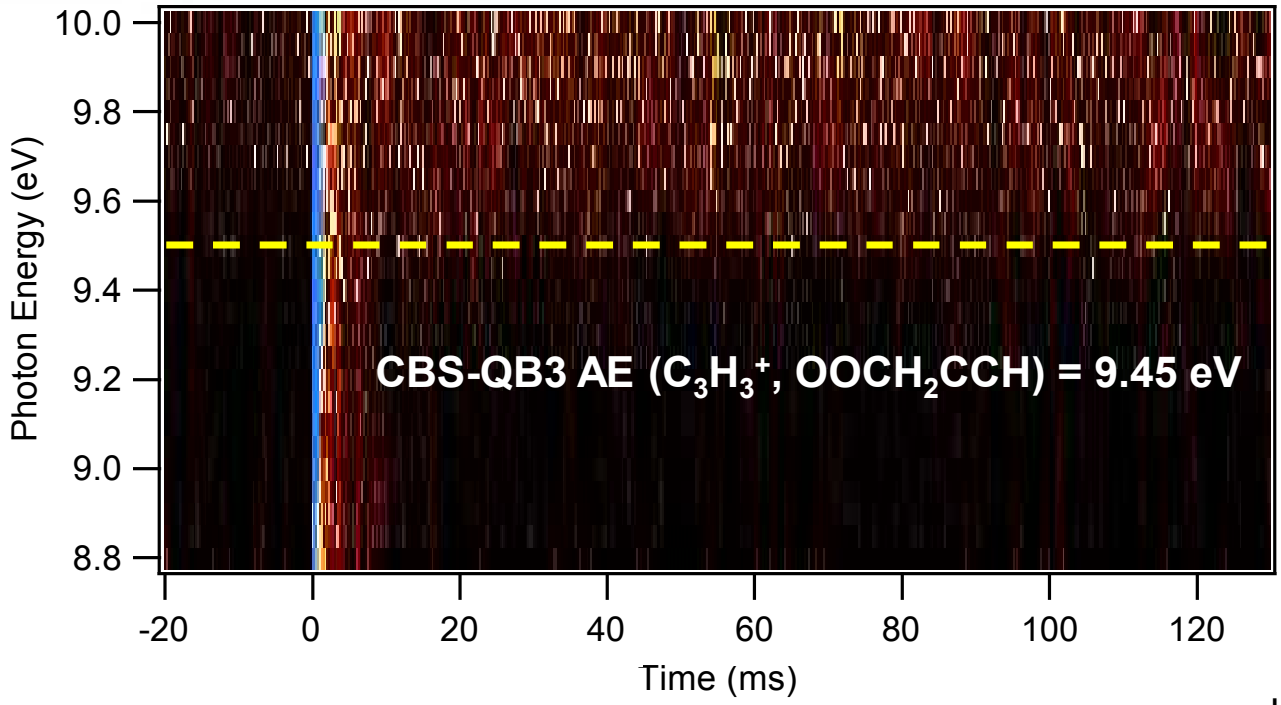
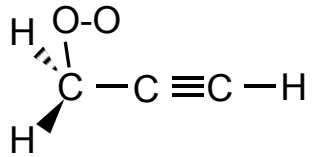
Rule

“Alkylic-type peroxy radicals dissociative ionize, with the exception of methylperoxy, whereas alkenyl-type peroxy radicals have stable singlet ground electronic state cations.”

Appearance of $C_3H_3^+$ fragment



- Dissociative ionization of the alkylic-type propargylperoxy 
- Electron detachment from the $\sigma_{C\text{-}O}$ MO, followed by resonance stabilization

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Acknowledgements

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Chemical Dynamics Beamline 9.0.2

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