



Ketohydroperoxide Formation and Decomposition in Cl-atom Initiated Oxidation of *n*-Butane and Neopentane: Achievements and Challenges

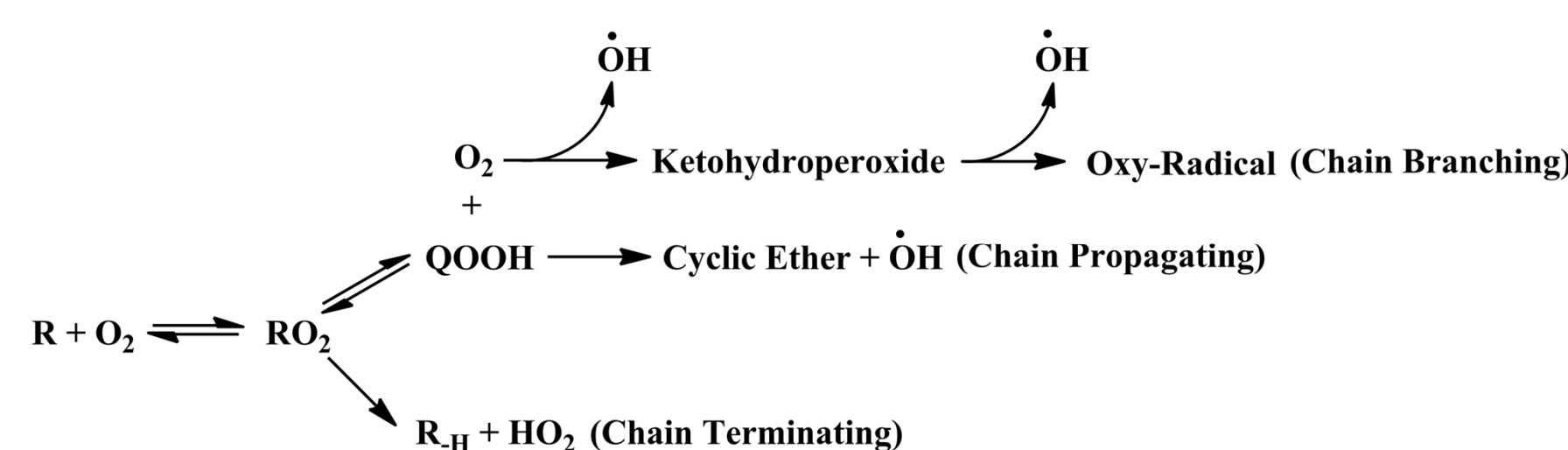
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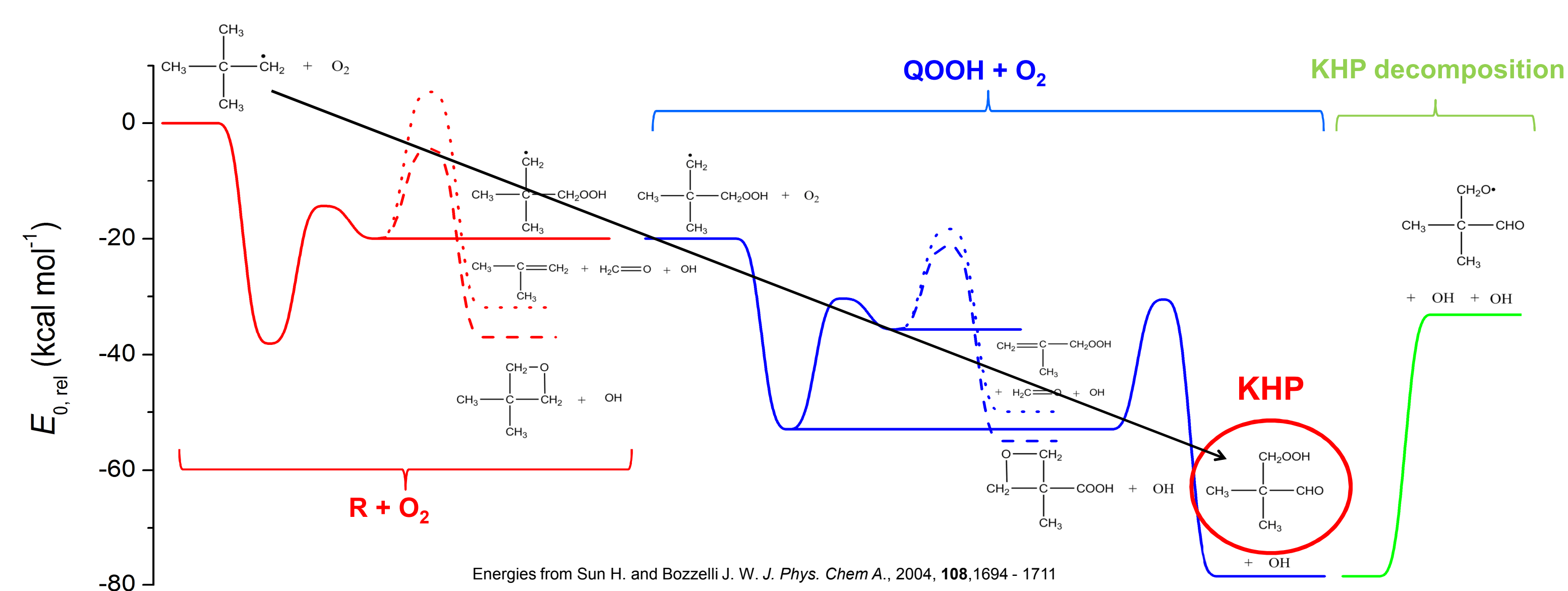
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Introduction

- Autoignition chemistry plays crucial role in the development of modern, high-efficiency, low-emission engine technologies.
- Oxidation of fuel radicals R and especially reaction channels which lead to chain-branching are essential for autoignition and ketohydroperoxides (KHP's) are a marker of this chemistry.

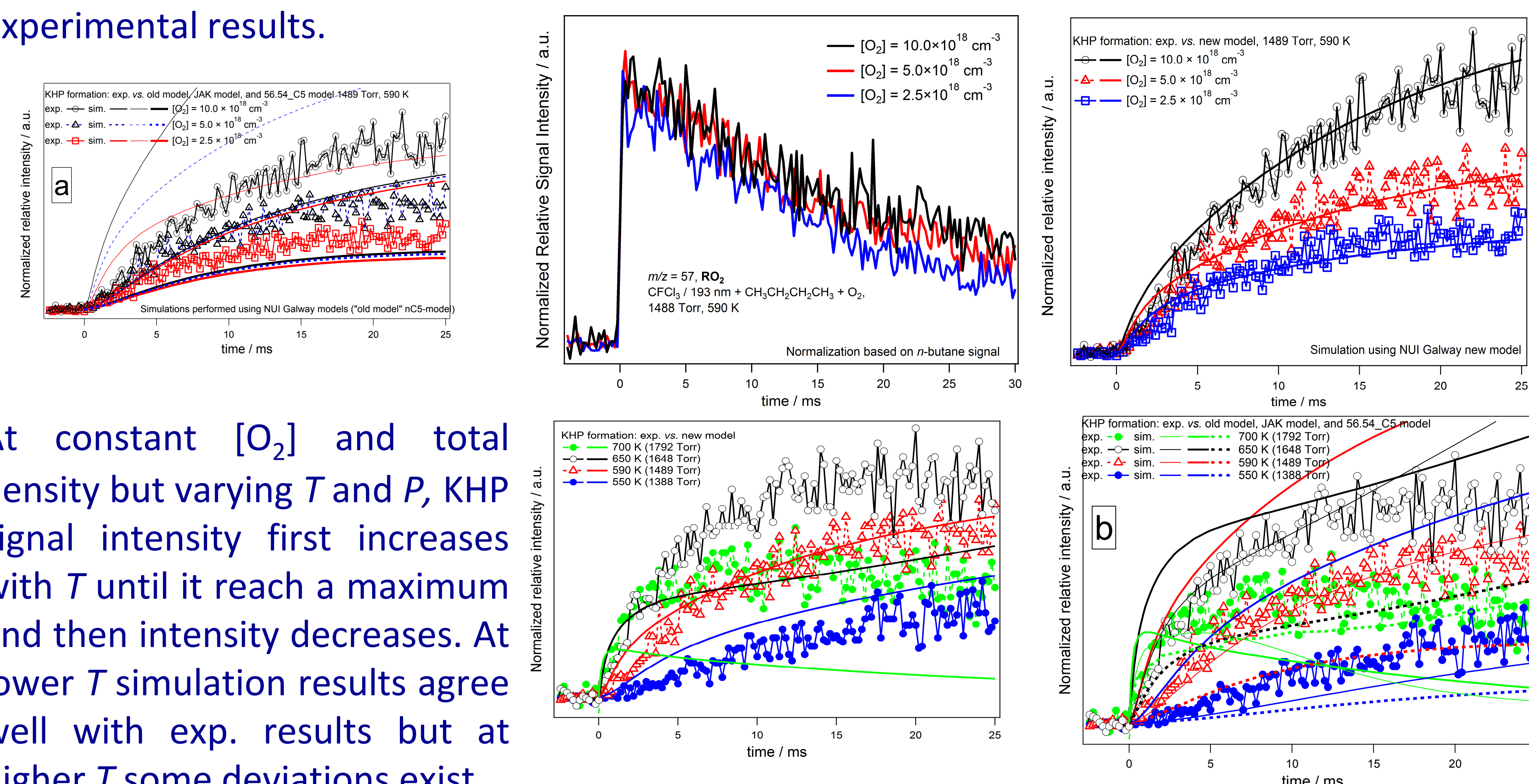


- Fuel radicals of the current work are different: neopentyl radical has no β -hydrogens and alkene + HO_2 channel is absent while 1-butyl + O_2 and 2-butyl + O_2 radicals constitute a smallest system with low-temperature behavior of larger hydrocarbons. R + O_2 and QOOH + O_2 potential energy surfaces where R = neopentyl radical, clearly demonstrate that KHP formation is a “down-hill” process along lowest energy path.



Results

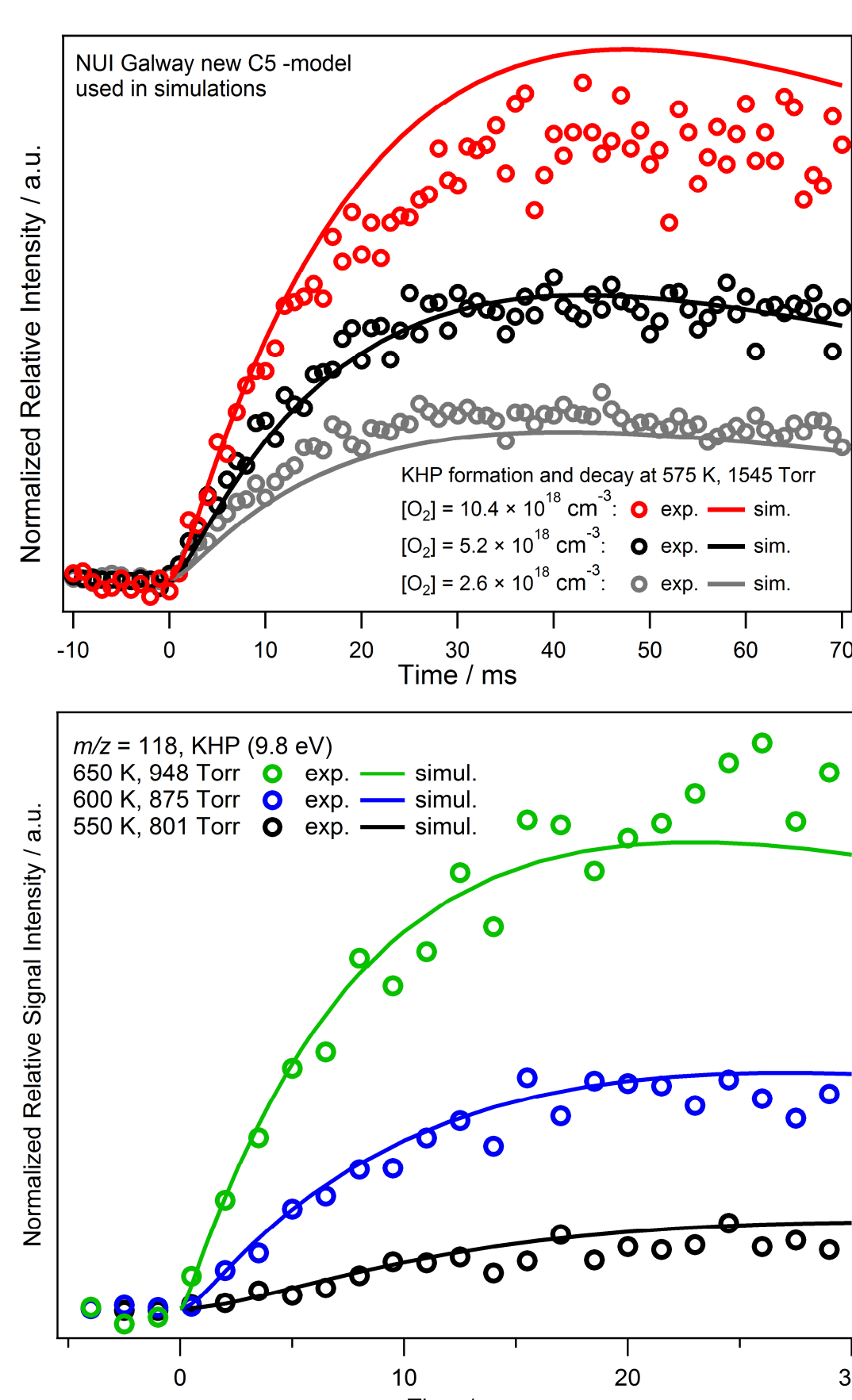
- In *n*-butane oxidation, ketohydroperoxides ($\text{C}_4\text{H}_8\text{O}_3$) are formed at $m/z = 104$ in $\text{Cl} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{O}_2$ system. At constant T , P but varying $[\text{O}_2]$, RO_2 signal intensity and decay rate are unchanged whereas intensity of KHP signal at $m/z = 104$ clearly increases with $[\text{O}_2]$ but the time-behavior remains the same. NUI Galway new model agree well with experimental results.



At constant $[\text{O}_2]$ and total density but varying T and P , KHP signal intensity first increases with T until it reach a maximum and then intensity decreases. At lower T simulation results agree well with exp. results but at higher T some deviations exist.

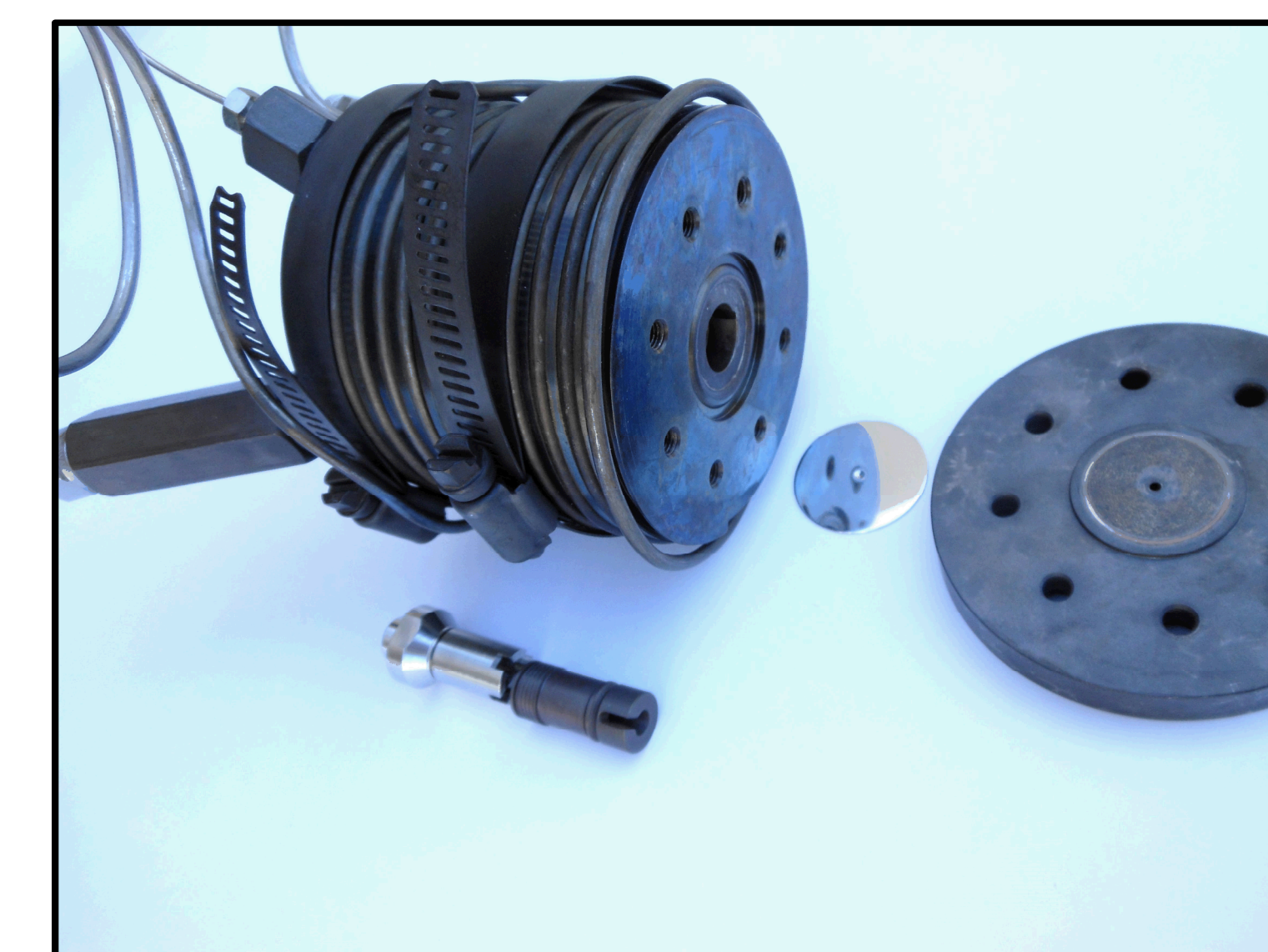
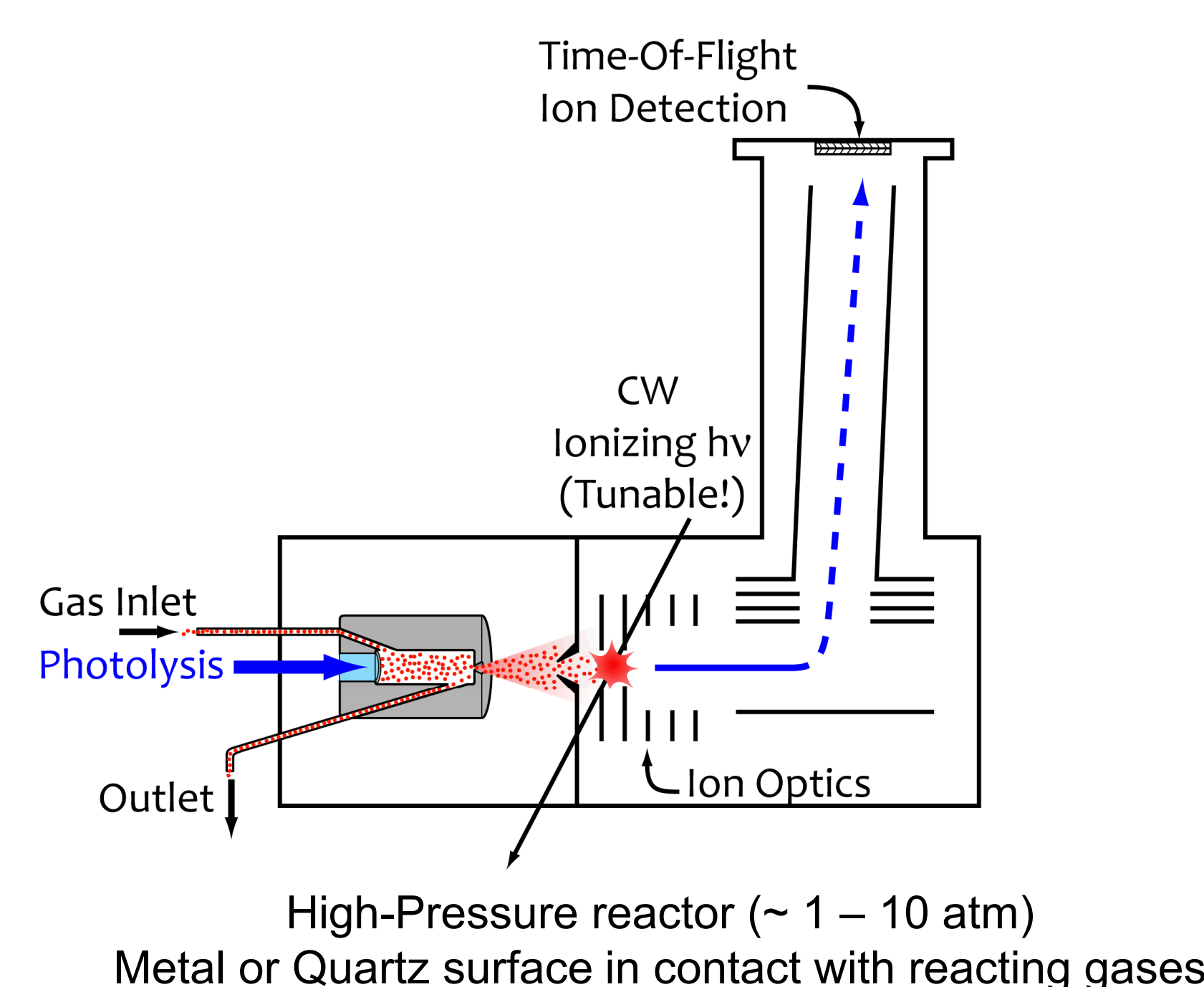
- In neopentane oxidation, ketohydroperoxide ($\text{C}_5\text{H}_{10}\text{O}_3$) is formed at $m/z = 118$ in $\text{Cl} + (\text{CH}_3)_4\text{C} + \text{O}_2$ system. Similar to above, experiments performed at constant T , P but varying $[\text{O}_2]$, RO_2 signal intensity and decay rate are unchanged whereas intensity of KHP signal at $m/z = 118$ clearly increases with $[\text{O}_2]$ but the time-behavior remains the same. NUI Galway new model agree well with exp. results.

In experiments performed at constant $[\text{O}_2]$ and total density while varying T and P , the KHP signal intensity rapidly increases with T . Simulation results agree well with exp. results.



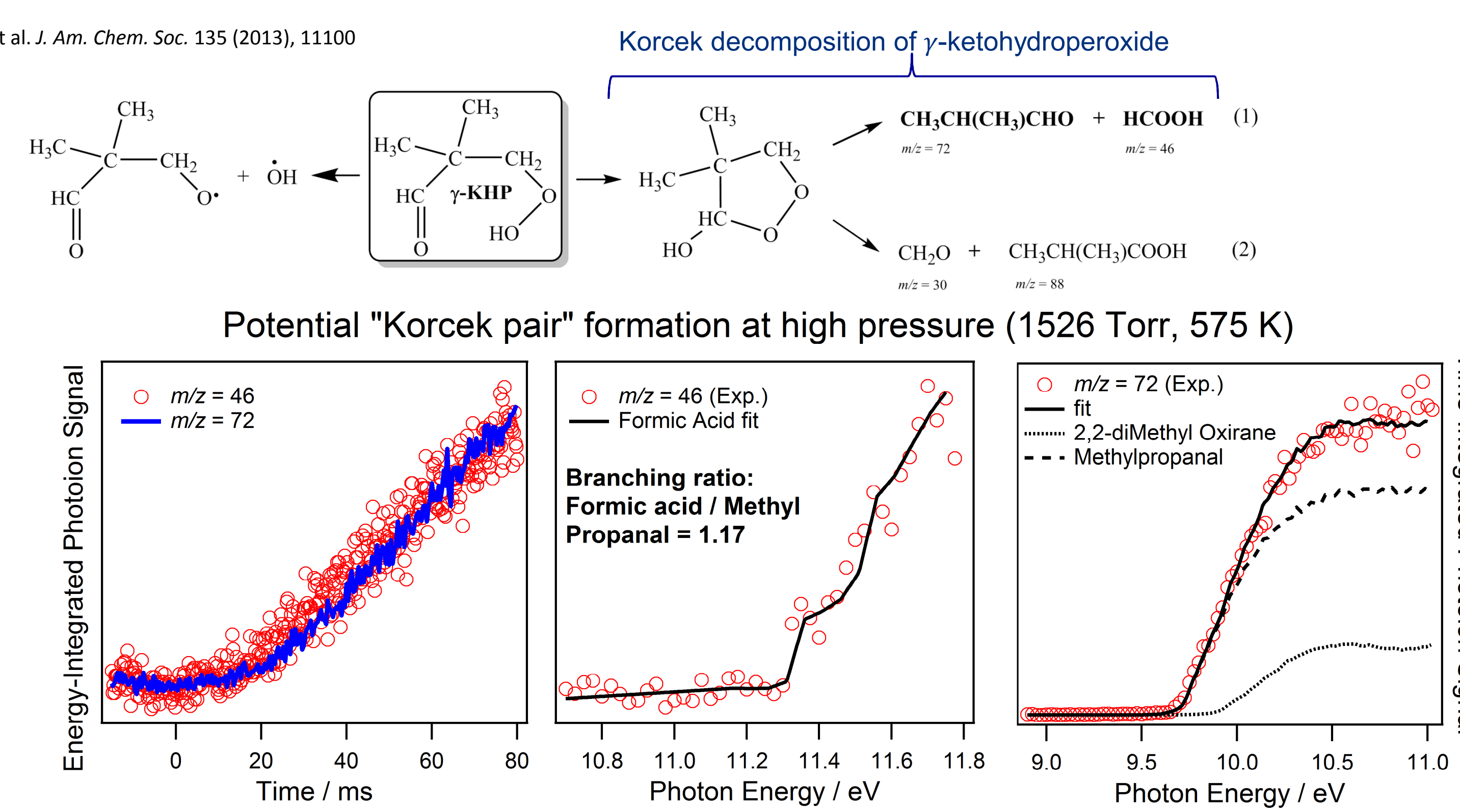
Experimental: Laser photolysis – flow reactor coupled to a TOF-MS with synchrotron photoionization

- We study Cl-atom initiated oxidation chemistry of neopentane and *n*-butane using a High-Pressure (HP) reactor under 500 – 700 K and 1 – 7 atm conditions.
- Radical chemistry is initiated by excimer laser photolysis at 193 nm/ CFCl_3 or 248 nm/ $(\text{COCl})_2$.
- HP Inconel reactor is sampled through small hole at the end-plate of the reactor (*i.e.* parallel with the laser beam axis). A beam formed into a vacuum is intersected by ionizing VUV synchrotron light and ions formed are separated using orthogonal-acceleration time-of-flight mass spectrometer. Full mass-spectra are taken at 20 μs intervals, providing simultaneous detection of all masses with high sensitivity due to single-ion counting.



- KHP decomposition *via* suggested Korcek decomposition of γ -ketohydroperoxide* mechanism leads to aldehyde + acid products, not to reactive OH + oxy-radicals that are needed for chain-branching. In case of neopentane, lowest energy Korcek decomposition products are formic acid and methylpropanal, which are both observed in this work.

* Jalan et al. J. Am. Chem. Soc. 135 (2013), 11100



Discussion: Achievements thus far and Current & Future Challenges

- Very recently we have performed the first direct time-resolved experiments where KHP formation is unambiguously observed. KHP formation has been measured as a function of temperature, pressure, and $[\text{O}_2]$ to better understand kinetics and mechanism of KHP formation and also to compare with and test models developed to simulate autoignition. In case of *n*-butane oxidation, it is even possible to determine a single isomer of KHP that is formed. We are also able to observe KHP decomposition and detect products of Korcek decomposition reaction.
- Still current and future challenges exist. Probably the most significant challenge is lack of absolute photoionization cross section of any KHP, effectively preventing to determine KHP product yields and branching ratios. KHPs also seem to be decomposed efficiently on heated quartz or metal walls, resulting in difficulties to experimentally determine *gas-phase* decomposition products of KHPs. Depending on a system, several KHP isomers are possible which might be difficult to separate experimentally.