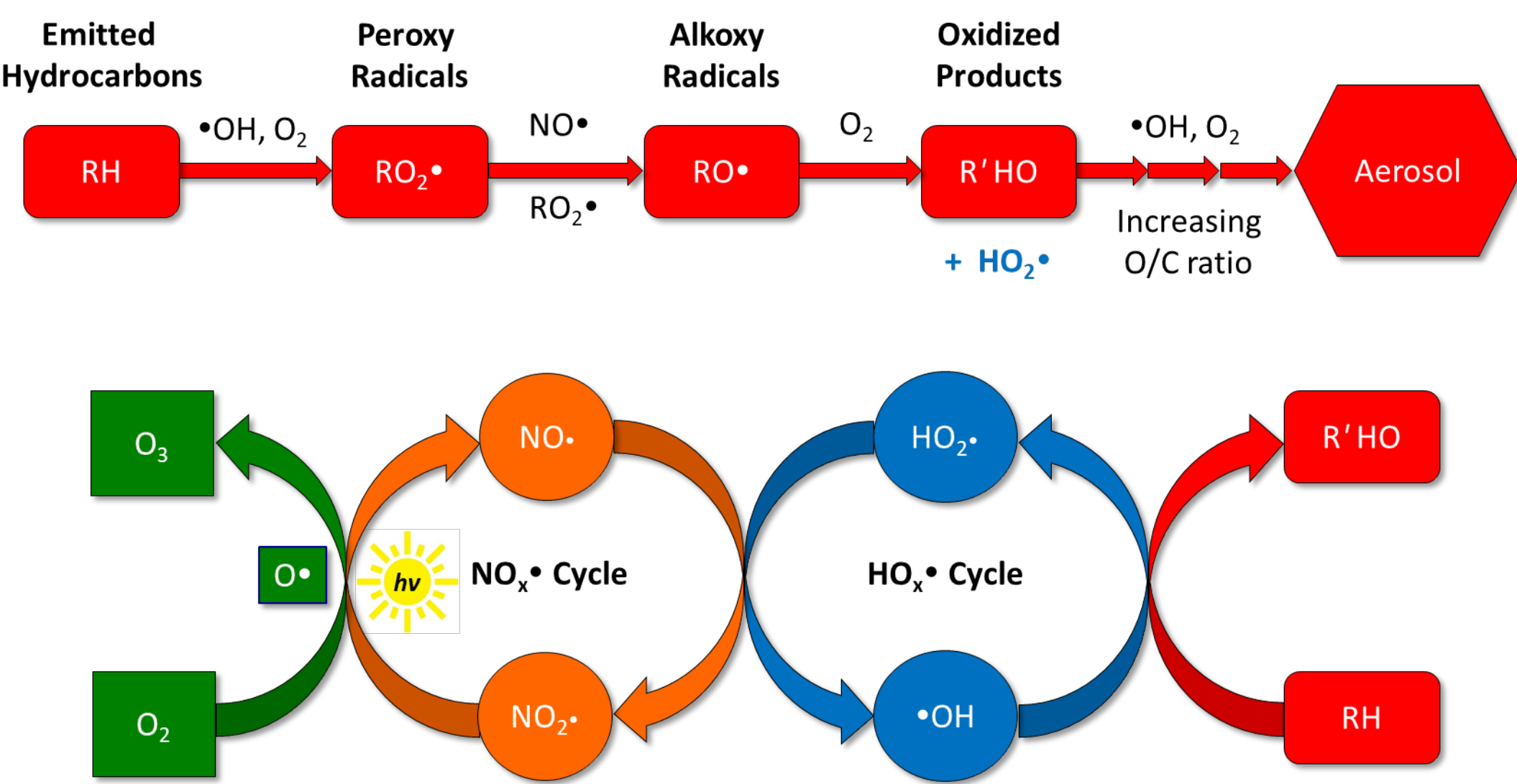


# Kinetics and Spectroscopy via Multiplexed Photoionization Mass Spectrometry

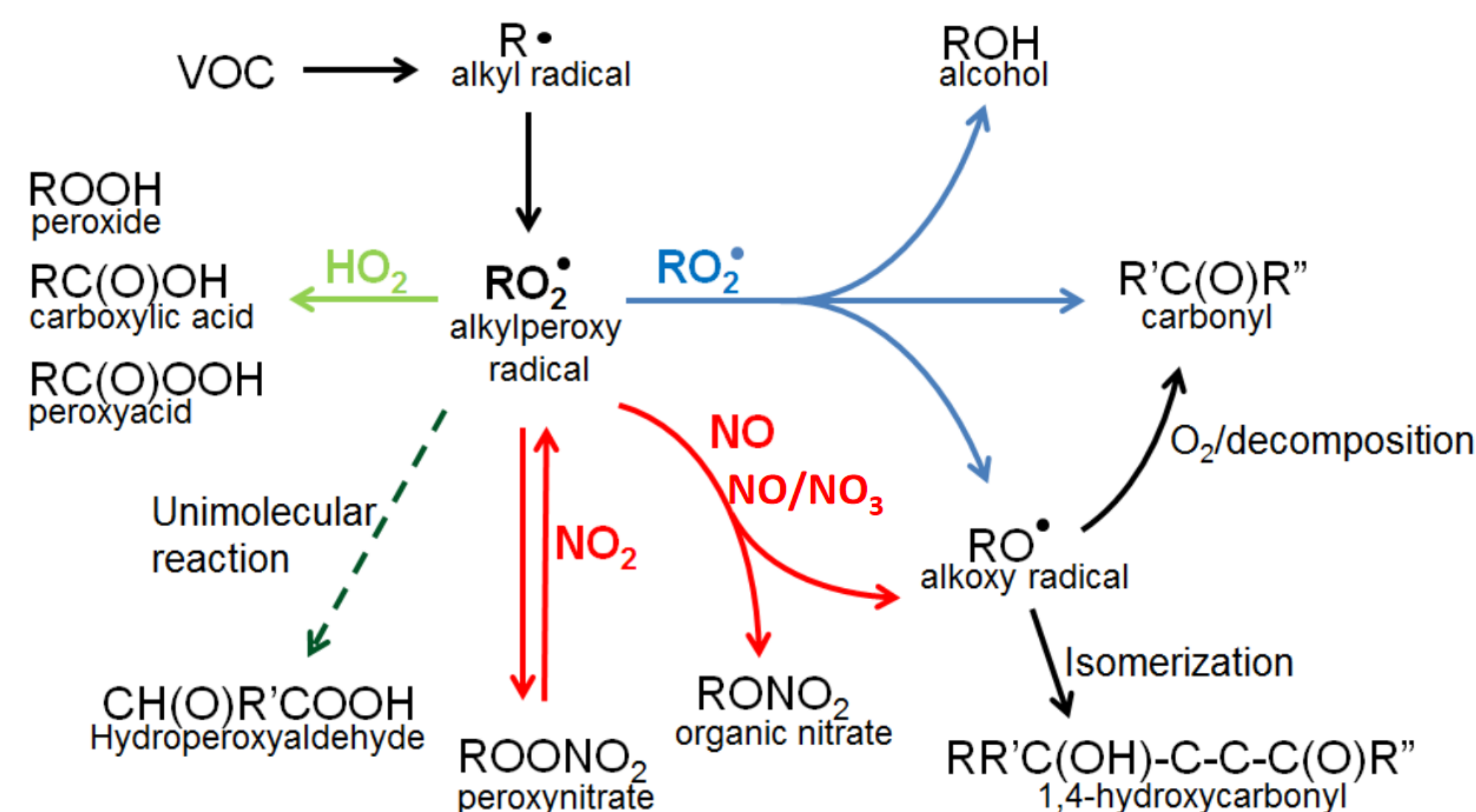
## Okumura Group

### Chemistry of Air Pollution

- Organic peroxy radicals play a central role in the chemistry of the atmosphere.
- Chain reactions of these radicals form a variety of highly oxygenated moieties, which condense to form aerosols, with significant impact on human health and climate
- Reactions with NO and HO<sub>2</sub> drive photochemical production of ozone in troposphere, a main component of urban smog

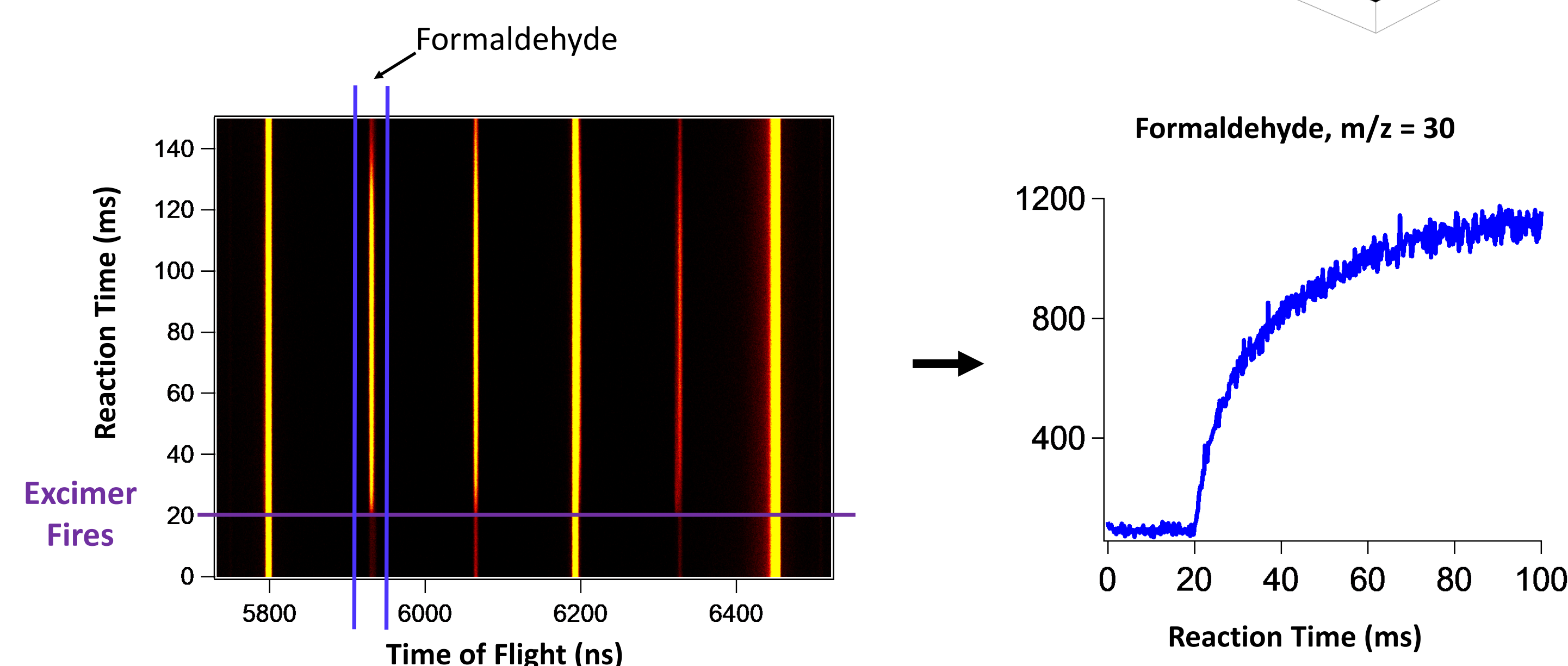
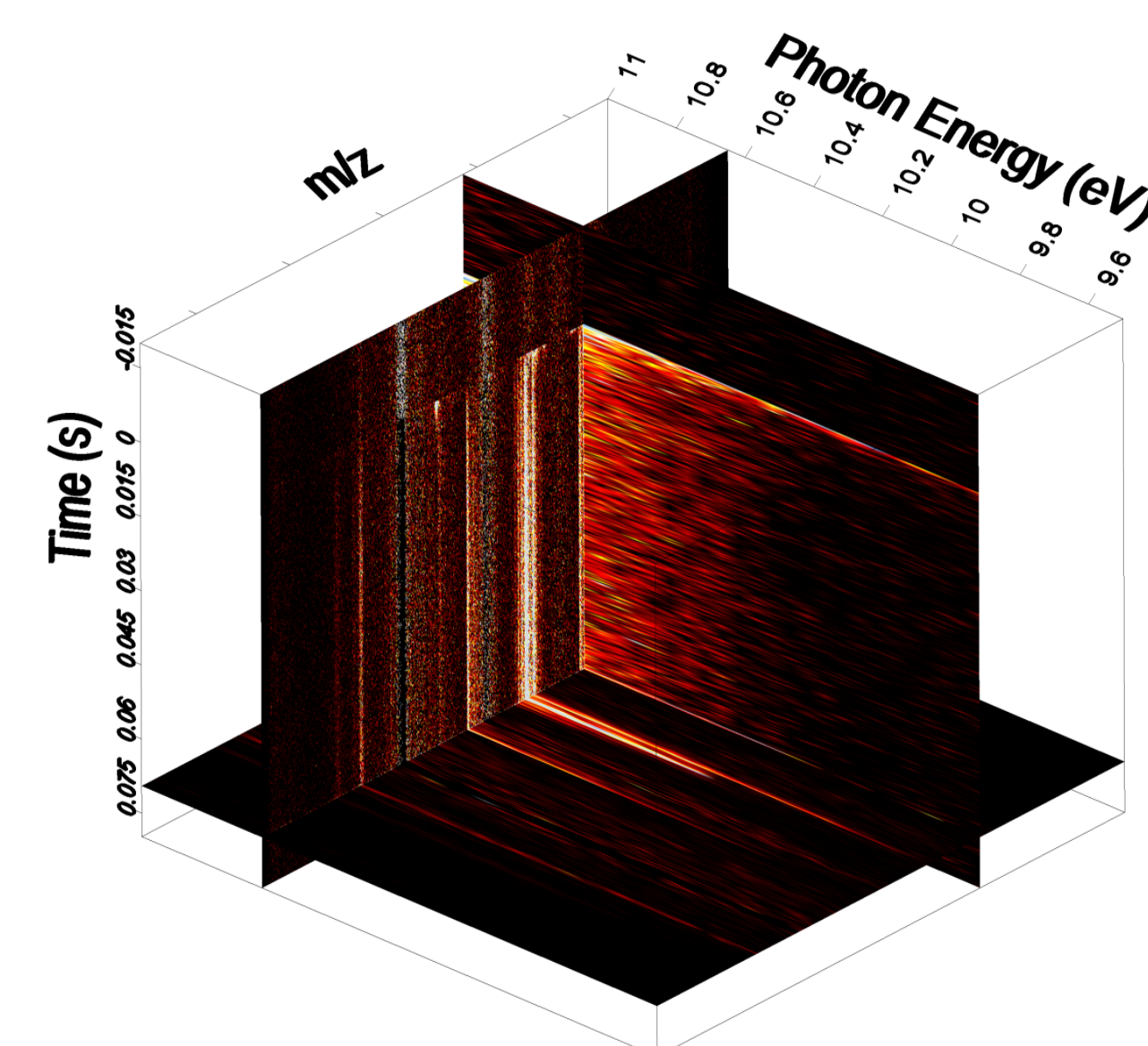


Complex interrelationships make isolating individual reactions difficult



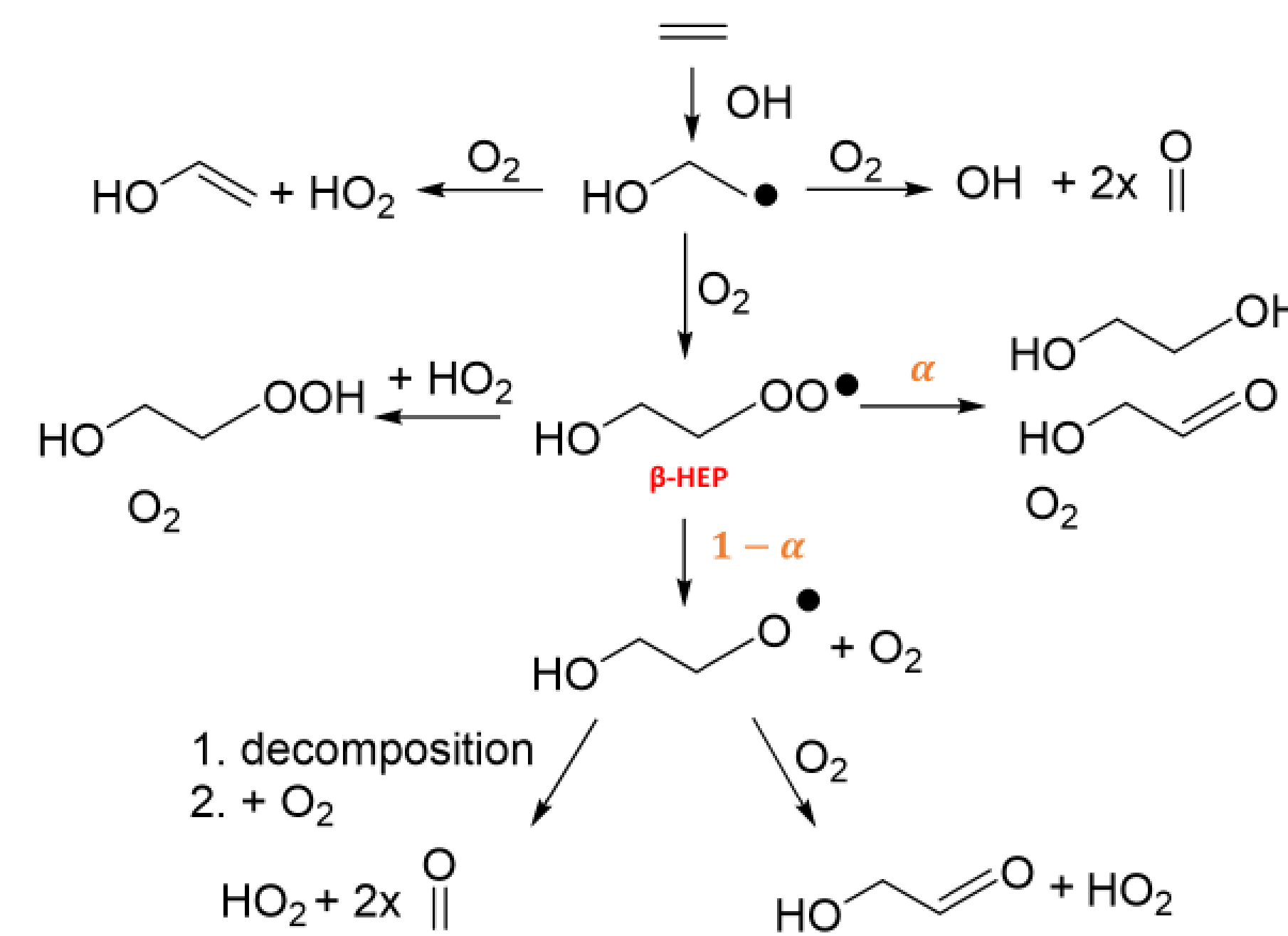
Our approach: multiplexed photoionization mass spectrometry

- Collect full mass spectrum every 20  $\mu$ s over the course of 0 – 150 ms, giving kinetics as a function of mass
- Tunable photon energy from synchrotron at Lawrence Berkeley Labs yields selective ionization of same-mass species

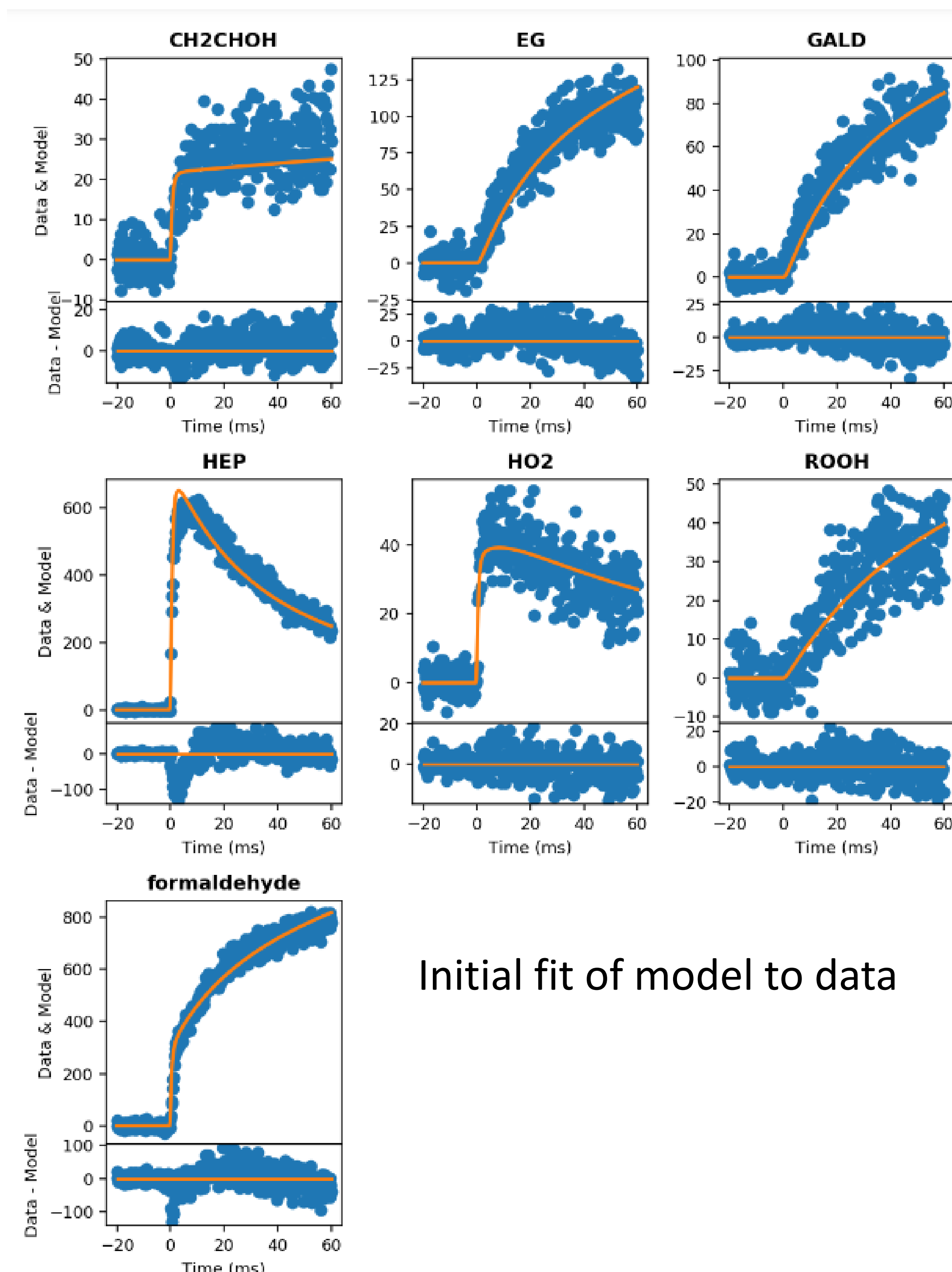


### Peroxy Radical Kinetics

- $\beta$ -HEP serves as a model system for OH-initiated oxidation of alkenes
- It was reported that its self reaction was enhanced in the presence of water through a H-bonded complex
- Only disappearance of  $\beta$ -HEP observed; effects on branching fraction  $\alpha$  unknown



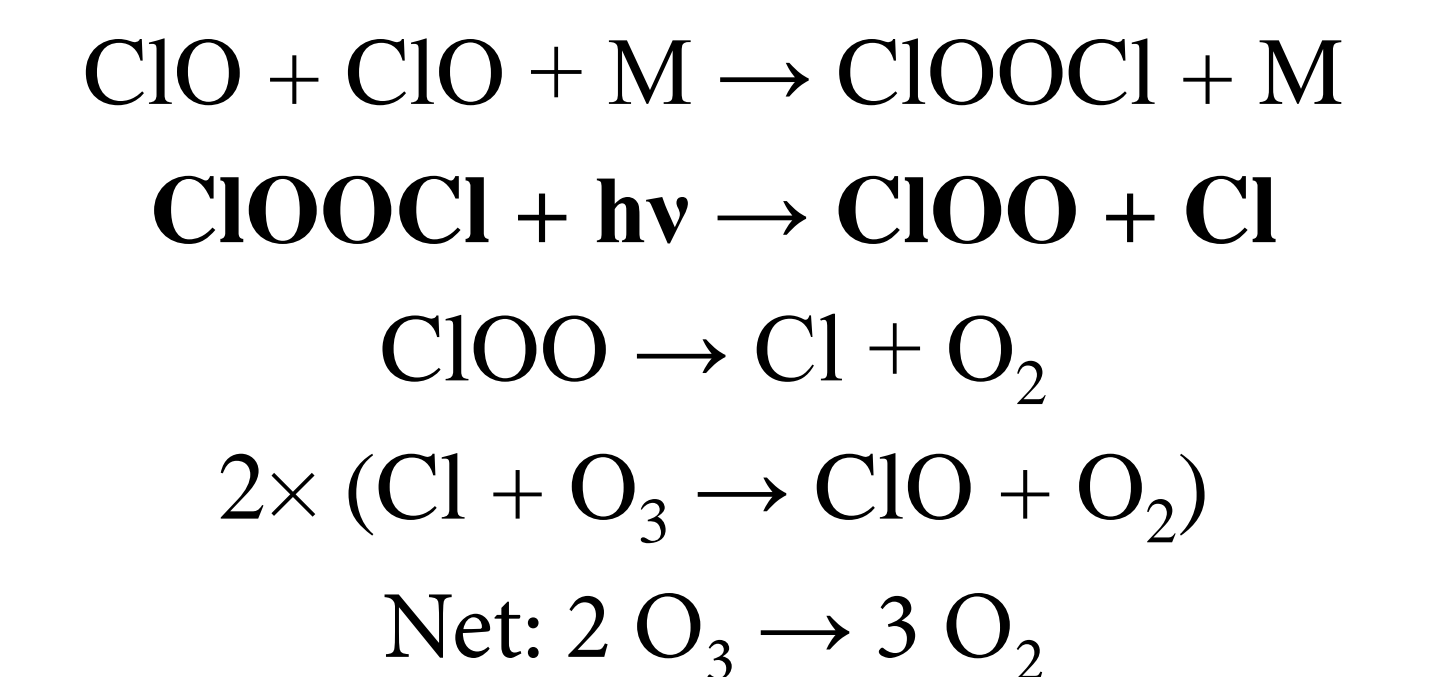
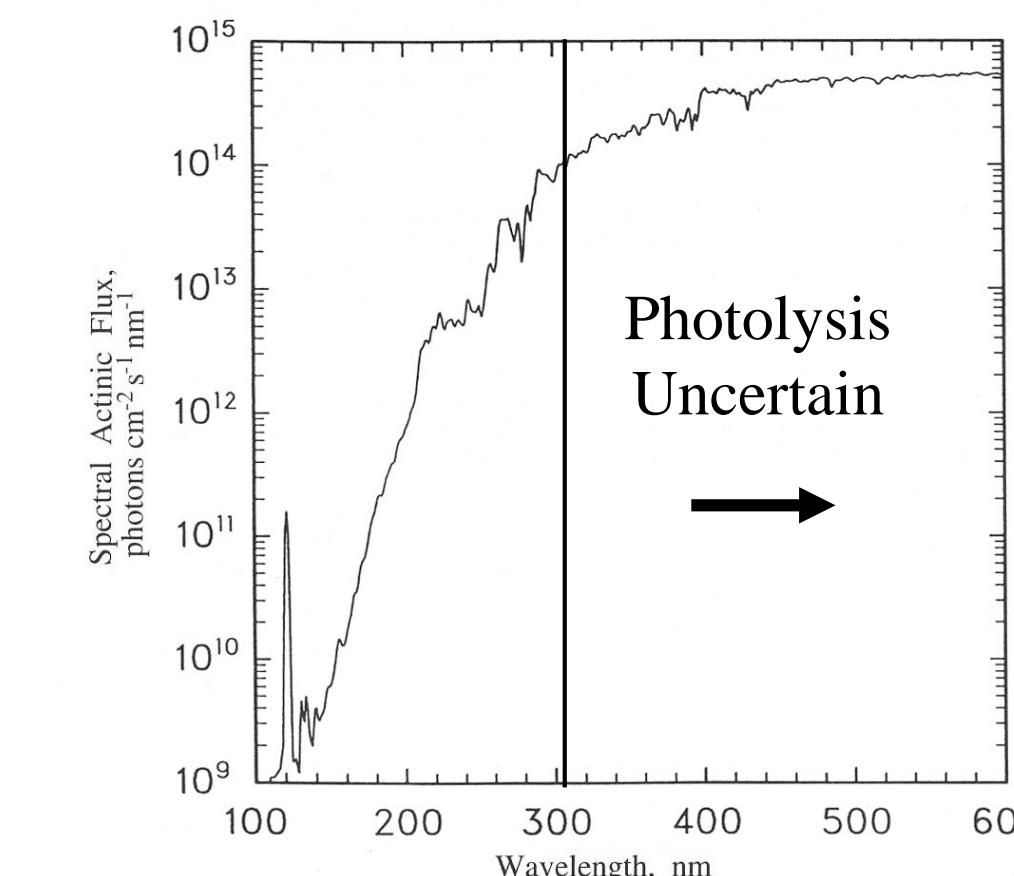
- Using MPIMS, we can observe all species except HOCH<sub>2</sub>CH<sub>2</sub>· and HOCH<sub>2</sub>CH<sub>2</sub>O·
- By varying water concentrations and fitting to a kinetic model, branching fractions can be determined



Initial fit of model to data

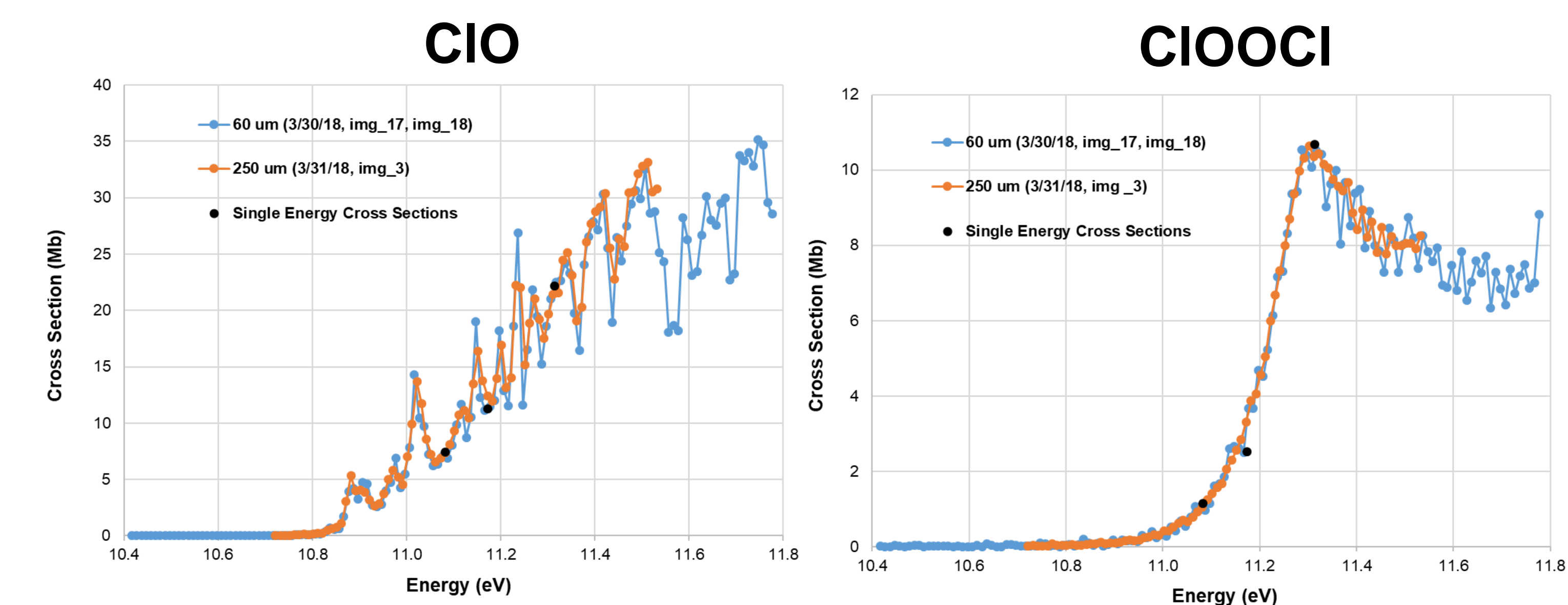
### Ozone Depletion Chemistry

- ClO<sub>x</sub> chemistry important in the stratosphere, especially in ozone destruction
- Photolysis products never measured for  $\lambda > 308$  nm



**Strategy:** produce ClOOC1 from ClO + ClO and measure depletion/products of ClOOC1 photolysis longwave of 308 nm

- Currently measuring photoionization cross section of ClO, ClOOC1 to put concentrations on absolute scale
- Photoionization spectrum of ClO shows structure from Rydberg autoionization resonances  $\rightarrow$  fundamental chemical physics



### Future Work

- Photolysis cross section of ClOOC1
- Photoproduct branching ratios for ClOOC1 photolysis
- Construction of photoionization mass spectrometer at Caltech using high-harmonic generation of an ultrafast laser

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