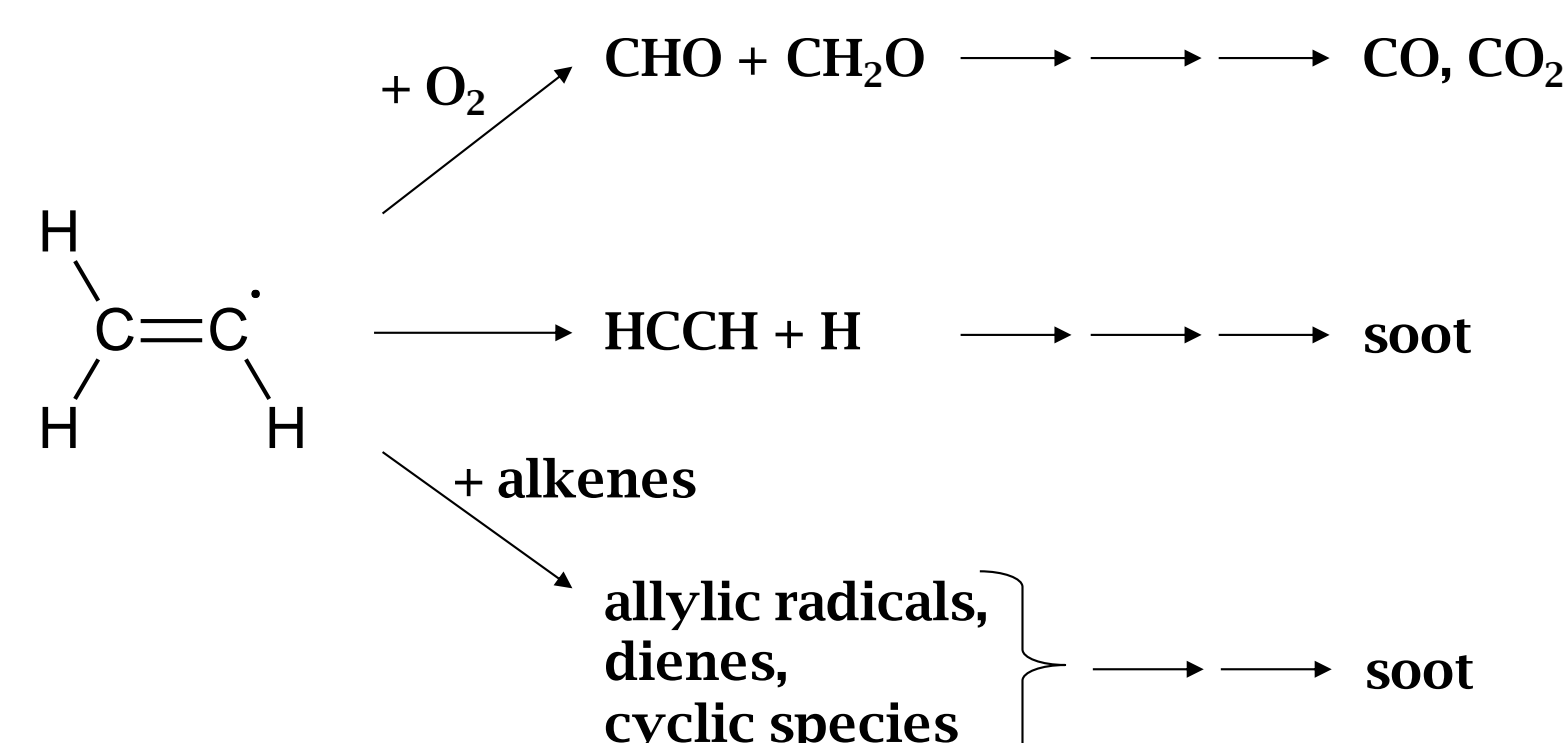


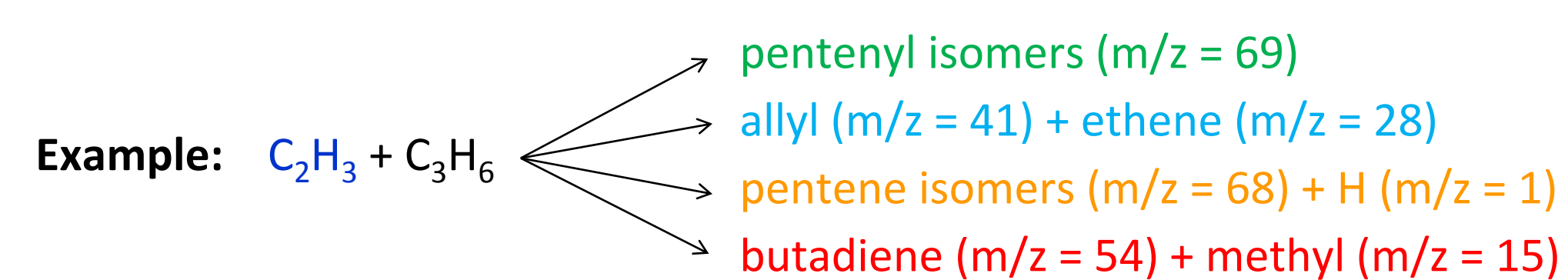
Vinyl + Propene Reaction: Measuring the Product Distribution

Chemical Kinetics of Interest

The reactions of vinylic and allylic radicals are important in combustion and pyrolysis systems. In particular, the reactions of vinyl radicals with various alkenes and the reactions of vinyl and allyl radicals with themselves are thought to be important in carbon-growth processes and soot formation.

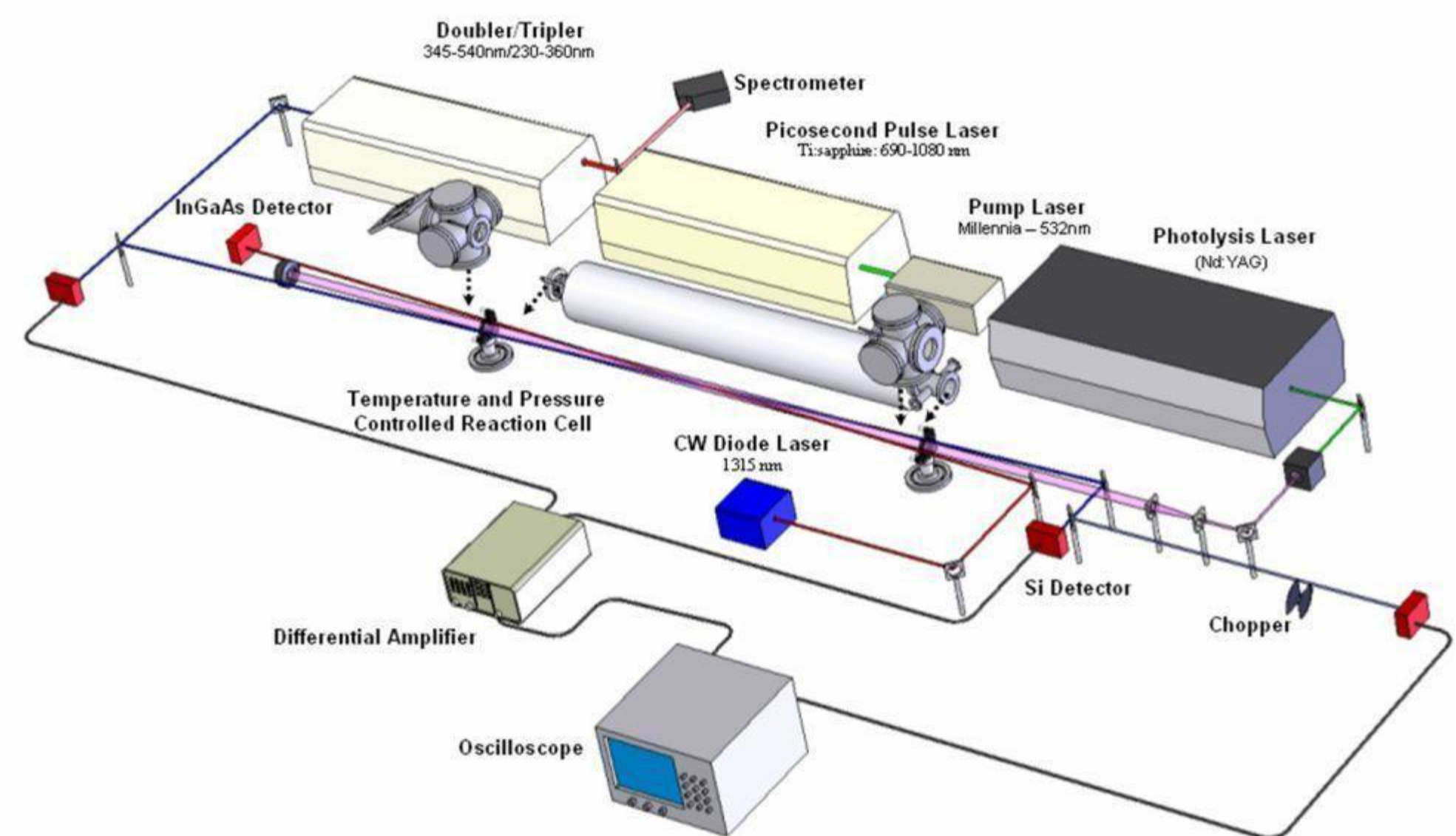


Vinyl + propene reaction unique in that allyl radicals in allyl + ethene product channel can be seen using laser absorption technique.

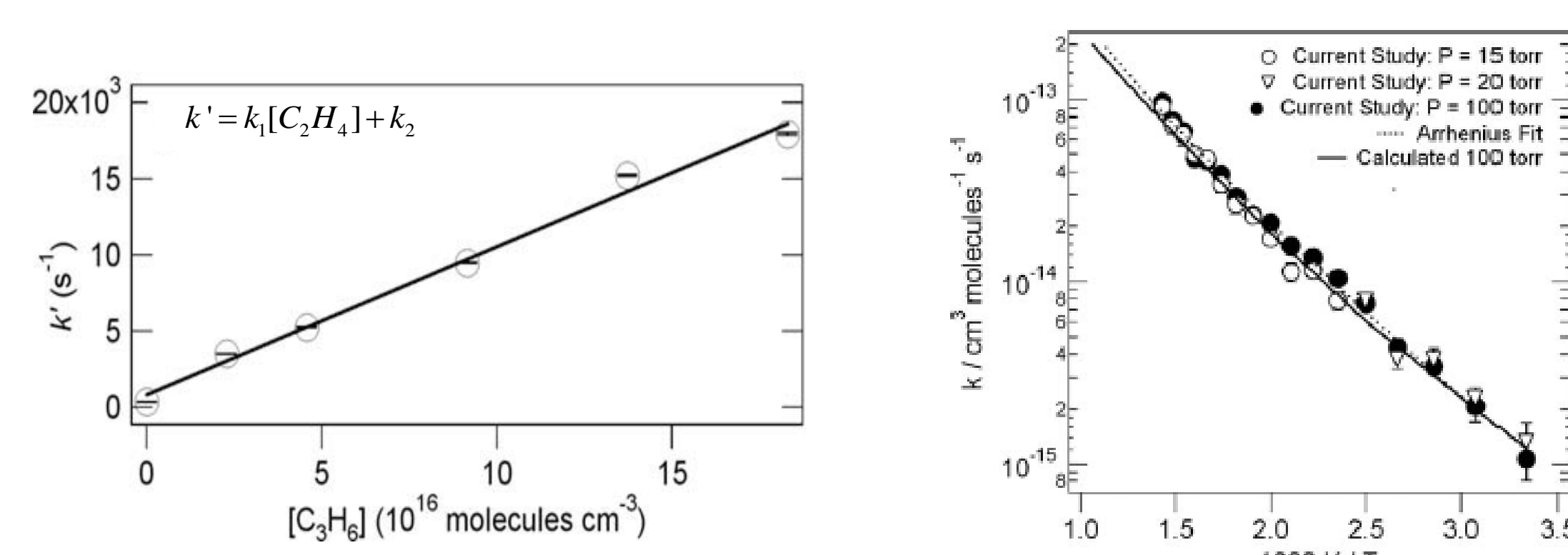


Laser Absorption Spectrometry

- LAS gives high resolution overall reaction rate by measuring the reactant concentration
- Sometimes a particular product, and thus its branching ratio, can be measure



The gas inside the reaction cell is photolyzed by the fourth harmonic (266 nm) output of a Nd:YAG photolysis laser and the transient concentration of the resulting radicals is measured via absorption spectrometry using the frequency doubled/tripled output of a Ti:sapphire laser. The experiments are typically performed under pseudo-first order conditions (i.e. a large excess of the alkene).



Plotting the pseudo-first order rate constant (k') versus the propene concentration gives the reaction rate of interest (k_1) as the slope of the resulting line (left). The overall reaction rate measured and calculated at several pressures agree to within experimental uncertainty (right).

Ismail, H.; Goldsmith, C. F.; *et al.* *J. Phys. Chem. A* **111**, 6843-6851 (2007).

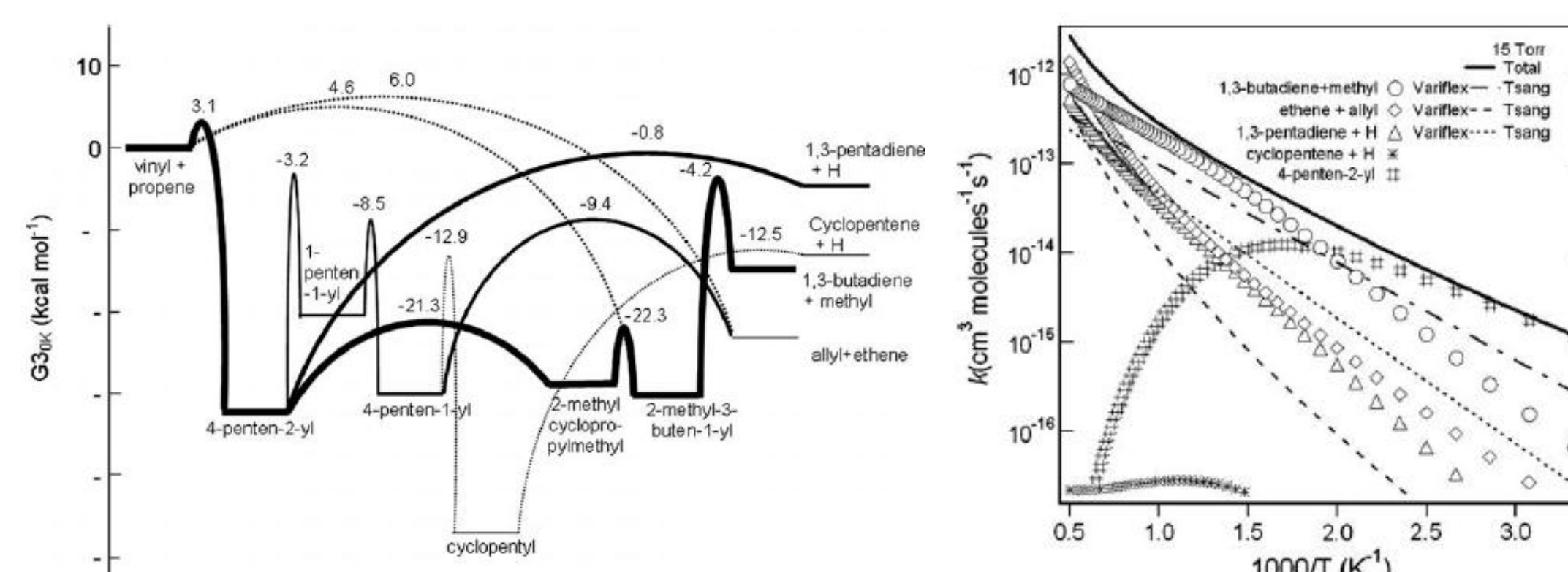
Goldsmith, C. F.; Ismail, H.; *et al.* *Proc. Combust. Inst.* **32**, 139-148 (2009).

Acknowledgements

We are grateful to the U.S. Dept. of Energy, the U.S. Dept. of Defense, the U.S. National Science Foundation for funding the laser absorption work, and we thank the King Abdullah University of Science and Technology (KAUST) and the Combustion Energy Frontier Research Center (CEFR) for funding the PI TOF-MS project. Thanks also to the R.W. Field group and MIT's Harrison Spectroscopy Laboratory for equipment and other assistance.

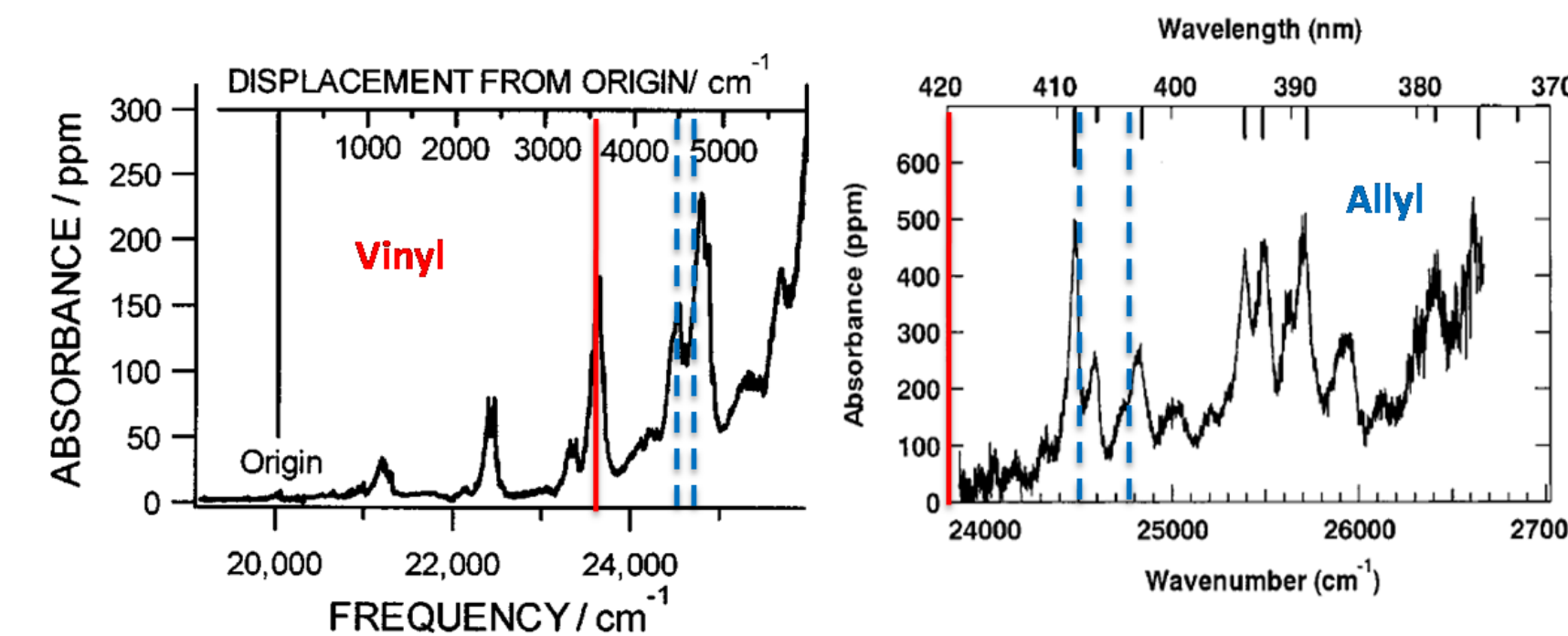
Theoretical and Experimental Product Branching Ratios

- Product branching determined by C.F. Goldsmith *et al* using temperature and pressure dependent RRKM/ME simulations

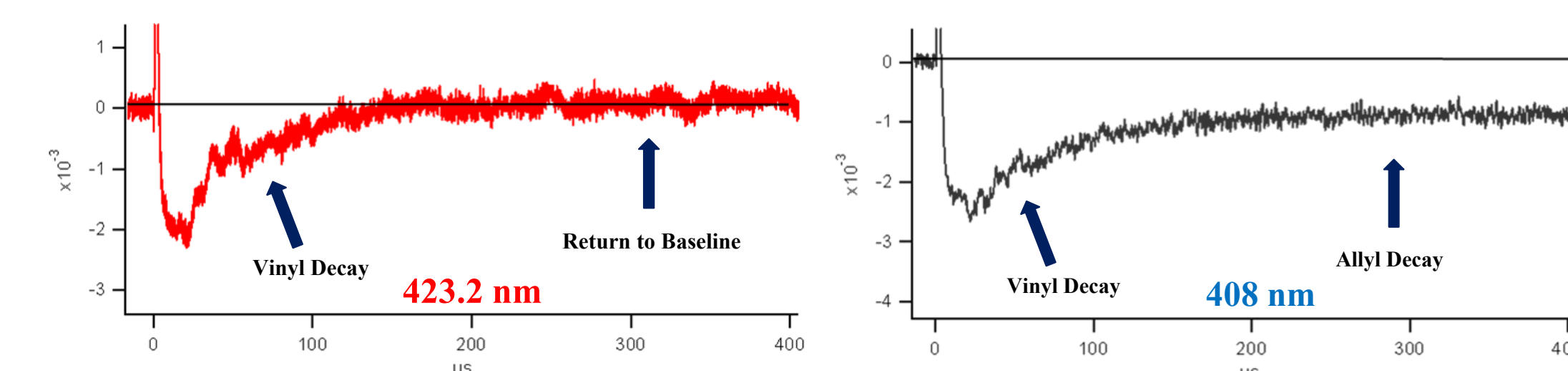


Potential energy surface (PES) generated by G3 compound method (left). Pressure dependent reaction network for all product channels (right).

- Allyl + ethene product branching determined using LAS technique and de-convoluting the contributions to the abs. signal from vinyl and allyl



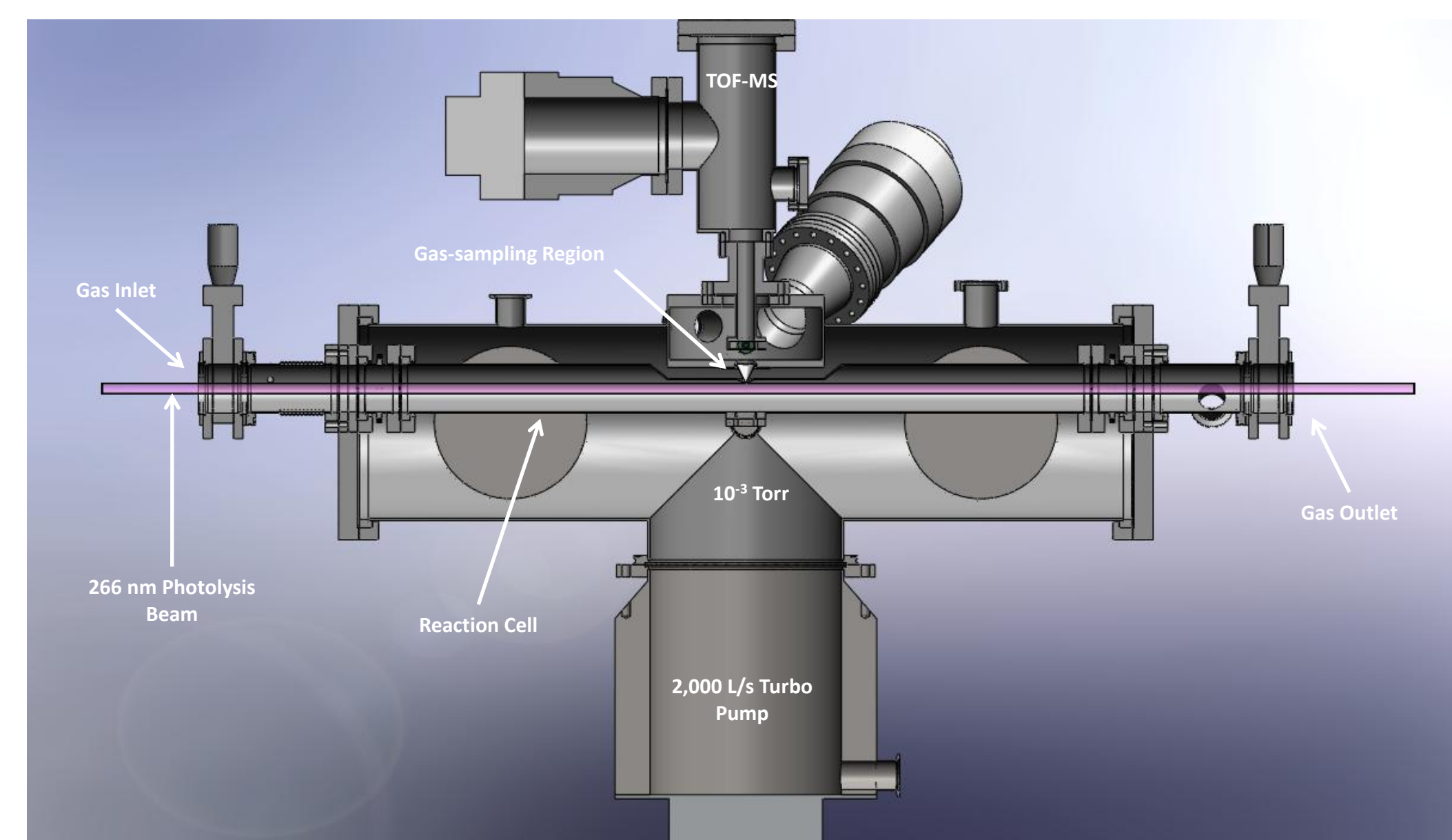
Vinyl radical (left) and allyl radical (right) absorption spectra. Absorption at typical vinyl line (423.2 nm, red line) has no absorption from other species with absorption at typical allyl lines (404 nm and 408 nm, blue lines) shows simultaneous absorption.



Vinyl radical decay with immediate return to baseline is observed at 423.2 nm (left) while a biexponential decay is observed at 404 nm and 408 nm (right) due to absorption from allyl radical, which is a resonantly stabilized free radical.

Photoionization Time-of-flight Mass Spectrometer (PI TOF-MS)

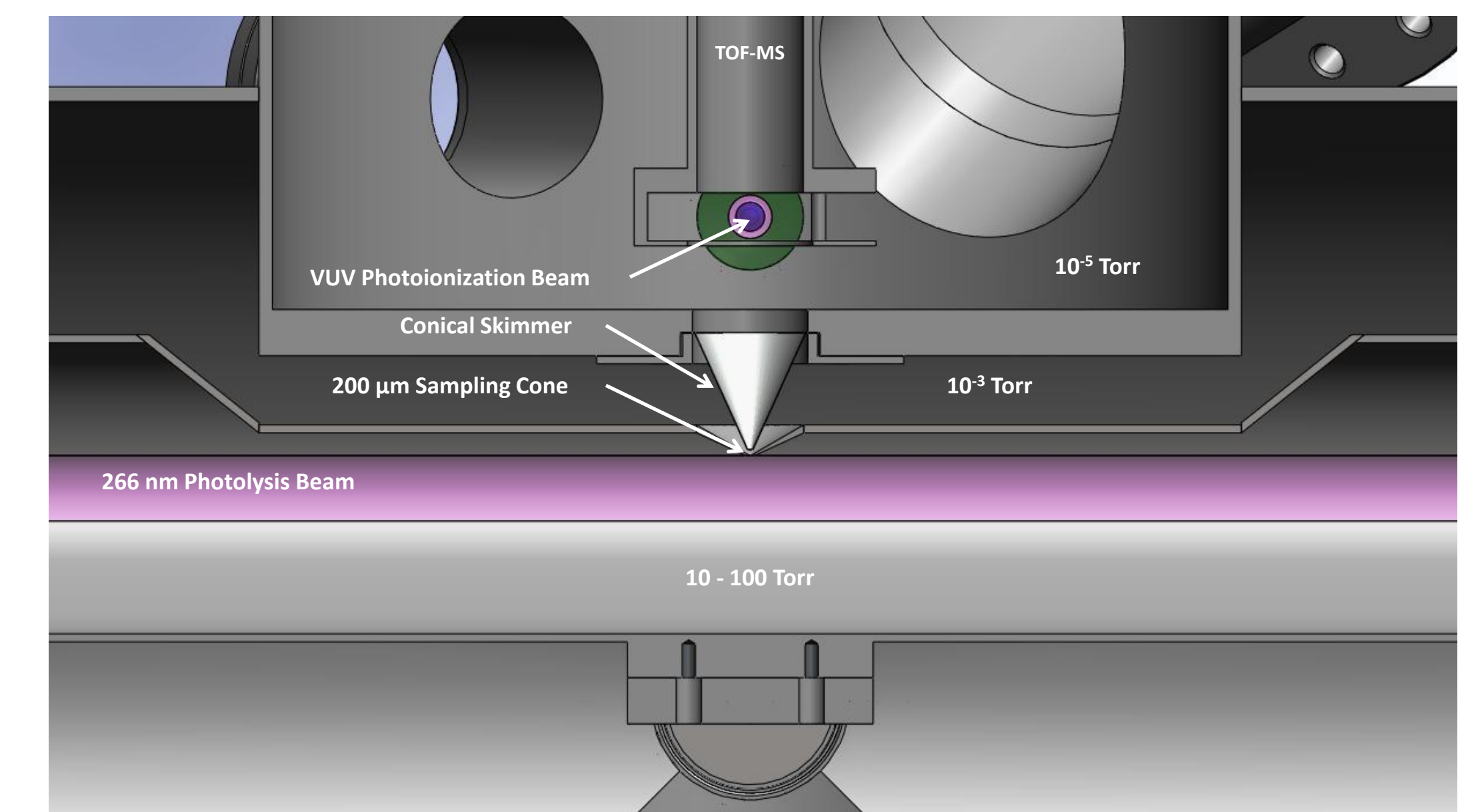
- Time-resolved PI TOF-MS yields transient mass spectra from which chemical kinetic rates can be determined
- The branching for all isomeric product channels with discrete mass-to-charge ratios can be simultaneously determined
- Only the center of the tube is photolyzed to avoid wall reactions and complications from heterogeneous chemistry
- Tube is large enough to allow Herriott multipass laser absorption techniques to be simultaneously performed



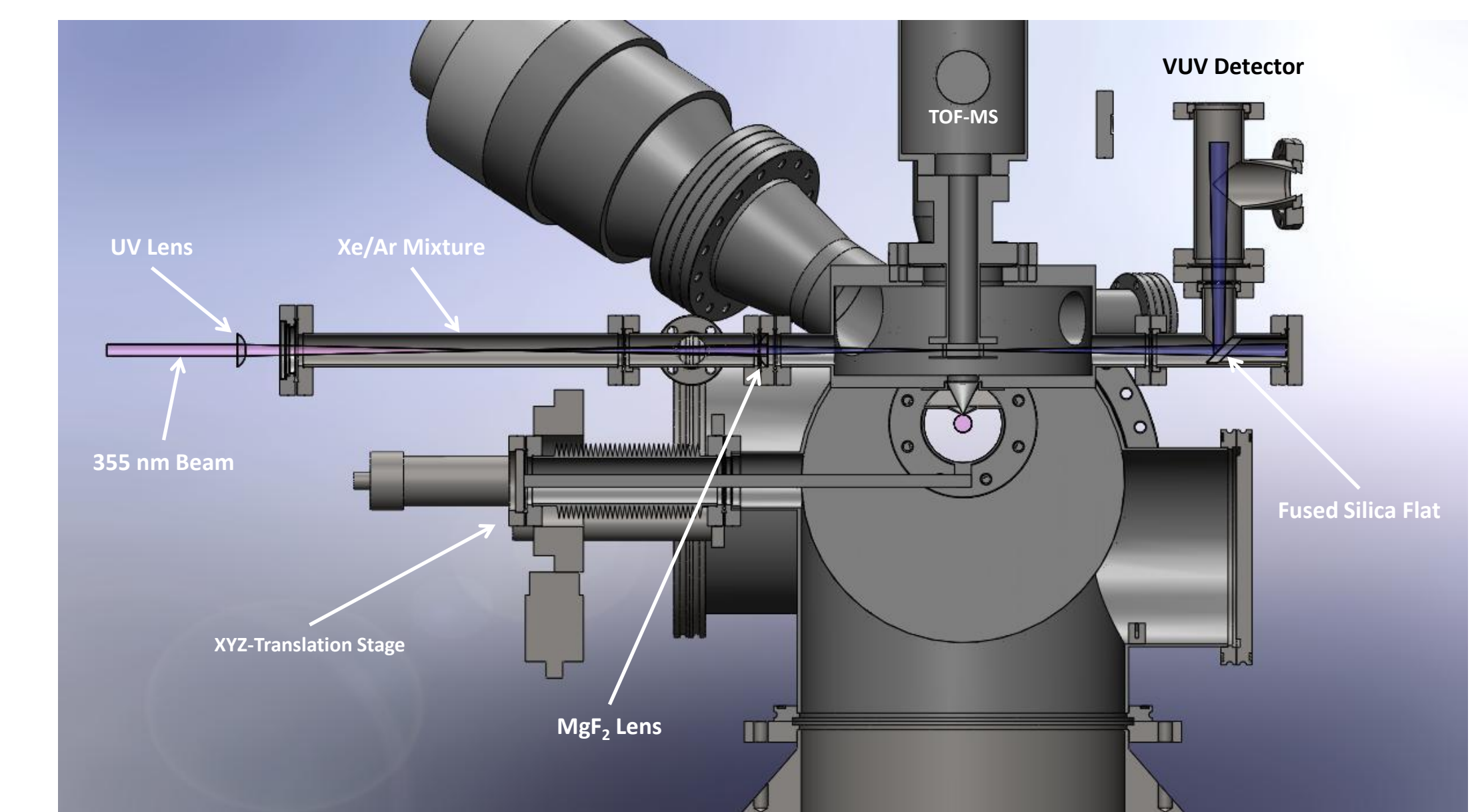
Front cross section showing the 2.5" OD reaction cell and co-axial 15 mm diam. photolysis beam passing through the middle of the chamber. The reactive gas is sampled via a small pinhole in the sampling cone tip in the center of the chamber.

Vacuum Ultraviolet Photoionization (VUV PI) Details

- VUV PI imparts less energy into the molecules and thus produces less ion fragmentation than other methods like electron impact
- VUV light is produced by frequency tripling the third harmonic (355 nm) output of a Nd:YAG laser using a Xe:Ar gas mixture
- Mass spectra at different reaction times are obtained by varying the delay time between the photolysis laser and the photoionization laser



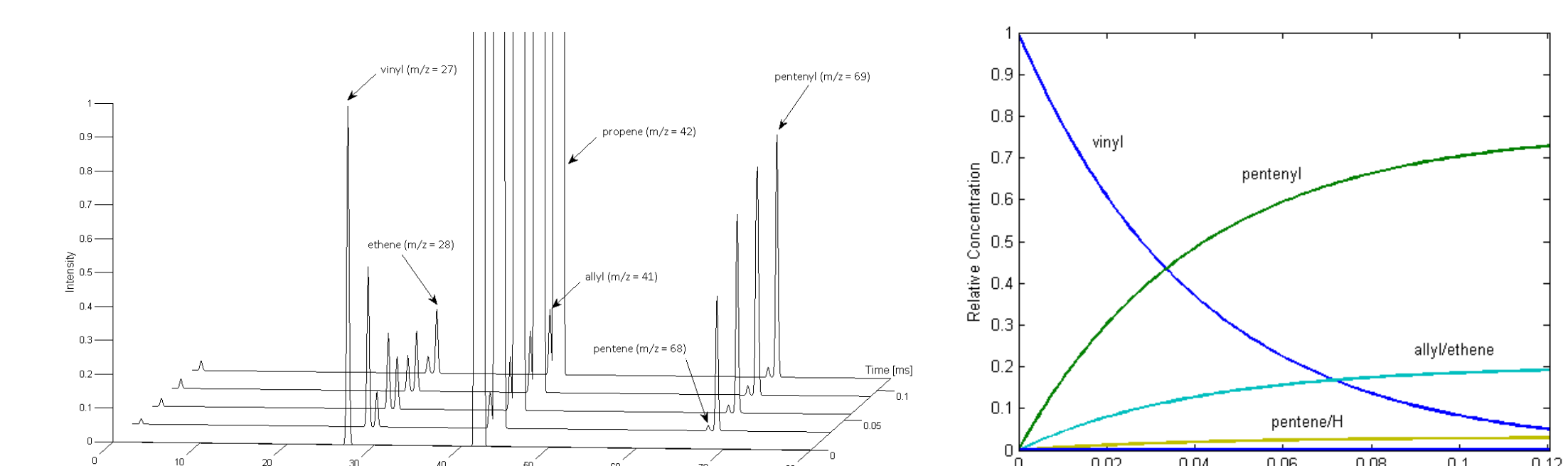
Close-up of the gas sampling region showing how the sampled gas is cooled and thus all reactions are quenched in transit to the TOF-MS by supersonically expanding and then skimming the gas to create a molecular beam.



Side cross section showing the VUV PI generation scheme used to ionize the sampled gas and the XYZ-translation stage used to align the gas-sampling cone relative to the conical skimmer.



The Kore TOF-MS (top right) is shown mounted on the chamber (bot. right), which has been mounted to a custom cart along with all of the associated electronics (left).



Simulated data calculated using the theoretical rates for the vinyl + propene reaction system is shown in mass spectra form (left) and in concentration form (right). We hope to soon take the actual data.