

Reaction of cyclopentadiene with $\text{CH}(\text{X}^2\Pi)$ radicals, a new route toward the formation of benzene

O. Durif¹, K. Caster², T. Selby³, F. Goulay², S. D. Le Picard¹

¹Institut de Physique de Rennes, UMR 6251 Université de Rennes 1/CNRS, 35042 Rennes, France

²Department of Chemistry, West Virginia University, Morgantown, WV 26506, United States

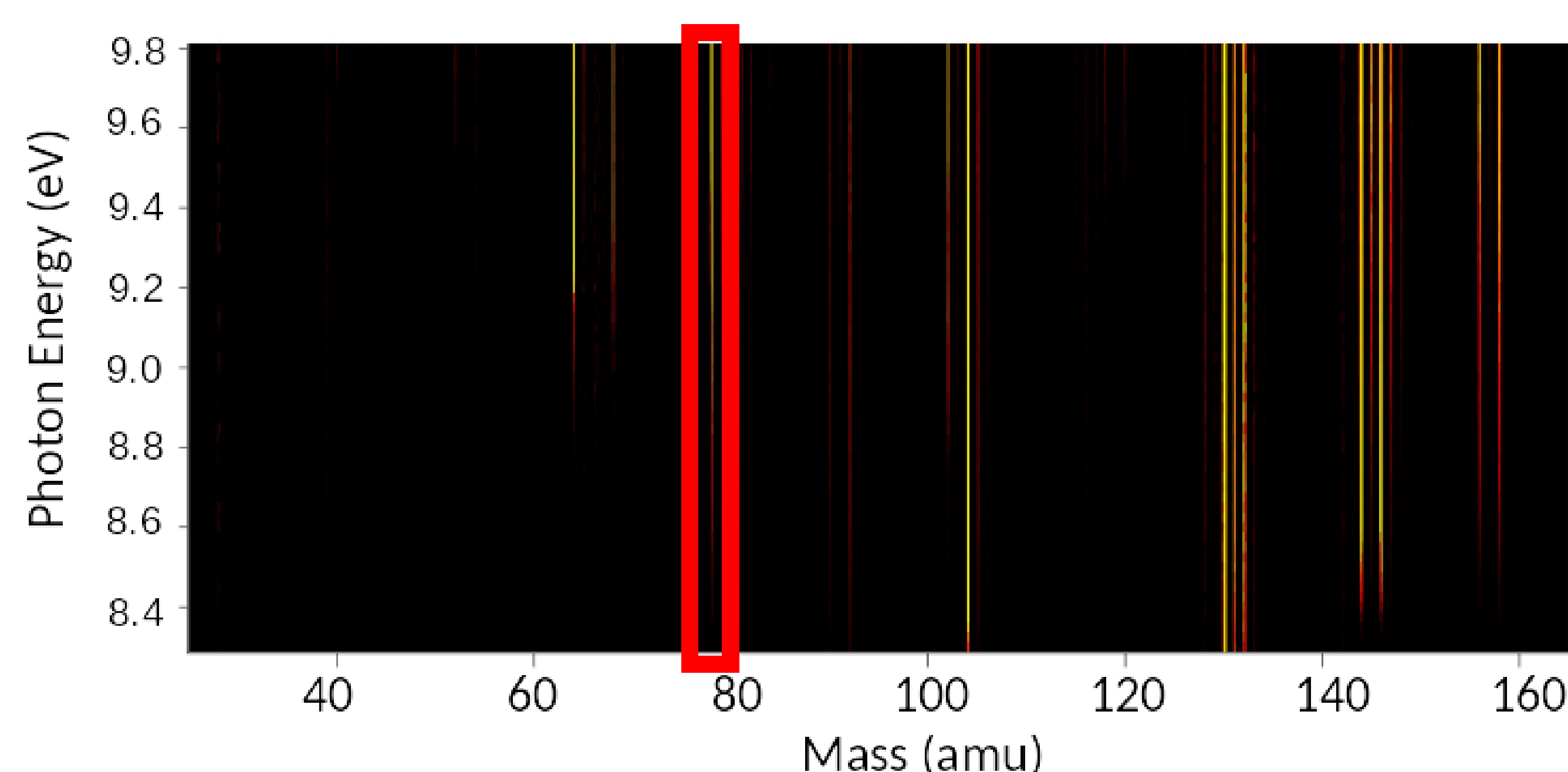
³Department of Chemistry, University of Wisconsin Colleges, Madison, WI 53715, United States

INTRODUCTION

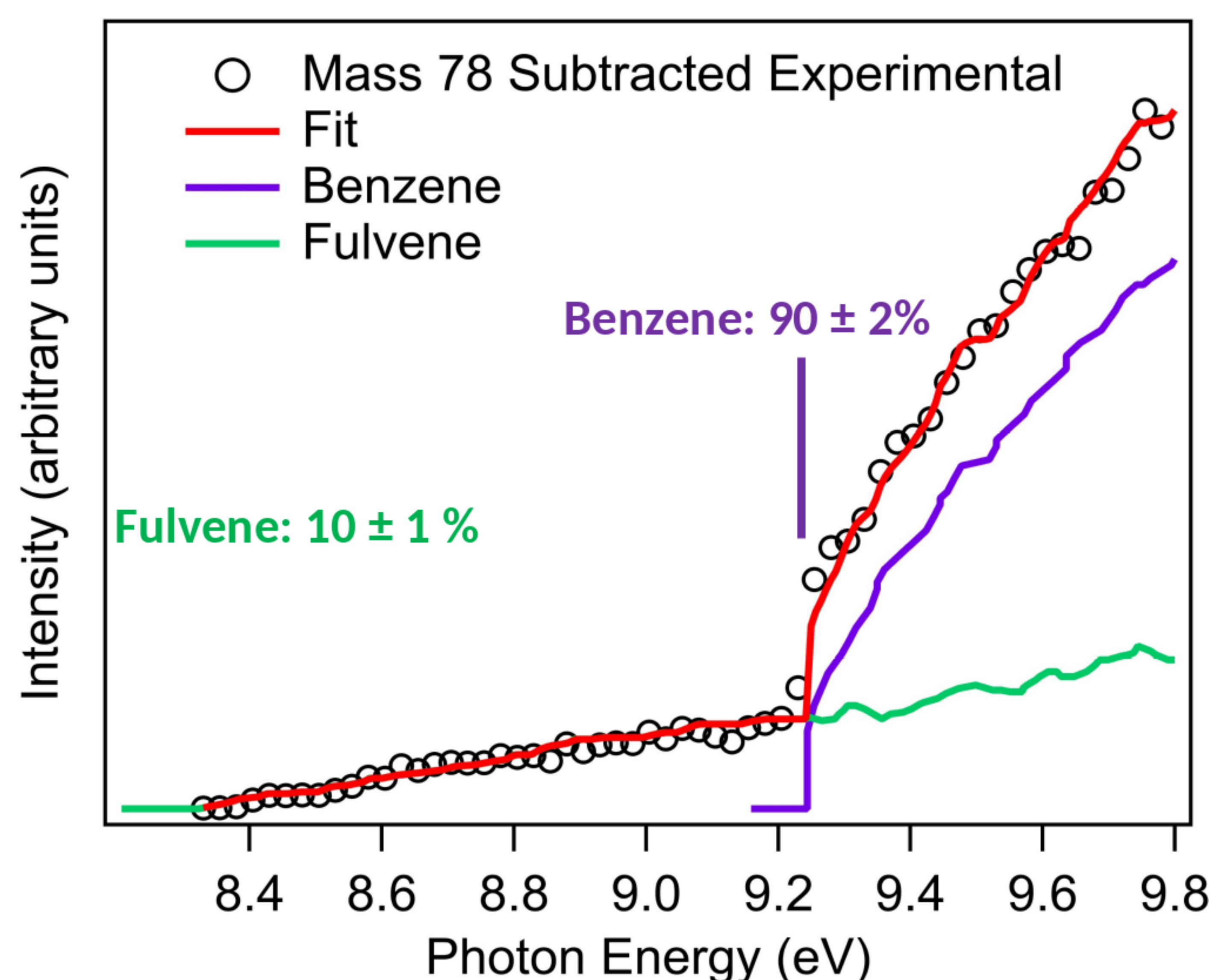
In the present work we investigated the reaction of cyclopentadiene (C_5H_6) with the combustion relevant radical CH leading to the formation of C_6H_6 isomers identified as fulvene and benzene. The formation of these aromatic ring molecules has been characterized experimentally using the kinetic apparatus from the chemical dynamics beamline at the Advanced Light Source at Berkeley, completed by computational investigation of the potential energy surface. This study provides new valuable insight into the mechanism behind the formation of benzene and fulvene in carbon rich environments.

Keywords: kinetics, branching ratio, benzene formation, cyclopentadiene reaction, chemical dynamics.

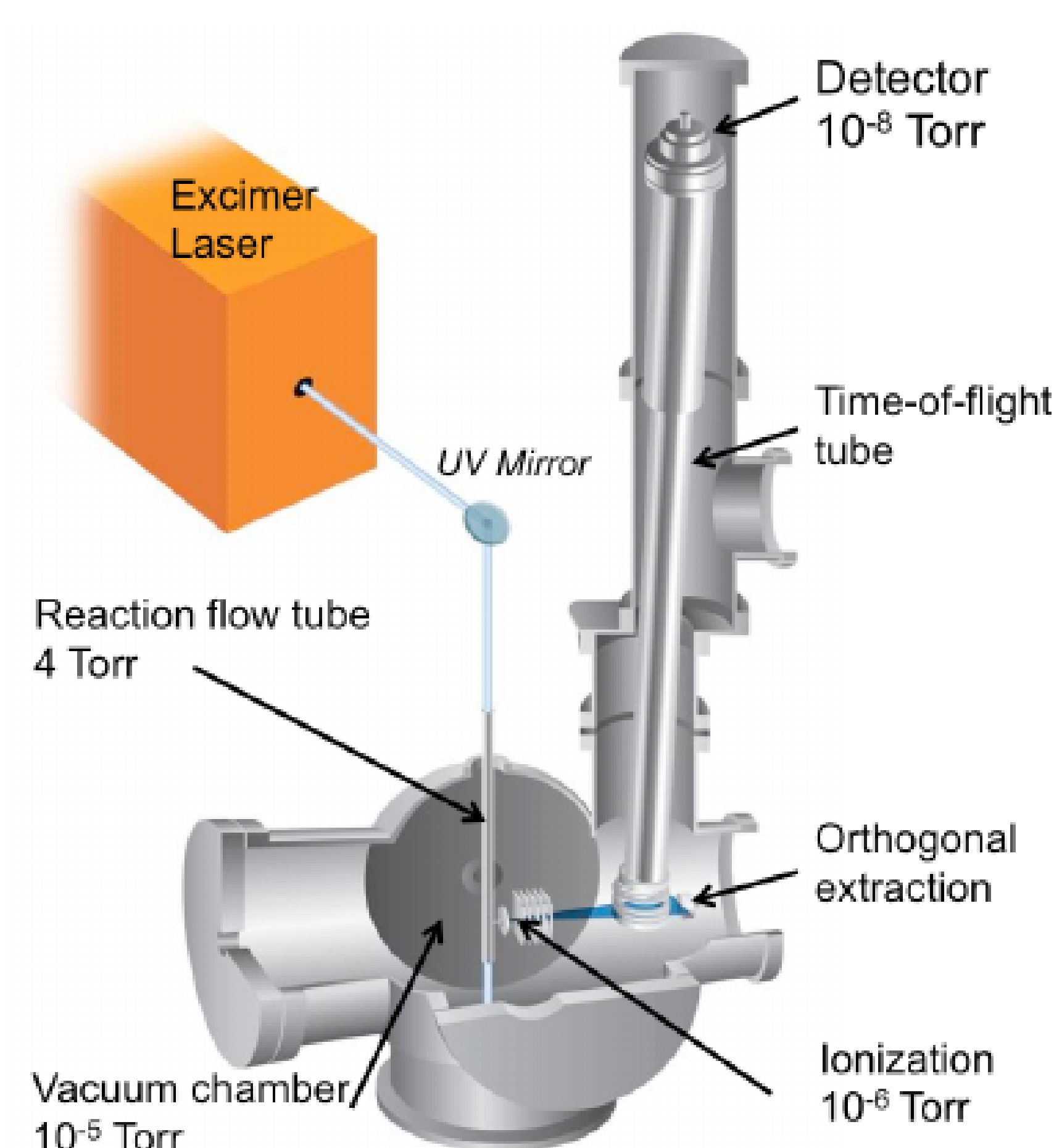
ENERGY AND TIME RESOLVED MASS SPECTRA



PHOTOIONIZATION EFFICIENCY SPECTRUM



MULTIPLEX KINETIC DIAGNOSTIC AT THE ALS



- Pressure 2-8 Torr
- Temperature 298-800 K
- CH radical produced by laser photolysis of CHBr_3
- CPD produced by thermal cracking of DCPD

Signal recorded as function of

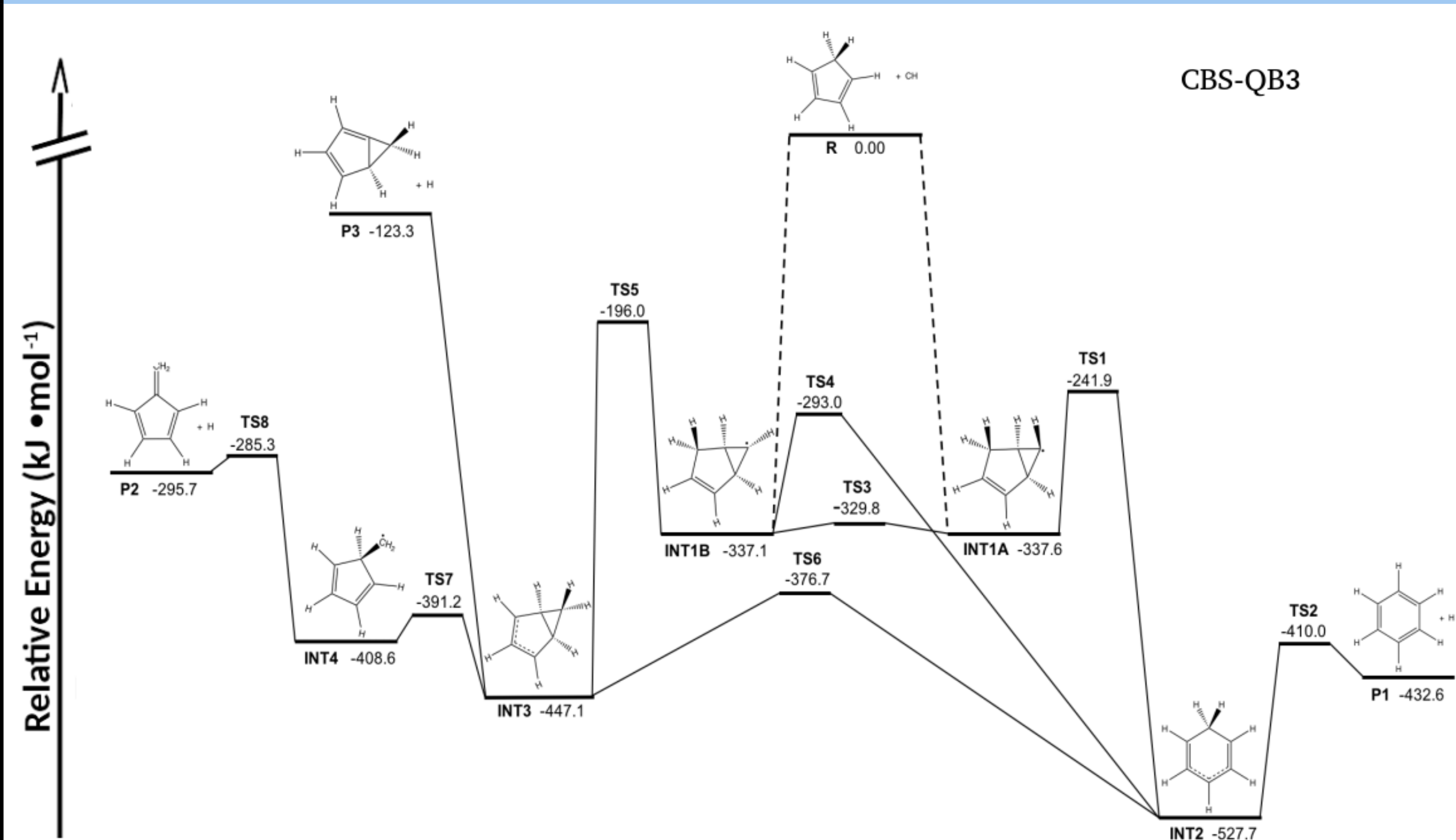
1. Mass-to-charge ratio
2. Reaction time
3. Photoionization energy

BIMOLECULAR RATE COEFFICIENT

Additional data by pulsed laser photolysis-laser induced fluorescence (PLP-LIF) at West Virginia University.

$$k = (2.7 \pm 1.3) \times 10^{-10} \text{ cm}^3/\text{s at 5.4 Torr and 300K}$$

POTENTIAL ENERGY SURFACE



MASTER EQUATION - MESMER RESULTS

- Benzene - 95 %
- Fulvene - 5 %

No Pressure/Temperature Dependence !

CONCLUSION

The data show that cycloaddition is the most likely entrance channel. Following the barrier-less addition, the bicyclic reaction intermediate can either ring open to give the resonance stabilized C_6H_7 radical or isomerize through transfer of a hydrogen atom from the sp^3 carbon of cyclopentadiene to the carbon from the initial CH radical. The 6-member ring intermediate can then directly decompose to give benzene and a H-atom. The initial intermediate may also lead to fulvene through ring opening and H-elimination.