



Photodissociation dynamics of acetylacetone

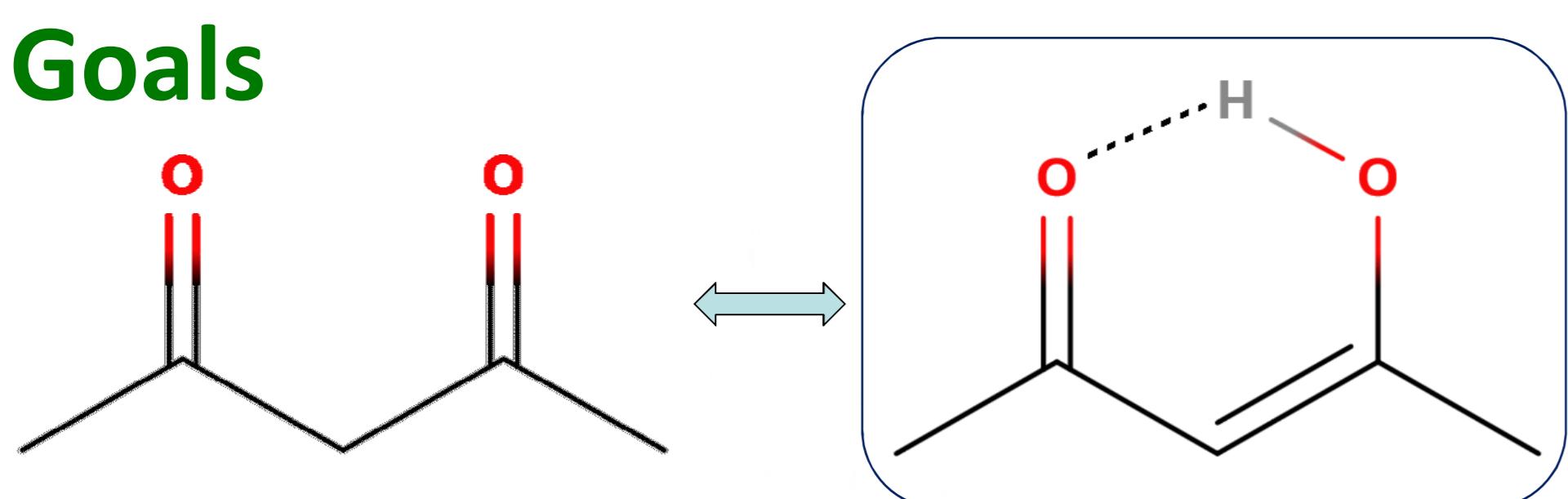
Ivan Antonov¹, Ming-Wei Chen¹, Krisztina Voronova², Bálint Sztáray², Leonid Sheps¹, David L. Osborn¹

Combustion Research Facility, Sandia National Laboratories

¹ 7011 East Ave., MS 9055, Livermore, California 94551 USA

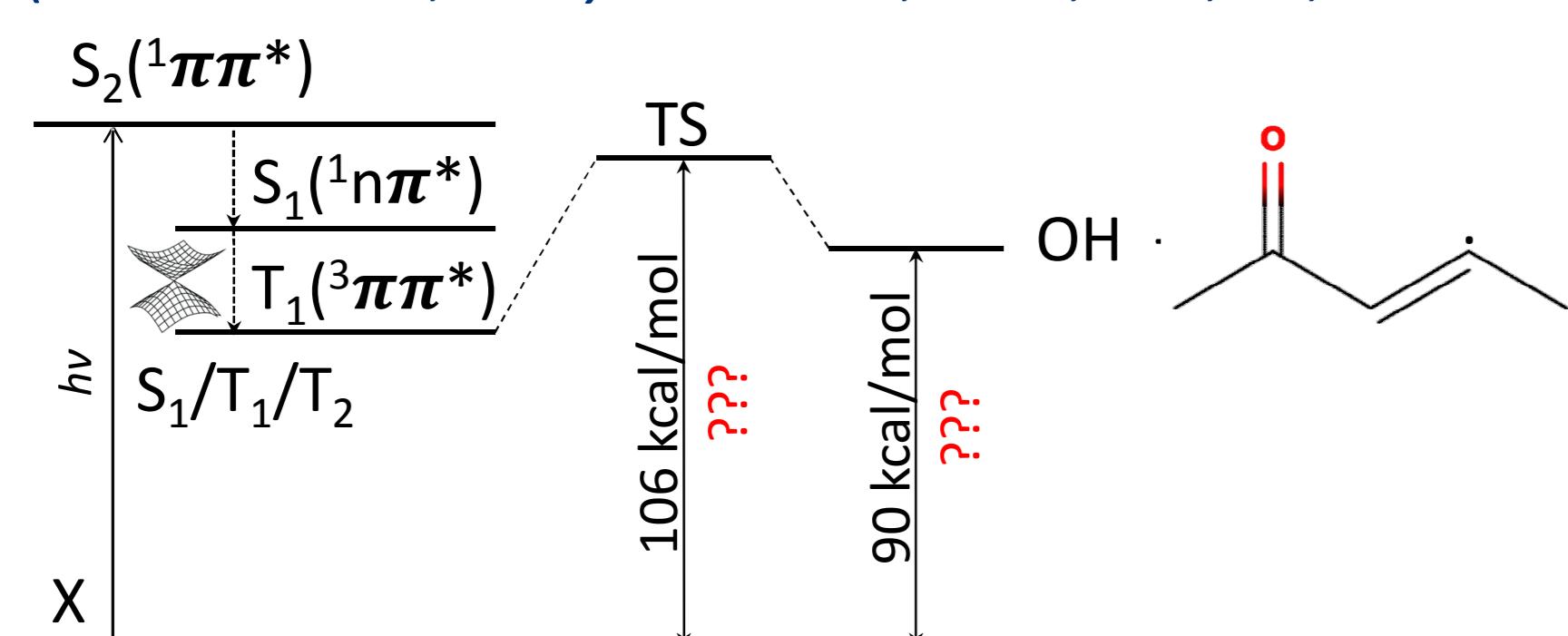
² Department of Chemistry, University of the Pacific, Stockton, CA, USA

Goals



Prospective high-P and T source of OH radicals for kinetic studies

- Stable in the gas phase up to 750 K (Al-Awadi et al, *Int. J. Chem. Kinet.*, 1995, **27**, 517-523).
- Cross-section at 266 nm $\sim 4 \cdot 10^{-17} \text{ cm}^2$ (Nakanishi et al, *Bull. Chem. Soc. Japan*, 1977, **50**, 2255-2261).
- Was used in recent LIF study of trans-butene + OH reaction (Antonov et al., *J. Phys. Chem. A*, 2015, **119**, **28**, 7742-7752)



"The preferential C-C bond cleavage over C-O bond cleavage is more predominant at 266 and 248 nm compared to 193 nm..." – Upadhyaya et al, *JCP*, 2003, 2590

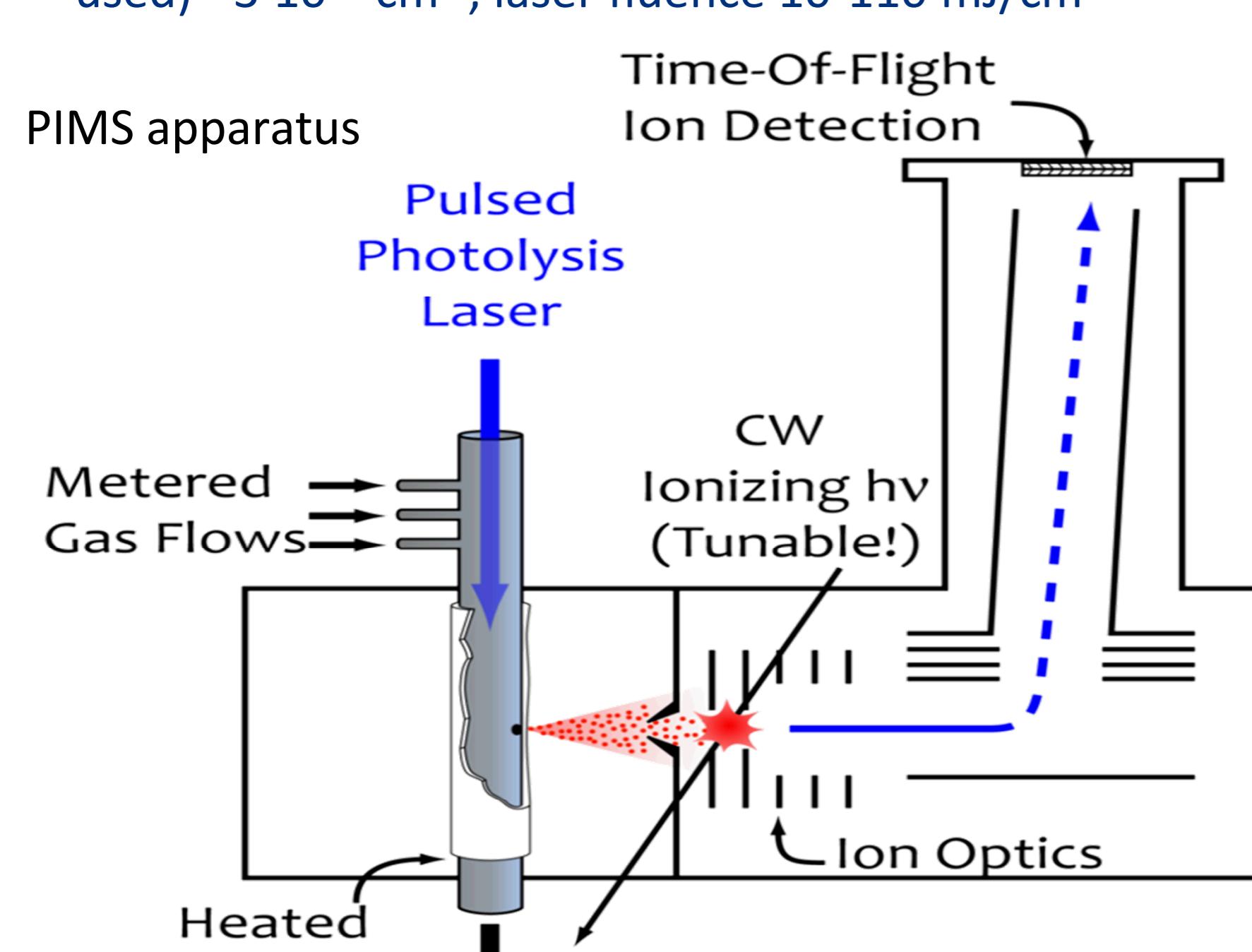
"OH loss is the dominant channel after 266 nm excitation" – Xu et al., *JPCA*, 2004, 6650

"The C-O fission pathway is the predominant dissociation process in the $T_1(3\pi\pi^*)$ state... Keto-enolic tautomerization takes place with little probability for acetylacetone in the gas phase" – Chen et al., *JPCA*, 2006, 4434

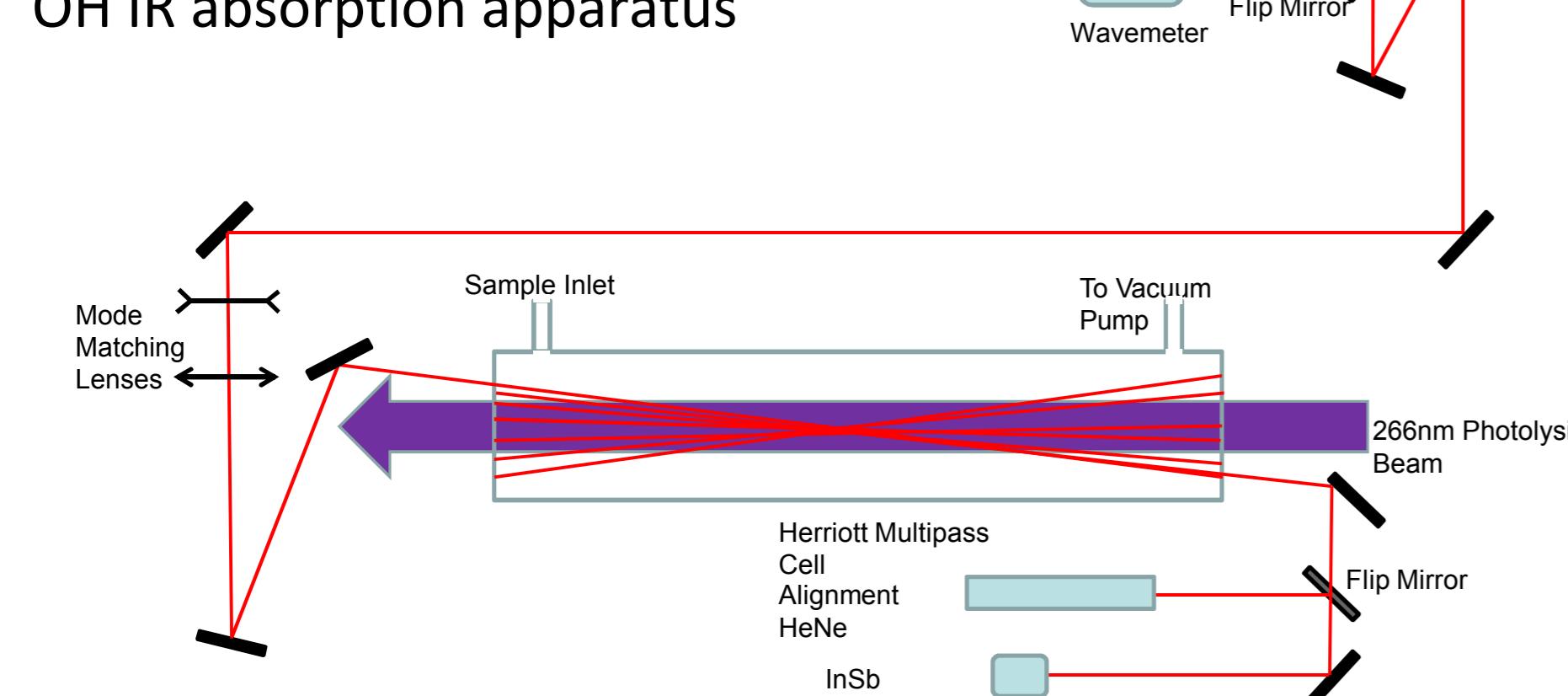
Our goal is to test existing mechanism of AcAc photodissociation at 266 and 248 nm and determine if there are any other photochemical pathways needed to be taken into account

Experimental

- Photodissociation of AcAc was studied with PIMS and OH transient absorption at T=300-600 K at 248 and 266 nm
- PIMS is synchrotron based photoionization mass spectrometry coupled to a flash photolysis flow reactor with continuous sampling. Tunable VUV at 8.5-11 eV was used.
- OH was detected in a multipass IR absorption cell integrated in a (separate) flash photolysis flow reactor
- [AcAc] - $2 \cdot 10^{12} \text{ cm}^{-3}$ (PIMS) or $1 \cdot 10^{14} \text{ cm}^{-3}$ (absorption), $[\text{O}_2]$ (when used) - $3 \cdot 10^{16} \text{ cm}^{-3}$, laser fluence $10-110 \text{ mJ/cm}^2$

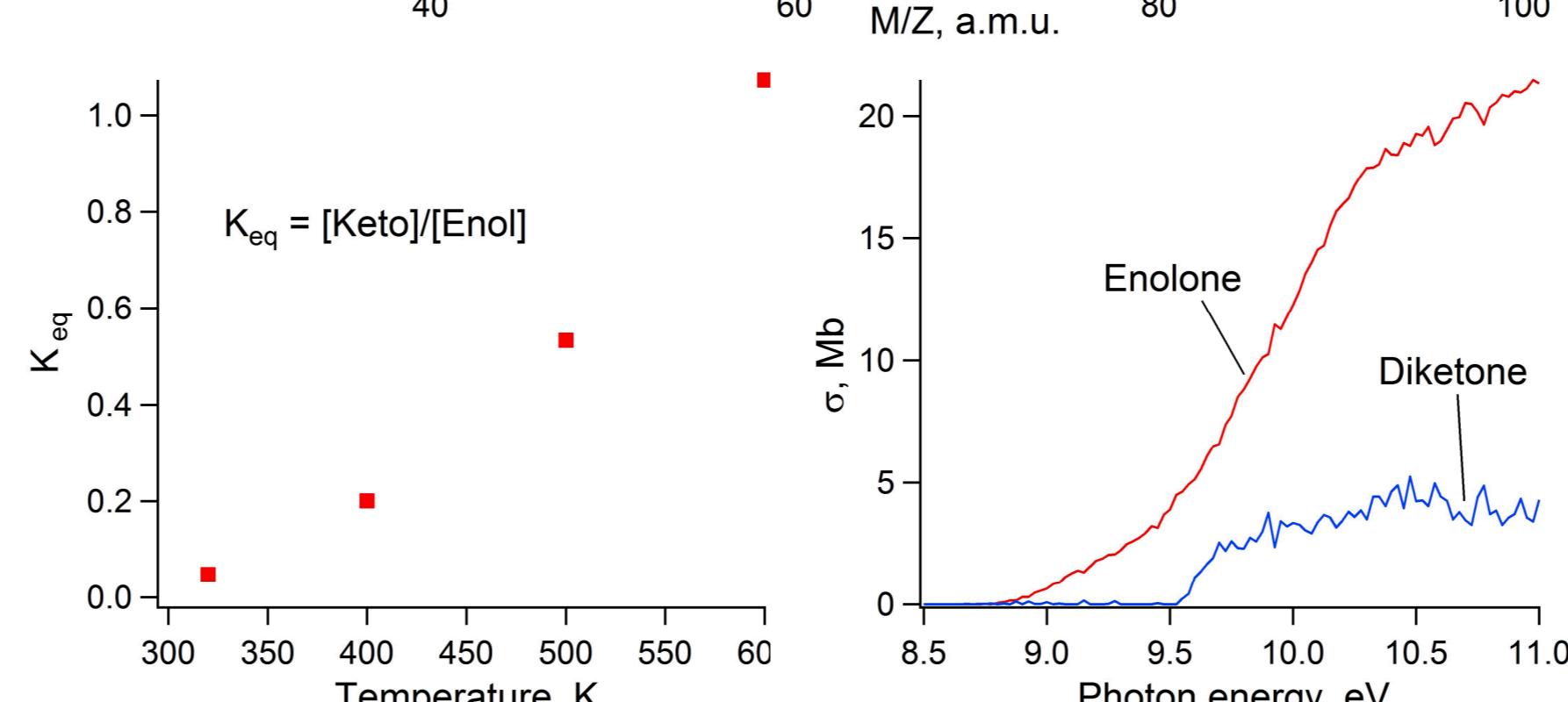
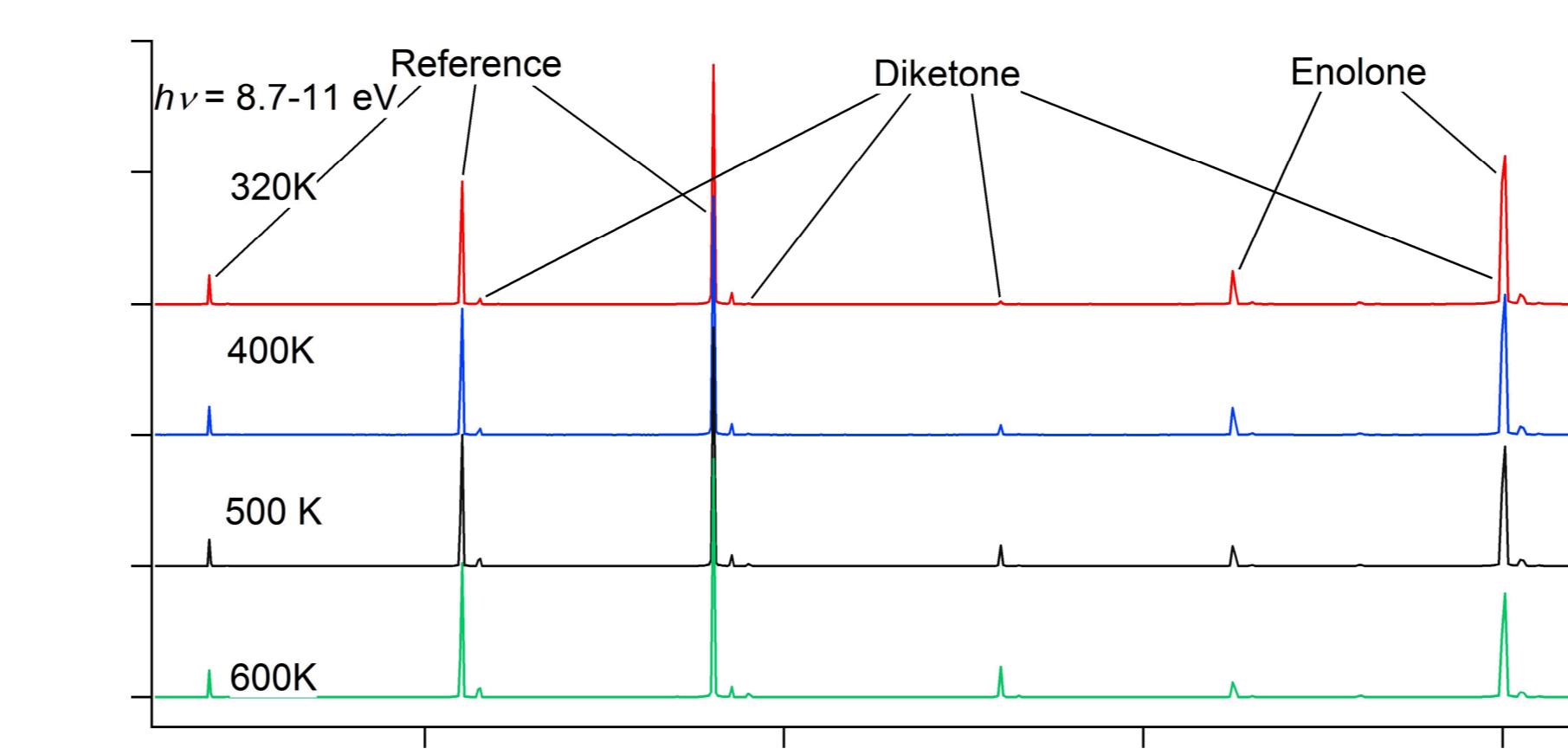


OH IR absorption apparatus

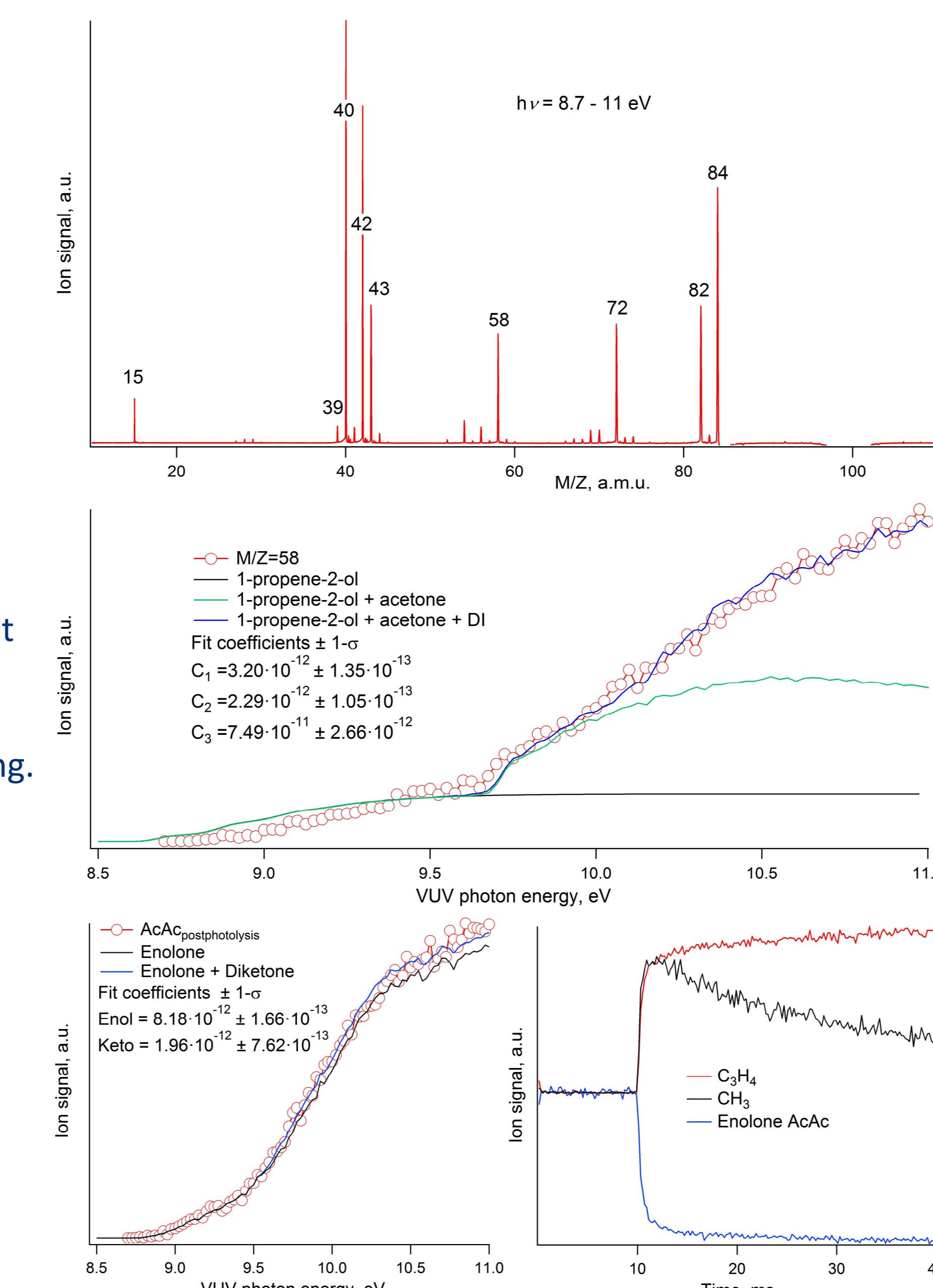


Results

Measurement of diketo-enolone equilibrium constant and absolute PI spectra



Identification of photolysis products using PI spectra and time evolution

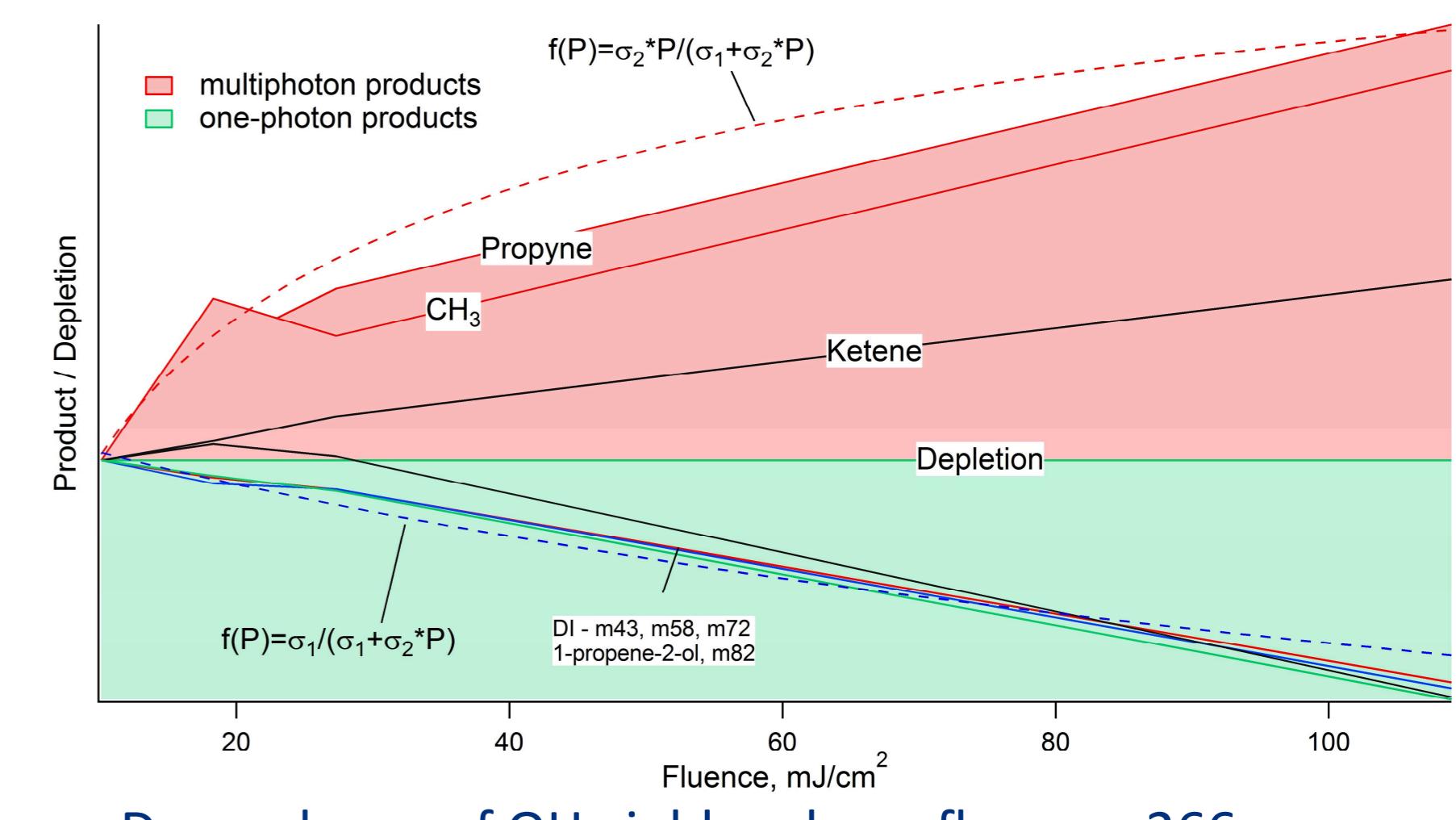


Summary of identified products

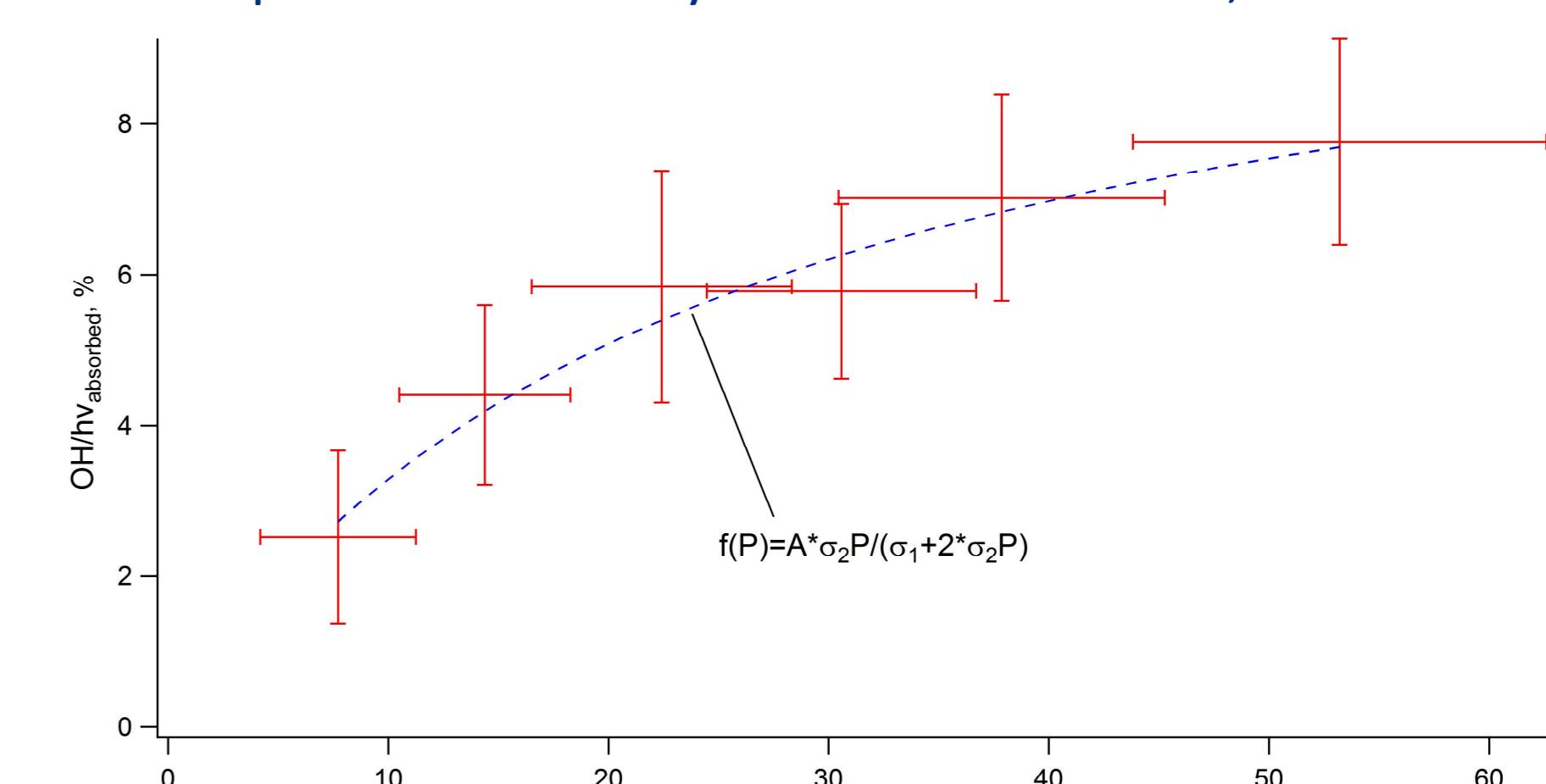
M/Z	Composition	Yield, % at 248 nm	Identification
15	CH_3^+	24	Methyl
16	CH_4^+	5	Methane
18	H_2O^+	17	Dihydrogen monoxide
39	C_3H_3^+	1	Propargyl
40	C_3H_4^+	2	Allene
		19	Propyne
42	$\text{C}_2\text{H}_2\text{O}^+$	8	Ketene
43	$\text{C}_2\text{H}_3\text{O}^+$?	DI of diketo-AcAc
58	$\text{C}_3\text{H}_6\text{O}^+$	2	1-propene-2-ol
		2	Acetone
		?	DI of diketo-AcAc
72	$\text{C}_4\text{H}_8\text{O}^+$?	DI of diketo-AcAc
82	$\text{C}_5\text{H}_6\text{O}^+$?	Co-fragment of H_2O elimination
84	$\text{C}_4\text{H}_4\text{O}_2^+$?	Co-fragment of CH_4 elimination
100	$\text{C}_5\text{H}_8\text{O}_2^+$	8	Diketo-AcAc

Discussion

Dependence of products on laser fluence, 248 nm

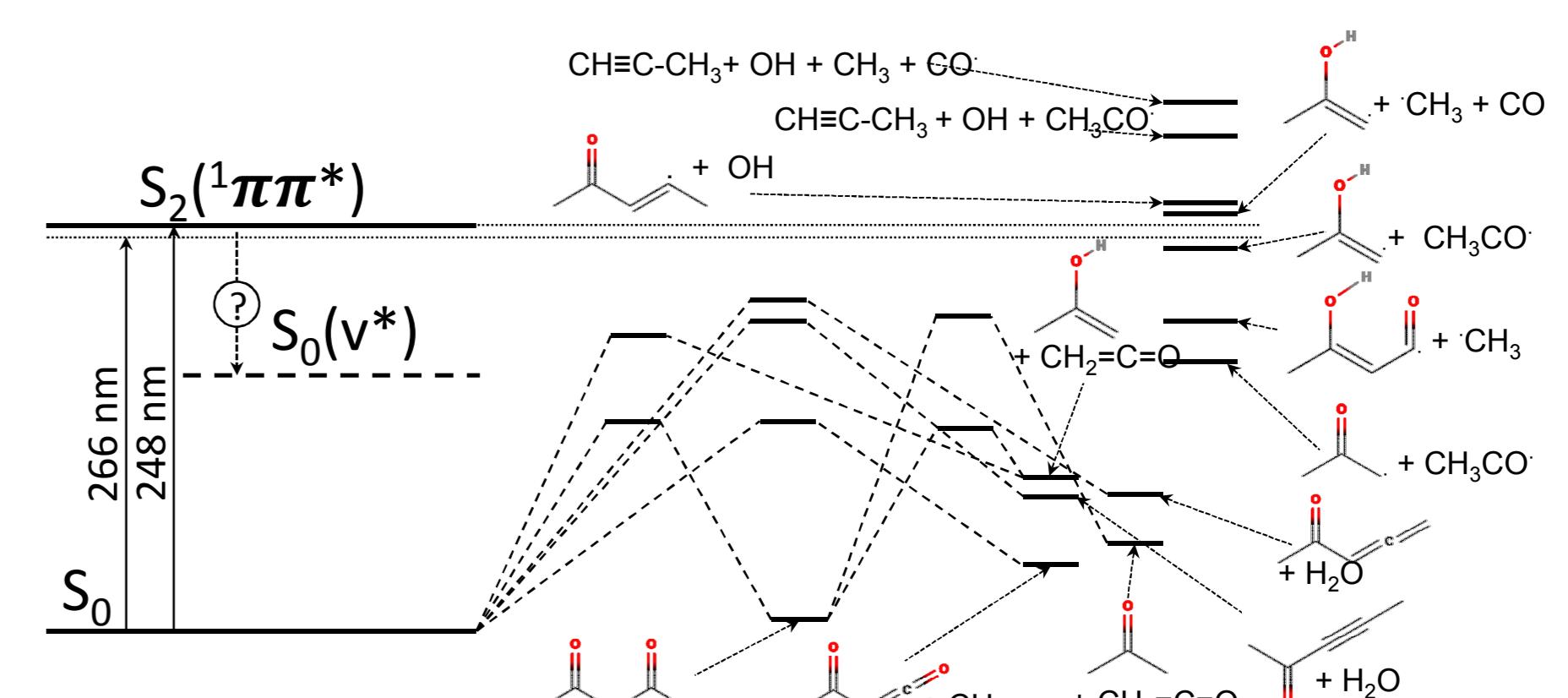


Dependence of OH yield on laser fluence, 266 nm

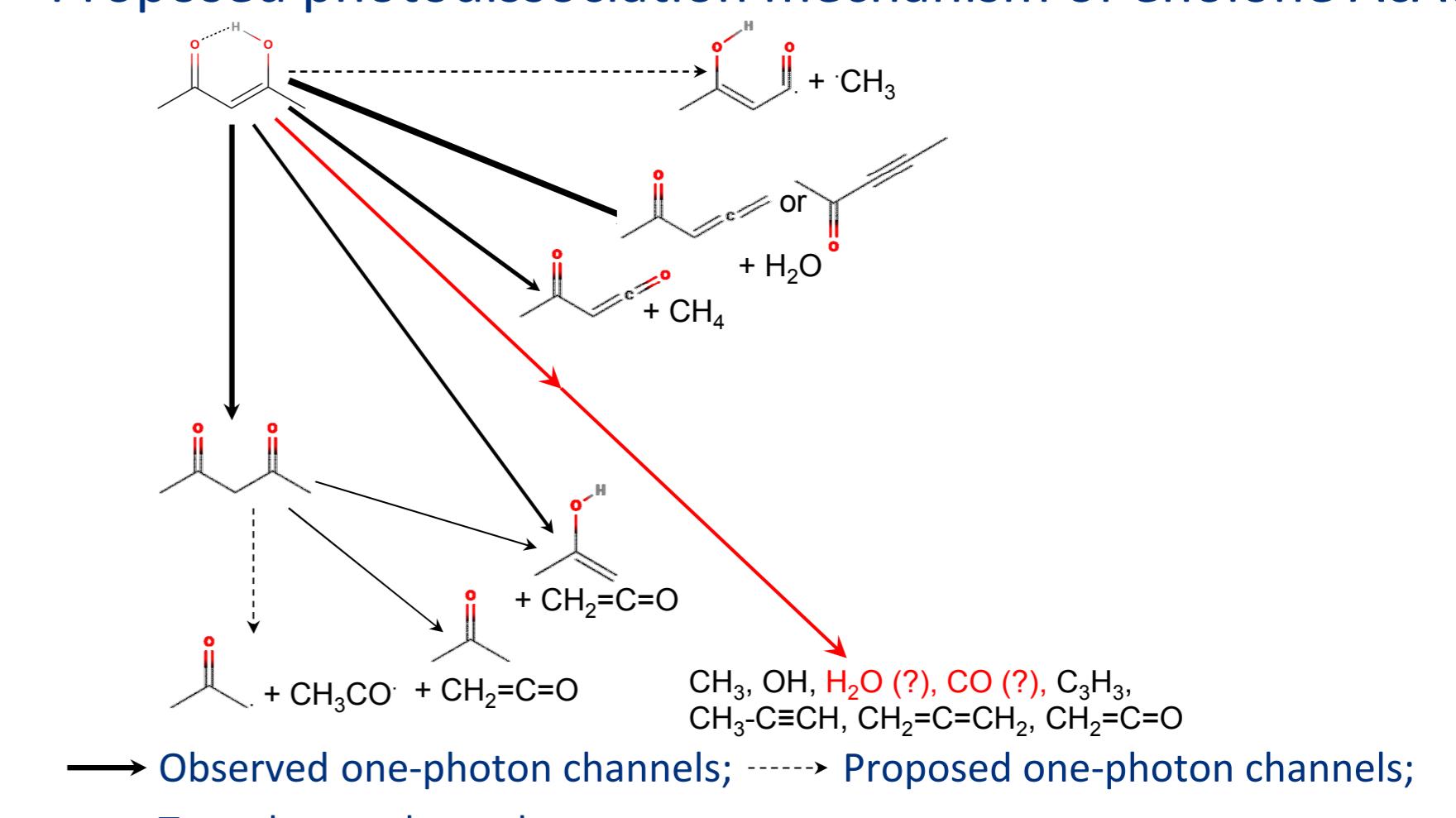


*Dashed lines are simulations of 1- and 2-photon products behavior in a high depletion limit

Calculated energies of photolysis products and selected transition states on the ground electronic state



Proposed photodissociation mechanism of enolone AcAc



Conclusions

- AcAc photodissociation at 248 and 266 nm was studied with PIMS and OH absorption. We observed >15 new photolysis products. Previous studies focused on OH only and should be revised.
- 2-photon processes play a significant role in AcAc photolysis at the laser fluence levels applied.
- OH radical is not a dominant product of AcAc photolysis. OH yield is $<10\%$ and power-dependent.
- We propose a new 1-photon dissociation mechanism that involves only S₀ surface.
- AcAc can be an intense source of OH radicals at high P and elevated T. One need to pay attention to how the photolysis products may interfere with the chemistry or product detection.

LS and IA were supported through the Argonne-Sandia Consortium on High-Pressure Combustion Chemistry (FWP# 2009ANL 59044). MWC and DLO were supported by the Division of Chemical Sciences, Geosciences, and Biosciences, BES/USDOE. KV and BS were supported by the National Science Foundation (CHE-1266407) Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.