BROOKHAVEN NATIONAL LABORATORY

Mass-Resolved Imaging of Products from Surface Photoreactions

Matt Kershis, Amanda Muraca, Michael White

Surface Chemical Dynamics Group

Chemistry Division, Brookhaven National Laboratory

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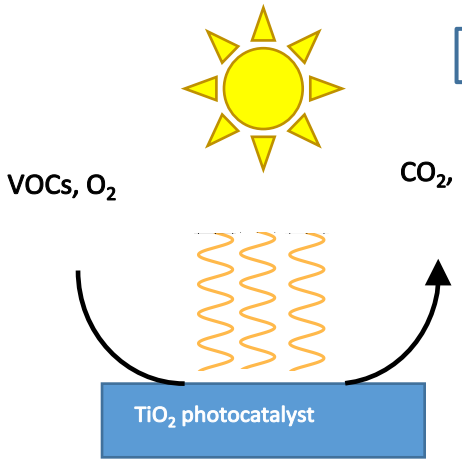
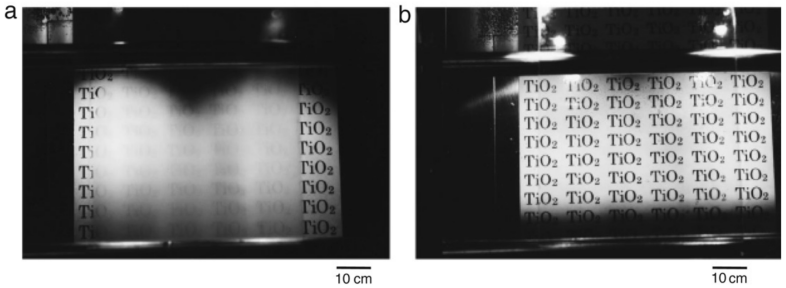
Photooxidation on TiO_2 surfaces

- Liquid or gaseous organic molecules adsorb on TiO_2 surfaces, decompose when irradiated with UV light ($h\nu > 3$ eV or $\lambda < 400$ nm). TiO_2 is a semiconductor with 3.1 eV band gap.
- Oxygen usually needed to facilitate decomposition
- Useful in environmental remediation, anti-fogging coatings, self-cleaning coatings



Anti-fogging coatings



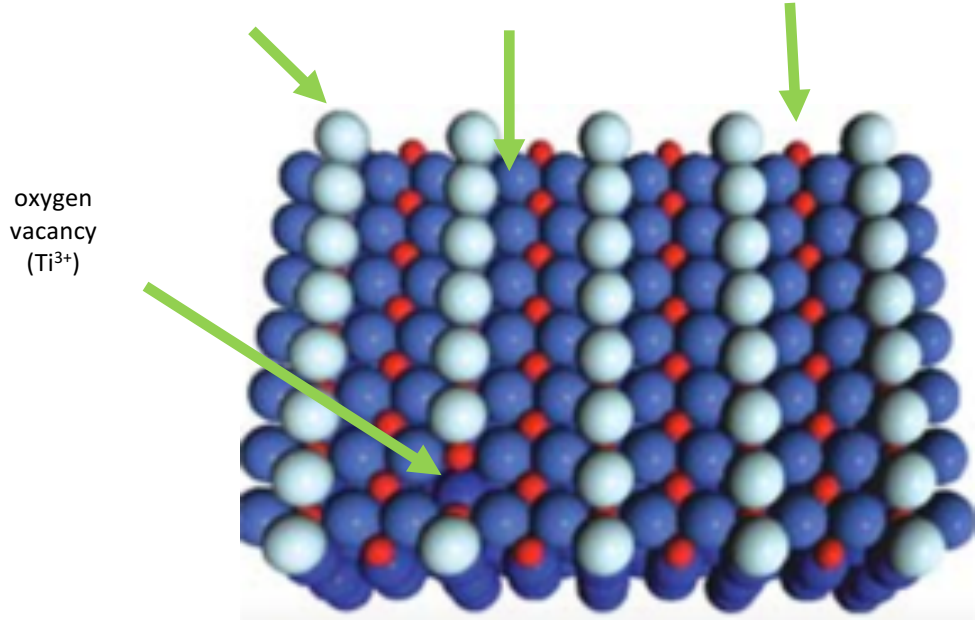
Watanabe et. al *Thin Solid Films* 351 (1999) 260-263

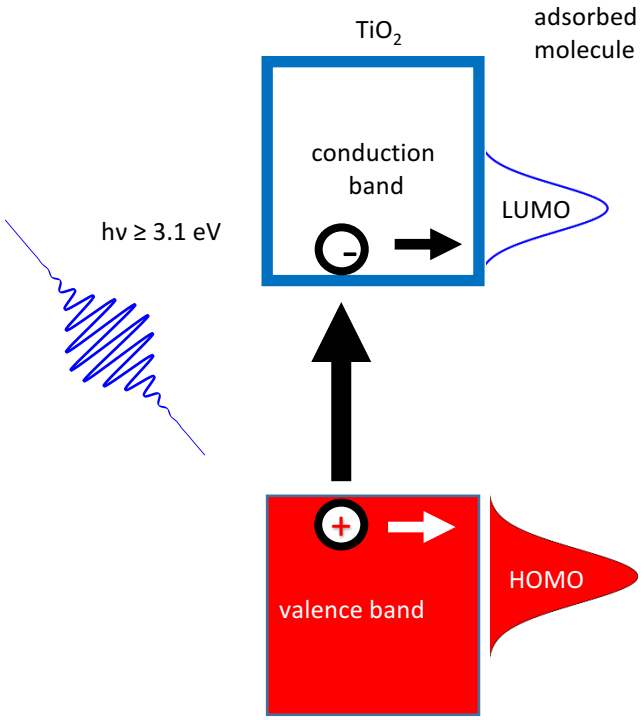
Self-cleaning, photocatalytic coatings

Source: news.thomasnet.com

TiO_2 as a model photocatalyst

- TiO_2(110) facet ideal for fundamental studies
  - Stable, well-understood surface structure
- We study reactions of small ketones (acetone, butanone, etc.)



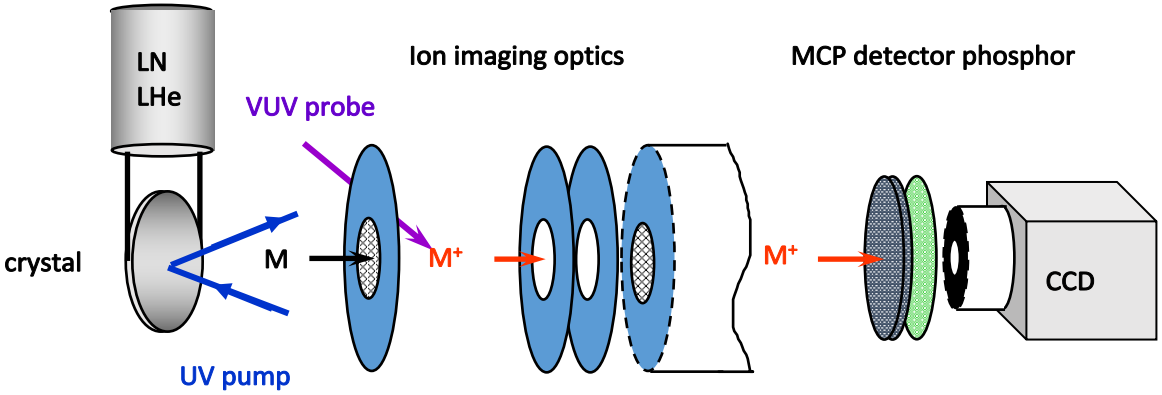


Pang et. al, *Chem. Soc. Rev.*, **2008**, 37, 2328-2353

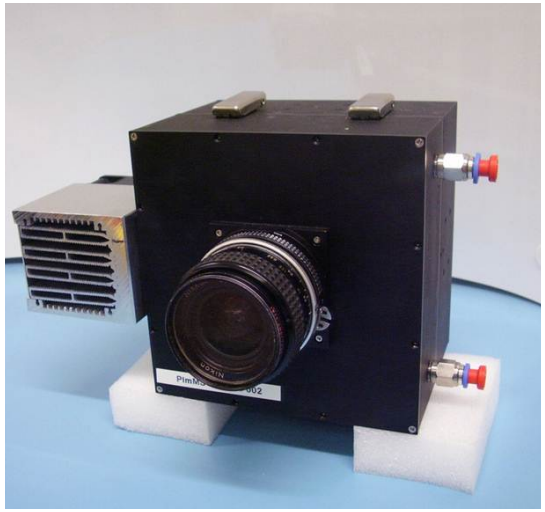
Velocity map imaging for surfaces

Time-resolved imaging – TimePix (previously PImMS)

- angular distributions for individual mass products simultaneously on single dose
- Distinguish photoproducts from ion fragmentation
- New insights to dynamics



PImMS* Camera
Oxford/Physics
Andrei Nomerotski



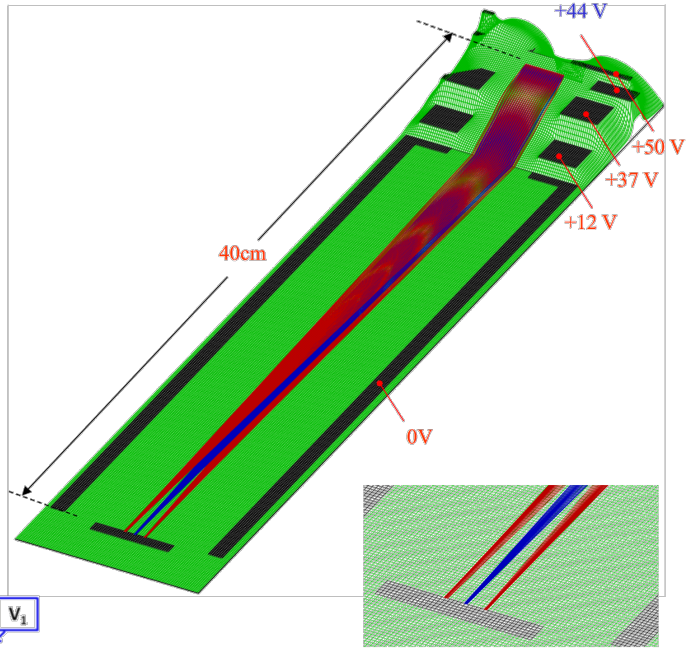
- 25 ns time resolution over 200 μsec window
- 72x72 pixels, 70x70um^2
- 500 frames per sec (USB)
- 360x360 pixel sensor in testing

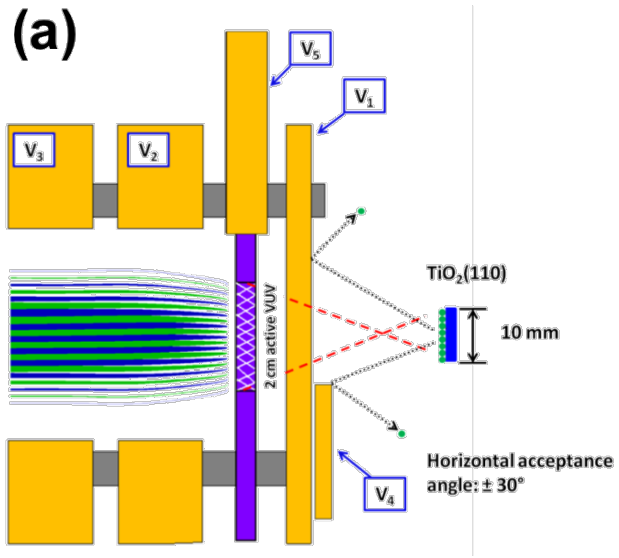
*PImMS ≡ pixel imaging mass spectrometry

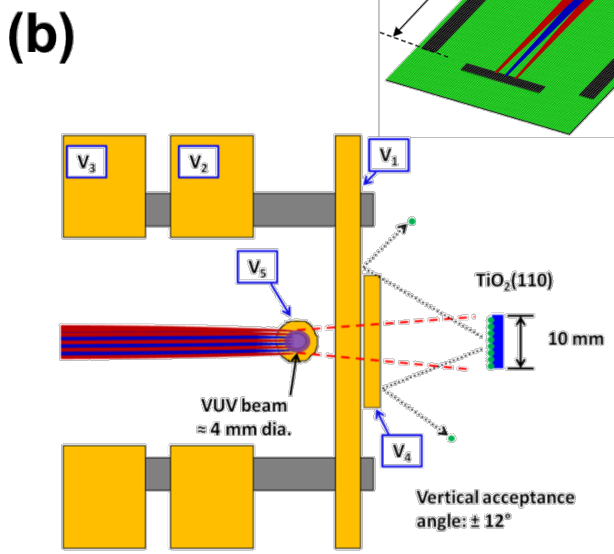
Surface velocity map imaging (VMI) for angular distributions

- In principle, distinguish primary products from fragments
- all trajectories focused to same point regardless of position
- Finite detection capability
  - Limited angular acceptance
  - Can be theoretically modeled

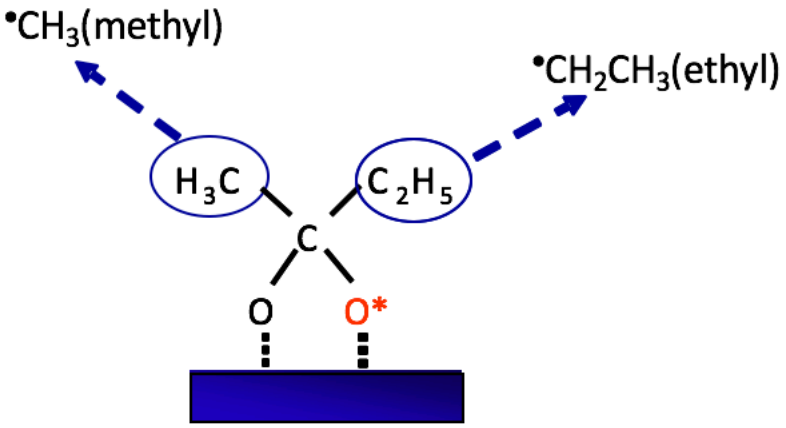
a) horizontal acceptance angle (parallel to lab floor)
b) vertical acceptance angle (perpendicular to lab floor)







2-butanone photooxidation: Multiple reaction products



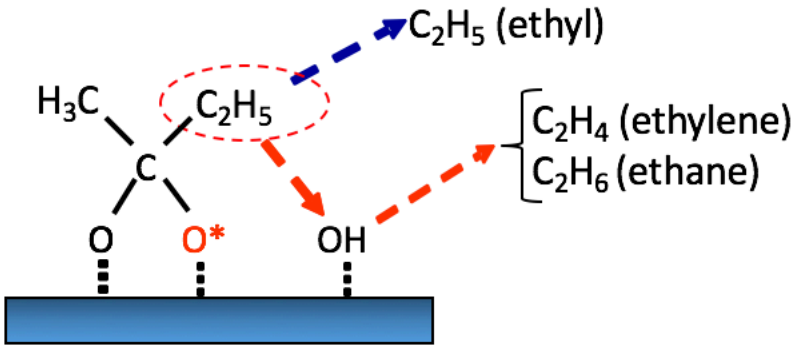
Both methyl and ethyl products possible

- ethyl radical primary product
- bond energies differ < 1-2 kJ/mole

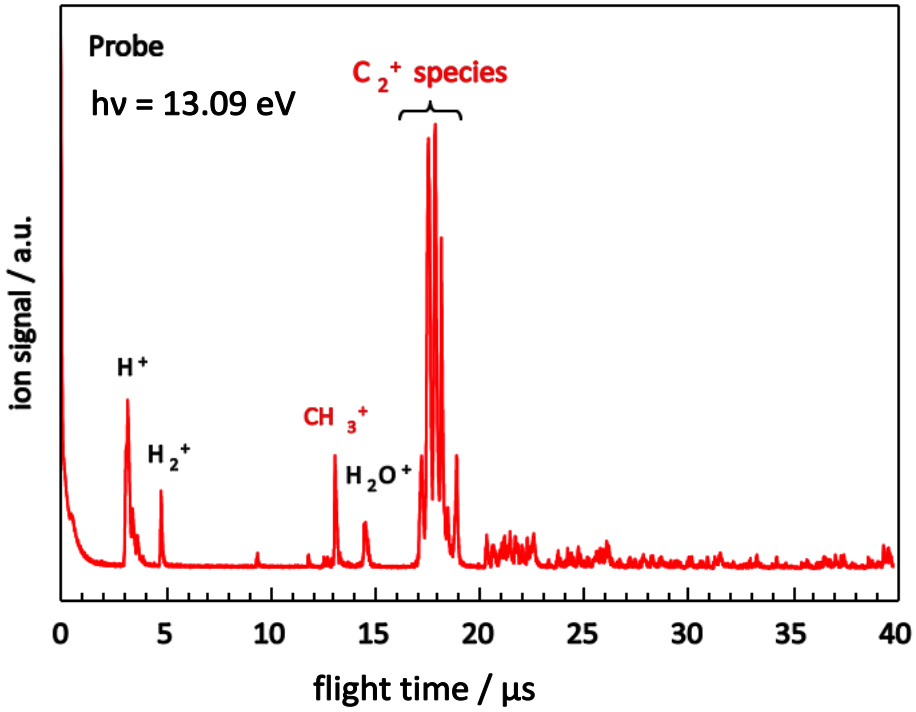
Henderson, Surf. Sci. 602, 3188 (2008)

Electron-impact mass spec

- Observe masses 27-30
- Assigned to secondary chemistry of photo-generated radicals



Time of flight MS, VUV ionization

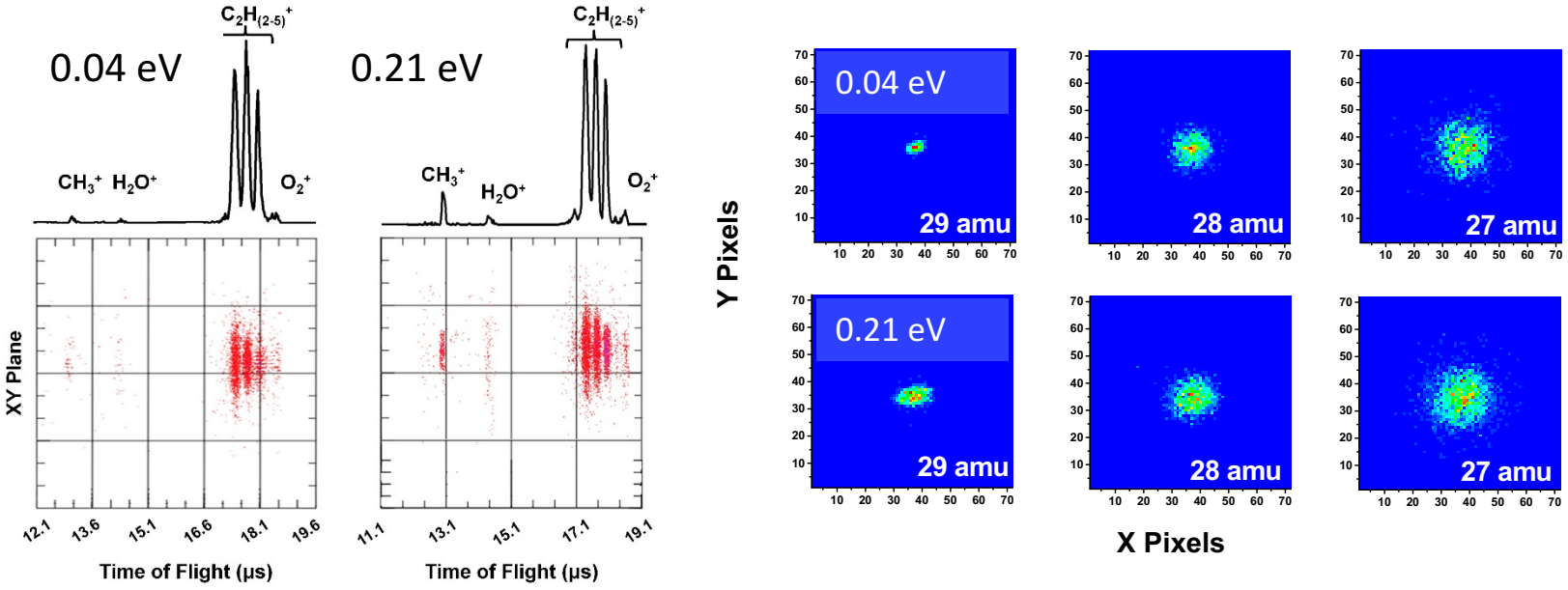


Wilson et. al, *J. Phys. Chem. C* 2013, 117, 9290-9300

Evidence for fragmentation

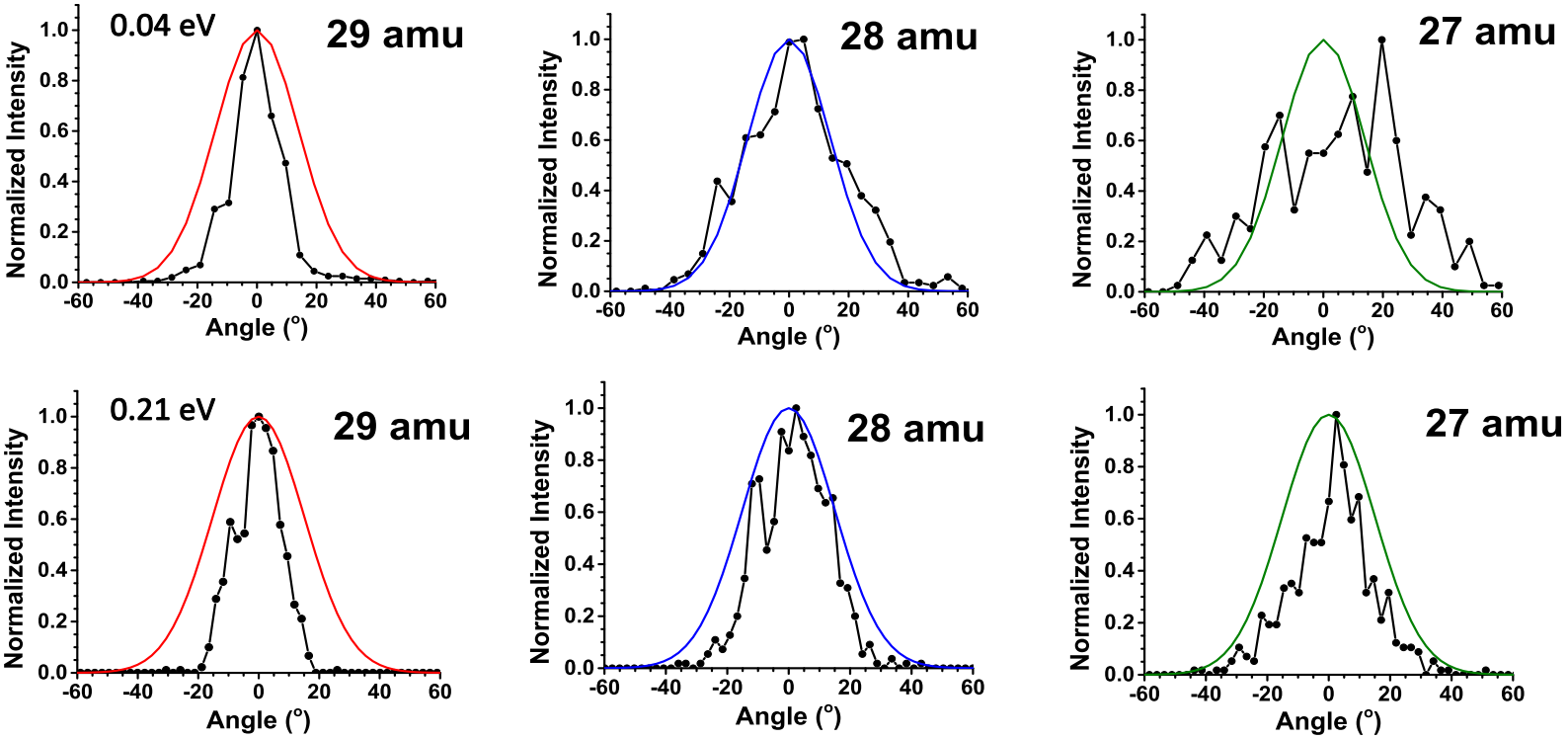
Data collected at two different fragment kinetic energies

Similar fragmentation pattern



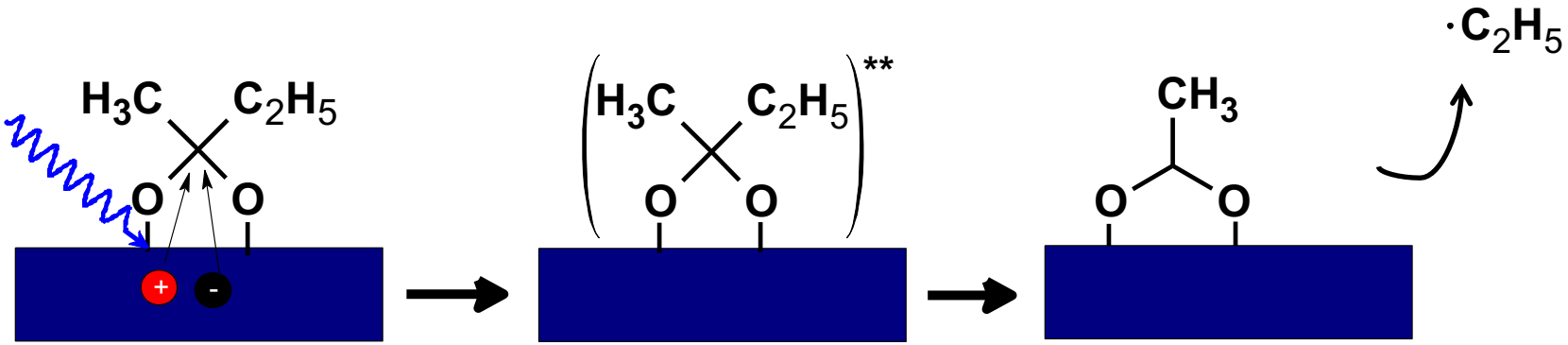
Angular distributions

- Detector functions show acceptable angular probability distribution of apparatus
- valid angular distribution data must fit within these functions



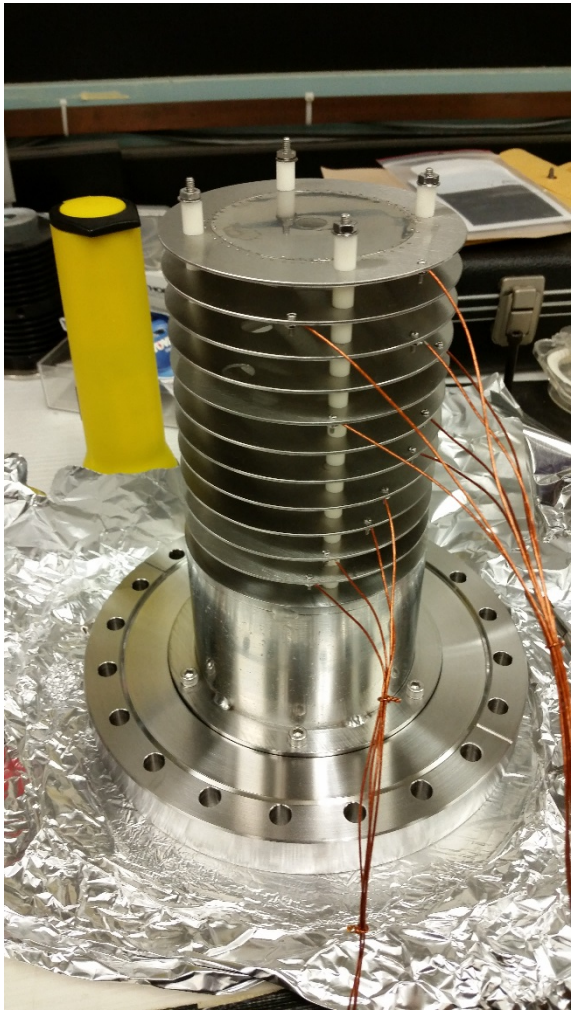
Conclusions

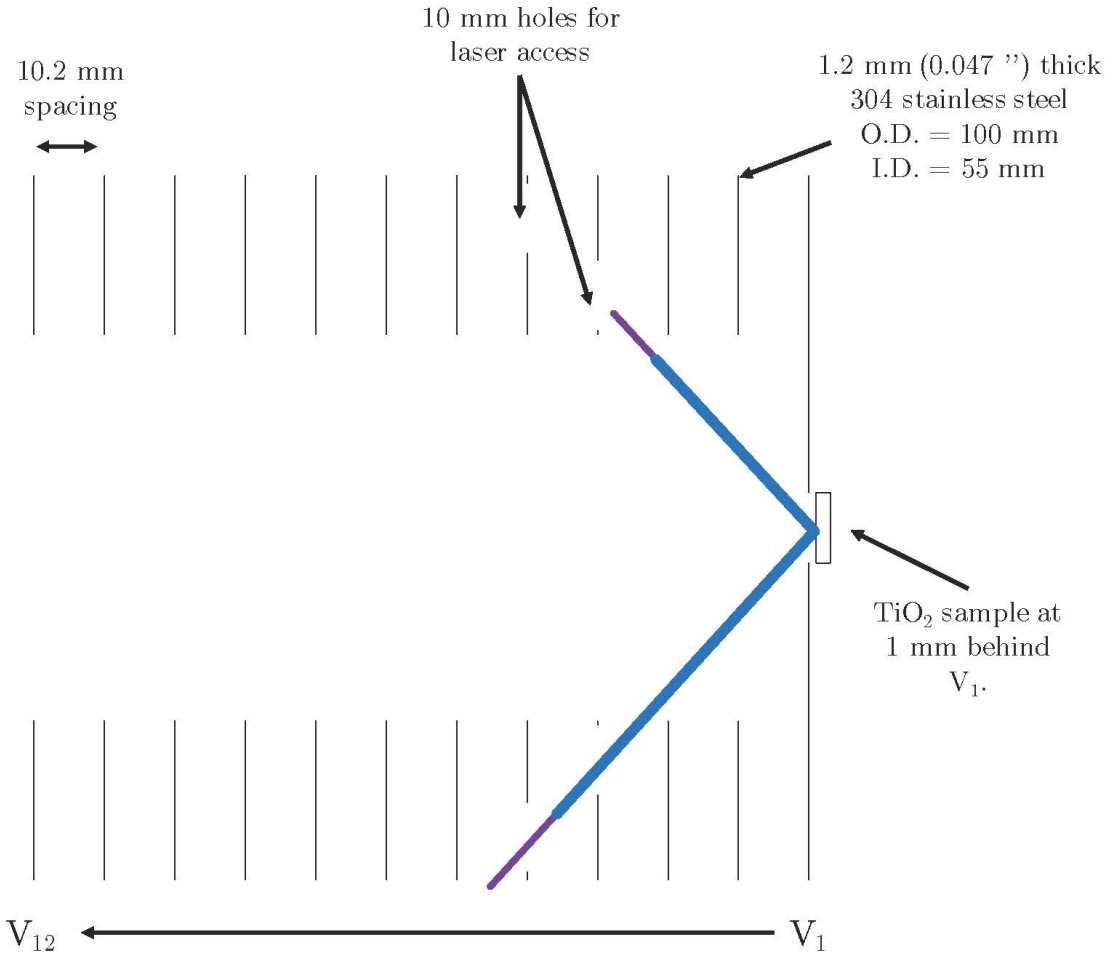
- Successful demonstration of novel imaging technique for mechanistic surface photochemistry
  - results consistent with previous studies – ethyl radical primary product for butanone photooxidation
  - presents significant time savings over conventional pump-probe techniques



Current/Future work

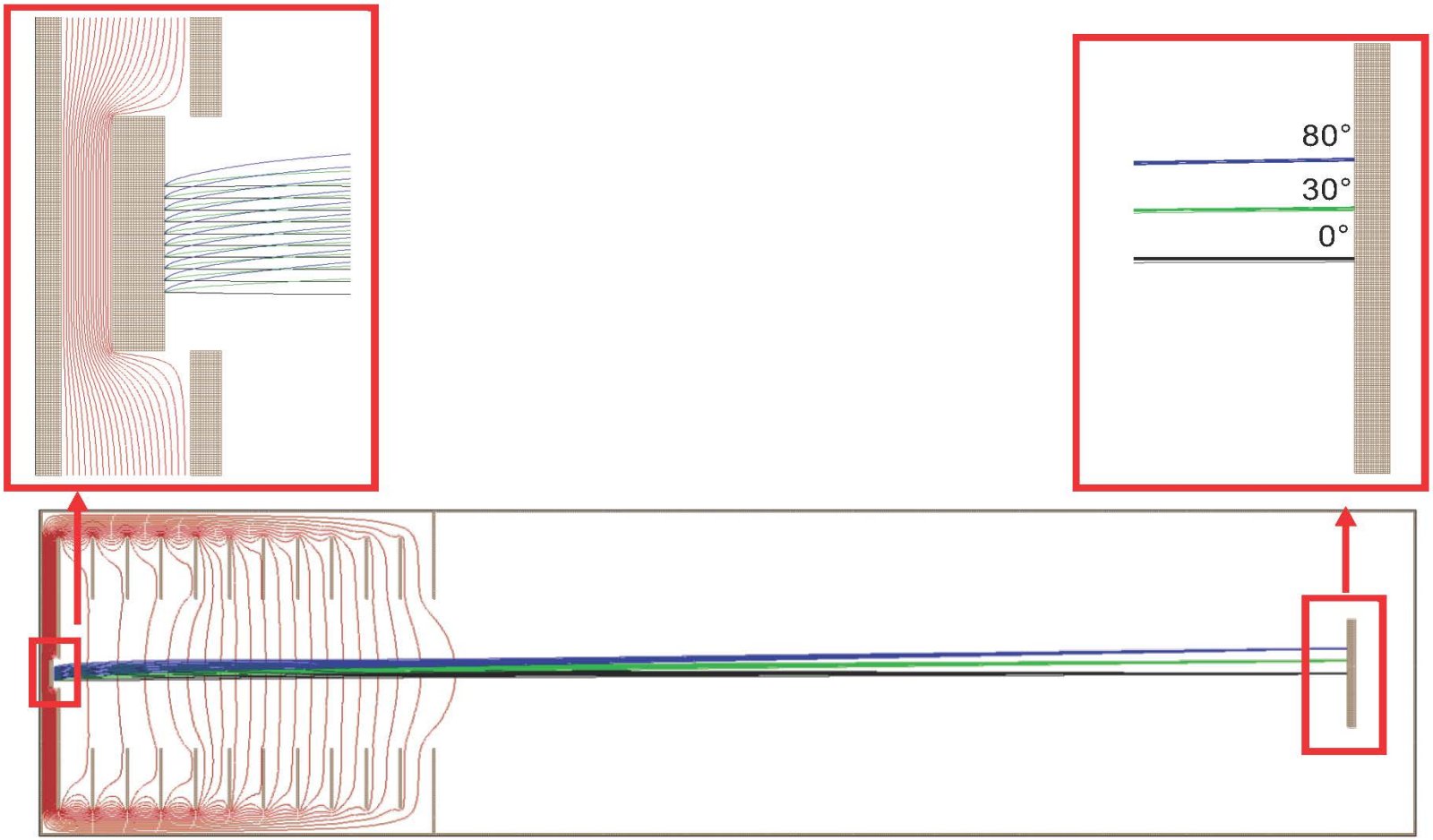
- Built new TOF-MS/VMI detector for femtosecond studies of surface reaction dynamics
  - Want to study reaction dynamics in “real-time”
  - Co-linear pump-probe scheme – ionize products at surface, as they’re made





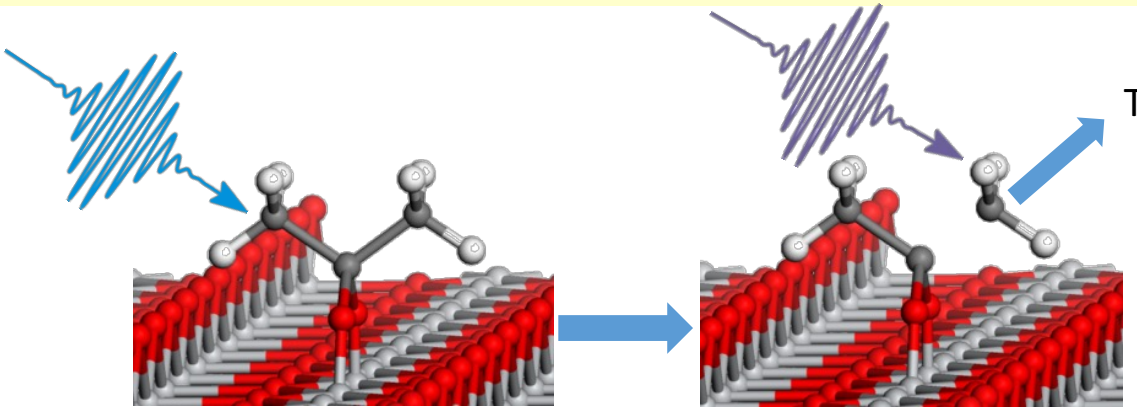
Detector performance:
SIMION Calculations

- Ions flown at various initial trajectories, each group focused to same point regardless of initial position on surface
- Angular acceptance greatly improved over previous design



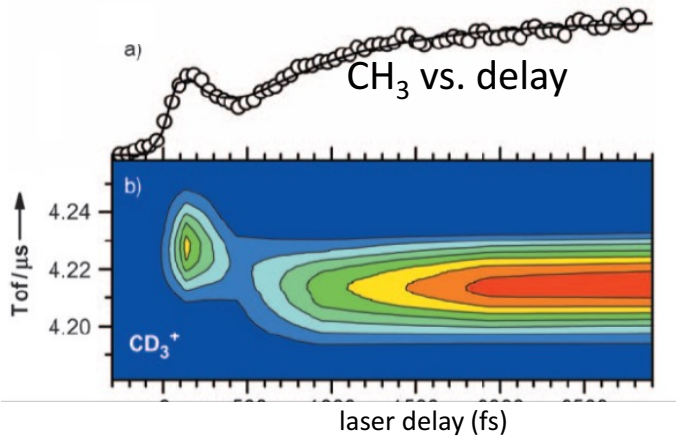
Time-Resolved Studies of Photocatalysis

Use ultrafast lasers to follow excitation and fragmentation processes in real time



Photoexcite surface with "pump" pulse create electron hole pairs

Electron transfer leads to fragmentation
Ionize ejected fragment as it leaves surface

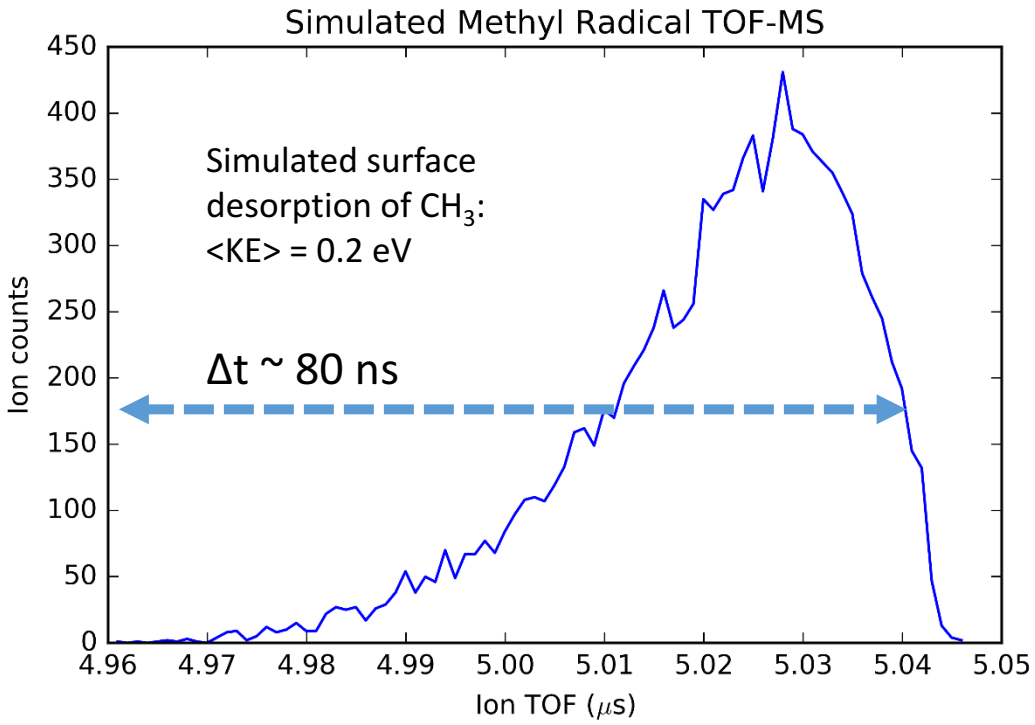


Correlation of methyl evolution time and KE

Vaida & Bernhardt, *Rev. Sci. Instrum.* **81**,104103 (2010); *CPPC* **804**, 11 (2010)

Imaging requirements

- Kinetic energy – from TOF profiles (requires detector modeling in SIMION)
- New detector – mass peaks in 80 ns window
- Would like camera timing resolution pushed to ~1 – 5 ns.



Summary

- Hope to extend studies of surface-mediated reactions using TimePixCam and femtosecond laser techniques
- “Ultimate Experiment”:
  - Kinetic energy – from TOF profiles (requires detector modeling in SIMION)
  - Images – angular distributions as discussed previously (but greater acceptance angles)
  - Relate to ultrafast evolution of photoproducts - comprehensive picture of reaction dynamics