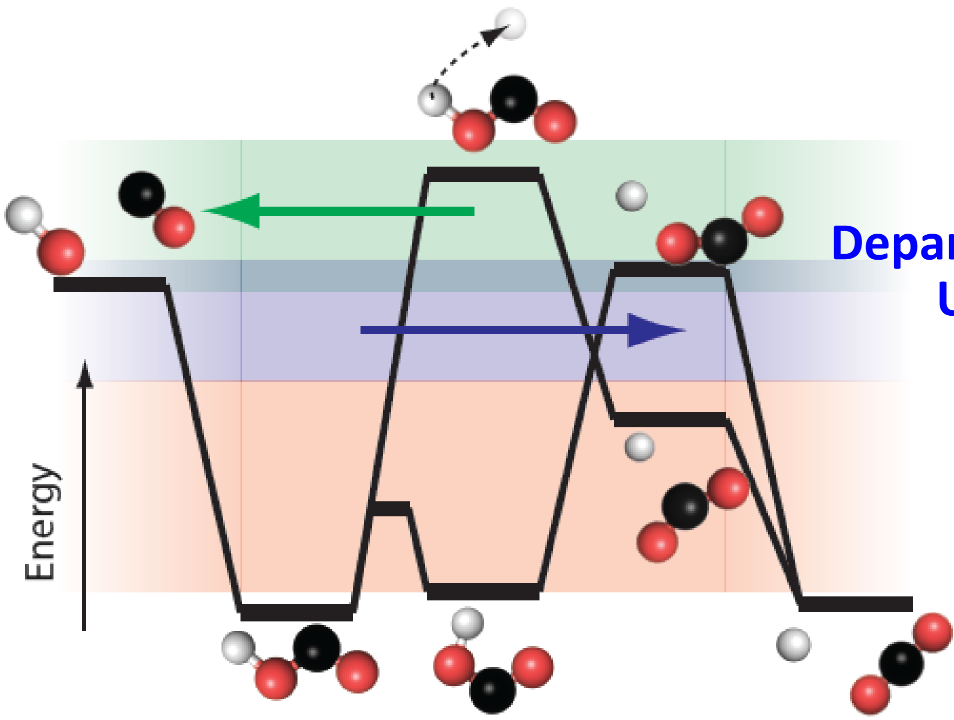
Electrostatic Ion Beam Trap for the Study of Molecular Reaction Dynamics



ROBERT E. CONTINETTI

Department of Chemistry and Biochemistry
University of California San Diego

Fundamental Interactions with Atom and Ion Traps
Weizmann Institute, December 3, 2012

University of California San Diego

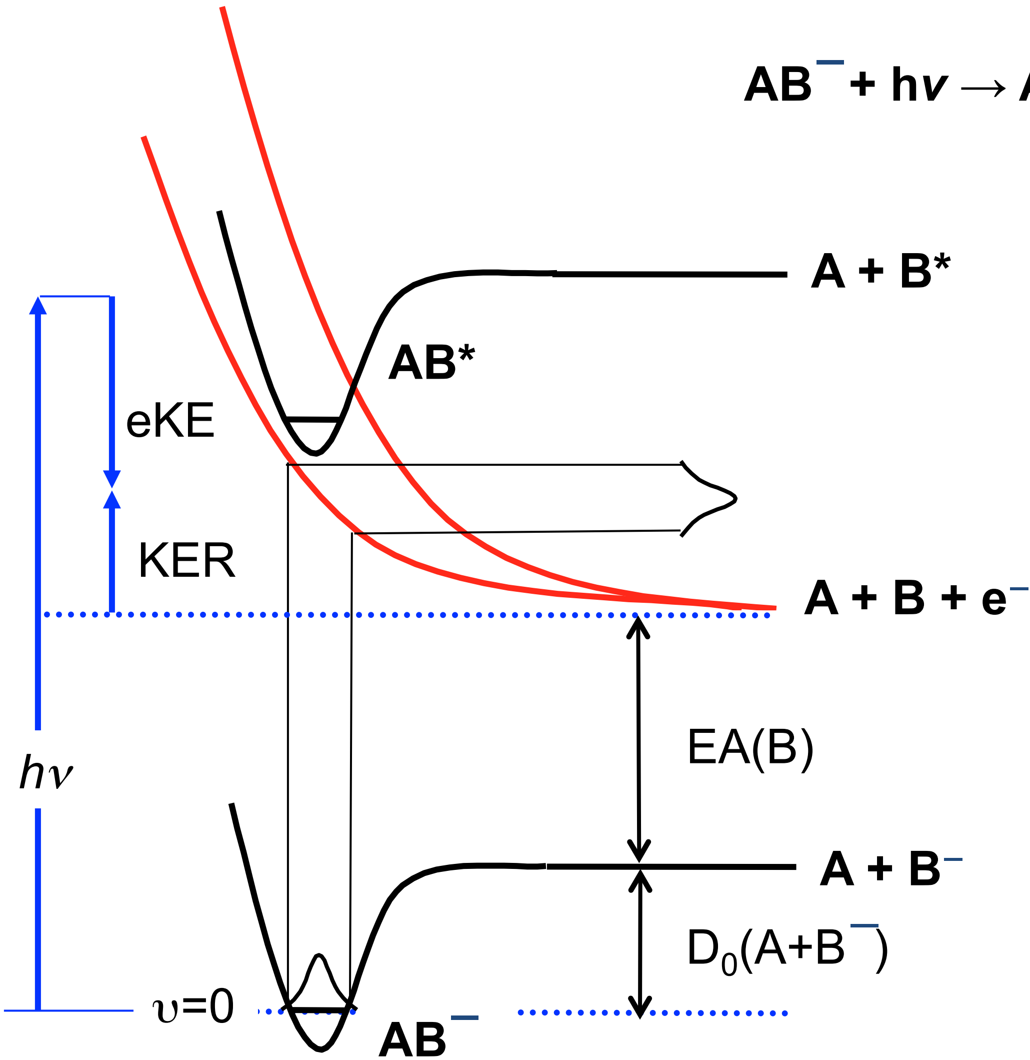
Overview

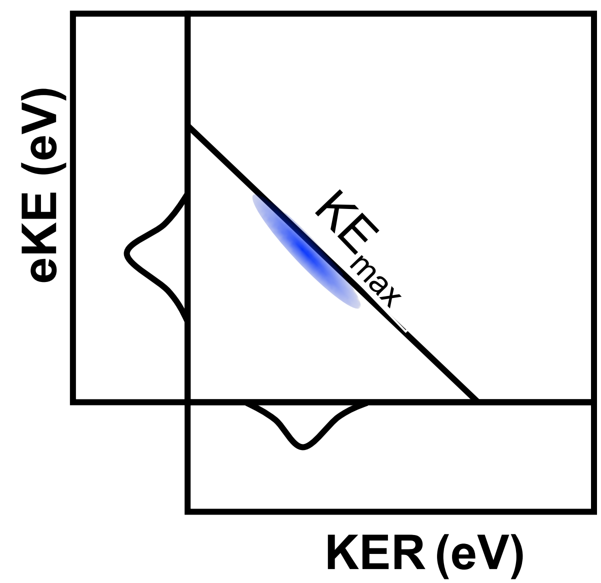
- Dissociative Photodetachment – Probing Transient Neutrals using Coincidence Spectroscopy
- Photoelectron-Photofragment Coincidence – O_4^-
- Experimental Techniques – Electrostatic Ion Beam Trap
- $HOCO^-$, HOCO and the OH + CO → H + CO_2 reaction
- Photoelectron Spectroscopy
    - Electron Affinities and Vibrational Spectra of HOCO
- Experimental determination of the tunneling barrier
    - HOCO/DOCO → H/D + CO_2
- Future

Neutralization Probes of Dissociative States

Direct Dissociative Photodetachment (DPD)

$$AB^{-} + h\nu \rightarrow A + B + e^{-}$$





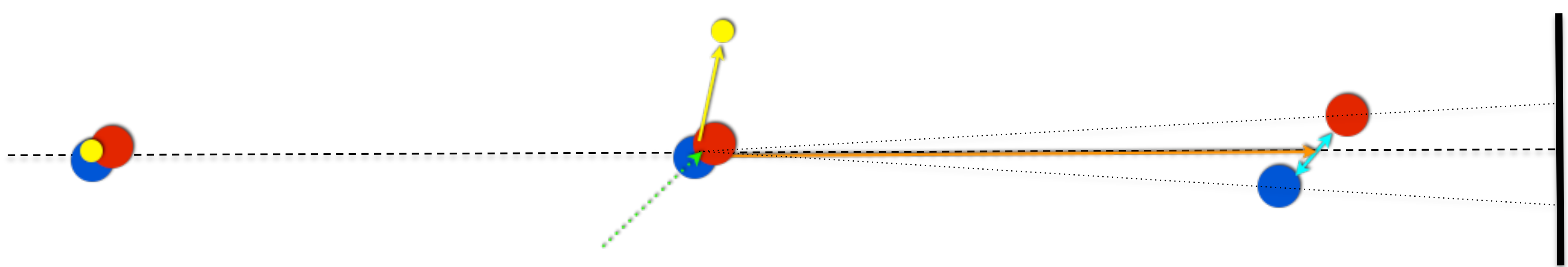
Photoelectron-photofragment coincidence (PPC) spectrum

$$KE_{max} = eKE + KER$$

Photoelectron-Photofragment Coincidence Experiments

- Create precursor anion of interest
- Detach a single electron, collect it and resulting neutral fragments in coincidence (Dissociative Photodetachment)
- Full kinematic measurement of dissociation event

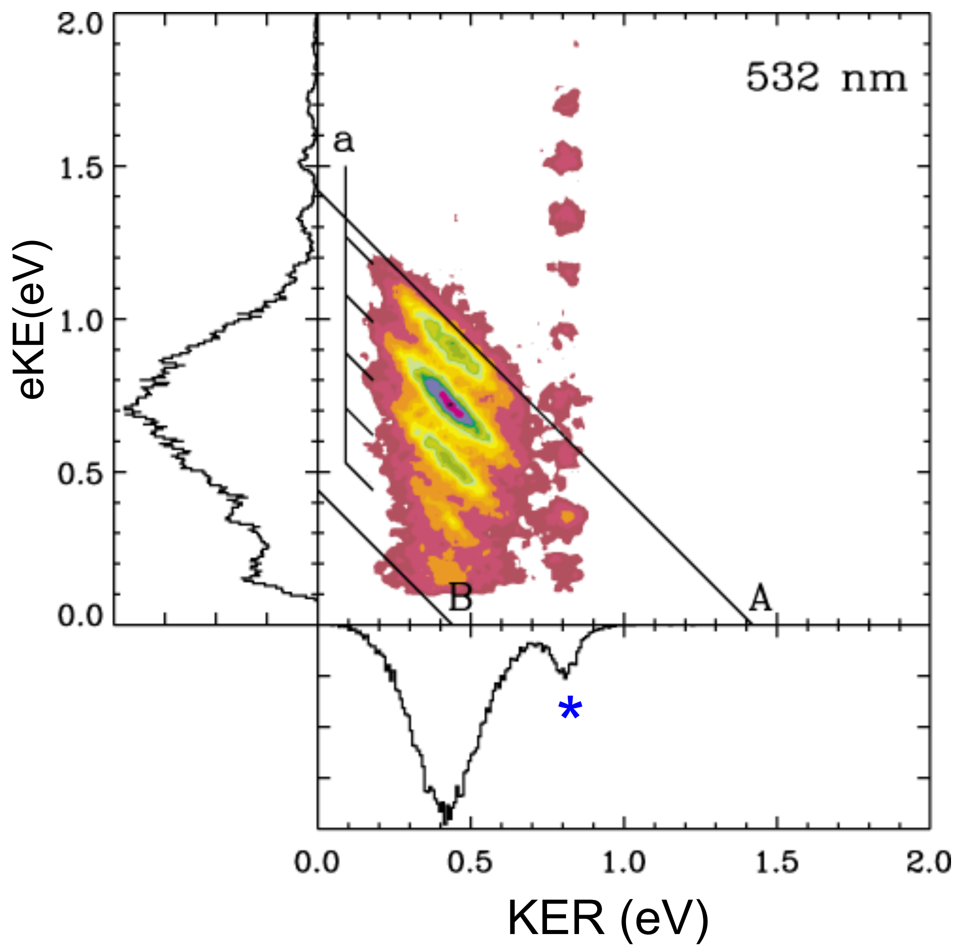
$$AB^- + h\nu \rightarrow A(KER) + B(KER) + e^-(eKE)$$



Dissociative Photodetachment of O_4^-

$O_4^- + h\nu \rightarrow O_2\,(^3\Sigma_g^-) + O_2\,(^3\Sigma_g^-) + e^-$ ***532 nm (2.33 eV)***

$^*O_4^- + h\nu \rightarrow O_2^-\,(^2\Pi_g) + O_2\,(^1\Delta_g)$



PPC Spectrum

Diagonal bands:

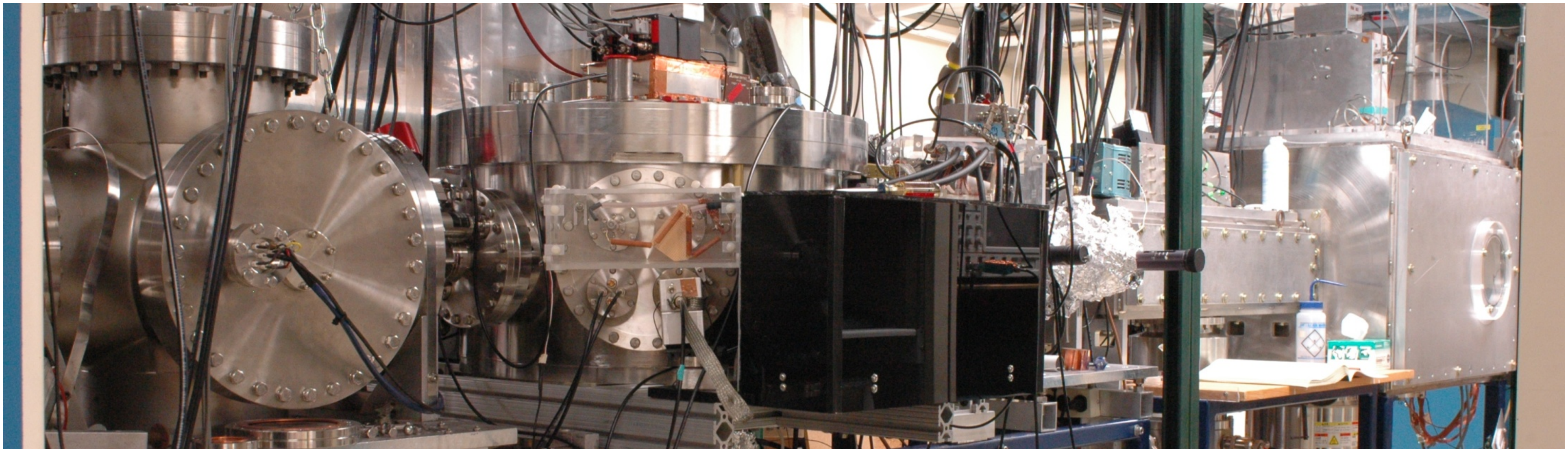
O_2 product vibrations
Low rotational excitation

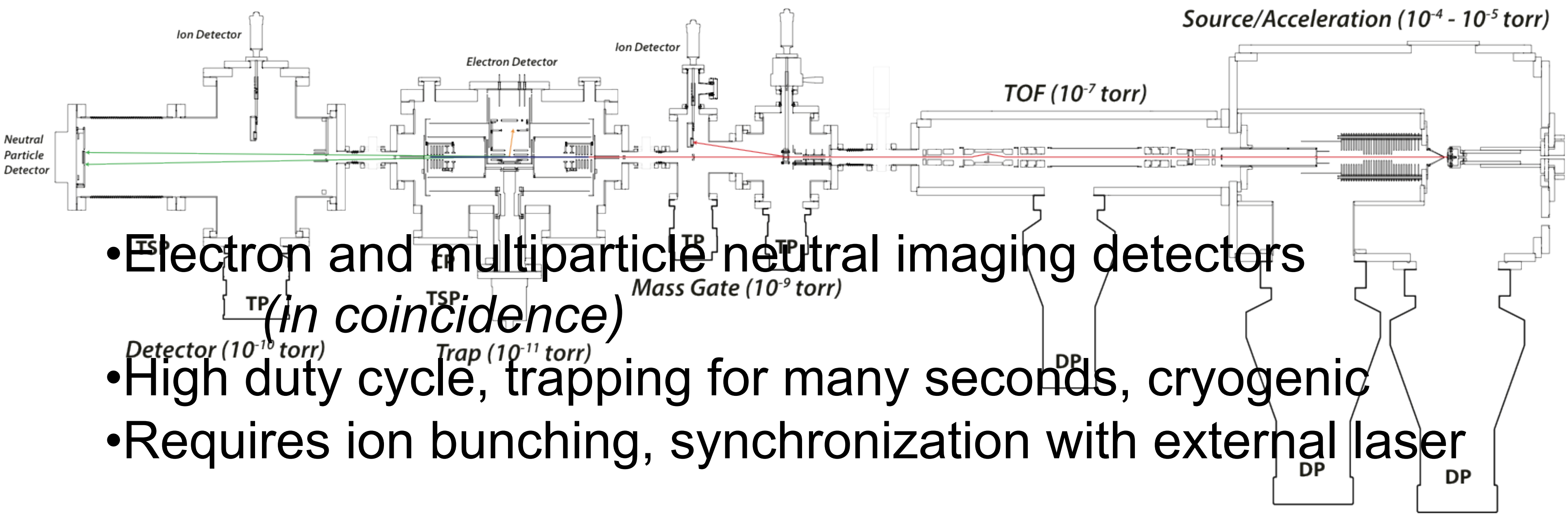
Vertical Spots:

2-photon signal – Photodissociation followed by Photodetachment

Hanold, Garner and Continetti
Phys. Rev. Lett. **77**, 3335 (1996)

Photoelectron-Photofragment Coincidence Spectrometer



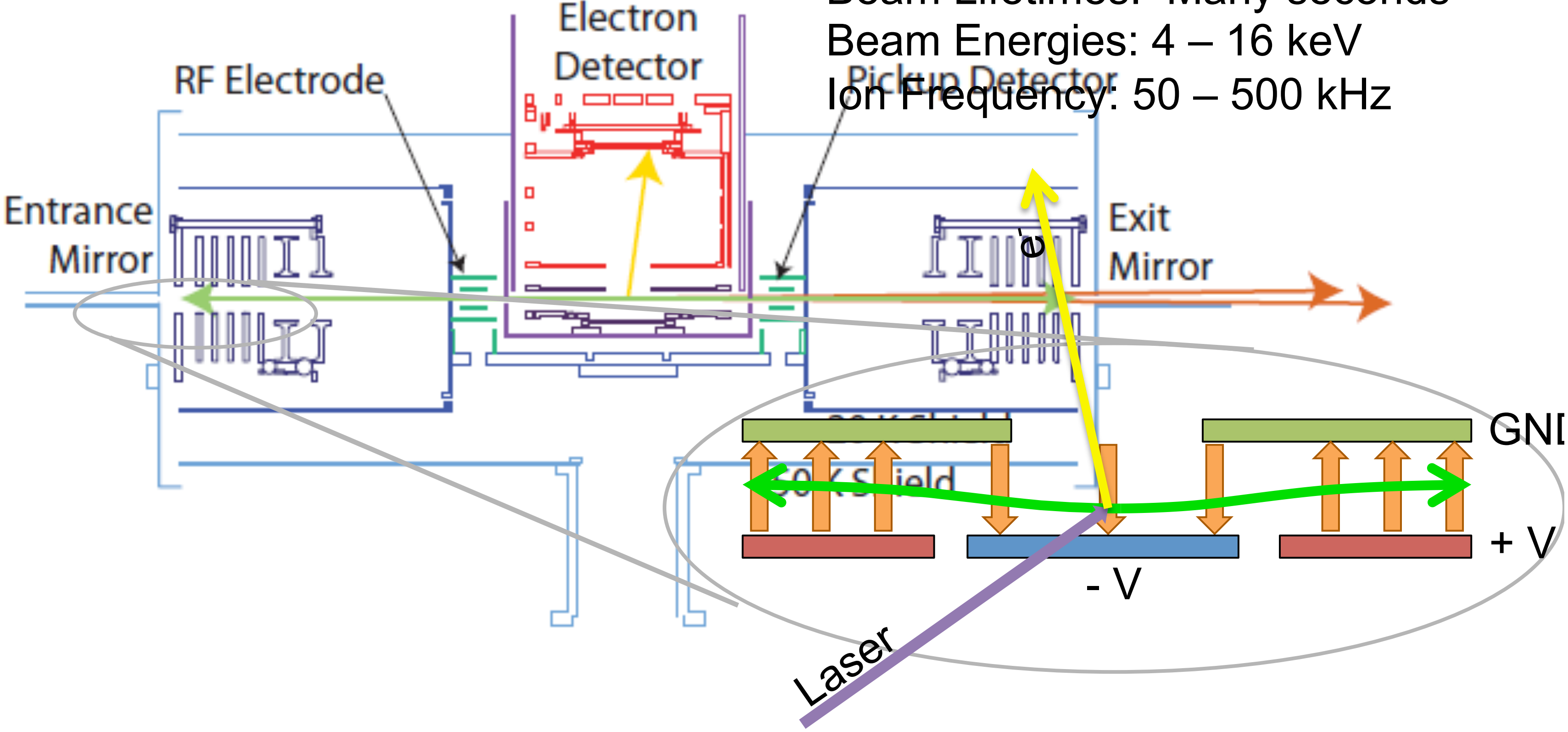


- Electron and multiparticle neutral imaging detectors *(in coincidence)*
- High duty cycle, trapping for many seconds, cryogenic
- Requires ion bunching, synchronization with external laser

Linear Electrostatic Ion Beam Trap

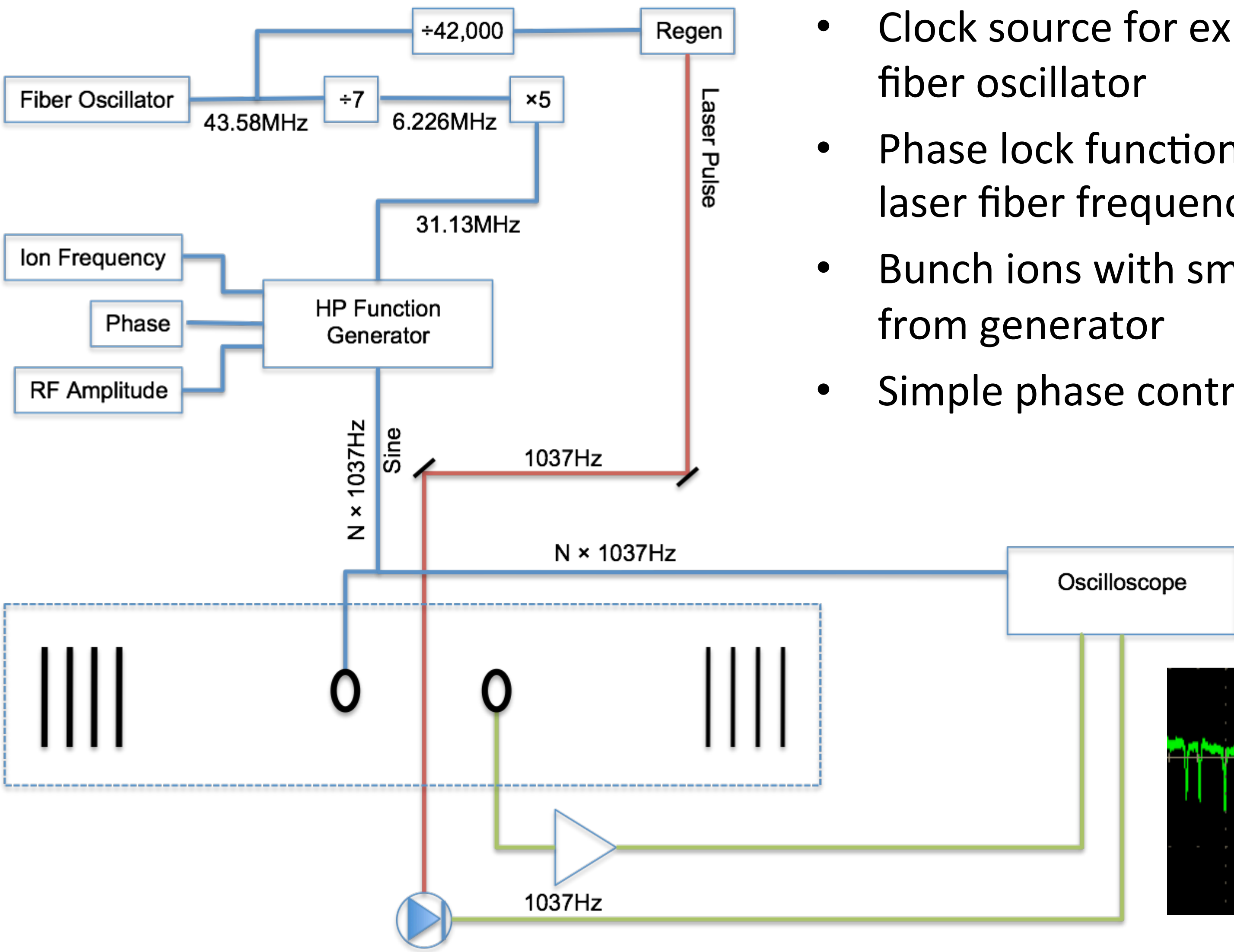
Zajfman and co-workers (1997)

Beam Environment: ~ 20 K
Background Pressure: ~ 10^{-11} torr
Beam Lifetimes: Many seconds
Beam Energies: 4 – 16 keV
Ion Frequency: 50 – 500 kHz

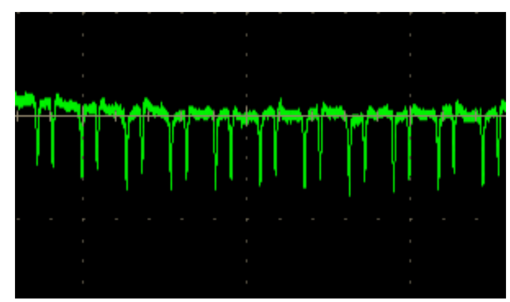


C.J. Johnson *et al.*, Rev. Sci. Instrum. **82**, 105105 (2011)

Ion Bunching and Synchronization

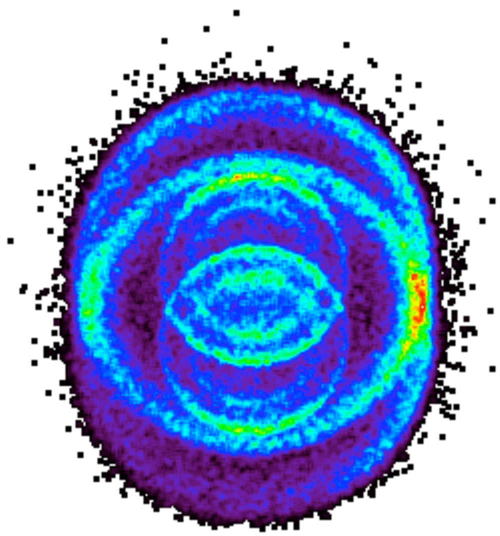


- Clock source for experiment is laser fiber oscillator
- Phase lock function generator to laser fiber frequency
- Bunch ions with small RF voltage from generator
- Simple phase control

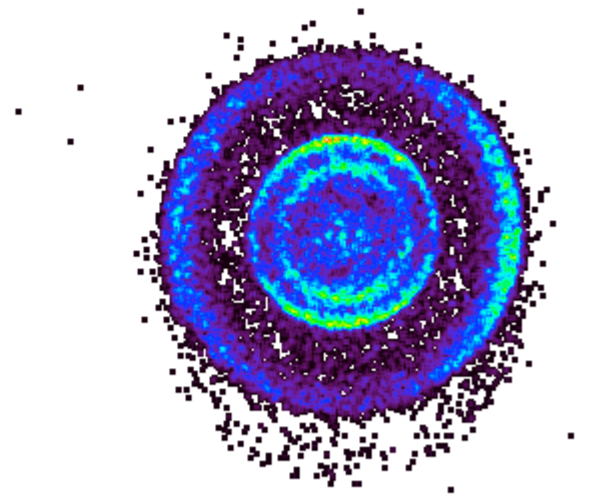


Ion Bunching and Synchronization

Fast Beam – Significant Photoelectron 'Doppler' Effect
Vinoxide – $C_2H_3O^-$ photodetached at with 3.2 eV photons



Unbunched – Doppler Shift
(Multi-mass experiments)

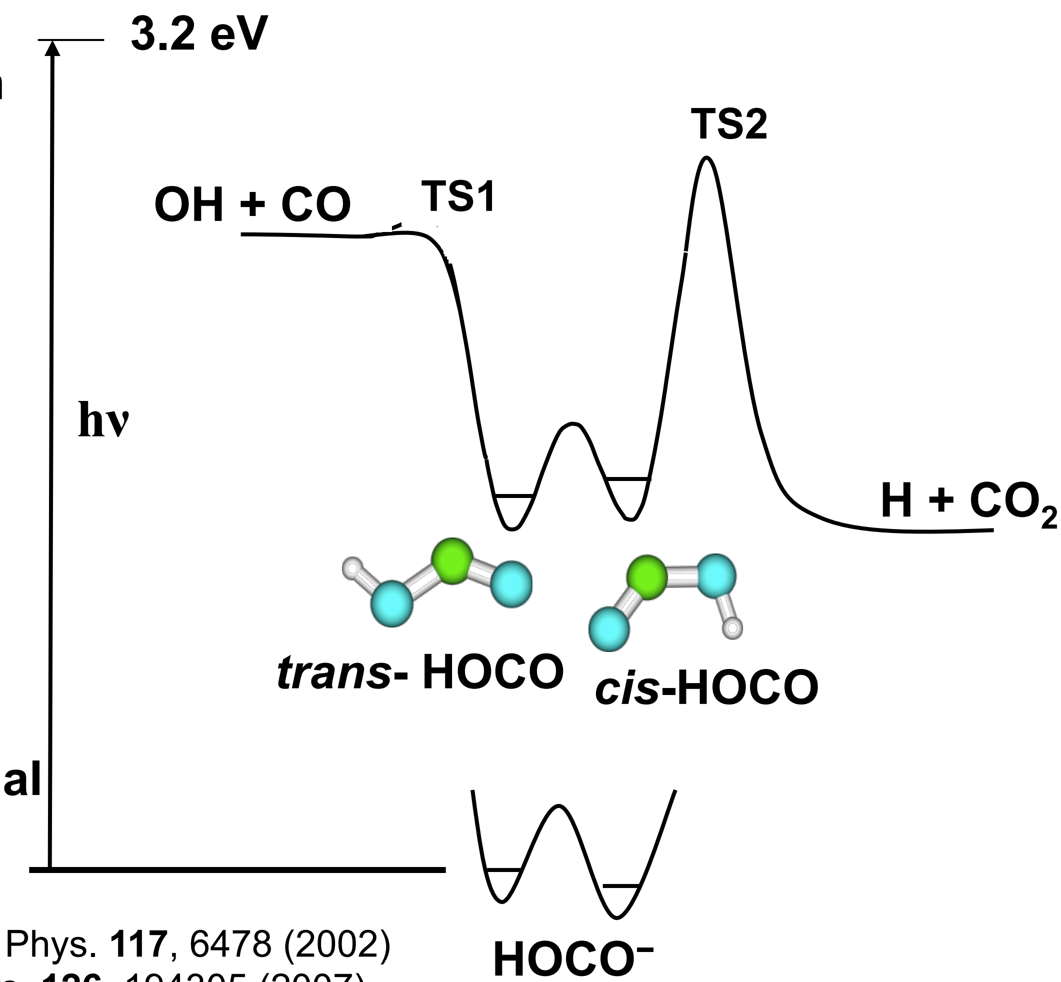


Bunched and phase-locked to laser

Neutral particle coincidence can be used to clean-up unbunched mode
(with a loss of duty cycle)

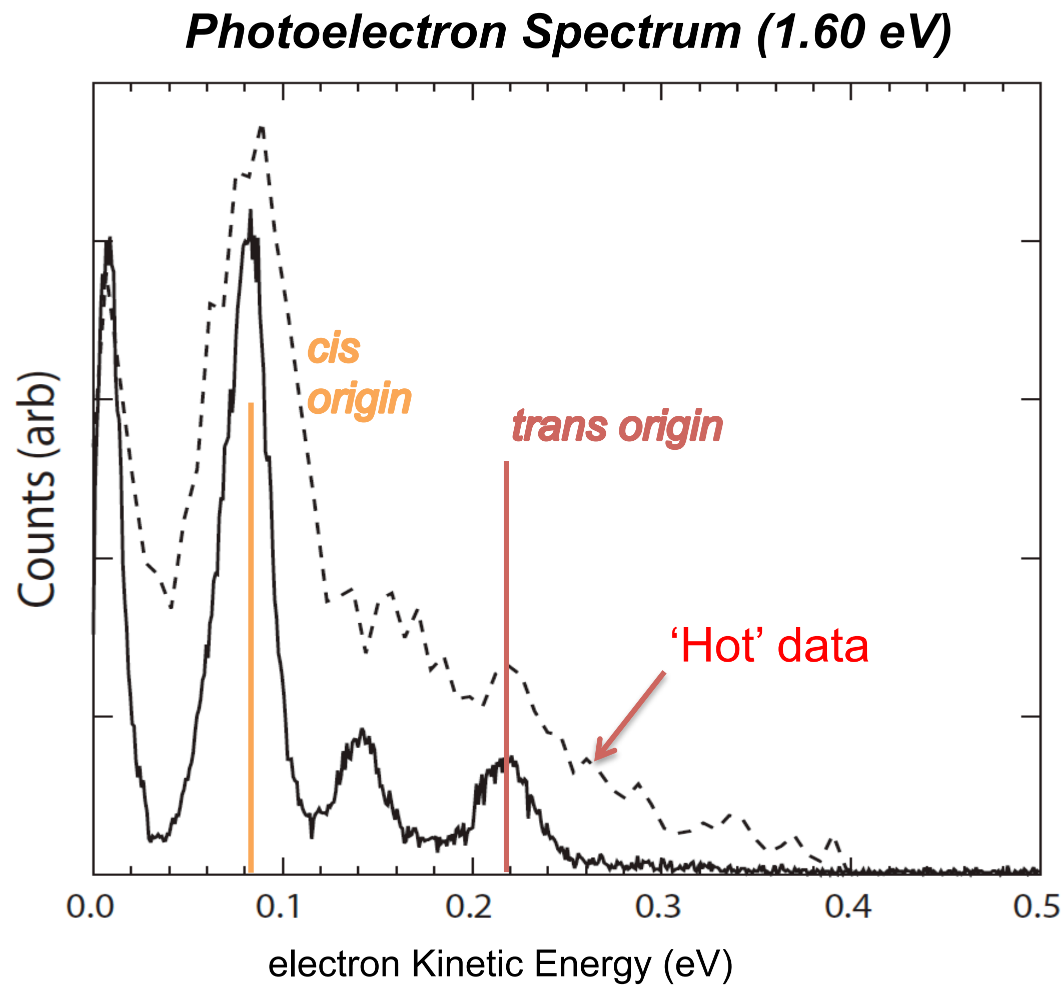
OH + CO → HOCO → H + CO_2*

- **Important source of heat in hydrocarbon combustion.**
- **Mediates CO, CO_2, and OH concentrations in lower atmosphere.**
- **Kinetics, spectroscopy, quantum chemistry and dynamics studies**
- **Previous studies: Sequential DPD of $HOCO^-$**



Clements, Continetti, Francisco, J. Chem. Phys. **117**, 6478 (2002)
Lu, Hu, Oakman, Continetti, J. Chem. Phys. **126**, 194305 (2007)
Lu, Oakman, Hu, Continetti, Mol. Phys. **106**, 595 (2008)

Cold, Vibrationally Resolved Photoelectron Spectra



'Hot' data: Lu and Continetti, PRL **99**, 113005 (2007)

Revised adiabatic electron affinities (AEA's) [(2)]

cis-HOCO: 1.43 eV[(1)] → 1.51 eV

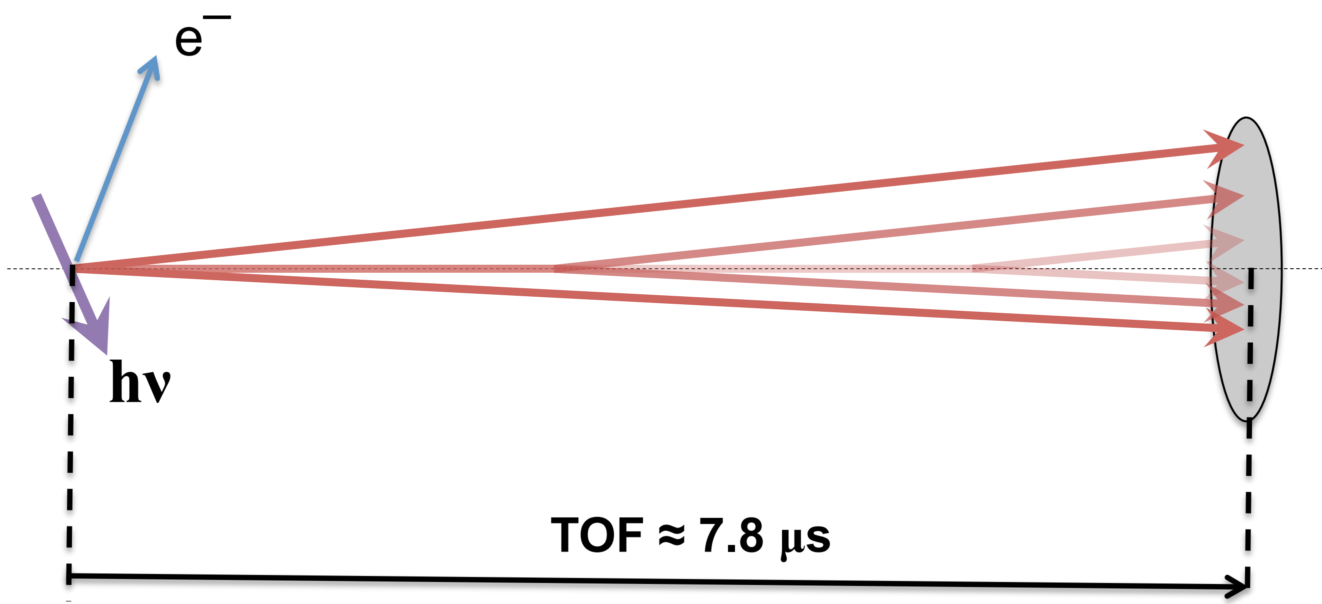
trans-HOCO: 1.30 eV[(1)] → 1.37 eV

(1) Clements, Continetti and Francisco 2002
CCSD(T) / 6-311++G(3df,3pd)

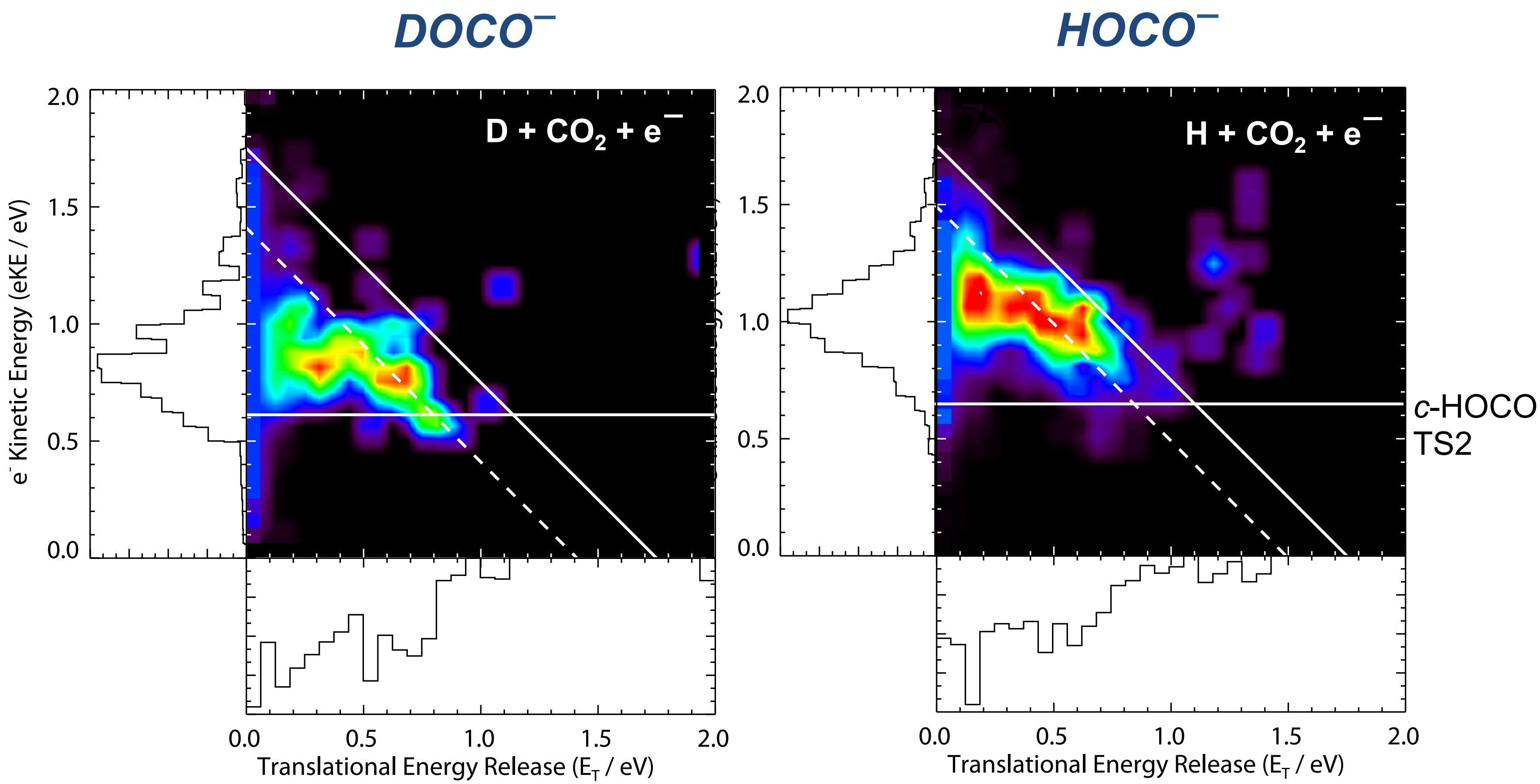
(2) Harding and Stanton – HEAT procedure
CCSD(T) / ANO basis set

Photoelectron-Photofragment Coincidence Spectroscopy

- ***Record photoelectron spectra in coincidence with stable HOCO ; H + CO_2 ; OH + CO***

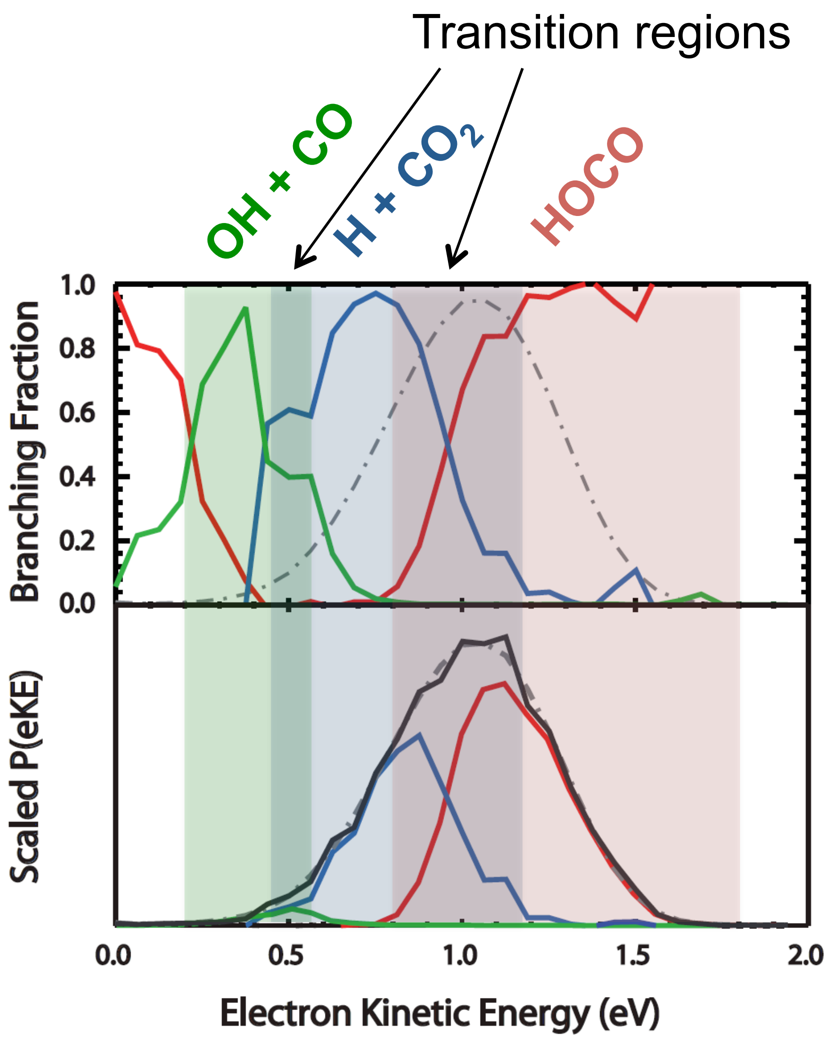


Isotope Effects – Tunneling Below the Barrier

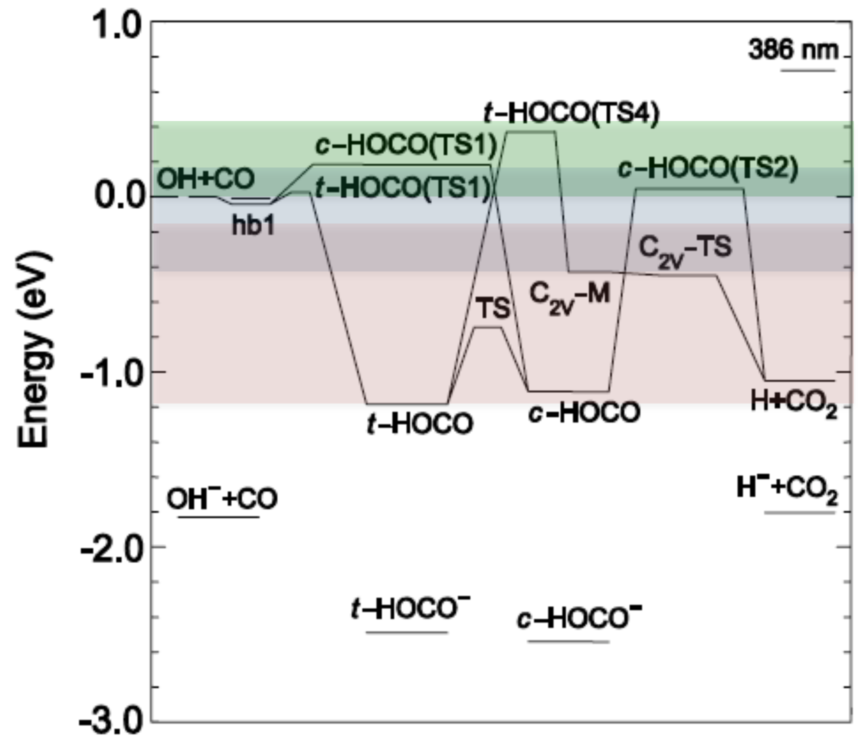


- Turnover towards $E_T = 0$ – onset of long-lived HOCO/DOCO radicals
- Tunneling rate drops dramatically in DOCO: ≈ 0.2 eV higher in the well
- $E_{int} \approx 0.2 - 0.3$ eV

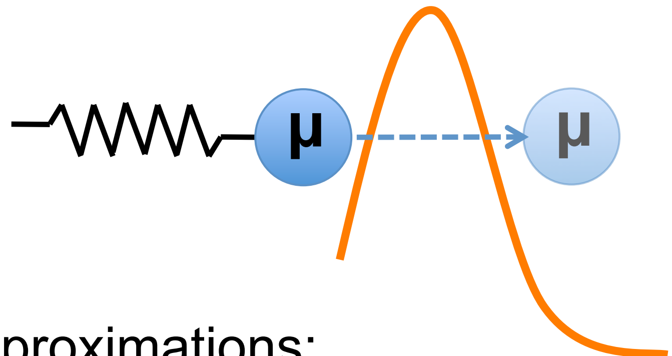
Product Branching Fractions



- Processes occurring over > 6 orders of magnitude of time
- Extract lifetimes as a function of E_{int}?



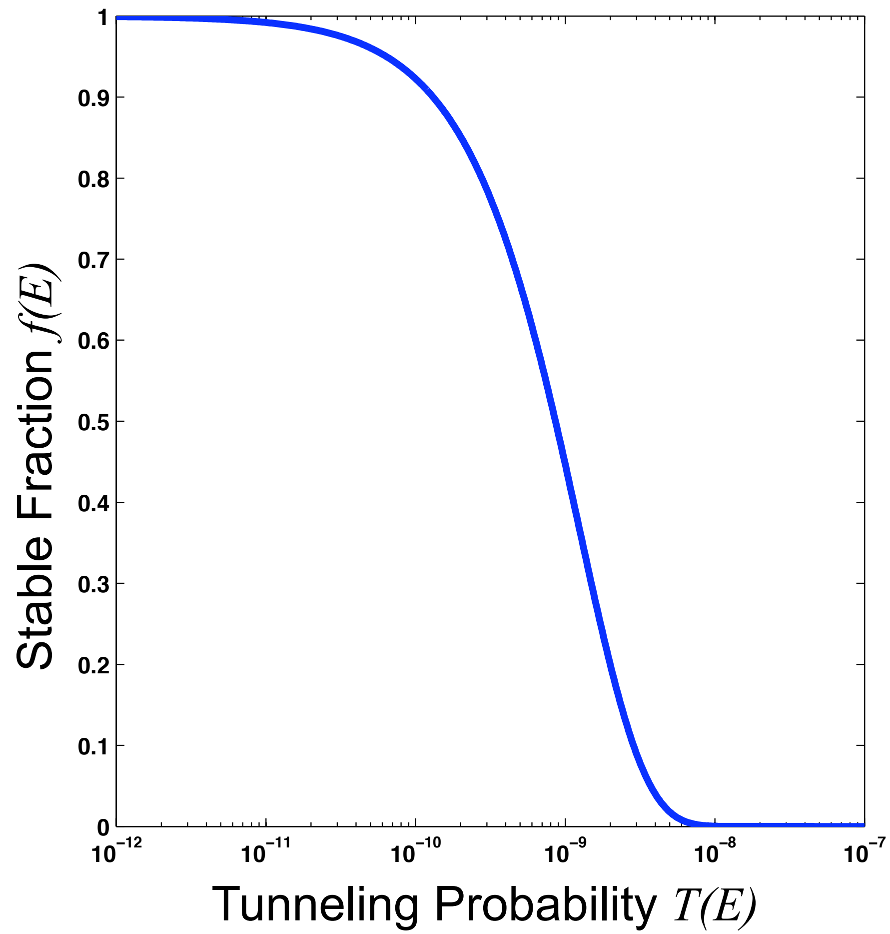
Model for Tunneling HOCO → H + CO_2



Approximations:

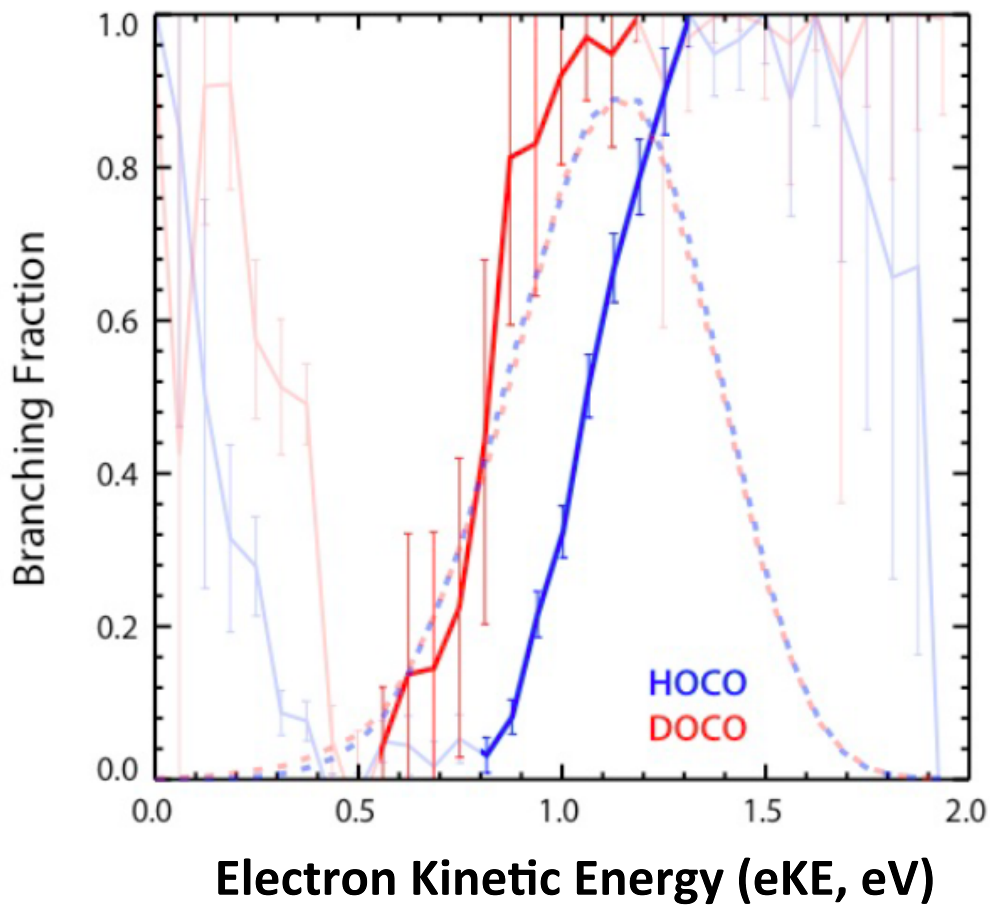
- Reaction coordinate
  simple harmonic oscillator
  H-OCO   D-OCO
- 1 dimensional dynamics
- *f(E)* – stable fraction
- N = ω_{OH} x *TOF*

$$f(E) = (1 - T(E))^N$$



Semiclassical Tunneling Model

$f(E_{int})$



$E_{int} = E_{h\nu} - EA - eKE$

$$f(E_{int}) = (1 - T(E_{int}))^N \qquad N = \omega_{OH}\, x\, TOF$$

Generating a Model Potential

Two interacting states

$$V_{a,b}(r) = \frac{V_1(r) + V_2(r)}{2} \pm \sqrt{\left(\frac{V_1(r) - V_2(r)}{2}\right)^2 + H_{12}(r)^2}$$

Adiabatic curve generated by a 'predissociated' Morse oscillator

$$V_1^0(r) = D_e\left[1 - \exp\{-\alpha(r - r_e)\}\right]$$

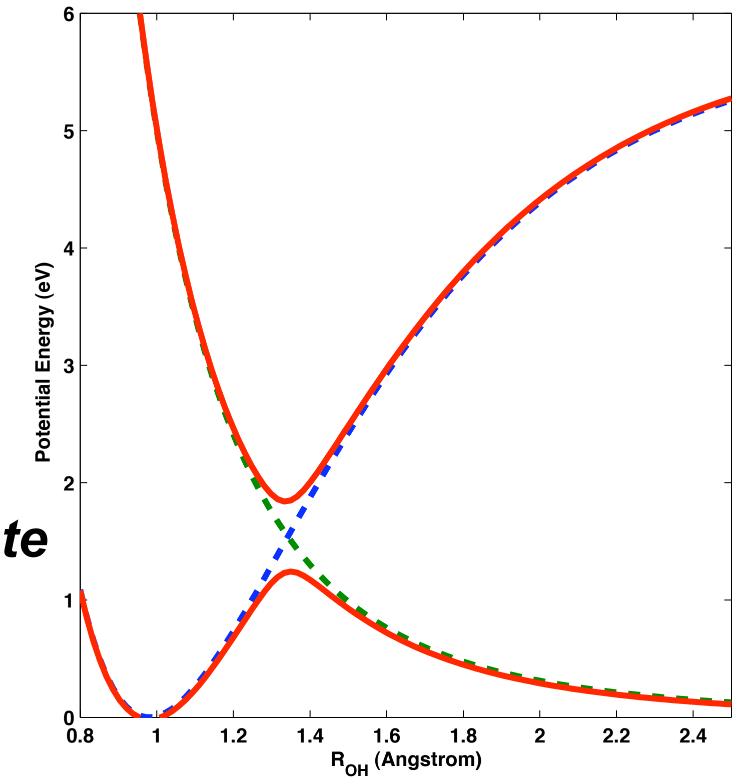
$$V_2^0(r) = Ar^{-n}$$

$$H_{12}(r) = H_{12}^0 \exp\{-a|r - r_c|\}$$

Fix Morse well-depth D_e and r_e

D_e: dissociation to H + CO_2 A($^1B_2$) state (5.70 eV)

r_e: 0.98 Å (CCSD/aug-cc-pVTZ)



Semiclassical Tunneling Model – WKB Approximation

Use WKB approximation - Works for arbitrary potentials V(r)

$$T(E_{int}) \approx \exp\left\{-2\int_{r_1(E_{diss})}^{r_2(E_{diss})} \sqrt{\frac{2\mu}{\hbar^2}(V(r) - E_{diss})}\,\mathrm{d}r\right\}$$

Not all internal energy is along the H-OCO reaction coordinate

- ***Assume reaction promoted by vibration in H-OCO***
- ***Include some fraction of residual internal energy (quasi – 1D)***

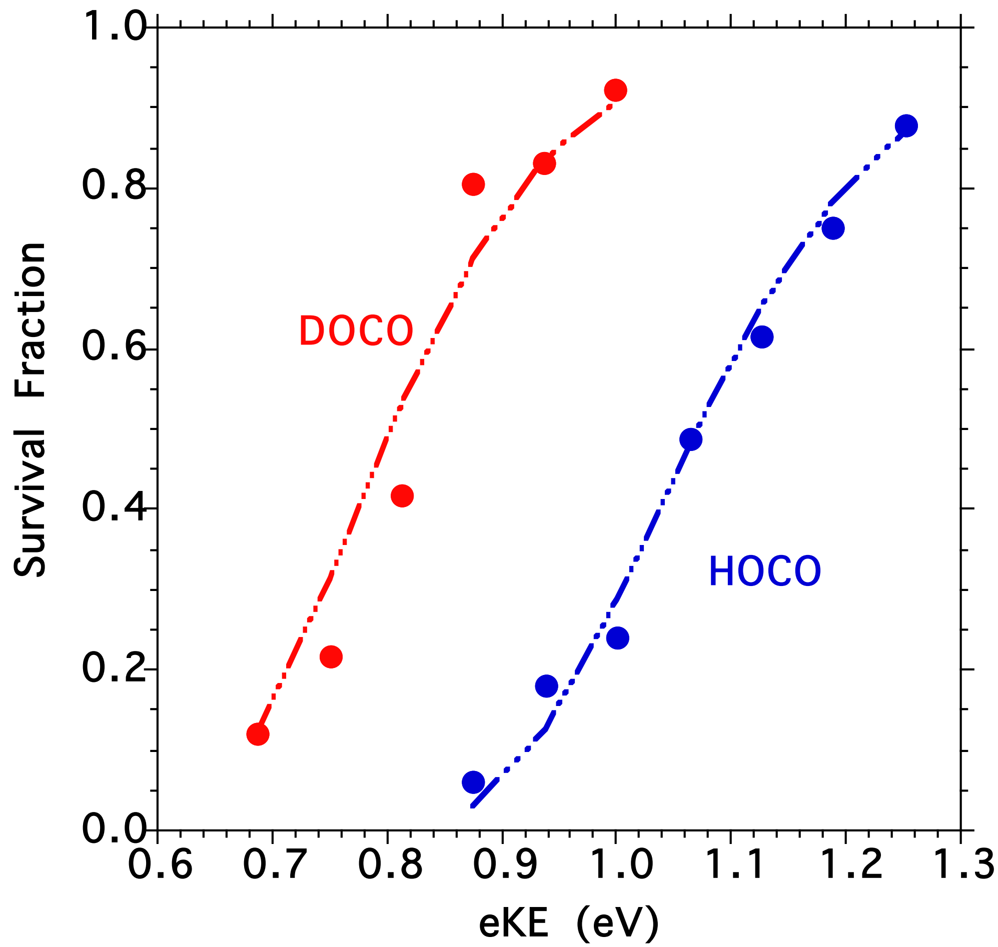
$$E_{diss} = (v_{max} + 1/2)\,h\nu_{OH/OD} + \chi\left[E_{int} - (v_{max} + 1/2)\,h\nu_{OH/OD}\right]$$

Equate WKB result to experimental tunneling coefficients - Optimize V(r)

Experiment ***Model***

$$\ln\left[1 - f(E)^{\,\omega_{OH}\, t_{flt}}\right] = -2\int_{r_1(E)}^{r_2(E)} \sqrt{\frac{2\mu}{\hbar^2}(V(r) - E)}\,\mathrm{d}r$$

Tunneling Model Fit to the Experimental Branching Fraction



- v_{max} = 2 for DOCO
- v_{max} = 1 for HOCO

Best Fit Parameters

$a = 0.05\ eV^{-1}$

$\alpha = 1.96$

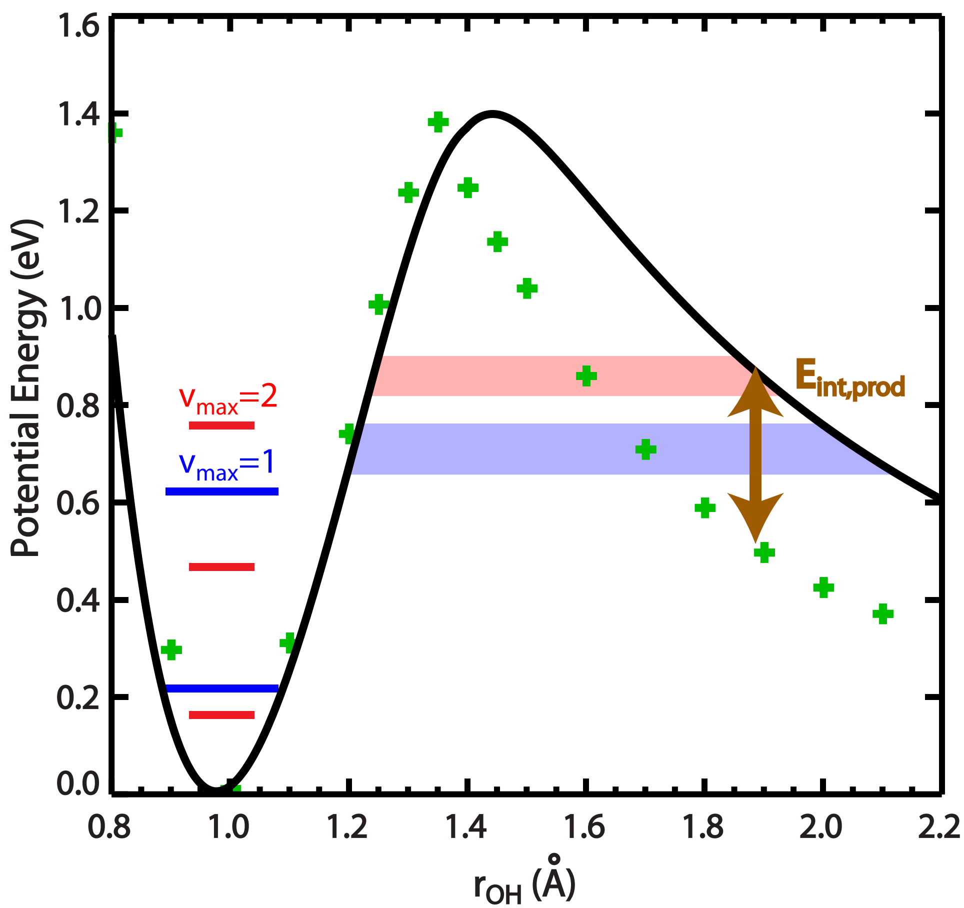
A = 4.02 eV

N = 2.27

$H_{12}^{0} = 0.49$ eV

$\chi = 0.19$

Experimentally Extracted Barrier



- Simultaneous optimization of HOCO and DOCO experimental data
- $E_{int,prod}$ ~0.3 eV predicted, consistent with experiment!

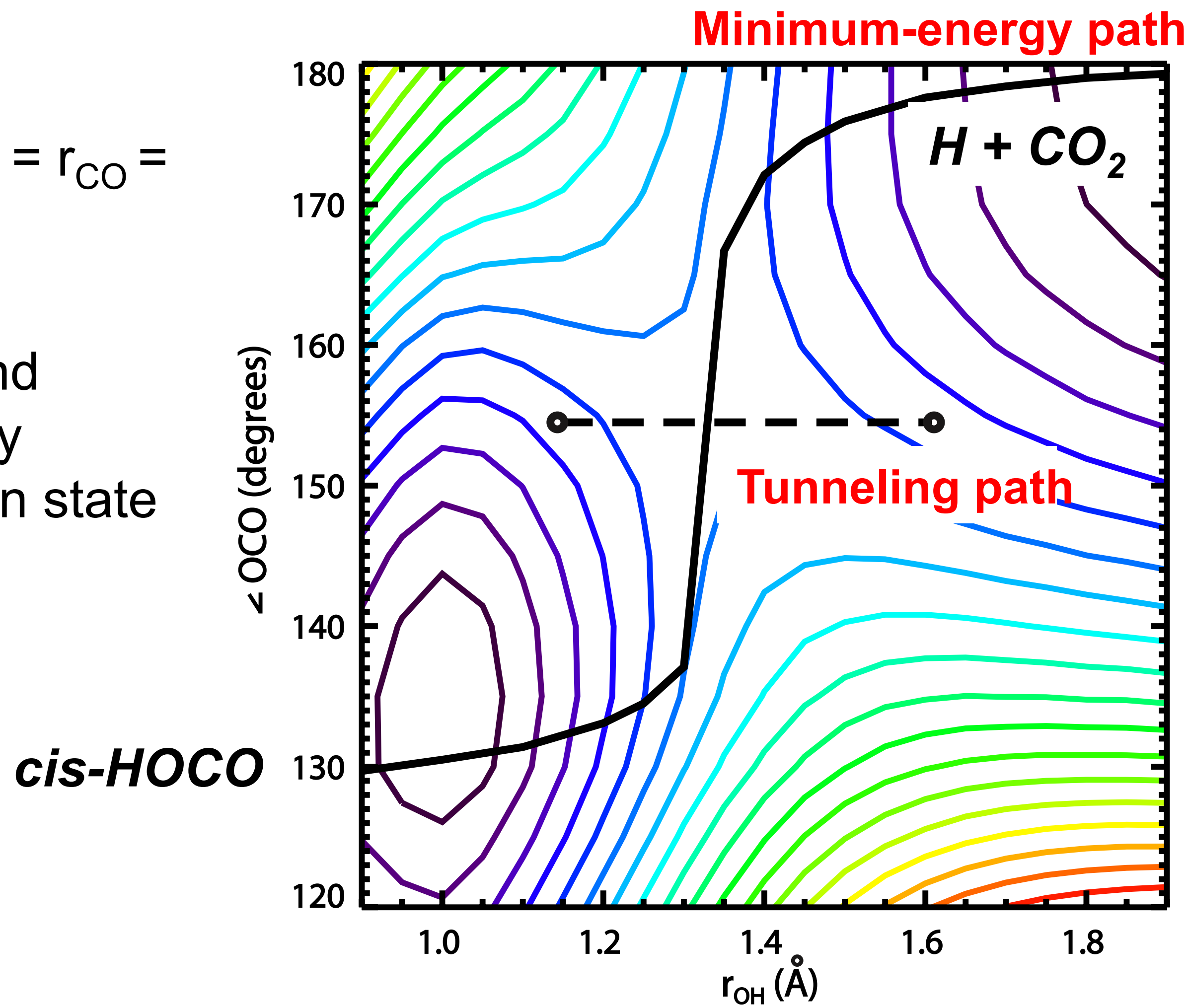
Experimental

Minimum Energy
(Fully relaxed)
CCSD/aug-cc-pVTZ

Johnson *et al.* J. Chem. Phys. **134**, 171106 (2011)

Tunneling Reaction Pathway

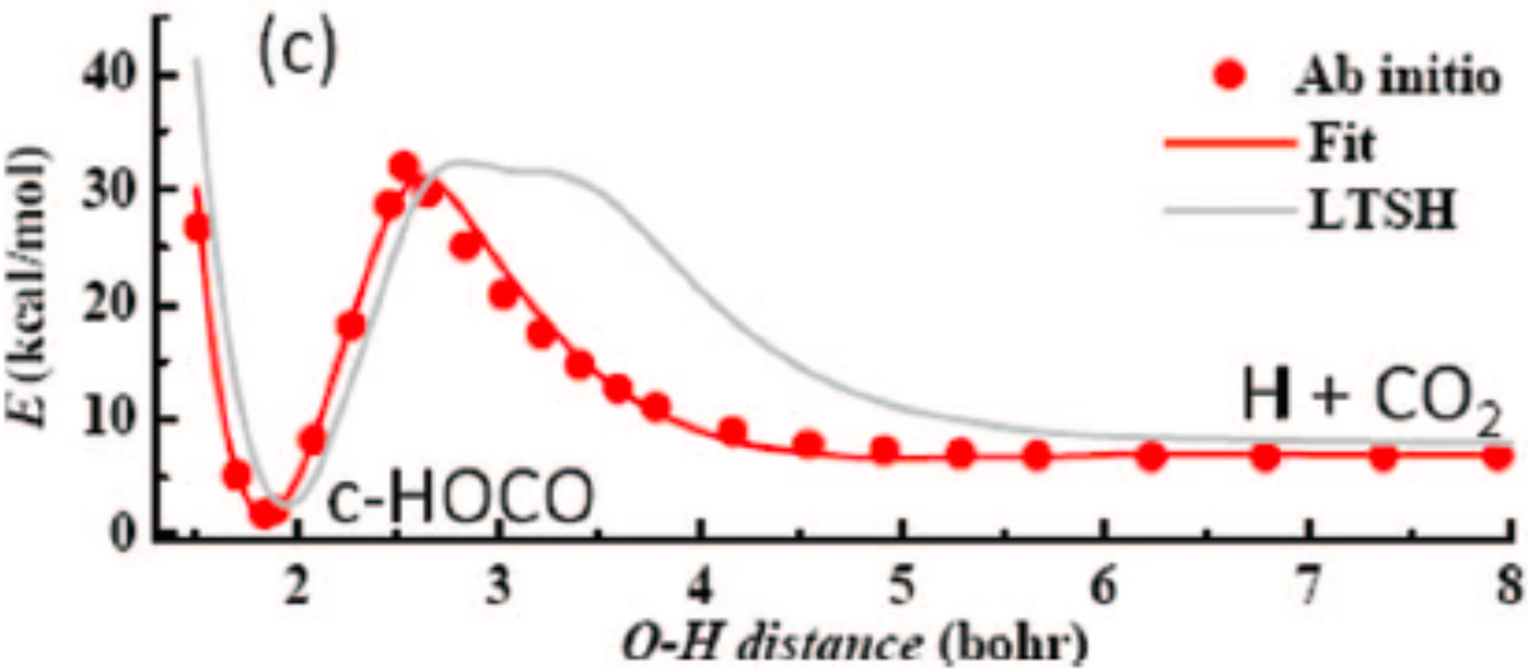
- Slice through PES at $r_{OC} = r_{CO}$ = 1.18 Å
- Minimum energy path and tunneling path essentially orthogonal near transition state



A New Global Potential Energy Surface

Communication: A chemically accurate global potential energy surface for the HO + CO → H + CO_2 reaction

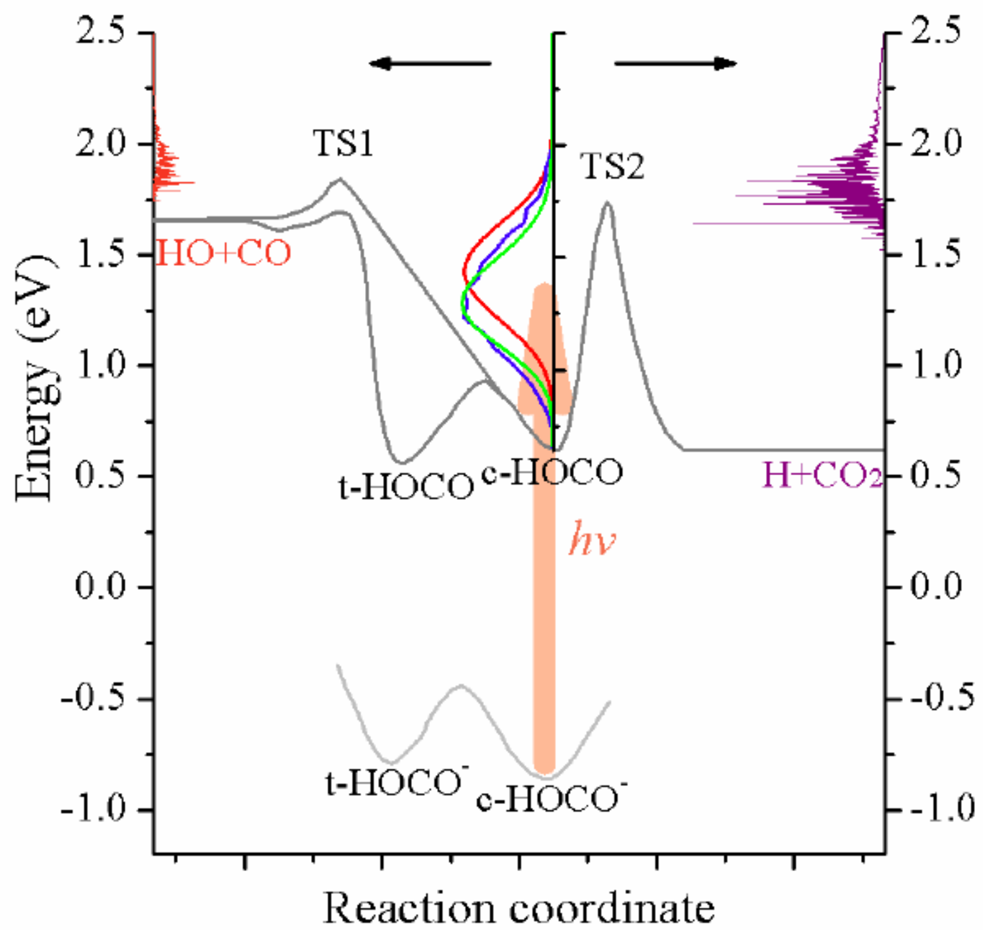
Jun Li,[1] Yimin Wang,[2] Bin Jiang,[3] Jianyi Ma,[1] Richard Dawes,[4] Daiqian Xie,[3]
Joel M. Bowman,[2] and Hua Guo[1,a)]



Fit – CCSD-1/d Potential Energy Surface

J. Chem. Phys. **136**, 041103 (2012)

Quantum Wavepacket Dynamics on an ab initio Potential Energy Surface



CCSD-2/d Potential Energy Surface

- 6-D (green) reproduces experimental photoelectron spectrum much better than 5-D (red)
- picosecond lifetime tunneling resonances observed below TS2 in 5-D simulations
- Difficult to capture microsecond time-scale deep tunneling observed in experiment

Ma, Li and Guo, Phys. Rev. Lett. **109**, 063202 (2012)

Conclusions

- ***Photoelectron-Photofragment Coincidence Spectroscopy in an Electrostatic Ion Beam Trap***

- ***Photodetachment of $HOCO^-$ and $DOCO^-$:***
  Three competing channels:

  $$HOCO^- \rightarrow \begin{cases} HOCO + e^- \\ H + CO_2 + e^- \\ OH + CO + e^- \end{cases}$$

- ***Vibrational frequencies; cis AEA = 1.51 eV, trans AEA = 1.37 eV***

- ***The $HOCO \rightarrow H + CO_2$ tunneling pathway is significant: implications for high-pressure combustion / atmospheric oxidation?***

- ***Effects of vibrational excitation? Future Experiments***

Acknowledgments

Experiment

Dr. Chris Johnson

Dr. Berwyck Poad

Ben Shen

Ab Initio Theory

Prof. John Stanton
Dr. Michael Harding

Univ. Texas, Austin

Support: U.S. Department of Energy