Electrostatic Ion Beam Trap for the Study of Molecular Reaction Dynamics

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Fundamental Interactions with Atom and Ion Traps
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Overview

- Dissociative Photodetachment – Probing Transient Neutrals using Coincidence Spectroscopy
- Photoelectron-Photofragment Coincidence – $\text{O}_4^-$
- Experimental Techniques – Electrostatic Ion Beam Trap
- $\text{HOCO}^-$, HOCO and the $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$ reaction
- Photoelectron Spectroscopy
  - Electron Affinities and Vibrational Spectra of HOCO
- Experimental determination of the tunneling barrier
  - $\text{HOCO/DOCO} \rightarrow \text{H/D} + \text{CO}_2$

Future
Neutralization Probes of Dissociative States

Direct Dissociative Photodetachment (DPD)

\[ AB^- + h\nu \rightarrow A + B + e^- \]
**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 $O_4^-$

$O_4^- + h\nu \rightarrow O_2 (^3\Sigma_g^-) + O_2 (^3\Sigma_g^-) + e^-$

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

532 nm (2.33 eV)

Diagonal bands:

$O_2$ product vibrations
Low rotational excitation

Vertical Spots:

2-photon signal –
Photodissociation
followed by
Photodetachment

Hanold, Garner and Continetti
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)
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$^-$

Cold, Vibrationally Resolved Photoelectron Spectra

Revised adiabatic electron affinities (AEA’s) \(^{(2)}\)

- cis-HOCO: \(1.43 \text{ eV}^{(1)} \rightarrow 1.51 \text{ eV}\)
- trans-HOCO: \(1.30 \text{ eV}^{(1)} \rightarrow 1.37 \text{ eV}\)

‘Hot’ data: Lu and Continetti, PRL 99, 113005 (2007)

(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 + CO₂; OH + CO

\[ \text{TOF} \approx 7.8 \mu s \]
Isotope Effects – Tunneling Below the Barrier

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

- Processes occurring over > 6 orders of magnitude of time
- Extract lifetimes as a function of $E_{\text{int}}$?
Model for Tunneling HOCO → H + CO₂

Approximations:

• Reaction coordinate
  simple harmonic oscillator
  H-OCO    D-OCO
• 1 dimensional dynamics
• \( f(E) \) – stable fraction
• \( N = \omega_{OH} \times TOF \)

\[
f(E) = (1 - T(E))^N
\]
Semiclassical Tunneling Model

\[ f(E_{int}) = (1 - T(E_{int}))^N \]

\[ E_{int} = E_{hv} - EA - eKE \]

\[ N = \omega_{OH} \times TOF \]
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

\[ V_1^0(r) = D_e \left[ 1 - \exp\{-\alpha(r - r_e)\} \right] \]
\[ V_2^0(r) = A r^{-n} \]
\[ H_{12}(r) = H_{12}^0 \exp\{-a |r - r_c|\} \]

Fix Morse well-depth \( D_e \) and \( r_e \)
\( D_e \): dissociation to \( \text{H} + \text{CO}_2 \) \( ^1\text{B}_2 \) 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 $V(r)$

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

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)

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

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

**Experiment**

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

**Model**
Tunneling Model Fit to the Experimental Branching Fraction

- $v_{\text{max}} = 2$ for DOCO
- $v_{\text{max}} = 1$ for HOCO

Best Fit Parameters
- $a = 0.05 \text{ eV}^{-1}$
- $\alpha = 1.96$
- $A = 4.02 \text{ eV}$
- $N = 2.27$
- $H_{12}^0 = 0.49 \text{ eV}$
- $\chi = 0.19$
Experimentally Extracted Barrier

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

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

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
Communication: A chemically accurate global potential energy surface for the HO + CO → H + CO₂ reaction

Jun Li,¹ Yimin Wang,² Bin Jiang,³ Jianyi Ma,¹ Richard Dawes,⁴ Daqian Xie,³ Joel M. Bowman,² and Hua Guo¹,ᵃ

Fit – CCSD-1/d Potential Energy Surface

Quantum Wavepacket Dynamics on an ab initio 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

Conclusions

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

- Photodetachment of HOCO$^-$ and DOCO$^-$: Three competing channels:
  - $\text{HOCO}^- \rightarrow \text{HOCO} + e^-$
  - $\text{HOCO}^- \rightarrow \text{H} + \text{CO}_2 + e^-$
  - $\text{HOCO}^- \rightarrow \text{OH} + \text{CO} + e^-$

- 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
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