Ammonia & Oxidation State Sensing Based on Catalyst-Tipped Optical Fibers

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Cross-Cut Lean Exhaust Emissions Reduction Simulations

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U.S. DEPARTMENT OF ENERGY

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Outline

I. Motivation & Approach

II. Ammonia Sensing with CuZSM5

III. Copper Zeolite Luminescence

IV. Summary & Next Steps

V. Acknowledgements

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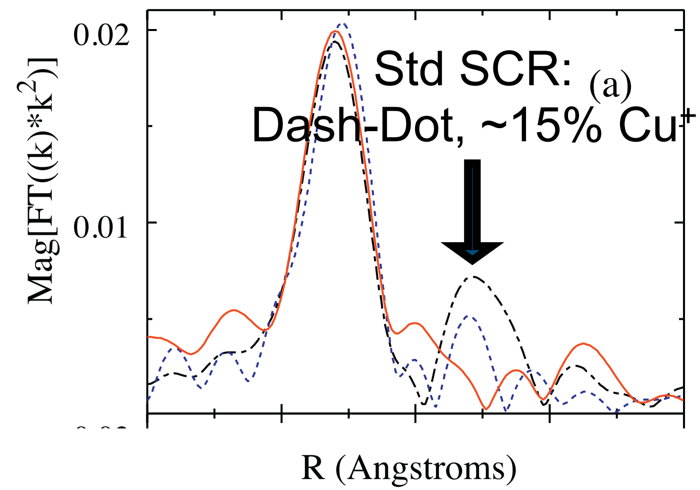
NH_3 & Cu State Impact SCR Catalyst Performance

Global Reactions

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$	Standard SCR
$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$	NO_2 SCR
$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$	Fast SCR

- Storage, utilization of NH_3 is critical to development, controls
- Ribeiro, et al, 2012: EXAFS, operando XANES identifies differences in Cu oxidation state ratios for Fast & Slow vs. Standard SCR

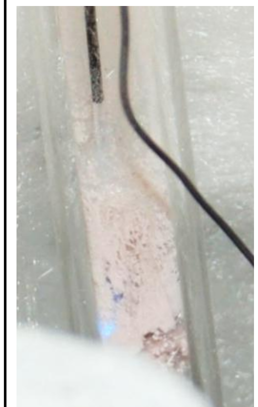
Fast SCR: Solid line, no Cu^+



J.-S. McEwen et al. / Catalysis Today 184 (2012) 129–144

Using Light to Detect NH_3 & Cu State

- Cu state changes yield visible response

In-Situ Picture					
Temp	450°C	450°C	450°C	450°C	35°C
Gas	Air	Hydrogen	Air	Ammonia	Air
Color	Gray	Pink	Gray	Pink	Blue

* Gas conditions defined as "H_2": 40%H_2, balance inert; "NH_3": 1000ppm NH_3, balance inert.

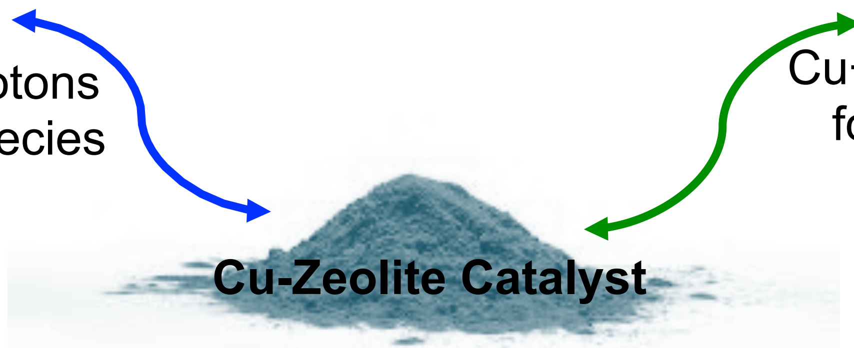
Hydrogen & ammonia effect common changes to optical absorbance in CuZSM5. Similar results are also seen in CuCHA.

Using Light to Detect NH_3 & Cu State

- Cu state changes yield visible response
- Unique optical accessibility of Cu redox couple
  - Route to ammonia, other redox-active species assessment
  - Simplified approach to monitor redox state of Cu centers

Laser provides photons that excite Cu+ species

Cu+ species emit photons for sensitive detection



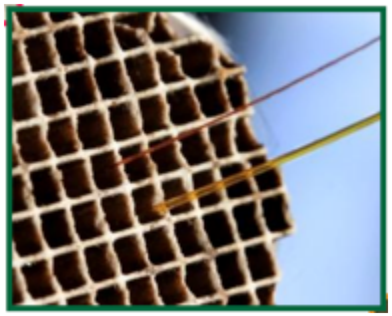
Cu+ species vibrationally relax & undergo intersystem crossing to lowest vibrational state of excited molecular electronic level

Not luminescent $Cu^{+2} + e^{-} \leftrightarrow Cu^{+1}$ ***Luminescent***

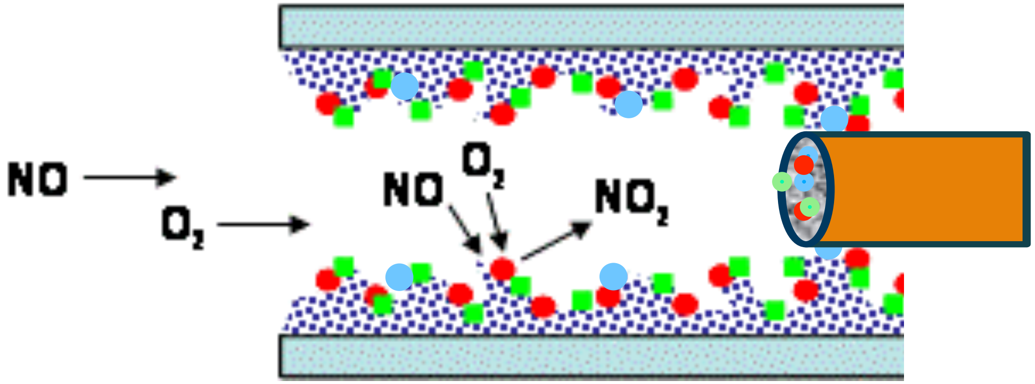
Intra-Catalyst Optical Sensing of Gases and Cu State

Motivation: Enhance catalyst state monitoring, modeling, design & control

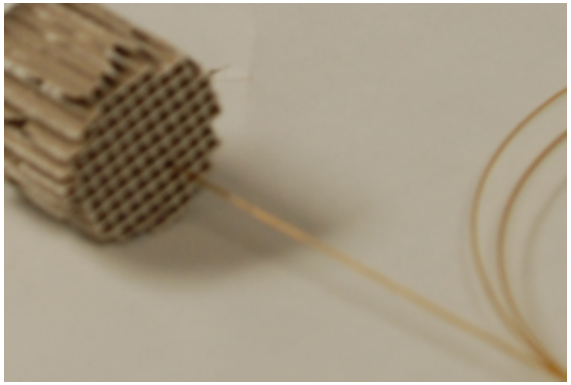
- Map intra-catalyst spatial NH_3 distributions
- Understand oxidation state, rxn network distribution & nature
- Assess ageing, operation at low temp
- Inspired by self-diagnosing "smart catalysts"



Exhaust gases interact with catalyst material on monolith **and** tip of fiber



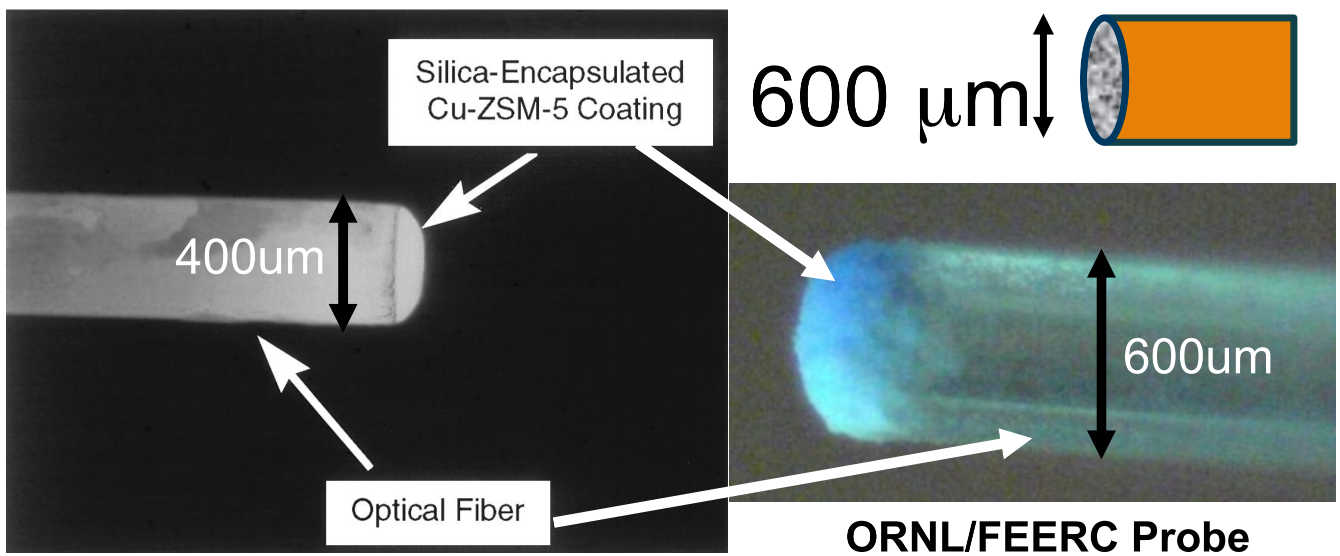
Catalyst material-tipped fiber fits easily into channels of monolith



Minimally Invasive Fiber Probe Fabrication

- Fused silica optical fiber commercially available
- Sol gel tip: porous matrix holds catalyst material
- Tuning the measurement for speed & sensitivity:
  - Zeolite identity
  - Sol gel precursor molecule/delivery solvent/sol gel viscosity
  - Catalyst powder loading level
  - Thickness of tip coating

Sensor Material-Tipped Optical Fiber

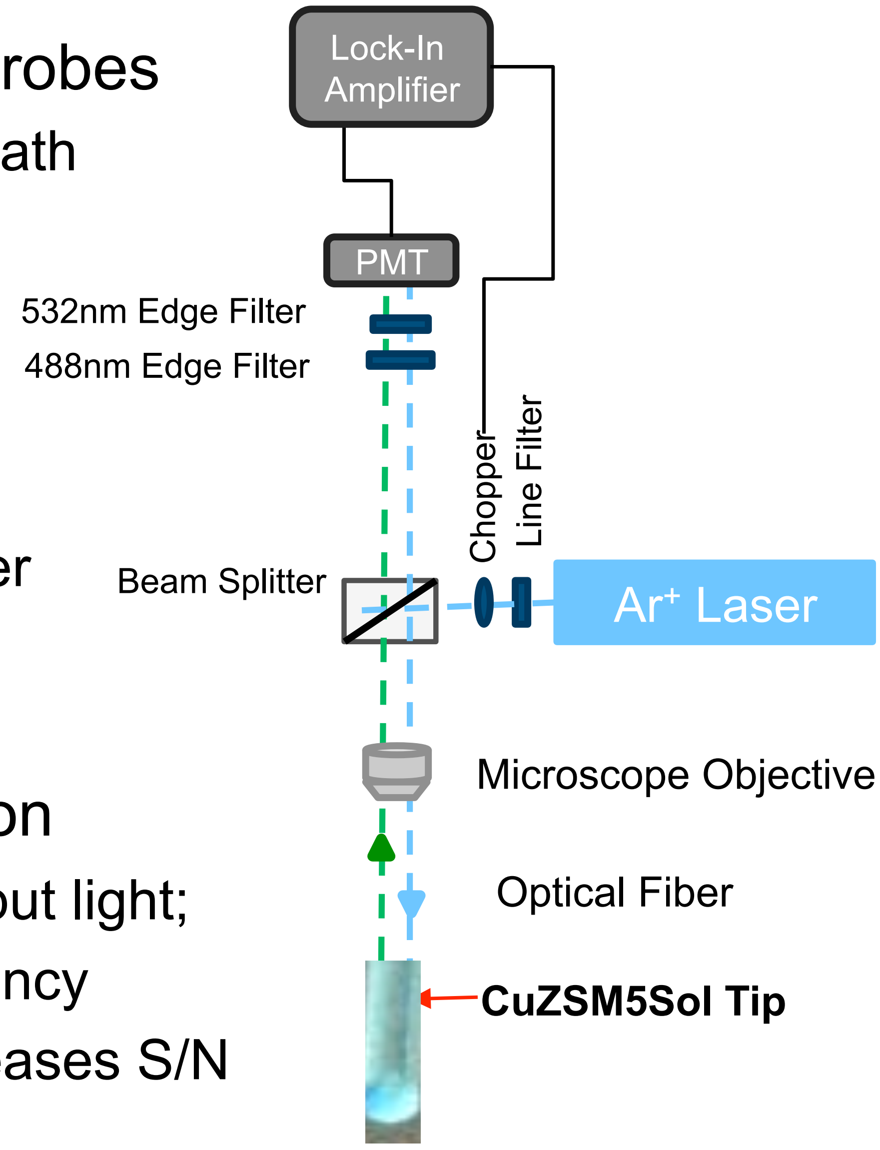


ORNL/FEERC Probe

Appl. Optics, 38(25), 5306-5309; **1999**.

Sensitive Detection Allows Catalyst Monitoring

- Single-entry, micron-footprint probes
  - Common excitation, collection path
  - Optimized collection of signal
- Laser-induced fluorescence
  - High signal to background ratio
  - Holographic filters minimize laser background
- Lock-in amplifier signal detection
  - Apply frequency signature to input light; detect outputs with same frequency
  - Phase-locking significantly increases S/N



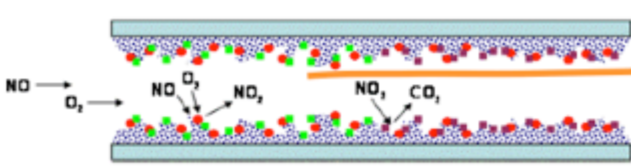
Outline

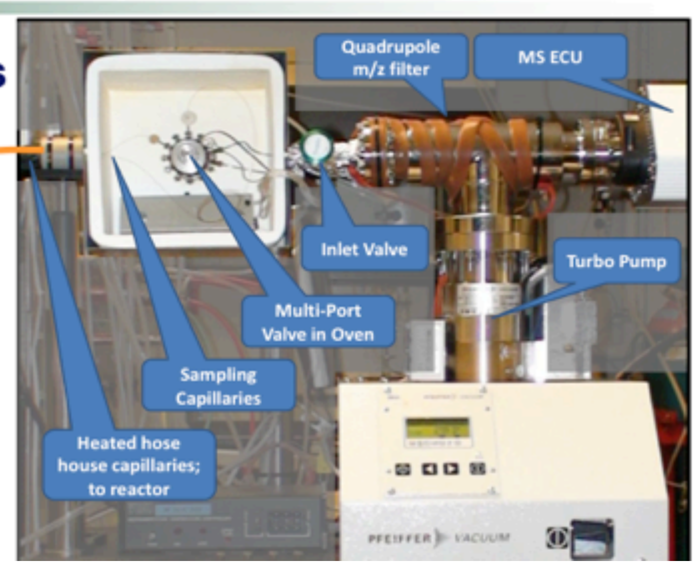
Ammonia Sensing with Cu Zeolite – Tipped Fiber

- Previous work: SPACI-IR, SPACI-MS
  - Gas phase NH_3 concentration indicates NH_3 storage
  - Stoichiometry of NH_3 gives reaction rate
  - Infer control strategies from these spatiotemporal measurements
- Optical methods allow complementary spatiotemporal info
- NH_3 slip control for general exhaust applications

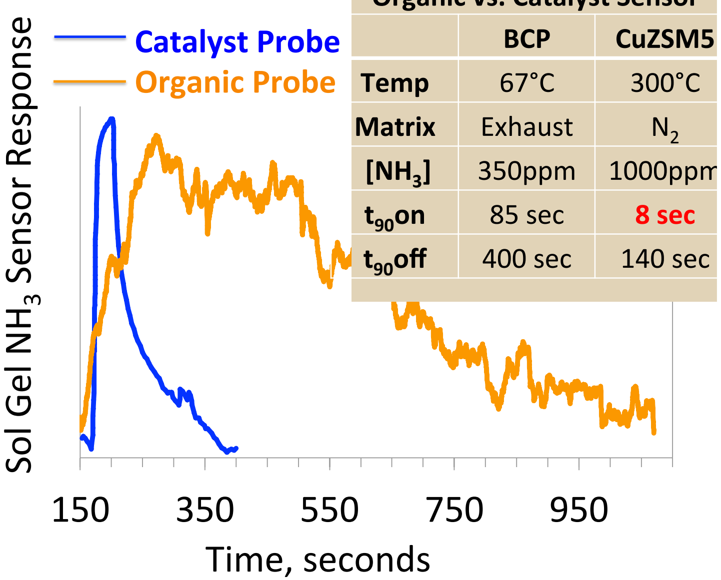
SpaciMS : Spatially Resolved Capillary Inlet MS

Quantifies transient species distributions within operating chemical reactors via direct capillary sampling to a mass spectrometer



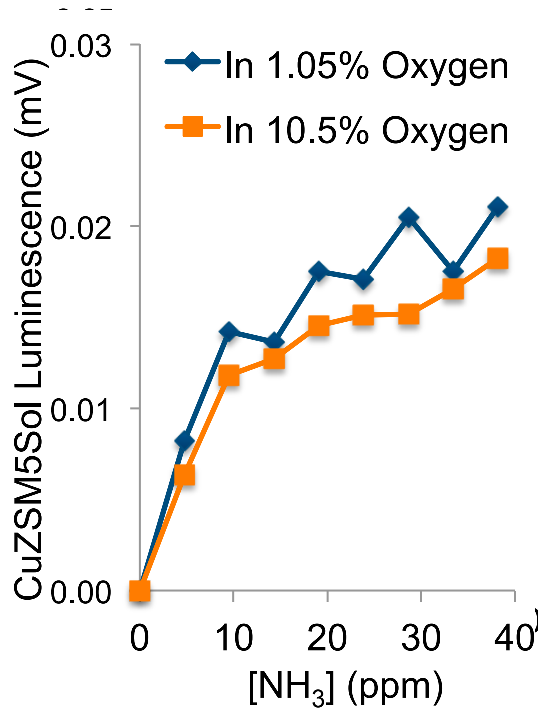


NH_3 Sensing at Diesel-Exhaust $[O_2]$ & Temps

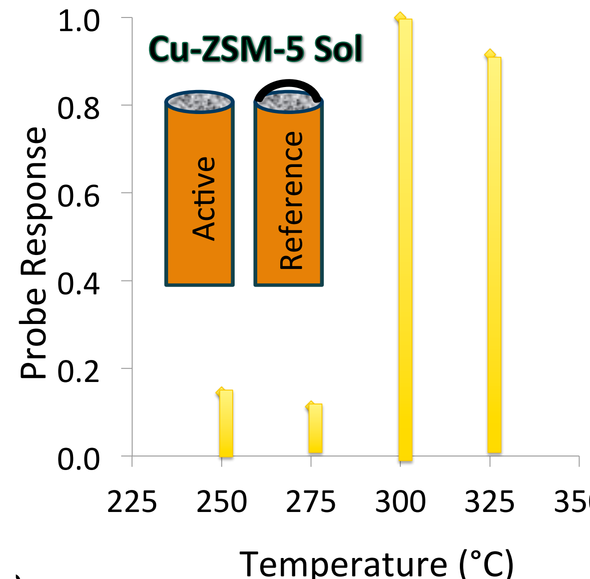


Response to NH_3 transient: Organic vs. Catalyst Sensor	BCP	CuZSM5
Temp	67°C	300°C
Matrix	Exhaust	N_2
$[NH_3]$	350ppm	1000ppm
t_{90}on	85 sec	8 sec
t_{90}off	400 sec	140 sec

- Transient responses of organic & inorganic catalyst transducers
- Comparison indicates favorable performance of inorganic.



- Response same 1%-10% O_2.
- Cu^+ luminescence quenching by O_2 is not an issue at diesel-SCR $[O_2]$.



- Thermal response varies due to
  - ✓ Lattice dehydration
  - ✓ Auto-reduction
  - ✓ Boltzman distribution
- Thermal Reference fiber
  - ✓ Passivated catalyst

Ultimately, Cu oxidation state is detected variable

Outline

I. Premise of Work

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III. **Copper Zeolite Luminescence**

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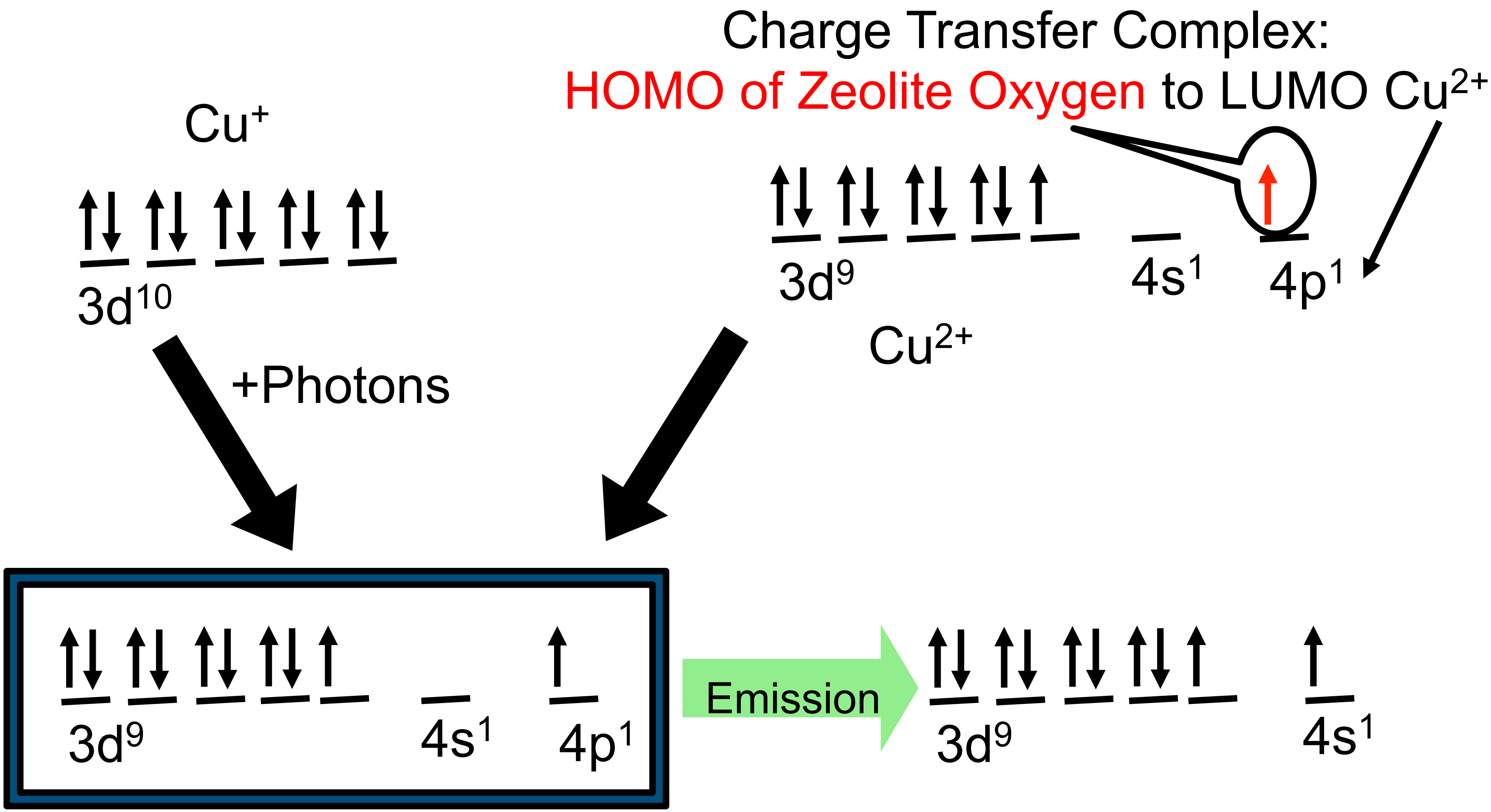
***Origins* of Cu-Zeolite Luminescence**

Not luminescent $Cu^{+2} + e^{-} \leftrightarrow Cu^{+1}$ ***Luminescent***



Method can measure both Cu^{+} and certain Cu^{2+} species

Differentiating Luminescence from Cu^{+} and Cu^{2+}

Strategies for Discerning Luminescent Centers

- Excitation wavelength multiplexing
- Luminescence lifetimes

Approaches Being Pursued

- Concurrent UV and visible excitation with diverse frequency signatures
- Generate calibration datasets in materials, gaseous environments matched to XANES literature data for comparison

Summary & Next Steps:
Developing diagnostics to address the next barriers to *efficiency improvements*

- Improved diagnostics allow broader development applications
  - Single-port, minimally invasive, probe
  - Spatial, temporal resolution in real-time, intra-monolith or on-engine
- Engine exhaust application in SCR catalysts
  - SCR control: oxidation state, coordination of copper
  - NH_3 utilization & slip
  - Urea decomposition & distribution
  - Monitor for catalyst poisons (P, S species)
- Future work: NH_3 Sensing
  - Improve speed & sensitivity by tuning fabrication; expand catalyst materials used
  - Develop thermal reference fiber
  - Apply in complex exhaust gases & compare to SPACI intra-cat measurements
- Future work: Cu Oxidation State Assessment
  - Concurrent UV and visible excitation with diverse frequency signatures
  - Generate calibration datasets in materials, gaseous environments matched to XANES literature data for comparison

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