

Tuning the Ultrafast Energy Flow in Molecular Scale Materials

VISTA Seminar

November 12, 2025

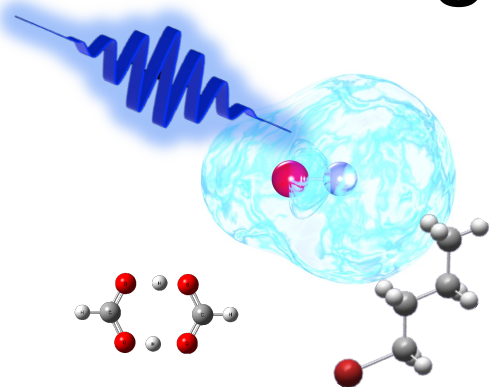
Scott G. Sayres

ssayres@asu.edu

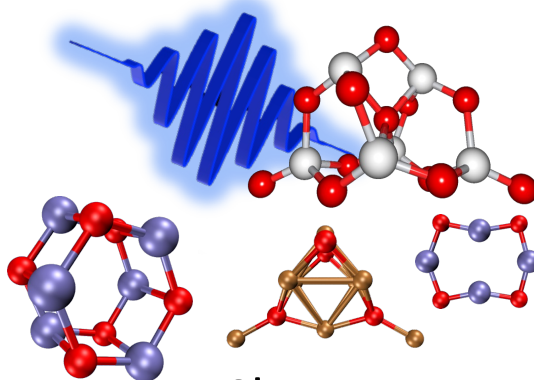
<https://sites.google.com/asu.edu/sayreslab>

Sayres Group

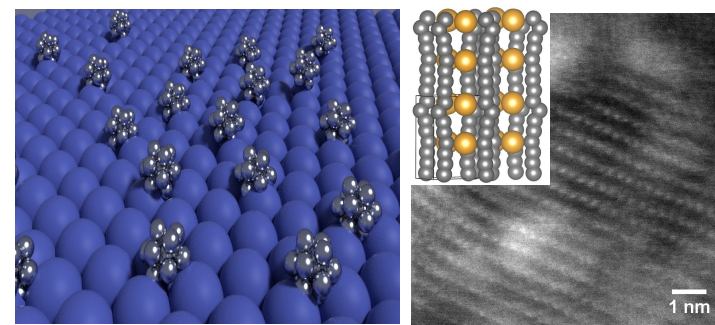
Ultrafast light/matter Interaction



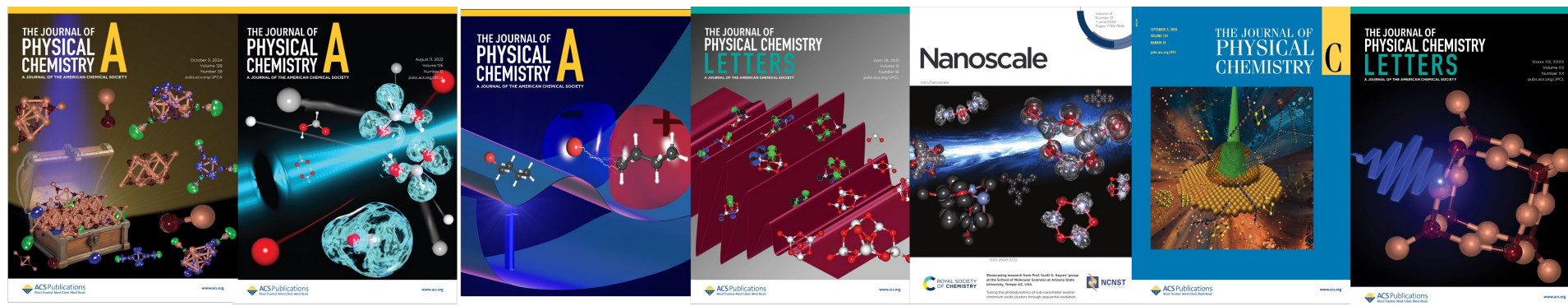
Molecules



Clusters



Cluster Assembled
Materials



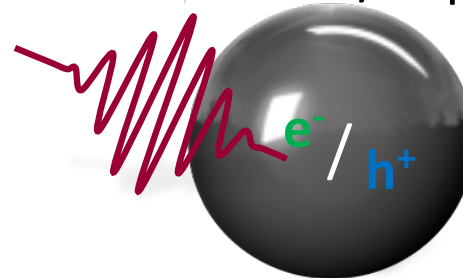
Photoexcitation/Photocatalysis



Photovoltaic Cell
(Solar Energy)

Step 1: Absorption

Create e^-/h^+ pair

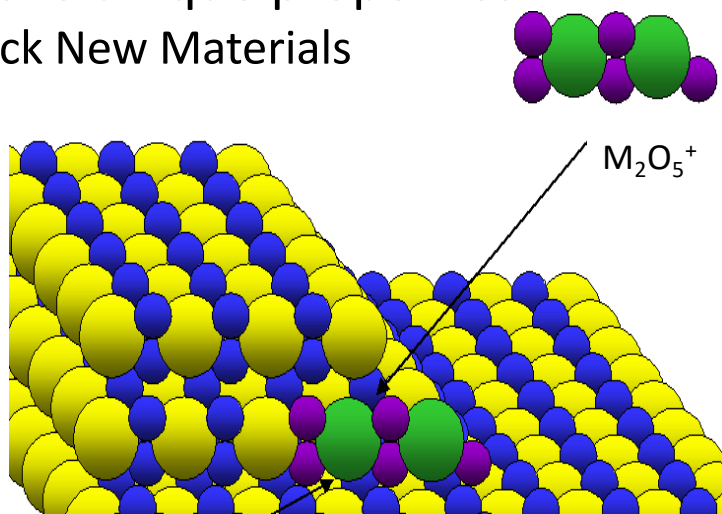


Step 2: Charge Carrier Separation
hindered by recombination

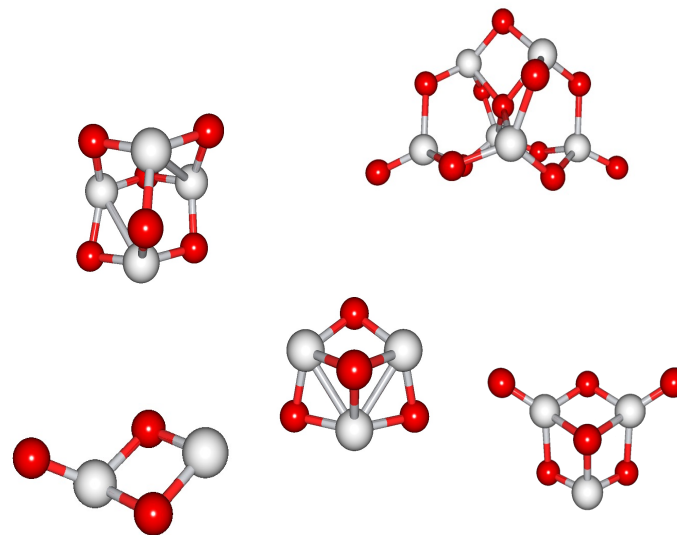


Clusters: Nature's Building Blocks

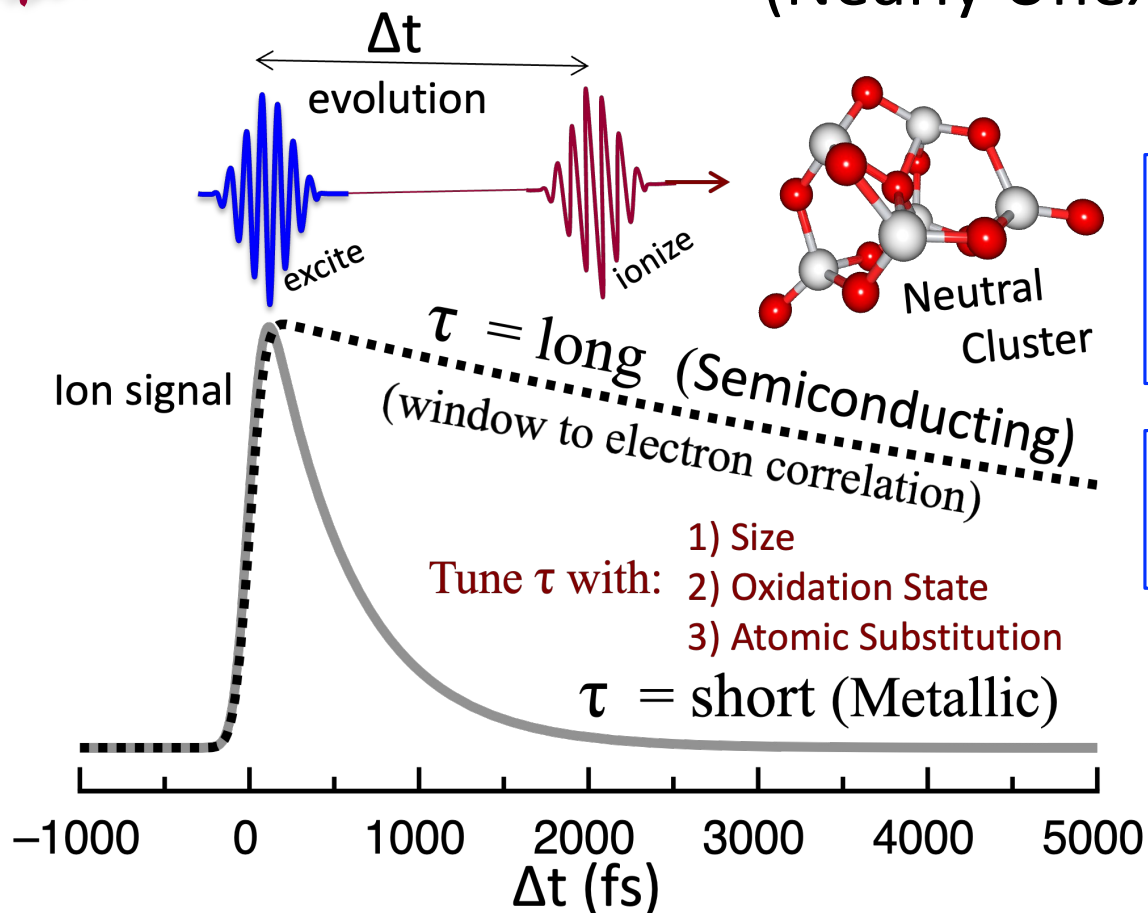
- Clusters are models of surfaces in chemical processes
- Cluster reactions produce similar products to bulk
- Clusters as catalysts themselves (with far higher activity)
- Ultimate Tunable Stoichiometry (not achievable in bulk)
 - Offer exquisite control over electron correlation
- They have unique properties!
 - Unlock New Materials



J. Phys. Chem. B 106, 6136 (2002)



Neutral Cluster Dynamics (Nearly Unexplored)

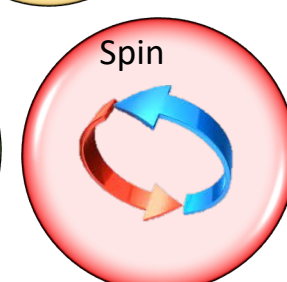
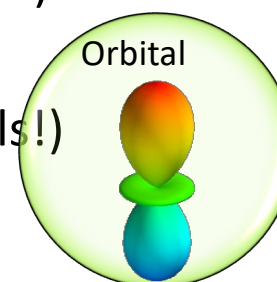
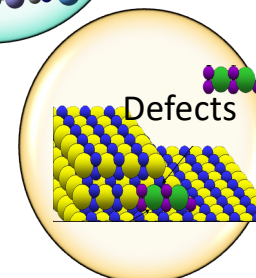
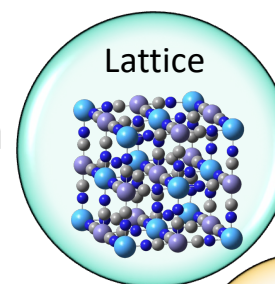


A good photocatalyst has a lifetime sufficient to drive chemical transformation

Develop strategies to understand and extend

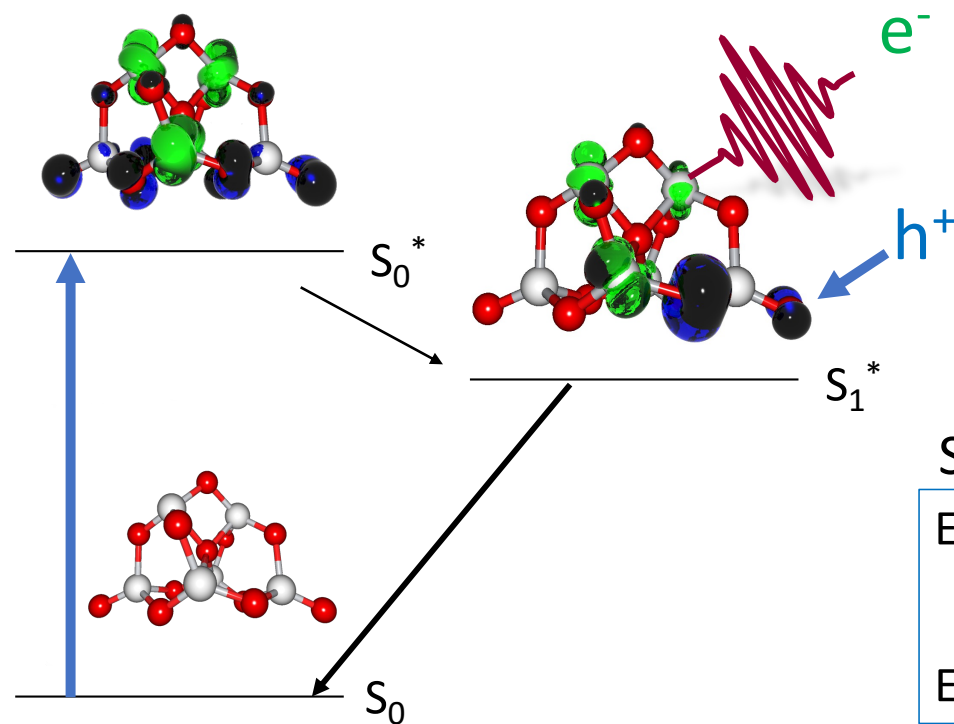
Dynamics: Window to New Phenomena

1. Identify structural features that drive carrier localization/separation, polaron/exciton formation
 - Consecutive growth using building blocks of same stoichiometry
2. Change dynamics/behavior with atomic precision (Every atom counts!)
 - Ultimate Tunable Stoichiometry (not achievable in bulk)
 - Tunable d-electron density (stoichiometry)
 - Mimic defect sites in catalysis (or unlock new materials!)
3. Onset of Metallic / Bulk Behavior?



22 47.867 Ti Titanium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.693 Ni Nickel	29 63.546 Cu Copper
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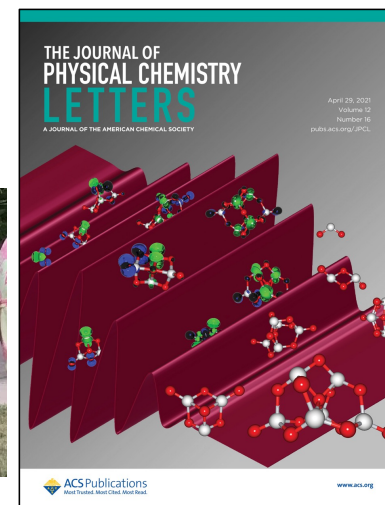
Example: Neutral $(\text{TiO}_2)_6$



Jacob Garcia



Lauren Heald



Synergy : Experiment and Theory

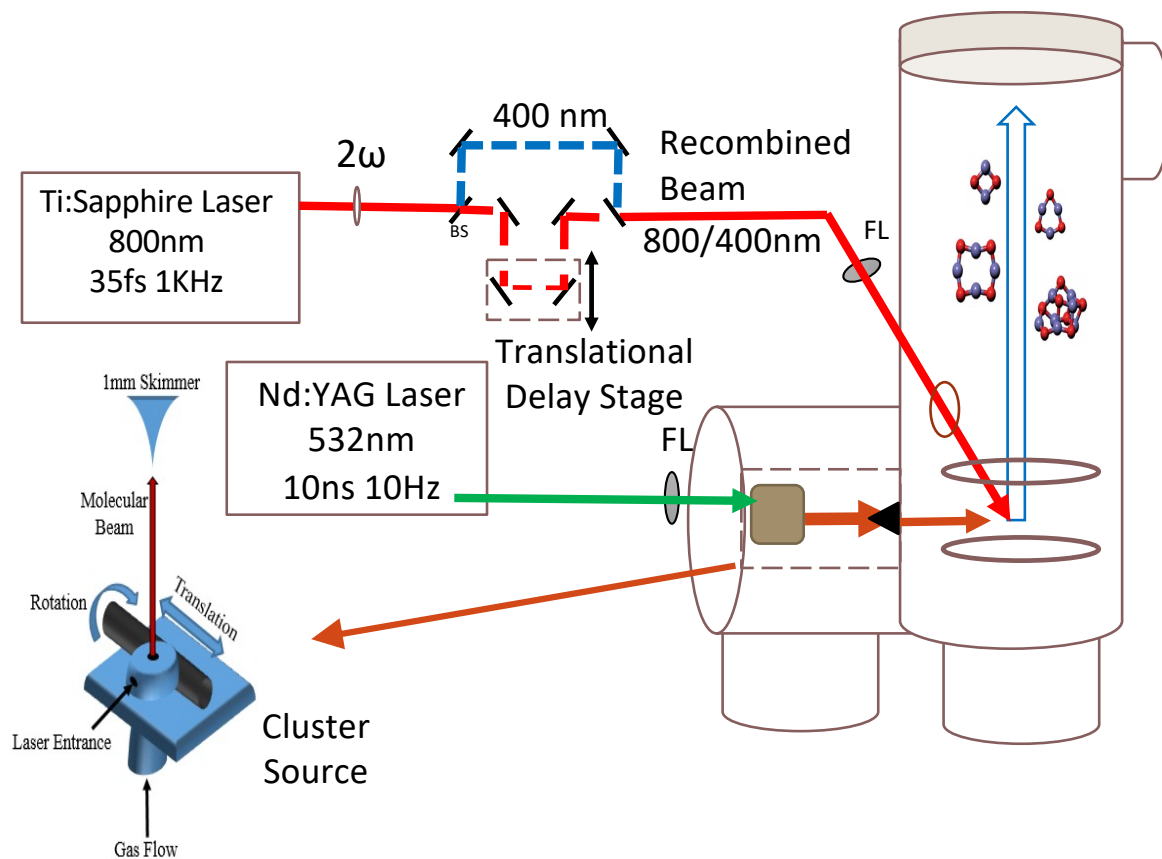
Experimentally monitor the ability to ionize
Related to electronic relaxation rate

Employ TD-DFT for excited state information

JPCL, 2021, **12**, 16, 4098–4103
J. Chem. Phys., 2021, **155**, 211102.
J. Phys. Chem A, 2022, **126**, 211-220

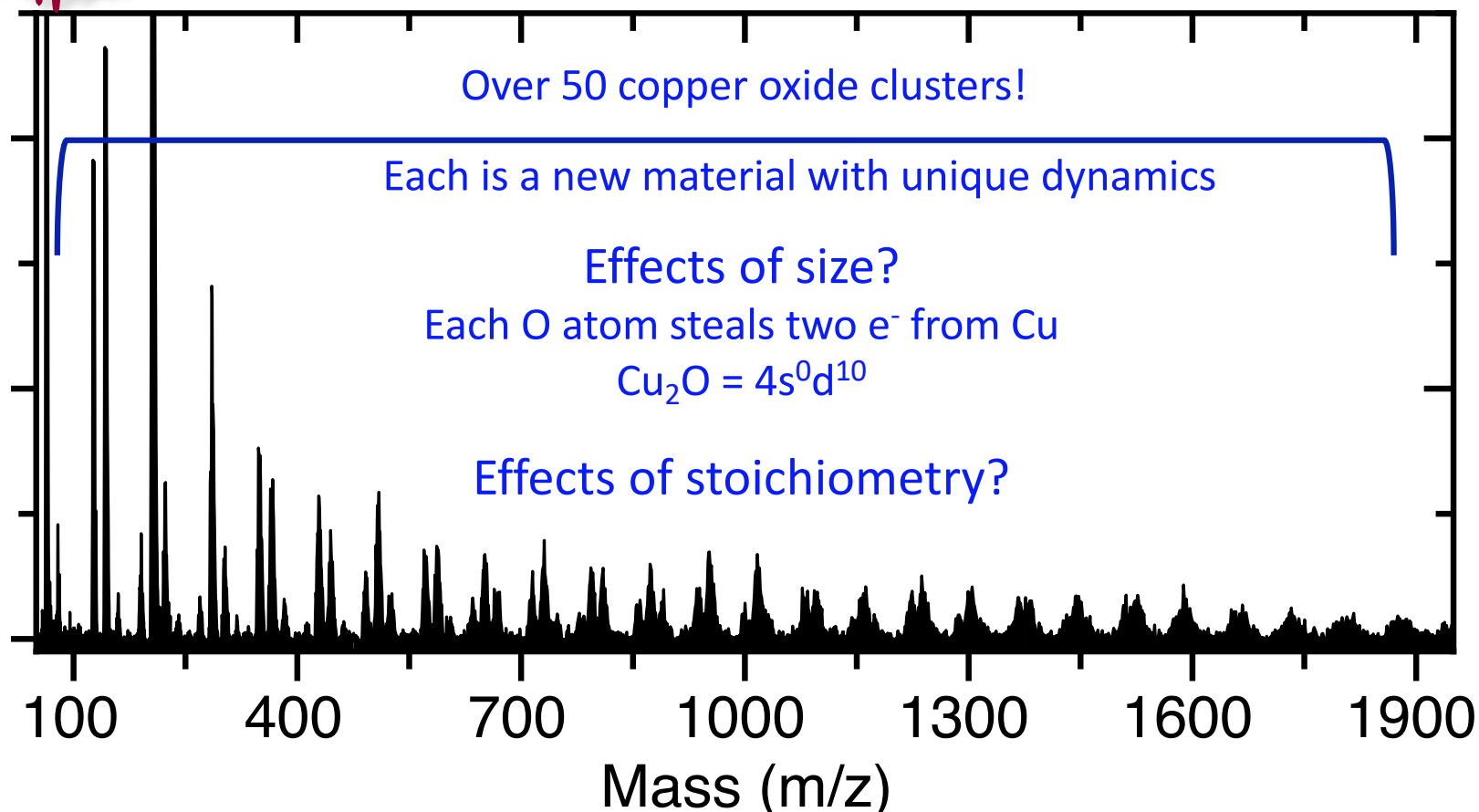
Experimental Setup

Our “Beakers”



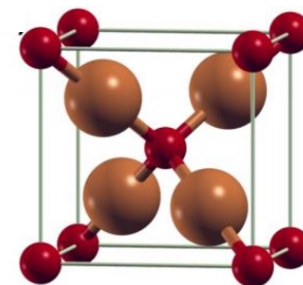
Garcia, Sayres PCCP 22, 24624 (2020)

Neutral Copper Oxide Clusters

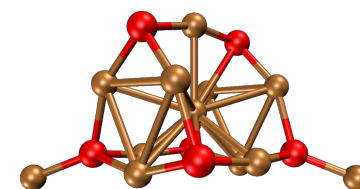


J.Phys.Chem.Lett, **16**, 7107-7114 (2025)

New Structures

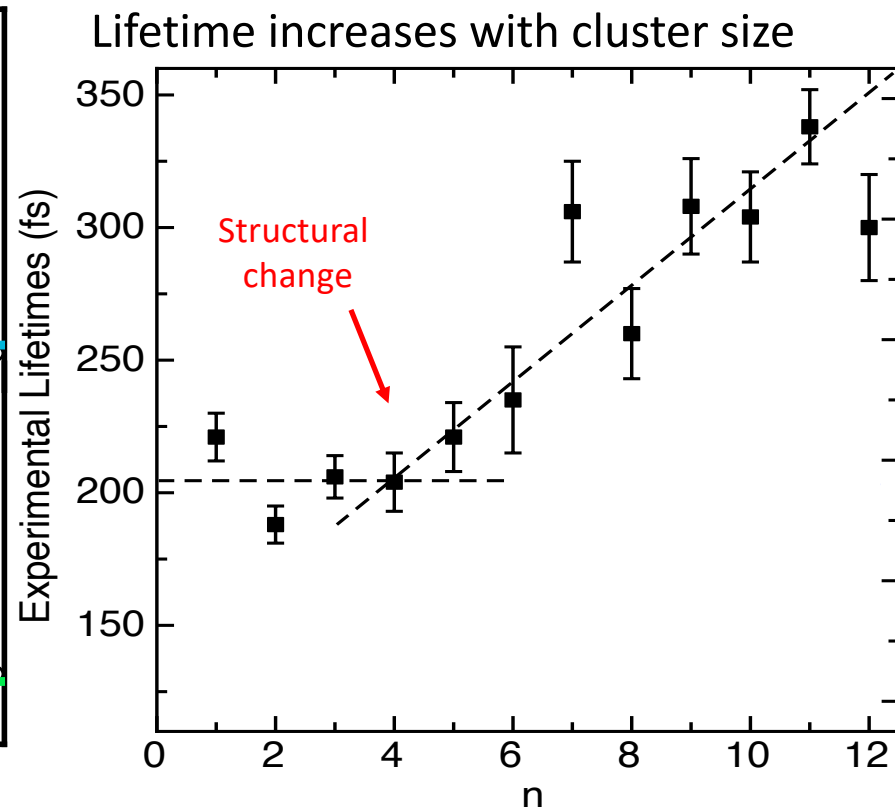
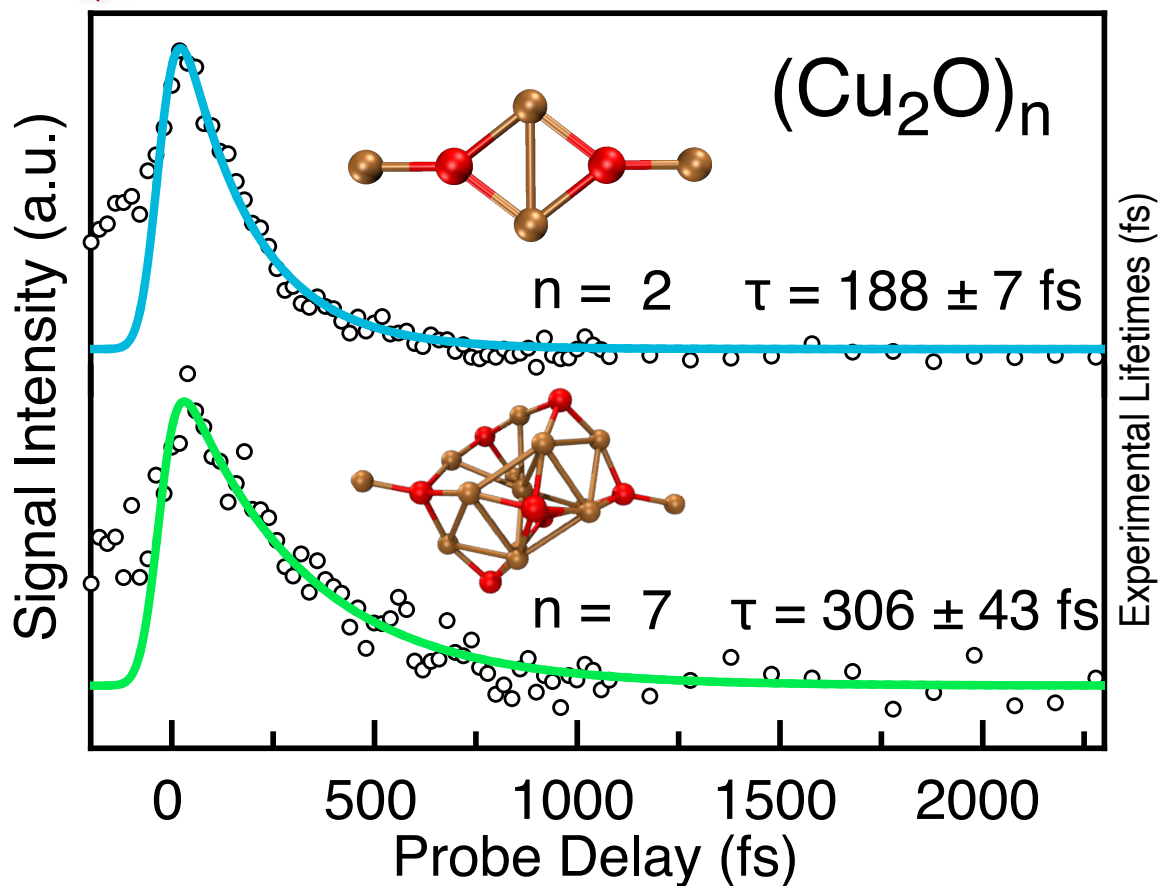


bulk



$(\text{Cu}_2\text{O})_6$

Excited State Lifetimes of $(\text{Cu}_2\text{O})_n$ [$4s^0d^{10}$]



Topological Parameters

Relaxation enhanced by overlap of electron and hole?

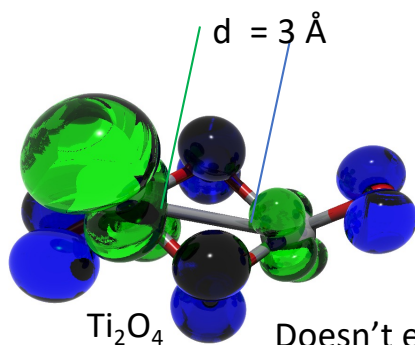
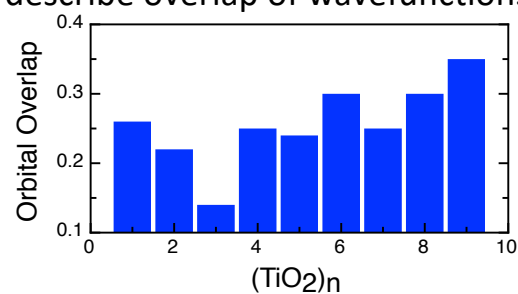
Lamda parameter, used in organic molecules to describe overlap of wavefunctions

$$\Lambda = \frac{\sum_{o,v} C_{ov}^2 O_{ov}}{\sum_{o,v} C_{ov}^2}$$

All values < 0.35

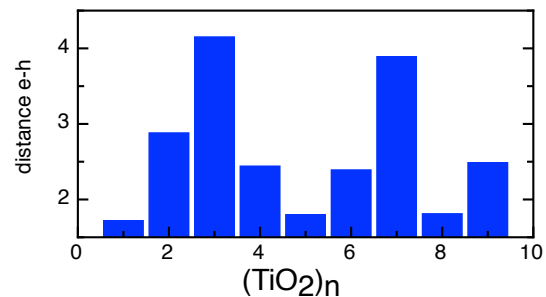
Indicates highly ionic (almost no overlap)

Doesn't explain lifetimes

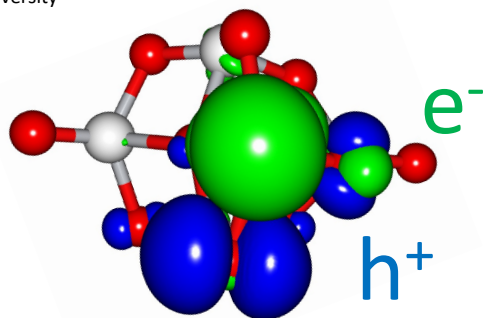


Doesn't explain lifetimes

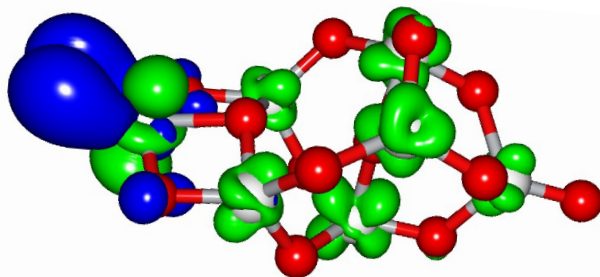
Distance between e-h



Carrier Localization (S_1) (polaron formation)

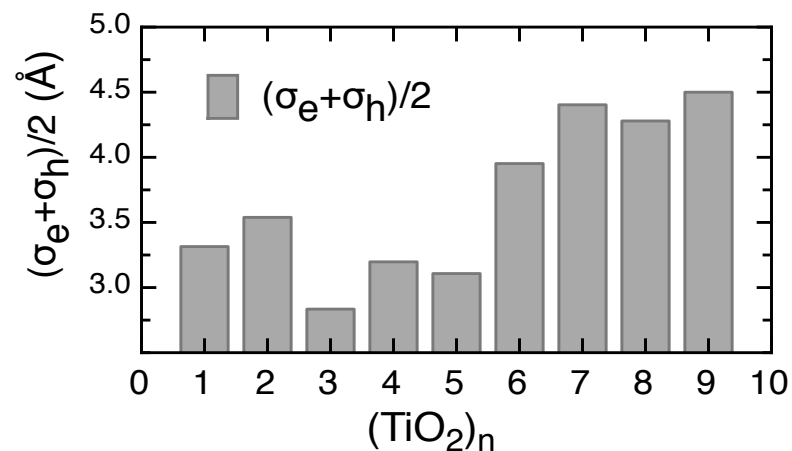
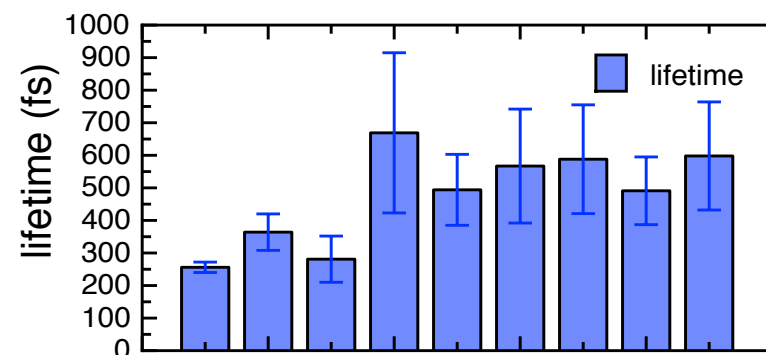


$(\text{TiO}_2)_5$: both localize (faster relaxation)



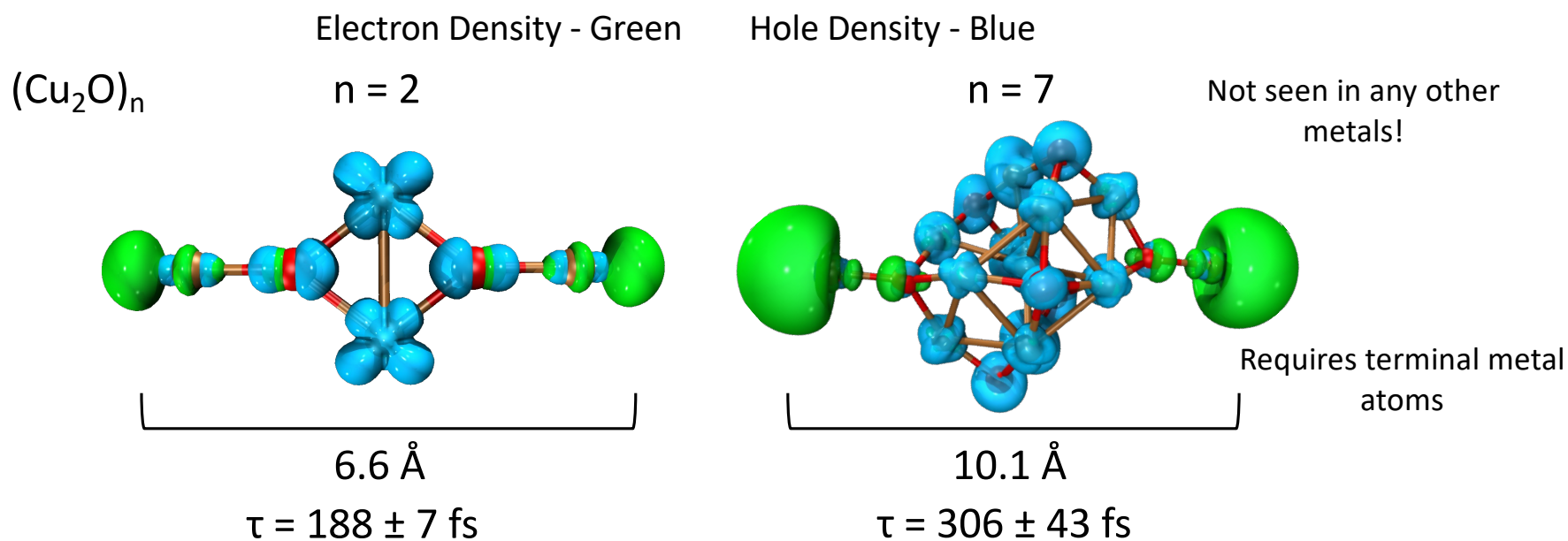
$(\text{TiO}_2)_7$: electron delocalized (slower)

1. Carrier localization is strongly tied to relaxation lifetime
2. If electron localizes it is a bound exciton pair
3. Certain geometric (structural) features extend lifetime



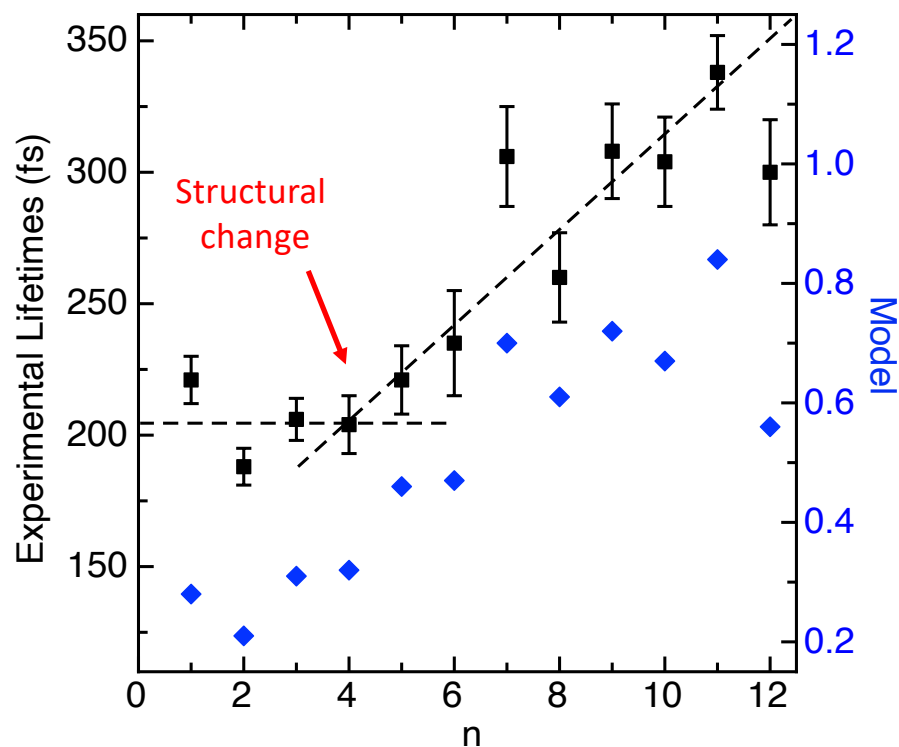
Rydberg Excitons

TD-DFT calculations reveal Rydberg excitons on terminal Cu atoms.



Electron delocalization proportional to relaxation lifetime

$(\text{Cu}_2\text{O})_n$ Clusters – d^{10}



Electron Delocalization Index (EDI)

$$EDI = 100 \times \sqrt{\int [\rho^{ele}(r)]^2 dr}$$

- Similar lifetimes for $n < 5$
- Relaxation **Slows** with size
- τ tied to e^- delocalization
(even capturing the small details)



Chase Rotteger



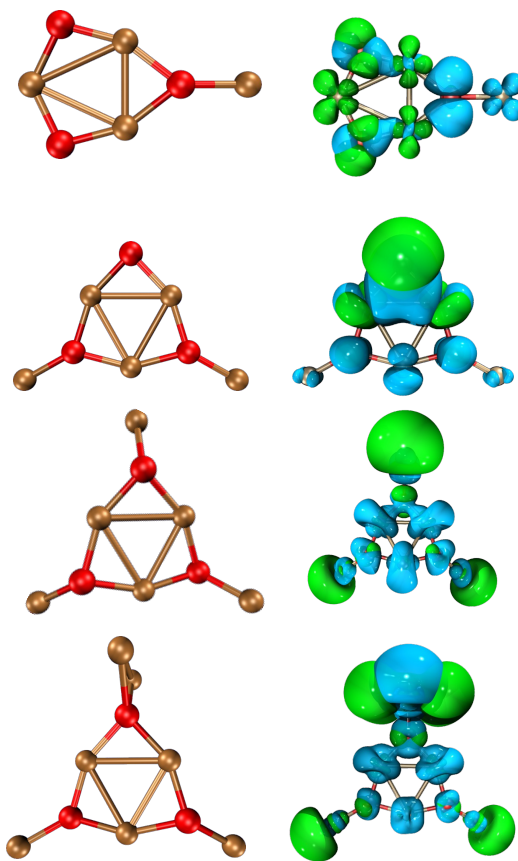
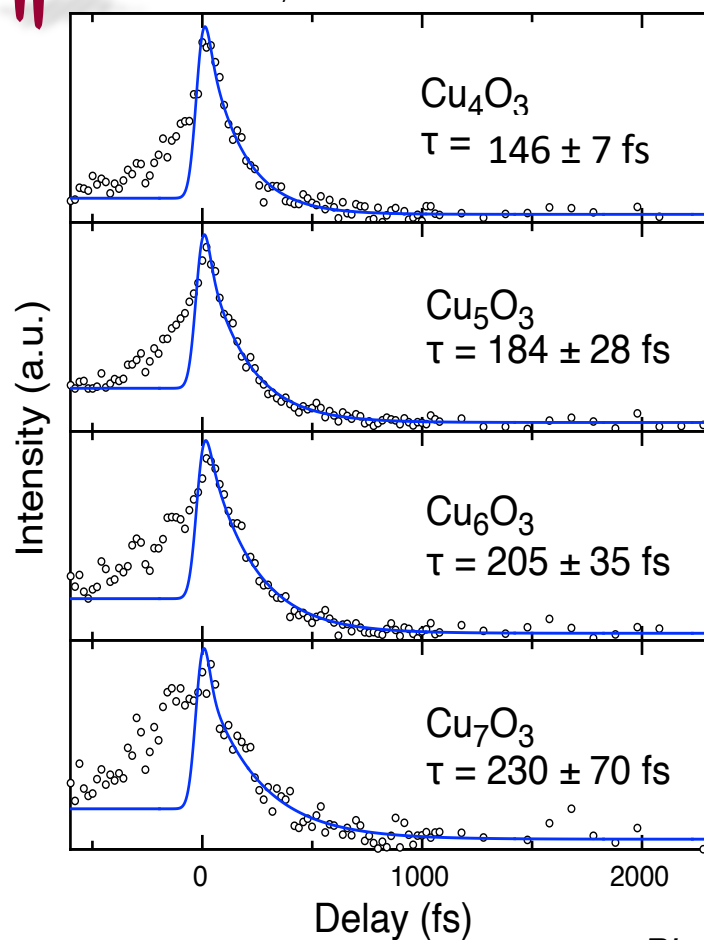
Carter Jarman



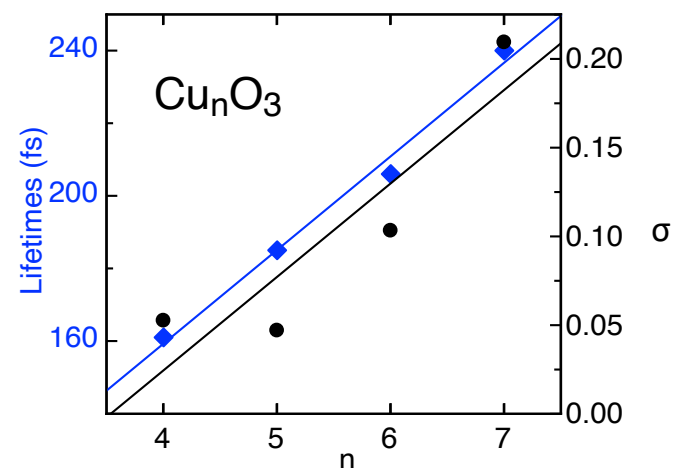
Madison Sobol

J.Phys.Chem.A, **128**, 8466 (2024)

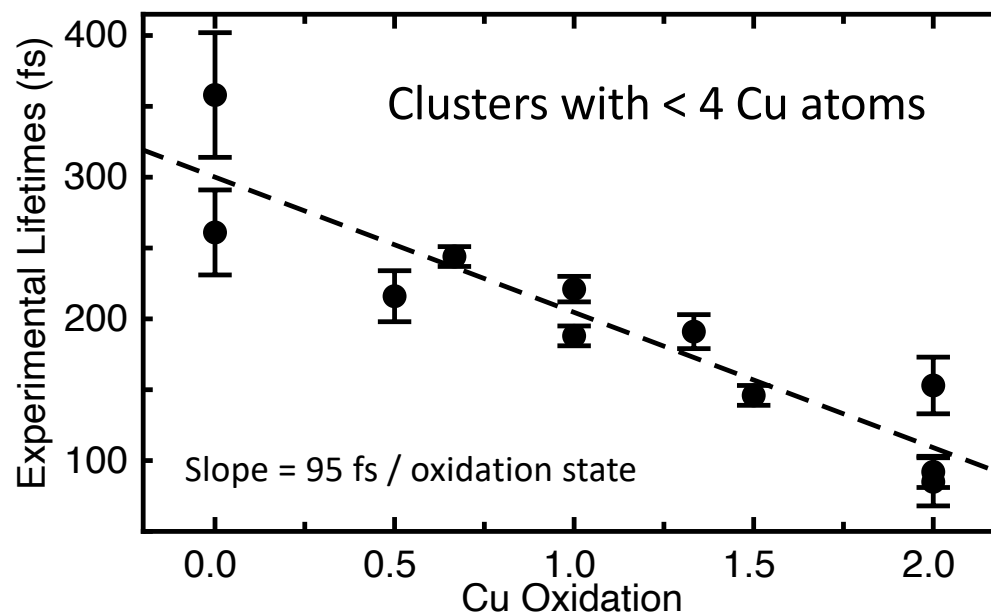
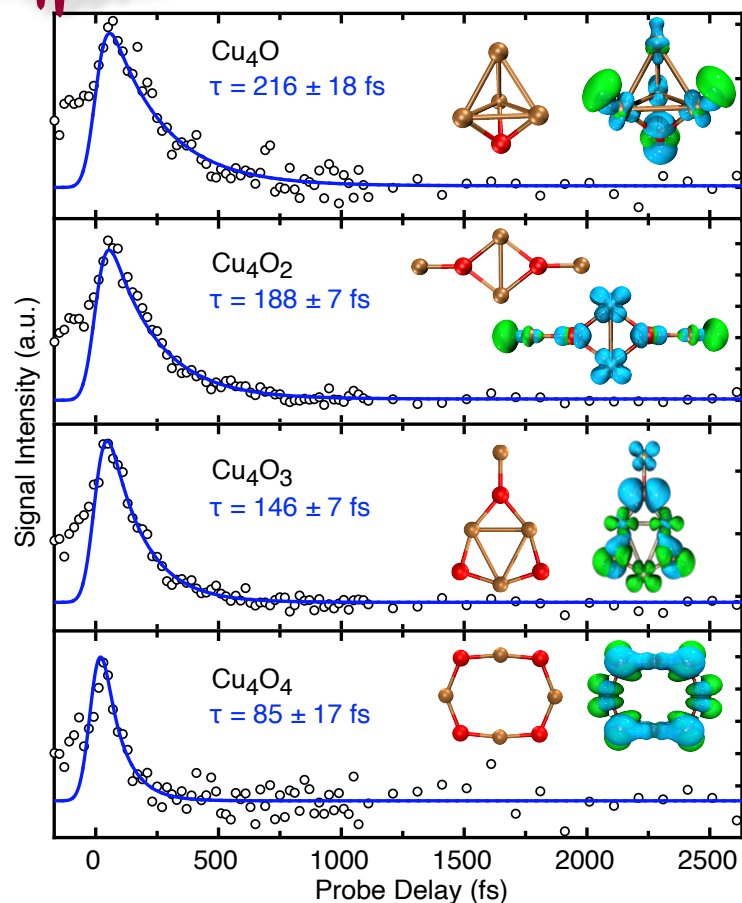
Stoichiometry: tune #d-electrons



- Lifetimes increase $\sim 20 \text{ fs}$ with each Cu atom
- Proportional to delocalization

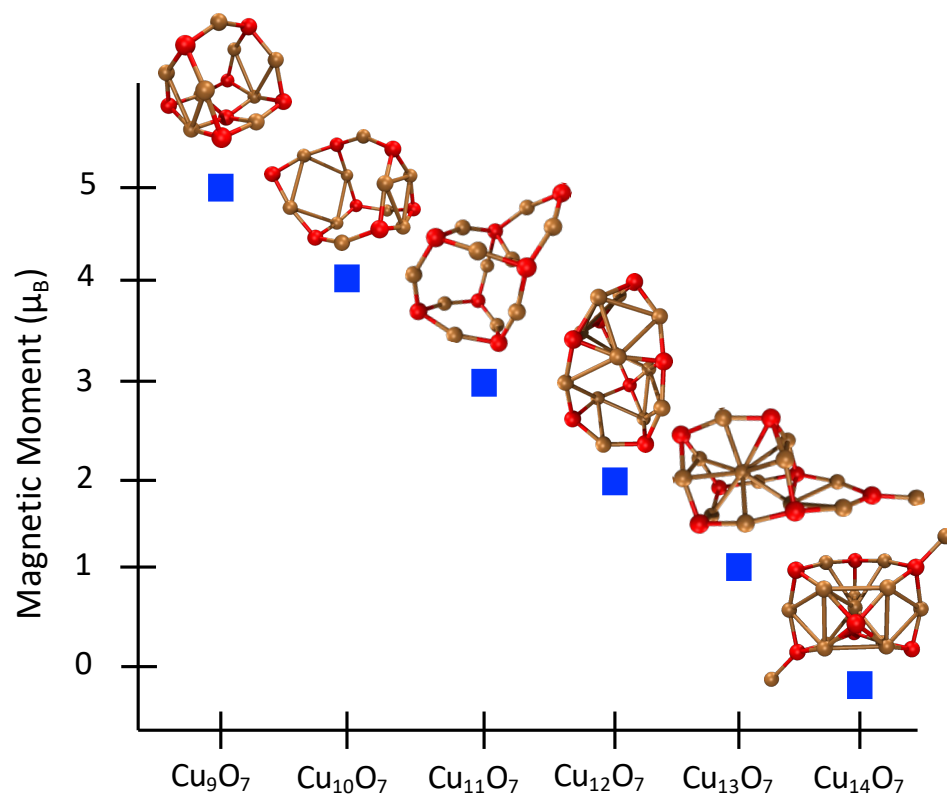


Linear Stoichiometric Behavior



- Lifetimes increase $\sim 20 \text{ fs}$ per Cu atom
- Lifetimes decrease $\sim 40 \text{ fs}$ per O atom
- Proportional to delocalization
- Related to $\#d$ -electrons available (correlation)

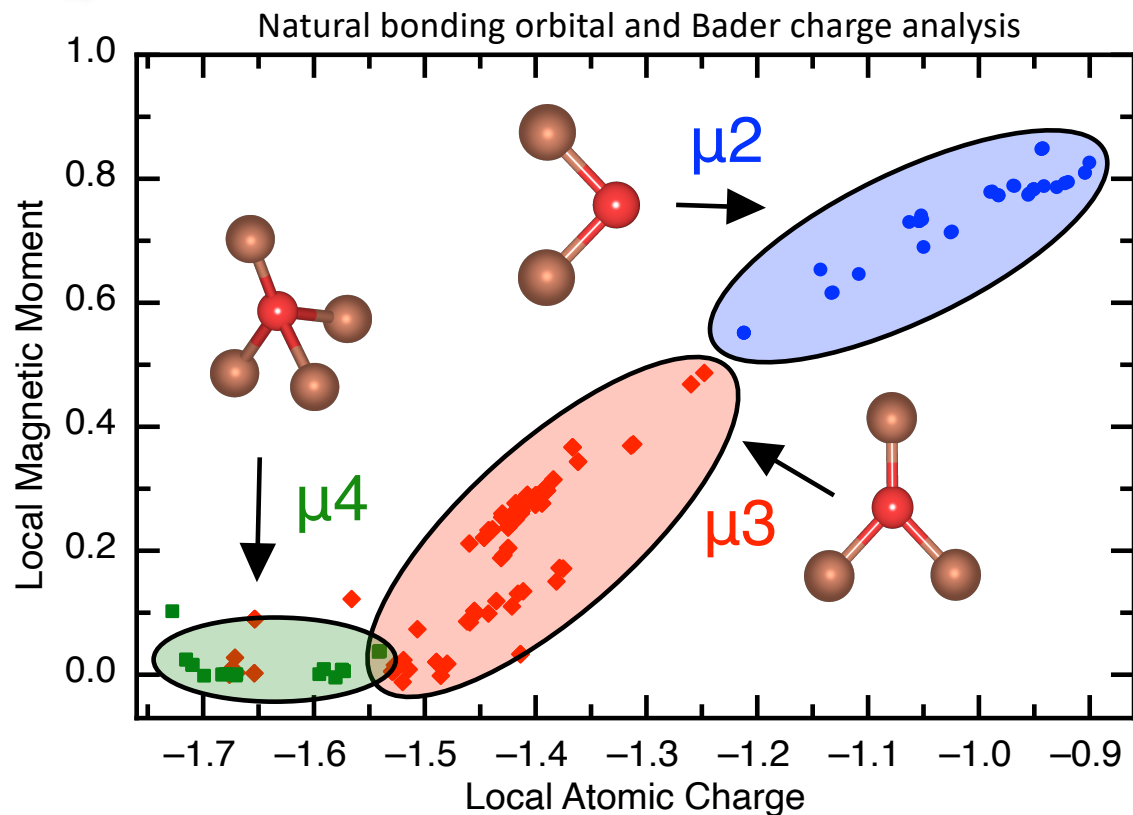
Ferromagnetically Coupled Magnetic Moments



- Ferromagnetic coupling plays a large role in structure determination
- Magnetic moment decreases with each additional Cu atom.
- Predictable magnetic moment is universal for all series.

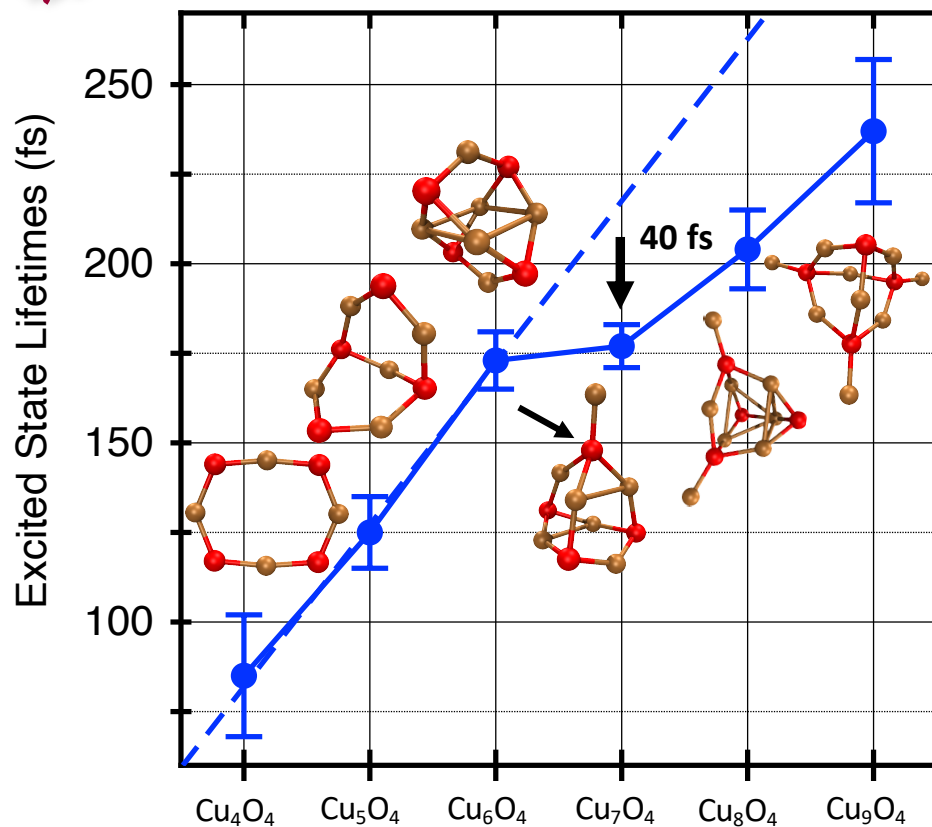
J.Phys.Chem.A, **129**, 8982 (2025)

Oxygen Coordination!



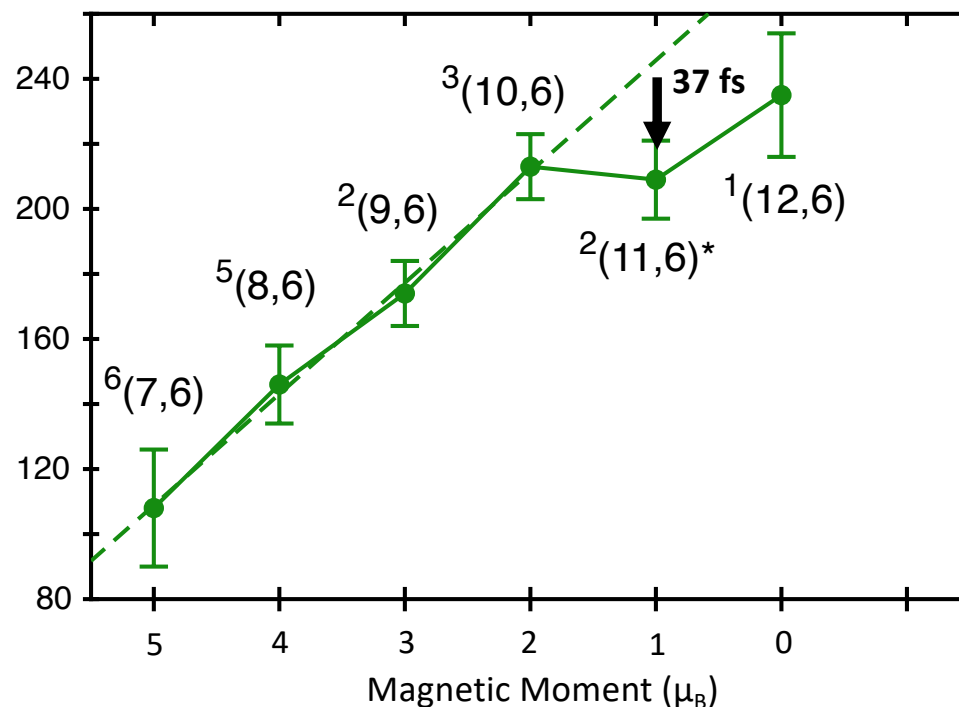
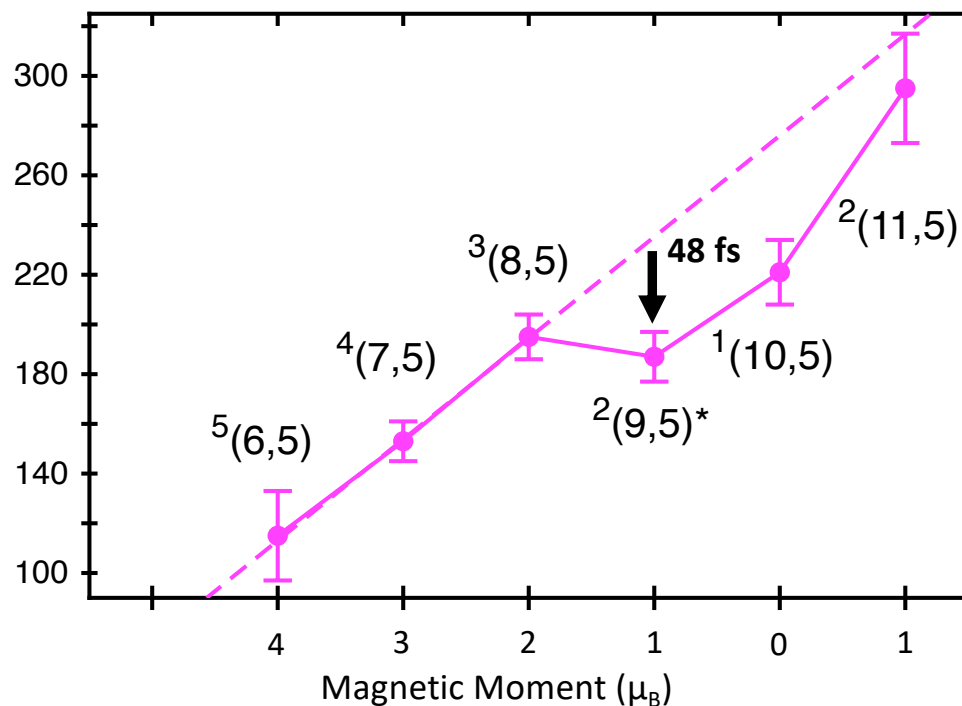
- Not only are total magnetic moments predictable, but local atomic moments as well.
- Ferromagnetic moments are tied to structure (selective magnetism).
- Bulk CuO and Cu₂O only contain tetrahedrally coordinate (μ_4 -O) atoms
- Recent CuO studies report magnetic behavior on surfaces and in nanoparticles.

Lifetimes Influenced by Cu Atoms



- Lifetimes increase with each Cu atom.
- Shorter lifetimes for clusters with large ferromagnetic moments and charge-carrier overlap.
- Terminal atoms attached to a $\mu_4\text{-O}$ atom facilitate faster relaxation (~25%).

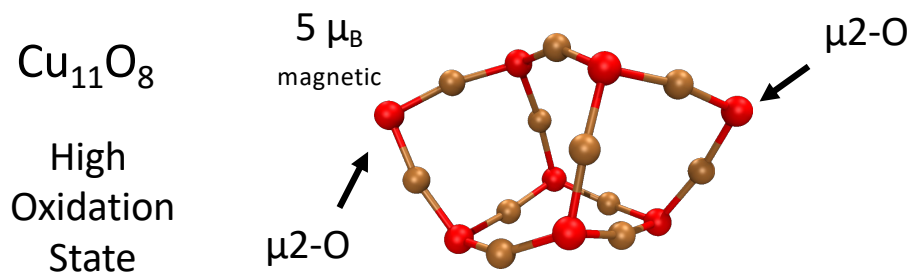
Trendline Deviation Tied to μ_4 -O Atom



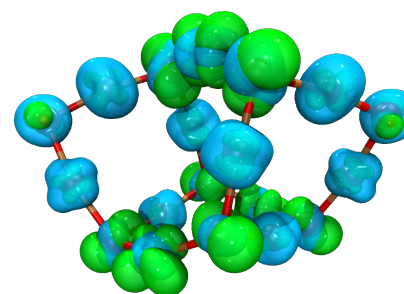
The decrease from expected lifetime occurs with the appearance of the μ_4 -O atom.

Tunable Lifetimes and Ferromagnetism

Structural Features



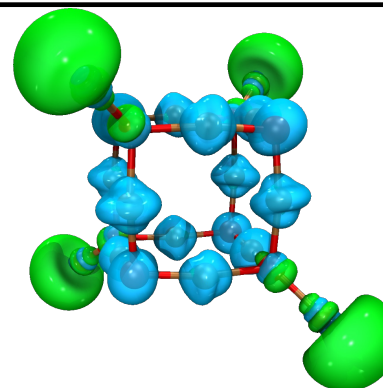
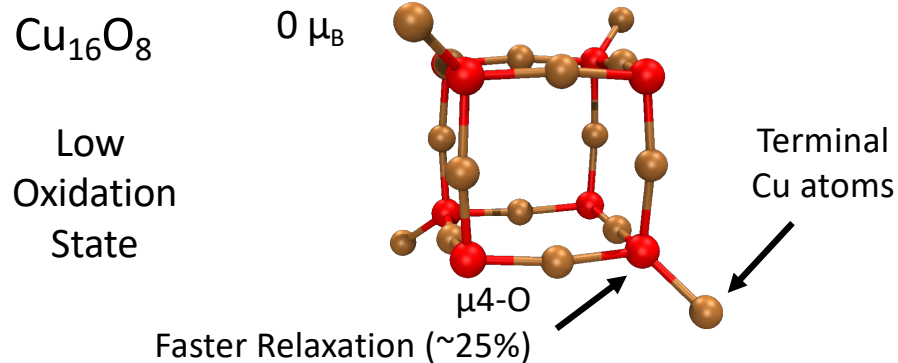
Excitations



Overlapped and localized charge carrier densities

$$\tau = 131 \pm 16 \text{ fs}$$

~100% increase

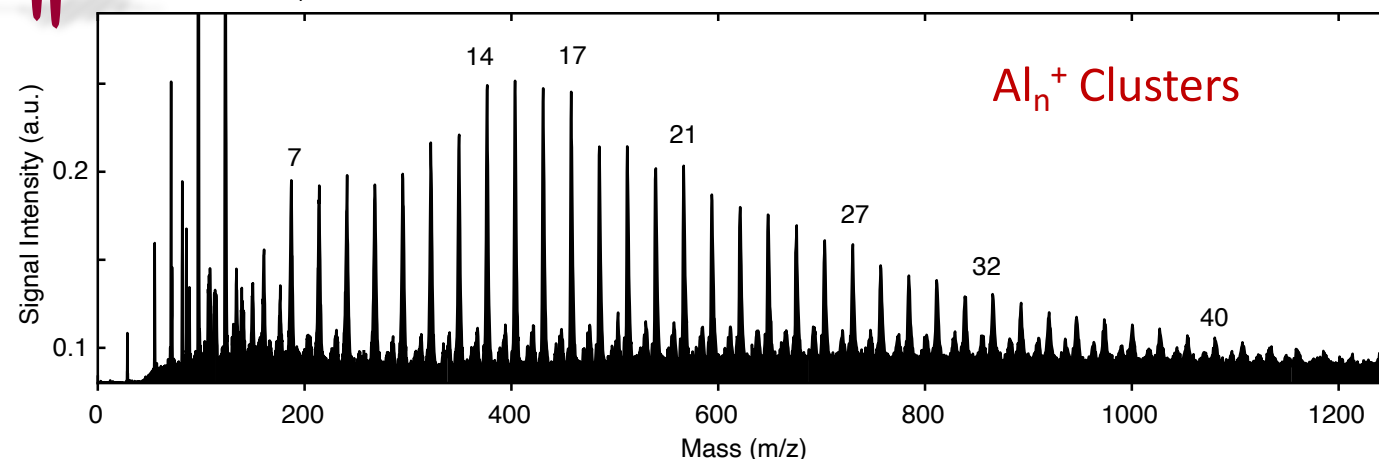


Diffuse and delocalized electronic densities with large charge carrier separation

$$\tau = 260 \pm 18 \text{ fs}$$

J.Phys.Chem.A, **129**, 8982 (2025)
J.Phys.Chem.Lett, **16**, 7107-7114 (2025)

Neutral Clusters?

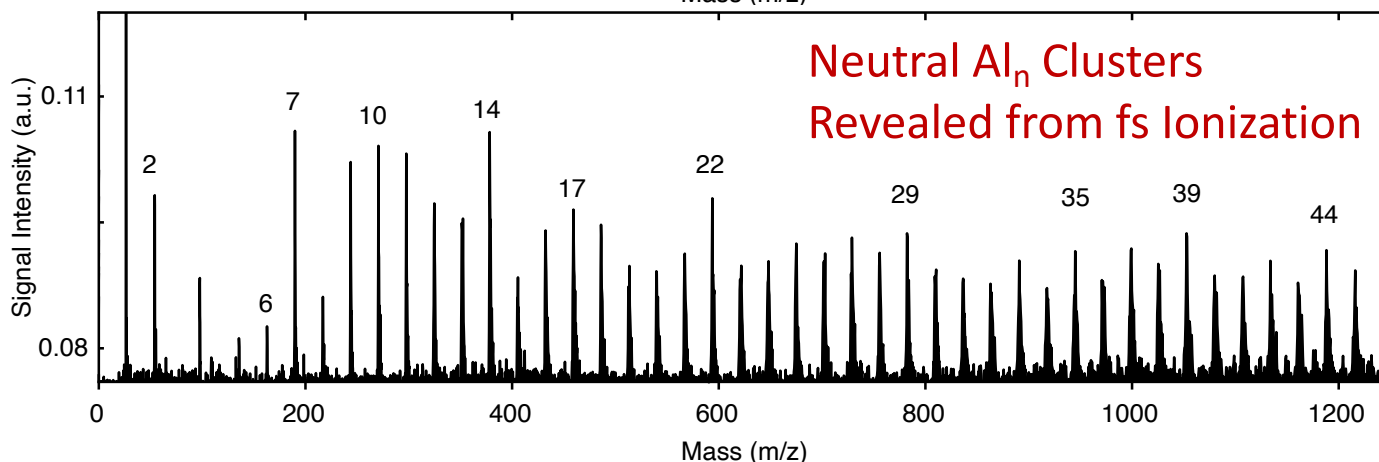


Chase Rotteger



Carter Jarman

Nearly Gaussian
Distribution
(Collision limited)



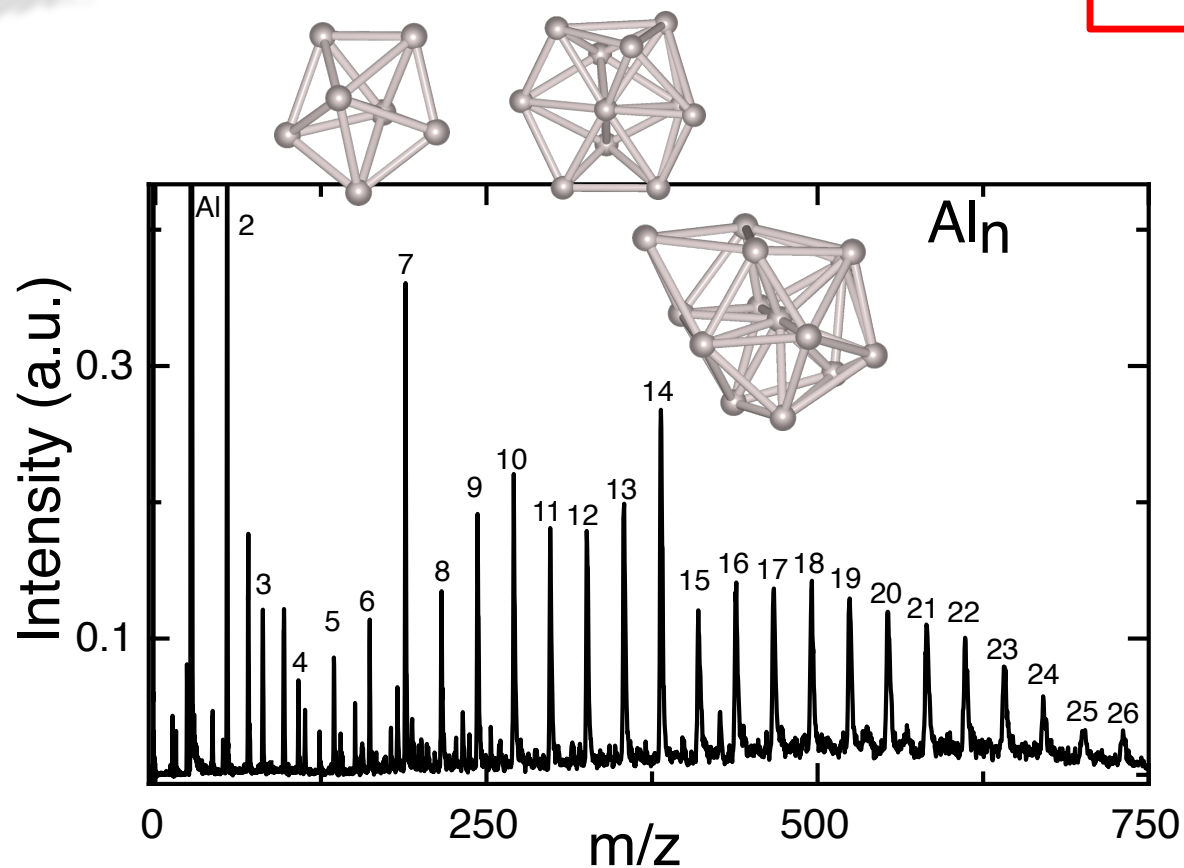
Strong-field Ionization
is sensitive to
Ionization Potential

Reveals Magic
Clusters!

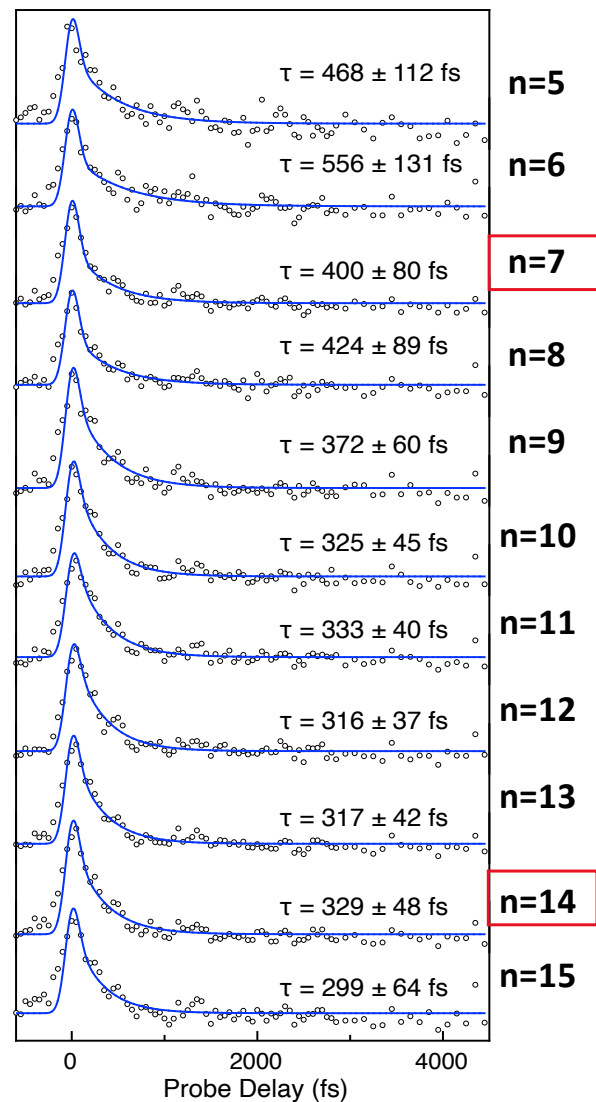
Nanoscale, 2024, **16**, 13516-13524

Magic Behavior?

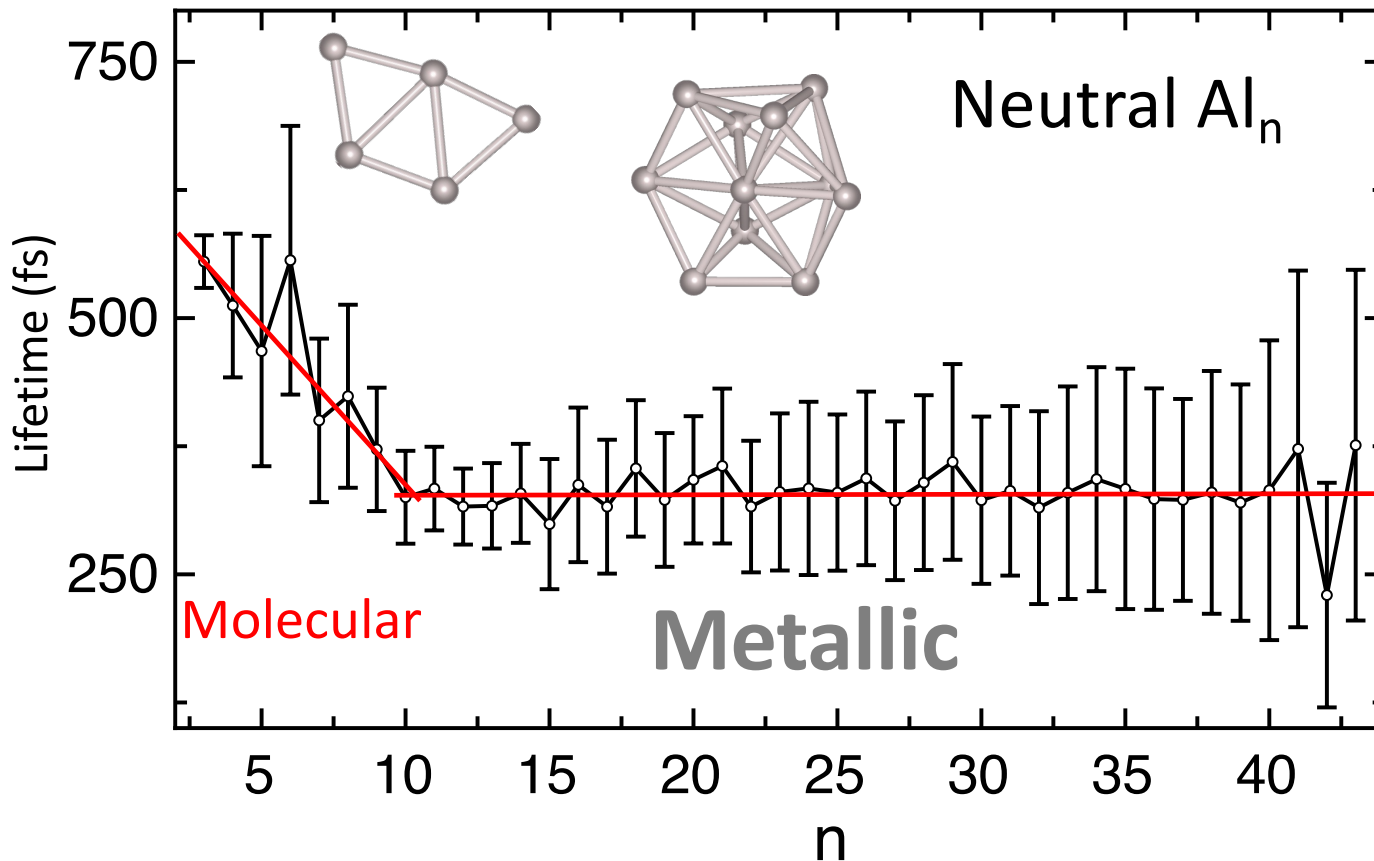
-NO



Nanoscale, 2024, **16**, 13516-13524

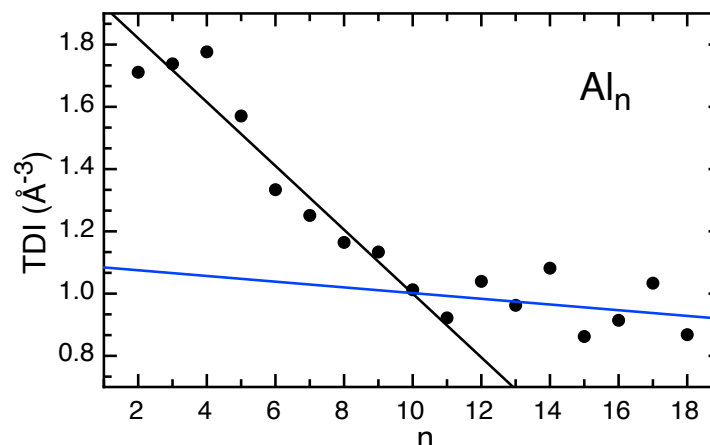
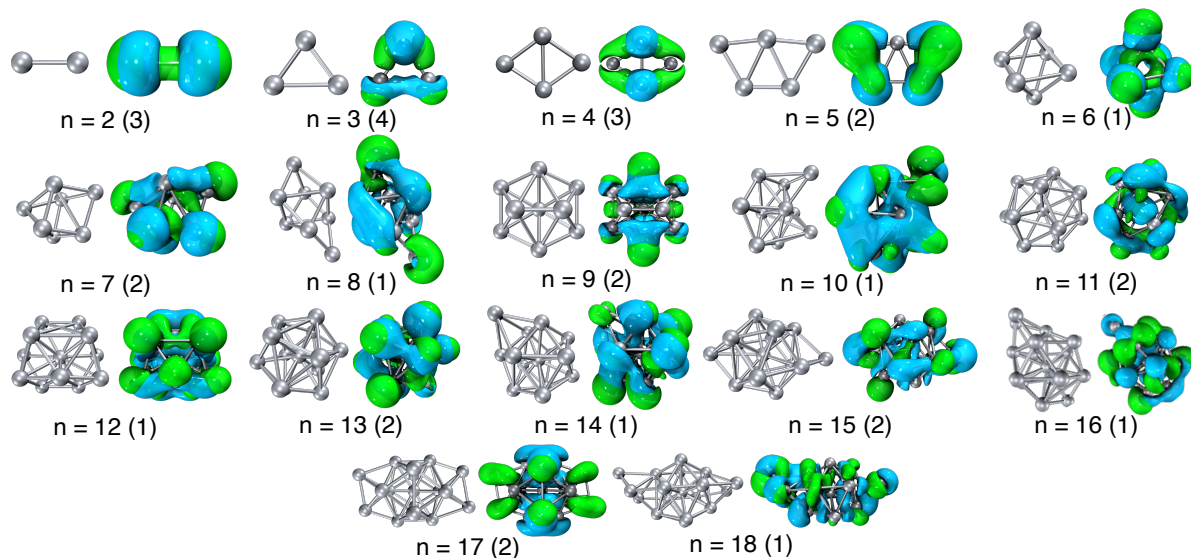


Onset of Metallic Behavior



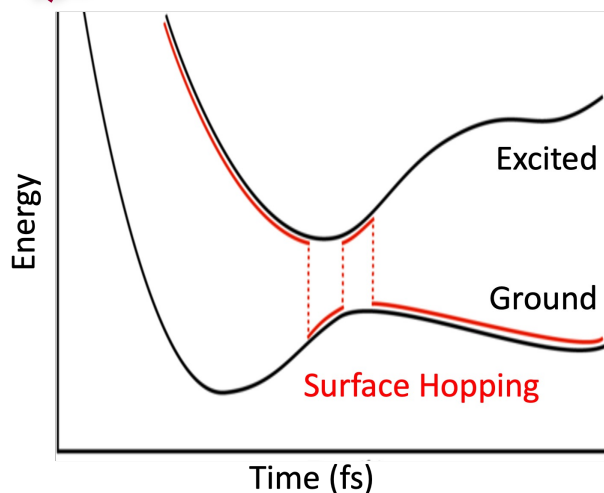
1. No obvious magic behavior
2. 2-D vs. 3-D structures
3. s/p hybridization at $n = 9$ (onset of metallicity)
(Phys. Rev. Lett. **81**, 1909)
4. Reaches bulk lifetime ~ 300 fs

Charge Carrier delocalization



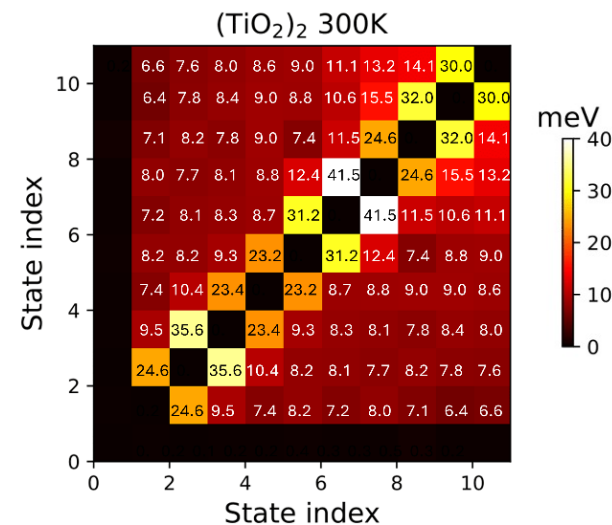
Total delocalization index decreases (similar to lifetime) with size until $n \sim 9$ which demonstrates transition

Non-Adiabatic Molecular Dynamics (NAMD)



$$\rho = \begin{bmatrix} (c_i \psi_i)^2 & c_i c_j \psi_i \psi_j \\ c_j c_i \psi_j \psi_i & (c_j \psi_j)^2 \end{bmatrix}$$

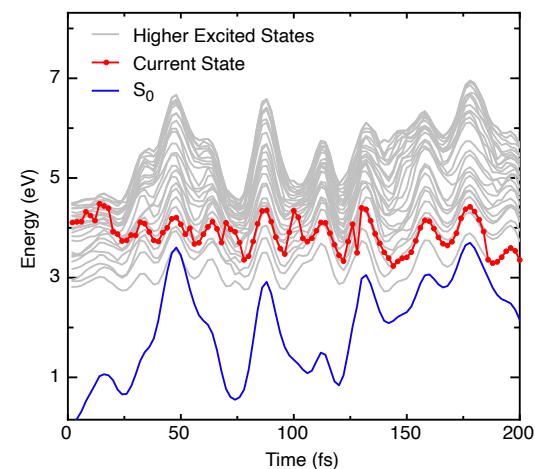
Non-Adiabatic Coupling (NAC) terms



Tully-Hammes-Schiffer (TSH) formula

$$d_{i,j} \left(t + \frac{\Delta t}{2} \right) \approx \frac{\langle \Psi_i(t) | \Psi_j(t + \Delta t) \rangle - \langle \Psi_i(t + \Delta t) | \Psi_j(t) \rangle}{2\Delta t}$$

J. Am. Chem. Soc. **2025**, *147*, 40900–40909



New Era in Theory

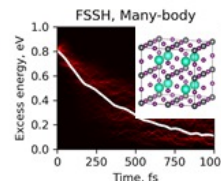
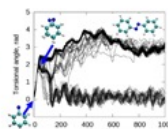
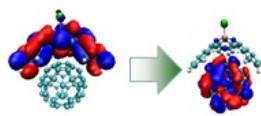
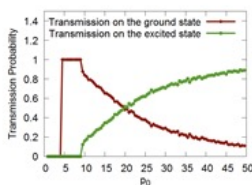
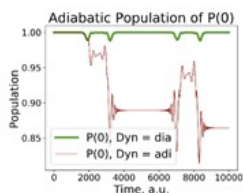


UNIVERSITAT DE
BARCELONA

**University
at Buffalo**

Ehrenfest & TSH methods, model problems

Atomistic NA-MD workflows



Principles:

- modularity and reusability
- “methodology prototyping”
- versatility
- abstract & atomistic
- C++/Python

Libra



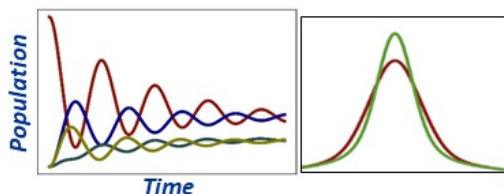
Interfaced with:

- DFTB+
- QE and eQE
- cp2k
- GAMESS
- Gaussian
- more coming...

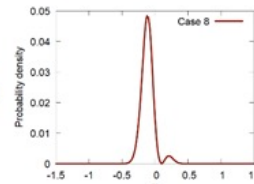
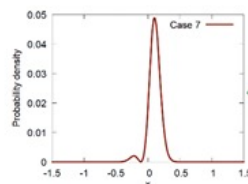


Miguel Recio-Poo

Dynamics of open quantum systems



Quantum Dynamics and DVR

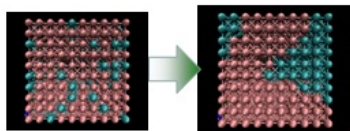


Alexey V. Akimov

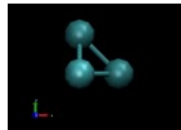


Ángel Morales-García

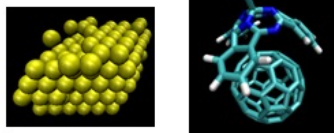
Lattice Monte Carlo



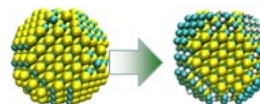
Rigid body



Classical MD



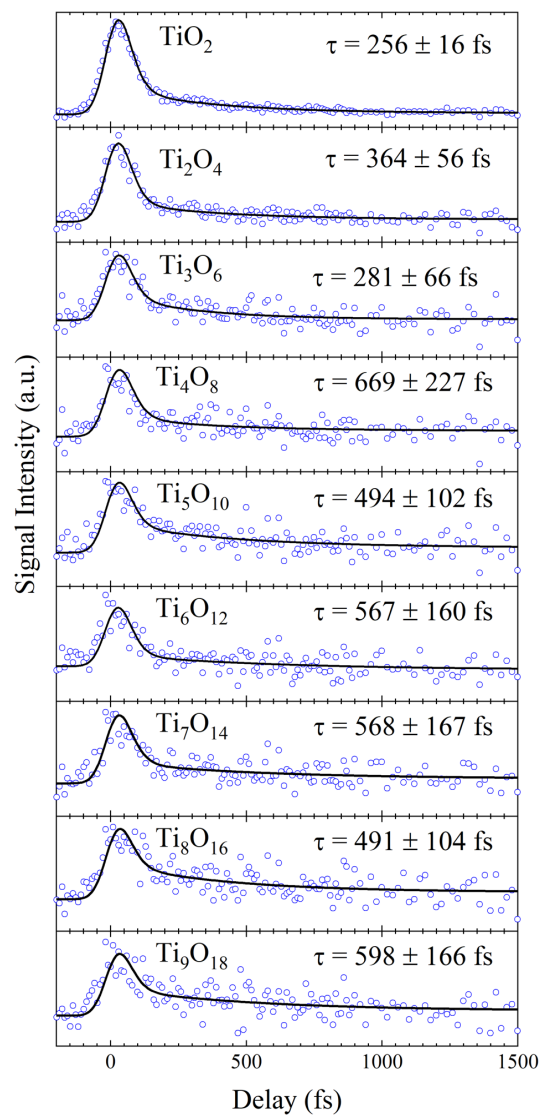
QD builder



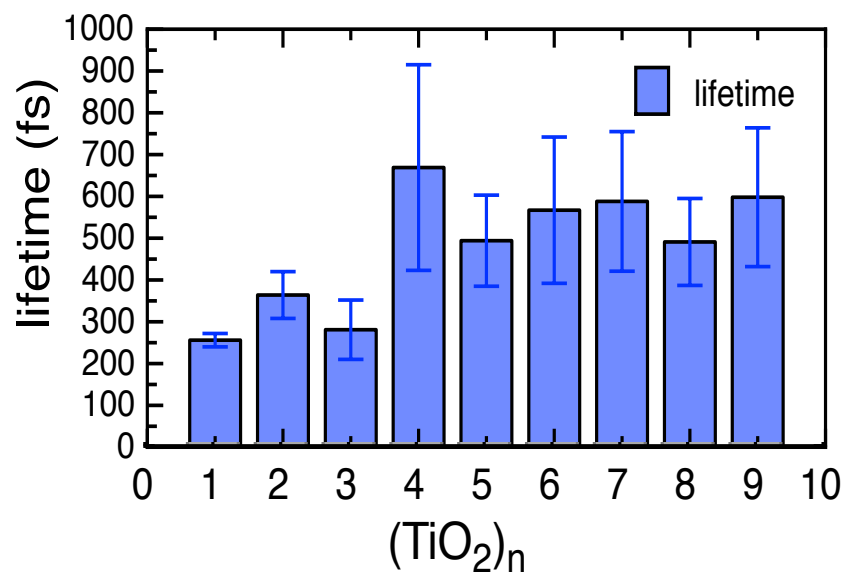
Stefan T. Bromley



Francesc Illas

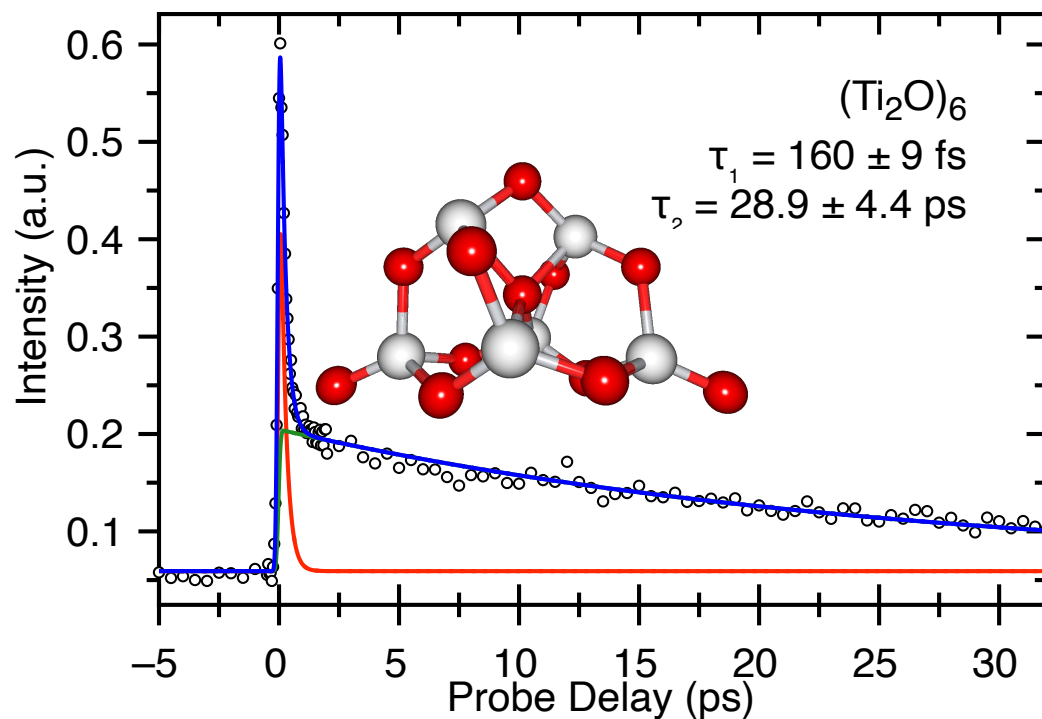


$(\text{TiO}_2)_n$ Lifetimes – d^0



Even/Odd alternation
Even clusters have longer lifetimes!
Slowly increases in lifetime with size

$(\text{TiO}_2)_n$ Revisited [d^0] (now with 266 nm excitation)



Conclusively Identify two relaxation Mechanisms!

J. Am. Chem. Soc. **2025**, 147, 40900–40909



Chase Rotteger

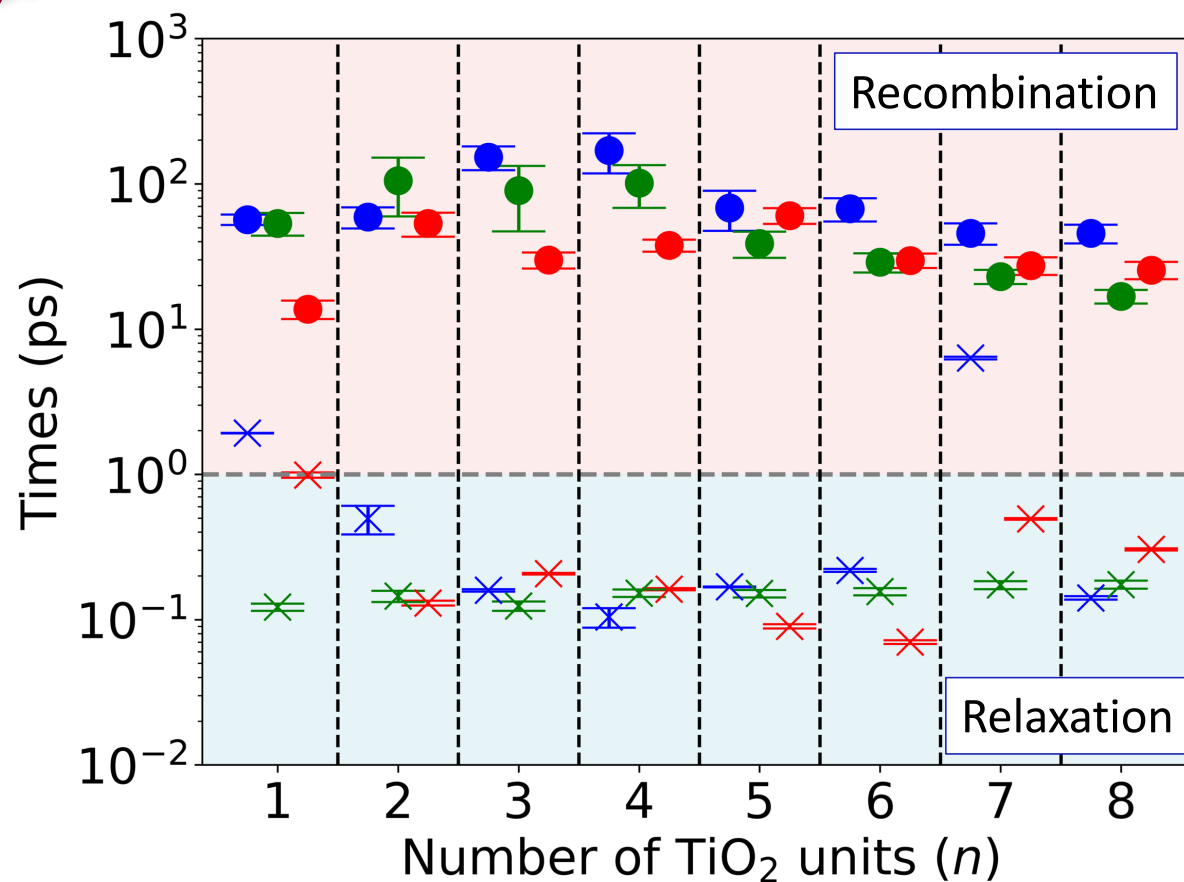


Hannah Rucker

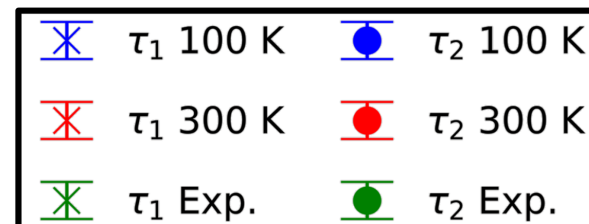


Liz Ballman

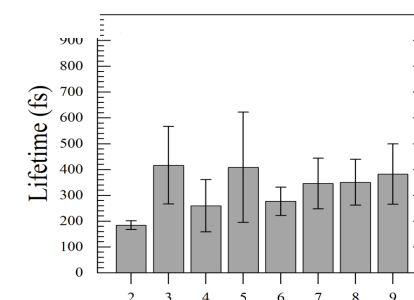
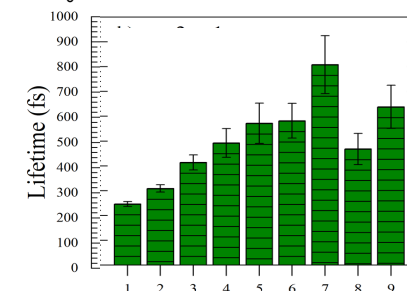
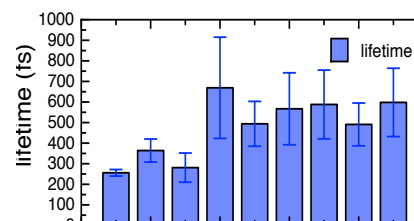
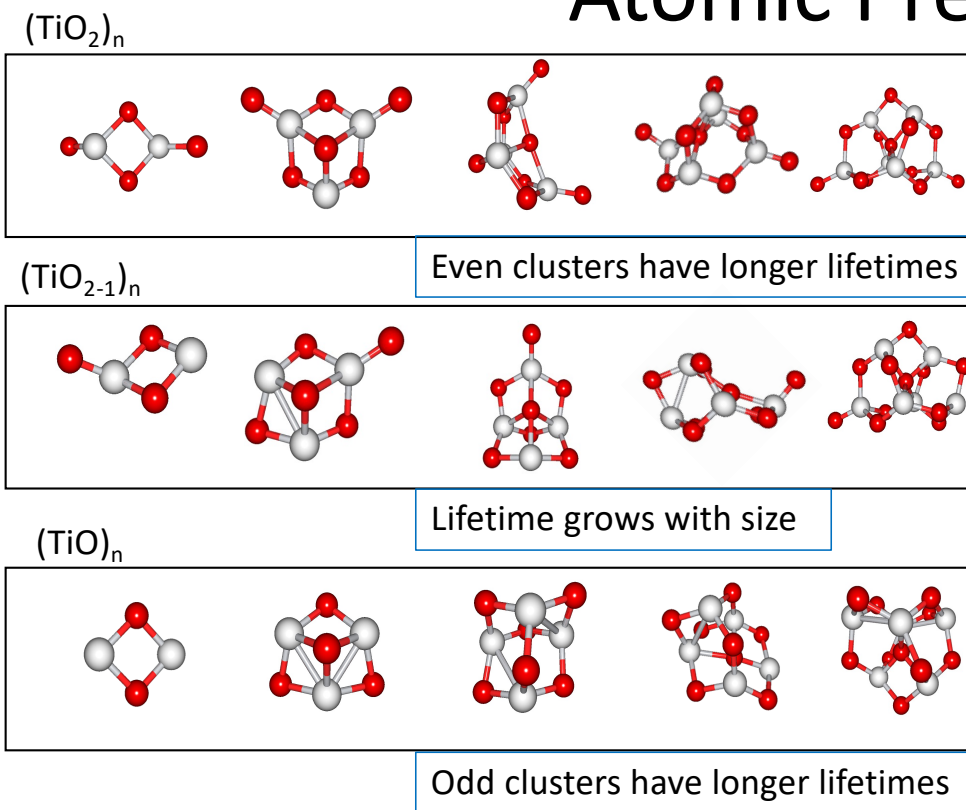
Experiment/Theory Agreement



Two orders of magnitude apart



Neutral Titanium Oxide clusters: Atomic Precision

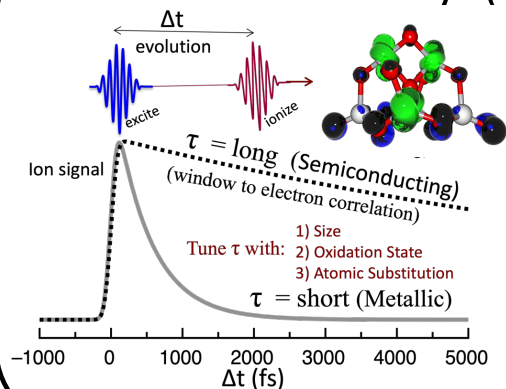


J. Chem. Phys., 2021, **155**, 211102

J. Phys. Chem A, 2022, **126**, 211-220

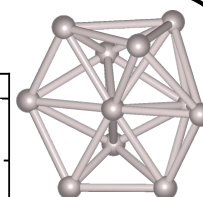
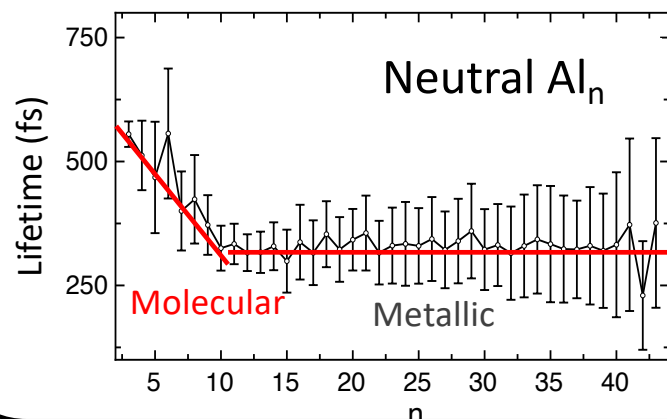
Conclusions

Ultimate Tunability: (e^- correlation)



Carrier localization in S_1 is strongly tied to lifetime (similar to Kasha's rule)

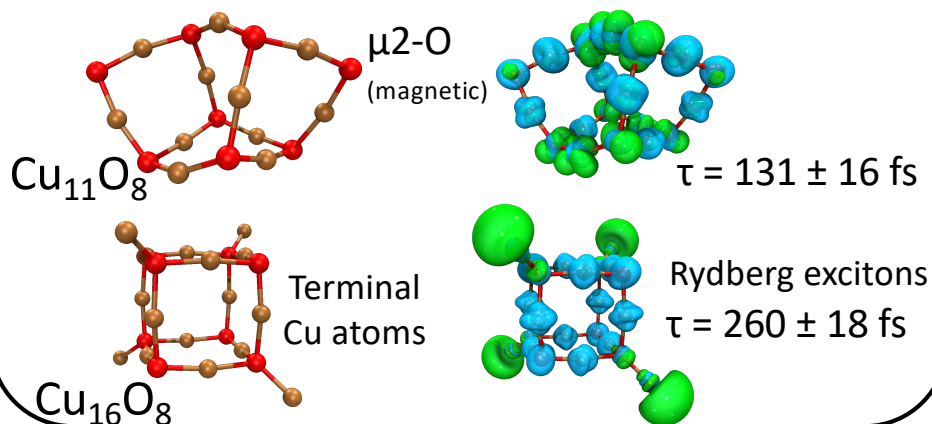
Onset of Metallic Behavior



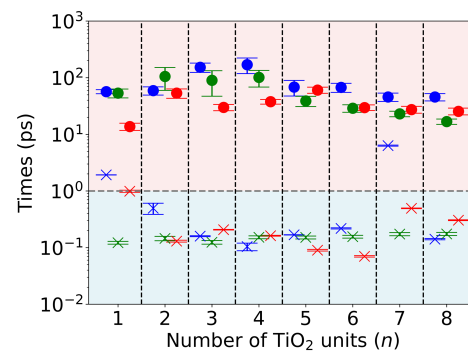
Transition
 $n = 9$

Change in
structure

Importance of Oxidation States



Predicting Excited State Lifetimes



Recombination
To $S_0 \sim 100$ ps

Relaxation to
 $S_1 < 1$ ps

Benchmarking NAMD Calculations

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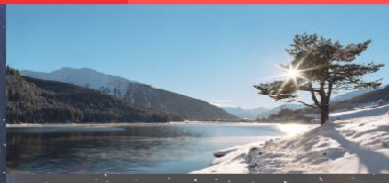


Symposium on Size Selected Clusters

S3C²

THE

... and Complexes



8. – 13. March 2026
Davos | Switzerland

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