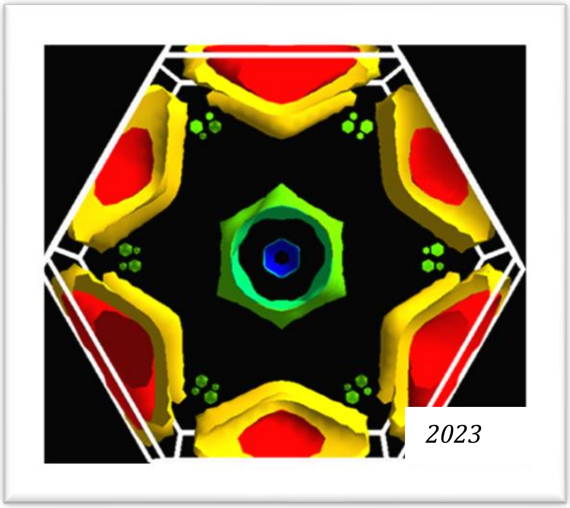
2023


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International Conference on Chemical Bonding

August 23-27, 2025.

Kauai, HI, USA

Sponsors:

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International Conference on Chemical Bonding – 2025

Dedicated to the memory of Professor Alexander Boldyrev, a founding organizer of this conference since its inception in 2013.

Technical Program

Friday, August 22

Arrival & registration. The registration starts at 5pm in the lobby of Sheraton Kauai Coconut Beach Resort.

Saturday, August 23

Morning: Opening. Bonding appetizer plate. *Presiding: Alina Sergeeva*

8:30 – 8:45 am	Anastassia, Lai-Sheng, Ivan - Introductory remarks
8:45 – 9:20 am	Lai-Sheng Wang (Brown University, USA) *"Collaboration with Alex: My Memories of Professor Alexander I. Boldyrev"*
9:20 – 9:55 am	J. V. Ortiz (Auburn University, USA) *"New-Generation Electron-Propagator Concepts in Chemical Bonding Theory"*
9:55 – 10:30 am	Mark S. Gordon (Iowa State University, USA) *"An Unbiased Story of the Origin of the Chemical Bond in Molecules"*
10:30 – 10:45 am	*Coffee Break*
10:45 – 11:20 am	Ángel Martín Pendás (Universidad de Oviedo, Spain) *"To Use or Not to Use References: That is the Question"*
11:20 – 11:55 am	Kenneth D. Jordan (University of Pittsburgh, USA) *"On the Nature of Positron Binding to Atoms and Molecules"*
11:55 – 12:30 pm	Puru Jena (Virginia Commonwealth University, USA) *"From Superhalogens to Superatoms: Design and Applications"*

Afternoon: *Presiding: Anastassia Alexandrova*

Session A: Small Systems, Big Effects: Delocalization, Currents, Magnetism

3:00 – 3:35 pm	Thomas Heine (TU Dresden, Germany) *"Magnetic Carbon"*
3:35 – 4:10 pm	Masaichi Saito (Saitama University, Japan) *"Creation of σ-Delocalization Systems Based on Non-bonded Tellurium Atoms"*
4:10 – 4:45 pm	Dage Sundholm (University of Helsinki, Finland) *"Orbital Contributions to Magnetically Induced Current Density Susceptibilities"*
4:45 – 5:00 pm	*Coffee Break*

Session B: Density Perspective on Bonding

5:00 – 5:35 pm	Amanda Morgenstern (University of Colorado, Colorado Springs, USA) *"Gradient Bundle Analysis of Molecules in External Electric Fields"*
5:35 – 6:10 pm	Dmitry Zubarev (IBM Almaden Research Center, USA) *"From SMILES to Charge Densities: Evolution of Foundational Models in Chemistry"*

07:00 – 10:00 pm ***RECEPTION***

Sunday, August 24

Morning: Materials, Dynamics, and Interfaces *Presiding: Maxim Kulichenko*

8:30 – 9:05 am	Jack P. Simons (University of Utah, USA) *"Alex Boldyrev's influence on my science"*
9:05 – 9:40 am	Philippe Sautet (University of California, Los Angeles, USA) *"Minority Active Sites in Heterogeneous Catalysis"*
9:40 – 10:15 am	Boris I. Yakobson (Rice University, USA) *"Chemical Bonds Alive, in Structures and in Process Dynamics"*
10:15 – 10:30 am	*Coffee Break*
10:30 – 11:05 am	Sergei Tretiak (Los Alamos National Laboratory, USA) *"From Probing Chirality to Chirality Transfer Mechanisms at Organic-Inorganic Interfaces"*
11:05 – 11:40 am	Scott L. Anderson (University of Utah, USA) *"Cluster Size, Composition, and Support Effects on the Catalytic Activity of Supported, Sub-Nano Pt_n"*
11:40 – 12:15 pm	Longjiu Cheng (Anhui University, China) *"Bonding Rules of Conjugated π Electrons: 2D Superatomic-Molecule Theory"*

CONFERENCE PHOTO: 12:30 pm

Afternoon: d- & f-Block *Presiding: Nikolay Tkachenko*

3:00 – 3:35 pm	Anastassia N. Alexandrova (University of California, Los Angeles, USA) *"Chemical Bonding in ^{229}Th-Doped Materials: Development of New Generation Nuclear Clocks"*
3:35 – 4:10 pm	Michael Shatruk (Florida State University, USA) *"High-Symmetry Lanthanide Complexes as Clock-Transition Qubits"*
4:10 – 4:45 pm	Michael D. Morse (University of Utah, USA) *"Bond Dissociation Energies of d- and f-block Diatomic Molecules"*
4:45 – 5:00 pm	*Coffee Break*
5:00 – 5:35 pm	Stefanie Dehnen (Karlsruhe Institute of Technology, Germany) *"Multinary Clusters: Metal Atoms in Their Element(s)"*
5:35 – 6:10 pm	Kirk Peterson (Washington State University, USA) *"Accurate Coupled Cluster-Based Bond Dissociation Energies of the Actinide Halides: Steps towards Understanding the Actinide-Halide Bond"*
6:10 – 6:45 pm	Ivan Popov (Washington State University, USA) *"Dissecting Electron Density in Low-Valent U-Arene Interactions"*

Monday, August 25

Professional Networking, Off-Site Team Meetings, and Exploration Day

Tuesday, August 26

Morning: *Presiding: Lai-Sheng Wang*

Session A: Bonding in Boron-Based Species

8:30 – 9:05 am	Si-Dian Li (Shanxi University, China) *"Fluxional Bonds and Boron Bonds in Chemistry"*
9:05 – 9:40 am	Wan-Lu Li (University of California, Los Angeles, USA) *"Lanthanide/Actinide-Doped Boron Nanoclusters"*
9:40 – 10:15 am	Alexander M. Spokoyny (University of California, Los Angeles, USA) *"Redox-Active Boron Clusters"*
10:15 – 10:30 am	*Coffee Break*

Session B: Gas-Phase Clusters and Spectroscopy

10:30 – 11:05 am	Xue-Bin Wang (Pacific Northwest National Laboratory, USA) *"Photoelectron Spectroscopy Study of Hydrated Hydroxide Anions and Host-Guest Complexes"*
11:05 – 11:40 am	Teng-Teng Chen (The Hong Kong University of Science and Technology, China) *"Cavity-Enabled Enhancement of Intramolecular Vibrational Redistribution over Pseudorotation by Two-Dimensional Infrared Spectroscopy"*
11:40 – 12:15 pm	Stephen Kocheril (JILA and University of Colorado, Boulder, USA) *"Probing the Formation of Interstellar Benzene via Cold Sequential Ion-Molecule Reactions"*

Afternoon: *Presiding: Amanda Morgenstern*

Session A: Fundamentals and Applications of Chemical Bonding - I

3:00 – 3:35 pm	Julen Munárriz (Universidad de Zaragoza, Spain) *"A Statistical Approach to Chemical Bonding"*
3:35 – 4:10 pm	Alvaro Muñoz-Castro (Universidad San Sebastián, Chile) *"Multiple Aromatic Units within a Single Molecular Structure. Overall Aromaticity in Local Aromatic Aggregates"*
4:10 – 4:45 pm	Maksim Kulichenko (Los Alamos National Laboratory, USA) *"Accelerating Quantum Simulations with Graph Theory on AI Hardware"*
4:45 – 5:00 pm	*Coffee Break*

Session B: Biological Systems

5:00 – 5:35 pm	Cynthia Burrows (University of Utah, USA) *"On the Irrelevancy of Hydroxyl Radical to the Evolution of Human Cells"*
5:35 – 6:10 pm	Alina P. Sergeeva (Columbia University, USA) *"Molecular Engineering of Protocadherin Interactions: A Chemical Bonding Perspective on Astrocyte Self-recognition"*

Wednesday, August 27

<u>Morning</u>: Fundamentals and Applications of Chemical Bonding - II *Presiding: Julen Munárriz*

8:30 – 9:05 am	Cina Foroutan-Nejad (Polish Academy of Sciences, Poland) *“Collective Bonding”*
9:05 – 9:40 am	John McGrady (University of Oxford, UK) *“On the Interplay between Metal-Metal and Metal-Ligand Bonding in Zintl Clusters: Complementary Perspectives from DFT and MC-SCF”*
9:40 – 10:15 am	Giovanni Maestri (Università di Parma, Italy) *“A Journey into Molecular Complexity Accompanied by Strong Metal-Metal Bonds and Weak Dispersion Interactions”*
10:15 – 10:30 am	*Coffee Break*
10:30 – 11:05 am	Knut R. Asmis (Leipzig University, Germany) *“Gas Phase Clusters as Model Systems for Solid “Single Site” Catalysts”*
11:05 – 11:40 am	Nikolay Tkachenko (The University of Oklahoma, USA) *“Assessing and Amending Unphysical Potential Energy Surfaces in the D3 and D4 Dispersion Correction Models”*
11:40 – 12:15 pm	Aleksey Kuznetsov (Universidad Tecnica Federico Santa Marıa, Chile) *“Computational Study of the Complexes of P-core-modified Metalloporphyrins with Alkali Metal Cations”*

<u>Afternoon</u>: Clusters and Microdroplets *Presiding: Ivan Popov*

3:00 – 3:35 pm	Zhong-Ming Sun (Fudan University, China) *“Synthesis and Chemical Bonding of Aromaticity-Stabilized Group 14/15 Cage Compounds”*
3:35 – 4:10 pm	Xinxing Zhang (Nankai University, China) *“Investigation of Microdroplet Chemistry with Mass Spectrometry”*

Adjourn

4:20 pm – Departure to Luau (*Please note: transportation is not provided. We recommend using Uber/Lyft or coordinating a shared rental car with other participants*).

Abstracts

Saturday, August 23

Morning: Opening. Bonding appetizer plate.

Collaboration with Alex: My Memories of Professor Alexander I. Boldyrev

Lai-Sheng Wang
Department of Chemistry, Brown University, Providence, RI 02912, USA

Alex and I started our collaboration in 1998 and went on to co-author 91 high impact publications. In this talk, I will begin with my first meeting with Alex and trace our fruitful collaboration for a quarter of a century, from our first paper on superhalogens[1] to the last paper on copper-boron clusters.[2] Along the way, we made many significant discoveries and introduced new concepts, including pentatomic tetracoordinate planar carbons,[3] all-metal aromatic and antiaromatic clusters,[4-6] and d-aromatic transition metal clusters,[7] to name just a few. Together, we initiated the systematic elucidation of the structures and bonding of size-selected boron clusters,[8-10] opening a new area of research that continues to be pursued by my lab and many others. Alex was foremost a chemist, not just a theoretical and computational chemist. He was deeply aware of the limitations of any computational methods and was always seeking new concepts and ideas from calculations. His untimely passing was a profound loss to chemistry and he is dearly missed.

References:

1. X. B. Wang, C. F. Ding, L. S. Wang, A. I. Boldyrev, and J. Simons. First Experimental Photoelectron Spectra of Superhalogens and Their Theoretical Interpretation. *J. Chem. Phys*. **110**, 4763-4771 (1999).
2. W. J. Chen, A. S. Pozdeev, H. W. Choi, A. I. Boldyrev, D. F. Yuan, I. A. Popov, and L. S. Wang. Searching for Stable Copper Borozene Complexes in CuB_7^- and CuB_8^-. *Phys. Chem. Chem. Phys*. **26**, 12928-12938 (2024).
3. L. S. Wang, A. I. Boldyrev, X. Li, and J. Simons. Experimental Observation of Pentaatomic Tetracoordinated Planar Carbon Containing Molecules. *J. Am. Chem. Soc*. **122**, 7681-7687 (2000).
4. X. Li, A. E. Kuznetsov, H. F. Zhang, A. I. Boldyrev, and L. S. Wang. Observation of All-Metal Aromatic Molecules. *Science* **291**, 859-861 (2001).
5. A. E. Kuznetsov, K. A. Birch, A. I. Boldyrev, X. Li, H. J. Zhai, and L. S. Wang. All-Metal Antiaromatic Molecule: Rectangular Al_4^{4-} in the $Li_3Al_4^-$ Anion. *Science* **300**, 622-625 (2003).
6. A. I. Boldyrev and L. S. Wang. All-Metal Aromaticity and Antiaromaticity. *Chem*. *Rev*. **105**, 3716-3757 (2005).
7. H. J. Zhai, B. B. Averkiev, D. Y. Zubarev, L. S. Wang, and A. I. Boldyrev. δ-Aromaticity in $Ta_3O_3^-$. *Angew. Chem. Int. Ed*. **46**, 4277-4280 (2007).
8. H. J. Zhai, L. S. Wang, A. N. Alexandrova, and A. I. Boldyrev. On the Electronic Structure and Chemical Bonding of B_5^- and B_5 by Photoelectron Spectroscopy and *Ab Initio* Calculations. *J. Chem. Phys*. **117**, 7917-7924 (2002).
9. A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang. All-Boron Aromatic Clusters as Potential New Inorganic Ligands and Building Blocks in Chemistry. *Coord. Chem. Rev*. **250**, 2811-2866 (2006).
10. A. P. Sergeeva, I. A. Popov, Z. A. Piazza, W. L. Li, C. Romanescu, L. S. Wang, and A. I. Boldyrev. Understanding Boron through Size-Selected Clusters: Structure, Chemical Bonding, and Fluxionality. *Acc. Chem. Res*. **47**, 1349-1358 (2014).
11. T. Jian, X. N. Chen, S. D. Li, A. I. Boldyrev, J. Li, and L. S. Wang. Probing the Structures and Bonding of Size-Selected Boron and Doped-Boron Clusters. *Chem. Soc. Rev*. **48**, 3550-3591 (2019).

New-Generation Electron-Propagator Concepts in Chemical Bonding Theory

J. V. Ortiz
Department of Chemistry and Biochemistry, Auburn University
& Department of Chemistry, University of Florida

Chemists have a long history of explaining trends in bonding, spectra and reactivity in terms of molecular orbital (MO) concepts. Whereas MO theories began as qualitative tools of pattern recognition and prediction, they have been supplanted by related concepts with quantitative aspirations. *Ab initio* electron-propagator (EP) theory conserves the one-electron picture of molecular electronic structure by rigorously associating Dyson orbitals to observable properties. Examples include electron binding energies, total energies, dipole moments and transition intensities. Unlike other orbitals introduced for computational or pictorial convenience, Dyson orbitals have measurable amplitudes. A new generation of EP methods has surpassed its antecedents with respect to accuracy, efficiency and conceptual clarity. These advantages have enabled parameter-free applications to a variety of problems. Anion photoelectron spectra of nucleotides, green-fluorescent-protein chromophores and species with two or more diffuse, extra-valence electrons may be interpreted with EP calculations and concepts.

An Unbiased Story of the Origin of the Chemical Bond in Molecules

Mark S. Gordon
Department of Chemistry and Ames National Laboratory
Iowa State University
Ames, IA 50011

Most interpretations of the chemical bond rely on some intrinsic assumptions that reflect the point of view of the authors, thereby inserting an implicit bias into the approach. In contrast, the quasi-atomic orbital (QUAO) analysis is based on insights provided by the underlying wave function, with no implicit (or explicit) bias. The QUAO analysis naturally gives rise to the concept of the kinetic bond order (KBO), based on the fact that the energy lowering upon bond formation arises primarily from the kinetic energy due to interference of the wave functions from the combining atoms or collections of atoms. After the QUAO analysis is introduced, it will be demonstrated using several interesting applications.

To Use or Not to Use References: That is the Question

Ángel Martín Pendás,[a] Evelio Francisco[a]
[a] *Universidad de Oviedo, Oviedo, Spain*
E-mail: ampendas@uniovi.es

The use of reference states permeates the theory of chemical bonding. For some researchers, a chemical bond cannot be defined without due consideration of an initial state. For others, chemical bonds are intrinsic features of molecules, and it should be possible to define and characterize them without further reference. We recall that in the standard paradigm of chemical bonds being driven by kinetic energy lowering internal and external reference biases and analyze several other cases. We advocate that the use of real space analyses are as reference-less as possible[1].

[1] Á. Martín Pendás, E. Francisco, Nat. Commun (2022)13:3327; Á. Martín Pendás, D. J. L. Rodrigues, E. Francisco, Phys. Chem. Chem. Phys. 10.1039/d4cp04353g (2025)

On the Nature of Positron Binding to Atoms and Molecules

Kenneth D. Jordan,[1] Shiv Upadhyay,[1,2] and Anouar Benali[3,4]
[1]Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, USA
[2]Department of Chemistry, University of Washington, Seattle, WA, USA
[2]Argonne National Laboratory, Lemont, IL, USA
[4]QuBit Pharmaceuticals, Boston, MA, USA

Experimental studies reveal that a large number of atoms and molecules bind positrons. This includes many species that do not bind an electron to give a stable anion. Treating positron complexes with standard electronic structure methods is challenging due to the fact that when employing localized basis sets, angular momentum functions up to l =15 can be required for both the electron and positron basis functions can be required to achieve well converged results, making configuration interaction or coupled cluster calculations of positron affinities (PAs) of polyatomic molecules computationally prohibitive. We have approached this problem by using the diffusion Monte Carlo (DMC) method which has the advantage of being far less sensitive to the choice of basis set than approaches based on Slater determinants. Although DMC is a real-space method, for treating many-electron systems it is generally coupled with this fixed-node approximation which involves introducing a trial wave function to enforce nodal surface for exchange of electrons. In our work we employ multideterminant trial wave functions for the trial wave functions for subsequent DMC calculations on the systems of interest in the presence of and absence of the positron. Positron affinities are calculated for molecules up to benzene in size.

From Superhalogens to Superatoms: Design and Applications

Puru Jena
Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284

Four decades ago, Gennady Gutsev and Alexander Boldyrev predicted that clusters with suitable size and composition could be created with electron affinities larger than those of halogens as well as ionization potentials smaller than those of alkalis. Named, respectively, superhalogens and superalkalis, these predictions have been verified by experiments. Subsequently, it became apparent that these superions could also be created by using electron-counting rules other than the octet rule. Further, multiple electron-counting rules can be applied simultaneously to create hyperhalogens with even larger electron affinities. Today, hundreds of these species have been created and their applications in promoting unusual chemical reactions have been studied both theoretically experimentally. Equally important, these species can be used to design and synthesize a new generation of solar cells, electrolytes in Li and Na-ion batteries, and heterogeneous catalysts. This talk will provide an overview of this progress over the past four decades. I will illustrate how small clusters carrying multiple charges can be stabilized in the gas phase, how noble gas atoms can form chemical bonds at room temperature, how like charges can attract, and how a salt can be made with only superhalogens as building blocks. Time permitting, I will also discuss how these species can be used as building blocks of advanced solar cells, all solid-state Li ion batteries, and single-superatom catalysts.

Afternoon:

Session A: Small Systems, Big Effects: Delocalization, Currents, Magnetism

Magnetic Carbon

H. Yu[1] and T. Heine[1]
[1]*School of Science, TU Dresden, Germany*

It is generally accepted that carbon is the most versatile element of the periodic table, and it offers a plethora of compounds ranging from biology to materials science. While the list of fascinating properties carbon materials offer is long, they are not yet famous for magnetism.

Indeed, most carbon materials are diamagnetic. Defects, dopants and dangling bonds can introduce paramagnetic centers without the potential to generate magnetic ordering. Recently reported magic-angle twisted bilayer graphene may become ferromagnetic due to a half-filled flat band at the fermi level and spin-orbit coupling[1]. A spectacular early report on magnetic carbon in pressurized fullerenes[2] was found to be caused by defects and the paper has been retracted five years later.

We propose an alternative concept to generate carbon materials with strongly coupled magnetic centers. Our materials are based on molecular triangulene and its derivatives, aromatic molecules intrinsically carrying one or two unpaired electrons. Using covalent linkages that preserve electron conjugation, we construct two-dimensional polymers with honeycomb-kagome lattice. The magnetic coupling between the monomers is facilitated by the linker groups. This has been examined in detail for the dimers[3]. When extending this concept to 2D polymers, we predict magnetic carbon materials with intriguing electronic structure that includes orbital ferromagnetism, while it maintains the Dirac and flat bands which are characteristic for the honeycomb-kagome lattice of the underlying 2D polymer [4,5].

References:

[1] A. Sharpe E. J. Fox, A. W. Barnard, J. Finney, K. Watanabe, T. Taniguchi, M. A. Kastner, D. Goldhaber-Gordon, ACS Nano **21**, 4299 (2021).
[2] T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, A. V. Rakhmanina, Nature **413,** 716, (2001) (retracted).
[3] H. Yu, T. Heine, J. Am. Chem. Soc. **145,** 19303 (2023).
[4] H. Yu, T. Heine, Sci. Adv. 10 (2024) eadq7954
[5] H. Yu, Y. Jing, T. Heine, Acc. Chem. Res. 58 (2025) 61-72

Creation of σ-Delocalization Systems Based on Non-bonded Tellurium Atoms

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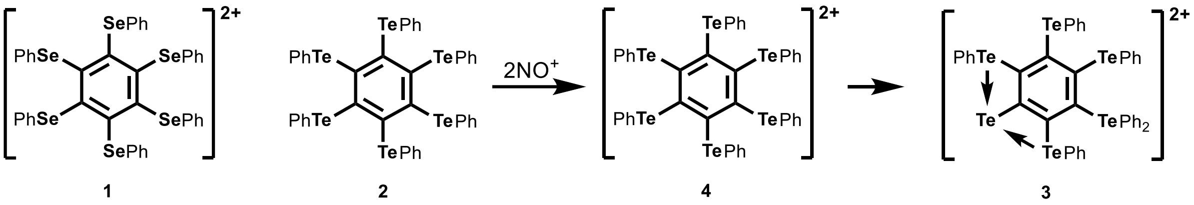
Electronic delocalization is one of the important fundamental phenomena to regulate electronic properties of molecules. Attention has mainly focused on extension of π- and σ-delocalization through bond axis to develop structural and materials chemistry. On the other hand, σ-delocalization can take place on non-bonded atoms. When atoms bearing lone-pair electrons are closely oriented in a certain rigid framework, σ-symmetric orbital interactions take place to increase a HOMO energy level.[1] We have focused on a benzene platform to fix selenium atoms, which are forced to interact with each other to create σ-delocalization on the periphery of the benzene ring. As the number of adjacent selenium atoms increases, the HOMO energy levels increase.[2] Oxidation of a hexa-selenium-substituted benzene afforded dication **1**, which possesses (σ+π)-double aromaticity.[3] These investigations prompted us to introduce a tellurium atom, the heaviest stable atom among the Group 16 atoms.

In this work, we demonstrate the first synthesis of hexa-tellurium-substituted benzene **2** and its less-substituted derivatives, which were obtained by the decomposition of **2** under the reaction conditions. Oxidation of **2** by two equivalents of oxidants afforded unexpected tellurenium cation **3**, which was probably formed via rearrangement of the expected dication **4**. Plausible reaction pathways are also discussed.



References:

1. a) Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5599; b) Roux, M. V.; Jiménez, P; Dávalos, J. Z.; Notario, R.; Juaristi, E. *J. Org. Chem.* **2001**, *66*, 5343; c) Norton, J. E.; Briseno, A. L.; Wudl, F.; Houk, K. N. *J. Phys. Chem. A* **2006**, *110*, 9887.

2. Saito, M.; Suzuki, T.; Takahashi, K.; Seko, S.; Furukawa, S.; Ishimura, K. *Chem. Lett.* **2023**, *52*, 97.

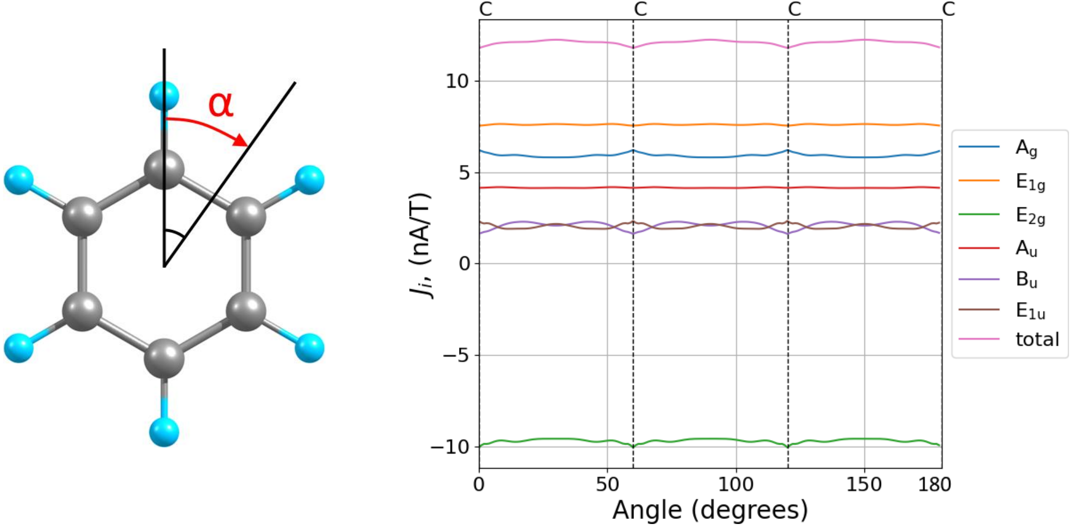
3. a) Hatanaka, M.; Saito, M.; Fujita, M.; Morokuma, K. *J. Org. Chem.* **2014**, *79*, 2640; b) Furukawa, S.; Fujita, M.; Kanatomi, Y.; Minoura, M.; Hatanaka, M.; Morokuma, K.; Ishimura, M.; Saito, M. *Commun. Chem.* **2018**, *1*, 60.

Orbital Contributions to Magnetically Induced Current Density Susceptibilities

Dage Sundholm, Rinat T. Nasibullin, Maria Dimitrova, Rashid R. Valiev

Department of Chemistry, Faculty of Science, A.I. Virtasen aukio 1, POB 55, FI-00014 University of Helsinki, Finland

We have developed and implemented a method to calculate orbital contributions to magnetically induced current density (MICD) susceptibilities in molecules.[1] In our GIMIC method, the gauge origin eliminated from the MICD expression by using gauge-including atomic orbitals (GIAO).[2] Orbital contributions to magnetically induced ring-current (MIRC) strengths and molecular magnetic properties are analyzed and visualized. We have studied the orbital contributions to the MIRC strengths of typical aromatic and antiaromatic organic molecules. We have also used the new approach in studies of orbital contributions to the MICD of all-metal clusters such as Al_4^{2-}, Al_4^{4-}, Cu_4^{2-}, and Bi_6^{2-}. The charge conservation of the MICD is not fulfilled for individual orbitals, whereas it holds for the sum of the orbital contributions of all orbitals in each irreducible representation of the molecular structure in the presence of the external magnetic field. The divergence of the MICD vanishes in the limit of complete basis sets when using the GIMIC method.[1,2]



Orbital contributions to the MIRC strength of benzene for each irreducible representation of the C_{6h} point group as a function on the angle of the integration plane.

References:

[1] R. N. Nasibullin, M. Dimitrova, R. R. Valiev, D. Sundholm, Chem. Sci. (submitted)

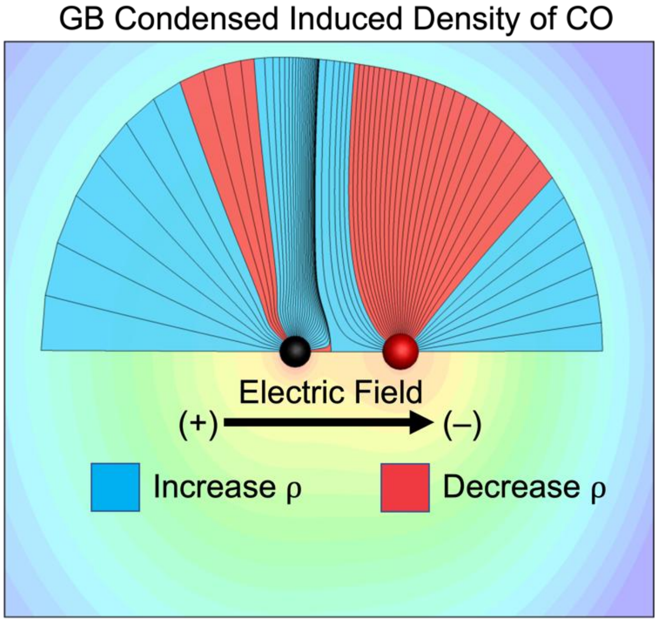
[2] J. Jusélius, J. Gauss, D. Sundholm, J. Chem. Phys. 121 (2004) 3952-3963.

<u>Session B:</u> Density Perspective on Bonding

Gradient Bundle Analysis of Molecules in External Electric Fields

Logan Epperson, Megan Mascarenas, Nikodemos Hughes, <u>Amanda Morgenstern</u>
University of Colorado, Colorado Springs, USA

Significant effort has recently been invested in manipulating electric fields to act as catalysts and for product selectivity. Reasonably strong electric fields can occur naturally, such as in enzymes and droplets, or can be externally applied to reactions such as in scanning tunneling microscopy experiments. Electric fields rearrange the charge density, ρ(r), but it is challenging to quantify these changes in a useful way and predict how the rearrangement of ρ(r) will affect chemical reactivity. The quantum theory of atoms in molecules (QTAIM) has been successful in uncovering some relationships between electric fields and ρ(r). However, electric fields tend to cause subtle changes in ρ(r), making it challenging to study the exact effect of electric fields using QTAIM alone. Gradient bundle analysis (GBA) is an extension to QTAIM that allows for a more detailed quantification of how ρ(r) is rearranged due to external factors. Specifically, GBA allows for analysis of ρ(r) rearrangement within atomic basins. This talk will use DFT calculations to show how gradient bundles can be used to understand ρ(r) rearrangement in terms of conceptual density functional theory. Specifically, gradient bundles are used to analyze changes in ρ(r) due to external electric fields through the condensed induced density of molecules. The rearrangement of ρ(r) *within* atoms is found to often be more significant than rearrangement *between* atoms, thus necessitating the use of GBA in understanding changes in reactivity due to electric fields. Furthermore, rearrangement of ρ(r) from electric fields will be shown to be distinct from rearrangement due to loss or gain of electrons from the entire molecule calculated with Fukui functions.



From SMILES to Charge Densities: Evolution of Foundational Models in Chemistry

Dmitry Zubarev
Senior Research Scientist at IBM Research, Mathematics of Computation Department

In this talk, we present two open-source foundation models from IBM Research that accelerate and extend computational chemistry workflows. First, SMI-TED, a self-supervised Transformer trained on 91 million SMILES, delivers state-of-the-art predictions of molecular properties and reaction yields. The emergent compositionality of the latent space of the model is favorable for few-shot learning. Next, 3DGrid-VQGAN encodes 3D electron density grids into compact, vector-quantized representations and reconstructs simulation-grade grids without expensive quantum calculations. Together, these models slash simulation costs, boost accuracy of property prediction, and enable generative molecular design. We'll close by outlining strategies to scale 3DGrid-VQGAN beyond single molecules, improve latent interpretability, and explore reasoning-based, agentic capabilities that improve accessibility and amplify impact of computational chemistry.

Sunday, August 24

<u>Morning</u>: Materials, Dynamics, and Interfaces

Alex Boldyrev's Influence on my Science

Jack P. Simons
University of Utah, USA

Minority Active Sites in Heterogeneous Catalysis

<u>Philippe Sautet</u>[1,2], Zihan Yang[2], Simran Kumari[1], Anastassia N. Alexandrova[2]
[1]Chemical and Biomolecular Engineering dep., University of California Los Angeles
[2]Chemistry and Biochemistry dep., University of California Los Angeles

We will show that rare, metastable catalytic sites play a paramount role to determine the activity of heterogeneous catalysts. These metastable active sites are created under under reaction conditions and are not present for the as prepared catalysts. The first example will concern the nature of active sites for the zirconia on copper inverse catalyst under the conditions of CO_2 hydrogenation to methanol. We consider a model three atom Zr cluster on a Cu(111) surface decorated with various O, OH and formate ligands. The approach combines Density Functional Theory, and grand canonical global optimization to study variable amount of adsorbates. Under reaction conditions, we observe a large number of compositions and structures with similar free energy for the catalyst, with respect to changing the type, number, and binding sites of the ligands. However, these catalyst configurations show highly distinct reaction energy and barriers for formate hydrogenation elementary steps. The highly dominant contributor to the rate constant is a high energy metastable state with low probability. We will discuss the limits of in situ spectroscopy to detect catalytic active sites. As a second example we will consider large PtNi nanoparticles (more than 10,000 atoms) for which the 3D local atomic structure and chemical composition was determined by atomic electron tomography. The experimental 3D atomic coordinates have used by first-principles trained machine learning to identify the active sites of the nanocatalysts, which are corroborated by electrochemical measurements. A striking feature is the difference of the ORR activity by several orders of magnitude among the surface Pt sites on the nanocatalysts. Furthermore, by analyzing the structure-activity relationship, we formulate an equation named the local environment descriptor to balance the strain and ligand effects and gain physical and chemical insight into the ORR active sites of the Pt alloy nanocatalysts. The ability to determine the 3D atomic structure and chemical composition of realistic nanoparticles, coupled with machine learning, could transform our fundamental understanding of the catalytic active sites and provide a guidance for the rational design of optimal nanocatalysts.

Chemical Bonds Alive, in Structures and in Process Dynamics

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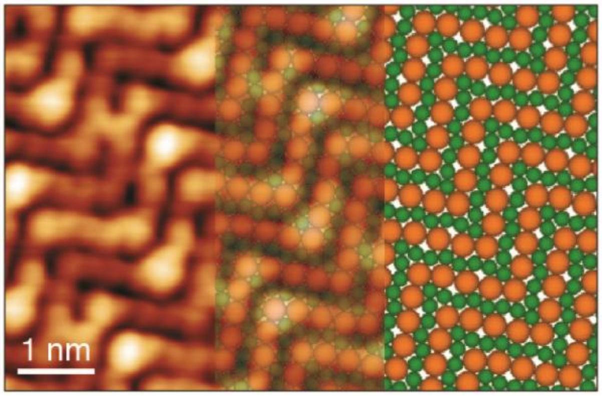

In a meeting dedicated to Alex Boldyrev, new "things boron" are not to be missed. I'd start briefly from a recent work on borophene vs 2D metal-boride "bifurcation" in the epitaxy [1]. Our early prediction of borophene synthesis [2] recommended Ag(111) or Au(111) surfaces as substrates but dismissed Cu, due to too strong B-Cu bonds… Neverthelss, experimenters still reported, quite prominently although quite ambiguous "borophene", which now [1] a thorough the STM images matching to DFT-determined structures (see Figure) proves to be a Cu_8B_{14} boride—being further of potential interest as a coveted UHTC ceramic coating. In the next recent example, the breaking of metallic bond and re-bonding to the nearby atoms covalently produces the switchable ON/OFF dynamics, in the heart of a memristor operation [3]. Lastly, although a big topic, I will try to share briefly emerging understanding of the solid state flash syntheses, accelerated by a Joule-heat spike [4]. In the example of YSZ, yttria stabilized zirconia, we argue that there is a feedback-loop mechanisms involving thermal sublimation of mobile O-sublattice, shifting the Fermi level in the crystal above the charge-transition level ($E_F > E_{CTL}$), which triggers the charge-state change of the Zr-vacancy defects, $V_{Zr}^0 \rightarrow V_{Zr}^{-4}$, giving it greatly higher diffusivity, which thus accelerates its dynamics and overall speeds up the kinetics of sintering.

1. H. Li, Q. Ruan, … B.I.Y.*, M.C. Hersam*, **Science Advances**, **11** eadv8385, (2025).
2. Y. Liu, E.S. Penev, and B.I.Y., **Angew. Chemie Intern. Ed.**, **52**, 3156 (2013).
3. Y. Huang, E.S. Penev, B.I.Y., **Nano Lett. 24**, 13037 (2024).
4. D.X. Luong, K.V. Bets, … B.I.Y.*, J.M. Tour*, **Nature**, **577**, 647 (2020).
5. *Fermi-level mediated flash sintering of oxide ceramics*, Q.-K. Li, E.S. Penev, B.I.Y., **manuscript**.

From Probing Chirality to Chirality Transfer Mechanisms at Organic-Inorganic Interfaces

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Chirality is a fundamental molecular property that plays a crucial role in biophysics and drug design. Our simulations demonstrate that X-ray Circular Dichroism (CD) can exploit the localized and element-specific nature of X-ray electronic transitions. X-ray CD therefore is more sensitive to local structures and the chirality probed with it can be referred to as local which in contrast to a conventional Optical CD probing the global molecular chirality. By considering several molecular cases, we find that XCD is capable of distinguishing dichroic contributions combing from a local chirality center and global molecular conformations, along with their complex interplay. We demonstrate that sterically-induced global distortions can be a dominant source of chirality, in the X-ray range, in some cases even destructively interfering with the dichroic response from the chiral center. We further we formulate the concept of chiral populations connecting distribute the dichroic response to the atomic orbital picture.

Inducing chiroptical activity into semiconductors is challenging due to difficulties of creating asymmetric crystal structures. We further explore chirality transfer in hybrid perovskite quantum dots capped with chiral ligands. Our atomistic modeling suggests the observed chirality transfer is best rationalized by a dipole – dipole coupling. To maximize the bulk effect, both strategic functionalization and limited conformationally degrees of freedom of the ligands are important for obtaining high-intensity nanomaterial chiroptical signatures through chirality transfer. These computational insights provide synthetic mechanistic guidelines towards improving chiroptical functionality in semiconductor nanomaterials.

Cluster Size, Composition, and Support Effects on the Catalytic Activity of Supported, Sub-nano Pt_n

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Sub-nano clusters can be highly active for a variety of catalytic and electrocatalytic reactions, but a major challenge is to stabilize the clusters against sintering, poisoning, and in the case of electrocatalysis, dissolution. Results will be presented for two types of catalysis. 1. High temperature decomposition of alkanes, where the issues are selectivity and cluster stability. 2. Electrocatalysis by small Pt_n on a variety of electrodes under both oxidizing and reducing conditions, where the issues are to anchor the clusters to prevent sintering and dissolution, while preserving high activity.

In the high temperature catalysis project, the goal is to selectively dehydrogenate alkanes to alkenes, with the alkenes desorbing rather than remaining on the surface, losing additional hydrogen, and depositing carbon (coke). We compare the chemistry of n-butane and iso-butane, and the desorption behavior of the corresponding alkenes on both Pt_n and Pt_nGe_m clusters deposited on alumina. The branched vs. linear alkane structure has an enormous effect on the catalyst selectivity, and while Ge addition suppresses coking effectively for both alkanes, in one case it also almost completely suppresses activity, while for the other, the activity actually increases. DFT calculations from the Alexandrova group provide insights into the factors that control selectivity and stability.

Electrocatalysis has been studied for electrodes prepared by both soft- and hard-landing of sub-nano Pt_n clusters on indium-tin oxide (ITO), fluorine-tin oxide (FTO), highly-oriented pyrolytic graphite (HOPG), and HOPG functionalized with nitrogen (N-HOPG). Activity and stability have been tested using the oxygen reduction reaction (ORR), the hydrogen evolution reaction (HER), and electrooxidation of primary and secondary alcohols. Finally, reactions have been studied both in a conventional benchtop electrochemical cell, and in a unique *in situ* electrochemical cell with no air exposure. For some reactions, air exposure has little effect, but for others it can passivate or activate the clusters. Detailed DFT theory by the Alexandrova group was used to probe the dynamics of energetic impacts of both Pt_n clusters and N_2/N ions on HOPG, and to predict trends in electrocatalytic activity.

Bonding Rules of Conjugated π electrons: 2D Superatomic-Molecule Theory

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Aromaticity is one of the most important concepts in chemistry. However, there is still no unified chemical insight for various systems with conjugated sp^2 carbon. Herein, we proposed a superatomic-molecule theory to build a generalized electron-rule for polycyclic conjugated hydrocarbons, fullerenes and 2D periodic materials [1-4]. Taking benzenoid units as 2D superatoms, polycyclic conjugated hydrocarbons and C_{60} can be seen as superatomic molecules consisting of bonded superatoms, resulting in local aromaticity. In superatomic molecules, π electrons are not totally delocalized, but localized in a single superatom forming superatomic lone pairs or shared by two atoms forming a superatomic bond, mimicking rules in classical valence bond theory. Moreover, two 2D superatomic crystals ($C_{18}H_6$ and

$C_{54}H_{18}$) are predicted to have fairly large band gaps (~1.8 eV), although the π electrons are conjugated and delocalized. The proposed superatomic-molecule theory provides generalized chemical insights into the nature of local aromaticity, which can be qualitatively evaluated by the chemical intuition given by superatomic Lewis structures.

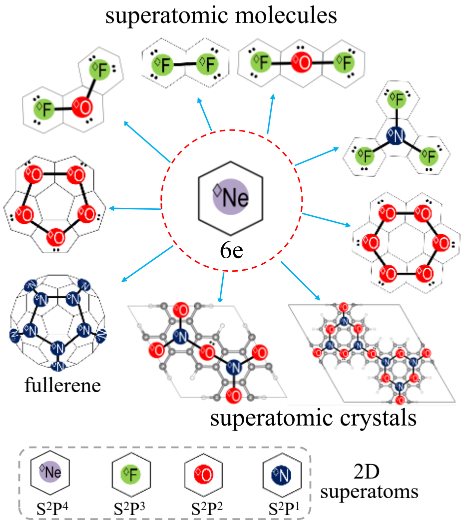

Fig. 1 Illustrations of 2D superatomic molecules

References:
[1] Li, D.; Yang, J.;* Cheng, L.* *Natl. Sci. Rev.* **2023**, 10(3): nwac216.
[2] Li, D.; Yan, C.; Yuan, Q.; Shi, L.; Cheng, L.* *Phys. Chem. Chem. Phys.* **2023**, 25(12): 8439.
[3] Yu, X.; Wu, P.; Yuan, Q; Yan, C.; Li, D.; Cheng, L.* *J. Phys. Chem. A* **2023**, 127, 7487.
[4] Guo, L.; Zhang, D.; Shen, K.; Yuan, Q.; Li, D.; Cheng, L.* *J. Phys. Chem. Lett.* **2024**, *15*, 5754-5760.

Afternoon: d- & f-Block

Chemical Bonding in ^{229}Th-doped Materials: Development of New Generation Nuclear Clocks

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The ^{229}Th isotope has a laser-accessible nuclear transition, not only in the gas phase, but also in ^{229}Th doped large-band gap solids. This feature should allow a number of exciting applications: the construction of a robust and portable optical nuclear clocs; exploration of nuclear superradiance; tests of fundamental physics; and, perhaps, a new temperature standard. Solid-state ^{229}Th nuclear clocks require a host material whose band gap is larger than the 8.4 eV nuclear transition energy. Other requirements include maximally uniform environment for every ^{229}Th atom to avoid broadening of the transition due to dipole-dipole interactions, minimal covalency of Th with the environment to prevent the formation of intragap electronic states that can interfere with the nuclear excitation or provide undesirable decay channels via hyperfine coupling, and preferably the lack of nuclear spins in the material host. Hence, this material design task is essentially a chemical bonding task. I will present several material hosts for ^{229}Th nuclear clocks that have been designed and tested experimentally.

References:
Pineda, S.V.; Chhetri, P.; Bara, S.; Elskens, Y.; Casci, S.; Alexandrova, A.N.; Au, M.; Athanasakis-Kaklamanakis, M.; Bartokos, M.; Beeks, K.; Bernerd, C.; Claessens, A.; Chrysalidis, K.; Cocolios, T.E.; Correia, J.G.; De Witte, H.; Elwell, R.; Ferrer, R.; Heinke, R.; Hudson, E.R.; Ivandikov, F.; Kudryavtsev, Yu.; Köster, U.; Kraemer, S.; Laatiaoui, M.; Lica, R.; Merckling, C.; Morawetz, I.; Morgan, H.W.T.; Moritz, D.; Pereira, L.M.C.; Raeder, S.; Rothe, S.; Schaden, F.; Scharl, K.; Schumm, T.; Stegemann, S.; Terhune, J.; Thirolf, P.G.; Tunhuma, S.M.; Van Den Bergh, P.; Van Duppen, P.;

Vantomme, A.; Wahl, U.; Yue, Z. *Radiative Decay of the ^{229m}Th Nuclear Clock Isomer in Different Host Materials.* **2025**, Phys. Rev. Res., 7, 013052.

Elwell, R.; Terhune, J. E. S.; Morgan, H. W. T.; Alexandrova, A. N.; Tran Tan, H. B.; Derevianko, A.; Hudson, E. R. *^{229}ThF$_4$ thin films for solid-state nuclear clocks.* **2024**, Nature, 636, 603-608.

Elwell, R.; Schneider, C.; Jeet, J.; Terhune, J. E. S.; Morgan, H. W. T.; Alexandrova, A. N.; Tan, H. B. T.; Derevianko, A.; Hudson, E. R. *Laser excitation of the ^{229}Th nuclear isomeric transition in a solid-state host.* **2024**, Phys. Rev. Lett., 133, 013201.

High-Symmetry Lanthanide Complexes as Clock-Transition Qubits

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Qubit is an elementary unit of quantum computation, allowing coherent superposition of states that can be initialized, manipulated, and read-out for quantum information processing. Molecular spin qubits are appealing due to their synthetic tunability and a broad range of spin states that can be incorporated by using various transition and lanthanide metal ions. The generally short coherence time, however, remains the major obstacle for implementation of molecular qubits in quantum computing technology. In this contribution, we demonstrate how this challenge can be addressed by using high-symmetry lanthanide complexes to achieve clock transitions,[1,2] characterized by a dramatically enhanced coherence time at specific values of resonant magnetic field. We use variable-frequency EPR spectroscopy to determine the clock-transition energy gaps for the ground-state doublets of crystal-field generated manifolds of ±m_J states and demonstrate the correlations of the gap magnitude to the geometry of the local coordination environment around the lanthanide ion. The nature of the ground states that lead to the clock transition is elucidated by theory.

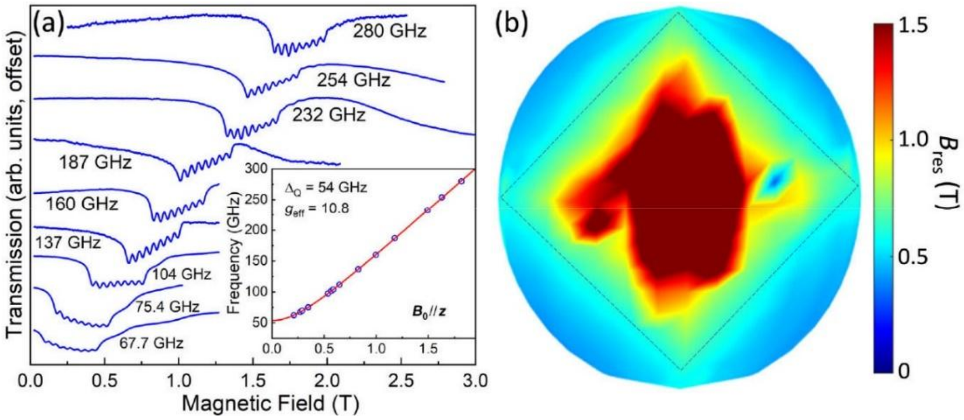

Figure 1. (a) Variable-frequency EPR spectra of a Ho metal-organic framework that exhibits a quantum clock transition at 54 GHz. (b) Spherical plot of the applied magnetic field, B_{res}, at the center of the spectrum at 80.6 GHz, viewed along the 4_1 crystallographic axis.

1. M. Shiddiq, D. Komijani, Y. Duan, A. Gaita-Ariño, E. Coronado, S. Hill, *Nature* **2016**, *531*, 348-351.
2. A. Gaita-Ariño, F. Luis, S. Hill, E. Coronado, *Nat. Chem.* **2019**, *11*, 301-309.

Thermochemistry from Spectroscopy: Bond Dissociation Energies of *d*- and *f*-block Diatomic Molecules

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This research group employs laser ablation/supersonic expansion sources to provide jet-cooled beams of small metal-containing molecules, which are then probed using resonant two-photon ionization (R2PI) spectroscopy and time-of-flight mass spectrometric detection. For molecules with open *d*- or *f*-subshells, we find that when the molecule is excited above the ground separated fragment limit, spin-orbit interactions and nonadiabatic processes allow it to dissociate on a nanosecond to sub-nanosecond time scale, allowing the onset of predissociation to be used to measure the bond dissociation energy (BDE) to high precision. In this talk I will discuss our BDE measurements of the LnCl molecules, which are then related to their electronic structure. A clear distinction is observed between LnCl molecules with $4f^n6s^1$ and $4f^{n-1}6s^2$ molecular configurations. Our laser system allows BDEs to be measured up to about 5.8 eV using the R2PI method. To measure the BDEs beyond this limit, we have devised a resonant three photon ionization (R3PI) process, which has been used to measure the BDEs of VO, RuC, RhC, OsC, IrC, and PtC to a precision of ±0.002 eV. If time permits, other recent developments from our laboratory will also be discussed.

Multinary Clusters: Metal Atoms in Their Element(s)

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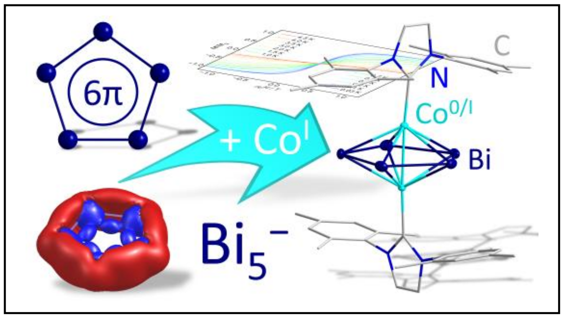
The synthetic access to cluster compounds and their numerous exciting properties have inspired many research groups worldwide to investigate them in the solid state, in solution, and in the gas phase.[1] In particular, clusters based on p-block elements in combination with d-/f-block metals have attracted a lot of attention,[2,3] with a recent focus on novel bismuth-based architectures.[4] Out of the many different synthetic approaches for corresponding clusters, we use Zintl anions in reactions with d- or f-block metal compounds to gain access to multinary clusters. Multimetallic clusters like $[K_2Zn_{20}Bi_{16}]^{6-}$,[5] $[Th@Bi_{12}]^{4-}$,[6] $[\{(cod)Ru\}_4Bi_{18}]^{4-}$,[7] or $[\{CpRu\}_3Bi_6]^{-}$,[8] $[Bi_6\{Zn(hmds)\}_2]^{2-}$,[9] or $[\{IMesCo\}_2Bi_5]$ (see figure)[10] demonstrate the broad range of unique structures and unprecedented bonding modes, including uncommon electronic as well magnetic features, and they also allow insight into cluster formation steps. In addition to these fundamental aspects, such species show potential for cluster-based bond activation, or as precursors for new intermetallics.



6π-Aromatic Bi_5^- and $[\{IMesCo\}_2Bi_5]$

References:

[1] Zhang, J.; Bu, X.; Feng, P.; Wu, T. *Acc. Chem. Res.* **2020**, *53*, 2261.
[2] Wilson, R. J.; Lichtenberger, N.; Weinert, B.; Dehnen, S. *Chem. Rev.* **2019**, *119*, 8506.
[3] McGrady, J. E.; Weigend, F.; Dehnen, S. *Chem. Soc. Rev.* **2022**, *51*, 628.
[4] Pan, F.; Peerless, B.; Dehnen, S. *Acc. Chem. Res.* **2023**, *56*, 1018.

[5] Eulenstein, A. R.; Franzke, Y. J.; Bügel, P.; Massa, W.; Weigend, F.; Dehnen, S. *Nat. Commun.* **2020**, *11*, 5122.
[6] Eulenstein, A. R.; Franzke, Y. J.; Lichtenberger, N.; Wilson, R. J.; Deubner, L.; Kraus, F.; Clérac, R.; Weigend, F.; Dehnen, S. *Nat. Chem.* **2021**, *13*, 149.
[7] Pan, F.; Wei, S.; Guggolz, L.; Eulenstein, A. R.; Tambornino, F.; Dehnen, S. *J. Am. Chem. Soc.* **2021**, *143*, 7176.
[8] Peerless, B.; Schmidt, A.; Franzke, Y. J.; Dehnen, S. *Nat. Chem.* **2023**, *15*, 347.
[9] Schmidt, A.; Rienmüller, J,; Weigend, F.; Dehnen, S. *Angew. Chem. Int. Ed.* **2025**, 64, e202417234.
[10] Rienmüller, J.; Peerless, B.; Paul, S.; Bruder F.; Wernsdorfer, W.; Weigend. F.; Dehnen S. *Nat. Chem.* **2025**, *17*, 547.

Accurate Coupled Cluster-Based Bond Dissociation Energies of the Actinide Halides: Steps towards Understanding the Actinide-Halide Bond

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An accurate coupled-cluster-based composite methodology is used to calculate the bond dissociation energies (BDEs) of the actinide halides AnX and AnX^+, where An=Ac-Cf and Md-Lr with X=F-I. In most cases a spinor-based CCSD(T) approach was utilized where spin-orbit was included at the orbital level. In the middle of the actinide row this was not possible due to strong multireference effects, and then a more standard Feller-Peterson-Dixon approach was used where SO was included as a correction to scalar relativistic CCSD(T) results. In all cases sequences of large correlation consistent basis sets were used in all-electron calculations with extrapolation to the complete basis set (CBS). The effects of outer-core correlation and QED were included in all cases. Comparison to recent experimental values for the Th and U halides demonstrate that the current strategy can obtain sub-kcal/mol accuracies for the BDEs. The trend of accurate BDEs across the actinide row is expected to lead to improved models for a fundamental understanding of actinide bonding.

Dissecting Electron Density in Low-Valent U-Arene Interactions

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Separating heavy elements remains one of the central challenges in nuclear waste management. A deeper understanding of actinide ligand interactions, particularly across multiple oxidation states, is essential for advancing the design of selective ligands used in nuclear separation chemistry. Low valent actinide complexes, while promising for their unique bonding and redox properties, often exhibit high reactivity that can lead to decomposition or disproportionation. This reactivity can be modulated through deliberate ligand design, including steric protection, the ability to accommodate excess electron density, and stabilization by intercalated counterions within the second coordination sphere. Deconvoluting the electronic structure of low valent U complexes presents a significant challenge. As the U 5*f* and 6*d* manifolds approach energetic degeneracy with ligand-based antibonding orbitals, competition between metal-centered and ligand-centered reduction increases, leading to ambiguity in assigning the metal's oxidation state.

In this talk, I will examine the nature and extent of metal to ligand backdonation in a series of low valent U arene complexes using DFT and *ab initio* multireference calculations. I will show that backdonation into arene π^* orbitals plays a critical role in stabilizing these reduced species, with the magnitude of backdonation increasing as the formal oxidation state of U decreases. Through electronic structure analysis in the formally U^{2+} and U^{1+} compounds, we assess the contributions of U 5*f* and 6*d* orbitals to this interaction and quantify the degree of electron delocalization onto the ligand framework. The results reveal that arene ligands can act as electron reservoirs, accepting substantial charge upon reduction of the complex and creating a notable divergence between the formal and physical oxidation states of the U center. These insights not only deepen our understanding of covalency in f element bonding but also offer guiding principles for stabilizing reactive low valent species relevant to nuclear chemistry and actinide reactivity design.

Tuesday, August 26

Morning:

Session A: Bonding in Boron-Based Species

Fluxional Bonds and Boron Bonds in Chemistry

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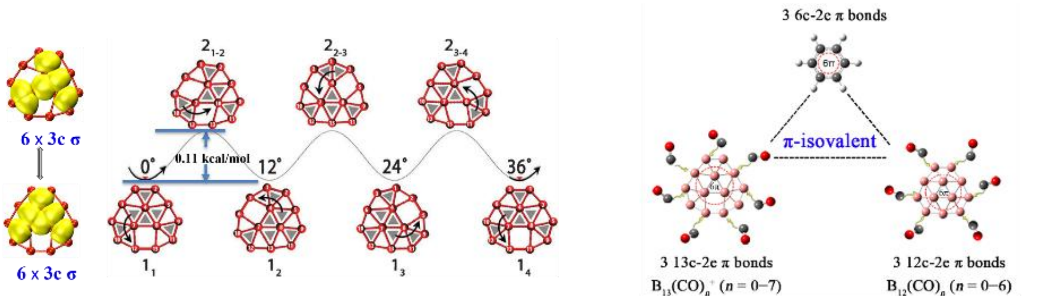
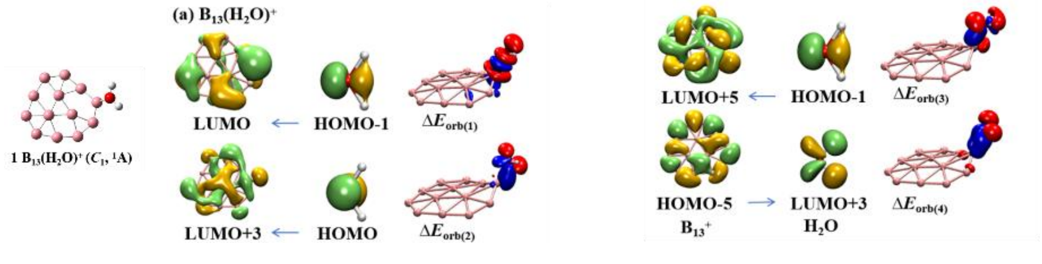
Boron (B[He]$2s^2 2p^1$) as a prototypical electron-deficient element exhibits unique structures and bonding in both its polyhedral molecules and bulk allotropes. We focus on the following topics in this presentation : (1) Structural and bonding characteristics of the cage-like $B_{40}^{0/-}$ and B_{39}^-, seashell-like $B_{28}^{0/-}$ and B_{29}^-, and bilayer $B_{48}^{0/-}$; (2) Fluxional bonds (FBs) in planar B_{11}^-、 B_{13}^+ and B_{19}^-, tubular Ta@B_{20}^- and La_2@B_{20}, cage-like bullvallene $C_{10}H_{10}$, and semibullvalene C_8H_8 and fluxional hydrogen bonds (FHBs) in small water clusters $(H_2O)_{1\text{-}6}$ and fluxional halogen bonds (FXBs) in molecular clusters and crystals; (3) Observation of boron carbonyl aromatics (BCAs) $B_{13}(CO)_n^+$ (n=1-7) anlogous to benzene and $B_{11}(CO)_n^+$ (n=1-6) and $B_{15}(CO)_n^+$ (n=1-5) with σ and π conflicting aromaticity; (4) Core–shell superpolyhedral boranes and carboranes and 1D and 2D borophanes in bottom-up approaches based on icosahedral $B_{12}H_{12}^{2-}$ by partial dehydrogenations; (5) Observation of boron bonds (BBs) in aromatic boron-water complexes $B_{13}(H_2O)_n^+$ (n=1,2) and $B_{12}H(H_2O)^+$ analogous to benzene.



(a) Fluxional bonds in B_{13}^+ **(b) Aromatic $B_{13}(CO)_n^+$ (n=1-7)**



(c) boron bonds (BBs) in $B_{13}(H_2O)^+$.

Fig.1 (a) Fluxional bonds (FBs) in B_{13}^+, (b) Boron carbonyl aromatics (BCAs) $B_{13}(CO)_n^+$ (n=1-7), and (c) Boron bonds (BBs) in boron-water complex $B_{13}(H_2O)^+$.

References:

[1] Zhai, H.-J.; Li, J. ; Li, S.-D. ; Wang, L.-S. et al, *Nat. Chem.* **2014**, **6**, 727-731.
[2] Chen, Q.; Li, S.-D. ; Wang, L.-S. et al, *ACS nano* **2015**, **9**, 754-760.
[3] Yan, Q.-Q.; Li, S.-D. et al, *Nano Research* **2025**, **18**, 94907288
[4] Yuan, R.-N.;Li, S.-D. et al, *J. Am. Chem. Soc.* **2024**, **146**, 31464–31471.
[5] Yuan, R.-N.; Li, S.-D. et al, Phys.Chem.Chem. Phys., **2025**, **27**, 7279.
[6] Zhang T.; Li, S.-D. et al., Joural of Cluster Science, **2025**, in revision.

Lanthanide/Actinide-Doped Boron Nanoclusters

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Lanthanide and actinide compounds are known for exhibiting diverse chemical bonding and oxidation states, owing to the variation in valence shells available for chemical bonding and the influence of relativistic effects. On the other hand, boron clusters have demonstrated tunable bonding activity due to their diverse geometries and electronic structures, which vary with cluster size. Leveraging the electron deficiency of boron clusters, doping with lanthanide or actinide metals introduces unique bonding patterns, non-traditional oxidation states, and enriched cluster geometries. To explore these systems, we recently developed a global minimum search package called San Diego Global Minimum Search (SDGMS). This package utilizes a "Strategic Escape" algorithm combined with supervised seed generation techniques to effectively identify global minimum structures of metal-doped boride clusters. Our studies revealed several intriguing discoveries: singly-doped "borozenes" exhibiting rare low oxidation states of lanthanide/actinide elements, doubly-doped "inverse sandwiches" with d-p δ unprecedented bonding configurations, and the first triply-doped metallo-borospherene.

These theoretical findings were validated through the comparison with experimental results obtained via photoelectron spectroscopy, confirming the predicted structural and electronic properties. This work advances the synthesis of lanthanide/actinide boride materials and deepens our understanding of stability and bonding in lanthanide and actinide chemistry.

Redox-Active Boron Clusters

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For the past decade,[1] our group has been dedicated to exploring the unique redox behavior of boron cluster molecules, with the aim of understanding and harnessing their remarkable properties for molecular and materials applications. Boron clusters can be considered three-dimensional aromatic systems with redox and photophysical profiles that stand in sharp contrast to those of traditional planar organic aromatics. In particular, we have focused on functionalized closo-dodecaborate derivatives, such as $B_{12}(OR)_{12}$ clusters, which display highly tunable, multielectron redox processes. Through detailed spectroscopic and electrochemical studies, we have mapped out their accessible redox states and translated this knowledge into practical uses, including catholytes and anolytes for redox flow batteries, as well as chemical dopants for conjugated polymers.

Our investigations have also highlighted the visible-light absorbing and strongly oxidizing behavior of fluoroaryl-substituted $B_{12}(OR)_{12}$ clusters, which act as photoexcitable weakly coordinating anions capable of promoting photooxidation reactions. Building on these discoveries, we extended our studies from solution-phase systems to the solid state by leveraging $[B_{12}(OH)_{12}]^{2-}$ as a stable building block for hybrid metal oxide composites. In these materials, the boron cluster serves as a thermally robust cross-linker that enhances electron transfer between oxide nanoparticles, providing improved performance in photocatalysis and supercapacitor electrodes. Beyond the dodecaborate-based molecules, our group has begun investigating vertex-differentiated clusters that incorporate both alkoxy and halogen substituents to expand the accessible electrochemical potential window.

In addition, we have explored smaller boron clusters, such as *closo*-hexaborates and *closo*-decaborates, which show less reversible redox chemistry but reveal valuable reactivity under oxidative conditions. These systems have been transformed through selective oxidation into alkyl boronate esters or converted to electrophilic species capable of unique arene borylation, opening new pathways for small molecule synthesis.

Collectively, these efforts establish boron clusters as a versatile and underexplored family of redox-active molecules. Their distinctive electronic and structural properties offer a powerful platform for developing advanced materials with tunable physical and electrochemical behavior, as well as creating innovative reagents for organic transformations. This talk will highlight key recent advances from our group and lay out future directions in this exciting area with a focus on understanding fundamental structure function relationship between molecular bonding and physical properties of the boron clusters.

1. Ready, A. D.; Nelson, Y. A.; Pomares, D. F. T.; Spokoyny, A. M. "Redox-Active Boron Clusters", *Acc. Chem. Res.* **2024**, *57, 9,* 1310-1324.

Session B: Gas-Phase Clusters and Spectroscopy

Photoelectron Spectroscopy Study of Hydrated Hydroxide Anions and Host-Guest Complexes

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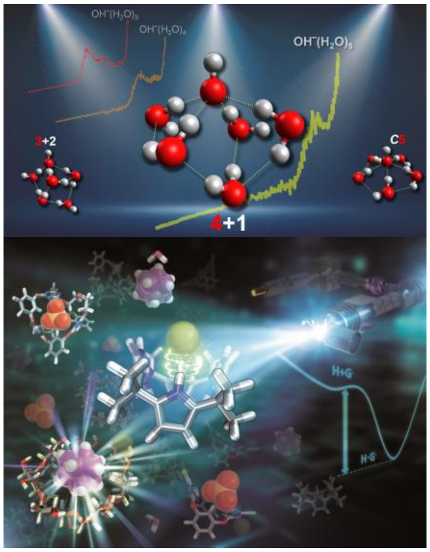
Size-selective cryogenic photoelectron spectroscopy (cryo-PES) coupled with electrospray ionization (ESI) source is a powerful experimental technique to investigate electronic structures and energetics of a wide variety of micro-solvated clusters and host-guest anionic complexes in the gas phase.[1] A key property associated with the behavior of hydroxide, one of the most important ions in aqueous chemistry, is the binding motif in its primary hydration shell. We carried out a joint experimental – theoretical study for hydrated hydroxide clusters $OH^-(H_2O)_n$ (n = 0-6). Our study, based on the first reported photoelectron spectra and high-level *ab-initio* calculations, determined the primary gas phase hydration shell of hydroxide containing four water molecules, and reconciled a long-standing debate on hydroxide solvation shell between previous IR action spectroscopic data and theory.[2] We conducted a series of studies to probe intrinsic anion-receptor interactions, precisely measured these noncovalent interaction strength and quantified detachment cross sections in various host-guest complexes.[3] We demonstrated that octamethylcalix[4]pyrrole (omC4P), a versatile organic host molecule, can behave like an alkali metal that reacts with various halogens/ pseudohalogens (X) to form charge-separated $omC4P^{+}\cdot X^{-}$ complexes via harpoon mechanism.[4]



Photoelectron spectroscopy of $OH^-(H_2O)_n$ (top) and host-guest complexes (bottom)

References:
(1) X.-B. Wang, *J. Phys. Chem. A*, **121**, 1389-1401 (**2017**); (2) W. Cao *et al. Sci. Adv.* **9**, eadf4309 (**2023**); (3) H. Sun *et al*. *Chem. Eur. J.* **30**, e202402766 (**2024**); (4) W. Cao *et al. Chem. Eur. J.* **30**, e202400038 (**2024**)

Cavity-Enabled Enhancement of Intramolecular Vibrational Redistribution over Pseudorotation by Two-Dimensional Infrared Spectroscopy

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Vibrational strong coupling (VSC) between molecular vibrations and microcavity photons yields a few polaritons (light-matter modes) and many dark modes (with negligible photonic character). Although VSC is reported to alter thermally activated chemical reactions, its mechanisms remain opaque.

To elucidate this problem, we followed ultrafast dynamics of a simple unimolecular vibrational energy exchange in iron pentacarbonyl [$Fe(CO)_5$] under VSC, which showed two competing channels: pseudorotation and intramolecular vibrational-energy redistribution (IVR)[1]. We found that under polariton excitation, energy exchange was overall accelerated, with IVR becoming faster and pseudorotation being slowed down. However, dark-mode excitation revealed unchanged dynamics compared with those outside of the cavity, with pseudorotation dominating. Thus, despite controversies around thermally activated VSC modified chemistry, our work shows that VSC can indeed alter chemistry through a nonequilibrium preparation of polaritons.

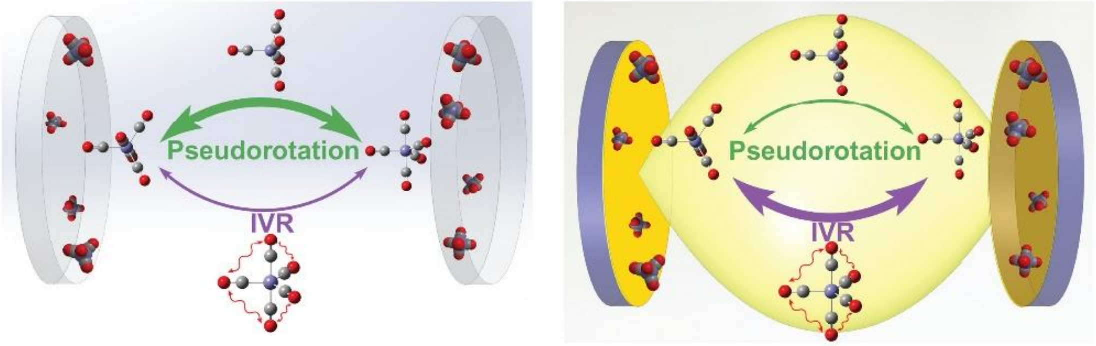

Figure 1: Schematic drawing showing that for $Fe(CO)_5$, while outside of the cavity, pseudorotation is the dominating channel (left); while under VSC, IVR becomes the dominant energy-exchange process and pseudorotation is suppressed (right).

Acknowledgements: This work has the support of National Science Foundation (USA)

References;

[1] T.-T. Chen, M. Du, Z. Yang, J. Yuen-Zhou, W. Xiong, *Science* **2022**, *378*, 790-794.

Probing the Formation of Interstellar Benzene via Cold Sequential Ion-Molecule Reactions

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The aromatic molecule benzene is considered the essential building block for larger polycyclic aromatic hydrocarbons (PAHs) in space. Despite benzene's importance in the formation of PAHs, the formation mechanisms of interstellar benzene are not well understood. A single ion-molecule reaction sequence is considered when modeling the formation of benzene in the interstellar medium, beginning with the protonation of acetylene. Although this process has been used to model the initial steps for formation of PAHs, it has not been experimentally measured. To explore this reaction mechanism, we have carried out the first experimental study of sequential ion-molecule reactions beginning with protonation of acetylene at single-collision conditions. Surprisingly, we find that the reaction sequence does not result in benzene and instead terminates at $C_6H_5^+$, which is unreactive toward both acetylene and hydrogen. This result disproves the previously proposed mechanism for interstellar benzene formation, critically altering our understanding of interstellar PAH formation.

Afternoon:
Session A: Fundamentals and Applications of Chemical Bonding - I

A Statistical Approach to Chemical Bonding

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While the orbital paradigm offers a valuable one-particle perspective of chemical systems, a rigorous understanding of electron distribution in real space remains of paramount importance in chemistry. Quantum chemical topology approaches have significantly advanced this goal by partitioning space into chemically meaningful regions. Notable examples include the Quantum Theory of Atoms in Molecules, which divides space into atomic basins, and the Electron Localization Function (ELF), which partitions it into electron-pair domains. These partitions can be coupled with electron number distribution functions (EDFs), providing a statistical description of the electron population within each region. This framework offers an intuitive yet rigorous reconstruction of fundamental c decomposition of chemical bonding hemical concepts and exploring exotic bonding regimes.[1]

Here, we present several recent advances in this field, including the extension of the EDF framework to a finer resolution by coupling it with the intersection of QTAIM and ELF domains (QTAIM∩ELF, or QEI). Performing EDF analysis on the QEI partition enables the decomposition of chemical bonding into contributions from each participating atom (Figure 1a). This unified perspective on electron sharing connects both Lewis-type constructs (e.g., bonds, lone pairs) and atomic basins. We demonstrate the power of this approach by applying it to a range of test systems.[2] Besides, we apply the EDF framework to understand chemical bonding within other challenging systems, such as the [4]-pyramidane family (Figure 1b), and systems containing the pentafluoroorthotellurate group (teflate, OTeF5), which is considered as a bulky analogue of fluoride ligand with relevance in synthetic chemistry (Figure 1c).[3]

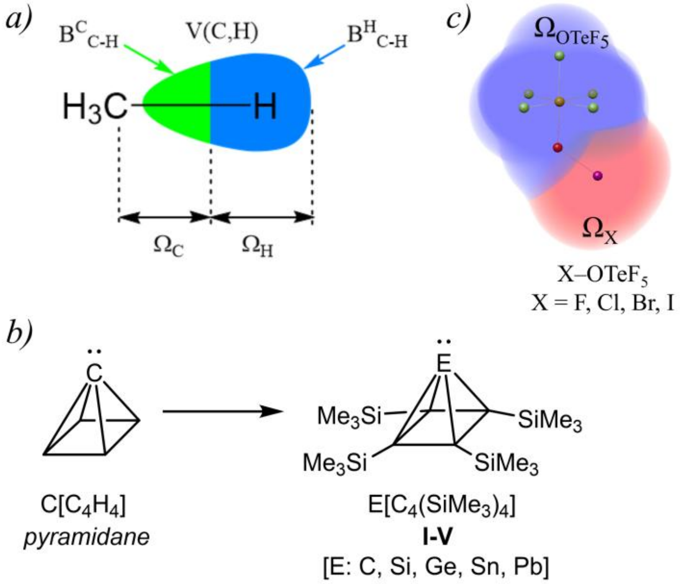

Figure 1. a) Simplified QEI partition for a hydrogenic V(C,H) basin, which represents the C – H bond of methane molecule. b) Parent pyramidane compound and derivatives studied in this contribution. c) Teflate structure and halogen-based derivatives.

[1] Á. Martín Pendás, E. Francisco, D. Suárez, A. Costales, N. Díaz, J. Munárriz, T. Rocha-Rinza, J. M. Guevara-Vela, *Phys. Chem. Chem. Phys.* **2023**, *25*, 10231–10262.
[2] D. Barrena-Espés, J. Munárriz, Á. Martín Pendás, *J. Chem. Phys.* **2024**, 160, 14.
[3] A. Pérez-Bitrián, J. Munárriz, K. B. Krause, J. Schlögl, K. F. Hoffmann, J. S. Sturm, A. N. Hadi, C. Teutloff, A. Wiesner, C. Limberg, S. Riedel, *Chem. Sci.* **2024**, *15*, 5564–5572.

Multiple Aromatic Units within a Single Molecular Structure. Overall Aromaticity in Local Aromatic Aggregates

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Conceiving a building-up approach to pursue a rational design and synthesis of functional materials, is an attractive strategy based on the controlled aggregation of multiple cluster building blocks. Spherical aromatic species as an extension to planar aromatics,[1,2] sustaining related magnetic properties, enabling an induced shielding cone behavior given from any orientation of the applied field.[3] This behavior contrast to planar species, which sustain such character under a parallel oriented external field mainly.[4] Here, we discuss the resulting aromatic characteristics for oligomers involving several building cluster units, encouraged by the understanding of how multiple spherical aromatic units behave together in the birth of extended linear arrays, highlighting the use of descriptors to locate spherical aromatic states and their related magnetic anisotropy, favoring the understanding of how multiple spherical aromatic units behave together towards in molecularly conceived materials.

References:

1 A. Hirsch, Z. Chen and H. Jiao, *Angew. Chemie Int. Ed.*, 2001, **40**, 2834–2838.
2 M. Kulichenko, N. Fedik, N. Tkachenko, A. Muñoz-Castro, Z.-M. Sun and A. I. Boldyrev, in *Aromaticity: Modern Computational Methods and Applications*, ed. I. Fernandez, Elsevier, 2021, pp. 447–488.
3 A. Muñoz-Castro, *Chem. Phys. Lett.*, 2013, **555**, 282–285.
4 A. G. Papadopoulos, N. D. Charistos and A. Muñoz-Castro, *ChemPhysChem*, 2017, **18**, 1499–1502.

Accelerating Quantum Simulations with Graph Theory on AI Hardware

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Advancing the simulation of large-scale atomistic systems requires quantum chemistry methods that are both accurate and computationally efficient. In this talk, I will present a scalable electronic structure framework that integrates graph-based linear-scaling theory (as implemented in the SEDACS[1] platform) with GPU-accelerated semi-empirical quantum chemistry (via PySEQM[2]). This combination enables fast and memory-efficient electronic structure calculations across multiple compute nodes, making it possible to simulate systems with more than 10,000 atoms. I will discuss the underlying algorithms, parallelization strategy, and GPU optimizations, along with detailed performance benchmarks and accuracy analysis. This work demonstrates how combining graph theory, semiempirical models, and modern hardware can unlock quantum simulations previously limited by cost and scalability.

References:

1. https://github.com/lanl/sedacs
2. https://github.com/lanl/PYSEQM

<u>Session B:</u> Biological Systems

On the Irrelevancy of Hydroxyl Radical to the Evolution of Human Cells

Cynthia Burrows
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After the Great Oxidation Event ca. 2.2 billion years ago, eukaryotes evolved to capitalize on O_2 as an electron sink while simultaneously controlling the cellular chemistry of Fe(II). Then and now, the classical Fenton reaction (Fe(II) + H_2O_2) presents an ordeal for cell survival due to the DNA/RNA damaging properties of the reactive oxygen species generated. I will show that life is made simpler for cells by the discovery that neither the highly reactive hydroxyl radical ($HO^{\bullet}$) nor a ferryl species (Fe(IV)=O) is formed in the cellular Fenton reaction. Instead, the presence of high intracellular concentrations of bicarbonate (20 – 100 mM) redirects the Fenton reaction to form carbonate radical anion ($CO_3^{\bullet -}$), a weaker and more selective oxidant. $CO_3^{\bullet -}$ reacts as a one-electron oxidant toward DNA and RNA focusing the oxidative damage on guanine bases.

Mammalian cells take advantage of this selective oxidation of G in two ways. (1) Guanine-rich sequences in regulatory regions of the genome (gene promoters) respond to oxidative stress in cells by turning redox-responsive genes on or off via guanine oxidation in G-quadruplexes. These DNA sequences are particularly evolved and conserved in mammals. (2) The ribosome, responsible for translation of mRNA to a peptide/protein, has evolved long GC-rich tentacles during evolution to humans. We will show that these sequences are RNA antennae that capture $CO_3^{\bullet -}$ from oxidative stress and $NO^{\bullet}/NO_2^{\bullet}$ from inflammatory stress; we will then speculate wildly about why they do this.

Acknowledgements: Co-authors Dr. Aaron Fleming and (soon-to-be) Dr. Justin Dingman have made enormous contributions to this work. NIH has funded us so far, currently via R35 GM145237.

Further reading:

1. A. M. Fleming, J. C. Dingman, and C. J. Burrows, "CO_2 protects cells from iron-Fenton oxidative DNA damage in E. coli and humans," *PNAS,* **2024**, *121,* e2419175121. <u>https://doi.org/10.1073/pnas.2419175121</u>.
2. A. M. Fleming and C. J. Burrows, "Why the ROS matters: One-electron oxidants focus DNA damage and repair on G-quadruplexes for gene regulation," *DNA Repair* **2025**, 103789. https://doi.org/10.1016/j.dnarep.2024.103789.

Molecular Engineering of Protocadherin Interactions: A Chemical Bonding Perspective on Astrocyte Self-Recognition

Alina P. Sergeeva
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Self-recognition is a basic cellular process that helps neurons avoid connecting to themselves. Clustered protocadherins (cPcdhs) are cell-surface proteins that recognize matching partners and shape brain development. Their random expression gives each neuron a unique identity, allowing it to distinguish itself from others. We found that a specific cPcdh isoform, γC3, is enriched in human and mouse astrocytes and acts independently to regulate astrocyte morphogenesis in the mouse visual cortex[1].

To interrogate the chemical basis of astrocyte self-recognition, we engineered γC3 chimeric proteins with redesigned extracellular domains that could bind heterophilically (to a partner), but not homophilically (to themselves). By co-expressing complementary heterophilic-binding γC3 chimeras in γC3-null astrocytes, we restored normal morphogenesis, whereas expression of individual chimeras alone did not rescue morphology; thus, demonstrating that γC3 trans interactions are both necessary and sufficient for proper astrocyte development.

Our design focused on how proteins bond at the molecular level. The extracellular cadherin domains of protocadherins use specific surface features to form precise interactions. By changing key amino acids at the protein-protein interface, we disrupted natural self-binding and created new, selective pairings. We also controlled the angles between domains, important for proper alignment and binding, by modeling and enforcing specific orientations. This work demonstrates how protein recognition can be engineered through both chemical and structural design.

References:

[1] J.H. Lee#, A.P. Sergeeva#, G. Ahlsén, S. Mannepalli, F. Bahna, K.M. Goodman, R. Xu, B.S. Khakh, J.A. Weiner, L. Shapiro, B. Honig, S.L. Zipursky. *Astrocyte morphogenesis requires self-recognition*. Nature (2025)
PMID: 40437095, DOI: 10.1038/s41586-025-09013-y

Wednesday, August 27

<u>Morning</u>: Fundamentals and Applications of Chemical Bonding - II

Collective Bonding

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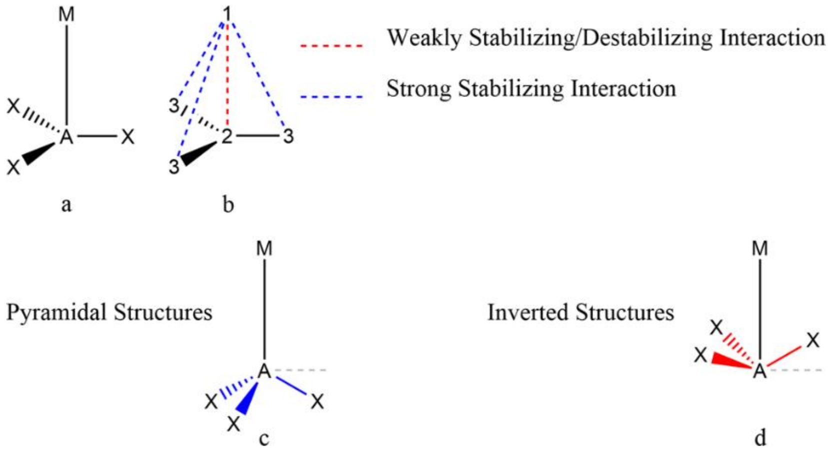
A century after G. N. Lewis introduced his foundational model of chemical bonding, its core principles remain central to our understanding of molecular structure. Traditionally, neighboring atoms in a Lewis structure are assumed to share stabilizing interactions. However, this assumption begins to falter at the boundary between covalent and noncovalent bonding. Our work reveals that, in certain molecules with the general formula MAX_3, where M is a metal, A a nonmetal, and X an electron-rich or electron-withdrawing group, the interaction between adjacent M and A atoms can be destabilizing. Remarkably, the overall structure is preserved due to strong interactions between electron-deficient metals and the X groups.[1–6] This phenomenon gives rise to unconventional structures, such as the inverted $LiCF_3$, where lithium interacts preferentially with fluorine atoms over the central carbon in the gas phase. Our recent investigations suggest that these *collective interactions* extend beyond organometallic compounds and offer insight into anomalous bond dissociation energies and stability trends across a wide range of molecules, from perhaloalkanes to the elusive cyclic C_6O_6. Our computational studies highlight the broad relevance of this concept in modern chemical bonding theory. I would present a full spectrum of transition from conventional to collective bonding as the electronegativity of bonded elements change, if I could visit you. Unfortunately, due to political reasons, I will not be able to meet you but I invite you to check the listed literature as well as the force coming publications for more information.



References:

1. Foroutan-Nejad, C. The Na···B Bond in NaBH3$^-$: A Different Type of Bond. *Angew. Chem. Int. Ed.* **59**, 20900–20903 (2020).
2. Sowlati-Hashjin, S. *et al.* Collective interactions among organometallics are exotic bonds hidden on lab shelves. *Nat. Commun.* **13**, 2069 (2022).

3. Šadek, V. *et al.* Reply to: On the existence of collective interactions reinforcing the metal-ligand bond in organometallic compounds. *Nat. Commun.* **14**, 3873 (2023).
4. Badri, Z. & Foroutan-Nejad, C. Classical versus Collective Interactions in Asymmetric Trigonal Bipyramidal Alkaline Metal–Boron Halide Complexes. *Chem. – Eur. J.* **n/a**, e202400156 (2024).
5. Pino-Rios, R., Báez-Grez, R. & Foroutan-Nejad, C. Anti-electrostatic cation⋯π-hole and cation⋯lp-hole interactions are stabilized via collective interactions. *Chem. Commun.* **60**, 400–403 (2024).
6. Bandeira, N. A. G., Martín Pendás, Á. & Foroutan-Nejad, C. Reply to: An approach to the resolution of the dispute on collective atomic interactions. *Nat. Commun.* **15**, 10403 (2024).

On the Interplay between Metal-Metal and Metal-Ligand Bonding in Zintl Clusters: Complementary Perspectives from DFT and MC-SCF

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Endohedral clusters present a fascinating challenge to theories of chemical bonding, simply because the nature of the interaction between the endohedral atom (or atoms) and the cage can vary from van-der-Waals'-like to strongly covalent. In the former case, the endohedral atom is held inside the cage only by the barrier to passing through the wall, whereas in the latter, charge transfer can influence the structure of the cage. In clusters with two or more endohedral metals, the situation is further complicated by the potential for metal-metal bonding, and the interplay between this and metal-cage bonding leads to a complex electronic landscape. In this presentation, I will discuss our latest work using both DFT and MC-SCF approaches, which give different but complementary perspectives on the nature of chemical bonding in this fascinating class of clusters.[1,2]

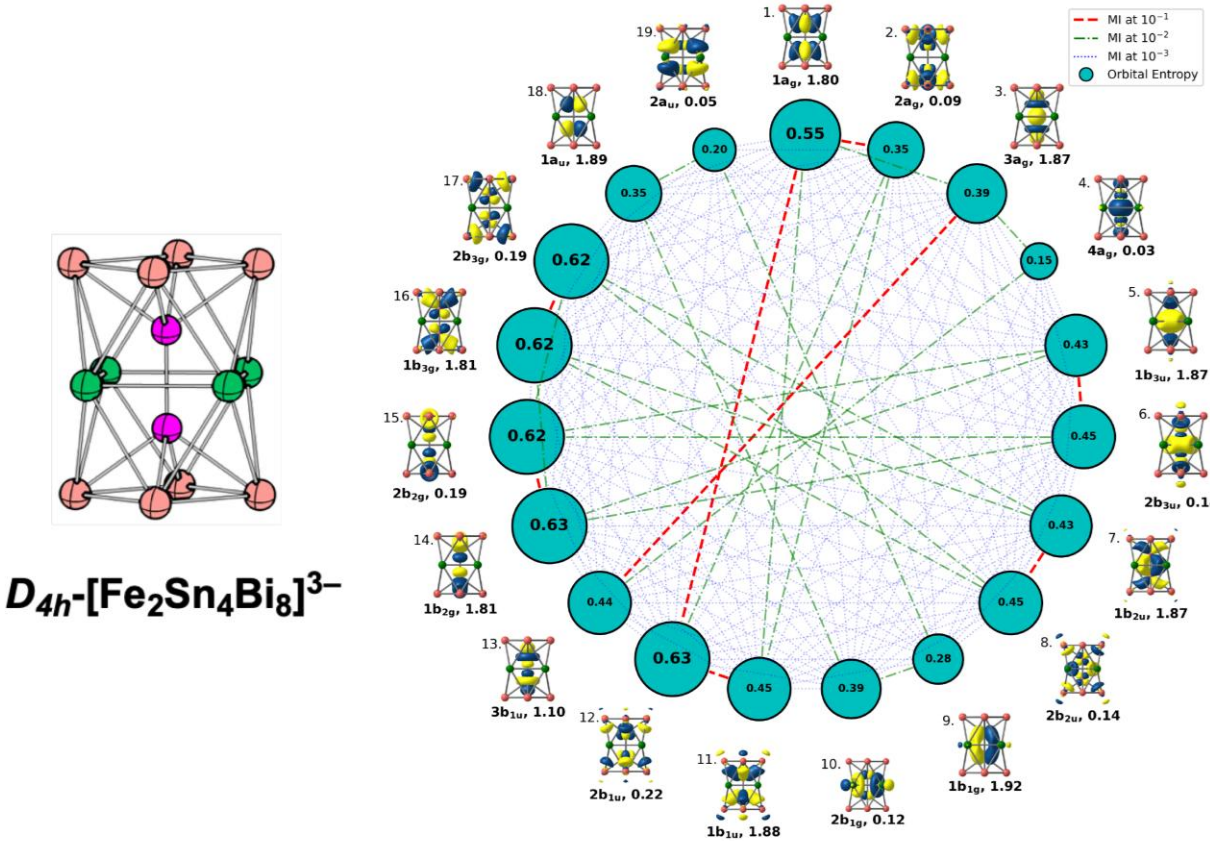

Figure 1. Orbital entanglement in $[Fe_2Sn_4Bi_8]^{3-}$.[2]

References:

1. W.-X Chen, Z.-S Li, H. W. T. Morgan, C.-C Shu, Z.-M. Sun, J. E. McGrady. Fe-Fe bonding in the rhombic Fe_4 cores of the Zintl clusters $[Fe_4E_{18}]^{4-}$ (E= Sn and Pb). *Chem. Sci.*, **2024**, 15 (13), 4981-4988.
2. Y.-N. Yang, Z.-S. Li, S. Mondal, L. Qiao, C.-C. Wang, W.-J. Tian, Z.-M. Sun, J. E. McGrady. Metal-metal bonds in Zintl clusters: Synthesis, structure and bonding in $[Fe_2Sn_4Bi_8]^{3-}$ and $[Cr_2Sb_{12}]^{3-}$. *Chin. Chem. Lett.*, **2024**, 35 (8), 109048.

A Journey into Molecular Complexity Accompanied by Strong Metal-Metal Bonds and Weak Dispersion Interactions

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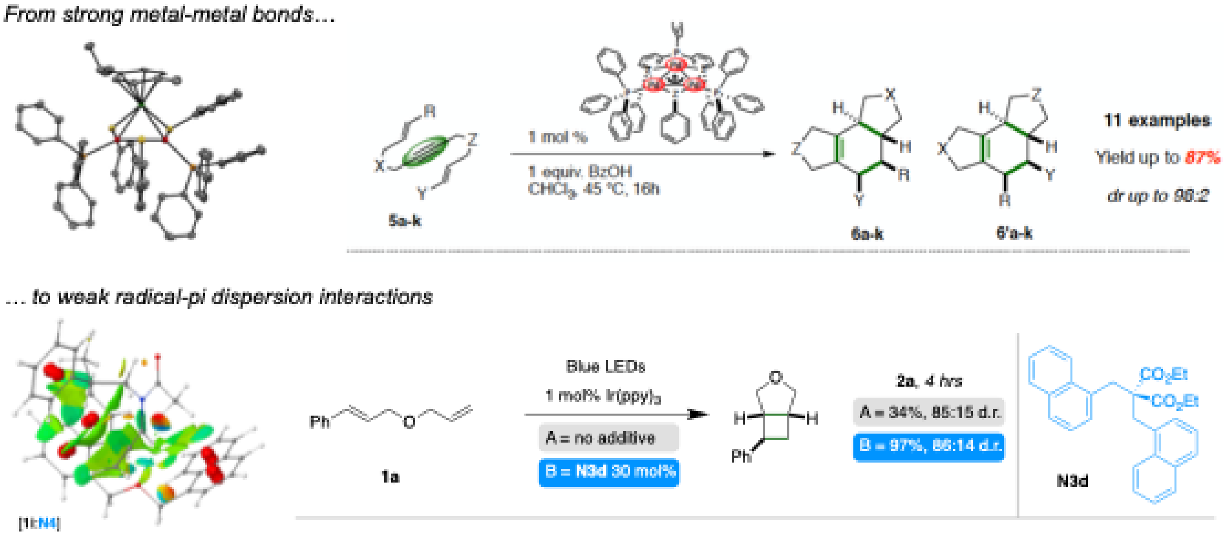
The exploitation of original bonding modes is a key tool to devise sustainable synthetic methods. As part of an ongoing interest in atom-economical cascades, the presentation will focus on the fundamental investigation of new catalytic strategies, which are applied to the ordered assembly of complex molecular architectures.

By eliciting the formation of strong, delocalized metal-metal bonds, it has been possible to synthesize trinuclear all-metal aromatic species and study their catalytic properties in several prototypical reactions. The combination of computational and experimental tools showed that the unique chemical robustness of these catalysts is precisely the result of their aromatic stabilization, making these entities the ideal link bridging homogeneous and heterogeneous catalysis.

Switching to the opposite end of the relative strength of bonding interactions, we recently highlighted the key role of radical-pi dispersion interactions in visible-light promoted energy-transfer cascades. The pi network of fused aromatic systems, such as naphthyl groups, can stabilize the transient triplet intermediates of several photochemical reactions through a stacking-like interaction with mono-occupied molecular orbitals. The trick proved crucial to unlock several challenging reactivities, including the first general Himbert-type dearomative *para*-cycloaddition on electronically unbiased arenes and the preparation of tricky *N*- heterocycles, such as azetidines, tropanes and bicyclic architectures that are pyridine bioisosters.



Gas Phase Clusters as Model Systems for Solid "Single Site" Catalysts

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Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Leipzig University, Germany

Gas phase metal oxide clusters are relevant as model systems of reduced complexity for heterogeneous catalysts, for example, as models for solid "single site" catalysts obtained by doping metal oxides. The influence of transition metal substitution (Fe, Co, Ni) on the structure and reactivity of small aluminum oxide clusters is studied using vibrational action spectroscopy paired with quantum chemistry.[1-3] Density functional theory (DFT) in combination with global structure optimization is used to identify low energy structures and to connect them to the experimental data. The reactivity of the aluminium oxide cations $Al_3O_4^+$ and $Al_8O_{12}^+$ is fundamentally different and can be tuned by transition-metal substitution. For example, the electronically closed-shell $Al_3O_4^+$ is unreactive towards hydrocarbons, while the radical $Al_8O_{12}^+$ even activates methane. The opposite is observed for the substituted systems $FeAl_2O_4^+$ and $FeAl_7O_{12}^+$, respectively. For the $Al_3O_4^+/FeAl_2O_4^+$ system we find evidence of valence isomerism. In summary, DFT calculations may accurately describe local minimum structures when transition metal atoms are present in these small metal oxide ions, but the relative energies are not predictive and an accurate description is challenging even for multi-reference methods.

References:

[1] W. Schwedland, T.C. Penna, H. Windeck, F. Müller, S. Leach, J. Sauer, X.R. Advincula, F. Berger, N. Ishida, K. Ohshimo, F. Misaizu, Y.-K. Li, A. Chakraborty, F. Horn, K.R. Asmis, *Chem. Sci.* **16**, 11999 (2025). 10.1039/D5SC02681D
[2] Y.–K. Li, F. Müller, W Schöllkopf, K.R. Asmis, J. Sauer, *Angew. Chem. Int. Ed.* **61**, e202202297, (2022). 10.1002/ANIE.202202297
[3] F. Müller, J.B. Stückrath, F.A. Bischoff, L. Gagliardi, J. Sauer, S. Debnath, M. Jorewitz, K.R. Asmis, *J. Am. Chem. Soc.* **42**, 18050 (2020). 10.1021/JACS.0C07158

Assessing and Amending Unphysical Potential Energy Surfaces in the D3 and D4 Dispersion Correction Models

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The University of Oklahoma, USA

The addition of dispersion corrections to density functionals is essential for accurate energy and geometry predictions. Among the most popular and computationally efficient approaches for accounting for London dispersion interactions within density functional theory are the D3 and D4 dispersion correction models. We demonstrate that these models can induce the appearance of unphysical minima on the potential energy surface (PES) when the coordination number of atoms changes. Optimizing to these artifactual structures can lead to significant errors in determining the interaction energy between two molecules and in estimating the system's thermodynamic properties. To resolve this issue, we propose a re-parameterization of the D3 and D4 models by introducing a modified C6AB functional form, which explicitly depends on the specific atom pairs being considered. These new models, are termed D3-Smooth (D3S) and D4-Smooth (D4S), are designed to smooth out the PES associated with the dispersion correction. Our results demonstrate that D3S and D4S effectively eliminate unphysical local minima while maintaining the quite satisfactory accuracy of the parent D3 and D4 methods in interaction energy benchmark sets.

Computational Study of the Complexes of P-core-modified Metalloporphyrins with Alkali Metal Cations

Aleksey Kuznetsov
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Tetrapyrrole macrocycles are ubiquitous compounds which have been receiving well-deserved attention from researchers around the world due to their prominent and versatile characteristics and a broadness of functionalities in diverse areas ranging from biology to technology [1]. Metal complexes of tetrapyrrole macrocycles are of particular interest because the metal centers are able to govern various chemical and physical properties of metalloporphyrins [1]. No studies of complexes formed by metal cations and metalloporphyrins have been found in the literature, although, for example, computational studies of p-complexes of alkaline metals (Li, Na, and K) with various non-aromatic, aromatic hydrocarbons, as well as heteroaromatic systems have been reported recently [2]. Motivated by this fact, we have performed comparative DFT studies of the complexes formed by the cations of alkali metals, $\mathrm{Li^+}$, $\mathrm{Na^+}$, and $\mathrm{K^+}$, with two regular metalloporphyrins, ZnP and NiP, and two phosphorus-core-modified metalloporphyrins [3], $\mathrm{ZnP(P)_4}$ and $\mathrm{NiP(P)_4}$. The B3LYP hybrid functional with the D2 version of Grimme's dispersion and 6-311++G(d,p) basis set were employed (B3LYP-GD2/6-311++G(d,p) approach), both in the gas phase and with implicit effects from benzene and water. We found the existence of various isomers for each complex studied, with significant binding energies, e.g., ca. 33 and 59 kcal/mol for $\mathrm{ZnP(P)_4\text{-}K^+}$ and $\mathrm{ZnP(P)_4\text{-}Li^+}$, respectively, and ca. 39 and 69 kcal/mol $\mathrm{NiP(P)_4\text{-}K^+}$ and $\mathrm{NiP(P)_4\text{-}Li^+}$, respectively (see Fig. 1 for the $\mathrm{ZnP(P)_4\text{-}K^+}$ and $\mathrm{NiP(P)_4\text{-}K^+}$ lowest-lying isomer). Binding energies, frontier molecular orbitals, charge distributions, molecular electrostatic potential distributions, and non-covalent interactions for the complexes studied were analyzed and compared. These results show potential applications of core-modified (metallo)porphyrins as metal cation sensors and for their complexes with metal cations as components of molecular building blocks.

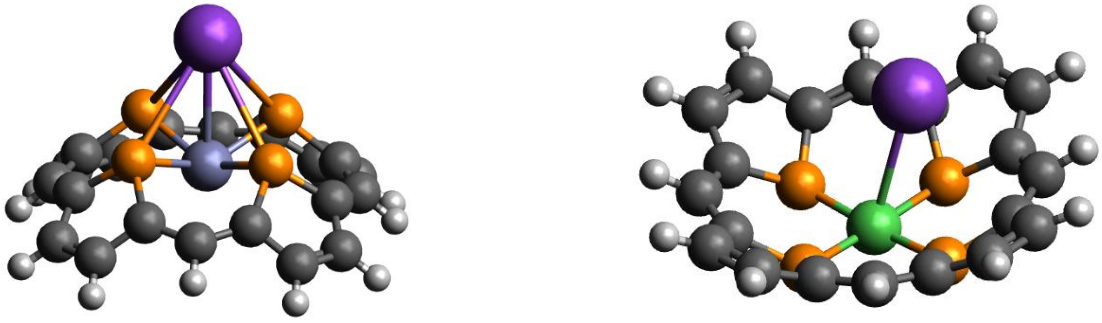

Figure 1. The lowest-lying isomer of $\mathrm{ZnP(P)_4\text{-}K^+}$ (left) and $\mathrm{NiP(P)_4\text{-}K^+}$ (right).

References:

1. K. M. Kadish, K. M. Smith, R. Guilard, Eds. Handbook of porphyrin science with applications to chemistry, physics, materials science, engineering, biology and medicine. Singapore: World Scientific 2010.
2. P. K. Ramya, A. Shivhare, M. M. Deshmukh and C. H. Suresh. From loose to tight: unveiling bond stretch isomerism in p-complexes of Li, Na and K. Phys. Chem. Chem. Phys., 2024, 26, 27054.
3. A. E Kuznetsov. Metalloporphyrins with all the pyrrole nitrogens replaced with phosphorus atoms, $\mathrm{MP(P)_4}$ (M=Sc, Ti, Fe, Ni, Cu, Zn). Chem. Phys., 2015, 447, 36-45.

Afternoon: Clusters and Microdroplets

Synthesis and Chemical Bonding of Aromaticity-Stabilized Group 14/15 Cage Compounds

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Since the discovery of benzene, the concept of aromaticity has revolutionized our understanding of electronic structure and stability, becoming one of the most fundamental principles in chemistry. In recent decades, this concept has expanded beyond organic molecules to include inorganic and all-metal clusters, opening new frontiers in the study of metal–metal bonding. However, synthesizing inorganic aromatic clusters remains highly challenging. Most known examples are ligand-stabilized planar rings, where ligands significantly influence both bonding and geometry. In contrast, ligand-free clusters retain the intrinsic bonding features of elements, making them ideal models for fundamental bonding studies. Yet, their synthesis—especially in the gas phase—is often hindered by low yields and structural complexity. Despite theoretical advances, limitations in modeling electron correlation and relativistic effects continue to impede reliable predictions. To date, experimentally characterized ligand-free inorganic aromatic clusters remain scarce and are typically limited to low-nuclearity species.

By employing a cross-phase synthetic strategy that combines high-temperature solid-state reactions with organometallic approaches, we have successfully synthesized a series of high-nuclearity inorganic clusters. In group 14, our work primarily focuses on Ge-based clusters, including σ-aromaticity-induced heterometallic supertetrahedral clusters [Zn$_6$Ge$_{16}$]$^{4-}$ and [Cd$_6$Ge$_{16}$]$^{4-}$, Ge$_9$-based sandwich-type aromatic clusters {(Ge$_9$)$_2$[η^6-Ge(PdPPh$_3$)$_3$]}$^{4-}$, the multi-locally aromatic [Ge$_{24}$]$^{4-}$, and a giant σ-aromatic cluster [Co$_3$@Ge$_6$Sn$_{18}$]$^{5-}$ that is analogous to H$_3^+$ and Li$_3^+$. Similarly, in group 15, our research has focused on heavy-element clusters, such as the spherical aromatic [Bi@Pd$_{12}$@Bi$_{20}$]$^{6-}$ and [Pn@In$_8$Pn$_{12}$]$^{3-/5-}$ (Pn=Sb, Bi), as well as the all-metal fullerene [K@Au$_{12}$Sb$_{20}$]$^{5-}$.

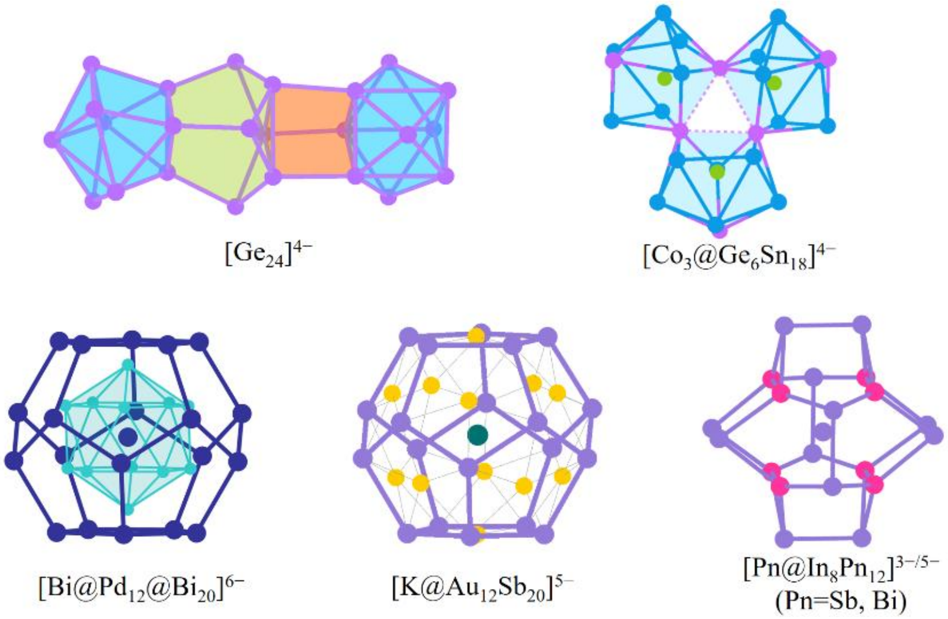
[Ge$_{24}$]$^{4-}$
[Co$_3$@Ge$_6$Sn$_{18}$]$^{4-}$
[Bi@Pd$_{12}$@Bi$_{20}$]$^{6-}$
[K@Au$_{12}$Sb$_{20}$]$^{5-}$
[Pn@In$_8$Pn$_{12}$]$^{3-/5-}$
(Pn=Sb, Bi)

Figure 1. Selected examples of aromatic main-group clusters.

Investigation of Microdroplet Chemistry with Mass Spectrometry

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Water is considered as an inert environment for the dispersion of many chemical systems. However, by simply spraying bulk water into micro-sized droplets, the water microdroplets have been shown to possess a large plethora of unique properties, including the abilities to accelerate chemical reactions by several orders of magnitude compared to the same reactions in bulk water, and/or to trigger spontaneous reactions that cannot occur in bulk water. A high electric field (~10^9 V/m) at the air-water interface of microdroplets has been postulated to be the probable cause of the unique chemistries. This high field can even oxidize electrons out of hydroxide ions or other closed-shell molecules dissolved in water, forming radicals and electrons. Subsequently, the electrons can trigger further reduction processes. In our lab, by showing a large number of such electron-mediated redox reactions, and by studying the kinetics of these reactions, we opine that the redox reactions on sprayed water microdroplets are essentially processes using electrons as the charge carriers. The potential impacts of the redox capability of microdroplets are also discussed in a larger context of synthetic chemistry and atmospheric chemistry.