

Sponsors:



International Conference on Chemical Bonding

Technical Program

Wednesday, June 21

Arrival and registration

Thursday, June 22

Morning: Opening. Bonding appetizer plate.

Presiding: Anastassia Alexandrova

- 8:30 – 8:45 am Alex, Anastassia, Lai-Sheng - Introductory remarks
8:45 – 9:15 am Tom Nilges (TU Munich, Germany)
“Low-dimensional Group 15 Semiconductors”
9:15 – 9:45 am Giovanni Maestri (Università di Parma, Italy)
“Connecting Homogeneous and Heterogeneous Catalysis with All-Metal Aromatics”
9:45 – 10:15 am Patrick Bultinck (Gent University, Belgium)
“Maximum Probability Domains – a New Tool in Chemical Bonding”
10:15 – 10:45 am Lai-Sheng Wang (Brown University, USA)
“Probing the Electronic Structure and Chemical Bonding of Size-Selected Boron and Doped-Boron Clusters Using Photoelectron Spectroscopy: From Borophenes to Metalloborophenes”
10:45 – 11:00 am *Coffee Break*
11:00 – 11:30 am Knut Asmis (Univeristät Leipzig, Germany)
“Unusual Properties of Boron-Containing Clusters Probed by Cryogenic Ion Trap Vibrational Spectroscopy”
11:30 – 12:00 am Bryan Wong (University of California, Riverside, USA)
“Anomalous Optoelectronic Properties of Nanostructures from DFT and TD-DFT Calculations”
12:00 – 12:30 am Otto Dopfer (TU Berlin, Germany)
“Structures of Silicon Ions and Clusters: Silane Ions and Doping on the Nanoscale”

Afternoon: Quantum effects in materials and interfaces

Presiding: Bryan Wong

- 3:00 – 3:30 pm Paul Weiss (University of California, Los Angeles, and CNSI, USA)
“Imaging, Understanding, and Leveraging Buried Interactions in Supramolecular Assemblies”
3:30 – 4:00 pm Richard Saykally (University of California, Berkeley, and LBNL, USA)
“On the Mechanism of Selective Adsorption of Ions to Aqueous Interfaces: Graphene/Water vs. Air/Water”
4:00 – 4:30 pm Tyrel McQueen (Johns Hopkins University, USA)
“The Rich Bonding Motifs of Quantum Materials”
4:30 – 4:45 pm *Coffee Break*
4:45 – 5:15 pm Vladimiro Mujica (Arizona State University, USA, and Yachay Tech, Ecuador)
“The Role of Hydrogen Bond in Electron Transport in Molecular Junctions”
5:15 – 5:45 pm Jeffrey Grossman (MIT, USA)
“Graphene and graphene-oxide based membranes for filtration”
5:45 – 6:15 pm Vijay Kumar (Shiv Nadar University, India)
“Novel nanostructures of boron: bowls, drums, cages, nanotubes, and atomic layers with Dirac cones”
6:15 – 6:45 pm Anastassia Alexandrova (University of California, Los Angeles, USA)
“Playing with electrons in 2D and 3D borides”
07:00 – 10:00 pm **RECEPTION at Kauai Beach Resort**

Friday, June 23

Morning: Bonding at nano and sub-nano scales

Presiding: Vijay Kumar

- 8:30 – 9:00 am Oleg Prezhdo (University of Southern California, USA)
“Chemical bonding steers excited state dynamics in nanoscale materials”
- 9:00 – 9:30 am Michael Heaven (Emory University, USA)
“Spectroscopic studies of the alkaline earth oxides and hypermetallic oxides”
- 9:30 – 10:00 am Ralf Kaiser (University of Hawaii at Manoa, USA)
“One Step at a Time - Unraveling the Formation of Interstellar Grains under Single Collision Conditions”
- 10:00 – 10:30 am Stefanie Dehnen (Philipps-Universität Marburg, Germany)
“Structures and Bonding in Multimetallic Cluster Anions”
- 10:30 – 11:00 am Miguel Castro (Universidad Nacional Autónoma de México)
“Structural and Electronic Properties of Small Vanadium, $V_n^{0,+}$, clusters and of the Hydrated V_nH_2O and $V_n^+H_2O$, $n \leq 13$, Systems”
- 11:00 – 11:15 am *Coffee Break*
- 11:15 – 11:45 am Israel Fernández (Universidad Complutense de Madrid, Spain)
“Reactivity and Bonding of Polycyclic Aromatic Hydrocarbons: Shape and Size Dependence”
- 11:45 – 12:15 pm Xuenian Chen (Henan Normal University, China)
“Bonding Analysis and Synthesis of Borane Complexes”
- 12:15 – 12:45 pm Marcela Beltran (Universidad Nacional Autonoma de Mexico)
“TBA”
- 12:45 – 13:15 pm Artem Oganov (Skolkovo Institute of Science and Technology, Russia, and Stony Brook University, USA)
“Computational Materials Discovery”

Afternoon: Bonding in heterogeneous catalysis

Presiding: Ping Yang

- 3:00 – 3:30 pm Gareth Parkinson (Technische Universität Wien, Austria)
“Single Atom Catalysis: A Surface Science Approach”
- 3:30 – 4:00 pm Evgeny Pidko (Eindhoven University of Technology, the Netherlands, and ITMO University, Russia)
“Confinement-induced reactivity in zeolite catalysis”
- 4:00 – 4:30 pm Philippe Sautet (University of California, Los Angeles, USA)
“Modeling chemical bond at electrochemical interfaces: an approach from first principles”
- 4:30 – 5:00 pm Sergey Kozlov (KAUST, Kingdom of Saudi Arabia)
“Simulations of alloys for catalysis”
- 5:00 – 5:15 pm *Coffee Break*
- 5:15 – 5:45 pm Ive Hermans (University of Wisconsin, Madison, USA)
“The Science and Serendipity behind the Unexpected Discovery of Boron Nitride as Selective Oxidation Catalyst”
- 5:45 – 6:15 pm Dennis Salahub (University of Calgary, Canada)
“Beyond structure: on the role of dynamics and entropy in nanocatalysis”
- 6:15 – 6:45 pm Xuemin Yang (Institute of Chemical Physics, Chinese Academy of Science, China)
“TBA”

Saturday, June 24

TOUR DAY

Sunday, June 25

Morning: Fundamentals

Presiding: Marat Talipov

- 8:30 – 9:00 am Mingfei Zhou (Fudan University, China)
"Infrared Spectroscopy of Donor-Acceptor Bonding Carbonyl Complexes"
- 9:00 – 9:30 am Eduard Matito (Euskal Herriko Unibertsitatea, DIPIC, Basque Country, Spain)
"Conjugation and aromaticity in large circuits"
- 9:30 – 10:00 am Jinlong Yang (University of Science & Technology of China, Hefei, China)
"Superatomic Molecule Theory of Metal Clusters"
- 10:00 – 10:30 am Maarten Goesten (Cornell University, USA)
"(Unusual) hypervalence"
- 10:30 – 11:00 am Dmitry Zubarev (IBM Research, Almaden, USA)
"Chemical Evolution in Structured Environments"
- 11:00 – 11:15 am *Coffee Break*
- 11:15 – 11:45 am Ángel Martín Pendás (Universidad de Oviedo, Spain)
"One-electron images in real space: Natural adaptive orbitals"
- 11:45 – 12:15 pm Tim Lee (NASA Ames Research Center, USA)
"Computational Study of the Formation of Prebiotic Molecules in Astrophysical Environments: Mixed Ices and Gas-Phase Conditions"
- 12:15 – 12:45 am Cherif Matta (Mount Saint Vincent University, Canada)
"TBA"

Afternoon: Challenging organometallics

Presiding: Maarten Goesten

- 3:00 – 3:30 pm Kit Cummins (MIT, USA)
"Generation, Reactivity Patterns, and Bonding in Singlet Phosphinidenes"
- 3:30 – 4:00 pm Jochen Autschbach (University of Buffalo, SUNY, USA)
"Bonding, localization vs. delocalization, and molecular properties"
- 4:00 – 4:30 pm Etienne Garand (University of Wisconsin-Madison, USA)
"Probing the structure and solvation of catalytic reaction intermediates"
- 4:30 – 5:00 pm Dong-Sheng Yang (University of Kentucky, USA)
"Organolanthanide Radicals Formed by Metal-Mediated Bond Activation of Small Hydrocarbons"
- 5:00 – 5:15 pm *Coffee Break*
- 5:15 – 5:45 pm Angela Wilson (Michigan State University, USA)
"TBA"
- 5:45 – 6:15 pm Ping Yang (Los Alamos National Laboratory, USA)
"Covelency in Actinide-Ligand Bonds"
- 6:15 – 6:45 pm Anne Andrews (University of California, Los Angeles, USA)
"TBA"

Monday, June 26

Morning: New materials: predictions and realizations

Presiding: Eduard Matito

- 8:30 – 9:00 am Svilen Bobev (University of Delaware, USA)
"Zintl Phases with Rare-Earth Elements"
- 9:00 – 9:30 am Eva Zurek (University at Buffalo, SUNY, USA)
"Theoretical Predictions of Superconducting Hydrides Under Pressure"
- 9:30 – 10:00 am Tim Strobel (Carnegie Institution for Science, USA)
"Accessing metastable states with pressure: synthetic pathways to new materials with exceptional properties"
- 10:00 – 10:30 am Tatiana Timofeeva (New Mexico Highlands University, USA)
"Intramolecular Interactions from X-ray Diffraction Data as a Tool of Understanding Crystal Properties"
- 10:30 – 11:00 am Choong-Shik Yoo (Washington State University, USA)
"Chemistry in Dense Solid Mixtures"
- 11:00 – 11:15 am *Coffee Break*
- 11:15 – 11:45 am Thomas Heine (Leipzig University, Germany)
"Chemical bonding in two-dimensional crystals"
- 11:45 – 12:15 pm Dylan Jayatilaka (University of Western Australia, Australia)
"TBA"

Afternoon: Bonding at nano and sub-nano scales

Presiding: Anastassia Alexandrova

- 3:00 – 3:30 pm Marat Talipov (New Mexico State University, USA)
"Long-Bonding Interaction Between Two Radicals as a Source of Novel Molecules"
- 3:30 – 4:00 pm Ryan C. Fortenberry (Georgia Southern University, USA)
"The Brightest of Vibrational Transitions: Proton-Bound Complexes"
- 4:00 – 4:30 pm Alexander Boldyrev (Utah State University, USA)
"Homocatenation"

Abstracts

Low-dimensional Group 15 Semiconductors

T. Nilges, M. Köpf, D. Pfister, M. Baumgartner, C. Ott

Synthesis and Characterization of Innovative Materials Group
Technical University of Munich, Department of Chemistry
Lichtenbergstrasse 4, 85748 Garching b. München, Germany
E-mail: tom.nilges@lrz.tum.de

Element allotropes of phosphorus, like orthorhombic black, violet or fibrous phosphorus gained reasonable interest in the past years due to their electronic properties and their ability to be delaminated into quantum-confined two-dimensional nano sheets or fibers [1]. Here, we present an easy access to this class of low-dimensional semiconductors and provide selected applications afterwards. Black phosphorus, violet phosphorus and arsenic-substituted black phosphorus were used to fabricate field effect transistors and sensors. A selection of these features are presented [2-4].

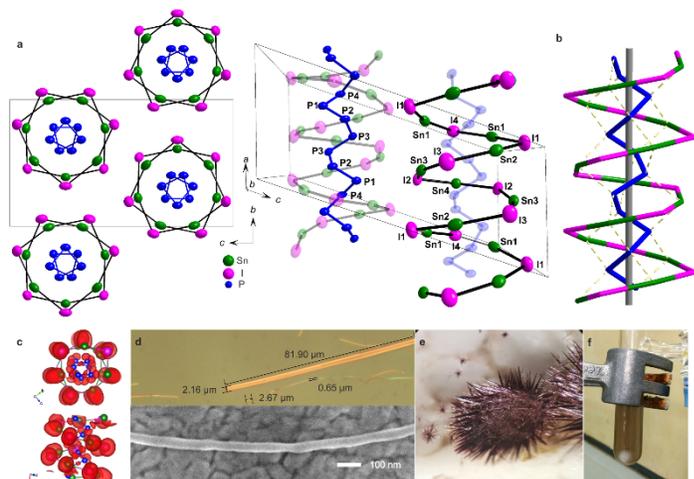


Fig. 1. Double helical SnIP, sections of the crystal structure (a,b), ELF calculations featuring the covalent and van der Waals type interactions (c), Crystal morphology and microscope picture of SnIP (d, e) and suspension of delaminated nano particular SnIP in chloroforme.

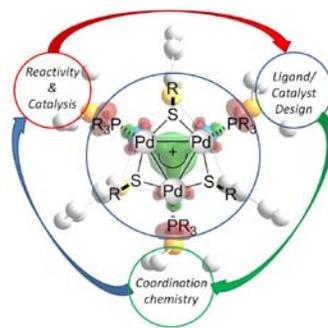
Another emerging class of quasi one-dimensional semiconductors are based on helical polyphosphide substructures [5]. Recently, the first pure inorganic, atomic-scale double helix compound SnIP was reported [6]. The material consists of hexagonally stacked double helices formed by phosphorus and [SnI] single helices. Due to the unusual structure it combines the mechanical properties of polymers and the electronic properties of main group semiconductors. Based in this structure prototype a homologues series of double helical main group semiconductors were predicted featuring intriguing electronic properties, like for instance band gaps between 1 and 2.5 eV [7].

- [1] A. Carvalho, M. Wang, X. Zhu, A. S. Rodin, H. Su, A. H. Castro Neto, **Nat. Rev. Mater.** (2016), 1, 16061.
- [2] A. N. Abbas, B. Liu, L. Chen, Y. Ma, S. Cong, N. Aroonyadet, M. Köpf, T. Nilges, C. Zhou, **ACS Nano** (2015), 9, 5618.
- [3] B. Liu, M. Köpf, A. A. Abbas, X. Wang, Q. Guo, Y. Jia, F. Xia, R. Wehrich, F. Bachhuber, F. Pielnhofer, H. Wang, R. Dhall, S. B. Cronin, M. Ge, X. Fang, T. Nilges, C. Zhou, **Adv. Mater.** (2015), 27, 4423.
- [4] F. Baumer, Y. Ma, C. Shen, A. Zhang, L. Chen, Y. Liu, D. Pfister, T. Nilges, C. Zhou, **ACS Nano** (2017), DOI: 10.1021/acsnano.7b00798.
- [5] A. S. Ivanov, A. J. Morris, K. V. Bozhenko, C. J. Pickard, A. I. Boldyrev, **Angew. Chem. Int. Ed.** (2012), 51, 8330.
- [6] D. Pfister, K. Schäfer, C. Ott, B. Gerke, R. Pöttgen, O. Janka, M. Baumgartner, A. Efimova, A. Hohmann, P. Schmidt, S. Venkatachalam, L. van Wüllen, U. Schürmann, L. Kienle, V. Duppel, E. Parzinger, B. Miller, J. Becker, A. Holleitner, R. Wehrich, T. Nilges, **Adv. Mater.** (2016), 28, 9783.
- [7] M. Baumgartner, R. Wehrich, T. Nilges, **Chem. Eur. J.** (2017), DOI: 10.1002/chem.201700929.

CONNECTING HOMOGENEOUS AND HETEROGENEOUS CATALYSIS WITH ALL-METAL AROMATICS

Giovanni Maestri

Department of Chemistry, Life Sciences and Environmental Sustainability, Università di Parma, 17/A Parco Area delle Scienze, 43124 Parma - Italy (giovanni.maestri@unipr.it)



Pivoting on a family of stable trinuclear clusters featuring delocalized metal-metal bonds,¹ the lecture will present key aspects of the synthesis, stereoelectronic properties² and catalytic applications^{3,4} of these prototypical sub-nanometric metal surfaces.

These scaffolds can be readily prepared through a single synthetic step from commercial reagents. They could incorporate both palladium and platinum nuclei, allowing one to access and study all-metal heteroaromatics. These complexes can catalyze the reduction of alkynes to cis-alkenes under transfer hydrogenation conditions with complete selectivity coupled with unmatched activity. Ongoing developments will present the access to multinuclear complexes in which the metal triangle acts formally as an aromatic donor-ligand for a Lewis acid and the development of cascades involving polyunsaturated linear organic substrates for the diastereoselective assembly of multiple carbon-carbon bonds.

References

1. Synthesis of Triangular Tripalladium Cations as Noble-Metal Analogues of the Cyclopropenyl Cation. *Angew. Chem. Int. Ed.* **2014**, *53*, 1987.
2. A Simple Synthesis of Triangular All-Metal Aromatics Allowing Access to Isolobal All-Metal Heteroaromatics. *Chem. Eur. J.* **2015**, *21*, 12271.
3. Catalytic Semireduction of Internal Alkynes with All-Metal Aromatic Complexes *Chem. Cat. Chem.* **2015**, *7*, 3266
4. Boosting catalyst activity in cis-selective semi-reduction of internal alkynes by tailoring the assembly of all-metal aromatic tri-palladium complexes. *Dalton Trans.*, **2016**, *45*, 15786.

MAXIMUM PROBABILITY DOMAINS A NEW TOOL IN CHEMICAL BONDING ANALYSIS

GUILLAUME ACKE, PATRICK BULTINCK*

Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium. Patrick.Bultinck@UGent.be

Classical chemical bonding theories such as those that rely on Lewis structures consider electron pairs to be somewhat “glued” in space. The usual dot notation for H_2O suggests that for each O-H bond a pair of electrons is somewhat fixed between both atoms while two free electron pairs are localised on the oxygen atom and are considered free electron pairs. This view along with VSEPR theory has allowed to interpret and even predict chemical structures from the simple composition of a molecule and its bonding pattern.

In contrast to this success, the physical reasoning needed to explain why these methods work so well has lagged behind significantly. The wave function should be the source of this information but in most cases of previous explanations, use was made of specific “intermediates” such as molecular orbitals or valence bond structures. Following the Copenhagen interpretation of a wavefunction, the probability of finding electron 1 in a volume element $d\mathbf{x}_1$, electron 2 in the volume element $d\mathbf{x}_2$ etc. is given by:

$$(1) \quad |\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

In the most common explanations, the key ingredient is the pair density matrix whereby the probability above is integrated over all electrons $3 \cdots N$.

$$(2) \quad \binom{N}{2} d\mathbf{x}_1 d\mathbf{x}_2 \int_{R^3} |\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

For our purposes we can proceed to computing the probability that two electrons are confined to a region $d\Omega$ in the following way:

$$(3) \quad \binom{N}{2} \int_{\Omega} d\mathbf{x}_1 d\mathbf{x}_2 \int_{R^3} |\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

However, this leads to a problem since we include not only the probability of having 2 electrons in Ω but also 3, 4, ... as there is no constraint on the other electrons. In this talk we reveal how the study of maximum probability domains can help foster insight in chemical bonding by shape optimisation of Ω as a domain that contains two and only two electrons:

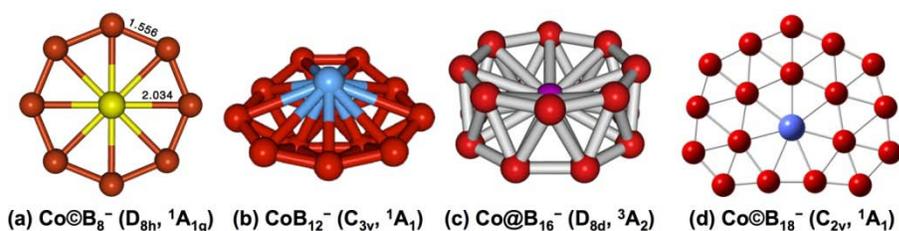
$$(4) \quad \binom{N}{2} \int_{\Omega} d\mathbf{x}_1 d\mathbf{x}_2 \int_{R^3 \setminus \Omega} |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n)|^2 d\mathbf{x}_3 \cdots d\mathbf{x}_N$$

Probing the Electronic Structure and Chemical Bonding of Size-Selected Boron and Doped-Boron Clusters Using Photoelectron Spectroscopy: From Borophenes to Metalloborophenes

Lai-Sheng Wang

Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

Joint studies using photoelectron spectroscopy and computational chemistry over the past decade have shown that small boron clusters possess planar structures [1,2], culminated in the discovery of the hexagonal B₃₆ cluster, that led to the concept of borophene [3]. The recent syntheses of borophenes on inert substrates have availed the opportunities to investigate the interesting properties of this new form of 2D materials [4]. Metal-doping can significantly change the electronic and structural properties of boron clusters. We have investigated boron clusters doped with a single Co atom and observed a number of interesting structures. For CoB₈⁻, we found that it forms a molecular wheel-type structure with a central Co atom coordinated by a monocyclic B₈ ring [5] (a), whereas CoB₁₂⁻ has a half-sandwich-type structure in which a quasi-planar B₁₂ cluster is coordinated to the Co atom [6] (b). A recent study on CoB₁₆⁻ has led to the discovery of Co-centered molecular drum [7] (c). A more recent finding concerns the planar CoB₁₈⁻ cluster, in which the Co atom is observed to be part of the 2D network [8] (d), suggesting the possibility of metalloborophenes, a potentially new class of 2D materials consisting of a boron network doped by transition metals. The talk will discuss these recent advances and the implications for borophenes and metalloborophenes.



References:

- [1] A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, L. S. Wang. All-boron aromatic clusters as potential new inorganic ligands and building blocks in chemistry. *Coord. Chem. Rev.* **2006**, 250, 2811-2866.
- [2] L. S. Wang. Photoelectron spectroscopy of size-selected boron clusters: from planar structures to borophenes and borospherenes. *Int. Rev. Phys. Chem.* **2016**, 35, 69-142.
- [3] Z. A. Piazza, H. S. Hu, W. L. Li, Y. F. Zhao, J. Li, L. S. Wang. Planar hexagonal B₃₆ as a potential basis for extended single-atom layer boron sheets. *Nature Commun.* **2014**, 5, 3113.
- [4] A. J. Mannix, B. Kiraly, M. C. Hersam, N. P. Guisinger. Synthesis and chemistry of elemental 2D materials. *Nat. Rev. Chem.* **2017**, 1, 0014.
- [5] C. Romanescu, T. R. Galeev, W. L. Li, A. I. Boldyrev, L. S. Wang. Transition-metal-centered monocyclic boron wheel clusters (M@B_n): A new class of aromatic borometallic compounds. *Acc. Chem. Res.* **2013**, 46, 350-358.
- [6] I. A. Popov, W. L. Li, Z. A. Piazza, A. I. Boldyrev, L. S. Wang. Complexes between planar boron clusters and transition metals: A photoelectron spectroscopy and ab initio study of CoB₁₂⁻ and RhB₁₂⁻. *J. Phys. Chem. A* **2014**, 118, 8098-8105.
- [7] I. A. Popov, T. Jian, G. V. Lopez, A. I. Boldyrev, L. S. Wang. Cobalt-centred boron molecular drums with the highest coordination number in the CoB₁₆⁻ cluster. *Nature Commun.* **2015**, 6, 8654.

- [8] W. L. Li, T. Jian, X. Chen, T. T. Chen, G. V. Lopez, J. Li, L. S. Wang. The planar CoB_{18}^- cluster as a motif for metallo-borophenes. *Angew. Chem. Int. Ed.* **2016**, *55*, 7358-7363.

Unusual Properties of Boron-Containing Clusters Probed by Cryogenic Ion Trap Vibrational Spectroscopy

Knut R. Asmis

*Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie
Universität Leipzig, Linnéstr. 2, 04109 Leipzig, Germany*

Boron is electron deficient and therefore has a strong tendency to share electrons. Consequently, boron compounds can exhibit pronounced delocalized bonding and aromatic behavior. These unusual electronic properties of elemental boron lead to a rich polymorphism. Infrared photodissociation (IRPD) spectroscopy of mass-selected ions, thermalized to cryogenic temperatures, combined with quantum chemical calculations allows for a detailed characterization of these unusual properties in gas phase clusters. Recent advances in the vibrational spectroscopy of pure boron cluster cations [1] and polyhedral closo-dodecaborate anions [2] are highlighted.

Comparison of the IRPD spectrum of the magic-number boron cluster B_{13}^+ to simulated IR spectra of low energy isomers from density functional theory (DFT) unambiguously reveal a planar boron double-wheel species (see Fig. 1). Born-Oppenheimer DFT molecular dynamics simulations show that B_{13}^+ exhibits internal quasi-rotation already at 100 K. Vibrational spectra derived from these simulations allow extracting the first spectroscopic evidence from the IRPD spectrum for the exceptional fluxionality of B_{13}^+ .

The closo-dodecaborate anion $\text{B}_{12}\text{Cl}_{11}^-$ spontaneously binds the noble gases (Ng) xenon and krypton at room temperature – a reaction typical of “superelectrophilic” dications. The electrophilic nature of the anion is confirmed spectroscopically by the observation of a blue shift of the CO stretching mode in the IRPD spectrum of $[\text{B}_{12}\text{Cl}_{11}\text{CO}]^-$ and theoretically by the investigation of its electronic structure. The orientation of the electric field at the reactive site of $\text{B}_{12}\text{Cl}_{11}^-$ results in an energy barrier for the approach of polar molecules and facilitates the formation of Ng-adducts that are not detected with reactive cations like C_6H_5^+ . Based on these studies the new chemical concept of “dipole discriminating electrophilic anions” is introduced.

References:

- [1] M.R. Fagiani, X. Song, P. Petkov, S. Debnath, S. Gewinner, W. Schöllkopf, T. Heine, A. Fielicke, K.R. Asmis, *Angew. Chem. Int. Ed.* **56** 501 (2017).

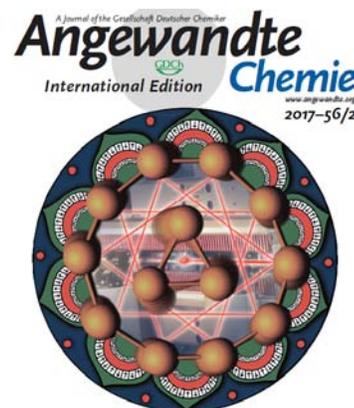


Fig. 1

[2] M. Rohdenburg, M. Mayer, M. Grellmann, C. Jenne, T. Borrmann, F. Kleemiß, V.A. Azov, K.R. Asmis, S. Grabowsky, J. Warneke, *Angew. Chem. Int. Ed.* In press (2017).

Anomalous Optoelectronic Properties of Nanostructures from DFT and TD-DFT Calculations

Bryan M. Wong

Department of Chemical & Environmental Engineering and Materials Science & Engineering Program, University of California-Riverside, Riverside, California

<http://www.bmwong-group.com>

Nanostructures with π -conjugated orbitals continue to provide fascinating systems for understanding and probing the unique chemical bonding interactions in nanomaterials. Although π -conjugation effects are intrinsically quantum-mechanical in nature (i.e., π -orbital delocalization/aromaticity has no classical analogue), these electronic effects have a profound impact on *real* material properties such as energy transfer, charge delocalization, and electron/hole mobility. Indeed, it is precisely these unique electronic effects that have ignited immense efforts in the synthesis of new conjugated nanostructures with the desired structural and electronic properties. In this presentation, I will highlight recent and ongoing work¹⁻³ in my group to understand the unusual optoelectronic properties that have emerged in recently-synthesized nanostructures. Specifically, we have discovered that the lowest excitation energy – in both cycloparaphenylene carbon nanorings and recently-synthesized porphyrin nanotubes – surprisingly becomes larger as the size is increased, *in contradiction with typical quantum confinement effects*. To rationalize these unusual electronic properties, we have carried out extensive investigations of excitonic effects by analyzing electron-hole transition density matrices, quasiparticle energy levels, and other electronic chemical descriptors using both DFT and time-dependent DFT. Based on our theoretical analyses, we find that both excitonic and aromatic effects play a vital role in understanding the unusual photoinduced dynamics in these nanostructures.

1. S. I. Allec, N. V. Ilawe, and B. M. Wong, “Unusual Bandgap Oscillations in Template-Directed π -Conjugated Porphyrin Nanotubes.” *Journal of Physical Chemistry Letters*, **7**, 2362 (2016).
2. B. M. Wong and J. W. Lee, “Anomalous Optoelectronic Properties of Chiral Carbon Nanorings...and One Ring to Rule Them All.” *Journal of Physical Chemistry Letters*, **2**, 2702 (2011).
3. B. M. Wong, “Optoelectronic Properties of Carbon Nanorings: Excitonic Effects from Time-Dependent Density Functional Theory.” *Journal of Physical Chemistry C*, **113**, 21921 (2010).

Structures of Silicon Ions and Clusters: Silane Ions and Doping on the Nanoscale

Otto Dopfer

Institut für Optik und Atomare Physik, TU Berlin, Germany

Doping of bare silicon clusters at the nanoscale is relevant for applications in materials science and astrochemistry. We present IR spectra and calculations of neutral and charged $\text{Si}_n\text{X}_m^{(+)}$ clusters with first row elements $\text{X}=\text{Be-O}$ generated in a laser desorption cluster source coupled to a molecular beam, a time-of-flight mass spectrometer, and an IR free electron laser [1-6]. Vibrational spectra of neutral Si_nX_m clusters are obtained by resonant IR-VUV photoionization, while those of cationic Si_nX_m^+ clusters are measured from IR photodissociation of cold mass-selected $\text{Si}_n\text{X}_m^+-\text{Xe}$ clusters. The structures are assigned by comparison to sophisticated DFT calculations combined with effective basin hopping and/or genetic algorithm search routines. It is shown, that the cluster structures and their bonding characteristics sensitively depend on the type and number of dopant atoms.

Silanes and their derivatives and ions are fundamental species in a variety of chemical disciplines, ranging from organic chemistry and materials science to astrochemistry and theory of chemical bonding. In contrast to hydrocarbon ions, almost no information is available for the corresponding Si_xH_y^+ cations. Here, IR spectra of Si_xH_y^+ produced in a supersonic plasma expansion of SiH_4 are inferred from photodissociation of cold Ne and Ar complexes obtained in a tandem quadrupole mass spectrometer coupled to an electron impact ionization source, an octopole ion trap, and an IR-OPO laser. The clusters are characterized in their ground electronic states by quantum chemical calculations to investigate the effects of ionization/protonation and Ar/Ne complexation on their geometric, vibrational, and electronic structure. We present initial results for Si_2H_6^+ , Si_2H_7^+ and Si_3H_8^+ , which have complex potential energy surfaces, with low-energy isomers featuring unusual three-center two-electron (3c-2e) bonding [8-10]. Some of these clusters exhibit the new concept of “charge-inverted” hydrogen bonding. Results on elusive protonated silanols will also be presented.

[1] M. Savoca, J. Langer, A. Lagutschenkov, D.J. Harding, A. Fielicke, O. Dopfer, *J. Phys. Chem. A* 117, 1158 (2013)

[2] M. Savoca, J. Langer, D.J. Harding, O. Dopfer, A. Fielicke, *Chem. Phys. Lett.* 557, 49 (2013)

[3] N.X. Truong, M. Savoca, D.J. Harding, A. Fielicke, O. Dopfer, *Phys. Chem. Chem. Phys.* 16, 22364 (2014)

[4] M. Savoca, J. Langer, D.J. Harding, D. Palagin, K. Reuter, O. Dopfer, A. Fielicke, *J. Chem. Phys.* 141, 104313 (2014)

[5] N.X. Truong, M. Savoca, D.J. Harding, A. Fielicke, O. Dopfer, *Phys. Chem. Chem. Phys.* 17, 18961 (2015)

[6] N.X. Truong, M. Haertelt, B. Jaeger, S. Gewinner, W. Schöllkopf, A. Fielicke, O. Dopfer, *Int. J. Mass Spectrom.* 395, 1 (2016)

[7] N.X. Truong, B. Jaeger, S. Gewinner, W. Schöllkopf, A. Fielicke, O. Dopfer, *J. Phys. Chem. C*, submitted (2017)

[7] M. Savoca, M.A.R. George, J. Langer, O. Dopfer, *Phys. Chem. Chem. Phys.* 15, 2774 (2013)

[8] M. Savoca, J. Langer, O. Dopfer, *Angew. Chem. Int. Ed.* 52, 1568 (2013)

[9] M.A.R. George, M. Savoca, O. Dopfer, *Chem. Eur. J.* 19, 15315 (2013)

Imaging, Understanding, and Leveraging Buried Interactions in Supramolecular Assemblies

Paul S. Weiss

California NanoSystems Institute and Departments of Chemistry & Biochemistry and Materials Science & Engineering, UCLA, Los Angeles, CA 90095

Structural domains in self-assembled systems are well known. The types of domain boundaries can be simplified by using symmetric building blocks. Likewise, interactions can be designed into the building blocks to add stability to the systems. By developing new imaging tools that let us visualize these interaction networks, we have discovered that buried networks can cross structural domain boundaries, regions of disorder, and substrate step edges in monolayer systems.¹⁻³ The interactions, their ranges and the consequences of these effects will be discussed.

1. Heads and Tails: Simultaneous Exposed and Buried Interface Imaging of Monolayers, P. Han, A. R. Kurland, A. N. Giordano, S. U. Nanayakkara, M. M. Blake, C. M. Pochas, and P. S. Weiss, *ACS Nano* **3**, 3115 (2009).
2. Defect-Tolerant Aligned Dipoles within Two-Dimensional Plastic Lattices, J. C. Thomas, J. J. Schwartz, J. N. Hohman, S. A. Claridge, H. S. Auluck, A. C. Serino, A. M. Spokoiny, G. Tran, K. F. Kelly, C. A. Mirkin, J. Gilles, S. J. Osher, and P. S. Weiss, *ACS Nano* **9**, 4734 (2015).
3. Mapping Buried Hydrogen-Bonding Networks, J. C. Thomas, D. P. Goronzy, K. Dragomiretskiy, D. Zosso, J. Gilles, S. J. Osher, A. L. Bertozzi, and P. S. Weiss, *ACS Nano* **10**, 5446 (2016).

On the Mechanism of Selective Adsorption of Ions to Aqueous Interfaces: Graphene/Water vs. Air/Water

Richard J Saykally

Department of Chemistry, University of California. Chemical Sciences Division, Lawrence Berkeley National Laboratory Berkeley, CA 94720-1460

The behavior of ions at aqueous interfaces has been a subject of much controversy for over a century. By exploiting the strong charge-transfer-to-solvent (CTTS) resonances of selected anions in aqueous electrolytes, their adsorption properties have been measured by deep UV-SHG spectroscopy methods for both air/water and graphene/water interfaces. Temperature and concentration dependences determined by both experiment and computer simulations for the air/water case reveal that the strong interfacial adsorption observed for weakly hydrated ions is enthalpically driven by hydration forces and impeded by a novel entropy effect (capillary wave suppression). Extension of this approach to the water-graphene interface reveals a surprising similarity to the air-water case, albeit with very different mechanistic details. Our recent development of a broadband deep UV SFG spectroscopy technique has produced detailed CTTS spectra of interfacial ions, for which comparisons with bulk CTTS spectra provide additional new insights.

Rizzuto, A.M., Irgen-Gioro, Shawn, Eftekhari-Bafrooei, A., Saykally, R. J. "[Broadband Deep UV](#)

Spectra of Interfacial Aqueous Iodide" *J. Phys. Chem. Lett.*, **7**, 3882-3885 (2016).

D.E. Otten, P. Shaffer, P. Geissler, R.J. Saykally, *Elucidating the Mechanism of Selective Ion Adsorption to the Liquid Water Surface*, PNAS **109**, 701(2012).

D. L. McCaffrey, S. C. Nguyen, S. J. Cox, P. L. Geissler, H. Weller, A. P. Alivisatos, and R. J. Saykally, *Selective adsorption of ions to the graphene-water interface studied by deep UV second harmonic generation spectroscopy and theory* In Preparation(2017).

The Rich Bonding Motifs of Quantum Materials

Tyrel M. McQueen

Department of Chemistry, Department of Materials Science and Engineering, Department of Physics and Astronomy, Institute for Quantum Matter, The Johns Hopkins University

<https://occamy.chemistry.jhu.edu>

A quantum material is loosely defined as a material in which there are one or more highly correlated degrees of freedom that often give rise to emergent behavior that appears greater than the sum of the individual interactions. In this talk, I will present our recent work on the discovery and synthesis of new quantum materials, with a particular focus on elucidating the physical principles underpinning not only the observed bonding motifs but also the process of their formation during synthesis. Examples will be drawn from our use of small atomic clusters, assembled into extended three dimensional frameworks, to realize new quantum magnetic states (e.g. condensed valence bonds in $\text{LiZn}_2\text{Mo}_3\text{O}_8$), our successful electron doping of a two dimensional kagome spin liquid, and the competition between localized and itinerant states, and d- and f- orbital contributions, in SmB_6 .

The Role of Hydrogen Bond in Electron Transport in Molecular Junctions

Micah Wimmer¹, Tarakeshwar Pilarisetty¹, and Vladimiro Mujica^{1,2}

¹Arizona State University School of Molecular Sciences Physical Sciences Center PSD-D102, Tempe, AZ 85287

²School of Chemical Sciences and Engineering, Yachay Tech, Yachay City of Knowledge, 100119-Urcuqui, Ecuador.

The use of local probe, e.g. STM, can shed new light on the properties of chemical bonds. We present a theoretical and computational study of electron transport in molecular junctions involving hydrogen bonds. While electron transport through covalent bonds has been extensively studied, in recent work the focus has been shifted towards hydrogen-bonded systems due to their ubiquitous presence in biological systems and their potential in forming nano-junctions between molecular electronic devices and biological systems.

This analysis allows us to significantly expand our comprehension of the experimentally observed result that the inclusion of hydrogen bonding in a molecular junction significantly impacts its transport properties, a fact that has important implications for our understanding of transport through DNA, and nano-biological interfaces in general. We have explored the implications of quiresonant transport in short chains of weakly-bonded molecular junctions

involving hydrogen bonds to interpret recent experiments by Nishino *et al* and explain the role of Fano resonances in the transmission properties of the junction.

Graphene and graphene-oxide based membranes for filtration

Jeffrey Grossman
MIT, USA

The use of nanoporous graphene-based films for filtration has recently emerged as a promising approach to reduce the energy consumption and capital costs of molecular separations. Graphene and graphene-oxide are two-dimensional materials with very high mechanical strength, favorable surface properties, and the potential to exhibit water permeability two orders of magnitude greater than that of the membranes used commercially today. The system-level benefits that these kinetics afford can only be realized if NPG material can be produced at scale. In this talk, I will highlight our computational and experimental work on the properties, synthesis, and performance of NPG-based materials for filtration applications.

Novel nanostructures of boron: Bowls, drums, cages, nanotubes, and atomic layers with Dirac cones

Vijay Kumar
Dr. Vijay Kumar Foundation, Gurgaon, Haryana 122001, India
Center for Informatics, School of Natural Sciences, Shiv Nadar University, Tehsil Dadri, Gautam Buddha Nagar, India

Boron is just before carbon in the periodic table and there has been much interest to explore if it can have nanostructures similar to carbon fullerenes and nanotubes. Research in past few years has shown novel structures of boron clusters as well as stabilization of atomic layers of boron called borophene. In this talk I shall discuss our recent findings from *ab initio* calculations on quasi-planar B₈₄ and other clusters stabilized with hexagonal holes [1]. Further studies have been carried out with doping of metal atoms in boron clusters. I shall present results on magic metal doped quasi-planar [2] and drum-shaped M@B₁₄ and M@B₁₆ (M = transition metal atom) [3] clusters whose stability has been understood using a disk jellium model with magic behavior at 12 and 24 valence electrons. Assemblies of such drum shaped clusters leads to the formation of nanotubes. For larger cluster sizes, metal doped cages have been obtained [4]. Further I shall present results on different atomic layers of boron stabilized on metal surfaces [5], and discuss the bonding character as well as Dirac-cone features in these systems.

Acknowledgements: I gratefully acknowledge my collaborators A.B. Rahane, P. Saha, N. Sukumar, J. Karthikeyan, and P. Murugan who contributed to these studies. The calculations were performed using Magus at SNU, CECRI machine as well as resources at VKF. Financial support from ITC-PAC is thankfully acknowledged.

- [1] A. B. Rahane and V. Kumar, *Nanoscale*, **7**, 4055 (2015).
- [2] P. Saha, A.B. Rahane, V. Kumar, and N. Sukumar, *Physica Scripta* **91**, 053005 (2016)
- [3] P. Saha, A.B. Rahane, V. Kumar, and N. Sukumar, *J. Phys. Chem. C* (2017)
- [4] A. B. Rahane, P. Saha, N. Sukumar, and V. Kumar, to be published.
- [5] J. Karthikeyan, P. Murugan, and V. Kumar, to be published.

Playing with electrons in 2D and 3D borides

Anastassia N. Alexandrova, P. J. Robinson, Zhihao Cui, Elisa Jimenez-Izal

Department of Chemistry and Biochemistry, University of California, Los Angeles, and California NanoSystems Institute, USA

I will present a prediction of several 2D materials with interesting electronic properties: isotropic and anisotropic conductivity, and magnetism. I will also present the new mechanism for how an extremely correlated solid, SmB_6 , exhibits the $\text{Sm}^{2+}/\text{Sm}^{3+}$ mixed valency. A highly non-adiabatic nature of the Sm-boron bonding is found responsible, as supported by Tyrel McQueen's experiment. The unifying theme of the findings to-be-presented is the promiscuous bonding nature of boron: when bound to metals, it can be covalent, cationic, or anionic, with a possible fluxionality between these bonding scenarios even at room temperature and without extra forces.

- [1] Nandula, A.; Trinh, Q. T.; Saeys, M.; Alexandrova, A. N. *Origin of Extraordinary Stability of Square Planar Carbon Atoms in Surface Carbides of Cobalt and Nickel*. *Angew. Chem. Int. Ed.* **2015**, *54*, 5312-5316.
- [2] Jimenez-Izal, E.; Saeys, M.; Alexandrova, A. N. *Metallic and Magnetic 2D Materials Containing Planar Tetracoordinated C and N*. *J. Phys. Chem. C* **2016**, *120*, Mark Gordon Festschrift Issue, 21685–21690.
- [3] Robinson, P.J.; Zhang, X.; McQueen, T.; Bowen, K. H.; Alexandrova, A. N. *SmB_6^- Cluster Anion: Covalency Involving f -Orbitals*. *J. Phys. Chem. A* **2017**, *121*, 1849–1854.
- [4] Cui, Z.; Jimenez-Izal, E.; Alexandrova, A. N. *Prediction of two-dimensional boron phase with anisotropic electrical conductivity*. *J. Phys. Chem. Lett.* **2017**, *8*, 1224–1228.
- [5] Robinson, P.J.; Zhang, X.; McQueen, T.; Bowen, K. H.; Alexandrova, A. N. *SmB_6 – a Non-Born-Oppenheimer Solid with a New Type of Mixed Valency*. **2017**, in preparation.

Chemical bonding steers excited state dynamics in nanoscale materials

Oleg V. Prezhdo

University of Southern California, Los Angeles

Our group's research focuses on modeling non-equilibrium processes in condensed phase systems explicitly in time-domain. We develop approaches for non-adiabatic molecular dynamics and time-domain density functional theory [1-4], and apply them to a variety of excited state electron-vibrational processes in nanoscale materials. The software to perform these simulations [5-7] are freely available at <http://gdriv.es/pyxaid>. A significant fraction of the efforts is motivated by photovoltaic and photo-catalytic applications. The talk will highlight the importance of chemical bonding in the excited state dynamics, including several, perhaps

counter-intuitive, examples investigated recently both by pump-probe spectroscopies and theoretically in our group.

Various chromophores are used to sensitize TiO₂ to achieve photo-induced charge separation. Most chromophores have a significant band-gap to avoid rapid electron-hole recombination. Surprisingly, graphene – a metal (!) – can be used as a chromophore as well. The charge separation is faster than the electron-hole recombination due to chemical bonding between TiO₂ and graphene [8].

Similarly, surface plasmon excitations of metallic particles leads to electron transfer to TiO₂ substrate. The traditional mechanism assumes that plasmons rapidly dephase into electron-hole pairs, and after that an electron is transferred. However, electrons and holes should rapidly recombine in metallic systems. Our simulations showed that charge separated states can form immediately during plasmon excitation [9]. The prediction was confirmed experimentally a year later [10]. This mechanism relies on strong interaction between metallic particles and TiO₂. In comparison, the traditional mechanism operates for metal on MoS₂, because the interaction is weak.

Long non-conjugated bridges between donor and acceptor species are viewed as insulators, slowing down electron transfer. A counter-intuitive observation, such bridge connecting a CdSe quantum dot and C₆₀ accelerates charge separation. We rationalize this experiment by strong electron-phonon coupling mediated by the high-frequency vibrations of the bridge [11].

Surface defects are viewed as a negative attribute of semiconductor quantum dots, and significant synthetic efforts are dedicated to eliminate them. Interestingly, Cd vacancies on CdS surface quench luminescence; however, S vacancies do not. We rationalize this by the ability of Cd-rich surfaces to “heal” defects much better compared to S-rich surfaces: excess non-metallic S is much more selective in creating chemical bonds than excess metallic Cd [12,13].

We also show that certain types of defects accelerate photo-induced charge separation in quantum-dot/molecular-chromophore systems, while maintaining slow charge recombination [14].

We demonstrate how the electron transfer mechanism changes from non-adiabatic to adiabatic as a result of chemical bonding induced by surface defects [15].

Finally, we will discuss Auger-type processes that are common in most nanoscale materials. In particular, in semiconductor quantum dots, they are responsible for fast losses of electron energy to heat. They energy loss can be avoided with hole trapping by appropriately bonded ligands [16]. Discovered recently in the experiment-theory collaboration [17,18], a new type of electron transfer – Auger assisted electron transfer – eliminates the Marcus inverted region and accelerates photon-induced charge separation. The mechanism relies on chemical interaction between the quantum dot electron donor and molecular acceptor.

1. C. F. Craig, W. R. Duncan, O. V. Prezhdo, “Trajectory surface hopping in the time-dependent Kohn-Sham theory for electron-nuclear dynamics”, *Phys. Rev. Lett.*, **95** 163001 (2005).
2. B. F. Habenicht, O. V. Prezhdo, “Electron and hole relaxation dynamics in a semiconducting carbon nanotube”, *Phys. Rev. Lett.*, **100**, 197402 (2008), chosen for *Virt. J. of Ultrafast Science*, June 2006.
3. S. R. Fischer, B. F. Habenicht, A. B. Madrid, W. R. Duncan, O. V. Prezhdo, “Regarding the validity of the time-dependent Kohn-Sham approach for electron-nuclear dynamics via trajectory

- surface hopping”, *J. Chem. Phys.*, **134**, 024102 (2011); chosen for Jan. 24, 2011 issue of *Virt. J. Nanoscale Sci. & Tech.*
4. L.-J. Wang, A. Akimov, O. V. Prezhdo, “Recent progress in surface hopping: 2011-2015”, *J. Phys. Chem. Lett.*, **7**, 2100-2112 (2016).
 5. A. V. Akimov, O. V. Prezhdo, “The PYXAID program for non-adiabatic molecular dynamics in condensed matter systems”, *J. Chem. Theor. Comp.*, **9**, 4959 (2013).
 6. A. V. Akimov, O. V. Prezhdo, “Advanced capabilities of the PYXAID program: integration schemes, decoherence effects, multiexcitonic states, and field-matter interaction”, *J. Chem. Theor. Comp.*, **10**, 789 (2014).
 7. S. Pal, D. J. Trivedi, A. V. Akimov, B. Aradi, T. Frauenheim, O. V. Prezhdo, “Nonadiabatic molecular dynamics for thousand atom systems: a tight-binding approach toward PYXAID”, *J. Chem. Theor. Comp.*, **12**, 1436 (2016).
 8. R. Long, N. English, O. V. Prezhdo, “Photo-induced charge separation across the graphene-TiO₂ interface is faster than energy losses: a time-domain ab initio analysis”, *J. Am. Chem. Soc.*, **134**, 14238 (2012); chosen for *JACS* Spotlight.
 9. R. Long, O. V. Prezhdo “Instantaneous generation of charge-separated state on TiO₂ surface sensitized with plasmonic nanoparticles”, *J. Am. Chem. Soc.*, **136**, 4343 (2014).
 10. K. Wu, et al., “Efficient hot-electron transfer by a plasmon-induced interfacial charge-transfer transition”, *Science*, **349**, 6248 (2015).
 11. V. V. Chaban, V. V. Prezhdo, O. V. Prezhdo, “Covalent linking greatly enhances photoinduced electron transfer in fullerene-quantum dot nano-composites: Time-domain ab initio study”, *J. Chem. Phys. Lett.*, **4**, 1 (2013).
 12. H. Wei, C. M. Evans, B. D. Swartz, A. J. Neukirch, J. Young, O. V. Prezhdo, T. D. Krauss, “Colloidal semiconductor quantum dots with tunable surface composition”, *Nano Lett.*, **12**, 4465 (2012).
 13. K. L. Sowers, Z. T. Hou, J. J. Peterson, B. Swartz, S. Pal, O. V. Prezhdo, T. D. Krauss, “Photophysical properties of CdSe/CdS core/shell quantum dots with tunable surface composition”, *Chem. Phys.*, **471**, 24-31 (2016).
 14. R. Long, N. J. English, O. V. Prezhdo, “Defects are needed for fast photo-induced electron transfer from a nanocrystal to a molecule: Time-domain ab initio analysis”, *J. Am. Chem. Soc.*, **135**, 18892 (2013).
 15. D. N. Tafen, R. Long, O. V. Prezhdo, “Dimensionality of nanoscale TiO₂ determines the mechanism of photoinduced electron injection from a CdSe nanoparticle”, *Nano Lett.*, **14**, 1790 (2014).
 16. D. J. Trivedi, L. J. Wang, O. V. Prezhdo, “Auger-mediated electron relaxation is robust to deep hole traps: time-domain ab initio study of CdSe quantum dots”, *Nano Lett.*, **15**, 2086-2091 (2015).
 17. H. Zhu, Y. Yang, K. Hyeon-Deuk, M. Califano, N. Song, Y. Wang, W. Zhang, O. V. Prezhdo, T. Lian, *Nano Lett.*, **14**, 1263 (2014).
 18. K. Hyeon-Deuk, J. Kim, O. V. Prezhdo, “Ab initio analysis of Auger-assisted electron transfer”, *J. Phys. Chem. Lett.*, **6**, 244 (2015).

Spectroscopic studies of the alkaline earth oxides and hypermetallic oxides

M. C. Heaven¹, D. J. Frohman¹, M. N. Sullivan¹, K. J. Mascaritolo¹, A. R. Dermer¹,
M. L. Theis¹, and W. M. Fawzy²

1. Department of Chemistry, Emory University, Atlanta, GA.

2. Department of Chemistry, Murray State University, Murray, KY

Our studies of group IIA oxides have two primary motivations. The first is associated with the potential for creating oxide ions under ultra-cold conditions. The alkaline earth atomic cations can be subjected to efficient laser cooling and captured as Coulomb crystals in radio frequency traps. Metal oxide ions may then be formed under conditions where they are sympathetically cooled by the surrounding atomic ions. Spectroscopic data for the oxide ions are needed for the characterization of internal state population distributions and state manipulations. Initial experiments of this kind have focused on diatomic ions (e.g., BaO⁺, CaO⁺). However, it is also apparent that ultra-cold polyatomic ions may be generated in a similar fashion. The Hudson group at UCLA has preliminary data indicating the formation of CaOBa⁺ in a Coulomb crystal. The neutral MOM hypermetallic oxides are of interest in their own right, having markedly multi-reference singlet ground states. We report electronic spectra and theoretical calculations for BeOBe, MgOMg and CaOCa. These measurements represent the first steps towards characterizing the MOM⁺ cations by means of two-color photoionization spectroscopy.

A second interest is in the ability of the oxides to form stable anions. For example, theoretical predictions for BeO⁻ yield an electron binding energy of 2.15 eV and the existence of two dipole-bound electronically excited states (Gutsev et al. CPL, **276**, 13 (1997)). We have examined these predictions by means of slow electron velocity map imaging spectroscopy. An accurate electron affinity, molecular constants for the anion and the binding energy of the first excited dipole bound state have been determined.

One Step at a Time - Unraveling the Formation of Interstellar Grains under Single Collision Conditions

Ralf I. Kaiser

Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822

ralfk@hawaii.edu

During the last years, the energetics and dynamics of elementary reactions of the simplest silicon-bearing radical, silylidyne (SiH), with hydrocarbons and with molecular oxygen under single collision conditions and the inherent formation of small silicon-bearing molecules have received considerable attention both from the experimental and theoretical viewpoints spanning astrochemistry, physical organic chemistry, and chemical bonding. An understanding of these dynamics is vital to explore the underlying molecular processes involved in the formation of (organo)silicon-bearing molecules in cold molecular clouds and in outflows of circumstellar envelopes of Asymptotic Giant Branch (AGB) stars as these species can act as molecular building blocks of interstellar silicates and silicon-carbide based grains. By merging crossed molecular beams with electronic structure calculations, we present new data on the formation and

structures of small (organo)silicon molecules in extraterrestrial environments. These studies yield a unified picture of the energetics and dynamics of ground state silylidyne radical reactions with prototype hydrocarbon molecules as well as with molecular oxygen and aid in a better understanding how molecular building blocks to interstellar grains are formed from the bottom up in extreme environments. Implications are also discussed how these interstellar grains can catalyze the formation of biorelevant molecules such as amino acids, glycerol, and phosphorus bearing molecules (phosphates, diphosphates) in cold molecular clouds as unraveled experimentally via exposure of interstellar analog ices to ionizing radiation and probing the newly formed molecules via single photo vacuum ultraviolet photoionization coupled with reflectron time of flight mass spectrometry.

R.I. Kaiser, X. Gu, *Chemical Dynamics of the Formation of the Ethynylsilylidyne Radical ($\text{SiCCH}(X^2\Pi)$) in the Crossed Beam Reaction of Ground State Silicon Atoms ($\text{Si}(^3P)$) with Acetylene ($\text{C}_2\text{H}_2(X^1\Sigma_g^+)$)*. Journal of Chemical Physics 131, 104311/1-6 (2009).

T. Yang, B. B. Dangi, P. Maksyutenko, R.I. Kaiser, L.W. Bertels, M. Head-Gordon, *A Combined Experimental and Theoretical Study on the Formation of the Elusive 2-Methyl-1-Silacycloprop-2-enylidene Molecule under Single Collision Conditions via Reaction of the Silylidyne Radical ($\text{SiH}(X^2\Pi)$) with Allene ($\text{H}_2\text{CCCH}_2; X^1A_1$) and D4-Allene ($\text{D}_2\text{CCCD}_2; X^1A_1$)*. J. Phys. Chem. A (Special Issue 50 Years Molecular Dynamics) 119, 12562-12578 (2015).

T. Yang, A.M Thomas, B.B. Dangi, R.I. Kaiser, *Untangling the Reaction Dynamics of the Silylidyne Radical ($\text{SiH}; X^2\Pi$) with Acetylene ($\text{C}_2\text{H}_2; X^1\Sigma_g^+$)*. Chem. Phys. Lett 654, 58-62 (2016).

T. Yang, B. B. Dangi, P. Maksyutenko, R.I. Kaiser, L.W. Bertels, M. Head-Gordon, *Formation of the 2-Methyl-1-Silacycloprop-2-Enylidene Molecule from Crossed Beam Reaction of the Silylidyne Radical ($\text{SiH}; X^2\Pi$) with Methylacetylene ($\text{CH}_3\text{CCH}; X^1A_1$) and D4-Methylacetylene ($\text{CD}_3\text{CCD}; X^1A_1$)*. The Journal of Physical Chemistry A 120, 4872-4883 (2016).

T. Yang, A.M. Thomas, B.B. Dangi, R. I. Kaiser, *Formation of the 2,3-Dimethyl-1-silacycloprop-2-enylidene Molecule via the Crossed Beam Reaction of the Silylidyne Radical ($\text{SiH}; X^2\Pi$) with Dimethylacetylene ($\text{CH}_3\text{CCCH}_3; X^1A_{1g}$)*. The Journal of Physical Chemistry A 120 7262–7268 (2016).

T. Yang, B.B. Dangi, A. Thomas, R.I. Kaiser, *A Combined Crossed Molecular Beam and Ab Initio Study on the First Gas-Phase Synthesis of 1-Silacyclopenta-2,4-diene (Silole; SiC_4H_6)* Angewandte Chemie – International Edition 55, 7983-7987 (2016).

Structures and Bonding in Multimetallic Cluster Anions

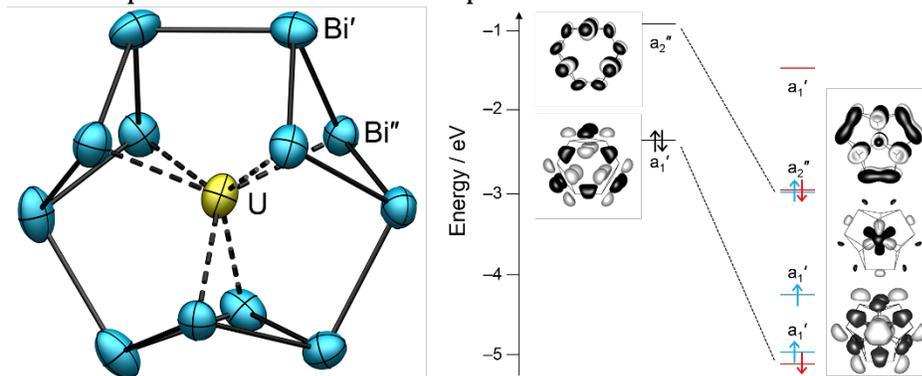
Stefanie Dehnen

Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany.

*dehnen@chemie.uni-marburg.de

Multinary, non-oxidic metallates as well as metallides have been actively investigated by many research groups over the past decades regarding basic properties as well as their potential use as innovative materials.¹ Recently, binary main group element aggregates proved to be useful synthetic tools for multinary transition metal-main group (semi-)metal clusters.²⁻⁴

Reactions of chalcogenidoetrelate ions $[E^{14}_x E^{16}_y]^{q-}$ ($E^{14} = \text{Ge, Sn, Pb}$; $E^{16} = \text{S, Se, Te}$) or the inversely polarized pnictogentriellide/tetrelide ions $[E^{13/14}_x E^{15}_y]^{q-}$ ($E^{13/14} = \text{Ga, In, Tl}$; Ge, Sn, Pb ; $E^{15} = \text{As, Sb, Bi}$) with transition metal (M) compounds lead to the formation of unprecedented cluster anions like $[\text{Rh}_3(\text{CN})_2(\text{PPh}_3)_4(\mu_3\text{-Se})_2(\mu\text{-PbSe})]^{3-}$, $[\text{U}@\text{Bi}_{12}]^{3-}$ (see figure) or $\{[\text{CuSn}_5\text{Sb}_3]^{2-}\}_2$. These exhibit unusual geometric and electronic structures that position them in between electron precise molecules and superatoms.⁵⁻¹⁰



Molecular structure and frontier orbital scheme of the intermetalloid cluster $[\text{U}@\text{Bi}_{12}]^{3-}$.

References:

- [1] P. Feng, X. Bu, N. Zheng, *Acc. Chem. Res.* 2005, 38, 293.
- [2] F. Lips, R. Clérac, S. Dehnen, *J. Am. Chem. Soc.* 2011, 133, 14168.
- [3] S. Santner, J. Heine, S. Dehnen, *Angew. Chem. Int. Ed.* 2016, 54, 886.
- [4] N.W. Rosemann, J.P. Eußner, A. Beyer, S.W. Koch, K. Volz, S. Dehnen, S. Chatterjee, *Science* 2016, 352, 1301.
- [5] B. Weinert, F. Müller, K. Harms, S. Dehnen, *Angew. Chem. Int. Ed.* 2014, 53, 11979.
- [6] G. Thiele, Y. Franzke, F. Weigend, S. Dehnen, *Angew. Chem. Int. Ed.* 2015, 54, 11283.
- [7] S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend, S. Dehnen, *Nat. Commun.* 2016, 7, 10480.
- [8] N. Lichtenberger, R.J. Wilson, A.R. Eulenstein, W. Massa, R. Clérac, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* 2016, 138, 9033.
- [9] R.J. Wilson, L. Broeckaert, F. Spitzer, F. Weigend, S. Dehnen, *Angew. Chem. Int. Ed.* 2016, 55, 11775.
- [10] R. J. Wilson, S. Dehnen, *Angew. Chem. Int. Ed.* 2017, 56, 3098.

Structural and Electronic Properties of Small Vanadium, $V_n^{0,+}$, clusters and of the Hydrated V_nH_2O and $V_n^+H_2O$, $n \leq 13$, Systems

Miguel Castro

Departamento de Física y Química Teórica, DEPg. Facultad de Química, Universidad Nacional Autónoma de México, Del. Coyoacán, México D.F., C.P. 04510, México

By means of density functional theory, BPW91-D2 all-electron calculations with dispersion corrections, the low-lying states of V_n and V_n^+ are studied in this work. The obtained results reveal that dimers motifs, acting as basic building blocks, produce distorted structures for these small clusters. The estimated properties for V_n and V_n^+ agree with experimental results for ionization energies (IE), dissociation energies, and IR spectra. We found that multiple isomers are involved in the spectrum of some V_n^+ ions and that the IEs are reduced considerably by water attachment in the V_n-H_2O systems. Water adsorption on the small vanadium clusters, V_n-H_2O and $V_n^+-H_2O$, $n \leq 13$, is quite important to understanding the features of the metal-solvation process, very difficult to determine experimentally. Through metal-oxygen bonding, V-O, water adsorption takes place on atop sites of the V_n^+ cations. This is confirmed by the results of vibrational analysis, which are in agreement with reported experimental findings, revealing small blue and red shifts of the bending frequency of the adsorbed water molecule. In neutral V_n-H_2O hydrogen bonding also contributes. Remarkably, in V_5-H_2O the metal atom lies in between the O and H atoms, forming agostic bonds, producing activation of the O-H bond: V_n clusters show some catalytic behavior in their interaction with water molecules.

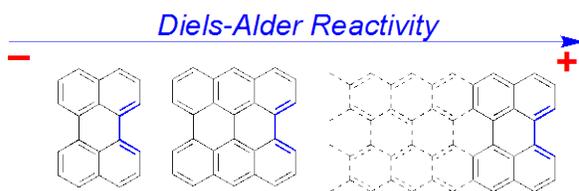
Reactivity and Bonding of Polycyclic Aromatic Hydrocarbons: Shape and Size Dependence

Israel Fernández

Departamento de Química Orgánica I, Facultad de CC. Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain, e-mail: israel@quim.ucm.

The Diels-Alder reactivity and selectivity involving Polycyclic Aromatic Hydrocarbons (PAHs) have been explored computationally within the DFT framework. To this end, the [4+2]-cycloaddition reactions between maleic anhydride and both planar PAHs^[1] and buckybowl^[2] have been studied by means of the Activation Strain Model^[3] (ASM) of reactivity in conjunction with the Energy Decomposition Analysis (EDA) method.

For bowl-shaped PAHs, it was found that there is a smooth convergence to the C_{60} barrier energy if the size of the buckybowl is increased (see Figure).^[5] Similarly, the process involving the bay regions of planar PHAs becomes more and more exothermic and the associated activation barriers become lower and lower when the size of the system increases.^[5] This enhanced reactivity follows an exponential behavior whose maximum can be extrapolated for the analogous process involving graphene. In addition, the influence of the presence of a metallabenzene fragment in the system on the reactivity shall be also discussed.^[6]



References:

- [1] E. H. Fort, P. M. Donovan, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 16006.
- [2] L.T. Scott, *Chem. Soc. Rev.* **2015**, *44*, 6464.
- [3] I. Fernández, F. M. Bickelhaupt, *Chem. Soc. Rev.* **2014**, *43*, 4953.
- [4] Y. García-Rodeja, M. Solà, F. M. Bickelhaupt, I. Fernández, *Chem. Eur. J.* **2016**, *22*, 1368.
- [5] Y. García-Rodeja, M. Solà, I. Fernández, *Chem. Eur. J.* **2016**, *22*, 10572.
- [6] Y. García-Rodeja, I. Fernández, *Chem. Eur. J.* **2017**, doi: 10.1002/chem.201700551.

Bonding Analysis and Synthesis of Borane Complexes

Xuenian Chen

School of Chemistry and Chemical Engineering, Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials, Henan Normal University, Henan, China, 453007

Boron, located in the second period and group 3A in the periodic table, is the only element of this group that can be considered nonmetallic. A family of well-known boron containing compounds is called boranes, which contain only boron and hydrogen. The deficiency in valence electrons is the typical property of such type of compounds that has attracted great attention of researchers. On the other hand, although boron is considered as nonmetallic element, it appears to be positive charge in borane complexes because the electronegativity of boron (2.0) is less than that of hydrogen (2.1). Thus, the hydrogen of boranes is “hydridic” or called hydride, e.g. they carry a partial negative charge which means that the hydride of boranes could show the Lewis base property. Therefore, boranes, such as the simplest borane, BH_3 , could be amphiprotic in terms of inorganic chemistry. It is capable of acting as either a Lewis acid using its empty orbital or a Lewis base using its hydride in different reactions. Boranes could also be described as either electrophiles or nucleophiles in terms of organic chemistry. The Lewis acid property of boranes is well-known, while its Lewis base property is little known. It is the nucleophilic of hydride of boranes that results in interesting reactions. In this topic, we will present several examples of hydride of boranes causing nucleophilic reactions which lead to the formation of new borane complexes.

References:

1. Chen, X.; Zhao, J.-C.; Shore, S. G. *Acc. Chem. Res.* , **2013**, *46*, 2666-2675.
2. Li, H.; Ma, N.; Meng, W.; Gallucci, J.; Qiu, Y.; Li, S.; Zhao, Q.; Zhang, J. Zhao, J.-C.; Chen, X.; *J. Am. Chem. Soc.*, **2015**, *137*, 12406-12414.
3. Chen, X.; Bao, X.; Zhao, J.-C.; Shore, S. G. *J. Am. Chem. Soc.*, **2011**, *133*, 14172-14175.
4. Chen, X.; Zhao, J.-C.; Shore, S. G. *J. Am. Chem. Soc.*, **2010**, *132*, 10658–10659.
5. Chen, X.; Zhang, Y.; Wang, Y.; Zhou, W.; Knight, D. A.; Yisgedu, T. B.; Huang, Z.; Lingam, H. K.; Billet, B.; Udovic, T. J.; Brown, G. M.; Shore, S. G.; Wolverton, C.; Zhao, J.-C. *Chem. Sci.*, **2012**, *3*, 3183-3191.
6. Chen, X.; Gallucci, J.; Campana, C.; Huang, Z.; Lingam, H. K.; Sheldon G. Shore, S. G.; Zhao, J.-C. *Chem. Commun.*, **2012**, *48*, 7943-7945.
7. Chen, X.; Bao, X.; Billet, B.; Shore, S. G.; Zhao, J.-C. *Chem.- Eur. J.* 2012, *18*, 11994 – 11999.

TBA

Marcela Beltran

Universidad Nacional Autonoma de Mexico

Computational Materials Discovery

Artem R. Oganov

Skolkovo Institute of Science and Technology, 5 Nobel St., Moscow 143026, Russia.

Stony Brook University, NY 11794-2100

Recent methods of crystal structure prediction have opened wide opportunities for exploring materials at extreme conditions and perform computational screening for materials with optimal properties for various applications. In my laboratory, we have developed a very powerful evolutionary algorithm USPEX [1,2], enabling prediction of both the stable compounds and their crystal structures at arbitrary conditions, given just the set of chemical elements. Recent developments include major increase of efficiency and extensions to low-dimensional systems and molecular crystals [3] (which allowed large structures to be handled easily, e.g. Mg(BH₄)₂ [4] and H₂O-H₂ [5]) and a new technique called evolutionary metadynamics [6].

Some of the results that I will discuss include:

1. Theoretical and experimental evidence for a new partially ionic phase of boron, γ -B [7] and an insulating and optically transparent form of sodium [8].
2. Predicted stability of “impossible” chemical compounds that become stable under pressure – e.g. Na₃Cl, Na₂Cl, Na₃Cl₂, NaCl₃, NaCl₇ [9], Mg₃O₂ and MgO₂ [10].
3. Novel compounds in the C-H-O, N-H and Mg-Si-O systems, and implications for interiors of giant planets.
4. Novel compounds of helium, stable at experimentally reachable pressures, Na₂He and Na₂HeO [11].
5. Extended techniques (e.g., multiobjective optimization [12]) and their applications to the discovery of novel superhard, thermoelectric etc. materials will be highlighted.

References

- [1] Oganov A.R. et al, *J.Chem.Phys.* **124**, 244704 (2006).
- [2] Lyakhov A.O. et al., *Comp. Phys. Comm.* **184**, 1172-1182 (2013).
- [3] Zhu Q. et al, *Acta Cryst.* **B68**, 215-226 (2012).
- [4] Zhou X.-F. et al, *Phys. Rev. Lett.* **109**, 245503 (2012).
- [5] Qian G.R. et al. *Sci.Rep.* **4**, 5606 (2014).
- [6] Zhu Q. et al, *Cryst.Eng.Comm.* **14**, 3596-3601 (2012).
- [7] Oganov A.R. et al, *Nature* **457**, 863 (2009).
- [8] Ma Y. et al, *Nature* **458**, 182 (2009).
- [9] Zhang W.W. et al, *Science* **342**, 1502-1505 (2013).
- [10] Zhu Q. et al., *Phys. Chem. Chem. Phys.* **15**, 7796-7700 (2013).
- [11] Dong X., et al., *Nature Chemistry*, in press (2017).
- [12] Kvashnin A.G., et al., *J. Phys. Chem. Lett.*, **2017** *8*, 755–764 (2017).

Single Atom Catalysis: A Surface Science Approach

Gareth S. Parkinson

Institute of Applied Physics, TU Vienna, Austria

**parkinson@iap.tuwien.ac.at*

Single atom catalysis is a rapidly emerging but controversial area of catalysis research that aims to maximize the efficient usage of precious metals through the use of single atom active sites [1]. Although catalytic activity has been demonstrated for several single atom catalyst systems, the inability to accurately characterize a catalyst based on single atom active sites ensures that the field remains controversial, and little is really known about how a single atom adsorbed on a metal oxide support can catalyze a chemical reaction. In this lecture, I will describe how we are addressing the crucial issues of stability and reaction mechanism using a surface science approach. The work is based on the magnetite (001) surface, which exhibits an unusual reconstruction based on subsurface cation vacancies [2]. A remarkable property of this reconstruction is that it stabilizes ordered arrays of metal adatoms (of almost any variety) with a nearest neighbor distance of 0.84 nm to temperatures as high as 700 K [3]. Crucially, because the geometry of the adatoms is uniform and precisely known, reactivity experiments are performed on a well-defined model system, and theoretical calculations can be performed to shed light on the mechanisms underlying catalytic activity and deactivation. Several examples of our recent work will be used to illustrate the trends we have discovered to date, including how strong CO adsorption destabilizes Pd and Pt adatoms leading to mobility and rapid sintering [4], and how extraction of lattice oxygen from the metal-oxide is central to catalytic activity in the CO oxidation reaction [5; 6].

- [1] X.-F. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis, *Accounts of Chemical Research* **46** 1740-1748 (2013); 10.1021/ar300361m
- [2] R. Bliem, E. McDermott, P. Ferstl, M. Setvin, O. Gamba, J. Pavelec, M.A. Schneider, M. Schmid,

- U. Diebold, P. Blaha, L. Hammer, G.S. Parkinson, Subsurface cation vacancy stabilization of the magnetite (001) surface, *Science* **346** 1215-1218 (2014); 10.1126/science.1260556
- [3] G.S. Parkinson, Iron oxide surfaces, *Surface Science Reports* **71** 272-365 (2016);
- [4] G.S. Parkinson, Z. Novotny, G. Argentero, M. Schmid, J. Pavelec, R. Kosak, P. Blaha, U. Diebold, Carbon Monoxide-Induced Adatom Sintering in a Pd-Fe₃O₄ Model Catalyst, *Nature Materials* **12** 724-728 (2013); 10.1038/nmat3667
- [5] R. Bliem, J. van der Hoeven, A. Zavodny, O. Gamba, J. Pavelec, P.E. de Jongh, M. Schmid, U. Diebold, G.S. Parkinson, An Atomic-Scale View of CO and H₂ Oxidation on a Pt/Fe₃O₄ Model Catalyst, *Angewandte Chemie International Edition* **54** 13999-14002 (2015); 10.1002/anie.201507368
- [6] R. Bliem, J.E.S. van der Hoeven, J. Hulva, J. Pavelec, O. Gamba, P.E. de Jongh, M. Schmid, P. Blaha, U. Diebold, G.S. Parkinson, Dual role of CO in the stability of subnano Pt clusters at the Fe₃O₄(001) surface, *Proceedings of the National Academy of Sciences* **113** 8921-8926 (2016); 10.1073/pnas.1605649113

Confinement-induced reactivity in zeolite catalysis

R. Rohling,^[a] E. Uslamin,^[a] E. Khramenkova,^[b] E. J. M. Hensen,^[a] E.A. Pidko^{[a,b]*}

^[a]*Inorganic Materials Chemistry, Department of Chemical Engineering & Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*

^[b]*Theoretical Chemistry group, Laboratory of Solution Chemistry for Advance Materials and Technologies, ITMO University, St. Petersburg, Russia*

Non-covalent interactions between the substrate molecules and confining environment of the enzymatic active sites give rise to molecular recognition, binding and catalytic transformations in many biological systems. Billions of years of evolutionary pressure have tailored the enzyme active site environments with functionalities precisely positioned to be complementary to the transition states of the reactions they catalyze.^[1] Typically the molecular recognition of substrates and transition states by enzymatic active sites stems from the concerted action of multiple non-covalent substrate-catalyst interactions that may be individually weak but collectively become very important.^[2] In chemocatalysis, however, conventional mechanistic models and reactivity theories predominantly focus on the so-called single-site rationalization of the catalytic phenomenon. In the respective models, the intrinsic chemistry of the isolated reactive ensemble is thought to be key to the catalytic performance of the overall system. In this lecture, I will discuss how the molecular recognition-type phenomena can become a dominant factor determining the catalytic performance of low-silica zeolite catalysts.

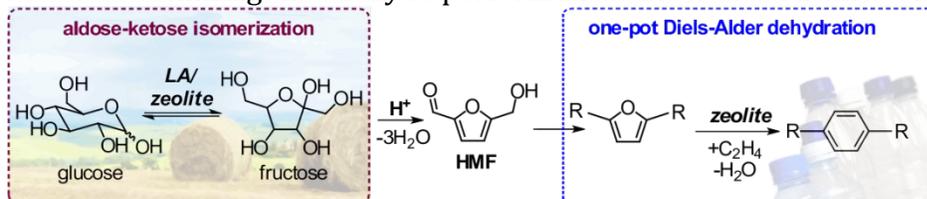


Figure 1. A principle scheme for the conversion of cellulosic biomass to aromatics

As a showcase example, we will discuss a Diels-Alder cycloaddition Dehydration (DAD) reaction of DMF with ethylene over cation-exchanged zeolites to produce bio-aromatic products^[3] (Figure 1). A crucial finding of this study is that the catalytic performance of low-silica zeolites is governed by a concert action of all accessible cationic-sites inside the zeolite micropores. The DAD reactivity does not follow the Lewis acidity trend of the exchangeable cations. For all elementary steps of the DAD process, molecular recognition effects are the main factors that determine the kinetics of the individual transformations. The optimal properties of the confinement space for this reaction are provided by KY zeolite. Catalytic experiments confirm the theoretically predicted reactivity trends.

[1] A.J. Neel, M. J. Hilton, M.S. Sigman, F. Dean Toste, *Nature* **2017**, *543*, 637

[2] S.J. Bencovic, S.A. Hammes-Schiffer, *Science* **2003**, *301*, 1196

[3] J.J. Pacheco, M.E. Davis, *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 8363

Modeling chemical bond at electrochemical interfaces: an approach from first principles

Philippe Sautet ^a, Stephan N. Steinmann^b

a) Department of Chemical and Biomolecular engineering, University of California, Los Angeles, Los Angeles, CA 90095, United States

e-mail: sautet@ucla.edu

*b) Univ Lyon, CNRS, Laboratoire de Chimie, Ecole Normale Supérieure de Lyon
46 allée d'Italie, 69007 Lyon Cedex 07, France*

Electrified interfaces are central for electrocatalysis, batteries and molecular electronics. Experimental characterization of these complex interfaces with atomic resolution is highly challenging. First principles modeling could provide a link between the measurable quantities and an atomic scale understanding. However, such simulations are far from straightforward. Although approaches that include the effect of the potential and the electrolyte have been proposed, detailed validation has been scarce and "indirect" since atomically resolved experimental studies of systems that can be convincingly simulated are scarce.

We will discuss in this lecture how bonding between a molecule and a metal surface is affected by the applied potential. After presenting CO₂ adsorption on Ni and Cu, we introduce in this lecture the adsorption of pyridine on Au(111) as a convenient and relevant model: the adsorption mode of pyridine switches as a function of the electrochemical potential. We demonstrate that the primitive surface-charging model gives qualitatively correct results at a low cost. For quantitative agreement, however, the model needs to include a more realistic description of the electrical double layer. Approximating the latter through the linearized Poisson-Boltzmann equation leads to a quantitative improvement, lowering the error in the transition potential from 1 V to acceptable 0.3 V. The inclusion of the size of cations or anions can be performed through a hybrid QM/MM type calculation. Hence, we demonstrate the qualitative usefulness of the surface charging method, the excellent agreement that can be obtained by

slightly more sophisticated electrolyte models, and the picture provided for the chemical bonding at an electrified interface.

References

- 1) Stephan N. Steinmann and Philippe Sautet “Assessing a First Principles Model of an Electrochemical Interface by Comparison with Experiment”
J. Phys. Chem. C 120, 5619–5623 (2016)
- 2) Stephan N. Steinmann, Carine Michel, Renate Schwiedernoch, Jean-Sebastien Filhol, Philippe Sautet
“Modelling the HCOOH/CO₂ Electrocatalytic Reaction: When Details Are Key
ChemPhysChem 16, 2307 – 2311 (2015)”

Simulations of alloys for catalysis

S. M. Kozlov, Z. Cao, L. Falivene, L. Cavallo

KAUST Catalysis Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

Alloys are widely employed in heterogeneous catalysis because their properties as well as their cost can be easily tuned by the alloy composition. Despite of the constantly increasing interest in the chemistry of alloys, many alloy formulations are still unexplored. Although simulations can greatly accelerate the development of novel alloy catalysts, they remain challenging due to the exceptional structural complexity of alloy particles. Moreover, reliable simulations require the knowledge of the 3D alloy structure with atomic resolution, which is rarely ever available from the experiment. At the same time, obtaining realistic alloy structure from simulations represents a global optimization problem, which can be solved only for systems with <100 atoms.

First, I will introduce a new method to generate realistic models of alloy particles for catalytic studies [1]. This method is based on topologic energy expressions and allows one to obtain realistic structures of alloy nanoparticles with thousands of atoms. This method has been shown to have essentially DFT accuracy for a diverse set of nanoalloys with core-shell (e.g. PtCo), ordered (PdZn), Janus (CuNi) and intermediate (PdCu, PtSn) structures. I will also demonstrate a recent application of this method to simulations of nanoparticles of arbitrary shapes and at arbitrary temperatures [2].

Second, I will discuss how tuning the composition of a nanoalloy may improve its catalytic properties. I will demonstrate this for NiCo alloys, which are able to maintain long term catalytic activity in the dry reforming of methane (DRM) reaction, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$, unlike their monometallic components [3]. Whereas Ni catalyst gets deactivated by coke formation and Co catalyst gets deactivated by oxidation, NiCo alloys balance the amount of surface C and O to remain active.

Finally, I will talk about electrochemical stability of Pt-based alloys [4]. This is a timely topic because high cost of Pt and its gradual leaching under high electrode potentials limit the commercial potential of fuel cell technologies. Although some Pt alloys with inexpensive metals are highly active electrocatalysts (per gram of Pt), these alloys may be also more prone to

leaching. I will present a simple way to evaluate the on-set electrode potential for alloy leaching, discuss the trends for various alloys and identify those with superior electrochemical stability at high electrode potentials.

References

- [1] S.M. Kozlov, G. Kovács, R. Ferrando, K.M. Neyman, How to determine accurate chemical ordering in several nanometer large bimetallic crystallites from electronic structure calculations, *Chem. Sci.* (2015) 3868–3880. doi:10.1039/C4SC03321C.
- [2] G. Kovacs, S.M. Kozlov, K.M. Neyman, Versatile Optimization of Chemical Ordering in Bimetallic Nanoparticles, *J. Phys. Chem. C.* (2017) acs.jpcc.6b11923. doi:10.1021/acs.jpcc.6b11923.
- [3] B. AlSabban, L. Falivene, S. M. Kozlov, A. Aguilar-Tapia, S. Ould-Chikh, J.-L. Hazemann, L. Cavallo, J.-M. Basset, K. Takanabe, In-operando elucidation of bimetallic CoNi nanoparticles during high-temperature CH₄/CO₂ reaction, *under revision*
- [4] S.M. Kozlov, Z. Cao, L. Cavallo, Electrochemical Stability of Pt-based alloys, *in preparation*

The Science and Serendipity behind the Unexpected Discovery of Boron Nitride as Selective Oxidation Catalyst

Prof. Ive Hermans

University of Wisconsin – Madison, USA

The oxidative dehydrogenation of propane (ODHP) as a method of “on-purpose” propylene production has the potential to be a game-changing technology in the chemical industry.¹ However, even after decades of research establishing supported vanadium oxide as the state-of-the-art catalyst for ODHP,^{2,3} selectivity to the olefin product remains too low to be commercially attractive because of facile over-oxidation of propylene into CO and CO₂ (CO_x).

During this presentation I will bring the story of how we discovered that hexagonal boron nitride (h-BN) and boron nitride nanotubes (BNNTs) are highly selective catalysts for the ODHP reaction (see Figure 1).^{4,5} Despite structurally similar materials (graphene and carbon nanotubes) showing catalytic activity for partial oxidations in recent years, BN materials have yet to be explored for their own catalytic activity. Kinetic and spectroscopic insights will be combined with computational predictions to shine light on potential reaction mechanisms.

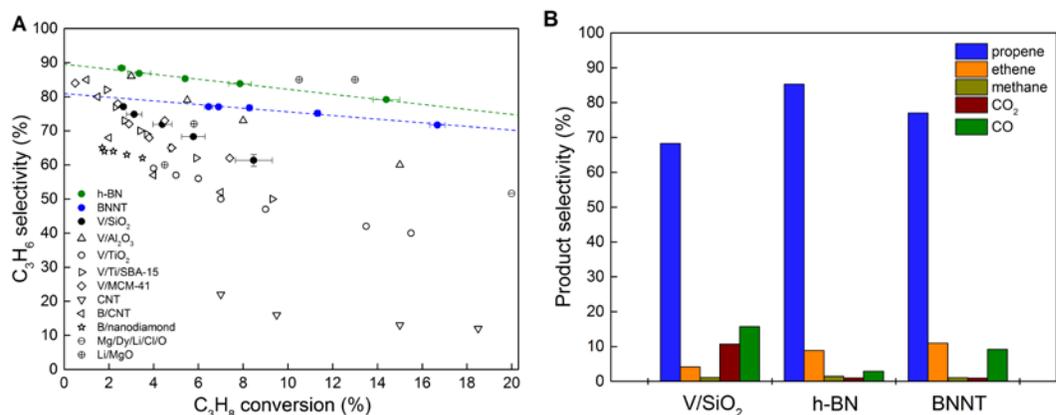


Figure 1. (A) Selectivity to propylene plotted against propane conversion for ODHP, comparing h-BN (green), BNNT (blue) and V/SiO₂ (black) to previously reported catalysts (open shapes); (B) Comparisons of product selectivity between V/SiO₂ ($X_{C_3H_8}$ =5.8%), h-BN ($X_{C_3H_8}$)=5.4%) and BNNTs ($X_{C_3H_8}$ =6.5%). Product selectivities are represented by colored bars.

References

1. T. Degnan, *Focus on Catalysts*, 2 (2016) 1
2. C. Carrero, R. Schlogl, I. Wachs, R. Schomaecker, *ACS Catal.*, 4 (2014) 3357
3. J. Grant, C. Carrero, A. Love, R. Verel, I. Hermans, *ACS Catal.*, 5 (2015) 5787
4. J. Grant, C. Carrero, F. Goeltl, J. Venegas, P. Mueller, S. Burt, S. Specht, W. McDermott, A. Chieragato, I. Hermans, *Science*, 354 (2016) 1570
5. J. Grant, C. Carrero, J. Venegas, A. Chieragato, I. Hermans, US Patent Application 15/260,649.

Beyond structure: on the role of dynamics and entropy in nanocatalysis

Dennis R. Salahub

Department of Chemistry, CMS – Centre for Molecular Simulation, IQST – Institute for Quantum Science and Technology and Quantum Alberta, University of Calgary, Canada

We are attempting to develop a multiscale, multimethodology approach to the modeling of chemical reactions in complex environments. Our main methods are Density Functional Theory (DFT), Density Functional Tight Binding (DFTB), Quantum Mechanical/ Molecular Mechanical (QM/MM) methods for both DFT and DFTB and the ReaxFF reactive force-field. The paradigm for the field is shifting from structure and potential-energy surfaces to dynamics and free-energy.

I will report progress on applications in the areas of nano-catalysis for oil sands upgrading.

Nano-catalysis for oil sands upgrading: We have recently completed the first multiscale study of the hydrogenation of benzene by molybdenum carbide nanoparticles in a hydrocarbon MM environment including the important anharmonic entropic effects that contribute greatly to the free-energy profile. We have recently embarked on a similar exploration of Ni-ceria catalysts for

the water gas shift reaction. To date we have performed periodic DFT (VASP) calculations for the three important (100), (111) and (110) surfaces of ceria with Ni present either as an adsorbate or as a substitutional dopant. The behavior of oxygen vacancies in relation to the formation of Ce^{3+} has been elucidated. These DFT calculations will eventually be used in the parameterization of DFTB. I will report progress.

TBA

Xuemin Yang

Institute of Chemical Physics, Chinese Academy of Science, China

Infrared Spectroscopy of Donor-Acceptor Bonding Carbonyl Complexes

Mingfei Zhou

Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China. E-mail: mfzhou@fudan.edu.cn

Carbon monoxide is one of the most important ligand in inorganic and organometallic chemistry. It can bind to a host of neutral and charged transition metal as well as main group metal centers in forming diverse metal carbonyl complexes. The bonding interactions between carbon monoxide and metal center can be described using the Dewar–Chatt–Duncanson model, which involves σ donation from the carbon lone-pair 5σ orbital to the metal and concomitant π back-donation of electron density from the metal $d(p)$ orbitals into the $2\pi^*$ antibonding orbitals of CO. This talk will present our recent results on the preparation of a number of neutral and charged metal carbonyl complexes either in gas phase or in solid noble gas matrices, which are studied using infrared photodissociation spectroscopy and matrix isolation infrared absorption spectroscopy. Vibrational spectroscopic combined with state-of-the-art quantum chemical calculations unveiled unusual structure and bonding properties of these complexes.

CONJUGATION AND AROMATICITY IN LARGE CIRCUITS

E. Matito,^{abc} I. Casademont,^{ab} E. Ramos-Cordoba,^{abd} M. Torrent-Sucarrat,^{abce}

^a*Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), Donostia, Euskadi (Spain).*

^b*Donostia International Phys. Center (DIPC), Donostia, Euskadi (Spain).*

^d*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Euskadi, (Spain).*

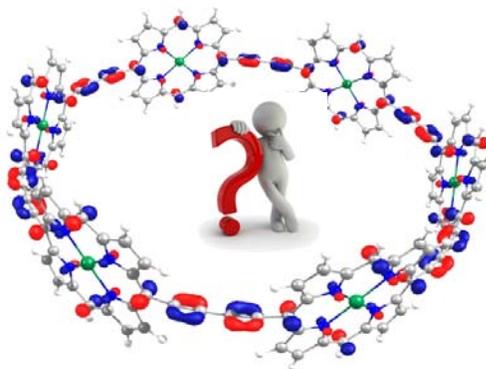
^e*Kenneth S. Pitzer Center for Theor. Chem., Univ. Cal. Berkeley, SFO (USA).*

^e*Organic Chem. Dep., Centro de Innovación en Química Avanzada (ORFEO-CINQA), Donostia, Euskadi (Spain).*

e-mail:ematito@gmail.com

We introduce a new electronic aromaticity index, AV1245,¹ consisting of an average of the 4-center multicenter indices (MCI) along the ring. AV1245 measures the extent of transferability of the delocalized electrons between bonds 1–2 and 4–5, which is expected to be large in conjugated circuits and, therefore, in aromatic molecules. AV1245 is a size-extensive measure carrying a low computational cost that grows linearly with the number of ring members; it does not rely on reference values and it does not present limitations concerning the nature of the atoms. Unlike current multicenter delocalization indices,² AV1245 is especially suited to study the conjugation in large circuits such as those occurring in expanded porphyrins or polymeric chains.

In this talk we present the index and a few applications, including the study of a six-porphyrin nanoring template complex in various oxidation states.³ AV1245 permits to understand the local and global changes of aromaticity occurring in the complex upon oxidation.



References:

1. Matito E., *Phys. Chem. Chem. Phys.*, **18**, 11839 (2016).
2. Feixas F., Matito E., Poater J., Solà M., *Chem. Soc. Rev.* 44, 6434 (2015)
3. Peeks M.D., Claridge T.D.W., Anderson H.L., *Nature* 541, 200 (2017)

Superatomic Molecule Theory of Metal Clusters

Jinlong Yang

Hefei National Laboratory for Physics Sciences at Microscale, University of Science & Technology of China, Hefei, Anhui, 230026, People's Republic of China

jlyang@ustc.edu.cn

[Http://staff.ustc.edu.cn/~jlyang](http://staff.ustc.edu.cn/~jlyang)

In cluster science, the concept of superatom is a major finding and has been widely explored. In this talk, we extend superatoms to superatomic molecules. We introduce a new concept of super valence bond, of which superatoms can share both valence pairs and nuclei for shell closure thus forming delocalized super bonding. Using Li clusters as a test case, we theoretically find that metal clusters can mimic the behavior of simple molecules in electronic shells. It is found that Li₁₄, Li₁₀, and Li₈ clusters are analogues of F₂, N₂, and CH₄ molecules, respectively, in

molecular orbital diagrams and bonding patterns. Using this concept, we explain the stability of some thiolate-protected gold clusters and construct the diamond-like Au cluster crystal. This new concept shows new insights in understanding the stability of clusters and designing the cluster-assembling materials.

(Unusual) hypervalence

Maarten Goesten
Cornell University, USA

Hypervalence is perhaps as old as the octet rule, and throughout the decades, theory has taken different paths to think of it. There appears room for a semantic discussion on hypervalence. And in this lecture, we make an attempt. We discuss the bonding traits that we associate with hypervalence, and how those translate to trends in the Periodic Table. But predominantly, we investigate the borders of our thinking on hypervalence. There, we discuss three case studies: (i) six-coordinate group 13 complexes, (ii) fluoride in a silicate double-4-ring, and (iii) a $[\text{CsO}_4]^+$ cation.

Chemical Evolution in Structured Environments

Dmitry Zubarev
IBM Research, Almaden, USA

In this talk I will discuss two facets of the computational reconstruction of prebiological reaction networks. One is prediction/educated guessing of the missing parts of reaction networks informed by the observed reactions. The other is constraints imposed by the structured environments hosting reaction networks on the outcomes of chemical reactions. Reaction network proposed by John Sutherland will be our sand box.

One-electron images in real space: Natural adaptive orbitals

Ángel Martín Pendás and Evelio Francisco
Dpto. Química Física y Analítica. Universidad de Oviedo. Spain
angel@fluor.quimica.uniovi.es

We introduce a general procedure to construct a set of effective one-electron functions in chemical bonding theory which remain physically sound both for correlated and non-correlated electronic structure descriptions and that are able to capture inter-particle correlations beyond

the first-order density matrix. These functions, which we call natural adaptive orbitals (NAOs) [1,2], decompose the n-center bonding indices used in real space theories of the chemical bond into one-electron contributions. For the n=1 case, they coincide with the domain natural orbitals [3] used in the domain-averaged Fermi hole analysis introduced by R. Ponec. We examine their interpretation in the two-center case, and show how they behave and evolve in simple cases. Orbital pictures obtained through this technique converge onto the chemist's molecular orbital toolbox if electron correlation may be ignored, and provide new insight if it may not. Natural adaptive orbitals are endowed with unique features, providing both qualitative and quantitative images of chemical bonding when electron correlation plays a significant role. An application to the conundrum of bonding in the dicarbon molecule is also offered.

- [1] E. Francisco, A. Martín Pendás, M. García-Revilla, R. Álvarez Boto. *Comput. Theor. Chem.* **1003** (2013) 71
- [2] M. Menéndez, R. Álvarez Boto, E. Francisco, A. Martín Pendás. *J. Comput. Chem.* 10.1002/jcc.23861 (2015)
- [3] R. Ponec. *J. Math. Chem.* **21** (1997) 323

Computational Study of the Formation of Prebiotic Molecules in Astrophysical Environments: Mixed Ices and Gas-Phase Conditions

Timothy J. Lee

Space Science and Astrobiology Division, NASA Ames Research Center

In recent years, our group has studied the formation mechanisms of the various RNA and DNA bases (Uracil, Cytosine, Thymine, Guanine, and Adenine) in mixed water ices seeded with either pyrimidine or purine and irradiated under astrophysical conditions. Our computational studies have been used to interpret the results from laboratory experimental studies to help explain which bases are found, what other products are synthesized, and their relative abundances. One interesting conclusion from our work is that only condensed-phase formation mechanisms are found to be feasible with these multistep reaction mechanisms. We will describe our latest research in this series of studies and discuss what our results may mean for the origins of life studies. Our group has also been actively studying the formation of larger ringed organic compounds starting from small C₂ organic species in the gas-phase, as occurs in the outflow of carbon stars or in the interstellar medium. Most of these studies have also been performed in collaboration with laboratory experiments. We will also discuss the latest from our group for this series of studies.

TBA

Cherif Matta

Mount Saint Vincent University, Canada

Generation, Reactivity Patterns, and Bonding in Singlet Phosphinidenes

Christopher C. Cummins

MIT, USA

The parent phosphinidene molecule, PH, has an electron count of six at phosphorus and a triplet ground state. This reactive intermediate is thus a phosphorus analog of methylene, CH₂, and it should be remembered that phosphorus has similar electronegativity to that of carbon, with which it shares a diagonal relationship, and has thus been called “the carbon copy”. Carbenes have been stabilized famously in the singlet state by placing pi-donor substituents adjacent to the otherwise electron-deficient carbon center, creating the class of molecules now referred to as N-heterocyclic carbenes, NHCs. A similar approach can be taken in order to stabilize the singlet state of phosphinidenes, and this is an actively emerging area of research. Bertrand has reported on the synthesis and reactivity patterns of an isolable phosphinophosphinidene encaged by sterically demanding organic residues, and we are working on the thermal generation of aminophosphinidenes using a new class of anthracene-based molecular precursors. I will report on our progress directed at phosphinidene transfer to metal complexes and to unactivated olefins, as well as on our current best understanding of electronic structure and chemical bonding in these systems.

Bonding, localization vs. delocalization, and molecular properties

Jochen Autschbach

University at Buffalo, SUNY, USA

Some molecular properties depend very strongly on the extent of delocalized bonding. For example, linear and non-linear optical properties of organic pi chromophores may be sensitive to the extent of pi delocalization. For the purpose of this talk, covalent ligand to metal donation bonding is also considered as a form of delocalization (namely of a ligand lone pair). In Kohn-Sham DFT calculations, the extent of delocalization may depend greatly on the functional parametrization. We will present selected cases for which the Kohn-Sham delocalization error has been quantified and related to the extent of delocalization in organic pi systems and metal complexes. An over- or underestimation of the extent of delocalization can have dramatic effects on molecular optical and spectroscopic properties. We will also briefly discuss metal - ligand covalency in lanthanide complexes and spin-orbit effects on actinide-ligand bonds.

Probing the structure and solvation of catalytic reaction intermediates

Etienne Garand

Department of Chemistry, University of Wisconsin-Madison, USA

Understanding reaction pathways and mechanisms is vitally important for the rational design of catalysts. Towards that end, we developed a method based on a unique combination of

mass spectrometry and cryogenic ion vibrational spectroscopy to capture and characterize the reaction complexes formed during homogeneous catalytic processes. In our approach, an in-line electrochemical flow cell is incorporated into an electrospray ionization source, thereby allowing us to controllably form, and mass spectrometrically isolate, the product of each catalytic step. Moreover, the structures of these isolated ions can be directly probed in detail using infrared predissociation spectroscopy. In addition to experimental considerations, this talk will present the application of our approach to model systems as well as to the study of homogeneous catalytic water oxidation by the single metal center $[\text{Ru}(\text{tpy})(\text{bpy})(\text{H}_2\text{O})]^{2+}$ complex. This talk will also present recent technical developments that gave us the capability to perform controlled gas-phase chemistry and clustering in a separate temperature controlled ion trap. This allows us to access unstable reactive species via controlled ion-molecule reactions as well as microsolvated complexes.

Organolanthanide Radicals Formed by Metal-Mediated Bond Activation of Small Hydrocarbons

Dong-Sheng Yang

Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055 USA

Hydrocarbon compounds are the most abundant, low-cost stock for functionalized organic chemicals. Because of their chemical inertness, the transformation of the hydrocarbons to value-added products requires the activation of thermodynamically stable carbon-hydrogen and carbon-carbon bonds. Metal-mediated bond activation circumvents this problem by stimulating the inert hydrocarbons to react with other molecules. Organometallic radicals formed in the entrance channel and subsequent steps are transient and reactive and play essential roles in such activation reactions. In our work, metal-hydrocarbon reactions are carried out in a pulsed supersonic molecular beam source, and reaction intermediates and products are identified by time-of-flight mass spectrometry and investigated by mass-analyzed threshold ionization spectroscopy and quantum chemical calculations. In this talk, we will discuss lanthanide-hydrocarbon radicals formed by metal association and insertion, dehydrogenation, carbon-carbon bond breakage and coupling of small alkanes, alkenes, and alkynes. The discussion will include the bonding and structures, electronic states and energies, and formation mechanisms of the organolanthanide radicals.

TBA

Angela Wilson

Michigan State University, USA

Covelency in Actinide-Ligand Bonds

Ping Yang, Enrique R. Batista, Stosh A. Kozimor
Los Alamos National Laboratory, Los Alamos, New Mexico, 87545
Email: pyang@lanl.gov

The complicated electronic structure of actinide complexes leads to their versatility of chemical reactivity, spectral and magnetic properties, and dynamical behaviors. As the largest domestic source of low-carbon electricity, nuclear energy represents a critical tool available to meet the demand of increasing energy supply and reducing green house gas emission. It is instrumental to develop more efficient strategies for selective separation so as to allow for the reduction of the need for long-term waste storage. We will show that computational chemistry modeling can be used as an effective tool to provide a first-principle description yielding insight into these spectroscopic and dynamical properties of actinide complexes. We will discuss actinide-ligand bonding across the series and the excitation of ligand based core electrons using time-dependent density functional theory. The simulated spectra are found in good agreement with the high-quality direct experimental probing of the bonding using K-edge X-ray Absorption Spectroscopy, lending support to the computational description of chemical bonding.

- [1] ME Fieser, MG Ferrier, J Su, ER Batista, SK Cary, JW Engle, WJ Evans, JS Lezama Pacheco, SA Kozimor, AC Olson, AJ Ryan, BW Stein, GL Wagner, DH Woen, T Vitova, P Yang, *Chem Sci*. In Press. (2017)
- [2] M. Sturzbecher-Hoehne, P Yang, A D'Aléo, RJ Abergel, *Dalton Transactions*, **45**, 9912-9919 (2016)
- [3] ER Batista, RL Martin, P Yang, *Computational Methods in Lanthanide and Actinide Chemistry*, 375-400 (2015)
- [4] SG Minasian, JM Keith, ER Batista, KS Boland, JA Bradley, SR Daly, KA Kozimor, WW Lukens, RL Martin, D Nordlund, GT Seidler, DK Shuh, D Sokaras, T Tylliszczak, GL Wagner, TC Weng, P Yang, *J. Am. Chem. Soc.* **135**, 1864-1871 (2013)
- [5] LP Spencer, P Yang, SG Minasian, RE Jilek, ER Batista, KS Boland, JM Boncella, SD Conradson, DL Clark, TW Hayton, SA Kozimor, RL Martin, MM MacInnes, AC Olsen, BL Scott, DK Shuh, MP Wilkerson, *J. Am. Chem. Soc.* **135**, 2279-2290 (2013)
- [6] SG Minasian, JM Keith, ER Batista, KS Boland, DL Clark, SD Conradson, KA Kozimor, RL Martin, DE Schwartz, DK Shuh, GL Wagner, MP Wilkerson, LE Wolfsberg, P Yang *J. Am. Chem. Soc.* **134**, 5586-5597 (2012)

TBA

Anne Andrews
University of California, Los Angeles, USA

Zintl Phases with Rare-Earth Elements

Svilen Bobev

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA

bobev@udel.edu

Zintl phases are compounds of the alkali or alkaline-earth metals and the early post-transition elements. The electropositive metals are the “cations” and they donate their valence electrons to the electronegative elements from groups 13, 14 and 15, which in turn, form covalent bonds to form the anionic building blocks of the resultant structure. The electron transfer is typically considered to be “complete”, and all constituent atoms should attain closed-shell configurations. Many known solid-state compounds with a general formula $AE_{14}MPn_{11}$ (AE = alkaline-earth metal, Eu, and Yb; M = Group 13 elements Al–In, and Pn = Group 15 elements P–Bi) are Zintl phases. Using the archetype $Ca_{14}AlSb_{11}$ as an example, this relatively complicated formula (and bonding arrangement), achieves perfect charge-balance per the Zintl concept as follows: 14 Ca^{2+} cations, 4 isolated Sb^{3-} ions, one $[AlSb_4]^{9-}$ tetrahedron, and a $[Sb_3]^{7-}$ linear anion. Surprisingly, the trivalent Al in this structure can be replaced by Mn, which is nominally stabilized as Mn(II), i.e., a $3d^5$ ion. In fact, there are a number of manganese-bearing analogues already known, namely $AE_{14}MnPn_{11}$. While initially the latter compounds were believed to be isotopic and *isoelectronic* to $Ca_{14}AlSb_{11}$, subsequent studies showed them to exhibit metal-like electrical conductivities. These findings are in contrast with the expected semiconducting behavior predicted by the Zintl concept, raising doubts over the applicability of the simple rules for electron counting in the cited examples. Apparently, $AE_{14}MnPn_{11}$ are *not* valence precise compounds.

Our prior work on related compounds has shown that charge balancing issues also exist for $AE_{14}MPn_{11}$ (M = Zn and Cd), where the d^{10} metal atoms are clearly divalent. The structure in question must be very flexible and could be modulated in a variety of ways, via substitutions of both cations and anions. For example, the seemingly trivial substitution of Al^{3+} at the Mn site in $Yb_{14}Mn_{1-x}Al_xSb_{11}$, or via substitution of trivalent RE^{3+} cations (RE = rare-earth metals) in $Yb_{14-x}RE_xMnSb_{11}$, both cases of electron doping, leads to a marked decrease in the hole carrier concentration. In the current study, replacement of one AE^{2+} by one RE^{3+} ion is used to make intrinsic semiconductors. The report will focus on the syntheses, structures, and physical properties of rare-earth metal substituted series $Ca_{14-x}RE_xMnPn_{11}$ (RE = La–Nd, Sm, Gd–Dy; $x \approx 1$, Pn = Sb or Bi), demonstrating that the facile exchange of trivalent RE^{3+} for Ca^{2+} . These results indicate that the electronic transport properties can be continuously varied, hence, these materials could be of relevance to the development of new thermoelectrics.

Theoretical Predictions of Superconducting Hydrides Under Pressure

Eve Zurek

Department of Chemistry, University at Buffalo, SUNY, 331 NSC, Buffalo, NY 14260, USA

The pressure variable opens the door towards the synthesis of materials with unique properties, ie. superconductivity, hydrogen storage media, high-energy density and superhard materials, to name a few. Under pressure elements that would not normally combine may form stable compounds or may mix in novel proportions. As a result, we cannot use our chemical intuition developed at 1 atm to predict phases that become stable when they are compressed. To enable our search for novel BCS-type superconductors that can be synthesized under pressure we have developed *XtalOpt*, an open-source evolutionary algorithm for crystal structure prediction. *XtalOpt* has been employed to find the most stable structures of hydrides with unique stoichiometries that are superconducting under pressure. Herein, we describe our predictions of the hydrides of phosphorus, scandium and uranium at pressures that can be achieved in diamond anvil cells. The electronic structure and bonding of the predicted phases is analysed by detailed first-principles calculations.

Accessing metastable states with pressure: synthetic pathways to new materials with exceptional properties

Timothy A. Strobel,

Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, USA

E-mail: tstrobel@ciw.edu

Multiple allotropes and/or chemical compounds can be formed under various pressure / temperature conditions, and some of these could remain metastable under standard conditions for time scales as long as the age of the universe (in fact it is estimated that 50% of all known inorganic compounds are metastable ones!). But the number of known allotropes/compounds pales in comparison with the number of hypothetical ones with energetic feasibility. For any given thermodynamic state, thousands of energetically competitive structures are plausible, a subset of which will exhibit mechanical stability. Further subsets of these structures offer enticing physical properties that differ from those of thermodynamic ground states. Here, we delineate thermodynamic and kinetic synthesis methods (with an emphasis on high pressure) and discuss strategies and examples for accessing these states experimentally. We discuss the successful experimental realization of new forms of silicon and carbon and present developments in computational pathway prediction tools to guide synthetic efforts.

Intramolecular Interactions from X-ray Diffraction Data as a Tool of Understanding Crystal Properties

Tatiana Timofeeva,¹ Boris Averkiev,¹ Victor Khrustalev,² Konstantin Lyssenko²

¹*Department of Chemistry, New Mexico Highlands University, Las Vegas, NM, USA*

²*Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*

Many properties of molecular crystalline materials are defined by the molecular packing in crystals, which, in its turn, is defined by how these molecules interact with each other. This concept will be applied for several phenomena such as formation of different polymorphs of organic materials, formation of high density materials, and formation of acentric crystalline materials. Investigation of intermolecular interactions is based on high-resolution low temperature X-ray diffraction data and quantum chemical computations to analyze the electron density distribution in the areas of interactions and hydrogen bonds, and its interpretation in the framework of Bader's Atoms in Molecule (AIM) theory. As an example of formation of acentric crystal, an organic nonlinear optical (NLO) materials tosylate salt of N,N-dimethylamino-N'-methylstilbazolium (DAST) will be considered to demonstrate how NLO properties of this material are connected with its crystal structure organization. Two furazan derivatives will be presented as examples of molecular organization in crystals of high-density organic materials. Molecular packing in organic of polymorphs will be discussed on examples of several pharmaceutical materials.

Chemistry in Dense Solid Mixtures

Choong-Shik Yoo

Department of Chemistry and Institute for Shock Physics, Washington State University, Pullman, Washington 99164

The application of compression energy comparable to that of chemical bonds, but substantially greater than those of defects and grain boundaries in solids allows us to pursue novel concepts of high-pressure chemistry (or barochemistry) in materials development by design. At such extreme pressures, simple molecular solids covert into densely packed extended network structures that can be predicted from first principles. In recent years, a significant number of new materials and novel extended structures have been designed and discovered in highly compressed states of the first- and second- row elemental solids, including Li, C, H₂, N₂, O₂, CO, CO₂, and H₂O. These extended solids are extremely hard, have high energy density, and exhibit novel electronic and nonlinear optical properties that are superior to other known materials at ambient conditions. However, these materials are often formed at formidable pressures and are highly metastable at ambient conditions; only a few systems have been recovered, limiting the materials within a realm of fundamental scientific discoveries. Therefore, an exciting new research area has emerged on the barochemistry to understand and, ultimately, control the stability, bonding, structure, and properties of low Z extended solids. In this paper, we will present our recent research to develop hybrid low Z extended solids amenable to scale up synthesis and ambient stabilization, utilizing kinetically controlled processes in dense solid mixtures and discuss the governing fundamental principles of barochemistry.

* This work was performed in support of the NSF (*DMR-1203834*), DTRA (*HDTRA1-12-01-0020*), and DARPA (*W31P4Q-12-1-0009*).

Chemical bonding in two-dimensional crystals

Yu Jing, Agnieszka Kuc, Yandong Ma, Thomas Heine*

Wilhelm-Ostwald-Institute of Physical and Theoretical Chemistry, Leipzig University, 04316 Leipzig, Germany

Email: thomas.heine@uni-leipzig.de

Research on two-dimensional crystals (2DC) has skyrocketed since the discovery of graphene and its extraordinary properties. Soon after, it has been shown that virtually any layered material can be exfoliated to its monolayer form, and even more 2DC can be produced by on-surface synthesis. Strong quantum confinement is inherent in many 2DC. Creation of the Dirac point in graphene, the change from indirect to direct band gap in MoS₂ and other Group 6 transition metal dichalcogenides (TMDC) and the appearance of giant spin orbit splitting in Group 6 TMDC are striking examples from the literature.

In my talk I will extend this line of examples to systems that undergo semiconductor-metal transitions upon change of the number of layers. I will further rationalize the nature of interlayer interaction in these systems, showing that they indeed base on quantum confinement. Some new, unexpected 2DC based on natural minerals (covellite), on arsenic-type layered compounds (GeP₃) and on chalcophosphides will be discussed.

Finally, I will discuss on the interplay of magnetism and topological states and the lattice type in 2DC. I will show how topological states (Group 6 TMDC) and diamagnetism (Group 5 TMDC) can be turned on and off by a simple Stone-Wales-like geometrical transformation, and show that topological states in 2DC are not restricted to honeycomb lattices, but are also possible, for example, in penrose-tile crystals.

TBA

Dylan Jayatilaka

University of Western Australia, Australia

Long-Bonding Interaction Between Two Radicals as a Source of Novel Molecules

Marat R. Talipov

Department of Chemistry & Biochemistry, New Mexico State University, USA

Discovery and spectroscopic characterization of novel few-atomic molecular species is of essential importance for the fields of astrochemistry and atmospheric chemistry. Furthermore, some of the small molecules such as nitric oxide (NO), nitroxyl (HNO), nitrosothiol (HSNO) have been recognized as being important for biochemical processes. At the same time, it is well

possible that many other potentially important molecules have not been yet discovered simply because it is difficult to predict their existence based on the current theories of chemical bonding. For example, we recently investigated the mechanism of interaction of triplet diatomic nitrene HN with molecular oxygen and found that one of its intermediates, singlet HO—ON, could exist as a stable molecule even though its O—O bond is rather long (1.9 Å) and weak (~8 kcal/mol) [1,2]. We believe that the newly discovered (both theoretically [2] and experimentally [3]) HO—ON represents the first example of molecules that could exist due to a unique ‘long-bonding’ type of chemical bonding where two radical-bearing atoms are separated by a lone pair-bearing atom. Thus, one could envision the existence of other (yet undiscovered) molecular species in which two radical moieties are bound together by a similar bonding pattern. This talk will address the problems of electronic structure, thermodynamic stability, and reactivity of such molecular species.

Relevant publications:

- 1) M. R. Talipov, S. L. Khursan, R. L. Safiullin, “RRKM and *ab initio* investigation of the NH (X) oxidation by dioxygen”; *J. Phys. Chem. A*, **2009**, *113*, 6468.
- 2) M. R. Talipov, Q. K. Timerghazin, R. L. Safiullin, S. L. Khursan, “No Longer a Complex, Not Yet a Molecule: A Challenging Case of Nitrosyl O-Hydroxide, HOON”; *J. Phys. Chem. A*, **2013**, *117*, 679.
- 3) K. N. Crabtree, M. R. Talipov, O. Martinez, Jr., G. D. O’Connor, S. L. Khursan, M. C. McCarthy “Detection and Structure of HOON: Microwave Spectroscopy Reveals an O—O Bond Exceeding 1.9 Å”; *Science*, **2013**, *342*, 1354.

The Brightest of Vibrational Transitions: Proton-Bound Complexes

Ryan C. Fortenberry

Department of Chemistry and Biochemistry, Georgia Southern University

The search for new molecules in space has stagnated in many regards. 2016 reported one and only one new molecular detection with only a handful of detections in 2015. With ALMA online, the number of rotational lines observed has only increased but potentially served to inundate rotational analyses of molecular detection. However, the upcoming launch of JWST and the presence of SOFIA mean that novel molecular detections may be additionally-served by infrared (IR) observations of molecular vibrations. The brightest of vibrational transitions originate with proton-bound complexes. When a single proton has two ligands, the resulting vibrational frequency of the proton shuttling back and forth between the two displaces nearly all of the molecular charge while very little of the mass moves. Consequently, significant intensities arise from these vibrational motions implying that only relatively small column densities are required for observable transitions. Our work has shown that such transitions can be found from the far-IR even unto the near-IR and everywhere in between depending upon the ligands. Ligands thus far explored include nitrogen molecules, carbon monoxide, and even noble gas atoms. The methods employed have previously produced vibrational frequencies to within 1 cm⁻¹ of experiment in many cases. Finally, proton-bound complexes may be key reservoirs of carbon and

nitrogen in protoplanetary disks and may also be another byproduct of interstellar H_3^+ chemistry.

Homocatenation

Alexander I. Boldyrev

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah, USA

Homocatenation is an ability of atoms to form long chains. Carbon is the most famous element capable of forming extended $\text{C}_n\text{H}_{2n+2}$ chains. Other Group 14 congeners also form chains, though not as long as carbon due to the decreasing homonuclear sigma bond enthalpies. It has been shown before that atoms by acquiring an extra electron form compounds, which have geometric and electronic structures of neighboring atoms.¹ Using this concept, which has been called an electronic transmutation, we explored a possibility of homocatenation of elements from Groups 13 and 15. We have shown that boron avoids homocatenation in the B_nH_{n+2} chains.² We have also tested this concept on the example of $\text{Li}_n\text{B}_n\text{H}_{2n+2}$ species, which were expected to form stable $\text{C}_n\text{H}_{2n+2}$ like-chains. Using the Coalescence-Kick (CK) method, we found that indeed, the global minimum structures of the $\text{Li}_2\text{B}_2\text{H}_6$ and $\text{Li}_3\text{B}_3\text{H}_8$ clusters have the ethane-like $\text{B}_2\text{H}_6^{2-}$ and propane-like $\text{B}_3\text{H}_8^{3-}$ cores, respectively.¹ In a similar manner, we have further tested if we can “transmutate” Al^- into Si. The CK searches revealed that the $\text{Li}_2\text{Al}_2\text{H}_6$ and $\text{Li}_3\text{Al}_3\text{H}_8$ molecules have the ethane-like $\text{Al}_2\text{H}_6^{2-}$ and propane-like $\text{Al}_3\text{H}_8^{3-}$ cores, respectively.³ This prediction was subsequently confirmed experimentally by the Bowen group⁴ in the example of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ anion, produced in a molecular beam. Theoretical results confirmed that the global minimum structure of the $\text{Li}_2\text{Al}_3\text{H}_8^-$ anion adopts the propane-like $\text{Al}_3\text{H}_8^{3-}$ core. Importantly, Jones and co-workers have recently reported the synthesis of the solid-state compound containing the ethane-like $\text{Al}_2\text{H}_6^{2-}$ core.⁵ We have also probed the viability of this concept in the example of phosphorous. We have found that Li_5P_5 , Li_6P_6 , and Li_7P_7 clusters adopt double helix geometrical structures. Further extension of these clusters to an infinite LiP chain was found to preserve the double helix structure.⁶ Thus, we have confirmed that the P^- chain does mimic sulfur structure under high pressure. Nilges and co-workers⁷ have recently reported a synthesis of the first inorganic double helix compound composed of two helical chains: P^- helix and SnI^+ helix. Few other results, which are still in progress, will also be discussed.

1. J. K. Olson, A. I. Boldyrev, *Chem. Phys. Lett.*, 2012, 523, 83.
2. E. Osorio, J. K. Olson, W. Tiznado, A. I. Boldyrev, *Chem. Eur. J.*, 2012, 18, 9677.
3. J. T. Gish, I. A. Popov, A. I. Boldyrev, *Chem. Eur. J.*, 2015, 21, 5307.
4. I. A. Popov, X. Zhang, B. W. Eichhorn, A. I. Boldyrev, K. H. Bowen, *Phys. Chem. Chem. Phys.*, 2015, 17, 26079.
5. S. J. Bonyhady, N. Holzmann, G. Frenking, A. Stasch, C. Jones, *Angew. Chem. Int. Ed.* 2016, 10.1002/anie.201610601.
6. A. S. Ivanov, A. J. Morris, K. V. Bozhenko, C. J. Pickard, A. I. Boldyrev, *Angew. Chem. Int. Ed.*, 2012, 51, 33, 8330.
7. D. Pfister, K. Schäfer, C. Ott, B. Gerke, R. Pöttgen, O. Janka, M. Baumgartner, A. Efimova, A. Hohmann, P. Schmidt, S. Venkatachalam, L. van Wüllen, U. Schürmann, L. Kienle, V. Duppel, E. Parzinger, B. Miller, J. Becker, A. Holleitner, R. Wehrich, T. Nilges, *Adv. Mater.* 2016, 28, 9783.