INTERNATIONAL BUNSEN DISCUSSION MEETING



Gas Phase Model Systems for Catalysis

June 18-20, 2018 Ulm/Germany

International Bunsen Discussion Meeting



Gas Phase Model Systems for Catalysis – GPMC 2018

June 18 –20, 2018 in Ulm/Germany

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Following up to the very successful first GPMC conference held in April 2014 we meet now for the second time to discuss catalytic model systems in the gas phase. The previous GPMC conference in 2014 offered for the first time a platform to report and discuss in a focused way research on defined catalytic models employing gas phase techniques. We are convinced that the research area is developing fast and in interesting new directions. This follow up meeting GPMC 2018 thus aims at reflecting this development during the past four years and at discussing new perspectives.

The subjects treated will again be well focused with respect to the methodology of gas phase investigations with a particular emphasis on the high complementarity and comparability of experiment and theory. Yet, concerning the catalyzed reactions and the catalyst systems a wide spectrum ranging from metal atoms and clusters over oxide materials up to biologically relevant questions (enzymes, photosynthesis) will be covered.

The appeal of atomically defined reaction centers in the gas phase that mimic active sites of catalytic materials continues to fascinate the scientific community in particular as new experimental techniques are increasingly applied and defined gas phase systems are well suited for simulations employing state of the art quantum theoretical methods. Also the possibility to systematically vary the reactive system atom by atom or ligand by ligand renders gas phase models ideally suited to investigate effects like solvation, composition dependent reactivity, etc. on a strictly molecular level. In addition, as already emphasized at the GPMC 2014 conference, is there an ever increasing awareness of the importance of very small particles or molecular systems for real catalytic materials.

It is also a great pleasure to announce this time a special evening lecture that will provide us with a technological perspective on recent challenges in the catalytic sciences.



Metal atoms, ions, clusters – Organometallic catalysis

08:30	Conference opening and Welcome of the President of the Ulm University
09:00	Uzi Landman (INV 1) Old Questions, New Paradigms: nanocluster size-dependent catalytic reactivity, selectivity, structure sensitivity, and fluxionality
09:40	Fumitaka Mafuné (INV 2) Adsorption forms of NO on Rh [*] and Rh [*] revealed by infrared multiple photon dissociation
10:20	Coffee break
10:40	Kit Bowen (HT 1) Activation of H_2O , CO_2 , and CH_4 by single atomic metal anions
11:05	Detlef Schooss (HT 2) Hydrogen induced structure change of ruthenium clusters
11:30	Masashi Arakawa (HT 3) Nitridation mechanism of tantalum cluster cations by ammonia molecules: Contrast to other group 5 metals
11:55	Mikkel Jørgensen (HT 4) Mechanisms and reaction kinetics of catalytic reactions over small metal nanoparticles
12:20	Lunch
14:00	Richard O'Hair (INV 3) One-pot routes to synthesise amides, thioamides and amidines discovered by a mechanisms-based approach that integrates gas-phase studies, DFT calculations and solution-phase studies
14:40	Vlasta Bonačić-Koutecký (INV 4) Translating the $[LCu_{2,1}(H)]^{\dagger}$ – catalysed selective decomposition of formic acid into H_2 and CO ₂ from the gas phase into zeolite and metal-organic framework
15:20	Coffee break
15:40	Konrad Koszinowski (INV 5) Organometallic ate complexes: models for homogeneous catalysts
16:20	Mathias Schäfer (HT 5) Structure and reactivity of gas-phase phenylhydroxycarbenes: Hydrogen tunneling at room temperature
16:45	Christian van der Linde (HT 6) Electron catalyzed reactions in the gas phase involving $CO_3^{\bullet-}$ studied by FT-ICR mass spectrometry and quantum chemistry
17:10	Knut Asmis (HT 7) Methane Activation by $Al_8O_{12}^+$ vs. $Al_7FeO_{12}^+$ in the Gas Phase: Mass Spectrometry and Vibrational Spectroscopy
18:00	Evening Lecture: Martin Vollmer

INV 1

<u>Uzi Landman</u>

School of Physics, Georgia Institute of Technology, Atlanta, GA 30332

Identification and tuning the factors governing reactivity and selectivity have been central productive challenges in catalysis. Attempts were made to uncover organizing concepts, such as the Sabatier principle in the form of volcano plots, seeking correlations between characteristic properties through use of catalytic descriptors, obtained, almost exclusively, from surface science studies of extended catalytic systems. The advent of nanocatalysis brought key assumptions of the above approaches under scrutiny, and critical assessments of the adequacy of the above-noted framework - via systematic theoretical and experimental studies of reactivity, spectroscopy, and microscopic reaction pathways of sizeselected supported nanocatalysts and trapped gas-phase clusters - resulted in a paradigm shift. This led to selection of "catalytic tuning knobs" appropriate for the nanoscale, including: non-crystallographic nanocluster structures and their isomers, nanocluster dynamic fluxionality, nanocluster-support interactions, cluster composition and doping, reactivity variations caused by nanocluster charging effects, atom-by-atom variation of the atomic coordination and the nanocatalyst discrete electronic structure. This talk will address these issues and illustrate their study through combined experimental explorations on gasphase trapped and supported nanoclusters, coupled with first-principles theoretical investigations of size-dependent cluster electronic and atomic (geometrical) structures, vibrational and optical spectral characteristics, chemical bonding trends, reactivity, and catalyzed reaction pathways.

Acknowledgement: The results described in this talk resulted from productive collaborative work with scientists at the Georgia Institute of Technology (B. Yoon and R.N. Barnett), The Technical University of Munich, TUM (U. Heiz et al.) Ulm University (S.M. Lang, T.M. Bernhardt et al.), and Radboud University, Nijmegen (J.M. Bakker).

* Work at the Georgia Institute of Technology has been supported by the U.S Air Force Office for Scientific Research, and in part by the office of Basic Energy Sciences of the US Department of Energy.

<u>F. Mafuné</u>¹, T. Nagata¹, K. Koyama¹, S. Kudoh¹, K. Miyajima¹, J. M. Bakker² ¹ Department of Basic Science, The University of Tokyo, 3-8-1 Komaba, Meguro Tokyo 153-8902 Japan ² Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, the Netherlands

Rhodium is one of the most important elements in catalysts. The mechanism of NO reduction has been investigated for a few decades and the form in which NO adsorbs on a surface is known to be sensitive to temperature and surface coverage. As the reaction path varies depending on reaction conditions, the use of a gasphase cluster for investigation of the reaction mechanism can be very instructive.¹ As a basic information, the adsorption of NO on cationic Rh clusters, Rh_n^+ (n = 6–16), was studied by infrared multiple photon dissociation (IRMPD) spectroscopy using free electron laser (FELIX) in combination with DFT calculations.² The IRMPD spectra show that NO adsorbs molecularly on an on-top site of Rh_n^+ for all *n* studied, while for n = 7, 12, 13 and 14 evidence is found for second, bridging, adsorption site. Indeed, the DFT calculations suggest that molecular NO adsorption on a bridge site is more stable than on an ontop site for n = 7. Part of the NO adsorbs dissociatively on Rh_n^+ , and the ratio of dissociative adsorption depends on the size, n. For Rh_n^+ (n = 6, 8, 9), the dissociative form of NO is predicted more favorable than the molecular form by the DFT calculations, but experimentally observed ratios of dissociative adsorption were less than the prediction. The activation barrier existing between the molecular and dissociative adsorption was considered to hinder the NO dissociation. This inference is supported by the fact that NO dissociates readily by adding one Ta atom to the clusters with the O atom on the on-top site of



INV 2

Figure 1: IRMPD spectrum for $Rh_6^+(NO)$ and (b-e) vibrational spectra of the stable isomers of $Rh_6^+(NO)$ obtained by the DFT calculations. Blue, red, and dark-cyan balls stand for N, O, and Rh atoms, respectively.

the Ta atom. A reaction path for NO decomposition obtained by DFT calculations for octahedral Rh_5Ta^+ and Rh_6^+ suggests that the Ta oxygen affinity strongly reduces the energy barrier right before bond cleavage, facilitating NO dissociation.

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Activation of H₂O, CO₂, and CH₄ by Single Atomic Metal Anions

<u>Kit H. Bowen</u>¹, Gaoxiang Liu¹, Sandra Ciborowski¹, and Xinxing Zhang^{1*} and Sotiris Xantheas² and Evangelos Miliordos^{2#} and Ueli Heiz³, Martin Tschurl³, and Ulrich Boesl³

¹ Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, 21218, USA
 ² Pacific Northwest National Laboratory, Richland, Washington, 99354, USA
 ³Institute for Physical Chemistry, Technical University of Munich, 85748 Garching, Germany

We have used single platinum, palladium, and nickel atomic anions to activate single water molecules. Anion photoelectron spectra of $[Pt(H_2O)]^-$, $[Pd(H_2O)]^-$, and $[Ni(H_2O)]^-$, supported by high level calculations by Xantheas and Miliordos, identified not only the physisorbed, anion-molecule complexes, Pt⁻(H₂O), Pd⁻(H₂O), and Ni⁻(H₂O), but also the water-activated intermediates, HPtOH⁻, HPdOH⁻, and HNiOH⁻. In the case of the platinum/water system, we also have both photoelectron and computational evidence for the presence of the water-activated intermediate, H₂PtO⁻, and for the final products, PtO⁻ via its anion mass spectrum and H₂ as H₂⁺ in the cation mass spectrum. Clearly, single atomic Group 10 anions can activate single water molecules.

The platinum/water binary intermediates were then used to activate other molecules, e.g., CO_2 and CH_4 . Their tertiary anionic intermediates, $[Pt(H_2O)(CO_2)]^-$ and $[Pt(H_2O)(CD_4)]^-$, were themselves observed in our mass spectra. In addition to seeing the $[Pt(H_2O)(CO_2)]^-$ intermediate, we also observed its formate anion reaction product in mass spectra. Anion photoelectron spectra of these two tertiary intermediates and our own calculations complemented each other and revealed the presence of a formate moiety within $[Pt(H_2O)(CO_2)]^-$ and a methoxy moiety within $[Pt(H_2O)(CD_4)]^-$.

* Present address: Department of Chemistry, California Institute of Technology, Pasadena, California, USA

Present address: Department of Chemistry, Auburn University, Auburn, Alabama, USA

Hydrogen Induced Structure Change of Ruthenium Clusters

Dennis Bumüller^{1,2}, Eugen Waldt¹, Anna-Sophia Hehn², Reinhart Ahlrichs², Manfred M. Kappes^{1,2} and <u>Detlef Schooss</u>^{1,2}

¹Institut für Nanotechnologie, KIT, Postfach 3640, 76021 Karlsruhe, Germany ²Institut für Physikalische Chemie, KIT, Kaiserstr. 12, 76128 Karlsruhe, Germany

Supported ruthenium nanoparticles are the active species in the K al nanoparticle size range is on the order of a few nm. This has been rationalized in terms of the number density of active areas (B5-sites) for dissociative chemisorption of ellog Advanced Ammonia Process. Model studies have established that the optim N_2 present on the surface of the Ru nanoparticles. Calculations indicate that the number of B5 sites per total ruthenium mass should be strongly dependent on particle size.

We have studied the structures of bare and hydrogenated Ru-clusters $Ru_nH_m^-$ using trapped ion electron diffraction in combination with density functional theory in a size range of n=14 - 231 with varying hydrogen coverage. While for the bare clusters hexagonal layered or close packed fcc structures were found¹⁻², hydrogenation changes the structure type of the ruthenium core towards an icosahedral motif³. Density functional theory computations reveal the driving force behind this process to be the larger hydrogen adsorption energies for the icosahedral structure type. TIED measurements indicate that the hydrogen induced structure change extends up to ~ 200 ruthenium atoms - a size range which is identical to the onset of catalytic activity. Because icosahedral structures cannot accommodate B5-sites, this mechanism could provide an additional/alternative explanation for the size dependence catalytic activity at small particle sizes.

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Nitridation mechanism of tantalum cluster cations by ammonia molecules: Contrast to other group 5 metals

Masashi Arakawa,¹ G. Naresh Patwari,² Akira Terasaki¹

¹ Department of Chemistry, Kyushu University, Japan ² Department of Chemistry, Indian Institute of Technology Bombay, India

Tantalum nitride is an attractive material with a potential for various applications such as photocatalysts for H_2 evolution from water and copper diffusion barriers in microelectronics. Elucidation of nitridation mechanism of tantalum at the molecular level would supply a useful recipe for fabricating high-quality tantalum-nitride materials. In the present study, reactions of free tantalum cation, Ta^+ , and tantalum cluster cations, Ta_n^+ , with ammonia molecules were investigated to probe nitridation reactions step by step with precise control in the number of atoms and molecules involved in the reaction [1].

In the experiment, Ta_n^+ (n = 1-10) was generated by a magnetron-sputter cluster-ion source. They were thermalized through collisions with helium molecules cooled by liquid nitrogen, and were mass-selected and guided into a reaction cell filled with NH₃ molecules. The ions produced by the reaction were identified by a quadrupole mass analyzer, and the yield of each reaction product was measured as a function of the cluster size, n.

The reaction of monomer cation, Ta⁺, with two molecules of NH₃ leads to formation of $TaN_2H_2^+$ along with release of two H₂ molecules. The dehydrogenation occurs until the formal oxidation number of the tantalum atom reaches +5. On the other hand, all the tantalum cluster cations, Ta_n^+ , react with two molecules of NH_3 and form $Ta_nN_2^+$ with the release of three H₂ molecules. Further exposure to ammonia showed that $Ta_n N_m H^+$ and $Ta_n N_m^+$ are produced through successive reactions; this is achieved by alternate single and double dehydrogenation upon adsorption of every other NH₃ reactant molecule. The nitridation occurred until the formal oxidation number of tantalum atoms reaches +5 as in the case of TaN₂H₂⁺. These reaction pathways of tantalum atom and cluster cations are in contrast to those of other group 5 metals, i.e., vanadium and niobium clusters, which have been reported to produce nitrides with lower oxidation states [2,3]. The present results on nitridation of small clusters of group 5 metals illustrate correlation with their bulk properties: Tantalum is known to form bulk nitrides in the oxidation states of either +5 (Ta_3N_5) or +3 (TaN), whereas vanadium and niobium form only an oxidation state of +3 (VN and NbN) [4]. Along with DFT calculations, these findings reveal that nitridation is driven by the electron-donating ability of the group 5 element, i.e., electronegativity of the metal plays a significant role in determining the composition of metal nitrides.

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<u>Mikkel Jørgensen¹</u>, Henrik Grönbeck¹

¹ Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, Sweden

Heterogeneous catalysis relies on metal nanoparticles (NPs) supported on oxide surfaces. To study catalytic reaction kinetics, extended surfaces are often used as simplified model systems. However, NPs are composed of a range of different sites, which can lead to complex kinetic behavior. It is therefore desirable to explicitly consider the structure of NPs in kinetic modeling. Recently, we have achieved this by developing the Scaling Relations kinetic Monte Carlo (SRMC) method [1], where Density Functional Theory (DFT) and Generalized Coordination numbers [2] are used to describe the NP reaction energy landscape, and kinetic Monte Carlo is used to simulate reaction kinetics. In the present work, reactions on NPs are elucidated by SRMC simulations, where CO oxidation over Pt nanoparticles is used as an archetype reaction.

We find that the TOF on a NP depends critically on the reaction conditions, particle size, and the particle shape. The reaction mechanism on NPs differs fundamentally from extended surfaces as each elementary step can proceed where it is most efficient. In the present case, CO₂ formation proceeds over edges, however, the rate of this step depends on oxygen adsorption on the facets. Thus, the kinetics is determined by couplings between different regions of the NPs. To quantify the kinetic couplings, we disabled all reactions over different regions as shown in Figure 1, where the edge TOF is shown as a function of temperature. The edge-TOF drops significantly in response to disabling facets. Moreover, by investigating different particle shapes, we find that the TOF of each site depends on the detailed environment. Thus, the assembly of sites determines the catalytic activity, and not simply single sites.



HT 4

Figure 1. Turnover Frequency is plotted against temperature. Pressure: 20 mbar CO and 10 mbar O_2 .

Extended surface-models cannot capture crucial aspects of nanoparticle catalysis, which must be modeled with explicit NP model systems. The present kinetic couplings highlight that catalysis on NPs is a delocalized phenomenon, which is a consequence of the entire particle geometry. The SRMC method serves as a platform for modeling more complex reactions with NPs as model systems.

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One-pot routes to synthesise amides, thioamides and amidines discovered by a mechanisms-based approach that integrates gasphase studies, DFT calculations and solution-phase studies

<u>R. A. J. O'Hair</u>,¹ A. Noor,¹ Y. Yang,¹ J. Li,¹ W. Altalhi,¹ D. Wang,¹ G. N. Khairallah,¹ A. Ariafard,² A. J. Canty,³ and P. S. Donnelly¹

¹School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Melbourne, Victoria 3010, Australia.
²Department of Chemistry, Faculty of Science, Central Tehran Branch, Islamic Azad University, Shahrak Gharb, Tehran, Iran.
³School of Physical Sciences, University of Tasmania, Hobart, Tasmania 7001, Australia

Modern synthetic chemistry employs transition metal complexes to activate various organic compounds to promote or catalyse chemical bond formation. Palladium-catalysed cross-coupling reactions, which form C–X bonds (X = C, N, O, S etc.), have revolutionised synthetic chemistry. The amide functional group is arguably the most important structural motif in biology and chemistry. Nature uses amide bonds within natural products, peptides and proteins, and many synthetic agrochemicals, drugs and functional materials contain amides; the amide group is present in 1 out of 4 of all known drugs. The sulfur and nitrogen analogues, thioamides and amidines respectively, comprise other important classes of compounds with applications in medicinal and synthetic chemistry. The formation of amides by the coupling of carboxylic acids with primary amines is one of the most widely used chemical reactions in modern synthetic chemistry. Since most commonly applied amide formation methods have poor atom economy, alternative approaches for the synthesis of amides are a high priority.

We have embarked on a research program that blends gas-phase multi-stage mass spectrometry experiments and DFT calculations to probe the mechanisms of the elementary steps that underpin the discovery of new metal-promoted chemical transformations to prepare amides, thioamides and amidines. The new reactions are then translated to the solution phase for further mechanistic studies and to develop useful synthetic protocols. Three classes of "one pot" metal-mediated syntheses of amides, thioamides and amidines will be presented: ExIn (Extrusion-Insertion) reactions of aromatic carboxylic and sulfinic acids (eq. 1); and C-H insertion reactions (eq. 2).

 $ArXO_{2}H + RNCY \rightarrow ArC(Y)NHR + XO_{2}$ (1) $ArH + RNCY \rightarrow ArC(Y)NHR$ (2)

X = C, S; Y = O, S and NR.

Translating the [LCu_{2,1}(H)]+ – Catalysed Selective Decomposition of Formic Acid into H₂ and CO₂ from the Gas Phase into Zeolite and metal-organic frameworks

<u>Vlasta Bonačić-Koutecký</u>,^{1,2} Marjan Krstić,¹ Antonija Mravak,¹ Qiuyan Jin,³ George N. Khairallah,³ and Richard A. J. O'Hair³

¹ Center of excellence for science and technology—integration of Mediterranean region (STIM) at Interdisciplinary Center for Advanced Sciences and Technology (ICAST) at University of Split, Poljička cesta 35, 21000 Split (Croatia)

² Chemistry Department, Humboldt University of Berlin, Brook-Taylor-Strasse 2, 12489 Berlin (Germany)

³ School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, 30 Flemington Rd, Parkville, Victoria 3010 (Australia)

Translating a homogenous catalyst into a heterogeneous catalyst requires a fundamental understanding of how the catalyst "fits" into the zeolite and how the reaction is influenced. Previous studies of bimetallic catalyst design identified a potent copper homobinuclear catalyst, $[(L)Cu_2(H)]^+$ for the selective decomposition of formic acid. Here, a close interplay between theory and experiment shows how to preserve this selective reactivity within zeolites. Gas-phase experiments and DFT calculations showed that switching from 1,1-bis(diphenylphosphino)-methane ligand to the 1,8-naphthyridine ligand produced an equally potent catalyst. DFT calculations show that this new catalyst neatly fits into a zeolite which does not perturb reactivity, thus providing a unique example on how "heterogenization" of a homogenous catalyst for the selective catalysed extrusion of carbon dioxide from formic acid can be achieved, with important application in hydrogen storage and in situ generation of H₂. The above results motivated us to investigate the selective decomposition of formic acid driven by [(L)Cu(H)], L=bipyridine which is a part of highly porous aluminum based metal-organic framework in order to design new materials for the heterogenous catalysis.

Organometallic ate complexes: models for homogeneous catalysts

Konrad Koszinowski,¹ Tobias Parchomyk,¹ Thomas Auth,¹ Sebastian Weske,¹ Richard A. J. O'Hair^{1,2}

¹ Institut für Organische und Biomolekulare Chemie, Universität Göttingen, Germany ² School of Chemistry, University of Melbourne, Australia

Homogeneous transition-metal catalysis provides effective means for the formation of new carbon-carbon bonds. Transition-metal catalyzed cross-coupling and C–H activation reactions are therefore heavily exploited in modern organic synthesis. With the exception of palladium-based methods, the mechanisms of these reactions remain poorly understood. This lack of knowledge prevents systematic and rational progress in the development of new and better catalysts.

To obtain detailed insight into the mechanism of transition-metal catalyzed coupling reactions, we consider organometallic ate complexes as models of the catalytically active intermediates (Scheme 1). Electrospray ionization permits the transfer of these anionic species from solution into the gas phase, where their microscopic reactivity can be probed by tandem mass spectrometry. In this way, we avoid the problems of ill-defined starting conditions, bimolecular consecutive reactions, or equilibration processes, all of which severely complicate analyses in solution.



Scheme 1: Selected organometallic ate complexes suggested as models for catalytic intermediates

We apply this approach to examine the prototypical elementary steps of reductive elimination, transmetallation, as well as radical transfer and elucidate the role of electronic, steric, and counter-ion effects.^[1-3]

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Structure and Reactivity of Gas-Phase Phenylhydroxycarbenes: Hydrogen Tunneling at Room Temperature

<u>Mathias Schäfer</u>,¹ Mathias Paul,¹ Katrin Peckelsen,¹ Jonathan Martens,² Jos Oomens,^{2,3} Giel Berden,² Albrecht Berkessel,¹ Anthony J. H. M. Meijer⁴

 ¹ Department für Chemie, Institut für Organische Chemie, Universität zu Köln, Greinstrasse 4, 50939 Köln, Germany, mathias.schaefer@uni-koeln.de
 ² Institute for Molecules and Materials, Radboud University, Nijmegen, FELIX Facility, Toernooiveld 7, 6525 ED Nijmegen, Netherlands
 ³ van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, Netherlands
 ⁴ Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

We report initial spectroscopic evidence for H-tunneling at room temperature, observed in hydroxy- [4-(trimethylammonio)phenyl]carbene in the gas phase. This carbene is generated by decarboxylation of oxo[4-(trimethylammonio)phenyl]acetic acid upon collision induced dissociation (CID) tandem mass spectrometry, and structurally characterized by isomer-selective two-color infrared-infrared-spectroscopy and high-level DFT calculations. The charge-tagged phenyl-hydroxycarbene undergoes clean 1,2-H-shift to the corresponding aldehyde, evidenced by isomer-selective IRMPD- depletion experiments. The deuterated (OD) carbene analogue showed negligible 1,2-D-shift reactivity, providing clear evidence for hydrogen atom tunneling in the H-isotopomer. This is the first experimental confirmation that hydrogen atom tunneling can govern 1,2-H-shift reactions at room temperature; a result of broad significance for a wide range of (bio)chemical processes, including enzymatic transformations and organocatalysis.

Mathias Schäfer, Katrin Peckelsen, Mathias Paul, Jonathan Martens, Jos Oomens, Giel Berden, Albrecht Berkessel, Anthony J. H. M. Meijer, Hydrogen Tunneling Above Room Temperature: A Gas-Phase Study of Phenylhydroxycarbene, *Journal of the American Chemical Society* **139** (2017) 5779–5786.

Electron catalyzed reactions in the gas phase involving CO₃^{•-} studied by FT-ICR mass spectrometry and quantum chemistry

<u>C. van der Linde¹</u>, W. K. Tang,² C.-K. Siu², M. Ončák¹, M. K. Beyer¹

¹ Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria ² Department of Biology and Chemistry, City University of Hong Kong, Hong Kong SAR, China

The carbonate radical anion $CO_3^{\bullet-}$ and the mono- and dihydrated species $CO_3^{\bullet-}(H_2O)_{1,2}$ are important intermediates in tropospheric negative ion chemistry. The route to $CO_3^{\bullet-}$ formation is well established, starting from an electron via O_2^- and O_3^- to $CO_3^{\bullet-}$ [1]. Despite its radical character, only a small number of reactions involving CO₃^{•-} are known. Using FT-ICR mass spectrometry, we studied the reactions of $CO_3^{\bullet}(H_2O)_{0.1.2}$ with formic acid, acrylic acid and propene. For formic acid and propene, signal loss is observed as the dominant first reaction step, indicating the formation of neutral reaction products accompanied by electron detachment. For acrylic acid, the first reaction step is transfer of O^{-} , and electron detachment occurs later in the reaction sequence. In all cases, the electrons are quantitatively scavenged by SF₆, corroborating that the signal loss is due to electron detachment. In the atmosphere, the electrons lead again to formation of CO_3^{\bullet} , closing a catalytic cycle (see Figure 1 for the reaction with HCOOH). This suggests that gas-phase electrons play an important role as catalysts in atmospheric negative ion chemistry. Quantum chemical calculations of the potential energy surface of the reactions provide information on neutral reaction products. E.g. oxidation of formic acid to CO₂ and water is the thermochemically favored reaction path [2]. The spectroscopy of $CO_3^{\bullet-}(H_2O)_{1,2}$ reveals a delicate interplay between hydration and distribution of spin density.



Figure 1: Catalytic cycle of CO₃[•] generation and its reaction with formic acid [2].

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Methane Activation by $Al_8O_{12}^+$ vs. $Al_7FeO_{12}^+$ in the Gas Phase: Mass Spectrometry and Vibrational Spectroscopy

Marcel Jorewitz,^a Sreekanta Debnath,^{a,b} Stephen Leach,^c Joachim Sauer,^c Knut R. Asmis^a

^a Wilhelm-Ostwald-Institut, Universität Leipzig, Linnéstr. 2, D-04103 Leipzig, Germany ^bFritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany ^cInstitut für Chemie, Humboldt-Universität zu Berlin, Unter den Linden 6, D-10099 Berlin, Germany

Recent interest in hydrogen-atom transfer (HAT) reactions induced by C-H activation of main group metal oxides at low temperatures is motivated by identifying efficient HAT catalysts which are free of precious/transition metals. Important insights can also be gained from investigations on gas phase model systems and these have mainly focused on characterizing metal oxide clusters in the context of methane activation. Schwarz, Sauer and coworkers used mass spectrometry in combination with electronic structure calculations to show that oxygen- centered radicals like $(A_2O_3)^+$ (n = 3, 4 ad 5) readily abstract an H-atom from methane to form a methyl radical $(CH_4 + M-O)^+ \rightarrow CH_3^+ M-OH^+)$.[1]

Here, we use ion trap mass spectrometry and infrared photodissociation spectroscopy in combination with density functional theory calculations to study the key intermediates of methane activation by AO in more detail, in particular, under multiple collision thermalization at variable temperature. The HAT reaction yield increases with decreasing temperature (300-100 K), confirming the barrier-free nature of this highly exothermic reaction. Interestingly, formal substitution of an Al^{3+} by a Fe³⁺-center suppresses the reactivity completely. IRPD spectra of He-tagged $A_8O_{12}^+$ and FeA₇ O_{12}^+ confirm that the substitution is isomorphic, occurs nearly exclusively adjacent to the oxygen-centered radical, leading to the reduction of the terminal O-atom and formation of a Fe⁴⁺ center.

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Evening Lecture

Innovation Driver in Catalysis: An Industrial Perspective

<u>Martin Vollmer</u>

Clariant Int. Ltd., Switzerland



Metal oxides and spectroscopy

09:00 Helmut Schwarz (INV 6) The Methane challenge: C-H bond activation by metal oxides and metal carbides 09:40 Joachim Sauer (INV 7) Structure and reactivity of metal oxide gas phase clusters compared to solid catalysts 10:20 Coffee break 10:40 Akira Terasaki (HT 8) Chemical analysis of oxygen storage/release processes in cerium-oxide cluster ions by X-ray absorption spectroscopy 11:05 Martin Tschurl (HT 9) Tantalum cluster cations and their oxides in the activation of methane under multi-collision conditions 11:30 Toshiaki Nagata (HT 10) Geometrical structures and reactions of cerium oxide cluster cations studied by ion mobility mass spectrometry 11:55 Tobias Lau (HT 11) Molecular iron oxides: Iron in the remarkable +7 oxidation state 12:20 Lunch 14:00 Lai-Sheng Wang (INV 8) CO oxidation by size-selected Au clusters: From gas-phase clusters to ligandprotected clusters with in situ active sites 14:40 Mark Johnson (INV 9) Trapping and vibrational characterization of small molecule activation in homogeneous catalysis with cryogenic ion chemistry and spectroscopy 15:20 Coffee break 15:40 Gereon Niedner-Schatteburg (HT 12) Non Haber-Bosch iron clusters 16:05 André Fielicke (HT 13) Activation of carbon dioxide by anionic transition metal clusters 16:30 **Joost Bakker** (HT 14) IR spectroscopic characterization of the reaction products of methane activation by 5d transition metals 16:55 Marko Förstel (HT 15) Gas phase UV/VIS spectroscopy on Au_4^+ 17:20 Masahiko Ichihashi (HT 16) Formation and infrared photodissociation spectroscopy of cluster complexes $Co_m^+ He_n$ Conference dinner "Bootshaus" 20:00

The Methane Challenge: C–H bond Activation by Metal Oxides and Metal Carbides

<u>Helmut Schwarz</u>, Maria Schlangen, Lei Yue, Shaodong Zhou, Caiyun Geng, Xiaoyan Sun, Sason Shaik, Jilai Li, Thomas Weiske

Institut für Chemie, Technische Universität Berlin, 10623 Berlin, Germany

In this lecture we will discuss a story of one molecule (methane), a few metal-oxide cationic clusters (MOCCs), dopants, metal-carbide cations, oriented-electric fields (OEFs), and a dizzying mechanistic landscape of methane activation! One mechanism is hydrogen atom transfer (HAT), which occurs whenever the MOCC possesses a localized oxyl radical (M–O[•]). Whenever the radical is delocalized e.g., in $[MgO]_n^{\bullet+}$ the HAT barrier increases due to the penalty of radical localization. Adding a dopant (Ga₂O₃) to [MgO]₂⁺⁺ localizes the radical and HAT transpires. Whenever the radical is located on the metal centers as in $[Al_2O_2]^{\bullet+}$ the mechanism crosses-over to proton-coupled electron transfer (PCET), wherein the positive Al center acts as a Lewis acid that coordinates the methane molecule, while one of the bridging oxygen atoms abstracts a proton, and the negatively charged CH₃ moiety relocates to the metal fragment. We provide a diagnostic plot of barriers vs. reactants-distortion energies, which allows the chemist to distinguish HAT from PCET. Thus, doping of $[MgO]_2^{*+}$ by Al₂O₃ enables HAT and PCET to compete. Similarly, [ZnO]^{•+} activates methane by PCET generating many products. Adding a CH₃CN ligand to form [(CH₃CN)ZnO]^{*+} leads to a single HAT product. The CH₃CN dipole acts as an OEF that switches off PCET. $[MC]^+$ cations (M = Au, Cu) act by different mechanisms, dictated by the M⁺–C bond covalence. For example, Cu⁺, which bonds the carbon atom mostly electrostatically, performs coupling of C to methane to yield ethylene, in a single almost barrier-free step, with an unprecedented atomic choreography catalyzed by the OEF of Cu⁺.

Structure and Reactivity of Metal Oxide Gas Phase Clusters Compared to Solid Catalysts

Joachim Sauer

Institut für Chemie, Humboldt-Universität, Unter den Linden 6, 10099 Berlin, Germany

We study gas phase clusters as models for solid catalysts,^[1] "the active site in isolation". For metal oxides, we are interested in the question how the structure and reactivity of gas phase clusters differ from those of the bulk phase with the same composition. We use density functional theory (DFT) to perform global structure optimizations (genetic algorithm). To verify the global minimum structures, we calculate IR spectra and compare them with the ones obtained for mass-selected clusters by photodissociation (IRPD) and multiple photon dissociation (IRMPD) spectroscopy.^[2,3]

In this lecture we focus on aluminium oxides. We look at compounds with an $Al_3(\mathbb{Z}_2-OH)_3$ core^[4] both as molecular crystal and in the gas phase, and we examine the interaction of water molecules with $Al_3O_4^+$. The unambiguous assignment of the vibrational spectra of these systems allowed to identify characteristic spectral regions for O–H stretching modes of different types of hydroxyl groups in aluminium oxide/water systems.^[3]

We substitute Fe for Al in $(Al_2O_3)_4^+$ whose reactivity towards methane has been studied in the past^[2] and examine the structure and reactivity changes caused by the substitution. Here we are facing the accuracy limits of DFT. Application of more reliable wave-function-based methods is very challenging, and sometimes fully converged results cannot be obtained with presently available methodology even for triatomic system like FeO₂^{+[5]} or FeO₂⁻.

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Chemical analysis of oxygen storage/release processes in cerium-oxide cluster ions by X-ray absorption spectroscopy

Akira Terasaki,^{1,2} Tetsuichiro Hayakawa,² Masashi Arakawa¹

¹ Department of Chemistry, Kyushu University, Japan ² East Tokyo Laboratory, Genesis Research Institute, Inc., Japan

Cerium oxide is an important material for catalysts in redox processes. It works efficiently in oxygen storage/release as the oxidation state of cerium changes flexibly between Ce(III) and Ce(IV). To gain insights into the mechanism of catalysis, isolated clusters provide us with a good model system representing an active site of such a catalyst. Here we report X-ray absorption spectroscopy (XAS) of size-selected cerium-oxide cluster ions, where the chemical states of both cerium and oxygen are characterized by taking advantage of the element-selective feature of XAS [1,2].

The experiment was performed at Photon Factory in High Energy Accelerator Research Organization (KEK-PF) located in Tsukuba, Japan. Cerium-oxide cluster ions, $Ce_mO_n^+$, were produced by magnetron sputtering of a metallic cerium plate under a trace amount of oxygen flow. The cluster ions were stored in a linear quadrupole ion trap after mass-selected by a quadrupole mass filter. Then they were irradiated with tunable soft X-ray from the synchrotron. The X-ray was tuned in the spectral ranges of both Ce M-edge and O K-edge. Absorption of the X-ray was measured via detection of fragment ions (such as CeO_2^+ , CeO^+ , Ce^+ , and Ce^{2+}) by a time-of-flight (TOF) mass spectrometer.

We have performed systematic measurement on a series of $Ce_3O_n^+$ clusters (n = 4-7), which illustrates how the chemical states of cerium and oxygen evolve as a function of oxygen content in the cluster [2]. The Ce M-edge spectra were compared with those of reference samples of bulk CeF₃, representing Ce(III), and bulk CeO₂, representing Ce(IV). It was found that cerium is in the Ce(III) state in $Ce_3O_4^+$, whereas it is in the Ce(IV) state in $Ce_3O_6^+$ and $Ce_3O_7^+$. The cerium in $Ce_3O_5^+$ was interpreted as a mixture of Ce(III) and Ce(IV). On the other hand, the O K-edge spectrum of $Ce_3O_4^+$ exhibited only one main peak, whereas additional pre-edge peaks showed up at the low-energy side for $Ce_3O_{5-7}^+$. These results were interpreted by referring to geometric structures of the clusters obtained by DFT calculations. The present study reveals a plausible scenario of oxidation of $Ce_3O_4^+$ to $Ce_3O_7^+$. In addition, it is shown that XAS provides novel experimental evidence for evaluating the structural models proposed by computational studies.

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Tantalum Cluster Cations and Their Oxides in the Activation of Methane under Multi-Collision Conditions

<u>Martin Tschurl</u>¹, Jan F. Eckhard¹, Tsugunosuke Masubuchi¹, Nikita Levin¹, George Goddard¹, Ueli Heiz¹

¹ Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technical University of Munich, Germany

Tantalum-based systems exhibit promising properties in the activation of methane. For example, in heterogeneous catalysis they enable a coupling to ethane with the concomitant release of molecular hydrogen.[1] Also in gas phase systems, this element is one out of a few, for which the atomic cation facilitates the dehydrogenation of CH_4 .[2] Besides bare tantalum, also its oxide cations exhibit an interesting reactivity. In this regard, TaO_3^+ has recently been found to undergo reaction with methane, which suggests the formation of value-added products.[3] While systems comprising one and, only recently, two [4] tantalum atoms have been studied, the reaction properties of tantalum clusters and their oxides still remain elusive.

In this work it is shown that tantalum clusters offer a rich chemistry in the reaction with methane under multi-collision conditions. Governed by their size and oxidation state, they exhibit different reaction pathways and end products. For most clusters the dominant reaction mechanism involves an insertion into the C-H bond. The cleavage of this bond is found to be the rate determining step. However, while the (partial) oxidation of the clusters in most cases result in an increase in their reactivity, higher degrees of cluster oxidation lead to a complete change of reaction behavior. As products from dehydrogenation steps may undergo further reaction with molecular oxygen, the formation of value-added products such as formaldehyde is enabled. Furthermore, indications are found that a particular cluster-oxide species undergoes reaction in a catalytic way, which seems to occur via a C-C coupling reaction forming ethane.

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Geometrical structures and reactions of cerium oxide cluster cations studied by ion mobility mass spectrometry

Toshiaki Nagata, Jenna W. J. Wu, Motoyoshi Nakano, Keijiro Ohshimo, Fuminori Misaizu

Department of Chemistry, Graduate School of Science, Tohoku University, Japan

Cerium oxide (CeO₂) is a widely used catalyst, which promotes many important reaction processes such as automobile exhaust gas purification. Gas-phase cerium oxide clusters have been studied as simplified models for those catalytic reactions. In this study, we have investigated geometrical structures and NO-adsorption reactions of cerium oxide cluster cations, Ce_nO_m⁺, by ion mobility mass spectrometry (IMMS).

The cluster cations were generated by laser vaporization of a CeO₂ rod in He gas pulse. Collision cross sections (CCSs) of the ions were measured by IMMS utilizing a He buffer gas filled ion-drift cell. To assign the ion structures, candidate structures were optimized by density functional theory (DFT) calculations. Corresponding theoretical CCSs were simulated and then compared with the experimentally obtained CCSs. Present results for Ce₂O₃⁺, Ce₃O₄⁺, Ce₃O₅⁺, and Ce₅O₉⁺ were in consistent with those from a previous infrared spectroscopic study [1]. However, for Ce_nO_{2n}⁺ (n = 2-5) ions, present results suggested more compact structures than previously proposed ones based on DFT calculations [2]. These compact structures of Ce_nO_{2n}⁺ have less terminal oxygen atoms, which are presumed to be reactive sites (Figure 1).

Furthermore, reactions of $Ce_nO_m^+$ cluster ions with nitric oxide were also examined. $Ce_nO_{2n}^+$ reacted with NO to form $Ce_nO_{2n}(NO)^+$, as previously reported [3]. After the reaction, the ions were analyzed by IMMS to obtain their experimental CCSs. The CCSs of $Ce_nO_{2n}(NO)^+$ ions increased by 2–6 Å² from $Ce_nO_{2n}^+$ by adsorption of NO (Figure 2). As an example, candidate structures of $Ce_4O_8(NO)^+$ based on a structure of $Ce_4O_8^+$ were obtained by DFT computations. A structure whose theoretical CCS reproduces the experimental CCS holds a NO₂ moiety from the adsorbed NO and an O atom of $Ce_4O_8^+$ on the terminal site.



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Molecular Iron oxides: Iron in the Remarkable +7 Oxidation State

R. Lindblad,^{1,2} V. Zamudio-Bayer,^{2,3} C. Bülow,^{2,4} M. Timm,^{2,4} A. Ławicki,² K. Hirsch,² A. Terasaki,⁵ B. von Issendorff,³ <u>J. T. Lau</u>^{2,3}

 ¹ Department of Physics, Lund University, 22100 Lund, Sweden
 ² Institut für Methoden und Instrumentierung der Forschung mit Synchrotronstrahlung, Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany
 ³ Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany
 ⁴ Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin, Germany
 ⁵ Department of Chemistry, Kyushu University, Fukuoka 819-0395, Japan

The smallest molecular iron oxides containing only a single iron center, FeO_n^+ with n = 1 - 4, have been studied by x-ray absorption and x-ray magnetic circular dichroism spectroscopy in a cryogenic ion trap. This allows us to separately probe transitions into metal and oxygen centered orbitals, to detect orbital and spin magnetizations and to determine chemical species. Analysis of the line shape and excitation energy shifts at the oxygen K edge and iron $L_{2,3}$ edge spectra give independent evidence of the unusual +7 oxidation state of iron, the highest that has been demonstrated so far in the ground state of any iron compound, in low-spin FeO_3^+ . This highest oxidation state of iron goes along with electron delocalization into strongly hybridized molecular orbitals, leading to reduced local 3d character at the iron site, and to spin pairing in molecular orbitals with a resulting low-spin state. This causes reduced local 3d electron density in the vicinity of the 2p core hole and leads to blue shifts of the iron 2p - 3d excitation energy of 0.7 - 0.9 eV per formal oxidation state because of reduced corehole screening.

CO Oxidation by Size-Selected Au Clusters: From Gas-Phase Clusters to Ligand-Protected Clusters with *In Situ* Active Sites

Lai-Sheng Wang

Department of Chemistry, Brown University, Providence, RI 02912, USA

The discovery of the remarkable catalytic properties of gold nanoparticles on oxide supports has stimulated extensive investigations of the structures and reactivity of size-selected gold clusters, which provide excellent models to gain insight into the catalytic mechanisms of nanogold. It was found that the Au₂₀ cluster possesses a highly symmetric pyramidal structure with all 20 gold atoms on the cluster surface [1]. The Au₂₀ pyramid was expected to exhibit interesting catalytic and optical properties, if bulk quantities can be obtained. In this talk, I will report our effort toward the syntheses of the Au₂₀ pyramid using phosphine ligands. Initial effort using triphenylphosphines demonstrated that the Au₂0 pyramid could be synthesized in solution (Figure 1a) [2]. Further effort to increase the yield and selectivity using long-chain diphosphine ligands resulted in the first crystallization of an Au₂₂ cluster (Figure 1b), consisting of two Au₁₁ fragments linked by four ligands [3]. The 8 Au atoms at the interface of the two Au₁₁ fragments are not coordinated, providing in situ active sites for chemisorption. By dispersing the Au_{22} clusters on different oxide substrates (Figure 1c), its CO oxidation activity has been investigated [4]. It was found that the as-deposited Au_{22} cluster is catalytically active toward CO oxidation. On reducible substrates (TiO₂ and CeO₂), the CO oxidation takes place by CO activation on the Au₂₂ cluster and then reacts with lattice O atoms to form CO₂ via the Mars-van Krevelen mechanism. For non-reducible substrate (Al₂O₃), both CO and O₂ are activated by the Au₂₂ cluster to produce CO₂ via the Langmuir-Hinshelwood mechanism.



Figure 1. (a) Calculated structure of the Au_{20} pyramid coordinated by four triphenylphosphine ligands [2]. (b) The crystal structure of the Au_{22} cluster coordinated by six diphosphine ligands [3]. (c) Schematic depiction of an Au_{22} cluster deposited on an oxide substrate and the CO+O2 reactions [4].

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Trapping and vibrational characterization of small molecule activation in homogeneous catalysis with cryogenic ion chemistry and spectroscopy

Mark Johnson

Department of Chemistry, Yale University, New Haven, CT 06520, USA

We describe the application of cryogenic ion chemistry techniques to capture and structurally characterize small molecules docked at the active sites of transition metal catalysts. Our strategy involves isolating the resting state of the catalysts using a controlled atmosphere ESI interface, and then opening a coordination site on the metal through collision-induced dissociation of charged ligands. This allows substrate molecules (CO_2 , H_2O_1 , N_2O , CO, N_2) to be docked onto the active site using a temperature-controlled ion trap. These complexes are then transferred to a second, cryogenic ion trap where they are tagged with H₂ or N₂ for acquisition of their vibrational spectra using predissociation spectroscopy in a linear action regime. These measurements highlight the critical role played by the oxidation states of the metal centers in determining both the binding motifs and degree of small molecule activation. This issue is explored in depth in the case of Ni(I) vs Ni(II) with two ligand scaffolds: The Ni cyclam system and a distorted variation of this ligand, which was specifically designed by the Krüger group to support a stable Ni(I) center. We will present new methods for the preparation and control of unstable oxidation states using ion-ion recombination in a non-dissociative mode (ET-noD). In the case of Ni cyclam, the product was characterized using IRMD (with Jos Oomens at FELIX). Isomer-selective spectroscopy is also generally available where necessary using two color, IR-IR double resonance. Variations on the double resonance capability will also be discussed that promise to enable measurement of intra-cluster reaction kinetics.

Non Haber-Bosch Iron clusters

Sebastian Dillinger, Jennifer Mohrbach, Annika Steiner, Matthias P. Klein, Marc H. Prosenc, and <u>Gereon Niedner-Schatteburg</u>

> Fachbereich Chemie, TU Kaiserslautern, Germany gns@chemie.uni-kl.de

Iron is generally accepted as an efficient catalyst for reductive nitrogen activation, and it is efficiently applied in ammonia synthesis. While the optimized protocol (by Mittasch et al.) invokes promotors such as potassium, naked Iron is an active catalyst in itself.

We have investigated the behaviour of naked transition metal clusters under cryo conditions, and we have published a series of spectroscopic and kinetic studies of the nitrogen adsorption onto size selected Cobalt and Nickel clusters [1-4], as well as a case study of Nitrogen N_2 and Hydrogen H_2 co-adsorption onto a selected Ruthenium cluster⁵. In the course of these studies we chose to investigate Iron clusters and Iron-Rhodium nanoalloys as well.

To our outmost surprise we found some Iron clusters reluctant to attach neither Nitrogen N_2 nor Hydrogen H_2 . Careful consistency checks confirm these findings while the interpretation is still pending, further experimental work in progress. This presentation puts the current level of understanding to the stage and presents all unpublished work.



Figure 1: DFT calculations (PBE0/cc-pVDZ) of Fe_{17}^+ suggest a geometry with an almost smooth cluster surface and an electronic 51tet high spin state.

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Activation of carbon dioxide by anionic transition metal clusters

André Fielicke

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Metal clusters are frequently used as model systems for low coordinated sites of extended surfaces and their study can provide valuable insights into the mechanisms of surface reactions. In many cases, however, there is still a lack of information on their structures and the relationship between structure and chemical behaviour. Using vibrational spectroscopy of gas-phase clusters one can obtain information about the clusters' structure or the behaviour of adsorbed species. The latter provides valuable insights into the binding geometry, the activation of bonds within the ligands or reactions occurring on the clusters' surface. Cluster size specific data can be obtained using infrared multiple photon dissociation (IR-MPD) spectroscopy.

Here we present results of studying the reactions of anionic cobalt, rhodium, and platinum clusters with carbon dioxide (CO₂). As a relevant greenhouse, cost-effective processes for its fixation, activation and transformation into value-added products become technologically increasingly more important. One possible activation mechanism is a reduction via the transfer of an electron into the LUMO of CO₂ which has C-O antibonding character. Furthermore it breaks the degeneracy of this $2\pi_u$ orbital leading to a bent ground state structure of the CO₂⁻ anion. IR spectroscopy is sensitive to these structural changes as for instance the IR-inactive symmetric stretching mode of CO₂ becomes IR-active after symmetry lowering. Anionic metal clusters can serve as electron source for such activation mechanism.

IR-MPD spectra of the anionic complexes between CO_2 and Rh clusters show all the typical fingerprint of metal-bound CO_2^- , the IR spectra of the Co cluster complexes are rather different but can be explained by dissociation of the CO_2 into O and CO. Indeed the only bands observed in the IR spectra are very close to the positions found for complexes between CO and the anionic Co clusters.[1] Theoretical investigation on the level of density functional theory confirm that this dissociation is energetically feasible. CO_2 binding to small anionic Pt clusters shows a cluster size dependent behaviour with certain sizes promoting dissociation of CO_2 like seen in the case of Co while for other sizes the presumably initially formed CO_2^- species can be identified.

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IR spectroscopic characterization of the reaction products of methane activation by 5d transition metals

<u>J.M. Bakker</u>¹, V. Chernyy¹, S. Kuijpers¹, O.V. Lushchikova¹, O.W. Wheeler², C. J. Owen², G. C. Boles², P.B. Armentrout ², S.M. Lang³, T.M. Bernhardt³, R.N. Barnett⁴, and U. Landman⁴

¹ Radboud University, FELIX Laboratory, Nijmegen, the Netherlands ² University of Utah, Salt Lake City, United States ³University of Ulm, Germany ⁴Georgia Tech, Atlanta, United States

Methane, a key fossil fuel, is both difficult to transport and to convert to other energy rich chemicals because of the strong CH bond. This bond can be activated exothermically by clusters or ions of several 5d transition metals, while only moderately endothermic by others. We study the products formed upon activation of methane by several 5d ions, as well as by small gold clusters through IR photodissociation spectroscopy. In this talk, we will demonstrate that the observed activation can be characterized to evolve from strong for 5d metal ions, leading to carbene MCH_2^+ or carbyne hydride $H-MCH^+$ formation, to gentle and weak (methyl CH_3 formation and physisorption by intact CH_4 only) for Au cluster cations or through consecutive adsorption of multiple methanes. A thorough understanding of these processes will allow the rational design of activation catalysts.



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Gas phase UV/VIS spectroscopy on Au₄⁺

M. Förstel, W. Schewe, B. K. A. Jaeger and O. Dopfer

Inst. für Optik und Atomare Physik, Technische Universität Berlin

Part of the broad interest in the electronic properties of gold nanoparticles and clusters is due to their catalytic applications and properties [1]. Nanometer-sized gold-containing particles are discussed as oxygen activator, assisting in the oxidation of CO [2]. Small cationic gold cluster show size dependent C-H bond cleavage properties [3].

Here we present high resolution optical absorption spectra of Au_4^+ in the range of the first few optically active excited states, i.e. in the range of 400 to 600 nm. The spectra are obtained via laser-induced photodissociation spectroscopy. The Au_4^+ clusters are produced via laser desorption and are cooled to about 100 K via expansion through a cold nozzle. We observe at least four distinct excited states. All transitions are vibrationally broadened. We can quantify four vibrational frequencies of the lowest observed excited state. The spectral quality is improved by at least an order of magnitude with respect to resolution and signalto-noise ratio as compared to previous results [4]. For the first time, this allows a direct comparison of the experimental spectra with TD-DFT based Franck-Condon simulations, with the aim of distinguishing the two low energy isomers (rhombic and Y-shaped) of Au_4^+ .[5-7]



Figure 1: Photodissociation cross section of $Au_4^+ + hv \rightarrow Au_3^+ + Au$ as a function of excitation energy in the region of the 0-0 vibrational transition of the first observable electronic transition. Red and green traces were recorded using a dye laser with sub cm⁻¹ resolution. The black trace was recorded using an OPO laser with a resolution in the order of 5 cm⁻¹.

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Formation and Infrared Photodissociation Spectroscopy of Cluster Complexes Co_m⁺He_n

Masahiko Ichihashi¹, Hideho Odaka²

¹ Cluster Research Laboratory, Toyota Technological Institute, Japan ² East Tokyo Laboratory, Genesis Research Institute, Inc., Japan

Reactions of molecules adsorbed on metal (and metal compound) clusters have attracted much attention as promising nanocatalysts and a fundamental model of catalysts. In order to examine the mechanisms of the catalytic reactions, it is important to elucidate the geometric and electronic structures of the nanocatalysts, and we are moving toward a study on the nanocatalysts in helium clusters for infrared spectroscopy. Now we have developed a technique to form cluster complexes by use of low-energy collision between clusters. This can provide a significant amount of cluster complexes of helium clusters having metal clusters, and we demonstrate the formation of the cluster complexes including cobalt cluster ions and the spectroscopy.

Low-energy collision experiments were accomplished by using a merging-beam apparatus [1, 2]. In the collision of Co_m^+ (m = 1-7) with He_N ($\langle N \rangle = 1600-30000$), cluster complexes, $Co_m^+He_n$, were observed, and it was found that the total intensity of $Co_m^+He_n$ is inversely proportional to the relative velocity between Co_m^+ and He_N , though it levels off in a slightly high velocity region, and steeply decreases above 10^3 m/s. This profile suggests that the main interaction changes from the charge-induced dipole one to the hard-sphere type one with the increase of the relative velocity. At the higher velocities, Co_m^+ which collides with He_N at a large impact parameter cannot stop at the inside of He_N and passes through it.

Photodissociation spectra of $Co_m^+He_n$ were measured in the wavenumber range of 5000 7000 cm⁻¹. $Co_6^+He_n$ have relatively large intensity of photofragments in this region. This dissociation comes from the electronic excitation of Co_6^+ , and shows that Co_6^+ has an electronic transition in this low-energy (0.65–0.85 eV) region. A time-dependent density functional theory (TD-DFT) calculation supports that Co_6^+ has electronic transitions in this region. These low-lying excited states could be closely related to the reactivity of the clusters, and a typical example is shown in the reaction of Co_m^+ with NO.

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Doped Metal and Metal-Oxide Clusters

- 09:00 Sheng-Gui He (INV 10) Catalytic reactions mediated with gas phase hetero-nuclear metal oxide clusters 09:40 Alexander Gentleman (INV 11) Molecular versus dissociative CO adsorption on Nb-Rh nanoalloy clusters 10:20 Coffee break 10:40 Roy Johnston (HT 17) The effect of palladium doping on the stability and fragmentation patterns of cationic gold clusters 11:05 Albert Viggiano (HT 18) New insight into oxidation of CO by N₂O catalyzed by the mixed metal cluster $AIVO_4^+$ Luis Molina (HT 19) 11:30 Control of CO adsorption at platinum clusters by size and doping effects; insights from DFT simulations Jan Vanbuel (HT 20) 11:55 Hydrogen chemisorption on rhodium doped aluminum clusters
- 12:20 Conference closing
- 15:00 Possibility to participate in a lab tour

Catalytic reactions mediated with gas phase hetero-nuclear metal oxide clusters

<u>Sheng-Gui He</u> Institute of Chemistry, Chinese Academy of Sciences, P. R. China

Practical metal oxide catalysts are often mixed or multi-component metal oxides. Inspired by this fact, we have recently studied elementary and catalytic reactions of many hetero-nuclear metal oxide clusters with mass spectrometry and quantum chemistry calculations. An ion trap reactor and a fast-flow reactor were used to study ionic and neutral cluster systems, respectively. The M-Al-O (M = Au, Pt, Rh, Ir, Cu), Au-Ti-O, Cu-V-O clusters were prepared to react with CO and CH₄ and several catalytic cycles were identified (see Figure 1 for two examples). The hetero-nuclear metal oxide clusters are generally more catalytic than their homo-nuclear counterparts. The *electro-negativity ladder effect* has been proposed to account for the enhanced catalytic reactivity of the hetero-nuclear systems in oxidation of CO by O_2 .



Figure 1: Catalytic cycles for CO oxidation by O_2 mediated with (a) $Cu_2VO_{3-5}^-$ and (b) $AuAl_3O_{3-5}^+$ clusters

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Molecular versus Dissociative CO Adsorption on Nb-Rh Nanoalloy Clusters

<u>Alexander S. Gentleman</u>¹, Benjamin E. Atkinson¹, Christian F. Kerpal¹, Alice E. Green¹, Andreas Iskra¹, Mark A. Buntine², Matthew A. Addicoat³, John E. McGrady¹, Gregory F. Metha⁴, André Fielicke⁵ and Stuart R. Mackenzie¹

¹Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3QZ, United Kingdom

²School of Molecular and Life Sciences, Curtin University, Perth, Western Australia 6845, Australia
 ³School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, UK
 ⁴Department of Chemistry, The University of Adelaide, South Australia 5005, Australia
 ⁵Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Cluster science provides an opportunity to tune the properties of clusters of one element by doping with other atoms. This additional dimension enables new questions to be posed such as whether the properties of the new cluster are intermediate to those of pure clusters of the elements involved. Here, the reactivity of CO with niobium-rhodium bimetallic clusters (or "nanoalloys") and their oxide counterparts in all three charge states have been investigated using a combination of Infrared Multiple Photon Dissociation (IRMPD) spectroscopy and Density Functional Theory (DFT) calculations. Experimentally, molecular adsorption of CO to various Nb-Rh nanoalloy clusters is indicated by the ion signal depletion of the pertinent carbonyl complex upon irradiation with IR light resonant with the C-O stretching frequency, v(CO), of molecularly-bound CO. The absence of a v(CO) band for a particular cluster is interpreted as CO being dissociatively-bound.

Overall, binding sites and interaction strengths have been characterised as a function of cluster size, composition (including O), and charge-state by observing how v(CO) in the IRMPD spectra changes with these variables. Assignments have been made based on geometric information from DFT calculations. Additionally, reaction profiles constructed from various DFT-calculated minima and maxima provide detailed insight into the CO dissociation on bimetallic clusters, including C-O dissociation barriers, potential routes to facile CO dissociation, *etc.* The results of these recent experimental and computational investigations to date will be discussed in the presentation.



The Effect of Palladium Doping on the Stability and Fragmentation Patterns of Cationic Gold Clusters

<u>Roy L. Johnston</u>¹, Heider A. Hussein^{1,2}, Christopher J. Heard³, Piero Ferrari⁴, Jan Vanbuel⁴, André Fielicke⁵, Peter Lievens⁴, Ewald Janssens⁴

¹ School of Chemistry, University of Birmingham, United Kingdom
 ² Department of Chemistry, College of Science, University of Kufa, Iraq
 ³ Department of Physical and Macromolecular Chemistry, Charles University, Czech Republic
 ⁴ Laboratory of Solid State Physics and Magnetism, KU Leuven, Belgium
 ⁵ Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The search for stable cluster species has been an important subject ever since the discovery that cluster stability depends strongly on the number of atoms [1]. We analyze how the interplay between electronic structure and cluster geometry determines the stability and the fragmentation channels of Pd-doped cationic Au clusters, $PdAu_{N-1}^+$ (N=2-20) [2]. A combination of photofragmentation experiments [3] and density functional theory (DFT) calculations (employing the DFT-genetic algorithm approach [4]) is employed and very good agreement found between theory and experiment. Pd doping is found to modify the structure of the Au clusters, in particular altering the 2D to 3D transition size, with direct consequences for cluster stability. Analysis of the electronic density of states of the clusters show that, depending on cluster size, Pd delocalizes one 4*d* electron, giving an enhanced stability to $PdAu_6^+$, or remains with all $4d^{10}$ electrons localized, closing an electronic shell in $PdAu_9^+$ (Figure 1). It is observed that for most clusters, Au evaporation is the lowest-energy decay channel, although for $PdAu_7^+$ and $PdAu_9^+$ decay is mainly by Pd evaporation due to the high stability of the Au_7^+ and Au_9^+ fragmentation products. Recent studies, again combining theory and experiment, of CO adsorption on these clusters will also be discussed [5].



Figure 1: Comparison of the density of states of Au₉⁺ and PdAu₉⁺

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New Insight into Oxidation of CO by N₂O Catalyzed by the Mixed Metal Cluster $AIVO_4^+$

Albert A. Viggiano, Brendan C. Sweeny, Shaun G. Ard, and Nicholas S. Shuman

Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base, NM 87117

In recent years mixed metal clusters have offered new avenues with which to study subtle mechanistic details of catalysis. One such system is $AIVO_4^+$, which catalyzes reduction of CO by N₂O. Previous work by Schwartz et. al. identified likely reaction mechanisms with thermal kinetic data and density functional theory (DFT) calculations. The present work has expanded upon this, studying this system in a variable temperature selected ion flow tube (VT-SIFT) for the first time. Statistical modelling of the resultant temperature dependent kinetic data allowed for verification of the previously postulated reaction surfaces but with an important additional detail. While it was found that CO oxidation by AlVO₄⁺ does proceed through a barrier-less dissociation upon complexation with the terminal Al-O site, complexes formed on the vanadium site still play a role. While these complexes don't lead directly to CO oxidation, accessible transition states were found so that rearrangement of these complexes to those on the Al-O site are only moderately hindered. Only including contributions from all of the stable complexes allows one to adequately model the data, highlighting the importance of stereo-chemical effects in reactions such as these. In other words complexes of CO to both Al and V are formed and those on the V side either rearrange to those on the AI side or dissociate back to reactants. All products are formed through the Al-O-CO complex. The reaction of $AIVO_3^+$ with N₂O was also studied in the same manner in order to complete the catalytic cycle. Preliminary analysis indicates that the stereo-chemical effects are not as important in that reaction.

Control of CO adsorption at platinum clusters by size and doping effects; insights from DFT simulations

Luis M. Molina¹, J. A. Alonso,¹ P. Ferrari², V. E. Kaydashev², P. Lievens², E. Janssens²

¹ Department of Theoretical, Atomic and Optical Physics, Universidad de Valladolid (Spain) ² Laboratory of Solid State Physics and Magnetism, KU Leuven, (Belgium)

Platinum catalysts, when used in fuel cells, are very susceptible to poisoning by trace amounts of CO present in the H2 fuel. One way to reduce such poisoning is to alloy platinum with other transition metals. In this talk, we will report the results of an extensive experimental and theoretical study of the CO adsorption features of small pure and doped Pt-based nanoclusters [1]. Multiple adsorption of CO on clusters with a size of 10-20 atoms was found to be very sensitive to the presence of Nb and Mo dopants, with a single impurity altering CO binding energies by more than 0.5 eV. Our ab initio DFT simulations allow us to correlate the decreasing CO binding energies to an important electron transfer from the dopants, which have a marked preference towards high-coordinated positions at the center of the clusters. The analysis of the DOS gives further insight into the details of the dopantplatinum charge transfer and its relationship with the enhanced tolerance to CO poisoning. Finally, we will show the results of ab initio molecular dynamics simulations for the adsorption of CO at both pure and Nb-doped platinum clusters. In agreement with the experimental findings, thermal effects associated to cluster heating induced by CO adsorption show sizable variations with the presence of a single Nb dopant.



Figure 1: Projected DOS into the d states of impurity atom, and Bader charges on Pt_{19}^{+} , $NbPt_{18}^{+}$ and $SnPt_{18}^{+}$.

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Hydrogen chemisorption on rhodium doped aluminum clusters

<u>Jan Vanbuel</u>¹, Meiye Jia¹, Piero Ferrari¹, Sandy Gewinner², Wieland Schöllkopf², Minh Nguyen³, André Fielicke², Ewald Janssens¹

¹ Laboratory of Solid State Physics and Magnetism, KU Leuven, Belgium ² Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany ³ Department of Chemistry, KU Leuven, Belgium

Hydrogen is a clean and sustainable alternative to the use of fossil fuels for our energy supply. Despite having a high gravimetric energy density, the volumetric density of hydrogen is too low to be of practical use. Solid state storage of hydrogen in metal hydrides such as NaAlH₄ increases the volumetric density but often suffers from slow (de)hydrogenation kinetics or irreversibility. The study of clusters in the gas phase allows for a detailed understanding of the thermodynamics and kinetics at play and could aid in the development of improved hydrogen storage materials.

We investigated the interaction of hydrogen with $Al_nRh_2^+$ (n = 10-13) clusters by mass spectrometry and infrared multiple photon dissociation (IRMPD) spectroscopy performed at the FEL facility of the Fritz-Haber-Institut [1,2]. Comparing the IRMPD spectra with predictions obtained using density functional theory calculations allows for the identification of the hydrogen binding geometry. We observed a competition between molecular and dissociative adsorption: for n = 10 and 11, a single H₂ molecule binds dissociatively, whereas for n = 12 and 13, it adsorbs molecularly. Upon adsorption of a second H₂ to $Al_{12}Rh_2^+$, both hydrogen molecules dissociate and spillover to the aluminum. Theoretical calculations suggest that the molecular adsorption is not due to kinetic impediment of the hydrogenation reaction by an activation barrier, but due to a higher binding energy of the molecularly adsorbed hydrogen–cluster complex.



Figure 1: IRMPD spectra of $Al_{12}Rh_2H_{2m}^+$ (m = 1, 2). For m = 1, he bands at 800 cm⁻¹ and 1600 cm⁻¹ correspond to molecularly bound H_2 -M vibrational modes. For m = 2, only bands at 1900 cm⁻¹ are observed, corresponding to dissociatively adsorbed hydrogen.

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Activation of H₂O by Single Atomic Metal Anions

Sandra M. Ciborowski¹, Gaoxiang Liu¹, Xinxing Zhang^{1*}, Kit H. Bowen¹ and Sotiris Xantheas² and Evangelos Miliordos^{2#} and Ueli Heiz³, Martin Tschurl³, and Ulrich Boesl³

 ¹ Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, 21218, USA
 ² Pacific Northwest National Laboratory, Richland, Washington, 99354, USA
 ³Institute for Physical Chemistry, Technical University of Munich, 85748 Garching, Germany
 ^{*} Present address: Department of Chemistry, California Institute of Technology, Pasadena, California, USA

[#] Present address: Department of Chemistry, Auburn University, Auburn, Alabama, USA

The search for the production of clean energy, often in the form of hydrogen from the splitting of water, is a significant scientific challenge.¹⁻³ The activation of water molecules, which leads to water splitting, is accomplished by single Group 10 metal anions of platinum, palladium, and nickel. We present anion photoelectron spectra of $[Pt(H_2O)]^-$, $[Pd(H_2O)]^-$, and $[Ni(H_2O)]^-$. With the support of high-level calculations by Xantheas and Miliordos, the physisorbed, anion-molecule complexes, M⁻(H₂O), and the water-activated intermediates, HMOH⁻, where M = Pt, Pd, or Ni, were identified. The combination of experimental and computational methods also provided evidence of the intermediate, H₂PtO⁻ in the anion photoelectron spectrum, and of the final products, PtO⁻ in the anion mass spectrum and H₂⁺ in the cation mass spectrum. The single-atom anions of platinum, palladium, and nickel activated single water molecules to different extents.

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Sequential H₂O Activation and CO₂ Hydrogenation by Single Platinum Atomic Anion

Gaoxiang Liu, Sandra M. Ciborowski, Zhaoguo Zhu, Kit H. Bowen

Department of Chemistry, Johns Hopkins University, Baltimore, Maryland, 21218, USA

Water activation and CO_2 hydrogenation are two important reactions for generating clean energy and alleviating global warming. Recently, we have demonstrated that single platinum atomic anion can activate either H_2O or CO_2 molecules. For H_2O activation, we verified the existence of the activated intermediate HPtOH⁻. In this work, we integrated these two important activation processes together: the platinum/water binary intermediate, HPtOH⁻, was used to hydrogenate the other molecule, CO_2 . Their tertiary anionic intermediate, $[Pt(H_2O)(CO_2)]^-$, was observed in the mass spectrum. In addition to seeing the intermediate, we also observed the CO_2 hydrogenation product, formate. The anion photoelectron spectrum and DFT calculation complemented each other and revealed the presence of a formate moiety within $[Pt(H_2O)(CO_2)]^-$.

Probing the Infrared Signature from Structural Isomers of Metal-N₂O complexes

<u>Ethan M. Cunningham</u>, Alexander S. Gentleman, Peter W. Beardsmore, Alice E. Green, Andreas Iskra & Stuart R. Mackenzie

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

Metal cations and their interactions with ligands are widespread in chemistry, serving both as prototypes for bonding in inorganic and organometallic chemistry and playing a pivotal role in catalytic processes. The ligand of interest in this work, nitrous oxide, is a potent greenhouse gas,¹ implicated in depletion of stratospheric ozone.^{2,3} The atmospheric concentration of N₂O is estimated to be increasing between 0.5–0.9 ppb per annum largely due to anthropogenic sources such as fossil fuel usage and agriculture.¹ Methods of reducing N₂O, in particular by metal-catalyzed decomposition, are thus of great interest.⁴ In particular, significant attention has been directed towards reduction of N₂O to N₂ at metal centres. In this regard, N₂O can act as a clean and highly-selective oxygen donor for catalytic oxidation processes.

Here we report infrared laser photodissociation spectroscopy studies of $M^{+}(N_2O)_n$ -Ar, (M = Li, Al, Cu, Ag, Au, Co, Rh, Ir; n = 2-7) complexes in the region of the v₃ stretch of N₂O.⁵ Spectral bands are assigned with the help of density functional calculations of energetically low-lying isomeric structures. These clusters are analysed in terms of N₂O ligands binding *via* the N atom or the O atom resulting in characteristic shifts in the v₃ (N-N) stretch of the N₂O, providing an insight into the M⁺-N₂O binding and the barrier to internal rotation. In some cases, evidence of insertion reactions is also observed.

It is comparatively unusual for one ligand to bind in multiple arrangements, and the ability to selectively excite one binding motif over another, as demonstrated here, offers the tantalizing prospect of driving mode-selective reactivity in different structural isomers.



Figure 1: *Left* calculated potential energy surface for the Au⁺N₂O complex, *right* IR-REPD spectrum of Au⁺(N₂O)₂-Ar showing two spectrally distinct bands, N-bound (blue) and O-bound (red) N₂O.

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Size effects in the activation of CO₂ on platinum cluster anions

<u>Alice E. Green</u>,¹ Jasmin P. Justin,² Alexander S. Gentleman,¹ Wieland Schöllkopf,² Ethan M. Cunningham,¹ Andreas Iskra,¹ André Fielicke² and Stuart R. Mackenzie¹

¹ Physical and Theoretical Chemistry, University of Oxford, United Kingdom ² Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

 CO_2 has high potential as a C-1 feedstock, providing a potentially cheap and abundant source of carbon in industrially important reactions. With this in mind, we demonstrate the ability to tune the degree of CO_2 activation induced in molecules adsorbed on small transition metal clusters, by means of changing cluster size.

Here we report the results of IR free electron laser photodissociation experiments, exploring the nature of carbon dioxide binding on isolated platinum cluster anions, Pt_n^- (*n*=4-7). The CO₂ binding motifs observed illustrate clear size-dependence, indicative of a change from molecular to dissociative (i.e. completely activated) adsorption. Of potential practical significance, CO₂ is observed to be molecularly-bound but highly activated on the Pt_4^- tetramer cluster anion. It is trapped behind a barrier to dissociation on the potential energy surface, which prevents access to the global minimum, dissociated structure.



Towards imaging the dynamics of C-H bond activation by transition metal ions

Jennifer Meyer, Franziska Krammer, Tim Michaelsen, Björn Bastian, Roland Wester

Institute for Ion Physics and Applied Physics, University of Innsbruck, AT

We present an experiment aiming at imaging the reaction dynamics of transition metal cations with small molecules like methane and hydrogen. Our aim is to get a deeper understanding of the factors steering the reactivity of transitions metal mediated catalytic cycles by understanding the dynamics of the elementary reaction steps.

Gas phase experiments can help to understand complex reaction systems by providing model systems and investigating individual elementary reactions one by one [1-3]. The use of crossed beams in combination with velocity map imaging allows the measurement of differential cross sections [4]. These give insight into the dynamics of the reaction and thus how atoms rearrange during a reaction and how energy is partitioned within the available degrees of freedom. Our group has investigated reaction dynamics ranging from charge transfer reactions to complex organic transformations [5,6].

First experiments are planned on the activation of methane by tantalum Ta^+ , iron Fe^+ and iron oxide FeO^+ cations. We have built a laser vaporization source and interfaced it with a velocity map imaging spectrometer. Here, we present first experimental results along the way towards imaging the C-H bond activation. We have characterized the ion beams of Fe^+ and Ta^+ produced by laser vaporization using velocity mapping. The first reaction to be investigated will be the reaction of $Ta^+ + CH_4$. The main product channel is the formation of the carbene $TaCH_2^+$ under hydrogen elimination. The reaction takes place at room temperature and will allow us to optimize the experimental setup.

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P6

Caiyun Geng,[†] Thomas Weiske,[†] Jilai Li,^{†,‡,*} Sason Shaik,^{§,*} and Helmut Schwarz^{†,*}

[†]Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 115, 10623 Berlin, Germany

[‡]Institute of Theoretical Chemistry, Jilin University, Changchun 130023, PR China [§]Institute of Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

The thermal activation of the C–H bond of methane by the diatomic carbide cations $[M-C]^{+}$ of the first row 3d transition metals Sc – Zn was elucidated by quantum chemical calculations at the NEVPT2//CASSCF level. Experimentally the reactivities were verified for M = Ti, V, Fe and Cu by using Fourier transform ion cyclotron resonance mass spectrometry. According to theory, $[M-C]^+$ species with M = Sc, Ti, V, Cr, Cu and Zn are able to activate methane at ambient conditions. In contrast, much too high energy barriers prohibit abstraction of a hydrogen atom for M = Mn, Fe and Co. $[Ni-C]^+$ is predicted to exhibit a small barrier and may react under multiple collision conditions. The theoretical analysis shows that the transfer of a hydrogen atom from methane to the metal carbide cation proceeds via proton-coupled electron transfer for M = Sc - Co. Classical hydrogen-atom transfer is involved only in the case of Ni, while the metal carbides of Cu and Zn follow a hydride transfer mechanistic scenario. [Cu–C]⁺ is the only carbide that reacts by an unprecedented, synchronous transfer of two hydride ions to produce directly $[Cu(C_2H_4)]^{\dagger}$. One of the more important and quite unexpected findings concerns the role of spin density at the hydrogen-acceptor carbide site. While this feature is so crucial for $[M-O]^{\dagger}/CH_4$ couples, it is much less important for the C-H bond activation chemistry of metal-carbide cations of the 3d transition metal series.

Gas-phase Reactivities of Silicon-Containing Ions for C–H Bond Activation and Catalytic Redox Reactions

Xiaoyan Sun¹, Shaodong Zhou^{1,2}, Lei Yue¹, Maria Schlangen¹, Helmut Schwarz¹

¹ Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

² Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, 310027 Hangzhou, P. R. China

Silicon oxide constitutes one of the most important catalyst support widely used in many large-scale chemical transformations.^[1] Understanding the mechanistic aspects of bond activation by silica catalysts is still rather limited despite the many surface-characterization methods used in condensed phase. Studies on gas-phase reactions of oxide clusters have provided meaningful insight concerning the elementary steps of catalytic processes, and fundamental physical and chemical behavior of catalytic materials have thus been revealed at a strictly molecular level.

The recent results in our group regarding the reactivities of the silicon-containing cations for the C–H bond activation of methane and catalytic redox reaction $CO + N_2O \rightarrow CO_2 + N_2$ in the gas phase are presented. The cluster ions $[OSiOH]^+, ^{[2]} [Si_2O_5H_2]^+, ^{[3]}$ and $[Si_2O_4]^{+[4]}$ can efficiently activate methane under thermal conditions. Furthermore, $[Si_2O_x]^+$ (x = 2-5) can mediate the catalytic reduction of N₂O by CO, and three sequential oxygen-atom transfers with full catalytic redox cycles are acchieved at room temperature.^[5] All these results may serve as the first step to interpret effects of silica support or its catalytic active role which have been extensively studied in the related condensed phase.



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Cryo IR Spectroscopy of N_2 and H_2 on Ru_8^+

<u>Annika Steiner</u>¹, Sebastian Dillinger¹, Matthias P. Klein¹, David C. McDonald II², Michael A. Duncan², Manfred M. Kappes³, and Gereon Niedner-Schatteburg¹

 ¹Fachbereich Chemie and Forschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany
 ²Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA
 ³Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

It is a pending challenge to characterize the interaction of N_2 and H_2 with transition metal surfaces and clusters in detail. We have utilized our tandem cryo trap instrument to investigate N_2 adsorption on Co [1], Ni [2] and Rh [3] clusters.



Figure 1: The instrumental setup with different sequences of adsorption on the Ru₈⁺ cluster.

Here, we present the cryo IR spectra of $[Ru_8(H_2)_1]^+ l = 1 - 8$, $[Ru_8(N_2)_m]^+ m = 1 - 8$, and the coadsorbed $[Ru_8(H_2)_1(N_2)_4]^+$ and $[Ru_8(N_2)_4(H_2)_1]^+$ species in isolation. The $[Ru_8(H_2)_1]^+$ species with l > 1 reveal bands in the region of 1800 cm^{-1} to 1880 cm^{-1} , which are a strong evidence for the formation of a hydride species. The $[Ru_8(N_2)_m]^+$ species reveal features redshifted to the free N₂ vibration (2300 cm⁻¹) in the region of 2190 to 2300 cm⁻¹, which are attributed to the vibration of head on adsorbed N₂. The H₂-N₂-coadsorbates $[Ru_8(H_2)_1(N_2)_4]^+$ and $[Ru_8(N_2)_4(H_2)_1]^+$ species reveal spectral differences in the hydride region of the IR spectra. We interpret these differences to different positioning of the hydrides on the Ru cluster. This positioning is influenced by the sequence of adsorption (first H₂ and then N₂ or first N₂ and then H₂) and the possibility of migration of the hydrides on the Ru₈⁺ cluster [4].

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Spectroscopic characterization of copper clusters for catalytic CO₂ fixation

<u>O.V. Lushchikova</u>^a, D.M.M. Huitema^a, L. Visscher^b, Z. Jamshidi^b, J.M. Bakker

^aFELIX Laboratory, Radboud University, Toernooiveld 7c, 6525 ED Nijmegen, the Netherlands ^bCenter for multi scale modeling, VU University, De Boelelaan 1081, 1081 HV Amsterdam, the Netherlands

The catalytic recycling of CO_2 to liquid fuels, such as methanol, may help to control the atmospheric CO_2 content and, therefore, reduce climate change and its societal impact. Currently, methanol is produced industrially from syngas (CO_2 -CO-H₂) under high temperature and pressure conditions over a Cu catalyst. A broad range of studies suggests that the most active parts of the industrial catalyst are Cu nanoparticles.

To increase understanding of this reaction, we study the interaction of CO₂ and H₂ with copper clusters as well-defined model systems with many undercoordinated adsorption sites. First, we elucidate the structure of cationic Cu clusters through IR photodissociation spectroscopy of their complexes with Ar. The structures are assigned based on the comparison of experimental IR spectra in the 70-300 cm⁻¹ spectral range with spectra calculated using density functional theory (DFT), and, for select sizes, with Born-Oppenheimer molecular dynamics (BOMD). In subsequent steps, we are currently examining the reactions of Cu clusters with CO₂ and H₂.



Figure 1: Figure: Experimental spectrum of $Cu_7^+Ar_3$ (top panel) and spectra calculated using BOMD and DFT calculations

Gas phase UV/VIS spectroscopy on Au₄⁺

M. Förstel, W. Schewe, B. K. A. Jaeger and O. Dopfer

Inst. für Optik und Atomare Physik, Technische Universität Berlin

Part of the broad interest in the electronic properties of gold nanoparticles and clusters is due to their catalytic applications and properties [1]. Nanometer-sized gold-containing particles are discussed as oxygen activator, assisting in the oxidation of CO [2]. Small cationic gold cluster show size dependent C-H bond cleavage properties [3].

Here we present high resolution optical absorption spectra of Au_4^+ in the range of the first few optically active excited states, i.e. in the range of 400 to 600 nm. The spectra are obtained via laser-induced photodissociation spectroscopy. The Au_4^+ clusters are produced via laser desorption and are cooled to about 100 K via expansion through a cold nozzle. We observe at least four distinct excited states. All transitions are vibrationally broadened. We can quantify four vibrational frequencies of the lowest observed excited state. The spectral quality is improved by at least an order of magnitude with respect to resolution and signalto-noise ratio as compared to previous results [4]. For the first time, this allows a direct comparison of the experimental spectra with TD-DFT based Franck-Condon simulations, with the aim of distinguishing the two low energy isomers (rhombic and Y-shaped) of Au_4^+ .[5-7]



Figure 1: Photodissociation cross section of $Au_4^+ + hv \rightarrow Au_3^+ + Au$ as a function of excitation energy in the region of the 0-0 vibrational transition of the first observable electronic transition. Red and green traces were recorded using a dye laser with sub cm⁻¹ resolution. The black trace was recorded using an OPO laser with a resolution in the order of 5 cm⁻¹.

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Preparation of binary ruthenium-siliconoxide-cluster for COmethanation

P. Walter, S. M. Lang, T. M. Bernhardt

University of Ulm, Institute of Surface Chemistry and Catalysis, Germany

Currently, one of the most important research areas in energy science is the electrochemical energy conversion. The conversion can be accomplished in fuel-cells, in which a mixture of hydrogen- and oxygen-gas is electrochemically converted to produce energy. The platinum catalyst in fuel-cells reacts very sensitive to carbon monoxide, which is present in the feed-gas, due to the production process of hydrogen, and which poisons the platinum catalyst irreversible. To maintain the long-term activity of the platinum catalyst and hence the fuel cell, a refinement of the feed-gas is crucial. One way to achieve a carbon monoxide free hydrogen gas is to convert carbon monoxide via methanation to methane, which is harmless to the platinum catalyst. A catalytic system based on ruthenium clusters supported on zeolites appears promising to achieve this goal. Ruthenium nano-particles smaller than 1 nm showed a very high activity and selectivity for the methanation-reaction of carbon monoxide [1,2].

To further examine the catalytic properties of ruthenium clusters a new experimental setup was designed based on the magnetron sputter technique to produce clusters of various sizes. A quadrupole mass filter in combination with an ion trap allows the probing of size selected clusters and their catalytic behavior. In particular, binary ruthenium-siliconoxide-clusters will be prepared this way to study mechanistic details of the zeolite-supported ruthenium catalyzed CO methanation reaction.



Figure 1: Product mass spectrum (intensity in arbitrary units) obtained after the gas-phase reaction of Ru_4^+ with CO and D_2 for 0.1 s. The corresponding calculated DFT structure of $H_5Ru_4(CO)_{12}^+$ is shown as an inset (Ru, C, O, and H atoms are indicated by green, gray, red and white spheres, respectively). (DFT Calculations by V. Bonačić-Koutecký) [2]

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Gold clusters as catalysts for the selective conversion of methane: New insights from IR multi photon dissociation spectroscopy

<u>Sandra M. Lang</u>,¹ Thorsten M. Bernhardt,¹ Valeriy Chernyy,² Joost M. Bakker,³ Robert N. Barnett,⁴ Uzi Landman⁴

¹Institute of Surface Chemistry and Catalysis, University of Ulm, Germany ²Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands ³Institute for Molecules and Materials, FELIX Laboratory, Nijmegen, The Netherlands ⁴School of Physics, Georgia Institute of Technology, Atlanta, Georgia, USA

Amongst all the metals gold exhibits the least inclination to undergo chemical reactions with other elements. It is therefore even more surprising that few nanometer sized gold particles and gold clusters consisting of very few atoms display excellent catalytic properties. Mild reaction conditions and the propensity to activate molecular oxygen for the selective oxidation of small hydrocarbon molecules render gold clusters ideally suited for environmentally friendly and sustainable catalytic oxidation chemistry. A major, hitherto unsolved problem in this respect is the selective activation and partial oxidation of the smallest hydrocarbon, methane. The selective activation of the stable sp3-C-H bond is exceedingly difficult and complex.

In order to demonstrate the ability of small gold clusters to activate methane, we previously performed gas phase reaction kinetics experiments in an octopole ion trap [1, 2]. These experimental studies revealed the particular catalytic properties of the gold dimer Au_2^+ to activate methane and to convert two methane molecules to ethylene at thermal reaction conditions [1]. These experiments have now been complemented by infrared multi photon dissociation experiments employing the free electron laser FELICE at the University of Nijmegen [3]. These spectroscopy investigations demonstrated that the interaction of methane with small gold cluster cations leads to selective C-H-bond dissociation and the formation of hydrido-methyl complexes $H-Au_x^+-CH_3$. The unique selectivity offered by these gold clusters originates from a fine interplay between the closed-shell nature of the gold d-bands, which in principle should leave them unavailable for binding with methane, and relativistic effects that make them available. Such fine balance in fundamental interactions could prove a 'tunable' feature in rational catalyst design.

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Catalytic Investigations and Stabilities of AuPd Sub-nanometre Clusters

Heider A.Hussein and Roy L. Johnston

School of Chemistry, University of Birmingham, Birmingham B15 2TT, United Kingdom

Sub-nanometre clusters can be defined as groups or aggregates of a few to tens of metal atoms which are below 1.0 nm in size. These clusters may contain the same atoms, giving pure clusters, or two or more different atoms presenting hetero-clusters. These clusters are attracting significant interest, e.g. in catalysis, where they offer the advantages of size-selection and tuning of selectivity or reactivity.

I will present the BPGA-DFT approach, with applications to: the study of the segregation and 2D-3D transition in (4-18) atom mono- and bi-metallic clusters of Au and Pd. We performed global optimization calculations on gas-phase and MgO(100)-supported subnanometre AuPd alloys. The energetics, structures, and tendency of segregation have been evaluated by different stability criteria such as binding energy, excess energy, second difference in energy, and adsorption energy. The role of cluster size, presence of Pd doping, and effect of MgO(100)-surface were found to be significant, and non-monotonic in altering cluster stability and structural behaviour. The ability of the approach in searching for putative global minimum has been assessed against a systematic homotop search method, which shows a high degree of success. I will also mention recent calculations on the direct DFT global optimisation of sub-nanometre mono-cationic Au-Pd clusters.

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Cryo kinetics and IR spectroscopy of N₂ adsorbed to size selected Rhodium and Rhodium Iron alloy cluster cations

<u>Matthias P. Klein</u>¹, Amelie A. Ehrhard¹, Annika Steiner¹, Sebastian Dillinger¹, Jennifer Mohrbach¹, and Gereon Niedner-Schatteburg¹

¹ Fachbereich Chemie and Forschungszentrum OPTIMAS, TU Kaiserslautern, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany

It is a pending challenge to characterize the interaction of N_2 and H_2 with transition metal surfaces and clusters in detail. We have utilized our tandem cryo trap instrument to investigate N_2 adsorption on Fe, Co [1], Ni [2], Rh [3] and Ru [4] clusters.

Here, we recorded N₂ adsorption kinetics and InfraRed-PhotoDissociation (IR-PD) spectra of the isolated cluster adsorbate complexes $[Rh_i(N_2)_m]^+$ i = 6 - 15 and m = 1 - 16. In conjunction with DFT modelling, the measurements allow for assignments of the adsorbate arrangement and the cluster core structure. The observed adsorption limits m_{max} reveal a strong cluster size dependency, some of the clusters reveal an additional intermittent adsorption limit. A single maximum adsorption limit is interpreted in terms of a smooth cluster surface, a pronounced intermittent maximum is indicative of a rough surface with non-equivalent surface atoms. By combination of IR-PD spectroscopy and DFT modelling we could observe a spin quenching with increasing N₂ coverage as well as an adsorption induced relaxation of the cluster structures for Rh₆⁺, Rh₇⁺, and Rh₉⁺ [4].

The spectroscopic analysis of equiatomic $[Rh_nFe_n(N_2)_m]^+$ cluster cations allows for discriminating Rh and Fe adsorption sites and reveals a preference for adsorption of N₂ to Rh sites.



Figure 1: An additional N₂ most likely adsorbs to a Rh site on a $[Rh_3Fe_3(N_2)_6]^+$ cluster.

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Dehydrogenation Processes Using Mixed Silicon Clusters Si_nM (n = 2, 3; M = Si, Be, Mg, Ca) As a Catalyst

Dieu Hang Tran¹, Minh Tho Nguyen¹

¹Department of Chemistry, University of Leuven, Belgium

High-accuracy quantum chemical calculations were carried out to study the mechanisms and catalytic abilities of various mixed silicon species SinM toward first step of methanol activation and water splitting reactions.[1-3] Potential-energy profiles were constructed using the coupled-cluster theory with extrapolation to complete basis set CCSD(T)/CBS. Concerning the methanol activation reaction, the cleavage of the O-H bond is favored over that of the C–H bond. Most importantly, the energy barriers for the O–H bond breaking on the singlet Si₃, Si₂Ca, and Si₃Ca clusters are found to be lower than the previously reported results for metal clusters, catalytic metal surfaces, metal oxides, etc. In the case of water splitting reactions, substitution of a Si atom in Si₄ by an earth alkaline metal induces a substantial reduction of the energy barrier for the (rate-limiting) first O - H bond cleavage of water dimer. The most remarkable achievement upon doping is a disappearance of the overall energy barrier for the initial O-H bond cleavage in water dimer. Of the three binary Si₃M clusters considered, dehydrogenation of water dimer driven by Si₃Be is the most kinetically and thermodynamically favorable pathway. In comparison to another cluster such as Al₆ and nanoparticles Ru₅₅, energy barriers for water dimer dissociation on Si₃M are much lower. The small mixed Si clusters thus appear as efficient alternative reagents for O - H dissociation, methanol activation and hydrogen production from water dimer and most probably in other dehydrogenation processes from the X–H bonds of organic compounds. This study proposes further searches for other mixed silicon clusters as realistic gas phase reagents for crucial dehydrogenation processes in such a way they can be prepared and conducted in experiment.

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Chemical processes in van der Waals complex TiO₂-O₂ as a model of photocatalytic processes on the surface of titanium dioxide: An ab initio investigation

Alexey V. Baklanov^{a,b}, Georgii A. Bogdanchikov^{a,b},

^a-Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia ^b-Novosibirsk State University, Novosibirsk 630090, Russia

Titanium dioxide (TiO_2) based materials are most widely used photocatalysts. Oxidative processes on the surface of photocatalyst proceed with participation of oxygen. It is known that singlet oxygen is generated when TiO_2 is UV-irradiated in the presence of oxygen [1]. Very recently we have revealed that singlet oxygen can react without barrier with TiO₂ giving rise to a stable titanium peroxide [2] shown in Figure 1. Taking into account high reactivity of superoxides the mechanism of its formation is interesting. In the presented work the processes of peroxide formation are investigated for interaction of TiO₂ with both singlet and ground triplet states of oxygen. Two approaches CAS(12,8)/6-311+G(2d,2p) and CCSD/6-311+G(2d,2p) are applied. It is found that both singlet and triplet states of oxygen give rise to peroxide TiO_4 via conical intersections with the singlet and triplet charge-transfer states of TiO₂-O₂ pair. In contrast with a singlet potential energy surface (PES) the reaction on the triplet PES has essential barrier on the way to superoxide. Revealed triplet and singlet states of peroxide have near equal energy close to 30 kcal/mole with similar equilibrium geometry. The demands to the geometry of reacting pair provided by orbital symmetry conservation rules are considered.



Figure 1. The structure of stable titanium peroxide TiO₄.

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How Do Ligand Effect, Electric Field, and Relativistic effect work? A Story from Thermal Methane Activation via the Zinc-oxide Triads

<u>Lei Yue¹</u>, Helmut Schwarz¹

¹ Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

The thermal reactions of bare diatomic zinc-oxide triads $[MO]^{*+}$ and the ligated complex $[(CH_3CN)MO]^{*+}$ (M = Zn, Cd, Hg) towards methane have been explored by gas-phase ion/molecule reactions combined with high-level quantum chemical calculations. When methane reacts with two lighter congeners $[MO]^{*+}$ (M = Zn, Cd), it generates $CH_3^{*}/[M(OH)]^{+}$, $HO^{*}/[M(CH_3)]^{+}$, and CH_3OH/M^{*+} . In contrast, the reaction of $[(CH_3CN)MO]^{*+}$ with CH_4 gives rise to a single product, $CH_3^{*}/[(CH_3CN)(MOH)]^{+}$, resulting from hydrogen-atom abstraction. The origin of the remarkable ligand effect on mechanistic switch are discussed and modeled by an oriented external electric field (OEEF).^[1]

Interestingly, protonated formaldehyde $[CH_2OH]^+$ has been generated as a major product only for the $[HgO]^{*+}/CH_4$ couple. Mechanistic insight is provided by high-level quantum chemical calculations, and relativistic effects are suggested to be the root cause for the unexpected thermal production of $[CH_2OH]^+$ from $[HgO]^{*+}/CH_4$.^[2]



Figure 1: a) thermal methane activation variants induced by a) ligand effect and oriented external electric field (OEEF),^[1] b) relativistic effects.^[2]

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On the Origin of the Distinctly Different Reactivity Behavior of Ruthenium in [MO]⁺/CH₄ Systems (M = Fe, Ru, Os)

Xiaoyan Sun,¹ Shaodong Zhou,^{1,2,*} Lei Yue,¹ Maria Schlangen,¹ and Helmut Schwarz^{1,*}

¹ Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

² Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, 310027 Hangzhou, P. R. China

The thermal gas-phase reactions of $[RuO]^+$ with methane have been explored by using FT-ICR mass spectrometry complemented by high-level quantum chemical calculations. In contrast to the previously studied $[FeO]^+/CH_4$ and $[OsO]^+/CH_4$ couples which bring about oxygen/hydrogen atom transfers and dehydrogenation, respectively, $[RuO]^+/CH_4$ produces selectively $[Ru(CH)_2]^+$ and H_2O but with much lower efficiency. Various mechanistic scenarios were uncovered, and the associated electronic origins were revealed by high-level quantum chemical calculations. It is the subtle interplay of spin-orbit coupling efficiency, orbital overlap, and relativistic effects that causes the reactivity differences observed for the $[MO]^+/CH_4$ couples (M = Fe, Ru, Os).



Figure 1: Simplified Potential energy surface and selected structural information for the reaction of $[RuO]^{+}$ with CH_4 .

Water oxidation reaction with manganese oxide clusters

N. T. Zimmermann, S. M. Lang, T. M. Bernhardt

Institute of Surface Chemistry and Catalysis, University of Ulm, Germany

One of the fundamental biological reactions, the catalytically activated water-splitting, takes place at an inorganic mono-calcium tetra-manganese penta-oxygen (CaMn₄O₅) cluster. To probe fundamental concepts of the water splitting reaction and to aid the design of artificial water-splitting molecular catalysts we prepare free manganese-oxide clusters as welldefined model systems and study their reactivity in an ion trap experiment. Recent studies from our laboratory mainly focused on the stoichiometric $Mn_4O_4^+$ cluster. Reactivity experiments in conjunction with infrared-vibrational spectroscopy have demonstrated that this tetra-manganese-tetra-oxygen cluster adsorbs multiple water molecules and deprotonates water by hydroxylation of the oxo-bridges of the cluster [1-4].

To improve the reactive properties of manganese-oxide clusters and to potentially enable the oxidation of water we have now extended our studies to non-stoichiometric clusters. In particular, clusters with an increased formal oxidation state of the manganese atoms are expected to show improved properties as an oxidizing catalytic agent for water [5]. Therefore, we focused our investigations on the reactivity of oxygen-rich species $Mn_xO_y^+$ (x < y) towards D_2O and H_2O .



Figure 1: Mass spectra of manganese oxide clusters without (a) and with (b) additional O₂ gas in the target chamber.

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Gas-phase experiments with calcium-manganese-oxide clusters

Silvia Mauthe, Sandra M. Lang, Thorsten M. Bernhardt

Institute of Surface Chemistry and Catalysis, University of Ulm, Germany

Calcium-manganese oxides are of great current interest regarding the biomimetic activation and oxidation of water. However, few is known so far concerning the activity of calciummanganese-nanoclusters in this reaction. Therefore, in this contribution, the possibility to prepare free calcium-manganese-oxide clusters as well-defined model system in the gasphase is investigated with the further aim to study their activity as water splitting catalysts. To probe fundamental concepts of the water splitting reaction and to aid the design of artificial water-splitting molecular catalysts we studied their reactivity in an ion trap experiment.

The catalytically activated water-splitting takes place at an inorganic mono-calcium tetramanganese penta-oxygen (CaMn₄O₅) cluster. For this reason, we investigated the pentamer species with addition of a calcium atom in the gas-phase. In particular, clusters with an increased formal oxidation state of the manganese atoms are expected to show improved properties as an oxidizing agent for water. Therefore, we focused our investigations on the reactivity of oxygen-rich species CaMn_xO_y⁺ (x<y) towards D₂O and H₂O.

Theoretical perspective on the $FeAI_7O_{12}^+$ cluster. Structure, vibrations and spin.

<u>Stephen Leach</u>¹, Knut Asmis,² Joachim Sauer¹

¹ Department of Chemistry, Humboldt University Berlin, Germany ² Wilhelm Oswald Institute for Physical and Theoretical Chemistry, University of Leipzig, Germany

The cluster $Al_8O_{12}^{+}$ has a predicted structure which deviates from that expected from the corundum structure [1]. It features a terminal Al-O bond with high spin density on the apical oxygen, suggesting radical oxygen. This explains its HAT reactivity as observed with methane [2]. IRPD data has been collected for the mono-substituted cluster $FeAl_7O_{12}^{+}$. Its reactivity towards methane is found to be reduced. In this work DFT calculations are carried out to ascertain the cluster connectivity and to characterize the Fe center. Vibrational analysis supports that the cluster connectivity is unchanged and that Fe substitutes at the apical position as shown in figure 1. The reduced reactivity is explained by the loss of the radical oxygen in favour of Fe(IV) and closed shell oxygen. Although high spin d⁴ Fe(IV) is predicted to be most stable at the hybrid GGA functional level, lower spin states exhibit shorter bonding distances for the Fe-O unit, these correlate with higher calculated stretching frequencies which better match the unusually high frequency signal observed.



Figure 1: IRPD spectrum from K. Asmis. With proposed structure from DFT inset.

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FT-ICR MS studies of thiomolybdate clusters as model catalysts for hydrogen evolution

Aristeidis Baloglou, Milan Ončák, Christian van der Linde, Martin K. Beyer

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

Molybdenum sulfide-based catalysts have the potential to replace platinum as a hydrogen evolution reaction (HER) catalyst in electrochemical water splitting.¹ A better understanding of the reaction mechanisms contributes to the targeted optimization of the catalysts. In this contribution, individual reaction steps are investigated quantitatively employing precisely defined gas-phase models, like [${}^{92}Mo_3S_{13}$]²⁻ and [${}^{92}Mo_2S_{12}$]²⁻. Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) is used, as it is an excellent tool to examine ion-molecule reactions in the gas phase,² including catalytic cycles. By combining FT-ICR MS with IR and UV/VIS laser spectroscopy, the reactants, products and reactive intermediates can be further characterized. For example, IR-spectroscopy experiments on protonated [H⁹²Mo₃S₁₃]⁻ show a distinct H-S stretching vibration (Fig. 1). Comparing this result with density functional theory (DFT) calculations suggests that the proton is bound to an edge disulfide unit of the cluster.



In gas phase, the cluster $[Mo_3S_{13}]^{2-}$ unfolds from the highly symmetrical Mo₃-ring structure, found in the solid state, to form irregular structures with a variety of mono- and disulfide ligands. Structural changes are also expected for molybdenum sulfide clusters deposited on electrodes. Investigation of the structural flexibility and chemical properties of the different sulfur moieties contributes to an understanding of the catalytic activity of molybdenum sulfide surfaces.

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A Gas-Phase Model for Dissecting Transmetallation Reactions at the Molecular Level

<u>Thomas Auth</u>¹, Konrad Koszinowski,¹ Richard O'Hair²

 ¹ Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstraße 2, 37077 Göttingen, Germany
 ² School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, 30 Flemington Rd, Parkville, Victoria 3010, Australia

Transmetallation is a key elementary step for both the stoichiometric preparation of organometallic reagents and transition-metal catalyzed cross-coupling [1,2]. Despite this great importance of transmetallation reactions, only little is known about their fundamental mode of operation and mechanistic details [3].

Inspired by crystallographic data related to the transmetallation of silver salts with tetraarylborates [4,5], we have studied solutions of AgOTf and LiBPh₄ in MeCN with ESI mass spectrometry in order to obtain information at a strictly molecular level. The ESI mass spectra showed $M_n(BPh_4)_{n+1}^-$ and $M_n(BPh_4)_{n-1}^+$ species (M = Li, Ag), whose unimolecular reactivity was probed by collisional activation. In line with the results from quantum chemical calculations, we observed transmetallation for anionic and cationic tetraphenyborate-containing silver complexes whereas the lithium counterparts merely dissociated. Moreover, the quantum chemical calculations revealed that the transmetallation steps are energetically less demanding than the subsequent dissociation of the corresponding product complexes.

In conclusion, by means of the powerful combination of gas-phase experiments and quantum chemical calculations, we were able to tackle the questions of how transmetallation depends on the metal, the charge and the oligomeric state for tetraphenylborate-containing complexes. The versatility of this approach holds great promise for a systematic and comprehensive investigation of transmetallation reactions.



Figure 1: Gas-phase reactivity and transmetallation transition structure of [Ag(BPh₄)₂]⁻.

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Hydrated Metal Ions M⁺(H₂O)_n as Model Systems for Photochemical Production of Hydrogen

M. Ončák, T. Taxer, D. Muß, E. Barwa, J. Franke, C. van der Linde, M. K. Beyer

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

Hydrated metal ions $M^+(H_2O)_n$ are well-defined systems that enable the study of fundamental chemical processes under controlled conditions, both experimentally and theoretically. Even for a low number of hydrating water molecules, they show non-intuitive trends in the electronic ground state as well as in excited states, as seen e.g. in the case of $Mg^+(H_2O)_n$ clusters.[1,2] Investigation of hydrated transition metals is further complicated by the absence of clear reactivity trends already in the electronic ground state.[3]

Here, we study the $M^+(H_2O)_n$ clusters, M = Mg, Al, V, with a focus on photochemical evolution of hydrogen. To measure the photodissociation spectra, we use a Fourier-

transform ion cyclotron resonance mass spectrometer (FT-ICR MS) coupled to a tunable OPO laser system. At the same time, we model photochemical behavior employing methods of theoretical chemistry: *ab initio* calculations, spectrum modeling within the reflection principle or Franck-Condon approximation and molecular (photo)dynamics.

We show that hydrated Mg^+ and Al^+ have similar photochemical behavior while for hydrated V^+ , its transition metal character induces more complicated photochemistry with many low-lying electronic states. We also discuss the importance of two-photon processes in hydrogen evolution.



Figure 1: Scans along the hydrogen evolution coordinate in $Mg^+(H_2O)_n$, n = 1-2, in various electronic states, calculated at the EOM-CCSD/aug-cc-pVDZ level of theory. Vertical excitation energy is marked by a violet arrow.

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Infrared Multiple Photon Dissociation of Copper Formate Clusters

Tobias Pascher, Milan Ončák, Jozef Lengyel, Christian van der Linde and Martin K. Beyer

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

Copper and copper oxides are widely investigated for their catalytic properties [1,2]. It was shown that the calcination of copper salts can lead to highly active catalysts [3] and that copper hydride-based catalysts show a distinct reactivity [4]. Here elementary steps in the calcination of copper formate are investigated in the gas phase by the means of infrared multiple photon dissociation of $Cu_n(HCO_2)_{2n+1}$, n=1-4. The clusters are prepared using electrospray ionization, transferred into the cell of a 9.4 T Fourier transformation - ion cyclotron resonance mass spectrometer and irradiated in the wavelength range of 2500 - 4475 nm by a tuneable optical parametric oscillator.

Three intense absorption bands were found in the wavelength range of 3400 - 3900 nm that shift depending on the size of the cluster and oxidation state of the copper ions. By deuterating the C-H bonds, the character of the vibrations involving C-H/D motion is confirmed and absorptions of C-O combination bands/overtones are identified.

The decomposition of the ions was investigated by measuring dissociation kinetics at the relevant absorption bands. The dissociation of copper formate ions was found to lead towards copper hydrides through a reaction cascade. The decomposition cascade along with the calculated structures (theory level: B3LYP/def2TZVP) and reaction energies are illustrated in Figure 1. The decomposition is induced predominantly through a hydrogen transfer under the elimination of CO₂ for small cluster sizes (starting with Cu_n(HCO₂)_{2n+1}; $n \le 2$). For larger clusters ($n \ge 3$), the fragmentation was found to take place predominantly through the evaporation of copper formate molecules.



Figure 1: The structure and decomposition of copper formate anions along with the zero-point corrected reaction energies, calculated on the B3LYP/def2TZVP level of theory.

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Photochemistry of $Mg^{+}(H_2O)_n$, n=1-5: Experiment and Theory

Thomas Taxer, Milan Ončák, Erik Barwa, Christian van der Linde, Martin K. Beyer

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

There has been a long history of studies¹⁻⁴ on hydrated metal ions in the gas phase over the last decades. The study of such cluster systems is important to understand the transition of various properties, like dissociation energy or reactivity, from single molecules to the bulk. In the ground state, these systems are already well understood while few studies are available on their excited state reactivity. Here, we investigate the photochemistry and spectroscopy of hydrated magnesium ions $Mg^+(H_2O)_n$, (n=1-5).

The experiments were performed on an FT-ICR-MS, using a laser vaporization ion source. Clusters were generated from a target consisting of isotopically enriched ²⁴Mg (99.9%) and supersonic expansion into high vacuum, along with a gas pulse of helium seeded with water vapor. A tunable, pulsed UV/VIS/NIR-laser system was used to induce photodissociation. Dissociation mass spectra were recorded in a wavelength range from 240 nm up to 2,000 nm and compared with *ab initio* calculation using both single- and multi-reference methods and various approaches to absorption spectra modeling (reflection principle, Franck-Condon approximation).



Figure 1: Comparison of our experimental photodissociation spectra with an earlier experiment² and theoretical calculations.

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Atomic Gold-Mediated Homocoupling of Haloalkanes in Gas-Phase and Solid Neon Matrix

<u>Satoru Muramatsu</u>¹, Xuan Wu², Mohua Chen², Kiichirou Koyasu^{1,3}, Mingfei Zhou², Tatsuya Tsukuda^{1,3}

¹ Department of Chemistry, The University of Tokyo, Japan ² Department of Chemistry, Fudan University, China ³ Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Japan

Recently it has been revealed that Au nanoparticles and clusters catalyze various C–C coupling reactions, which are initiated by activation of $C(sp/sp^2)$ –X (X: halogen) bond via oxidative addition [1]. In contrast, catalytic activation of $C(sp^3)$ –X bond in haloalkanes has been regarded as a challenge due to electron-rich nature of sp³ carbon [2]. This work demonstrates a high potential of Au atoms in anionic and neutral states for promotion of homocoupling reactions of CH₃I via the C–I bond activation [3,4].

Laser-ablated Au⁻ anions were allowed to react with CH_3I molecules in the gas-phase. Mass spectrometry and photoelectron spectroscopy on reaction products identified the oxidative addition product $[CH_3-Au-I]^-$ and AuI_2^- as major products. Reaction pathway exploration using Global Reaction Route Mapping (GRRM) program [5] indicated that $Au^$ and CH_3I afforded $[CH_3-Au-I]^-$ in a barrierless reaction, which further reacted with another CH_3I to form AuI_2^- together with a coupling product C_2H_6 (Figure 1); the calculated pathway is highly exothermic and shows no activation barrier with respect to the reactant ($Au^- + CH_3I$).

Reaction of neutral Au atoms with CH₃I was investigated in solid neon matrix at ~4 K, where neutral species can be detected by means of infrared (IR) absorption spectroscopy. The spectra after the reaction indicated the formation of the neutral oxidative addition product [CH₃–Au–I], as well as an intermediate of the homocoupling reaction [(CH₃)₂–Au–I₂] (Figure 1). GRRM calculations suggested the contribution of electronically excited Au atoms in formation of these species. Then, IR spectra was recorded after visible light irradiation on the sample, which directly characterized the coupling product C₂H₆, associated with consumption of [(CH₃)₂–Au–I₂]. This result demonstrates that photo-assisted homocoupling of CH₃I was promoted on the Au atom.



Figure 1: Reaction pathway of homocoupling of CH_3I by $Au^{0/-}$. The optimized structures of $[CH_3-Au-I]^{0/-}$ and $[(CH_3)_2-Au-I_2]^{0/-}$ (B3LYP/cc-pVTZ-PP (Au, I), cc-pVTZ (C, H)) are shown.

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A laser vaporization source for generation of chemically modified metal clusters

<u>Nikita Levin</u>¹, Tsugunosuke Masubuchi¹, Jan F. Eckhard¹, George Goddard¹, Martin Tschurl¹, and Ulrich Heiz¹

¹ Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technical University of Munich, Germany

In recent decades metal clusters of nano- and subnanosizes revealed peculiar sizedependent chemical and physical properties, which are different of those of bulk states. Clusters of these sizes have proved to be excellent models to investigate catalytic reactions on the molecular level, which allows for further improvements in terms of efficiency and cost in the realm of surface and heterogeneous catalysis. Advances in cluster production techniques have made it possible to generate and characterize a variety of clusters composed of various elements. The high frequency laser evaporation source described by Heiz et al. [1] has turned out to be a powerful tool to investigate reactions on trapped metal clusters in gas phase as well as in heterogenous catalysis under UHV conditions. The sufficient thermalization of the cluster plasma, which is created upon the irradiation of a metal target by a laser beam, is achieved by a well-timed inflow of buffer helium gas, controlled by the specially designed home-built piezo valve. While the discussed setup is capable of an efficient production of bare metal clusters, their chemical modification (e.g. their oxidation) can only be performed with limited control over the reaction parameters. Therefore, the setup has been modified accordingly in order to enable reaction of clusters with a reactant gas under multi-collisional conditions. This has been done by the attachment of a pulsed solenoid valve to the clusters source. This second valve enables the introduction of reactant gases by pre-filling the second waiting room (the reactor volume in the expansion channel)[2]. The metal clusters are expected to be generated in the first waiting room located at the metal target, in which they also undergo thermalization. In the second waiting room, the as-formed clusters are allowed to react with gaseous reactants. The aim of this design is to efficiently produce metal clusters over a wide size range with various metalto-adsorbate ratios under thermalized conditions, which are similar to those in the ion trap[3]. This methodology enables to produce reaction intermediates and study their reaction properties in the ion trap. With this approach it becomes possible to split up complex reactions into individual reaction steps, which can be analyzed separately from each other.

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A versatile electrospray ionization source for x-ray absorption studies of free molecules

M. Timm¹, C. Bülow^{1,2}, V. Zamudio-Bayer¹, R. Lindblad^{1,3}, B. v. Issendorff², J. T. Lau^{1,2}

¹ Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany ² Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany ³ Lund University, 22100 Lund, Sweden

X-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) spectroscopy in a cryogenic linear ion trap, combined with a magnetic field, is now well established as a useful tool for the study of electronic structure und magnetic properties of gaseous cluster and molecular ions. By combination of magnetron sputtering and gas-phase ion chemistry in a hexapole collision cell, a wide range of samples, from transition metal clusters [1] to organometallic complexes [2] to metal oxide clusters [3] is now routinely accessible.

To even further increase the range of samples, we have recently installed a dedicated electrospray ionization (ESI) source that will allow us to compare the electronic structure and spin state of gaseous ions to the same ions in solution. First results on $Fe(bpy)_3^+$ will be presented.



Figure 1: Left: CAD drawing of the ESI source showing, from left to right: the capillary (transmitting the molecular ions from the ambient pressure into the vacuum), the ion funnel (focusing the molecules) and the entrance of the hexapole ion guide. Right: Mass spectrum of size selected $Fe(bpy)_{3}^{2+}$, showing the parent cluster ion along with a few percent of $Fe(bpy)_{2}^{2+}$ from collision induced dissociation in the ion trap.

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Experimental setup with a ring electrode ion trap to study gasphase reactions

D. Wagner, S. M. Lang, T. M. Bernhardt

Institute of Surface Chemistry and Catalysis, University of Ulm, Germany

To study the reactive and catalytic properties of metal clusters we recently built a new setup consisting of a magnetron sputter source to produce metal clusters of different sizes, a multipole mass filter for the selection of clusters of interest, an ion trap to store the clusters for up to a few seconds, and a time-of-flight mass spectrometer for the characterization of the reaction products.

It is planned to replace the so far used octopole ion trap with a ring electrode ion trap, based on the concept of Gerlich and co-workers [1] and the design of Asmis et. all [2]. The ring electrode ion trap contains 24 single ring electrodes and an entrance and an exit electrode whereby the potentials of every electrode can be applied separately. For the storage of clusters the applied potential is a superimposition of a direct current and an alternating current in the radio frequency range. Due to the separate control of the direct current on each ring electrodes, it is possible to apply a potential ramp on the ring electrodes which leads to a well-defined extraction of reaction products. This enhances the intensity of peaks and leads to a better signal to noise ratio and resolution for measurements with the time-of-flight mass spectrometer.



Figure 1: 3D-CAD sectional drawing of the ring electrode ion trap

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3D high resolution diffractive imaging of ultrafast melting in silver clusters

J. Jordan¹, S. Dold², P. Behrens¹, <u>Nils Bernhardt¹</u>, A. Heilrath¹, L. Hecht¹, B. Langbehn¹, F. Seel¹, R. Tanyag³, A. Ulmer¹, S. Walz¹, J. Zimmermann^{3, 1}, I. Barke⁴, H. Hartmann⁴, R. Irsig⁴, N. Iwe⁴, F. Martinez⁴, K. Oldenburg⁴, K. Meiwes-Broer⁴, B. Kruse⁴, C. Peltz⁴, C. Bomme⁵, J. Correa⁵, S. Düsterer⁵, B. Erk⁵, B. Manschwetus⁵, R. Treusch⁵, T. Fennel⁴, B. v. Issendorff², T. Möller¹, D. Rupp^{1, 3}

¹ IOAP, TU Berlin, Germany
 ² Universität Freiburg, Germany
 ³ MBI Berlin, Germany
 ⁴ Universität Rostock, Germany
 ⁵ FLASH, DESY, Germany

Short wavelength free electron lasers such as FLASH in Hamburg provide unprecedented insight into the dynamics of nanoscale objects. The high intensity and short pulses render high resolution imaging of single nanoparticles in free flight possible.

Single silver clusters with a broad size distribution (tens to hundreds of nanometers) were produced with a magnetron sputter cluster source and imaged in a single-particle diffraction-before-destruction approach. In a previous work, this procedure has successfully been used to identify a large variety of structural motifs [1]. This was possible by utilizing wide angle scattering, which reveals structural information about particle shape and orientation from single-shot images.

In a very recent beamtime, we tried to improve the resolution of the imaging method while keeping the 3D information. Therefore, we used intense pulses at a wavelength of 5 nm and a large, sensitive pnCCD detector close to the interaction region. Using the increased resolution, we tried to image laser-induced melting. The clusters were excited with a long pulsed 400 nm laser, coupling to the Mie-plasmon frequency of the silver nanoparticles, and imaged with the FEL.

In this work, the setup of this recent experiment will be presented, first insight into the data will be given, and preliminary results will be discussed.

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Α

Addicoat, M. A.	
Ahlrichs. R	
Alonso, J. A	
Altalhi, W	
Arakawa, M	
Ard, S. G	
Ariafard, A.	
Armentrout, P. B.	
Asmis, K. R.	
Atkinson, B. E	
Auth, T	15, 69

В

Bakker, J. M	58
Baklanov, A. V	52
Baloglou, A	58
Barke, I	77
Barnett, R. N	58
Barwa, E	72
Bastian, B5	51
Beardsmore, P. W4	19
Behrens, P7	77
Berden, G1	16
Berkessel, A1	16
Bernhardt, N7	77
Bernhardt, T. M	76
Beyer, M. K 17, 68, 70, 71, 7	72
Boesl, U	17
Bogdanchikov, G. A	52
Boles, G. C	33
Bomme, C7	77
Bonačić-Koutecký, V1	14
Bowen, K. H	18
Bülow, C	75
Bumüller, D1	10
Buntine, M. A	10

С

Canty, A. J.	
Chen, M	73
Chernyy, V.	
Ciborowski, S. M	
Correa, J.	77
Cunningham, E. M.	

D

Debnath, S	
Dillinger, S.	
Dold, S.	77
Donnelly, P. S	
Dopfer, O	
Düsterer, S	77

Ε

Eckhard, J. F	
Ehrhard, A. A	60
Erk, B	77

F

41, 43, 44

G

Geng, C	23, 52
Gentleman, A. S	40, 49, 50
Gewinner, S	
Goddard, G	
Green, A. E	
Grönbeck, H	

Н

Hartmann, H	
Hayakawa, T	
He, SG	
Heard, C. J	
Hecht, L	
Hehn, AS	
Heilrath, A	
Heiz, U	9, 26, 47, 74
Hirsch, K	
Huitema, D. M. M	
Hussein, H. A	41, 59

I

40, 49, 50

J

Jaeger, B. K. A	
Jamshidi, Z	
Janssens, E	41, 43, 44
Jia, M	
Jin, Q	
Johnson, M	
Johnston, R. L.	41, 59
Jordan, J	
Jorewitz, M	
Jørgensen, M	
Justin, J. P.	50

К

Kappes, M. M	
Kaydashev, V. E	
Kerpal, C. F	
Khairallah, G. N	
Klein, M. P	
Koszinowski, K	15, 69
Koyama, K	
Koyasu, M	73
Krammer, F	

Krstić, M.	14
Kruse, B.	77
Kudoh, S	8
Kuijpers, S	

L

Landman, U	7, 33, 58
Lang, S. M.	33, 57, 58, 65, 66, 76
Langbehn, B	77
Lau, J. T	
Ławicki, A	
Leach, S	
Lengyel, J	71
Levin, N	
Li, J	
Li, Jilai	23, 52
Lievens, P	
Lindblad, R	
Liu, G	
Lushchikova, O. V.	

Μ

Mackenzie, S. R	40, 49, 50
Mafuné, F	8
Manschwetus, B.	77
Martens, J	
Martinez, F	77
Masubuchi, T	
Mauthe, S	
McDonald II, D. C.	54
McGrady, J. E	
Meijer, A. J. H. M	
Meiwes-Broer, K	77
Metha, G. F	
Meyer, J	51
Michaelsen, T	51
Miliordos, E	
Misaizu, F	
Miyajima, K	8
Mohrbach, J	
Molina, L. M	
Möller, T	77
Mravak, A	
Muramatsu, S	73
Muß, D	70

Ν

Nagata, T	
Nakano, M	
Nguyen, M	
Nguyen, M. T.	61
Niedner-Schatteburg, G	
Noor. A	
Nguyen, M. Nguyen, M. T. Niedner-Schatteburg, G. Noor, A.	

0

O'Hair, R. A. J.	13, 14, 15, 69
Odaka, H	
Ohshimo, K.	
Oldenburg, K.	77
Ončák, M.	17, 68, 70, 71, 72
Oomens, J	
Owen, C. J	

Ρ

15
71
11
16
16
77

R

S

Sauer, J	
Schäfer, M	
Schewe, W	
Schlangen, M	
Schöllkopf, W	
Schooss, D	
Schwarz, H	23, 52, 53, 63, 64
Seel, F	
Shaik, S	
Shuman, N. S	
Siu, CK	
Steiner, A	
Sun, X	
Sweeny, B. C	

Т

Tang, W. K	
Tanyag, R	
Taxer, T	
Terasaki, A	11, 25, 28
Timm, M	
Tran, D. H	61
Treusch, R	
Tschurl, M	9, 26, 47, 74
Tsukuda, T	

U

۷

van der Linde, C	
Vanbuel, J	41, 44
Viggiano, A. A	
Visscher, L	
Vollmer, M	
von Issendorff, B	

W

76
10
57
13
29
23, 52
15
51

Wheeler, O. W	. 33
Wu, J. W. J	. 27
Wu, X	.73

Χ

Xantheas, S

Y

Yang, Y				13
Yue, L	. 23,	53,	63,	64

Zamudio-Bayer, V	
Zhang, X	
Zhou, M	73
Zhou, S	23, 53, 64
Zhu, Z	
Zimmermann, J	77
Zimmermann, N. T	







We invite all participants of GPMC to contribute to a special issue "Gas Phase Model System for Catalysis" of the "Zeitschrift für Physikalische Chemie".

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EDITOR-IN-CHIEF K. Radoman	
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	Monday, 18 June 2018	Tuesday, 19 June 2018	Wednesday, 20 June 2018	
08:30	Conference Opening			
08:45	President of UUIm Welcome			
09:00 - 09:40	Uzi Landman	Helmut Schwarz	Sheng-Gui He	
09:40 - 10:20	Fumitaka Mafuné	Joachim Sauer	Alexander Gentleman	
10:20 - 10:40	Coffee break	Coffee break	Coffee break	
10:40 - 11:05	Kit Bowen	Akira Terasaki	Roy Johnston	
11:05 - 11:30	Detlef Schooss	Martin Tschurl	Albert Viggiano	
11:30 - 11:55	Masashi Arakawa	Toshiaki Nagata	Luis Molina	
11:55 - 12:20	Mikkel Jørgensen	Tobias Lau	Jan Vanbuel	
12:20 - 14:00	Lunch	Lunch	Conference Closure	
14:00 - 14:40	Richard O'Hair	Lai-Sheng Wang		
14:40 - 15:20	Vlasta Bonačić-Koutecký	Mark Johnson		
15:20 - 15:40	Coffee break	Coffee break		
15:40 – 16:20	Konrad Koszinowski	Gereon Niedner- Schatteburg	15:40 – 16:05	
16:20 – 16:45	Mathias Schäfer	André Fielicke	16:05 – 16:30	
16:45 – 17:10	Christian van der Linde	Joost Bakker	16:30 – 16:55	
17:10 – 17:35	Knut Asmis	Marko Förstel	16:55 – 17:20	
		Masahiko Ichihashi	17:20 – 17:45	
18:00 – 19:00	Evening Lecture Martin Vollmer Clariant Int. Ltd.	Poster Session	17:55	
		Conference Dinner	20:00	