Surface Science
Room 103C - Session SS+AS-ThA

Celebrating a Life in Surface Science: A Symposium in Honor of JOHN T. YATES, JR.

Moderators: John Russell, Jr., Naval Research Laboratory, Vincent Smentkowski, General Electric Global Research Center

2:20pm **SS+AS-ThA1 Introductory Remarks About Prof. John T Yates Jr. and his Scientific Legacy**, *V. Smentkowski,* General Electric Global Research Center*; **John Russell,*** US Naval Research Laboratory

Introductory remarks about Prof. John T Yates Jr. and his scientific legacy

2:40pm **SS+AS-ThA2 JOHN T. YATES, JR. - The Energizer Bunny (Invited Talk)***, **J. William Gadzuk,*** NIST

My friend and colleague John Yates was a joy to share life with. His perpetual enthusiasm, imagination, and sincere interest in whatever happened to be the topic of the moment whether a complex issue in surface science, the fate of an astronomically distant galaxy, the program for Lorin Maazel's next Pittsburgh Symphony concert, the well-being of his scientific "children" and real family, or speculation on what's likely to be tonight's specialties on the menu of our favorite Il Pizzico Restaurant near NIST, was infectious. John's retirement in 2006 from his chair at the University of Pittsburgh [which he went to from NBS/NIST in 1982] brought him to an emeritus-like guest faculty desk at the University of Virginia. Soon upon settling in at the university, his "desk" became an office became a full-fledged surface science lab with an active group of students and post docs supported by research grants that totaled among the highest within UVA chemistry, all of which was built up from scratch after John "retired". He was the only person I know who confessed that he really liked writing research proposals. He lived and executed his retirement with more excitement, energy, and enthusiasm than a young, tenure-seeking assistant professor; the energizer bunny personified.

I will present a number of anecdotal/amusing illustrative vignettes drawn from my experiences with "the energizer bunny" and discuss why his seminal JCP papers on thermal broadening in ESD [**51**,1264(1969)] and on resonance ESD [**90**,5793(1989)] were so influential in my own conceptualization and realizations in surface dynamics.

Finally, John and I had the privilege of being co-participants in two NIST Oral History interviews in 2014 and 15, once as a "target" and then as an interviewer [of each other]. This was a great way for us to summarize our nearly half a century of being a part of each other's life, a privilege that I feel very fortunate and honored to have had. [transcripts available upon request: gadzuk@nist.gov [mailto:gadzuk@nist.gov]]

3:00pm **SS+AS-ThA3 Polymer Precursors Studied by Mass Spectrometry, Ion Mobility and Computational Strategies (Invited Talk)***, **David M. Hercules,*** Vanderbilt University

There has been considerable interest recently in using mass spectrometry and related methods to address structures of complex systems, including block copolymers. Polyurethanes (PURs) are polymers that contain multiple "hard" and "soft" blocks that have different sequences of the same units along the chain. The ultimate goal in studying such materials would be the ability to determine the exact sequence along the chain and to correlate specific sequences with polymer performance. We have established a protocol on smaller molecules that can address this type of issue using the combination mass spectrometry, collision-induced dissociation, ion mobility spectrometry (IMS), and molecular dynamics simulations. A key component of the of the project is the synthesis of model PUR oligomers having authentic component sequences. The individual components are methylene diphenyl diisocyanate (MDI), bis-diol terminated polybutylene adipate (PBA), and 1,4-butane diol (BD), each containing 3 MDIs, 4 PBAs and 4 BDs (MW = 1910). The main collision-induced dissociation fragmentation reactions occur between the PUR and PBA carbonyl groups and BD hydrogen atoms. Additionally, a 1,3 H-shift reaction occurs between the PUR N-H group and BD oxygen. Different fragment ions are observed depending on the unit size and the sequences of the units in the chain. An important aspect of the research is to use IMS to separate compounds that have identical masses but different molecular-ion scattering cross sections. Computational strategies are important for calculation of IMS collisional scattering cross sections and to aid in the interpretation of fragmentation mechanisms. They help to identify synthetic targets that will show the largest effects of the experimental measurements.

3:20pm **SS+AS-ThA4 From Symmetry to Applications: One of Many Journeys Touched by John Yates (Invited Talk)***, **Ellen Williams,*** Advanced Research Projects Agency - Energy

In the 1970's John Yates spent a sabbatical year at Caltech, where he touched the lives of many students and postdocs working in the group of Prof. Henry Weinberg. My story starts as a young student, fascinated with symmetry and statistical mechanics, who was privileged to work in the laboratory with John, in those early days of surface science when it seemed that every observation opened new horizons.

I will provide highlights of some of the exciting research that followed from those early days of surface science, discussing the impact of scanning tunneling microscopy, the linkages of surface science and nano-electronics, and the practical impacts of many years of fundamental studies from the perspectives of industry and ARPA-E.

4:00pm **SS+AS-ThA6 A Tribute to John T. Yates Jr. and His Pioneering Work with Graphitic Surfaces (Invited Talk)***, **Patricia A. Thiel,*** Ames Laboratory

John T. Yates, Jr. directed pioneering work on graphitic surfaces. In one case, he and his group prepared graphene on SiC surfaces long before graphene was popularized. In another case, they developed a method to induce surface intercalation of Cs at a graphite surface. In this talk, I will review his contributions and describe the ways in which his work has inspired some of my own. For instance, we have studied adsorption, nucleation, growth, and reaction of dysprosium (Dy) on the basal plane of graphite, and the way that these phenomena are influenced by surface defects. Dysprosium islands nucleate homogeneously on terraces at room temperature. With increasing temperature the shape changes, with islands becoming taller and more facetted. At still higher temperature, Dy reactions with graphite to form carbide. Using the technique developed by John and his group, we can also induce surface intercalation at elevated temperature. We show that this surface intercalation differs significantly from bulk intercalation.

4:20pm **SS+AS-ThA7 Surface Science influenced by Dopants (Invited Talk)***, **Hajo Freund,*** Fritz Haber Institute of the Max Planck Society, Germany

Model systems are useful to establish structure/morphology reactivity relations in heterogeneous catalysis. Here we use a Metal-Insulator-Metal (MIM) structure to advice CO_2.

We had shown before that ultra-thin oxide films could be used as effective barriers to charge Au islands with electrons from the metal below the support. The idea is to use the electrons stored in the islands to activate molecules by electron transfer. Such a molecule is the energy economy relevant carbon-dioxide for example. We demonstrate adsorption of CO_2 at gold islands and the reversible formation of CO_2 anions and oxalates based on information from microscopy and spectroscopy.

We show how to transfer those ideas developed for thin film systems to bulk materials, where we use appropriate dopants within the support material to provide the electron source. The electron transfer to Au islands as well as the activation of oxygen will be demonstrated.

4:40pm **SS+AS-ThA8 Desorption: Out of the Vacuum, into the Liquid (Invited Talk)***, **Michael Grunze,*** KIT, Germany*; H.J. Kreuzer,* Dalhousie University, Canada

The first paper on thermal desorption John Yates published with Ted Madey was entitled: *Nitrogen Desorbs with Complex Kinetics*. Thermal Desorption Spectroscopy, in more and more sophisticated experimental set-ups including flow reactors, became then a prominent techniques in John´s Laboratory to study simple and complex surface chemical reactions. In this short report, we look further into "complex kinetics" and find that the theoretical framework of a thermally activated process can not be applied to the detachment of particles in a micro-fluidic shear-flow experiment.

The theoretical description of the desorption process treats bond breaking as a thermally activated process, which can be described by the Arrhenius equation. The activation energy and the pre-exponential factor can be determined from a series of TPD experiments with either varying coverage or at constant coverage, using different heating rates. Here we experimentally and theoretically analyze the detachment of microscopic polystyrene beads from different self-assembled monolayer (SAM) surfaces in a shear flow to develop a mechanistic model for the removal of cells from surfaces. The detachment of the beads from the surface is treated, as in thermal desorption experiments, as a thermally activated process to determine activation barrier and attempt frequency of the rate determing step in bead removal. The statistical analysis of the experimental shear detachment data, obtained in phosphate-buffered saline solution, results in an activation energy of detachment around 20 kJ/mol. This value is orders of magnitude lower than the adhesion energy measured by atomic force microscopy (AFM). The same order of magnitude for the adhesion energy measured by AFM is derived from ab initio calculations of the van der Waals interaction energy between the polystyrene beads and the SAM-covered gold surface. We hence conclude, that the rate determing step for detachment of the beads is the initiation of rolling on the surface (overcoming static friction), and not physical detachment as would be the case in a gas desorption experiment.

5:00pm **SS+AS-ThA9 Infrared Spectroscopy in Surface Science: The Legacy of John T. Yates, Jr. (Invited Talk)**, ***Michael Trenary,*** University of Illinois at Chicago

A constant theme throughout the long scientific career of John T. Yates, Jr. was the use of infrared spectroscopy to probe the properties of surfaces and of adsorbed molecules. In his very first publication in 1961, based on his PhD thesis from MIT, he used transmission infrared spectroscopy to study the interaction of carbon monoxide with alumina-supported nickel surfaces. He continued to use innovative methods of transmission infrared spectroscopy in his laboratories at the National Bureau of Standards, the University of Pittsburgh, and the University of Virginia. The final publication of his career, which appeared in 2016, featured transmission IR spectra of CO interacting with the surfaces of titania-supported gold. In addition to transmission IR spectroscopy of high-area powdered samples, he was also a leader in the use of reflection absorption infrared spectroscopy (RAIRS), also known as infrared reflection absorption spectroscopy (IRAS), a method that allows IR spectra to be obtained on small-area metal single crystals. RAIRS is one of the few surface science techniques that can be used both under UHV conditions as well as in the presence of an ambient pressure of gas. John Yates was a pioneer in bridging the so-called pressure gap by using RAIRS to probe gas-surface interactions in the presence of elevated gas pressures. Recent examples from other research groups will be presented to highlight the continuing impact John Yates has had in the use of infrared spectroscopy in surface science.

5:20pm **SS+AS-ThA10 From Surface Science to New Catalysts (Invited Talk)**, ***Ib Chorkendorff,*** Technical University of Denmark

In this presentation I will give a brief overview of how my post-doc with John T. Yates Jr. influenced my way of working and how that philosophy could be used too go from fundamental investigations of reactions on surfaces to actually understand and make new heterogeneous catalysts. First we shall discuss how mass-selected nanoparticles of CuZn alloys to elucidate the dynamics of the methanol synthesis catalysts. The produced nanoparticles will be compared to the conventional CuZnAl at 1 bar for synthesizing methanol from CO_2 and H_2 [1, 2, 3]. The methanol synthesis on CuZn will also be discussed with respect to our very recent findings of using alloys of NiGa for methanol synthesis [4]. The use of mass-selected nanoparticles will be further demonstrated for electrochemical Oxygen Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts by alloying Pt with early transition metals [5] or the lanthanides [6]. We have also shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [7] and PtGd alloys [8].

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5:40pm **SS+AS-ThA11 Activation of Carbon Dioxide on Metal and Carbide Surfaces (Invited Talk)**, ***Jingguang Chen,*** Columbia University

Converting CO_2 into valuable chemicals and fuels is one of the most practical routes for reducing CO_2 emissions while fossil fuels continue to dominate the energy sector. The catalytic reduction of CO_2 by H_2 can lead to the formation of three types of products: CO through the reverse water-gas shift (RWGS) reaction [1], methanol via selective hydrogenation [2], and hydrocarbons through combination of CO_2 reduction with Fischer-Tropsch (FT) reactions. In the current talk we will discuss some of our recent results in CO_2 conversion [3]. Our research approaches involve the combination of DFT calculations and surface science studies over single crystal surfaces, catalytic evaluations over supported catalysts, and in-situ characterization under reaction conditions. We will also discuss challenges and opportunities in this important research field [4].

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6:00pm **SS+AS-ThA12 Thermodynamic Control of TTF-TCNQ Molecular Layers on Metallic Surfaces (Invited Talk)**, ***Petro Maksymovych,*** Oak Ridge National Laboratory

Bulk molecular ionic solids exhibit a fascinating diversity of electronic ground states, including unconventional superconductivity. The electronic properties of these systems have historically avoided surface analytical studies due to the intrinsic difficulty with surface preparation. We are therefore pursuing epitaxial growth of charge-transfer compounds, toward understanding their fundamental properties and creating new kinds of metal-organic or organic-organic interfaces [1,2]. A primary challenge is to assure compatibility of supported epilayers with the redox processes so as to enable, enhance but not eliminate significant charge transfer and electron correlations with supported structures.

In this talk, I will discuss 2D molecular structures of TTF and TCNQ molecules supported on metal and graphitic surfaces. We established that these molecules self-organize into a "zoo" well-ordered structure with a wide-range of TTF:TCNQ ratios [3] - a marked deviation from a single stable 1:1 ratio in the bulk. We propose that the formation these structures is governed by a surface phase diagram that exhibits at least four distinct stable compositions. The diagrammatic picture explains many of the properties of such systems that often seem incidental: the morphology of epilayers, governed by nucleation and growth; coexistence and abundance of various phases, and the distinct molecular structure of phase boundaries. Using coupled image and computational analysis, we conclude that the observed shapes are dictated by the preferential formation of a well-defined “quad”-motif involving TTF(TCNQ) molecules coordinated by at least four of its matching neighbors. Thus enabled deterministic control is beneficial to both electronic properties of surface phases (which can develop local magnetic moments) and the formation of quasi-2D TTF-TCNQ solids, which develop decidedly non-bulk Mott-insulating state despite having 1:1 bulk ratio. We anticipate that these properties are quite general for multicomponent molecular compounds, providing new opportunities for self-organized and electronically interesting molecular systems.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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