Thursday Morning, November 12, 2009

Surface Science
Room: M - Session SS1+AS+TF-ThM

Surface Science of Hazardous Materials
Moderator: V. Grassian, University of Iowa

8:00am **SS1+AS+TF-ThM1 Interactions of Nerve Agents with Model Surfaces: Computational Approach**, *J.R. Leszczynski*, Jackson State University **INVITED**
The talk summarizes the results of recent studies performed by our group. They include modeling of interactions of selected nerve agents with model surfaces. Among studies nerve agents are soman, sarin, tabun and their surrogates. We investigated different types of surfaces: metals, metal oxides and clays. The study was performed using various techniques of non-empirical, ab inito methods. Among predicted characteristics are molecular geometries of resulting complexes, their interaction energies, electrostatic potentials, and IR spectra. We identified the most promised surfaces that facilitate decomposition of the selected nerve agents. Also, predicted differences between selected processes for nerve agents and their simulants will be discussed.

8:40am **SS1+AS+TF-ThM3** *Ab-Initio* **Computational Approaches to the Adsorption of Chemical Warfare Agents**, *V. Bermudez*, Naval Research Laboratory
Computational chemistry can be used to great advantage in dealing with chemical warfare agents (CWAs). Computation can be applied to reagents which are much too dangerous for routine experimentation as well as to non-traditional species which have not yet been (but could be) synthesized. Examples will be given from recent work[1] on the interaction of the simulant dimethyl methyphosphonate (DMMP) and the real CWAs Sarin and VX with γ-Al_2O_3 surfaces. The γ-Al_2O_3 surface acts as a Lewis acid (electron acceptor) when OH-free and a Brønsted acid (proton donor) when hydroxylated. Thus γ-Al_2O_3 is an excellent prototype for a wide range of other metal oxides. DMMP, Sarin and VX all adsorb in the same way and with a similar adsorption energy (ΔE_{ads}) which depends strongly on surface acidity. A coordinatively-unsaturated tetrahedral Al(T_d) site, which is a strong Lewis acid, forms an Al---O=P dative bond to the phosphonyl group. This is always the most favorable site, and an agent adsorbed by hydrogen bonding at an OH site will migrate to a bare Al(T_d) site if one is available. The γ-Al_2O_3 lowest unoccupied orbital is a surface state associated with the Al(T_d) site which lies just below the conduction band minimum. The energy of this state relative to vacuum is a quantitative measure of Lewis acidity and is directly reflected in ΔE_{ads}. The highest occupied orbital of the molecule is a non-bonding orbital on the phosphonyl O atom. The one-electron energy of this orbital also directly affects ΔE_{ads}. The hydroxylated surface forms Type I, II and III OH sites with O bonded to one, two or three Al's respectively. Brønsted acidity, and ΔE_{ads} for OH---O=P bond formation, increase in the order I<II<III with the Type I interaction being almost negligible. The amine group in VX is found to be a strong base, capable of deprotonating an acidic Type III OH site to form an ammonium ion even in the absence of a polar solvent. The electronic excitations of DMMP, Sarin and VX have also been investigated with the goal of identifying possible photochemical effects due to terrestrial solar radiation (TSR). This issue has been largely overlooked in previous agent-fate studies. DMMP and Sarin are insensitive at energies below ~7 eV; however, vapor-phase VX can be excited near 4.3 eV which is at the upper end of the TSR. The excitation threshold changes slightly for adsorbed VX, shifting to the red or to the blue depending on the nature of the surface. These results provide a predictive framework for understanding the effects of surface condition on the adsorption of VX and G-series CWAs on oxide surfaces.

(1) Supported by the Defense Threat Reduction Agency (DTRA)

9:00am **SS1+AS+TF-ThM4 Computational Prediction of Physical Properties and Environmental Reactivity of Nitro-aromatic and Hydrogen Reach Explosives**, *L.G. Gorb, F.C. Hill,* SpecPro, Inc., *E.N. Muratov, A.G. Artemenko,* A.V. Bogatsky Physical-Chemical Institute, Ukraine, *Y.I. Kholod,* Jackson State University, *V.E. Kuz'min,* A.V. Bogatsky Physical-Chemical Institute, Ukraine, *J.R. Leszczynski,* Jackson State University
Prediction of chemical and physical properties of explosives and products of their environmental degradation, instead of expensive and toxic chemical experiments, is a very important task from many points of view. Among them water solubility (SW) is an extremely important property of chemical compounds. It plays a major role in definition of migration and ultimate fate of chemicals in the environment. In particular, high solubility leads to expeditious distribution in water, i.e., chemicals that rapidly and completely dissolve in water will be transported along with the general flow of water. High SW is generally associated with a very low affinity for adsorption to solids in water, e.g., soil particles or sediment. In addition, high water solubility is associated with accumulation of contaminants in living organisms.

Water solubility values for twenty seven nitro-apomatic and hydrogen reach compounds with experimentally measured values were computed using the conductor-like screening model for real solvent (COSMO-RS) based on the density functional theory and COSMO technique. We have found that the accuracy of the COSMO-RS approach for prediction of water solubility of liquid nitro compounds is impressively high (the errors are lower than 0.1 LU). However, for some solid nitro compounds, especially nitramines, there is sufficient disagreement between calculated and experimental values. In order to increase the accuracy of predictions the quantitative structure–property relationship (QSPR) part of the COSMO-RS approach has been modified. The solubility values calculated by the modified COSMO-RS method have shown much better agreement with the experimental values (the mean absolute errors are lower than 0.5 LU). Furthermore, this technique has been used for prediction of water solubility for an expanded set of twenty three nitro compounds including nitroaromatic, nitramines, nitroanisoles, nitrogen rich compounds and some their nitroso and amino derivatives with unknown experimental values.

Finally, an application of COSMO-RS approximation to the prediction of environmental reactivity for hydrogen reach explosives (alkali hydrolysis in water) has been briefly discussed

9:20am **SS1+AS+TF-ThM5 A Material Approach to Enable Detection of Toxic Chemicals in Water by IR Spectroscopy**, *C.P. Tripp*, University of Maine **INVITED**
We are currently developing a detection system based on the principles of infrared (IR) spectroscopy that operates in heterogeneous aqueous environments and provides fast detection (< 10 min) and high sensitivity to chemical warfare agents and other toxic chemicals with minimal false alarms. The key enablers to using infrared spectroscopy for aqueous based detection are the development of materials that lead to selective and robust sampling protocols. In this talk, I will present new sampling methods that are based on the use of surface functionalized adsorbents and reactive thin films coated onto a porous and IR amenable support. The coatings chemically react with a predefined class of compounds and identification of the specific chemical is provided by IR spectral analysis. Examples of this approach for low level detection of cyanide, metals, pesticides, and chemical warfare agents in water will be demonstrated.

10:40am **SS1+AS+TF-ThM9 Surface Science and its Application to Energetic Materials**, *V.J. Bellitto, J.M. Kelley, D.N. Sorensen*, Naval Surface Warfare Center
Composite explosives and propellants are heterogeneous admixtures of crystalline powders in a rubbery binder. Materials such as aluminum are added to enhance specific performance criteria. The aluminum although improving performance in systems may not be efficiently consumed. Placement of explosives and propellants in closer proximity with the metal is expected to provide performance enhancements. The novel material should have more complete combustion and faster energy release rates as problems with heat transfer and diffusion rates are overcome.

We have undertaken a research effort to gain a fundamental understanding of the metal/explosive interaction. In performing experiments novel interfaces are produced which are not obtainable under ambient conditions. The research reveals possible avenues for the development of new energetic materials with improved performance.

In this work, X-ray photoelectron spectroscopy (XPS) was used to study the interaction of aluminum with cyclotrimethylenetrinitramine (RDX) and the resultant products analyzed via Differential Scanning Calorimetry (DSC). For RDX, the spectrum of the N 1s region has two easily discernable peaks assigned to the nitro group and ring structure nitrogen. Upon the initial interaction of aluminum with RDX, the N 1s spectrum reveals that the nitrogen peak associated with the nitro group is diminished compared to that of the ring structure. This is an indication of the preferential reaction of the nitro group with the aluminum, leaving the ring structure intact. The data also shows the preferential formation of aluminum oxide species over aluminum nitride species. Continued deposition of aluminum produces aluminum layers over the initial oxide layer. The DSC data demonstrates an increase in decomposition energy through the placement of metal directly onto the explosive surface.

11:00am **SS1+AS+TF-ThM10 Characteristics and Stability of Oxide Films on Plutonium Surfaces**, *H.G. García Flores*, University of Nebraska-Lincoln and Los Alamos National Laboratory, *A.L. Broach, D.P. Moore,* Los Alamos National Laboratory, *D.L. Pugmire*, Los Alamos National Laboratory and University of Nebraska-Lincoln

The oxidation of plutonium metal continues to be an area of considerable activity. The reaction characteristics have significant implications for production use, storage, and disposition of this reactive material. Developing an accurate physical model of the structures, oxidation states, and oxygen concentration gradients present during oxidation are essential to understanding this process. Traditionally, the stable oxides of plutonium have been thought to be plutonium sesquioxide (Pu_2O_3, O/Pu=1.5, Pu^{3+}) and plutonium dioxide (PuO_2, O/Pu=2.0, Pu^{4+}), existing in a layered structure on oxidized plutonium metal. Many studies of this system are performed under ultra-high vacuum (UHV) using surface sensitive techniques to probe oxidation states, electronic structure, and surface chemistry.

Here, we report on a detailed study using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to measure the relative concentrations of oxygen and plutonium, as well as the resulting oxidation states in the near-surface region. It has previously been shown that under UHV conditions, PuO_2 undergoes an auto-reduction reaction to the more stable Pu_2O_3. The auto-reduction of PuO_2 occurs as oxygen diffuses from the surface, through the oxide-film, to the metal-oxide interface.[1] The results of this study show a much greater than anticipated extent of auto-reduction and challenge the commonly held notion of the stoichiometric stability of Pu_2O_3 thin-films, especially in the presence of plutonium metal. The data indicates that a hypo-stoichiometric plutonium oxide (Pu_2O_{3-y}) exists at the metal-oxide interface. A new model of the plutonium/oxygen thin-film system will be proposed and its applicability to thicker-films will be discussed.

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[1] Morrall P, Tull S, Glascott J, Roussel P, 2007 *J.Alloys Comp.* **444-445** 352.

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