Final Report

1. DE-FG02-97ER45624 North Carolina State University

2. Theoretical Studies of Surface Reactions on Metals and Electronic Materials
   Principal Investigator: Jerry L. Whitten

3. April 23, 2012. Period covered by the report: December 1, 1996 - February 29, 2012

4. Description of Accomplishments

A. Overview
During the three year grant period, our research involved the following topics:

1) Adsorption and photochemistry of H_2O on palladium and silver;

2) Production of H_2 by photoinduced electron attachment to H_2O adsorbed on silver;

3) Photoinduced electron transfer to $Li(H_2O)_6^+ / Ag_{31}$ followed by dissociation of coordinated water to produce H_2 ;

4) Studies of H_2O liquid phase models and solvated H_3O^+ near a Ag (111) surface.

5) Production of hydrogen by photoinduced electron transfer to solvated H_3O^+ near a Ag (111) surface.

6) Solvation and hydrophobicity studies of hydrocarbon systems in which methods developed as part of the above studies were applied in a mass spectrometry collaboration.

7) Studies of the ground and excited states of TiO_2 ring systems and TiO_2 nanoparticles, including analysis of localized (excitonic) states corresponding to O2p to Ti3d localized excitations.

8) Collaborations with the Somorjai group on F doped TiO_2 and collaborations with the Lucovsky group on core electron spectroscopy of electronic materials.

A synopsis of these studies follows, and, in a separate section, abstracts of published and submitted papers are provided. One of the goals of this research is to learn more about fundamental processes involving photoinduced electron transfer to adsorbates on metals, in particular, those that lead to dissociation of water. Silver nanoparticles are chosen to represent the low end of catalytic activity, so as to delineate effects most directly associated with the dissociative electron transfer step. However, we also worked on palladium nanoparticles to take advantage of increased reactivity of that metal and its potential for hydrogen storage. In collaborative work with experimental investigations, the palladium catalyzed decomposition of butanoic acid was treated using high level electronic structure theory. For photoinduced processes at surfaces, key questions involve how electron transfer excited states are stabilized by

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the image charge or hole in the metal and whether dissociation occurs on the excited electronic state surface or by crossing over at some adsorbate geometry to the ground state surface. Differentiating between competing pathways depends on energy barriers and lifetimes in excited states.

Both the photochemical and catalytic studies require accurate electronic structure calculations to distinguish between competing pathways and to treat excited electronic states that lie above numerous states involving metal to metal excitations. In order to describe stretched chemical bonds and other aspects of electron correlation, we have based our work on high level many-electron theory: the full many-electron Hamiltonian is used, except for core-electron pseudopotentials for transition metal atoms, and wavefunctions are constructed by configuration interaction (CI). A formulation that allows excited electronic states embedded in a near continuum of lower energy states to be calculated accurately was developed and applied to the photoinduced electron transfer of adsorbates on metals.

A few general comments about the electron transfer processes of interest are appropriate. Since the cross-section for photon absorption is larger for a metal cluster than for the adsorbed water molecule, the excited electronic state that leads to the dissociation of water can be thought of as the result of photoemission from the metal followed by attachment of the photoemitted electron to water. An alternative language is to describe the excited state simply as one in which the electron density has been shifted toward the adsorbed water molecule, i.e., an electron transfer excited state. Both descriptions lead to the same physical result: the electronic state of interest in the water dissociation process is an electron transfer excited state of the H_2O-metal cluster system. This photoinduced excited state can evolve on the excited state potential energy surface or return at some point to the ground state surface and undergo further reaction. Energy barriers will determine whether a viable process exists in which H_2 can be formed leaving O or OH adsorbed on the surface, or whether ions can assist by steering the electron transfer to solvated water molecules. In this report, we explore several such systems and discuss the findings.

B. Theory
Electronic systems are described by a configuration interaction embedding method that is designed to give an accurate many-electron description of the adsorbate-surface region of a metal or oxide and electron transfer states. Many applications of the method to ground and excited states of adsorbates on metals have been reported previously and details of the method can be found in earlier publications and previous progress reports. A brief summary is given below.

Calculations are carried out for the full electrostatic Hamiltonian of the system (except for core electron potentials)

$$H = \sum_{i}^{N} [-\tfrac{1}{2}\nabla_i^2 + \sum_{k}^{Q}(\frac{-Z_k}{r_{ik}} + V_{ik}^{core})] + \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

Wavefunctions are constructed by self-consistent-field (SCF) and multi-reference configuration interaction (CI) expansions

$$\Psi = \sum_{k} c_k (n!)^{-1/2} det (\chi_1^k \, \chi_2^k \ldots \chi_n^k) = \sum_{k} c_k \Phi_k$$

In the present work, many of the electron transfer states of interest lie several eV above the ground state and even for the small, 30- or 40- atom metal clusters investigated many intervening lower energy states corresponding mainly to metal→metal excitations exist. Fig. 1 depicts a typical distribution of states.

In order to focus on electron transfer excited states relevant to the dissociation of water we proceed as follows. Initial single-determinant, self-consistent field (SCF) calculations on the ground state are carried out. We then seek to identify virtual orbitals from the calculation that contain appreciable contributions from water; typically, water basis functions contribute in varying amounts to many of the ground state virtual orbitals. To obtain this set of orbitals, we transform the virtual orbitals $\{\phi_k\}$ using an overlap projector. Excited states are constructed using this virtual orbital basis plus all orbitals that have significant exchange interactions with these orbitals. Proceeding in this way allows one to construct electronic states that are orthogonal to and effectively non-interacting with lower lying states and thereby assuring an upper bound on the excited state energy. See publications for details.
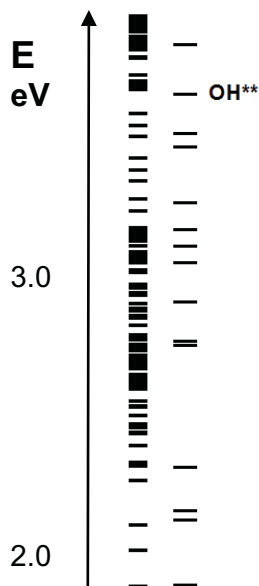

Figure 1. Electron transfer states of interest, denoted by OH**, embedded in a near continuum of lower energy states. Energies are from a CI calculation designed to identify all states arising from multiple excitations of the Ag_{31}/H_2O system that lie below electron transfer excited states that contain appreciable contributions from water orbitals. Energy levels on the right are single excitation states.

C. Photoinduced dissociation of water adsorbed on silver
Yu Zhang and J. L. Whitten, *Journal of Molecular Structure: THEOCHEM,* 903 (2009) 28-33.

Following structure optimizations, we investigated a) the photoinduced dissociation of water adsorbed on a silver cluster, Ag_{31}, and subsequent transfer of a H to a second nearby Ag_{31} cluster leaving OH on the first cluster (Fig. 2) and b) the photoinduced dissociation of water to produce H_2 directly (Fig. 3.)
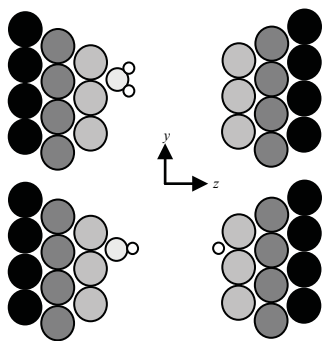
Figure 2. Dissociation of water and transfer of hydrogen.
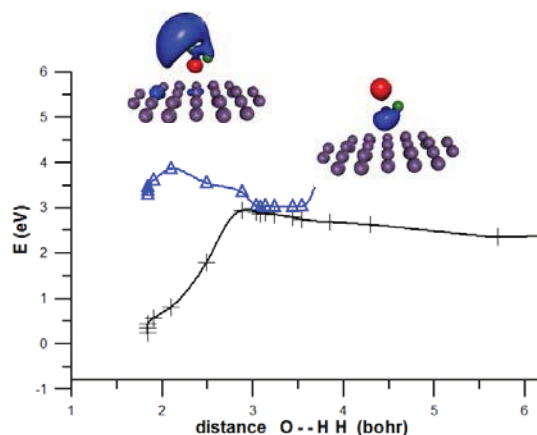
**Figure 3.** Electron attachment to water and formation of H_2

The ground state (lower curve in Fig 3.) shows a large energy barrier to formation of H_2 while the photoinduced excited state has only a small barrier on the excited state potential energy curve. After an OH stretch greater than 3.0 bohr (1.59Å) the excited state rises sharply in energy and dissociation can occur only if there is a crossover to the ground state potential. The insets in Fig. 3 are contour plots of the water molecular orbital occupied on the Ag→H_2O electron transfer excitation. The plots illustrate what turns out to be a general behavior for electron attachment to a molecule or region of a molecule with only sigma bonds: the orbital resulting from a Franck Condon excitation is Rydberg like, i.e., spatially large. In the early stages of stretch, the energy increases because the spatially large orbital only slightly affects the OH bond. On further stretch, the molecular orbital evolves toward a typical OH antibonding orbital which is spatially smaller with a well defined node between the nuclei, as depicted in the right inset. This shift in character leads to an energy decrease on further OH stretch as shown in Fig. 3. We see similar behavior in other systems.

The positive hole in the Ag cluster, formed on electron transfer to the adsorbed water molecule, plays an important role in stabilizing the excited state. First, the electron-hole attraction stabilizes electron distributions of both Rydberg and σ* character in the excited state. Second, as the system approaches the transition state, and one of the OH bonds is weakened, the hole plus increased covalent bonding of O with Ag causes a relaxation of H_2O^- toward shorter O-Ag surface distances. At the transition state, the O-Ag surface distance has decreased from the 5.44 bohr (2.93 Å) equilibrium value for neutral water, noted previously, to 3.55 bohr (1.88Å). As H_2 separates from Ag_{31}-O, the electron recombines with the positive hole and the evolution of H_2 proceeds on the ground state potential energy surface.

Next, we shift the Fermi level by a potential applied to the backside of the Ag_{31} cluster. Both positive and negative potentials are introduced by modifying the nuclear charge of each of the 12 atoms in the third layer to change the net charge of the layer to +0.72 |e| or -0.72 |e|. These are arbitrary choices designed only to be large enough to be realized in practice and show an effect. As a simulation of an electrode or capacitor, the model is actually better than might at first be supposed. The Ag_{31} cluster is sufficiently metallic that introduction of a net charge on the backside of the cluster is shielded by a shift in electron density so that to a first approximation only the Fermi level of the system changes. Fig. 4 shows that the positive/negative potentials

change the energy of the initial excitation, but do not change the general features of either the ground state or excited state potential energy curves. In particular, the increase in energy of the excited state in the early stages of OH stretch remains and crossover to the ground state surface is required for dissociation to occur.

Figure 4. Simulation of effects due to changes in the Fermi level of the Ag_{31} cluster. The backside of the silver cluster, indicated in the inset, is modified by changing the nuclear charge of each of the 12 atoms as indicated to give a net charge of $+0.72$ $|e|$ or -0.72 $|e|$.

D. Electron transfer to a solvated Li ion, Li(H₂O)₆⁺
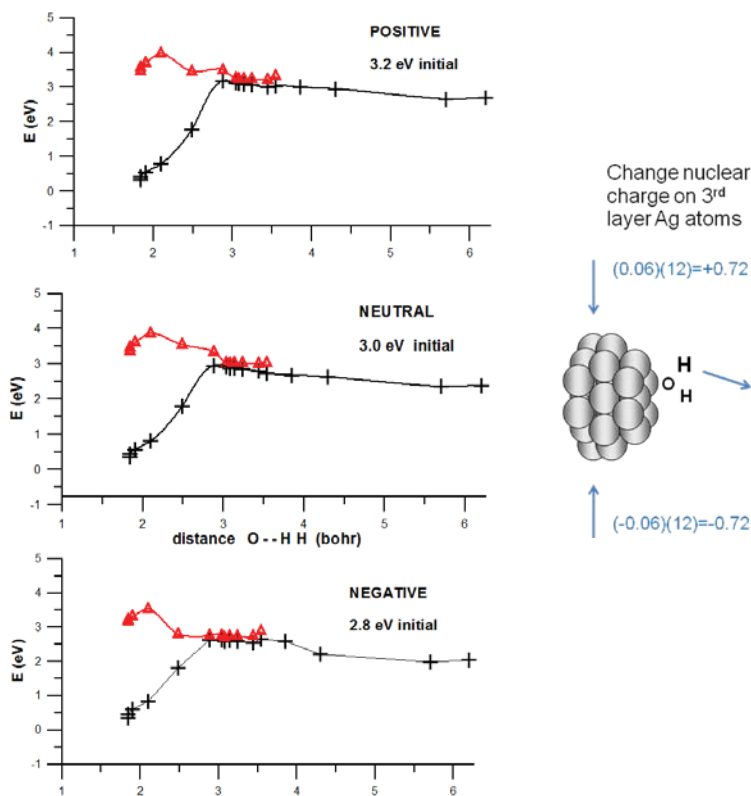
D. Electron transfer to a solvated Li ion, Li(H$_2$O)$_6$$^+$
Yu Zhang and J. L. Whitten, International J. Quantum Chemistry (2009), 109(15), 3541-3551.

Calculations were also performed on the photoinduced electron transfer to a solvated Li ion near the surface of a silver nanoparticle. The extent of solvation is taken to be $Li(H_2O)_6^+$. The small size of Li^+ also suggests that four solvated waters are likely to be found in solution. The Li^+ is fixed at an arbitrary distance of 11 bohr (5.82 Å) from the Ag(111) surface layer of nuclei and the solvated water molecules are as depicted in Fig. 5. The distance from Li^+ to the water solvation shell (the Li-O distance) is optimized and two of the solvated water molecules are allowed to rotate independently to their minimum energy orientation before and after electron transfer. There is no negatively charged counter ion in the model. In realistic simulations of a solution, all of the above points are important. The present investigation is limited to addressing the question of whether a positively charged species in solution can play a useful role in steering a photoemitted electron to a water molecule and thereby enhance dissociation to form H₂.
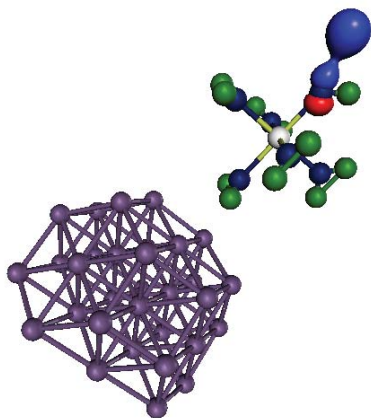
Figure 5. Electron attachment to $Li^+(H_2O)_6$. The diagram shows the initial orientation of the solvated water molecules and the contour diagram for the molecular orbital on water that is occupied after electron transfer.

Unlike, electron attachment to water, the orbital initially formed has much greater OH antibonding, as opposed to Rydberg, character. As a consequence, the increase in energy in the excited state seen at the early stages of OH---H stretch on electron attachment to adsorbed water does not occur and instead there is only a small gradual increase in energy with HO---H distance.

In Fig. 6, we explore whether a dissociating H atom can strip H off a second coordinated water molecule. It is helpful to think of the process in three steps: photoexcitation of the metal, subsequent electron transfer to one of the solvated water molecules in $Li(H_2O)_6^+$ and then a pathway in which $H(\delta-)$ approaches an acidic hydrogen $H(\delta+)\text{-}O\text{-}H(\delta+)$ of a different solvated water. In the final step, H_2 is formed by the reaction $H(\delta-) + H(\delta+) \longrightarrow H_2$. The energy of the excited state in Fig. 6 is seen to remain essentially flat or decreases slightly as H_2 is formed.
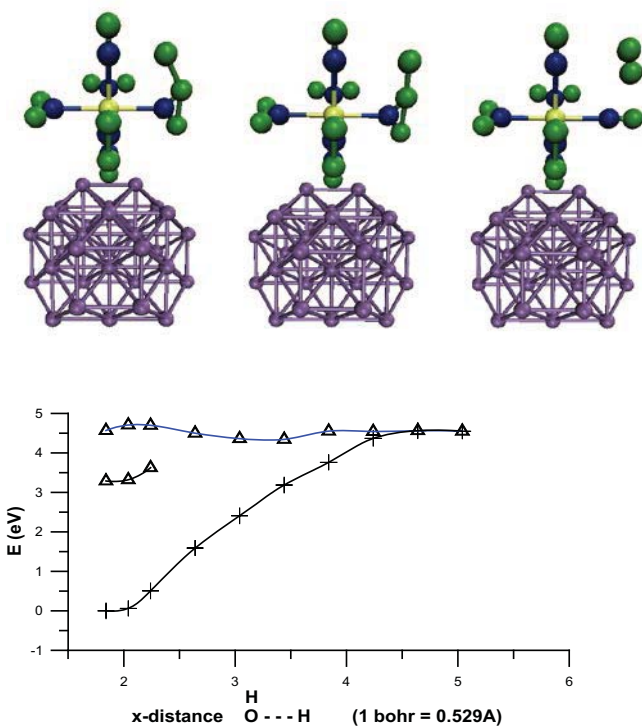

Figure 6 Photoinduced dissociation of water as a function of HO---H stretch for a trajectory of H moving from the initial water where electron attachment occurs toward a different solvated water molecule from which H is extracted to form H_2.

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In summary, in the photoinduced e-transfer to $Li^+(H_2O)_6$ near a silver surface, the calculations reveal a steering mechanism involving the interaction of a hydridic hydrogen formed from one solvated water molecule with an acidic hydrogen of a second solvated water. It would be interesting, and potentially useful, if H_3O^+ in aqueous solution would behave similarly and this possibility is currently being explored (see abstract section).

E. Dissociation of Water on a Palladium Nanoparticle

B. N. Papas and J. L. Whitten, Dissociation of water on a palladium nanoparticle, International Journal of Quantum Chemistry, 110, 3072–3079 (2010).

This section concerns studies of the interaction of a water molecule with the (111) surface of a 31-atom cluster of palladium atoms. Many-electron SCF and CI theory is used to describe the H_2O/Pd system. The focus of the investigation is the adsorption of water and the subsequent barrier to oxygen-hydrogen bond cleavage and hydrogen absorption into the cluster. We also explore the question of how electrically charging the palladium cluster (plus or minus one) affects the dissociation pathway and barriers.
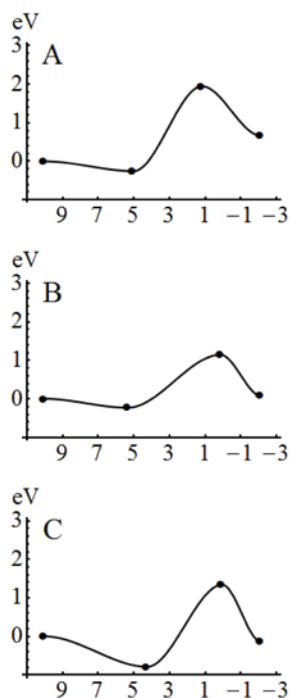

Figure 7. Potential curves for the dissociation $H_2O \rightarrow H + OH$ on Pd_{31}. From left to right, points are: separated system; adsorbed minimum; transition state; product. The horizontal axis is the distance of the penetrating hydrogen above the palladium surface plane of nuclei in bohr (1 bohr=0.529 Å) A: Cationic system; B: Neutral system; C: Anionic system.

We now consider water adsorbed on a Pd surface and the photoinduced dissociation reaction $H_2O \rightarrow OH + H$. The principal question is whether the dissociating H atom can penetrate into the lattice with an energy barrier significantly lower than for a ground state process. In order to describe the process, it is necessary to carry out calculations on highly excited states involving the water molecule adsorbed on the surface. The states of interest are electron transfer states arising from the excitation of Pd to create an electron-attached state of water and corresponding positive hole in the metal. Even for the small Pd particle considered in this work, there are many intervening lower energy excited states that involve metal to metal excitations. These states

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must be disentangled from the excited states of interest while preserving a variational bound. This is accomplished using the method described in an earlier section of the progress report.

In Fig. 8, the results of calculations on the lowest triplet and singlet states that have large contributions from water orbitals are reported; these states are the electron transfer states of interest. The energy of these states, the ground state and other higher energy states, are plotted vs. OH stretch for the dissociating H atom. Fig. 8A shows a dissociation pathway beginning with water adsorbed nearly parallel to the surface while Fig. 8B shows a pathway in which one
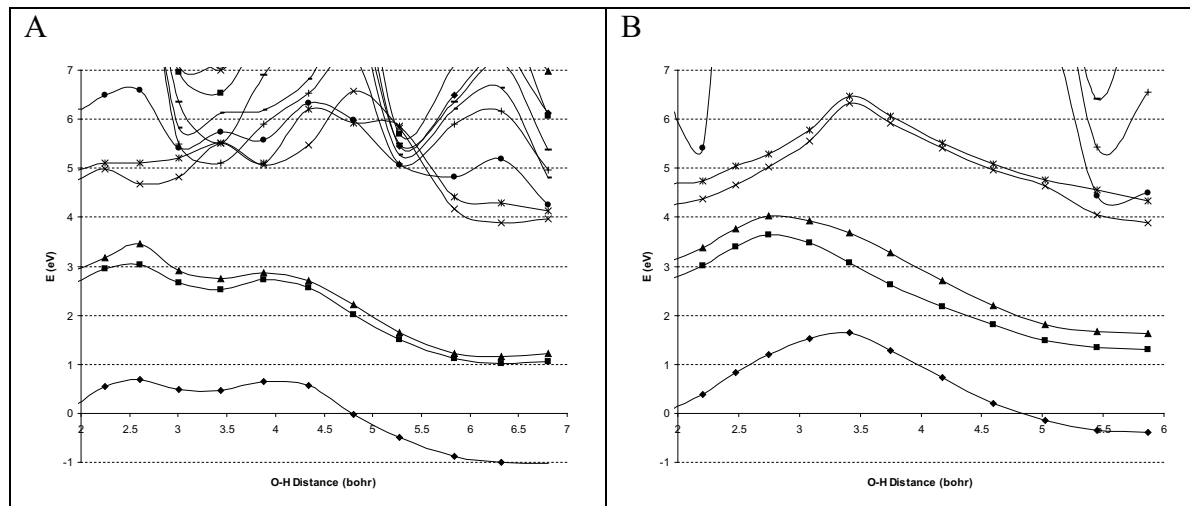
Figure 8. Ground and excited state behavior as O-H bond is lengthened so that dissociating hydrogen enters 3-fold site. A: Plane of initial water geometry parallel to plane of palladium layer 1; B: Breaking OH bond pointed towards 3-fold site.

of the hydrogens of the adsorbed water is initially pointing directly toward the three-fold Pd site. The figures differ in detail, but both have the common feature that the energy change on stretching one of the OH bonds in the excited state is much less pronounced than for dissociation on the ground state surface. The calculations reveal two possible pathways that could lead to dissociation of water and penetration of H into the particle interstitial sites. The first is to dissociate strictly on the excited state surface while the second involves an initial stretch on the excited state surface followed by relaxation back to the ground state. If the lifetime of the excited state is long enough to allow the ground state transition state geometry to be reached, the latter pathway leads to a final stage of dissociation along the ground state surface. Thus, with these caveats, both pathways are viable and need to be explored further. It is noted that the energy of the initial excitation to form the excited state is ~3 eV, a value still about 1 eV too high to make use of the intense portion of the solar spectrum. However, the present results are encourage further exploration and the possibility of using a thin metal film on a supporting surface to accomplish the separation of hydrogen and oxygen products.

F. TiO₂ ring structures

Titanium dioxide materials are widely used in heterogeneous catalysis and photochemistry. Many of the applications can be traced to the relatively low electronic band gap in TiO_2 of ~3.2 eV and the role vacancies play in electron transport and surface chemistry. Titanium dioxide nanoparticles are increasingly of interest. Because of their large surface to volume ratio, nanoparticles can enhance catalytic activity, and, in photocatalytic processes, longer excited state lifetimes may allow energy to be transferred to surfaces where non-thermal reactions with adsorbed species can occur. When the particle size is small, the states begin to resemble molecular electronic states and this quantum size effect alters the band gap of the material compared to a bulk phase. In solar applications, altering the band gap and prolonging excited state lifetimes through size effects, dopants and surface terminations are topics of great importance. The principal purpose of the present work is to examine a series of well-defined periodic systems to explore fundamental questions concerning delocalized and localized (excitonic) states.

We investigated a series of titanium dioxide ring structures, $(TiO_2)_{2n}$, n=3-9, by *ab initio* quantum theoretical methods. The study focuses on transitions from the ground state to the lowest triplet and singlet excited states and the extent of electron localization in the excited state, i.e., whether the excited state is most properly described as delocalized or as a localized electron-hole pair excitation. We calculated trends in the excitation energy for these well-defined geometrical structures $(TiO_2)_{2n}$ and compared with experiments on small TiO_2 clusters. Configuration interaction (CI) accounts for critical changes in electron correlation that occur in the ground and excited states, particularly when the excited state becomes localized. Although the total wavefunction must correspond to the symmetry of the Hamiltonian or nuclear framework, there is no fundamental symmetry requirement on individual molecular orbitals in a many-electron system. In small molecules, however, imposing symmetry on individual orbitals offers considerable conceptual and computational advantages, and, in the limit of infinite configuration interaction, will converge to the exact description of the electronic state.


$(TiO_2)_6$ $(TiO_2)_8$ $(TiO_2)_{10}$ $(TiO_2)_{12}$

$(TiO_2)_{14}$ $(TiO_2)_{16}$ $(TiO_2)_{18}$
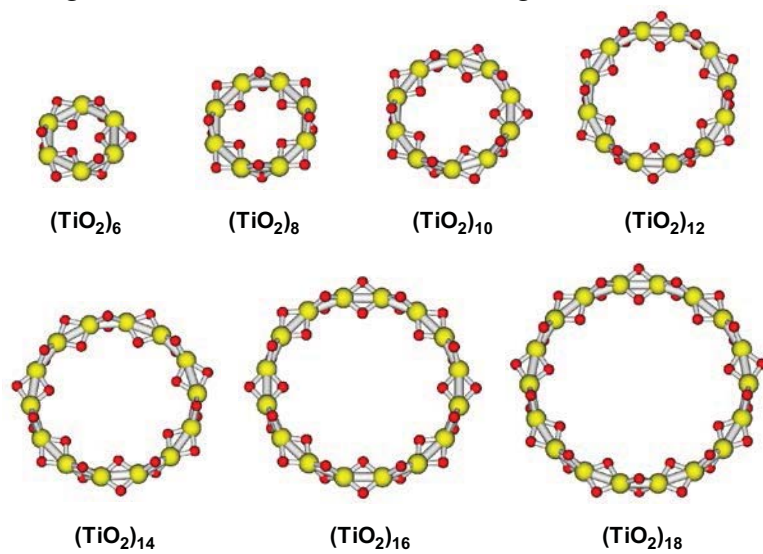
Figure 9. $(TiO_2)_{2n}$, n=3-9 rings.

Figure 10 depicts the localized holes found for the three types of oxygens using the triplet state of $(TiO_2)_{10}$ as an example. Figure 11 depicts the corresponding singly occupied orbitals which are largely localized on a nearest neighbor titanium. These figures demonstrate that the electron hole pair is very well described as an electron in a Ti 3d orbital and an oxygen 2p hole. The same high degree of localization is found for all other ring structures.
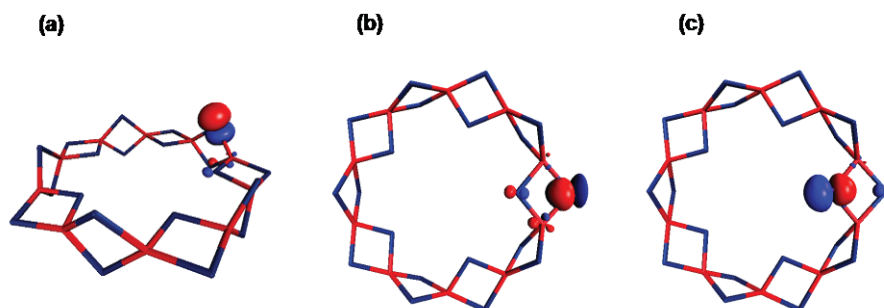
Figure 10. Three types of localized holes. In (a), the hole is on the out-of-plane oxygen relative to the plane of titanium nuclei; in (b), the hole is on the in-plane oxygen outside the titanium ring; and, in (c), the hole is on the inside, in-plane oxygen.
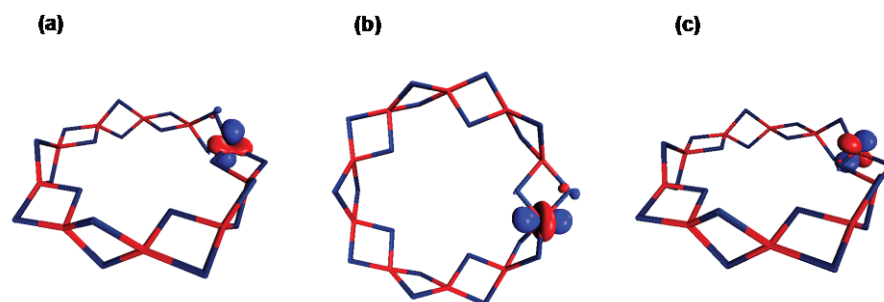
Figure 11. Types of Ti 3d localized electrons corresponding to the localized holes in Fig. 10.

Table 1. Excitation energies (in eV) for the singlet and triplet excited states of the out-of-plane, in-plane/outside and in-plane/inside hole location (see text) calculated by configuration interaction.

	out-of-plane		in-plane/outside		in-plane/inside		
	triplet	singlet	triplet	singlet	triplet	singlet	exptl.[a]
$(TiO_2)_6$	2.26	2.34	2.17	2.59	2.15	2.23	3.00
$(TiO_2)_8$	2.44	2.62	2.99	3.35	2.81	3.00	3.1
$(TiO_2)_{10}$	2.65	2.87	3.05	3.37	3.05	3.14	3.1
$(TiO_2)_{12}$	2.80	3.03	3.16	3.46	3.51	3.56	-
$(TiO_2)_{14}$	2.91	3.08	3.23	3.53	3.60	3.65	-
$(TiO_2)_{16}$	3.19	3.46	3.29	3.60	3.84	3.89	-
$(TiO_2)_{18}$	3.21	3.49	3.33	3.62	3.83	3.88	-

[a] PES experimental values for anions of unknown structure.

For the largest ring, $(TiO_2)_{18}$, the triplet and singlet excitation energies are between 3.2 eV and 3.9 eV for all locations of the O 2p hole. Although values for the ring structures should not necessarily correspond to bulk excitation energies, the ring values are fairly close to the bulk phase values of 3.0 eV (rutile) and 3.2 eV (anatase). Of particular interest is the singlet-triplet splitting which varies depending on the hole location. The singlet-triplet splitting is found to be almost negligible for the in-plane/inside hole location and large for the in-plane/outside location. The splitting for the out-of-plane location of the hole lies between these limits. The singlet-triplet splitting occurs because of the exchange interaction between the electron-hole orbitals and a variation in splitting suggests that the spatial extent of orbitals associated with the localized electron-hole pair may differ for the different hole locations.

The low transition energies to singlet excited states that range from 2.2 eV to 2.6 eV for rings $(TiO_2)_6$ and $(TiO_2)_8$ are intriguing and encourage exploration of ways to make use of these small structural units for solar radiation capture and possibly photoassisted catalysis, possibly by assembly of units on inactive supporting surfaces.

G. Mechanism for Direct Decarboxylation of Fatty Acids on Pd Surfaces
Henry Lamb, Laura Sremaniak and Jerry L. Whitten, J. Phys. Chem., to be submitted, (2011).

Heterogeneous catalysis is poised to play a key role in the future of biofuels and biorefining. Next-generation biofuels will be comprised of *hydrocarbons* like those in petroleum-derived fuels, making them "drop-in replacements" for existing fuels. Hydrocarbons for biofuels can be produced by deoxygenation of free fatty acids produced via triglyceride hydrolysis. Early work by Maier *et al.* demonstrated that Pd/SiO_2 is a highly active and selective catalyst for vapor-phase deoxygenation of carboxylic acids.

In this work, butanoic acid was investigated using high level electronic structure theory to elucidate the elementary steps involved in alkyl carboxylic acid decarboxylation on Pd surfaces.
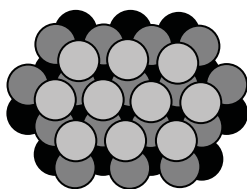
Fig.12. Top view of the (111) surface of the Pd-42 nanoparticle. Radii of the Pd atoms are shown at reduced size for clarity of visualization. The 10 surface Pd atoms and 6 of the Pd atoms in the second layer are described by flexible atomic basis (see text). The remaining atoms are described by effective potentials.

Butanoic acid is calculated to adsorb on the Pd(111) surface as an intact molecule with the –COOH group nearly parallel to the surface. After a series of steps, the molecule dissociates to form adsorbed CO_2 and adsorbed propane, propyl-COOH (ads) → propane(ads) + CO_2 (ads) .

The study reveals two viable pathways for the dissociation of butanoic acid to CO_2 and propane.
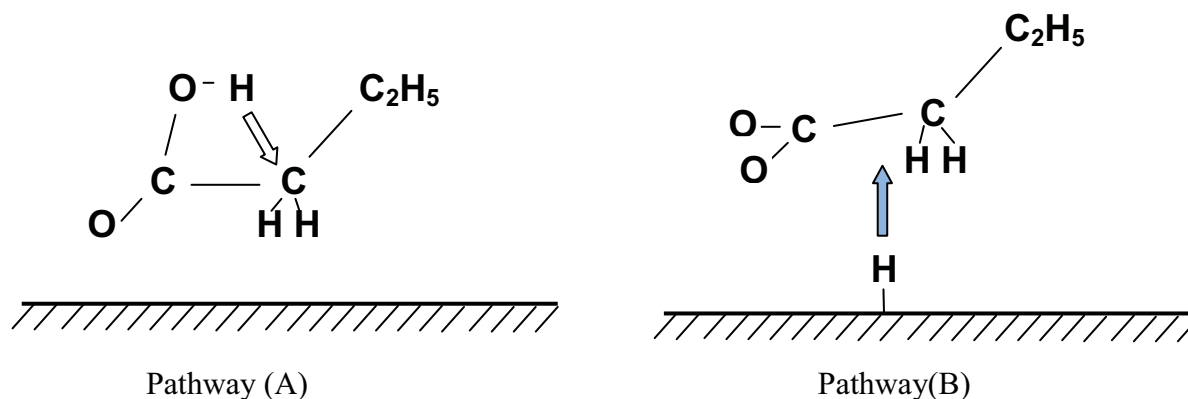
Pathway (A)   Pathway(B)

The first pathway (A), which we refer to as an intramolecular H transfer, involves initially a bending back of COOH to allow H to come close to the target carbon. A series of bond stretches and rotations occur to produce products. The second pathway (B) involves dissociation of H as the initial step and a subsequent transfer of H from the Pd surface to the target carbon. In both pathways, the surface plays a critical role in stabilizing intermediate geometries in which bonds are stretched and angular realignments occur. Both pathways involve essentially the same CO_2 and propane exit channels.

Fig. 13. H rotated back pathway. The three energy levels on the left are for gas phase butanoic acid far from the Pd surface, the energy of the adsorbed intact molecule and the barrier to rotating H through a perpendicular geometry.
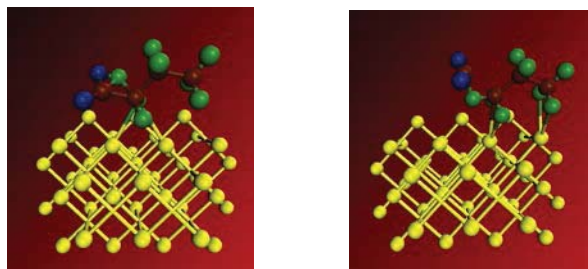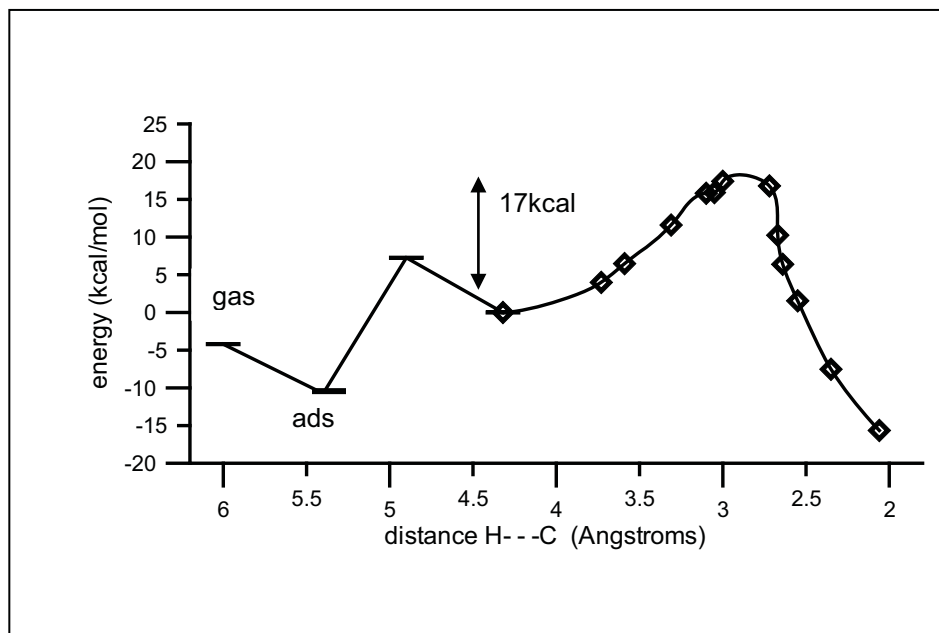
Fig. 14. Transition state for the H rotated back(left) and for an initial dissociation of H (right).

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Fig. 15. Pathway involving initial dissociation of H. The three energy levels on the left are for the adsorbed intact molecule, the dissociation of H to the most stable 3-fold Pd site and the barrier to move the H and propyl-COO fragments so that H is under the CC bond. The dashed line plots the energy vs. CC distance (changing the definition of the x-axis) for the CO_2 plus propane exit channel.
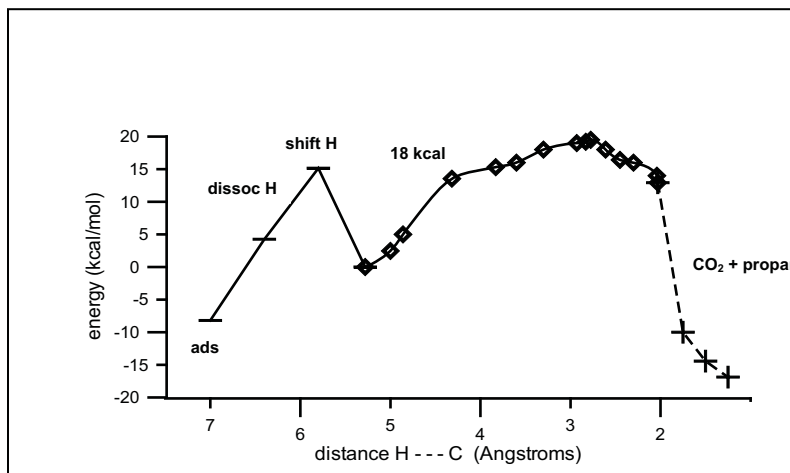
5. List of papers, DOE sponsored research DE-FG02-97ER45624

Publications and Abstracts of Papers, January 1, 2009- June 1, 2011
* DOE sponsored research Grant DE-FG02-97ER45624

A. Publications, 2009-2011

1. Yu Zhang and J. L. Whitten, Photoinduced dissociation of water adsorbed on a Ag cluster, *Journal of Molecular Structure: THEOCHEM,* 903 (2009) 28-33.

2. Williams, D. Keith; Comins, Daniel L.; Whitten, Jerry L.; Muddiman, David C. Evaluation of the ALiPHAT Method for PC-IDMS and Correlation of Limits-of-Detection with Nonpolar Surface Area, Journal of the American Society for Mass Spectrometry (2009), 20(11), 2006-2012.

3. Yu Zhang and J. L. Whitten, Photoemission into water adsorbed on metals: probing dissociative electron transfer using theory, International J. Quantum Chemistry (2009), 109(15), 3541-3551.

4. B. N. Papas and J. L. Whitten, Dissociation of water on a palladium nanoparticle, International Journal of Quantum Chemistry, 110, 3072–3079 (2010).

5. Shuford, Christopher M.; Comins, Daniel L.; Whitten, Jerry L.; Burnett, John C., Jr.; Muddiman, David C., Improving limits of detection for B-type natriuretic peptide using PC-IDMS: An application of the ALiPHAT strategy, Analyst (Cambridge, United Kingdom) (2010), 135(1), 36-41.

6. Takashi Tsuchiya and Jerry L. Whitten, Theoretical Study of the Molecular and Electronic Structures of TiO_4H_4, $Ti_2O_7H_6$, and $Ti_2O_6H_4$, *J. Phys. Chem. C*, 2011, 115 (5), pp 1635–1642

7. Takashi Tsuchiya and Jerry L. Whitten, Configuration interaction study of the ground and excited states of TiO_2 ring structures, Journal of Chemical Physics, 134, 114701-7 (2011).

8. Hyungtak Seo, L. Robert Baker, Antoine Hervier, Jinwoo Kim, J. L. Whitten, and Gabor A. Somorji, Generation of Highly n-Type Titanium Oxide Using Plasma Fluorine Insertion, *Nano Lett.*, 2011, 11 (2), pp 751–756.

9. Henry Lamb, Laura Sremaniak and Jerry L. Whitten Mechanism for Direct Decarboxylation of Fatty Acids on Pd Surfaces, J. Phys. Chem., to be submitted, (2011).

10. Gerry Lucovsky, Greg Parsons, Daniel Zeller, Kun Wu, B. N. Papas, Jerry Whitten, Rene Lujan, and Robert A. Street**,** Spectroscopic Detection of Medium Range Order in Device Quality Hydrogenated Amorphous Silicon, a-Si(H), Applied Phys. Lett, submitted, (2011)

11. B. N. Papas and J. L. Whitten, Silver as an electron supply for photo dissociation of a solvated hydronium ion, J. Phys. Chem., submitted, (2011).

12. Takashi Tsuchiya, Configuration Interaction Study of the Electron-hole States of $Ti_2O_6H_4$, Chemical Physics, submitted, (2011).

B. Abstracts of Papers listed in Section A, January 2009-June 2011.

1. Photoinduced dissociation of water adsorbed on a Ag cluster
Yu Zhang and Jerry L. Whitten, *Journal of Molecular Structure: THEOCHEM,* published online 26 January 2009 THEOCHEM (2009), 903(1-3), 28-33
Abstract. Theoretical electronic structure calculations are reported for the photoinduced dissociation of water adsorbed on a 31-atom silver cluster, Ag_{31} to produce H_2 and adsorbed O. Both ground and excited electronic state processes are considered. The excited electronic state of interest is formed by photoemission of an electron from the Ag cluster and transient attachment of the electron to the adsorbed water molecule. A very large energy barrier for H_2 formation (3.51 eV) is found for the ground state process while the barrier in the excited state is much smaller (0.47 eV). In the excited state, partial occupancy of an OH antibonding orbital facilitates OH stretch and the electron hole in the metal cluster stabilizes OH and O adsorbates. The excited state pathway for dissociation of water begins with the formation of an excited electronic state at 3.49 eV. Stretch of the OH bond up to 3.44 a.u. (1.82Å) occurs with little change in energy. In this region of OH stretch the molecule must return to the ground state potential energy surface to dissociate fully and to form H_2. Geometry optimizations are carried out using a simplex algorithm which allows the total energy to be calculated using configuration interaction theory.

2. Evaluation of the ALiPHAT Method for PC-IDMS and Correlation of Limits-of-Detection with Nonpolar Surface Area, Williams, D. Keith; Comins, Daniel L.; Whitten, Jerry L.; Muddiman, David C. Journal of the American Society for Mass Spectrometry (2009), 20(11), 2006-2012.

Note: This collaboration uses methods developed for other purposes with support from the current DOE grant, but otherwise is unrelated to the focus of the grant.

Abstract. PC-IDMS (protein cleavage coupled with isotope diln. mass spectrometry) expts. for two peptides, laminin nonapeptide and the N-terminal tryptic peptide of prostate specific antigen, were performed utilizing a variety of alkylating reagents. These expts. were conducted to investigate how hydrophobicity influences the limits-of-detection (LOD) by altering their electrospray ionization response. Nonpolar surface areas were calcd. for both peptides and all alkylating reagents to provide an est. of the hydrophobicity of the differently alkylated peptides.

3. Theoretical Treatment of the Dissociation of Butanoic Acid On Pd(111), Sremaniak, Laura S.; Whitten, Jerry L. Abstracts, 61st Southeast Regional Meeting of the American Chemical Society, San Juan, Puerto Rico, October 21-24 (2009), SRM-555.

Abstract. The dissocn. of butanoic acid on a Pd(111) surface of a nanoparticle is reported. First principles theor. methods (ab initio/CI) are used to describe metal-adsorbate bonding. In order to achieve high accuracy in the adsorbate-surface region of the cluster, an embedding theory is used. Butanoic acid initially binds to Pd(111) with the carboxyl group planar to the surface. A key step in the dissocn. of butanoic acid is the orientation of the adsorbate so that the acidic hydrogen can move to a three-fold site on the Pd surface. Dissocn. of the hydrogen is followed by stretch of the weakened OH bond.

4. Photoemission into water adsorbed on metals: probing dissociative electron transfer using theory, Yu Zhang and J. L. Whitten, International J. Quantum Chemisty (2009), 109(15), 3541-3551.

Abstract. The photoinduced dissociation of water adsorbed on a silver nanoparticle is explored using theory to probe reaction pathways that produce hydrogen. *Ab initio* configuration theory is used to describe the systems. A formulation that allows excited electronic states embedded in a near continuum of lower energy states to be calculated accurately is described.   Electron attachment of a photoemitted electron to adsorbed water can lead to the formation of H_2 at a very low energy barrier with oxygen remaining on the Ag surface. A large energy barrier to form H_2 plus adsorbed O is found for the ground state. The excited state has a much smaller barrier to OH stretch; however, to dissociate, the system must cross over from the excited state to the ground state potential energy surface.   The cross over point is near the transition state for a ground state process.   A characteristic feature of the excited state potential curve is an increase in energy in the early stages of OH stretch as the charge transfer state evolves from a state with considerable Rydberg character to one that has a typical OH antibonding molecular orbital. Another pathway releases a H atom leaving OH on the surface. Effects due to doping of a Ag nanoparticle with a K electron donor atom are compared with those caused by a Fermi level shift due to an applied potential. Results are also reported for electron transfer to a solvated lithium ion, $Li(H_2O)_6^+$, near the surface of a silver particle. A steering mechanism is found that involves the interaction of a hydridic hydrogen formed after electron transfer with an acidic hydrogen of a second solvated water molecule.

5. Dissociation of Water on a Palladium Nanoparticle.
Brian N. Papas, Jerry L. Whitten, International Journal of Quantum Chemistry, 110, 3072–3079 (2010).

Abstract. Ab initio SCF-CI theory has been used to examine the interactions of a single water molecule with a 31-atom nanocluster of palladium. Calculations are performed on singly-charged cationic and anionic particles in addition to the neutral system to determine effects of charging on the adsorption energy of water and the barriers to dissociation. Penetration of the dissociated H through the surface layer into an interstitial subsurface site is also examined. Adsorption energies of an intact water molecule fall in the range 0.2–0.8 eV, while the barrier to dissociation into a subsurface site is in the range 1.4–2.1 eV depending on the charge of the metal particle. Calculations on the photoinduced dissociation of water adsorbed on the Pd surface are also reported, and dissociation pathways with smaller energy barriers than found for the ground state are shown to exist.

6. Improving limits of detection for B-type natriuretic peptide using PC-IDMS: An application of the ALiPHAT strategy, Shuford, Christopher M.; Comins, Daniel L.; Whitten, Jerry L.; Burnett, John C., Jr.; Muddiman, David C., From Analyst (Cambridge, United Kingdom) (2010), 135(1), 36-41.
Note: This collaboration uses methods developed for other purposes with support from the current DOE grant, but otherwise is unrelated to the focus of the grant.

Abstract. Hydrophobic tagging of biomols. has been reported by our group and others to increase their ionization efficiency during electrospray ionization and facilitate their detection by mass spectrometry. As such, hydrophobic tagging should provide a viable method for augmenting MS-based quantification of low abundance proteins by decreasing their detection limits. Herein we have evaluated two com. alkylation reagents and several newly synthesized hydrophobic alkylation reagents for their utility in quantifying B-type Natriuretic Peptide, a low abundance cardiac biomarker, by protein cleavage.

7. Theoretical Study of the Molecular and Electronic Structures of TiO_4H_4, $Ti_2O_7H_6$, and $Ti_2O_6H_4$, Takashi Tsuchiya and Jerry L. Whitten, *J. Phys. Chem. C*, 2011, 115, pp 1635–1642.

Abstract. State-of-the-art multi-state configuration interaction (CI) calculations are performed for a series of titanium oxygen complexes chosen to identify features present in titanium oxide nanoclusters and titanium dioxide surfaces. All electrons are included in the calculations and transformation methods are employed to achieve high accuracy for the excitations of interest. The electronic structures of the ground and excited states are discussed and excitation energies are reported for different molecular conformations. Of particular interest is the high degree of localization of the electron-hole pair formed on electronic excitation leading to a description of the lowest excited state as an O2p hole Ti 3d-electron exciton for all systems investigated. Singlet and triplet excited states are resolved and energies of electronic states are reported as a function of molecular geometry.

8. Configuration interaction study of the ground and excited states of TiO_2 ring structures
Takashi Tsuchiya and Jerry L. Whitten, Journal of Chemical Physics, 134, 114701 (2011).

Abstract. Theoretical studies of the ground and lowest excited singlet and triplet states of a series of titanium dioxide ring structures, (TiO2)2n, $n = 3–9$, are reported. Calculations are based

on many-electron configuration theory, where energies of states and geometrical structures are determined by variational energy minimization. The lowest energy excited states correspond to excitations from oxygen 2p levels to unoccupied 3d orbitals on titanium. For each ring system, two types of excited state solutions are investigated: those that maintain periodic symmetry for individual orbitals and solutions that allow the symmetry to be broken. The latter solutions which correspond to localized states or excitons are found to be significantly lower in energy than the symmetric solutions. We compare the vertical excitation energy of these well-defined geometrical structures with size effects reported in experimental studies.

9. Generation of Highly n-Type Titanium Oxide Using Plasma Fluorine Insertion

Hyungtak Seo, L. Robert Baker, Antoine Hervier, Jinwoo Kim, J. L. Whitten, and Gabor A. Somorjai, *Nano Lett.*, 2011, 11 (2), pp 751–756

Abstract. Titanium oxide is a widely used metal-oxide semiconductor; its uses include catalysts, solar cells, transparent transistors, chemical sensors, and catalytic hot electron convertors. [1-7] Titanium oxide is considered intrinsically n-type because of native oxygen (O) vacancy donors. [8] However, O vacancy doping induces the formation of defect states in the bandgap, and at high O vacancy concentrations, a suboxide band structure forms that results in metallic transport, pins the Fermi level, and limits the excitation energy of hot carriers by charge trapping. [9-11] Consequently, O vacancy doping is not ideal for many metal-oxide semiconductor applications. A technique for true n-type doping of titanium oxide without the formation of mid-gap defect states would improve the efficiency of many current charge-based devices and expand the use of transition metal oxides to new applications. Here we show that plasma-assisted fluorine insertion passivates intrinsic defect states and that fluorine acts as an extrinsic n-type donor in titanium oxide. This enabled us to modify the Fermi level and transport properties of titanium oxide outside the limits of O vacancy doping. The origin of fluorine-induced surface electronic structure modification is also identified by *ab-initio* theoretical calculation. This expands the utility of titanium oxide for applications requiring highly n-type, low defect semiconductors. Potential applications include resistive switching memory devices, thin film transistors, high-efficiency solar cells, and photo- and support-catalysts.

10. Mechanism for Direct Decarboxylation of Fatty Acids on Pd Surfaces.

Henry Lamb, Laura Sremaniak and Jerry L. Whitten, J. Phys. Chem., to be submitted, (2011).
Abstract. Many-electron theory is applied to investigate the conversion of butanoic acid to propane and CO_2 on the (111) surface of a Pd_{42} nanoparticle. Butanoic acid weakly adsorbs exothermically on the surface as an intact molecule, $E_{ads} = 6.5$ kcal/mol. Subsequent dissociation of a hydrogen can occur and is endothermic by 12 kcal/mole or only 6 kcal in energy higher than butanoic acid in the gas phase. These values are reduced if the dissociation products move apart. The formation of CO_2 and propane can occur by two different pathways, and both involve precursor states. In a dissociated H pathway, H adsorbed on the surface reacts in a separate step with adsorbed propyl-COO. The energy of activation for this pathway was calculated as 18 kcal/mol. A second, intramolecular, pathway involves rotating the H of -COOH over an energy barrier toward the propyl carbon. Following a series of bond distortions the H is close enough to the target C to form a stretched H-C bond. The activation energy for this pathway is 17 kcal/mol. Both pathways have the same exit channel: After propane begins to form, the CO_2 linearizes and dissociation is downhill energetically and rapid. The overall reaction, forming CO_2 and propane adsorbed on the surface is 6.6 kcal/mol exothermic compared

to butanoic acid adsorbed on the surface. The results suggest that the dissociated H pathway can be influenced by predosing the surface with hydrogen; this would raise the energy of the precursor state and thereby decrease the activation barrier, however the presence of H also would facilitate reformation of reactants.

11. Spectroscopic Detection of Medium Range Order in Device Quality Hydrogenated Amorphous Silicon, a-Si(H)

Gerry Lucovsky, Greg Parsons, Daniel Zeller, Kun Wu, B. N. Papas and Jerry Whitten, N. C. State, Rene Lujan, and Robert A. Street, The Palo Alto Research Company.
Abstract. Hydrogenated amorphous silicon, a-$Si_{1-x}H_x$, with x ~ 0.1±0.02, is used in photovoltaic and thin film transistor devices. This a-Si(H) alloy can be deposited by the glow discharge method, remote plasma-enhanced chemical vapor deposition, or reactive magnetron sputtering. Two conditions are necessary for low densities of Si dangling bond defects: (i) a bonded monohydride, Si-H, concentration of 8 to 12%, and (ii) deposition, and/or a post-deposition anneal at ~250 to 300 °C. Second derivative Si $L_{2,3}$ soft X-ray absorption spectra are used to identify medium range order (MRO) beyond the short range order (SRO) of continuous random networks (CNRs) to explain the extra-ordinarily low defect densities of these alloys.

12. Silver as an electron supply for photo dissociation of a solvated hydronium ion.

B. N. Papas and J. L. Whitten, J. Phys. Chem., to be submitted, 2011.
Abstract. Dissociation pathways accessible upon excitation of an electron from a cluster of silver atoms to a solvated hydronium ion are examined using *ab initio* SCF-CI theory. Depending upon initial orientation of the hydronium relative to the silver surface, the electron attachment can occur at energies in the range of 1.22 eV to 3.05 eV. Rearrangement of solvating waters considerably dampens transition states to dissociation on the exited-state potential energy surface, such that fast dissociation of the hydronium would occur with no barrier. Both the H and H_2 product channels are exothermic pathways on the excited state surface and in several instances exothermic compared to the energy of the initial structure.

13. Configuration Interaction Study of the Electron-hole States of $Ti_2O_6H_4$.

Takashi Tsuchiya, Chemical Physics, submitted, (2011).
Abstract. Configuration interaction (CI) calculations were performed for $Ti_2O_6H_4$, and the excited electron-hole states were investigated. $Ti_2O_6H_4$ was constructed to model the defect site of the surface state of TiO_2 materials. Two strategies were applied for the description of the electronic structure of the excited state. One utilizes the symmetric, canonical orbitals and the other utilizes the symmetry-broken sets of orbitals. Although HF calculations produced a large difference in the state energy between two different descriptions of the electronic structure of the excited state, these two descriptions converged to be equivalent when the electron correlation effect is included by the large CI calculation. This implies that both the symmetric and symmetry-broken sets of orbitals may exist for the respective electron-hole states. The stability of the hole on the different oxygen sites was investigated. The hole non-adjacent to the localized electron is energetically more stable than the hole adjacent to the electron when the electron-hole distance is close. Therefore, the hole hopping from the adjacent site to the non-adjacent site may occur. This can lead to charge separation following the creation of the electron-hole pair. It is demonstrated that the excitation energy shifts monotonically as a function of the geometrical

change of the molecular structure. This suggests a potential of the band gap tuning of TiO_2 materials by means of the molecular-level local structure control.

6. Personnel
PI, Professor Jerry L. Whitten, summer support only from grant.

Postdoctoral research associate, Dr. Brian Papas. 100% support from grant. Dr. Papas worked closely with me on the development of parallel computing methods. He also carried out calculations on the photoinduced dissociation of water adsorbed on palladium and electron transfer to solvated H_3O^+ in aqueous solutions.

Postdoctoral research associate, Dr. Takashi Tsuchiya, 3 months support from DOE grant. Dr. Tsuchiya primary duties were associated with the UNC Chapel Hill EFRC Solar Center. When that support ended, Dr. Tsuchiya continued his work for three months on TiO_2 ring and nanoparticle systems.

Professor Gerry Lucovsky, faculty collaborator, Physics Dept. Joint research on metal/metal-oxide interfaces and core electron spectroscopy (no charge to grant).

Kun Wu, a graduate student jointly supervised with Professor Lucovsky. He worked closely with Dr. Papas and myself on calculations of $L_{2,3}$ spectra observed in synchrotron experiments and vacancy interactions in SiO_2.

Mr. Patrick White, undergraduate student. He has worked one summer on small projects to test various aspects of electron correlation ideas and calculations of the van der Waals surface area of molecules of interest to a mass spectrometry project (supported on a REU fellowship, no charge to grant).

Dr. Laura Sremaniak, faculty collaborator, Chemistry. Dr. Sremaniak, who is now serving as associate department chair, continued her collaboration with my research program at no cost to the DOE grant. She worked on palladium catalysis of the conversion of butanoic acid to propane plus CO_2.

7. Planned activities for next grant year
See the accompanying Renewal Proposal

8. Other support
Our research is currently supported only by the U.S. Department of Energy. I was a member of the DOE funded EFRC Solar Center at UNC-Chapel Hill and received a grant subcontract of $72,000 for the period August 1, 2009 to September 30,2010. My research with the Solar Center concerned TiO_2 systems which is a topic completely different from that associated with my DOE grant. The Solar Center subcontract ended September 30, 2010 and I withdrew from the Center effective that date.

9. Unexpended funds at the end of the current grant period are expected to be less that 10% of the award.