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The main goals of this program have been to develop new, more effective methods for performin accurae ab initio electronic structure calculations and to use these methods for the prediction of molecular structure, bonding and reactivity, especially for main group species and reactions of interest to the Air Force. Progress on the associated AASERT grant is include in this report. From the theoretical point of view, the principle accomplishements have been extensive development of approaches and codes for performing electronic structure calculations in parallel, continued development of methods for interfacing electronic structure calculations with dynamics, the development of a new model for treating solvation, and the development and implementation of a gridless approach to density functional theory. Applications have ranged from the development of very accurate and extensive potential energy surfaces for A + HB reactions (to interface with the experiments of Neumark and Zare) to the role of catalysts in the hydrosilation reaction and the formation of silsesquioxanes to extensive studies of reactions involved in both main group and transition metal chemical vapor deposition (CVD) to broad-based studies of cage molecules (using our new parallel capabilities) that are potential precursors for new materials, electronic and optical devices, and catalysts.

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# AFOSR FINAL REPORT
# THEORETICAL STUDIES OF SILICON AND RELATED ELEMENTS
# AFOSR F49620-95-1-0073

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The main goals of this program have been to develop new, more effective methods for performing accurate *ab initio* electronic structure calculations and to use these methods for the prediction of molecular structure, bonding and reactivity, especially for main group species and reactions of interest to the Air Force. *Progress on the associated AASERT grant is included in this report.* From the theoretical point of view, the principle accomplishments have been extensive development of approaches and codes for performing electronic structure calculations in parallel, continued development of methods for interfacing electronic structure calculations with dynamics, the development of a new model for treating solvation, and the development and implementation of a gridless approach to density functional theory. Applications have ranged from the development of very accurate and extensive potential energy surfaces for A + HB reactions (to interface with the experiments of Neumark and Zare) to the role of catalysts in the hydrosilation reaction and the formation of silsesquioxanes to extensive studies of reactions involved in both main group and transition metal chemical vapor deposition (CVD) to broad-based studies of cage molecules (using our new parallel capabilities) that are potential precursors for new materials, electronic and optical devices, and catalysts.

In the following pages, we summarize the progress of our recent AFOSR research, starting with theory/model developments and followed by applications.

## I. MODEL DEVELOPMENT

Calculations of accurate potential energy surfaces (PES's) for molecular isomerizations and dissociations and chemical reactions are highly compute-intensive, frequently requiring the use of very large basis sets and multi-reference wave functions. Multi-reference wave functions are especially critical when more than one electronic state is involved in the calculation. Therefore, a major effort in our group has been to increase the efficiency of the calculations by developing electronic structure codes that may be used on parallel computers.

Our philosophy has been to make the codes as general and (therefore) as portable as possible, so that they may be used in virtually any parallel environment. The platform used for

the parallel developments is GAMESS[1] [General Atomic and Molecular Electronic Structure System]. As developed in our laboratory, parallel GAMESS can be run using a modest number of workstations. A one-word option optimizes the performance, depending on whether several workstations of the same type or with different capabilities are being used. The same code may be run on larger "massively parallel" computers. For example, parallel GAMESS is generally available on the Intel Paragon and Cray T3E at the San Diego Supercomputer Center and the IBM SP2's at the Cornell Supercomputer Center, the Maui Center and the ASC. At the other end of the scale, GAMESS is now available on the Power Macintosh and Pentium Pro computers. This makes the full code available to virtually any user for a very small investment in hardware. A closely related activity is the development of front and back end graphical user interfaces for GAMESS. The main development here is a Macintosh program called MacMolPlt. Current features of MacMolPlt include the ability to visualize and rotate molecules in real time, animation of molecular vibrations, animation of minimum energy reaction paths or of classical dynamic trajectories, and visualization and real-time rotations of molecular wavefunctions. Both GAMESS and MacMolPlt are available at now cost to any user.

The currently distributed version of GAMESS includes parallel capability for essentially all types of wavefunctions, including Hartree-Fock (RHF, UHF, ROHF) and two-configuration (TCSCF or GVB) wave functions, and their associated analytic gradients[1] , analytic hessians[2] , and MCSCF and CI wavefunctions[3] . We have very recently developed a distributed data instruction (DDI) set that permits us to distribute large arrays of data across all of the nodes[4] . This allows us to avoid the use of replicated data and consequently increases the size of the problem that can be investigated. Second order perturbation theory (MP2) gradients have been implemented using this new method. This means that geometry optimizations, transition state searches, reaction path following and classical trajectories can all be performed using the parallel algorithms at all of these levels of theory. The scalability of the calculations with increasing numbers of nodes is close to ideal (100%) for up to 32 nodes, as long as the size of the application is increased as the number of nodes is increased. Very little efficiency is lost through 128 nodes, and significant speedups are obtained even with 512 nodes. The hessian algorithms do not yet scale as well, but a direct method that is under development is in progress[5] . The main participants in these endeavors are Dr. Graham Fletcher (Iowa State), Dr. Theresa Windus (ASC) and Dr. Galina Chaban (Iowa Stat). Ms. Chaban has recently developed a new method for converging MCSCF wavefunctions[6] . This is a combined second order-first order method that has considerable promise. It is already written to take adavntage of parallel hardware. The development of the DDI tool set and the MP2 gradients is the first step in the development of a general parallel algorithm for CI gradients.

We have also initiated the development and implementation of a density functional code[7] . Unlike most other implementations, we have chosen to use the analytic (gridless) method initially developed by Zhang and Almlof. This method makes use of the resolution of the identity (RI) to simplify integral evaluation. The RI approach is also used to facilitate the derivation and coding of energy first derivatives, enabling geometry optimizations, transition state determination reaction path following and moleclar dynamics simulations.

Closely connected to our developments of new approaches for treating larger systems is the development of new solvation models, in collaboration with Drs. Walter Stevens and Morris Krauss at CARB, and Drs. Ruth Pachter and Paul Day at Wright Laboratories. The *effective fragment potential* (EFP) method treats the solute (which could be a molecule, a reacting system, or a reacting system surrounded by a small number of solvent molecules) using *ab initio* wavefunctions. The solvent is simulated using solvent molecules (effective fragments) whose internal geometries are frozen, but which are otherwise free to move relative to each other and to the solute. The interactions between the fragments and the solute and between solvent molecules are described by a model potential that includes electrostatic, polarization, and exchange repulsion + charge transfer terms[8,9] . The first two terms in this model potential are obtained from *ab initio* calculations on the monomers (once and for all). The repulsive term is obtained by fitting to *ab initio* potential energy surfaces. The entire potential is added as one-electron terms to the *ab initio* Hamiltonian. The method has been implemented for both Hartree-Fock[8,9] and MCSCF[10] levels of theory. In both cases, the two parts (fragment and *ab initio*) are mutually iterated to self-consistency. The fragment-solute and fragment-fragment interaction terms and gradients have been derived and coded, as have the equations that allow us to follow minimum energy paths for reactions that occur in solution. We are currently developing molecular dynamics (MD) codes that will allow us to perform simulations of liquids and solvation dynamics. The model is now undergoing extensive testing and is in the most recently released version of GAMESS. The initial tests have been extremely encouraging. The EFP method agrees with full *ab initio* calculations for the geometries, barrier heights, vibrational frequencies, and minimum energy paths as the number of water molecules is increased in the internal rotation process of formamide[11] . Similar levels of agreement are being found in studies of water clusters[12] , the Menshutkin reaction[13] (ion separation reaction), a prototypical $S_N2$ reaction[14] , and solvation of electrolytes[15] .

The EFP method described in the previous section has one drawback: the repulsive potential relies on parameters that are fitted to *ab initio* calculations. This means that to extend the method beyond water would require many time-consuming calculations for each solvent of interest. To avoid this, we have been developing an alternative approach that avoids the need for fitted parameters[16] . This method is based on the use of localized orbitals and on the expansion

of the exchange repulsion as a power series in the overlap integral. Preliminary tests of this method are quite encouraging.

While the EFP method is primarily intended to open liquids and solvation to serious investigation, we have also been developing methods for the treatment of the solid state, particularly surface chemistry. Beginning with fused quantum mechanics (QM)/molecular mechanics (MM) methods developed by others, we have collaborated with Professor Larry Burggraf and James Shoemaker (AFIT) to develop an *ab initio* embedded cluster model to describe chemical reactions at surfaces[17]. The most exciting new strides are the development of methods to treat binary surfaces, such as SiC and SiN, and the use of massively parallel computers to maximize the size of the embedded (*ab initio*) cluster. While the method as developed is quite promising, there is much room for improvement, since we cannot easily perform constrained geometry optimizations or determine transition states for surface reactions, and the method for capping the cluster needs improvement. These areas are targeted for future development.

The study of PESs for chemical reactions often involves more than one electronic state. When this occurs, it is necessary to determine the spin-orbit coupling among these states. We have devised a general scheme for directly calculating the one-electron matrix elements and then using these results to parametrize the two-electron contributions, all using the GAMESS MCSCF programs. The predictive ability of this method for diatomics and small polyatomic molecules is quite good[18]. The next step is to develop general algorithms to permit the calculation of the full spin-orbit matrix elements. The first step in this process has been accomplished, since we now have a working all-electron two configuration (TC) SCF spin-orbit code. In collaboration with Professor Tom Furlani (SUNY-Buffalo) and Shiro Koseki (Mie University), we have initiated the development of a general CASSCF code for all-electron spin-orbit coupling.

Related to the foregoing discussion of potential energy surfaces is our development of new methods for using *ab initio* wavefunctions to explore classical trajectories "0n-the-fly", that is without prior the need for prior knowledge of the potential energy surface. Of particular importance are methods for treating surfaces that are highly curved, since then the role of tunneling is critical to an understanding of the dynamics. We have therefore developed a new method in which highly curved potential energy surfaces are treated correctly[19,20].

## II. STRAINED RING COMPOUNDS:MATERIALS PRECURSORS

It was discovered in the 1980's that the cage compounds known as cyclophanes can be synthesized such that the bridgehead hydrogen points inside the cage, toward the *trans*-annular benzene ring (endo position), rahter than outside (exo position). Professor Damrauer (University

of Colorado-Denver) attempted to synthesize the analogous compound in which the bridgehead carbon is replaced by a hydrogen, in order to explore the potential use for such compounds as materials precursors. However, these attempts were not successful. In an effort to understand why the endo silacyclophanes could not be made, we performed a series of calculations, making use of parallel GAMESS, to determine the preference for endo vs. exo, as a function of the nature of the bridgehead atom. It is found that when the bridgehead atom is C, the endo structure is preferred by about 13 kcal/mol, whereas the exo isomer is preferred by a huge 43 kcal/mol when the bridgehead atom is Si! The reason for this difference is that a C-H bond is polarized C(-)H(+), leading to a favorable electrostatic interaction between the positively charged H and the electron rich benzene ring. On the other hand, an Si-H bond is strongly polarized Si(+)H(-), leading to a repulsive interaction between an endo H and the benzene ring. This led us to propose increasing the size of the cage by one methylene group. Indeed, an expanded cage stabilizes the endo isomer of the silacyclophane by 40 kcal/mol, so that it is within 3 kcal/mol of the exo isomer[21] .

Silatranes are well known to be important materials precursors, while phosphatranes are among the strongest bases known (and therefore important catalysts). Again using the parallel capabilities of GAMESS, we have performed an extensive study of both series of compounds. For the silatranes, we have discovered[22] that the fundamental nature of the *trans*-annular Si-N bonding is a dative interaction between the N lone pair and the positive Si. The often invoked three-center two-electron bond plays only a minor role. Although it is usually assumed that the nature of the axial substituent has the greatest impact on the Si-N bond, we find that the nature of the adjacent (equatorial) atoms is more important. In fact, the most stable silatranes appear to be those in which these equatorial atoms are nitrogens (azasilatranes). A simple self-consistent reaction field (SCRF) model has been used to interpret the experimentally observed large shortening of the Si-N *trans*-annular bond in the condensed phase. The silatranes have a very large dipole moment, and this leads to a large electrostatic interaction with the solvent which in turn causes a large shortening of the bond. With regard to the phosphatranes[23] , we have predicted the gas phase basicities as a function of the equatorial atoms and substituents on the phosphorus. Both the precdicted geometries and basicities are in excellent agreement with the available experimental data. In addition, we have predicted some species which should be even stronger bases than those which have already been prepared. Our experimental colleagues at Iowa State (Verkade group) are attempting to synthsize these compounds.

Titanatranes are important as precursors for electronic devices, and Professor Verkade at Iowa State has characterized several titanatranes using X-ray crystallography. An unusual feature of the azatitantranes is that the axial Ti-N bond is actually shorter than the equatorial Ti-N distances. We have performed extensive calculations[24] on a series of azatitanatranes,

reproducing with excellent accuracy the observed crystal structures, including the reversal of axial vs. equatorial Ti-N distances. This reversal is nicely understood in terms of N lone pair backbonding, using localized molecular orbitals as an interpretive tool.

Large $(SiR_2O)_n$ siloxane rings, commonly referred to as $D_n$ play an important role in biomimetic laser-hardened materials. Since there are no reliable molecular mechanics force fields for this class of compounds, we have embarked on a series of calculations to predict their structures and relative isomer energies, and vibrational frequencies, in order to provide some *ab initio* data from which the development of force fields may be derived. To this end, RHF/6-311G(d,p) geometry optimizations have been performed on $D_3$, $D_4$, and $D_5$[25]. Contrary to previous calculations, $D_4$ is predicted to have a planar $D_{4h}$ structure. The larger $D_5$ species is found to have four isomers ($C_1$, $C_2$, $C_s$, $D_{5h}$) that are very close to each other in energy and structure. At the highest level of theory (MP2/6-3121G(d,p)//RHF/6-311G(d,p)), the $C_1$ structure is predicted to be the global minimum, but the relative populations of the various isomers vary with temperature.

The calculations described above on the $D_n$ rings have provided us with important insights needed to pursue the more complex problem of the mechanism(s) for formation of polyhedral oligomeric silsesquioxanes (POSS), cage compounds whose basic linkage is Si-O-Si. These POSS species hold great promise as viscosity modifiers. We have embarked on a systematic, long-term investigation of the potential energy surfaces of these compounds, beginning with the initial hydrolysis steps to form the precursor $R\text{-}Si(OH)_3$ and extending to the subsquent series of condensation reactions, the effect of modifying the pendant R groups, the role of solvent (using the EFP model discussed above), and the role of various catalysts[26]. The first series of calculation already emphasize the importance of solvent, since even one water molecule is sufficient to reduce the barriers for both the hydrolysis steps and the subsequent condensation steps from 20-30 kcal/mol to nearly zero. Likewise, both acid and base catalysis cause such stable ion-molecule complexes that barrier heights are reduced to zero.

Since their discovery several years ago, metallocarbohedrenes (met-cars) have caused great interest as possible precursors to nanoparticles. Met-cars have the general formula $M_8C_{12}$, where M is most commonly a group IVB element, especially Ti, Zr. Although there has been considerable experimental and theoretical interest in these species, there remain more questions than answers. Among the questions we have begun to probe are the fundamental molecular and electronic structures of met-cars in their low-lying electronic states, and the mechanisms of formation of the met-cars[27].

## III. HYPERVALENT BONDING

Hypervalent compounds (in which the central atom is bound to more than the 'normal' number of ligands), especially those containing silicon, have been implicated in the mechanisms of a variety of reactions used for the synthesis of coatings, optical devices, and materials precursors. We have therefore continued our extensive analyses of hypervalent Si and related elements.

We have recently completed an exhaustive study of the pseudorotation potential energy surfaces for $SiH_nX_{5-n}^-$ (X = F, Cl) compounds[28], using MP2/6-31++G(d,p) geometries. Minimum energy paths were determined in order to obtain a detailed understanding of these potential energy surfaces. We find that highly substituted compounds (i.e., n is small) exhibit the classical Berry behavior, with axial and equatorial minima and tetragonal transition states. On the other hand, when most substitutents are H, the equatorial structure itself tends to be a transition state, and axial substitutions seem to be the only stable ones. In many cases, Cl is very weakly bound and forms ion-dipole complexes, rather than true hypervalent species. The calculations also support an earlier qualitative work that interpreted -Cl and -F pseudorotation in terms of a simple electronegativity model.

## IV. Bonding.

The electronic structures of complexes arising from the formation of a double bond between a silylene and a high valent transition metal fragment have been investigated, using the LMO/MCSCF/CI method. A prime motivation for this work was that complexes of this type, unlike their C analogs, have so far eluded attempts at experimental characterization. We have concluded that (a) It is necessary to include electron correlation to obtain an adequate description of the MSi bond, whereas the $\sigma$ bond is well represented at the Hartree Fock level; (b) The kinetic and thermodynamic stability increase when H ligands and/or substituents are replaced by electronegative species; (c) Group VB MSi bonds are more stable than their Group IVB analogues; (d) MSi double bonds are stronger when the MSi bond is made more backbonding in nature. Strategies for designing stable M=Si species are suggested. The electronic structures of the transition metal-disilene complexes $MCl_2(Si_2H_4)$, with M = Ti, Zr, Mo, and W, and the complexes of disilene with $PtCl_3^-$ and $Pt(PH_3)_2$ have also been investigated[29]. This work has recently been summarized in an invited review.[30]

## V. POTENTIAL ENERGY SURFACES AND DYNAMICS

The details of A + HB potential energy surfaces is essential for the development of an understanding of a variety of AFOSR-supported experimental studies (for example, the

photodetachment experiments of Neumark). We have therefore embarked on a series of accurate calculations of such potential energy surfaces. The transition state for the Cl + HCl reaction is found to be nonlinear, albeit rather flat. It requires at least an MP2 or MCSCF+CI wavefunction to obtain a proper PES. This effort used MP2 and multi-reference CI wavefunctions to map the PES[31] . A large number of points on the PES have been obtained, and are now being fit to an analytical form, in preparation for an analysis of the dynamics of the reaction. Preliminary results suggest that an adequate treatment of the dynamics will require a detailed knowledge of the PES's for the excited state, as well as the $\sigma$ ground state. We have therefore performed extensive MCSCF calculations on both the ground and excited state potential energy surfaces. These potential energy surfaces have now been used to study the dynamics of the Cl + HCl reaction[32] . In a related development, the potential energy surface for the reaction H + HCl has been extensively studied, and the resulting surface used to predict the reaction kinetics.[33] A related, and much more challenging, problem is the investigation of the reaction I + HI. Once again, it is essential to investigate at least the lowest and $\sigma$ potential energy surfaces, but a complicating factor is the importance of spin-orbit coupling. Therefore, this study involves a collaborative effort with Professors Koseki (Mie University) and Yabushita (Keio University), both of whom have developed treatments of the spin-orbit problem.

The dynamics of $SiH_5^-$ pseudorotation has been investigated using the newly developed dynamic reaction path (DRP) method[34,35] . This method allows us to determine classical trajectories "on-the-fly", without prior knowledge of the potential energy surface. In the first study, both front- and side attack of $H^-$ on $SiH_4$ were studied using the symmetry constraints of $C_{3v}$and $C_{2v}$, respectively. The intramolecular vibrational energy transfer was studied by mapping the DRP and its corresponding momentun onto the normal modes of both reactants and products. These analyses reveal that Bery pseudorotation occurs repeatedly during the side attack, whereas the $S_N2$ reaction $H^- + SiH_4 \rightarrow SiH_4 + H^-$ often occurs upon front attack, depending on the initial relative velocity[34] . In the second study, the symmetry constraint was lifted. This investigation revealed that when approaching $SiH_4$ from either the side of the back, the $H^-$ changes its path toward a front attack, due to the high energy requirements for side or back attack. This results in a vibrationally active $SiH_5^-$ with accompanying pseudorotation[35] . A general discussion of the importance of interfacing electronic strutcure theory with dynamics methods has been discussed in an invited feature article in the Journal of Physical Chemistry[36]

The effect of ß-silyl substitution on stabilization of singlet (relative to triplet) carbene has been investigated[37] . It is found that there is indeed such a ß-silicon effect, due to the ability of ß C-Si (or C-Ge) bonds to twist into a position that permits electronic back donation from the C-Si bond into the empty p orbital on the carbene carbon.

The potential energy surfaces for several reactions related to *chemical vapor deposition* under investigation. In keeping with our increasing interest in transition metal CVD, analysis of the potential energy surface for the $TiH_3OH$ analog of silanol has been initiated[38]. A preliminary study was carried out on a series of $TiH_3X$ compounds (X = $CH_3$, $NH_2$, OH, $SiH_3$, $PH_2$, SH)[39]. The methyl compound is predicted to prefer an eclipsed, rather than a staggered structure, while the amino group is planar. The latter beahvior is consistent with the planar amino group found for $SiH_3NH_2$ in earlier work. The $SiH_3$ and $PH_2$ compounds are particularly interesting. Two isomers of $TiH_3SiH_3$ apparently exist. The less stable isomer is a "normal" staggered structure similar to ethane, whereas the global minimum is an "inverted" structure, in which the three silyl hydrogens point in toward Ti. This clearly occurs because Ti in this environment is electron deficient, much like B in boron hydrides. There are clear three-center Ti-H-Si bonds in this species. The phosphorus hydrogens in $TiH_3PH_2$ are also inverted, but here no evidence for three-center bonding is found. For both of these unusual species, the incorporation of electron correlation is critical to obtain even qualitatively correct structures.

Recent experiments indicate a "negative activation energy" in the insertion of $SiH_2$ into $SiH_4$ to form disilane. This suggests the existence of a long-range minimum on the PES. Using MP2/6-311G(d,p) calculations, we have found two $SiH_2$-$SiH_4$ complexes and two associated transitin states on the $Si_2H_6$ PES[40,41]. When zero point vibrational corrections or higher level correlation corrections are added, both barriers disappear. So, at best, there are very flat regions in these regions of the PES. In order to obtain a better understanding of the dynamics of this system, we initiated several "trajectory" calculations by separating the $SiH_2$ and $SiH_4$ to large distances with different orientations and allowed them to approach each other. Depending on the orientations the two fragments consistently found one of the two local minima. No starting point could be found such that the two fragments simply fell into the $Si_2H_6$ global minimum. The next step is to investigate this system using our new DRP methods.

Related to the $SiH_2$ insertions into silane are calculations on the addition of divalent silicon species to the ethylene double bond. Earlier calculations from this laboratory have found that the addition of $SiH_2$ to ethylene to form the three-mebered silirane ring occurs with no barrier. When chlorines are substituted for the hydrogens in silylene, we find a small (<5 kcal/mol) barrier for the addition[42]. In contrast, when highly electronegative fluorines are substituted, a very high barrier is found. These results have been interpreted in terms of the competing electrophilic vs. nucleophilic interactions between the silylene and ethylene as a function of substituent.

Damrauer and co-workers have studied the reactions of $HSiO^-$ with several neutral triatomic molecules. In order to understand the mechanism for this reaction, we performed a

detailed *ab initio* investigation of the reaction of $HSiO^-$ with $CO_2$[43]. The energetics were obtained using fourth order perturbation theory (MP4/6-311++G(d,p)) at MP2/6-31++G(d,p) geometries. These calculations predict, in agreement with experiment, that there are two important (low-energy) paths leading to $SiO + HCO_2^-$ and $HSiO_2^- + CO$. There are, in addition, two paths that lead to oxygen exchange. All four of these paths lie below the initial reactants $HSiO^- + CO_2$, explaining why both sets of products are observed.

Another fundamental problem involving $HSiO^-$ is the potential energy surface for the transfer of a proton from the neutral to the anion. Since there are two anion isomers ($SiOH^-$, as well as $HSiO^-$) and three neutral isomers ($H_2SiO$ and trans and cis HSiOH), there are several alternative reaction paths. All of these alternatives have been explored and compared using MP2 geometries and CCSD(T) energies[44]. A similar series of reactions have been studied for the ion-neutral pair ($HCSi^-$, $H_2CSi$)[45].

Considerable research has also been completed on reactions of cations. It is well known that cationic species are important in high energy CVD involving plasmas. We have therefore carried out[46] very acccurate calculations on the competing thermal decompostion mechanisms for $CH_3SiH_2^+$. Even though the most favorable thermodynamic product is $CH_3Si^+$, there is considerable production of $CH_2{=}SiH^+$, due to the relative barrier heights. That is, kinetics plays an important role in this mechanism. An unusual weakly bound complex has also been found on the potential energy surface, and this complex nicely explains the observed exchange reactions. We have also extensively mapped out the potential energy surface for the reaction of $Si^+$ with $CH_3SiH_3$.[47] This reaction has been studied experimentally at both thermal energies and at a range of higher temperatures. The calculated surface is in excellent agreement with all experimental data. Those reaction mechanisms for which all barrier heights are below the energy of the initial reactants correspond to the observed products for the threshold experiments, while those mechanisms that require the trversal of higher barriers give rise to products that are seen only at higher impact kinetic energies. Closely related to the reaction of $Si^+$ with $CH_3SiH_3$ is our more recent study of the reaction of $Si^+$ with $CH_2{=}SiH_2$, in order to determine the minima on the $Si_2CH_5^+$ potential energy surface[48]. In addition to the existence of several ion-molecule complexes, we have found two very low energy isomers. These two isomers may be interpreted as the results of reactions of $Si^+$ with silene and its isomer methylsilylene. The reaction of silene with $Fe^+$ has also been studied in the lowest quartet and sextet states.[49] Because of its partially occupied Fe valence s orbital, the sextet does not form as strongly bound complexes with silene as does the quartet. So, the quartet compounds are predicted to be lower in energy than the sextet compounds. As for the $Si^+$ surface, we find structures corresponding to both silene and methylsilylene on both the quartet and sextet surfaces. In each case, there is a large barrier separating the two isomers. This is consistent with the experimental observations of Bakhtiar

and Jacobson.

We have reported the existence of bond stretch isomerism in any silabicyclobutanes in which the bridgehead atoms are silicons. We have now mapped out the MEP connecting the two isomers in the tetrasila case at the GVB/6-31G(d,p) level of theory, calculated the projected vibrational frequencies along the path and predicted the free energy path for the reaction[50]. We have found that the size of the groups attached at the bridgehead positions determine whether the short bond or the long bond isomer is lower in energy. When the bridgehead substituent is hydrogen, the highest levels of theory predict that the short bond structure does not even correspond to a minimum on the potential energy surface. On the other hand, the short bond structure is the lower energy isomer when bulky t-butyl groups are placed in the bridgehead positions. The next step is to make use of variational transition state theory to investigate the dynamics and kinetics for the bond stretch isomerization reaction. An interesting feature of this investigation will be to ask how vibrational excitation affects the rate constants and tunneling probabilities.

The hydrosilation reaction, in which an Si-H bond adds across a C=C double bond, is very important, since it provides a source of Si-C bonds, precursors to silicon carbides. In a preliminary study[51] we investigated the addition of $SiH_4$, $SiH_3Cl$, and $SiHCl_3$ across the C=C bond of ethylene, as well as the addition of $SiH_4$ to propene. In the absence of a catalyst, the barriers for all of these reactions are found to be very high, in the range of 50-65 kcal/mol. The next step, of course, is to investigate the effect of the catalyst. Since the active catalytic species is thought to be divalent Ti, we have used $TiH_2$ to represent the catalyst[52]. What we find is that if the catalyst is allowed to attack ethylene first, forming a three-membered ring, the reaction with $SiH_4$ is facilitated, with all steps in the reaction, including intervening transition states, lying lower in energy than the reactants. The entire reaction path has been mapped using second order perturbation theory, followed by energetics at the CCSD(T) level of theory. We are now proceeding with analogous studies on more complex silanes and more realistic representations of the divalent Ti catalyst. Bis-silylation, in which an Si-Si bond is added across a CC double or triple bond has also been studied. In the absence of catalyst, the addition of disilane to ethylene also requires a very large barrier[53]. Even in the presence of $TiH_2$, however, the preferred reaction appears to be hydrosilation, rather than bis-silylation. We are still examining the potential energy surface for a facile mechanism for bis-silylation.

Collaborations with Professor Tom Barton (Iowa State) have led to several interesting mechanistic studies in silicon chemistry. The detailed potential energy surface for the isomerization of silylallene has been investigated with QCISD(T)/6-311G(d,p) energies at the MP2/6-31G(d) geometries[54]. The agreement with experimental thermodynamics and kinetics is excellent. In comparison with the isomerization of the parent allene, the silyl group was found to

migrate more easily than the hydrogen. The 1,3-migration that converts silylallene to silylpropyne has barriers of 55.8 and 52.9 kcal/mol for the forward and reverse reactions, respectively. These are roughy half the 1,3-hydrogen migration barriers in allene. In a combined experiment-theory investigation, the thermal isomerization of olefins to carbenes via a 1,2-silyl shift was examined[55] . No evidence of this rearrangement was found for acyclic vinyl silanes. Calculations show that for silyl migration the transition state is late and is, in fact, the carbene, while for carbon migration the TS is early and is considerably higher in energy than the resulting carbene.

There has been considerable interest for many years in the lowest singlet and triplet potential energy surfaces of Group IVA dihydrides, $XH_2$. The heavier $XH_2$ analogs (X = Sn, Pb) exhibit significant relativistic effects. We have studied the singlet and triplet potential energy surfaces for all five $XH_2$ compounds, in which the relativistic effects were included[56] . As expected, the spin-orbit couplings increase dramatically as the Group IVA element increases in mass. It is somewhat surprising, however, that the effect in $CH_2$ is not trivial.

A thorough study[57] of how the addition of successive water molecules shifts the gas phase zwitterion-neutral equilibrium of the amino acid glycine towards that of the solution phase has been carried out using MP2/DZP++ energies. It is found that two water molecules can stabilize the glycine zwitterion; that is, give rise to a potential energy minimumwith at least one vibrational level. The results were analyzed and interpreted using localized orbitals and the theory of localized charge distributions.

Four invited reviews have also resulted from our AFOSR-supported research. Two chapters have appeared in ACS Symposium series monographs on parallel computing[58,59] , a third review summarizes our work on transition metal-main group chemistry.[60] , and a fourth[61] focuses on main group chemistry.

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Jerry A. Boatz (currently, staff scientist, Edwards AFB)
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Dmitri Federov (admitted to Ph.D. candidacy)
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Theodore Packwood* (currently, employed in private sector)
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Jan H. Jensen (currently Assistant Professor of Chemistry, University of Iowa)
Graham Fletcher, postdoctoral research associate, Iowa State University
Grant Merrill, postdoctoral research associate, Iowa State University

## PRESENTATIONS AT MEETINGS

1. "Large Molecule Challenges", Workshop on Computational Aspects of Materials Chemistry, Wright Laboratories, Dayton, Ohio, September 1994 (INVITED)

2. "Potential Energy Surfaces for Large Molecules", National American Chemical Society Meeting, Anaheim, CA, April 1995 (INVITED).

3. B, Bode, "The Catalyzed Hydrosilation Reaction", Midwest Theoretical Chemistry Symposium, Evanston, IL, May 1995.

4. T. Taketsugu, "The Dynamic Reaction Path and Application to Pseudorotation", Midwest Theoretical Chemistry Symposium, Evanston, IL, May 1995.

5. "Water-Substrate Interactions", Pacific Basin Chemical Societies Meeting, Honolulu, HA, December 1995 (INVITED).

6. "Features and Applications of Parallel GAMESS", Maui Workshop on Parallel Computing, Maui Supercomputer Center, Kihei, Maui, HI, December 1995 (INVITED)

7. "Organosilicon Quantum Chemistry in Action", Organosilicon Symposium, Northwestern University, March 1996 (INVITED).

8. "The Effective Fragment Method for Solvation" (presented by Wei Chen), National ACS Meeting, New Orleans, March 1996.

9. "Interfacing Theory With Experiment", SUPER!96, Iowa State University, Ames, Iowa, April 1996 (INVITED).

10. "Ion-Molecule Reactions", Main Group Chemistry Symposium, Fargo, ND, June 1996

(INVITED).

11. "The Effective Fragment Method for Solvation", AFOSR Molecular Dynamics Meeting, Boulder, CO, June 1996 (INVITED)

12. "The Effective Fragment Method for Solvation", Great Lakes Regional ACS Meeting, Dayton, Ohio, June 1996 (INVITED).

13. "The Effective Fragment Method for Solvation", American Conference on Theoretical Chemistry, Park City, Utah, July 1996 (INVITED).

14. "Potential Energy Surfaces for the Reactions of Fe+ and Si+ With Silene", American Conference on Theoretical Chemistry, Park City, Utah, July 1996, presented by Jerzy Moc.

15. "A General Equation for Intermolecular Exchange", American Conference on Theoretical Chemistry, Park City, Utah, July 1996, presented By Jan Jensen.

16. "The Catalyzed Hydrosilation Reaction", American Conference on Theoretical Chemistry, Park City, Utah, July 1996, presented by Brett Bode.

17. "*Ab Initio* Studies of the Fe+ + CO Potential Energy Surfaces", American Conference on Theoretical Chemistry, Park City, Utah, July 1996, presented by Kurt Glaesemann.

18. "*Ab Initio* Study of the TiSiCC Analog of Cyclobutane", American Conference on Theoretical Chemistry, Park City, Utah, July 1996, presented by Vanda Glezakou.

19."The Effect of Solvation on the Menshutkin Reaction", American Conference on Theoretical Chemistry, Park City, Utah, July 1996, presented by Simon Webb.

20. "Mechanisms in Organometallic Chemistry", National American Chemical Society Meeting, Orlando, FL, August 1996 (INVITED).

21. "Current Status of Parallel GAMESS", Cornell Theory Center Workshop, October 1996 (INVITED).

22. "New Directions for Parallel Electronic Structure Theory", National ACS meeting, San Francisco, April 1997, INVITED.

23. "Gridless Density Functional Theory", National ACS Meeting, San Francisco, April 1997, presented by K. Glaesemann.

24. "Transition Metal-Main Group Multiple Bond Energies", National ACS Meeting, San Francisco, April 1997, presented by B. Bode.

25. "A New Second Order Convergence Method", National ACS Meeting, San Francisco, April 1997, presented by G. Chaban.

26. "The Effective Fragment Method for Solvation", National ACS Meeting, San Francisco, April 1997, presented by J. Jensen.

27. "An Approach to Parallel MP2 and CI Gradients", National ACS Meeting, San Francisco, April 1997, presented by G. Fletcher (INVITED)

28. "Quantum Chemistry Tools for Chemical Synthesis", AFOSR HEDM Meeting, Washington, DC, June 1997

29. "High Energy Isomers of N2O2, AFOSR HEDM Meeting, Washington, DC, June 1997, presented by G. Chaban.

30. "The Effect of Solvation on Chemical Processes", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997 (INVITED)

31. "Approximate Second Order Method for Orbital Optimization of SCF and MCSCF Wavefunctions", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by G. Chaban.

32. "Parallel SCF and MP2 Algorithms", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by G. Fletcher.

33. "Grid-Free Density Functional Theory", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by K. Glaesemann.

34. "An Approximate Formula for the Intermolecular Pauli Repulsion Between Closed Shell Molecules: Application to the Effective Fragment Method", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by J. Jensen.

35. "Ti-Carbohedrene: Structure, Energetics and Mechanism of Formation", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by V. Glezakou.

36. "Applications of the Effective Fragment Solvation Model: Water Clusters and Dynamic Reaction Coordinates", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by G. Merrill.

37. "Ab Initio Molecular Orbital Study of for the Mechanism of Formation of Silsesquioxanes", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by T. Kudo.

38. "Titanatranes", Ninth International Congress on Quantum Chemistry, Atlanta, GA, June 1997, presented by M. Schmidt.

## AWARDS AND HONORS

1. Editorial Advisory Board, Journal of Physical Chemistry

2. Editorial Advisory Board, Organometallics

3. Vice Chair, Theoretical Chemistry Subdivision, American Chemical Society, 1994-95

4. Chair-Elect, Theoretical Chemistry Subdivision, American Chemical Society, 1995-96

5. Chair, Theoretical Chemistry Subdivision, American Chemical Society, 1996-97

6. Secretary-Treasurer, Physical Chemistry Division, American Chemical Society, 1996-2001

## TRANSITIONS

In addition to the transitions reported last year, we have now transported our popular electronic structure code GAMESS to the Power Macintosh and to Intel Pentium systems running under LINUX. This means that our code (already distributed without charge to all users) can now be used on very inexpensive computers - for as little as $2,000 in hardware costs. While one would not run state-of-the-art computations on such a platform, it is ideal for code development, test runs and for educational purposes. Furthermore, one can configure such microcomputers with sufficient memory and disk to perform high-level calculations.