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1. Introduction. Significance and Review of Important Experimental Problems

Clusters constitute the "fourth" state of matter in that they form the important bridge between molecules and the bulk. Clusters have been the topic of astronomically increasing number of studies in recent years[1-161]. Transition metal clusters (TMC) in particular are extremely interesting candidates for both experimental[1-104] and theoretical[105-161] studies. Why are transition metal clusters so interesting? First the nature of bonding, the geometrical structure and the ground states of TMC are so unpredictable that they are very interesting. Numerous array of electronic states with varied spin multiplicities and different geometrical structures arise from the open shell d electrons. Even for a 'simple' transition metal dimer such as Ru_2[151], there are 112 electronic states arising from $Ru(^5F) + Ru(^5F)$ ground state atoms alone. Unlike some main group dimers it becomes impossible to predict a priori what would be the ground state of TM dimers, since numerous factors such as spin exchange stabilization energies and electron correlation energies counteract each other, thereby changing the relative ordering of electronic states as a function of level of theory. For example, at the zeroth order CAS-MCSCF level, the ground state of Zr_2 is a $^7\Sigma_u^+$ state, at an intermediate level it becomes $^3\Sigma_u^+$ and at the highest level it becomes $^1\Sigma_g^+$.[137]

The complex array of electronic states even for simple TM dimers and trimers leads to very complex electronic spectra with often overlapping and perturbed bands. The interpretation of the spectra becomes formidably difficult without the knowledge of low-lying electronic states acquired from theoretical calculations. Theoretical calculations can be extremely valuable in this regard as demonstrated by our previous calculations on small metal clusters [see the progress report for theory-experiment comparisons].

Theoretical calculations on transition metal clusters can provide important insight into the nature of metal-metal bonding, the involvement of

the metal d orbitals in chemical bonding and the nature of low-lying electronic states. Yet another important aspect of theory is the prediction and insight into the trends in both reactivity patterns and the periodicity. For example, why do platinum clusters behave differently from both palladium and nickel clusters? Why is it that gold clusters exhibit anomalous behavior in the noble metal group? What causes certain clusters to be unusually more stable compared to others? Why do certain clusters exhibit dramatically different photofragmentation patterns compared to others? What causes zig-zag variations in binding and ionization energies?

In recent years several experimental studies[71-91] have been carried out on the reactivities of transition metal clusters with H_2, N_2, O_2, CH_4 and other hydrocarbons. The gas phase reactivities of transition metal ions and small cluster ions have also been studied. These experimental studies have revealed several fascinating trends in the reactivities of transition metal clusters as a function of size. The state and site specificities of gas phase transition metal clusters are very intriguing. Theoretical studies of reactivities of clusters with small molecules could not only aid in unravelling the mysteries of transition metal cluster reactivities but also serve as useful models to comprehend competing processes in surface-molecule interactions and provide a sound basis to comprehend chemisorption.

Recent experimental investigations, which have employed a combination of techniques, such as the optical spectroscopy of jet-cooled clusters, UPS of negative ions of the clusters, laser-induced fluorescence (LIF), matrix-isolation spectroscopic methods, ion trapping methods, resonant two-photon ionization and dissociation spectroscopic techniques, collision induced dissociation of cluster ions formed in a nozzle expansion, ESR spectroscopy of matrix-isolated clusters, etc., have yielded a wealth of information on the electronic states and reactivities of metal clusters.[1-105] Comparable theoretical efforts to gain insight

and understanding on such volume of experimental material would take years due to the challenge posed by the d electrons to theorists.

There are very many exciting, fundamental and yet unresolved puzzles pertaining to transition metal clusters and their reactivities. For example, using an ingenious combination of the supersonic beam method and the fourier-transform ion cyclotron method Smalley and coworkers[15,16] have studied several metal cluster + H_2, D_2, N_2 reactions as a function of the cluster size. The reactivities of the ionic clusters were reminiscent of the neutral clusters in dissociative chemisorption. Similar reactivity studies have been made on cobalt, iron and Ni clusters by Smalley and coworkers as well as Riley and coworkers.[65] The Co_x and Nb_x clusters in particular, exhibit dramatic variation of reactivities with cluster size, while Ni_x clusters do not show any size dependence at all. For example, Nb_3-Nb_7 were found to be moderately reactive while Nb_8 and Nb_{10} are completely inert. The Nb_2^+ cluster also was found to be far more reactive in comparison to Nb_8^+ and Nb_9^+.

Recently Cox and coworkers[82] (Exxon) have reported the first experimental study on the reactivity of Pt_n clusters with CH_4 as well as palladium clusters[27] with H_2, D_2, N_2, H_4, CH_4, C_2H_4 and C_2H_6. The reactivities of these clusters showed dramatic size-dependence. Trevor et al.[82] find that Pt_2-Pt_5 are most reactive towards CH_4. A factor of 4 drop in reactivity was found to occur for Pt_6 and as the cluster size increased the number of hydrogen atoms retained was also found to increase. In contrast with other transition metal clusters, Pt_n exhibited a decrease in reactivity for larger clusters. These mind-boggling observations need to be explained.

Negative ion photodetachment spectroscopy is another method used to probe the electronic states of the neutral clusters. Lineberger and coworkers[14,23,23,60-64], Smalley and coworkers[12] as well as Cox and coworkers[30] have used this technique to study Au_n, Ag_n, Cu_n, Pt_n, Pd_n, and Ni_n.

The advantage of this method is that unlike conventional optical spectroscopy, electronic states to which transitions are symmetrically or dipole-forbidden can be observed using this method. Furthermore electron affinities as a function of cluster size can also be measured. However, usually only low-lying electronic states can be probed using this technique.

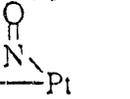
Weltner and coworkers[21,34,35,38] employ ESR spectroscopy to investigate small matrix-isolated transition metal clusters. The technique readily reveals information on the spin multiplicity of the ground state and the spin populations. The geometry of the cluster can be indirectly inferred. Several studies have been made by these authors on pure as well as mixed clusters such as Rh_3, Ir_3, MoPd, WPd, WPt, Cu_7, etc.

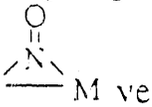
Morse and coworkers[39-43] have been studying mixed metal dimers and trimers such as Au_x, Ag_y, Pt_xPd_y, Pt_xNi_y, Cu_xAu_y, etc. ($x+y\leq 3$) using resonant two-photon ionization spectroscopy. Often the spectra are complicated with overlapping bands. It is impossible to unambiguously assign and interpret such spectra without the knowledge of theoretical studies.

T. Steimle of our department at ASU currently funded by DOE is proposing high-resolution spectroscopic studies on small mixed metal dimers, trimers and other small molecules containing transition metal atoms. Our proposed theoretical studies would be of immense use in both planning of these experiments and in the interpretation of experimental spectra. Prof. R. Field at MIT is also working on spectroscopic characterization of small transition metal hydrides and dimers. Our theoretical studies will be of use in these experimental studies too.

The existance of isomeric forms and the differences in the reactivities of isomers of clusters are very intriguing. For example, Hales et al.[57] have shown recently that there exist several clusters of Nb_x^+ with different isomers whose reactivity patterns varied dramatically. The structure specificity of these

isomers for reactivity with H_2 is certainly intriguing. El-Sayed and coworkers[68,69] have studied Br abstraction vs dehydrogenation in the gaseous Nb_x clusters by reacting with saturated and unsaturated organic bromides. It was found that Br abstraction takes place with all clusters while dehydrogenation occurs with only unsaturated compounds.

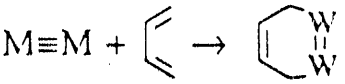
In recent years there have been numerous experimental studies pertaining to the reactivities of NO, CO, O_2, H_2, N_2, small hydrocarbons on surfaces.[93-104] These studies have revealed several fascinating trends. For example Yates and coworkers[95,96] find that NO and CO chemisorbed on stepped Pt (112) surfaces exhibit anisotropic vibrations. The amplitudes of motions perpendicular to the plane are 2-3 times larger than in plane motions. This suggests different type of structures formed, one possibly perpendicular to the plane involving  bridge bonds while the other in plane involving Pt-N = O end on bonds. There are several other studies on the chemisorption of NO and CO on Pt as well as noble metal surfaces.

Adsorbtion of NO on noble metal surfaces is complicated and not fully understood at present.[99] For example, photo-irradiation of adsorbed NO or O_2 on surfaces can lead to desorption, dissociation of the molecule, binding site rearrangement or synthesis of a new chemical species. There is also a question of orientational preferences (bridged versus atop) in NO and CO chemisorptions. The production of CO_2 in CO-chemisorption on oxidized surfaces is rather intriguing. In all these cases theoretical studies on small systems such as  versus M-N = O for M = Pt, Pd, Rh, Cu, Ag, Au, can provide significant insight into orientational and site specificities.

The chemisorption of ethylene (C_2H_4) on Pt surfaces is also extremely interesting. There are numerous experimental papers on the topic [see for

example Ref. 51]. Again there are two competing processes one leading to metal-carbon sigma bonds and the other primarily through single metal atom with C=C π bonds. Theoretical studies on $Pt_2 + C_2H_4$ and $Pt + C_2H_4$ can provide relative strengths of sigma and π-bondings and the primary mechanism involved in chemisorption of C_2H_4 on Pt surfaces.

In a recent experiment Chrisholm and coworkers (1991)[90] find that W_2 complexes reacts with 1,3 butadine analogous to the Diels-Alder reaction:



This is very exciting in that two metal atoms participate in a ring-closing reaction. Theoretical studies can provide significant new insight into M-M bonding in the product and the nature of activated complex for this reaction.

The above survey of experimental works on transition metal clusters and their reactivities demonstrate the need for accurate theoretical calculations to gain at least qualitative insight into the nature of the electronic states and for the interpretation of the observed spectra, reactivity, ionization potentials and electron affinity patterns. Calculations of electronic states of transition metal clusters are by far the most challenging tasks for theoreticians today. This is because of a combination of factors enumerated below:

(i) there are large numbers of electrons in heavy transition metal clusters

(ii) electron correlation effects arising from both d and s electrons are very large

(iii) relativistic and spin-orbit effects are extremely important

(iv) there is a large number of densely packed electronic states of varied spatial and spin multiplicities.

Any theoretical method, which fails to take into consideration even one of the above points, is likely to produce unreliable results. For example, the total number of electrons in Pt_2 is 156, 20 of which are active. The d correlation

effects are so large that CASSCF/CI treatment which included all 20 electrons in the active space is warranted. Relativistic and spin-orbit effects are extremely large for Pt_2[189]. Relativistic effects stabilize the 6s orbital of Pt leading to a $5d^9 6s^1$ ground state in comparison to $4d^{10}$ ground state for Pd. This produces considerable bonding in Pt_2. The $^3\Gamma_u(5_u)$ - $^3\Gamma_u(3_u)$ splitting for Pt_2 is 15 600 cm^{-1}. There are at least 22 electronic states with T_e < 16 000 cm^{-1} for Pt_2 and 11 λ-s states below 10 000 cm^{-1}.

The effect of relativistic corrections such as the mass-velocity correction, Darwin correction and the spin-orbit term on chemical properties have been addressed by many groups. Some of the significant developments in this area were made possible by early works of Professor K. S. Pitzer and coworkers, Jeff Hay and coworkers at Los Alamos National Lab, Krauss and Stevens at National Bureau of Standards, R. Pitzer at Ohio State University, N. Winter at Livermore Lab and so on. The PI was introduced to this area by Prof. K. S. Pizer at UC, Berkeley during his postdoctoral years (1980-82).

In 1982 when the first relativistic CI calculation was done on a diatomic we could do only calculations containing up to 3000 configurations. Today, we carry out calculations which contain up to 6 million configurations. While the basic method of generating relativistic effective core potentials (RECP) is still the same, we have made quantum leaps in our ability to handle systems of much larger magnitude and size such as Au_6. At present we can carry out CAS-MCSCF calculations which include up to 50 000 configurations and CI calculations which include up to 6 million. In 1982, the codes developed in collaboration with Professor K. S. Pitzer could handle only diatomics since these were based on Slater-type orbitals. Today we can handle transition metal clusters containing up to 8 atoms approximately, and smaller clusters with greater accuracies. This was made possible with significant and non-trivial code enhancements and modifications to both ALCHEMY II and the relativistic

CI codes by PI and his coworkers. These codes are running on the campus IBM 3090/600, Cray YMP at San Diego (contracted CI method of Siegbahn) and locally on IBM RISC/6000 systems dedicated to our group [see pages 60-62 for computational facilities]. We have also advanced the RCI method to compute density matrices, properties, natural orbitals and relativistic transition moments. Several new packages of codes had to be developed for these purposes.

The relativistic effective core potentials (RECPs) derived from relativistic numerical Dirac-Fock calculations have been proven of great utility in electronic structure calculations. The advantages of such a method are:

(i) it eliminates the unimportant core electrons

(ii) it avoids convergence problems

(iii) it brings down the configuration count in the CI calculations and

(iv) it facilitates inclusion of more basis functions for the valence space and additional diffuse and polarization functions

(v) core-valence correlation effects can be incorporated as additional terms in RECPs.

The general method of *ab initio* calculations has been discussed in the books by Schaefer[186]. Schaefer and coworkers[184] and others[182,183] have taken advantage of the graphical unitary group approach (GUGA) to many electron correlation problems by developing codes based on loop-driven GUGA. Likewise, Liu and Yoshimine[185] have developed the symbolic CI method which cuts down the time to do large scale CI calculations dramatically. The Siegbahn's contracted CI (CCI) method is especially useful for large scale CI in which contraction of configurations do not lead to substantial errors. In addition, more size consistent and extensive methods such as the averaged coupled pair formalism (ACPF) have been recently developed.

The approach we have adapted for the electronic structure of molecules containing heavy atoms combines the above advances in nonrelativistic direct CI technology by averaging the RECPs with respect to spin. The ARECPS which include all relativistic effects except the spin-orbit operator are included in MCSCF/direct CI calculations employing one of the techniques mentioned above. The spin-orbit operator is then introduced in a relativistic CI scheme. The details of these techniques will be discussed later. We have proven the utility of this approach with many calculations on transition metal compounds as well as many main group clusters (PI's publication list).

In the earlier three years (July 1, 1989-present) we have accomplished significant amount of work on smaller transition metal dimers, trimers and some tetramers (Cu_4, Ag_4, Au_4), Au_6 and their ions. Model calculations of $M + H_2$, $M^+ + H_2$ [M = third row TM atom] were also done. Extensive studies on $Pt_2 + H_2$ and $M_2 + H$ (M = Pt, Pd and Ni) were made. Yet there are several more extremely interesting systems which are completely unexplored. In addition larger clusters have also not been studied. Since we have our own computational facilities now (Appendix), we believe that we are poised to make significant developments and breakthroughs in this area.

In this proposal we identify several exciting completely new and unvisited problems pertaining to transition metal clusters. Our current proposal is not a simple extension of previous studies but comprises a brand new set of challenging and mind-boggling problems. We have identified and outlined several problems on pure transition metal clusters, bimetallic transition metal clusters (new endeavor), transition-metal carbide clusters (new), reactivity studies of TM clusters with C_2H_4, CO, NO, new etc. Hence all proposed reactivity studies are entirely different and substantially new. The significance of each system, the connection with experiment and how our proposed theoretical study will provide new insight and unravel mind-boggling

experimental questions are outlined in each subsection describing that compound or molecule.

2. Theoretical Method of Calculations

The general methodology of relativistic complete active space MCSCF (CASSCF)/configuration interaction (CI)/spin-orbit relativistic CI (RCI) is reviewed in my feature article[129] and shown in Fig. 1. Relativistic effective core potentials are generated from fully-relativistic Dirac-Fock calculations using the numerical DHF code of Desclaux.[174] The DHF calculations yield four-component spinor wave functions. The first two components are much larger than the last two components. For computation of chemical, valence and spectroscopic properties, Schwarz[175] has shown using the Foldy-Wouthuysen transformation that the effect of small components is ignorable. Relativistic effective core potentials constructed from the two-component spinors look as follows

$$U^{REP} = U_{LJ} + \sum_{\ell=0}^{L-1} \sum_{j=|\ell-1/2|}^{\ell+1/2} \sum_{m=-j}^{j} [U_{\ell j}(r) - U_{LJ}(r)] |\ell m j\rangle\langle \ell m j|.$$

where $U_{\ell j}$'s are the ℓj-dependent numerical radial potentials and $|\ell m j\rangle$'s are two-component spinors shown below.

$$|\ell m j\rangle = \begin{matrix} C(\ell\, 1/2\, j; m-1/2, 1/2)\, Y_{\ell, m-1/2} \\ C(\ell\, 1/2\, j; m+1/2, 1/2)\, Y_{\ell, m+1/2} \end{matrix}$$

where C(ℓ1/2j:m-1/2,1/2) etc. are the Clebsch-Gordan coefficients. The first component corresponds to the α spin while the second component corresponds

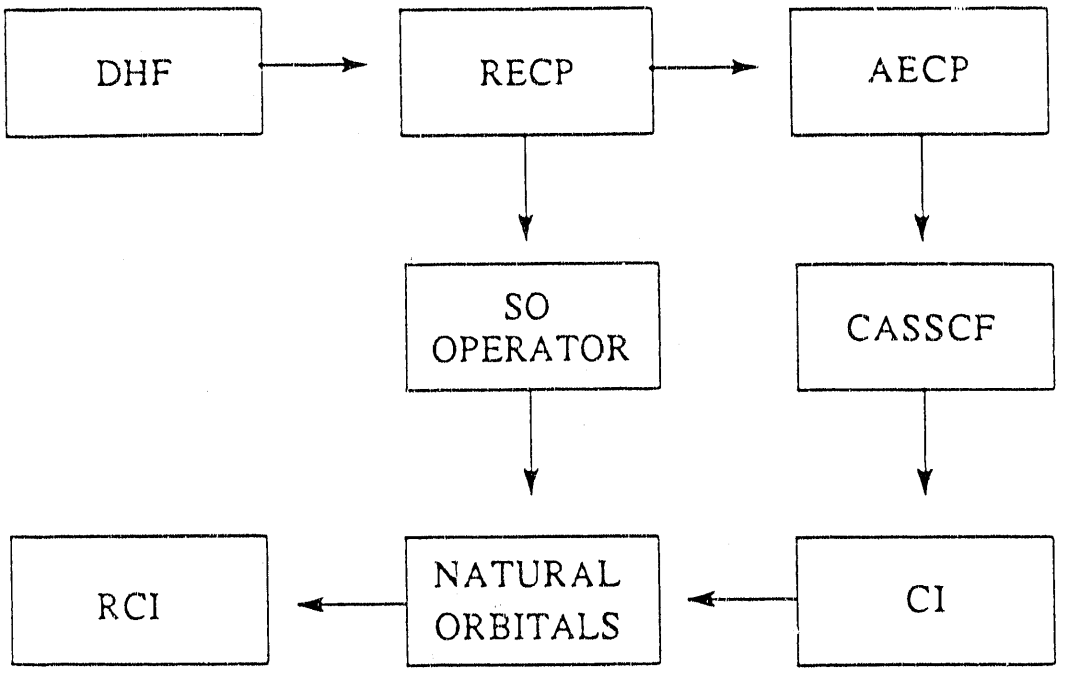


Fig. 1. Method of Calculations.

to the β spin. Thus as one can see from the above spinor, states of different spatial and spin symmetries are coupled by relativistic effects. This coupling is brought about by the spin-orbit coupling term, which, in fact can be expressed in terms of the RECPs as shown by Pitzer and coworkers as

$$U^{SO} = U^{REP} - U^{AREP} = \sum_{\ell=1}^{L} \Delta U_\ell^{REP} [\frac{\ell}{2\ell+1} \sum_{-\ell-1/2}^{\ell+1/2} |\ell, \ell+1/2, m><\ell, \ell+1/2, m|$$

$$- \frac{\ell+1}{2\ell+1} \sum_{-\ell+1/2}^{\ell-1/2} |\ell, \ell-1/2, m><\ell, \ell-1/2, m|],$$

where $\Delta U_\ell^{REP} = U_{\ell,\ell+1/2}^{REP} - U_{\ell,\ell-1/2}^{REP}$. The averaged RECPs take the following form:

$$U_\ell^{AREP} = U_L^{AREP} + \sum_{\ell=0}^{L-1} \sum_{m=-\ell}^{\ell} [U_\ell^{AREP}(r) - U_L^{AREP}(r)] |\ell, m><\ell, m|$$

The averaged RECPs thus exactly look like Kahn's ECPs and thus could be fit into non-relativistic MCSCF and CI codes. In recent years, Ermler and coworkers have reported Gaussian expansions for both AREPS and the spin-orbit operator based on the formalism of Pitzer and coworkers outlined above which could be used in *ab initio* computations conveniently. We have employed those RECPs in numerous investigations on diatomics, and clusters containing up to six atoms. [For details, see review articles Refs. 129-131.] We propose to use these potentials for most of the systems. For some systems, RECPs which include core-valence correlation corrections will be used. There is considerable progress in recent years on this aspect, especially by Meyer and coworkers.

Our objective is to use an accurate theoretical method which takes into account both electron correlation effects and relativistic effects including spin-orbit corrections. We have achieved this by modifying ALCHEMY II[129] package of non-relativistic codes to carry out relativistic CASSCF/CI/Relativistic CI calculations. In this method as shown in Fig. 1, the RECPs of the atoms are averaged with respect to spin. The RECP integrals generated are added to the one-electron integrals of ALCHEMY II. Then we carry out both MCSCF and CI calculations.

The orbitals for configuration interaction calculations are generated using the complete active space MCSCF (CASSCF) method[178] which yields approximate starting wave functions for CI calculations. In the CASSCF method active electrons (usually valence electrons) are distributed in all possible ways among a chosen set of orbitals referred to as internal orbitals. Then MCSCF wave functions are constructed by optimizing the orbitals in this configuration space. The other advantage of the CASSCF method is that it also yields the most important configurations which could then be used to do CI calculations.

The CI calculations we have carried out up to date are second-order CI (SOCI), MRSDCI (multi-reference singles + doubles CI) and restricted MRCI. The first two methods are more accurate in comparison to the last method. The SOCI calculations include all configurations in the CASSCF plus (i) configurations generated by distributing n-1 electrons in the internal space and one electron in the external space (n = number of active electrons), (ii) configurations generated by distributing n-2 electrons in the internal space and two electrons in the external space in all possible ways. The FOCI calculations include the first two sets described above for the SOCI. The MRSDCI calculations include a subset of configurations determined by the important configurations in the CASSCF (coefficient ≥ 0.07 or 0.05) as reference configurations and then allowing single + double excitations from those.

The largest CASSCF calculation carried out by our group to date included up to 50,000 configurations. The largest CI carried out to date by PI included about 6,000,000 configurations. We will be set up to carry out the large CIs locally using IBM RS/6000-550 models (at present 530 models) equipped with larger RAM. For further details of these computations, see Ref. 129.

The relativistic CI (RCI) calculations are carried out following CASSCF/CI. The CASSCF/CI calculations described above include electron correlation corrections as accurately as possible but neglect the spin-orbit coupling term which is far from negligible for molecules containing heavy atoms. I have now developed a relativistic CI method for polyatomics[187] which yields spin-orbit corrections with an accuracy of 5-10% of the experimental values. In the RCI calculations, the spin-orbit integrals are obtained for Gaussian basis sets using R. Pitzer's modified ARGOS codes.[173] The spin-orbit integrals are transformed over the natural orbitals obtained from the CASSCF/CI calculations and then added to the one-electron hamiltonian matrix at the relativistic CI step. There are several advantages of using natural orbitals obtained from

CASSCF/CI. First, these are superior to orbitals generated from a single configuration SCF. Second, they provide a convenient way of partitioning the external space as these orbitals are ordered in accordance to occupancies. Thus the spin-orbit coupling term is included variationally in the RCI.
In the RCI calculations, all configurations which mix in the presence of the spin-orbit coupling term are included as reference configurations. The inclusion of this term in the hamiltonian changes the normal single group symmetry of the molecule into spin double group. Thus all configurations which have the same symmetry in the spin double group would mix in the RCI calculations. For a diatomic all λ-s electronic states with the same Ω symmetry mix in the RCI calculations. For example, our 0_g^+ state RCI of Bi_2 included several reference configurations from several $^1\Sigma_g^+$ states, as well as $^3\Sigma_g^-$, $^5\Sigma_g^+$, $^3\Pi_g$ states.

The RCI of polyatomics can be illustrated using our earlier calculations on BiH_2^+.[188] We carried out CASSCF/SOCI calculations on three low-lying electronic states of BiH_2^+ ($^1A_1$, $^3B_1$, $^1B_1$) using a large valence (4s4p6d1f|4s4p4d1f) basis. The RCI was made with the natural orbitals generated from the SOCI calculations. The RCI calculations included all possible singles + doubles out of a multi-reference list determined in the C_{2v}^2 double group. Table I, shown below, gives a list of the most important electronic configurations and the electronic states arising from them in both C_{2v} and C_{2v}^2 groups. For the A_1 ground state, all configuration of the A_1 symmetry in Table I were included. The irreducible representations spanned by the various spin multiplets are obtained by correlating the three-dimensional rotation group representation $D^{(s)}$ (s=1 for triplet) into the C_{2v}^2 group. For example, the three triplet functions transform as A_2, B_1 and B_2 in the C_{2v}^2 group. The $(\alpha\beta+\beta\alpha)/\sqrt{2}$ of the triplet combination is A_2 while $(\alpha\alpha+\beta\beta)/\sqrt{2}$ and $(\alpha\alpha-\beta\beta)/\sqrt{2}$ transform as B_1 and B_2, respectively. Thus, for example, the RCI calculations of $^3B_1(A_2)$ would include $1a_1^2 2a_1 \alpha 1b_2^2 1b_1 \alpha$ and $1a_1^2 2a_1 \beta 1b_2^2 1b_1 \beta$ configurations

Table I. Possible configurations and electronic states of BiH_2^+.

Configuration	Electronic states	
	C_{2v}	C_{2v}^2
$1a_1^2 2a_1^2 1b_2^2$	$^1A_1$	A_1
$1a_1^2 2a_1^1 1b_2^2 1b_1^1$	$^3B_1$	A_2, B_2, A_1
	$^1B_1$	B_1
$1a_1^2 2a_1^2 3a_1^1 1b_2$	$^3B_2$	A_1, B_1, A_2
	$^1B_2$	B_2
$1a_1^2 2a_1 3a_1 1b_2^2$	$^3A_1$	B_1, B_2, A_2
	$^1A_1$	A_1
$1a_1^2 2a_1^2 1b_2^1 1b_1^1$	$^3A_2$	A_1, B_1, B_2
	$^1A_2$	A_2
$1a_1^2 2a_1 1b_2^2 1a_2$	$^3A_2$	A_1, B_1, B_2
	$^1A_2$	A_2
$1a_1^2 2a_1^2 3a_1 1b_2$	$^3B_2$	A_1, B_1, A_2
	$^1B_2$	B_2

as two of the possible reference configurations. Similarly, $^3B_1(A_1)$ is described by $1a_1^2 2a_1 \alpha 1b_2^2 1b_1 \alpha$, $1a_1^2 2a_1 \beta$ and $1b_2^2 1b_1 \beta$ configurations; these are added to the $1a_1^2 2a_1^2 1b_2^2$ configuration and other configurations which yield A_1 symmetry. In general, RCI matrix elements are complex. For molecules with C_{2v} or higher symmetry R. Pitzer and Winter[173] have shown that one could transform the RCI hamiltonian matrix into a real matrix by multiplying the imaginary configurations

with i ahead of time. This transformation is possible because spin-orbit matrix elements for such molecules are either purely real or purely imaginary. Our RCI code is a complex CI code although for molecules with C_{2v} or higher symmetry we will take advantage of the above transformation. The two advantages of this transformation are (i) memory saving, (ii) the CI matrix could be diagonalized with iterative large-scale diagonalization methods such as the Liu-Davidson method which extracts upper roots simultaneously together with the lowest root.

The spin-orbit coupling has dramatic impact on both geometries and energy separations of the electronic states of several molecules that we studied before [PbH_2, BiH_2^+, PoH_2, Ir_3, OsH_2, ReH_2, IrH_2, Pt_2, excited states of Au_3]. The Pt_2 spin-orbit splitting was found to be up to 10,000 cm^{-1}. While the $^1A_1$-$^3B_1$ separation of SnH_2 is 23.8 Kcal/mole, the spin-orbit splitting of the $^3B_1$ state is less than a kcal/mole, but this is not the case for PbH_2.

The dramatic change in the geometry of the A_1 component of $^3B_1$ is primarily a consequence of the mixing of $^3B_1(A_1)$ with the ground state ($^1A_1(A_1)$) which is brought about by the spin-orbit coupling. From the coefficients of the relativistic CI configurations, we showed that the $^3B_1(A_1)$ is actually made up of 67% $^3B_1(A_1)$ $1a_1^2 2a_1 1b_2^2 1b_1$, 24% $^1A_1(A_1)$ $1a_1^2 2a_1^2 1b_2^2$, 1.3% $1a_1^2 1b_2^2 1b_1^2$ $^1A(A_1)$, etc. The mixing between $^1A_1(A_1)$ ground state and $^3B_1(A_1)$ is thus quite significant.

The quadratically convergent CASSCF codes that we use have analytical gradients. This is especially important for larger clusters that we propose to investigate. Our plan is to use the gradient method for geometry optimization at the CASSCF level of theory. Then we will use a multi-dimensional multinomial fitting procedure (normally cubic polynomial) based on numerical Gaussian elimination method that we have developed for the direct CI geometry optimization. These procedures evaluate both first and second derivatives and

hence it is possible to determine if a stationary part is a minimum or a saddle point.

3. Proposed Theoretical Studies on Transition Metal Clusters

3.1. Pure transition metal clusters

3.1.1 Cu_n, Ag_n, Au_n (n = 6-8)

Our proposed studies on noble metal clusters will be focused mainly on larger clusters. The motivation for these studies are (i) Smalley's as well as Lineberger and coworkers' photodetachment spectra on Cu_n^-, Ag_n^-, Au_n^-; (ii) our theoretical study on Au_6; (iii) Van Zee and Weltner's experimental ESR study on Cu_7. As outlined in our progress report, negative photodetachment spectra of Cu_n^-, Au_n^- and Ag_n^- are now available for various sizes. While different structures of Au_6 have been already considered by us, this is not the case for Cu_6 and Ag_6. Au_6 is unusual in this group due to relativistic effects. Experimental spectra also seem to suggest that Au_6 is the only hexamer in this group which has an unusually large HOMO-LUMO gap. Consequently it would be of great interest to compute the geometries, binding energies, electron affinities, ionization potentials and other properties of Cu_6 and Ag_6, and compare the results with Au_6.

Our previous CASSCF/MRCI study on Au_6[148] has demonstrated that indeed it is possible to investigate such large clusters. In our previous study, we included the effect of 5d electron correlations employing the CASSCF/MRCI procedures. In addition, full second-order CI (SOCI) calculations were made which correlated the 6s electrons more completely. In this study the relative energy separations of the capped pentagon, octahedron and hexagon were considered for both Au_6^- and neutral Au_6. We employed a (3s2p3d) valence Gaussian basis which yielded 162 Gaussian functions. Since we carried out those calculations, our code capabilities have been enhanced to compute

integrals involving generalized Gaussian wave functions containing up to 250 contracted basis functions. We also have analytical gradients at the MCSCF stage of computations with dedicated IBM RISC/6000 530 systems which we propose to upgrade to 550E models equipped with 2.5 GB disk/system (total 10 GB). We will have more control on the disk space usage thereby allowing us to carry out calculations employing larger basis sets. The ALCHEMY integral codes can handle up to i functions and can retain only the spherical harmonic components of the Gaussian functions for higher angular momentum.

We propose to consider four possible structures shown in Fig. 2 as candidates for Cu_6 and Ag_6. This choice is governed both by our previous study on Au_6 as well as the works of Koutecký and coworkers[58,115] on Li_6, Na_6 and the other clusters. For the alkali metal clusters, both CP and distorted tribipyramidal (C_{2v}) structures are attractive candidates. We will employ relativistic effective core potentials (RECPs) which will uniformly retain the outer d and s shells of Cu and Ag atoms. Valence (3s2p3d) Gaussian basis sets of triple-zeta quality will be employed for both Cu and Ag atoms. At the CAS-MCSCF stage of the computation we will not allow excitations from the d orbitals. However, SOCI which does not include d excitations and MRCI which includes d excitations will be carried out. It is evident from our previous study on Cu_4, Ag_4, Ag_3, etc. that the effects of d-electron correlations must be included. At present, we can carry out CI calculations which include up to 4 million configurations on the IBM RS 6000-530 dedicated to our group and 6 million CSFs on the San Diego Cray YMP system, although the code operating on SDSC is based on Siegbahns's externally contracted CI (CCI). Note that upon upgrade of memory on our RS 6000 system we can carry out CI calculations up to 6 million configurations.

To demonstrate the feasibility of such studies we carried out preliminary calculations on Ag_6 on our IBM RS 6000 1530 system. The results of these

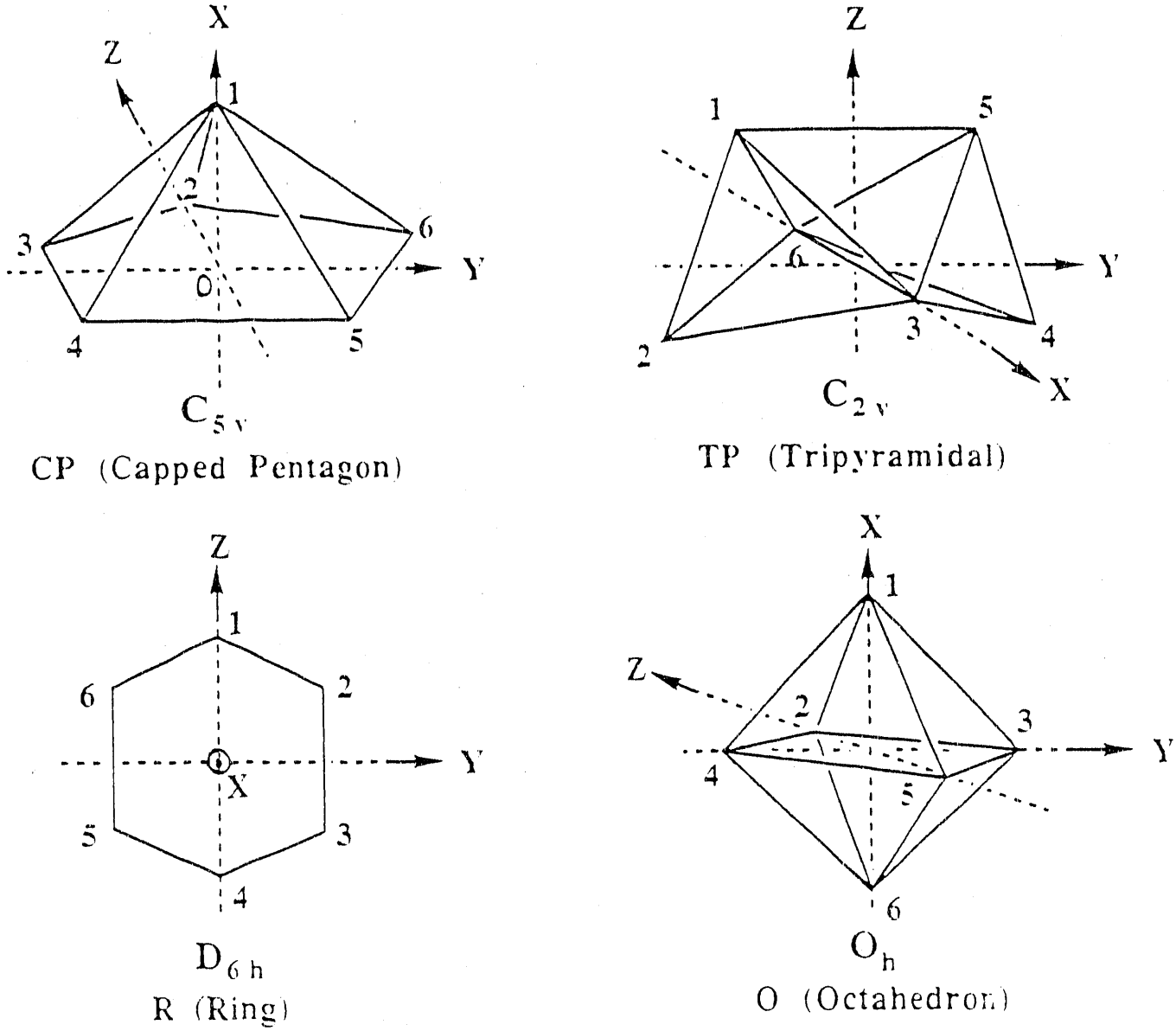


Fig. 2 Possible Structures for Cu_6 and Ag_6

calculations are shown in Table 1. We are in the process of completing similar calculations on Cu_6, Cu_6^+ as well as Ag_6^+. As seen from Table I, the energy separations are sensitive to the level of theory is employed. At all levels of

Table 1. Topology and energy separation of Ag_6.

			CASSCF		SOCI		MRCI	
Structure	Symmetry	State	R_e(Å)	E(eV)	R_e(Å)	E(eV)	R_e(Å)	E(eV)
CP-I	C_{5v}	$^1A_1$	1.27[a] (2.70)[b]	0.0	1.30 (2.71)	0.0	1.23 (2.68)	0.0
TP	C_{2v}	$^1A_1$	2.82	0.55	2.82	0.39	2.79	0.29
R	D_{6h}	$^1A_{1g}$	2.66	1.39	2.65	1.24	2.63	1.68
O	O_h	$^3T_{2g}$	2.83	1.22	2.84	0.94	2.80	0.8

[a] Origin-Cap distance. [b] Ag-Ag distance (see Fig. 2).

theory the CP structure prevails. However, the TP structure (Fig. 1) becomes closer and closer as the level of theory improved for Ag_6. This demonstrates the need to do the highest possible level of theory to unambiguously establish the structure and energy separations. However, usually the experimental spectra are sufficiently different for these structures to unambiguously assign the spectra.

Van Zee and Weltner[34,35] have obtained the ESR spectra of Cu_7 and Ag_7. From the spectra they interpret the structure of Ag_7 and Cu_7 to be a pentagonal bipyramid (PBP) with $^2A_2''$ ground state (D_{5h}). Howard et al. observed the ESR spectra of a Cu cluster in a C_6D_{12} matrix which was although attributed by these authors to Cu_5, Van Zee and Weltner subsequently assigned it to Cu_7. While there are theoretical studies on seven-atom alkali metal clusters which support the assignment of Van Zee and Weltner, at present there are no high-level *ab initio* calculations on Cu_7, Ag_7 and Au_7. Unlike the trimers, heptamers are in a $^2A_2''$ ground state and thus would not undergo Jahn-

Teller distortion. While the PBP structure is supported by the CP structure for the hexamer, accurate calculations are warranted. We propose to study all three heptamers using valence (3s2p3d) gaussian basis sets (226 basis functions) and RECPs which retain 11 outer electrons/atom in the valence space. CAS-MCSCF followed by restricted MRCI procedures including excitations from the d-shells will be allowed. The restriction in the MRCI will be imposed by partitioning the external space based on orbital occupancies for a smaller CI. Our objective is to keep the number of configurations below 6 million and yet obtain reasonably accurate results. We also need to compute the binding energy of a metal atom in M_6. This is done by computing the energy required to remove the apex atom from the CP structure

$$Ag_6 \rightarrow Ag_5 + Ag.$$

From these energies we could deduce the total atomization energies.

It would be very interesting to compare the structures, IPs, EAs and binding energies of all three hexamers to comprehend the impact of relativity on these clusters. We also propose to compute the IPs and binding energies of Cu_7, Ag_7 and Au_7.

Theoretical studies of eight-atom clusters would certainly be more challenging. Computations on Na_8 by Koutecký and coworkers[58] have yielded a $^1A_1$ ground state with tetra-capped tetrahedral symmetry (T_d). Figure 3 shows the possible structures we will consider for M_8 [M = Cu-Au]. To make our computations feasible, we propose to use a (3s2p2d) valence Gaussian basis set. At the CASSCF level, no excitation from the d shells will be allowed. At the CI stage, d-correlation effects will be incorporated only from the high lying d orbitals and by partitioning the external space based on a smaller CI scheme. The method cannot be used for computing binding energies but IPs and geometries should come out correct. Also the energy separations will be computed for various geometries in a consistent manner.

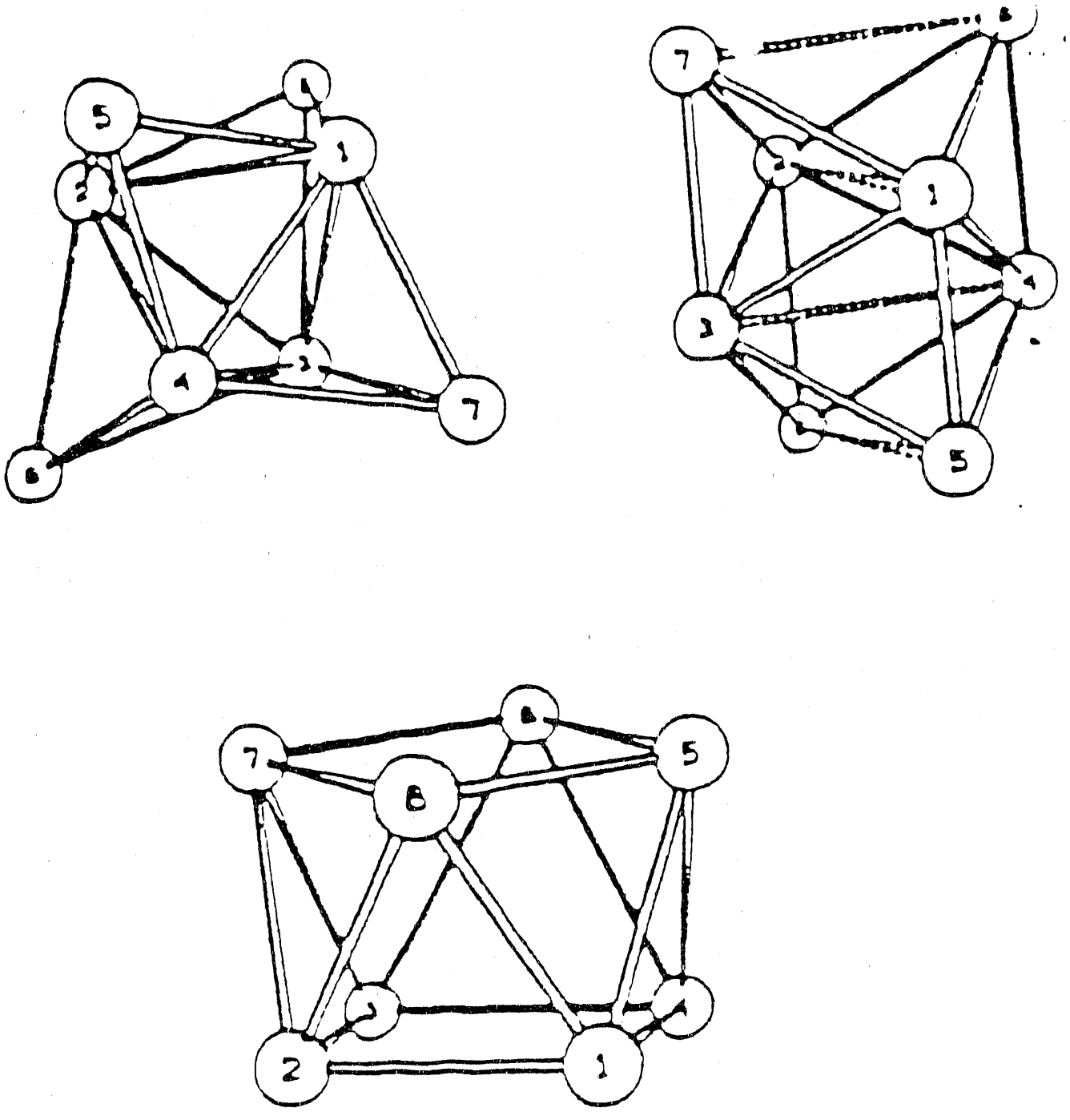


Fig. 3. Possible structures for M_8 [M = Cu-Au].

3.1.2. Ni_n, Pd_n, Pt_n [n = 4-6].

The structures and other properties of tetramers and larger clusters containing Ni, Pd and Pt are extremely important to investigate since (i) Pt, Pd, Ni group is one of the most important materials used in the heterogeneous

Ni group is one of the most important materials used in the heterogeneous catalysis, (ii) the dramatic differences in the properties of Pt clusters compared with Pd-clusters is fundamentally intriguing, (iii) there are increasing number of experimental studies on the structure, properties and reactivities of Ni, Pt and Pd clusters. A recent experimental study by Knickelbein, Yang and Riley[26] on photoionization of nickel clusters reveals dramatic variation of ionization potentials of Ni-clusters especially for $n \leq 11$. For example, the IP of Ni_4 (~5.7 eV) is considerably smaller than the IP of Ni_3 (6.2 eV) and Ni_5 (6.2 eV). At present theoretical calculations on Ni-clusters are limited to tight-binding method (Hückel theory), conducting spherical drop models, CNDO, and some *ab initio* methods with no or limited inclusion of electron correlation effects. As pointed out by Riley and coworkers, all those results are in poor agreement with the experiment. We presume that this is because these methods do not take into account electron correlation effects adequately leading to poor IPs. Our previous study on Pd_3^+, Ag_3^+, Ag_4^+, Au_4^+, etc. have shown that it is important to include electron correlation effects to a high order (CASSCF/MRSDCI+Q) for the computation of IPs and binding energies.

Theoretical studies of Pt_n and Pd_n clusters are more complicated by the fact that relativistic effects including spin-orbit effects are very important especially for platinum-clusters. We are in a unique position to include both electron correlation, spin-orbit effects and other relativistic effects to a high order through the use of CASSCF/MRCI/RCI methods on IBM RS/6000-530 systems dedicated to these projects.

A very recent scanning tunneling microscope study of Pt_2 and Pt_3 by Müller et al. (1991)[31] has confirmed the author's previously computed Pt-Pt distance in Pt_2.[189] The experimental average Pt-Pt bond length distribution on graphite was found to be 2.46 Å while our CASSCF/FOCI/RCI method yields 2.456 Å computed in 1987 for the 0_g^+ ground state of Pt_2. Müller et al. found for

Pt_3 two types of forms on graphite, one is almost linear and the other is triangular. Our computations on Pt_3 reveal that the triplet and singlet states are bent (triangular) while some high spin quintet states have linear structures. These agreements between theoretical predictions and the subsequent experiments are quite encouraging.

The agreement in the predicted density of electronic states and the vibrational frequencies computed in 1987[189] with a subsequent resonant two-photon spectra on Pt_2 by M. Morse and coworkers is also very important.[190] M. Morse and coworkers used our computed spectroscopic constants of Pt_2 to compute the partition function and hence the correct thermodynamic D_0^0 (Pt_2) which was found to be in excellent agreement with the spectroscopic value.

The author computed spectroscopic constants of 41 electronic states of Pd_2 in 1988[191]. Lineberger and coworkers[192] reported the negative ion photoelectron spectroscopy of Pd_2^- recently. Our computed $^3\Sigma_u^+(1_u)$-$^1\Sigma_u^+(0_u^+)$ splitting of Pd_2 is 4443 cm^{-1} compared to the experimental value of 4008 cm^{-1} obtained by Lineberger and coworkers[192]. Overall the density of states predicted by theory for Pd_2 is in good agreement with the observed spectra. Although the r_e values for Pd_2 states could not be deduced experimentally our predicted trends are in excellent agreement. Likewise our predicted triplet ground state for Pd_2 was also confirmed experimentally.

To demonstrate the feasibility of these studies, we have completed calculations of a few electronic states of Pd_4 recently. Our previous study on Pd_3 demonstrated that as the electron correlation effects are included to a higher-order the $^1A_1'$ state with equilateral triangular structure is lowered. Since Pd atom has a d^{10} (^1S) ground state, the $^1A_1$ state of Pd_4 formed from the excitation of some of the 4d electrons into 5s is an attractive candidate. As a

matter of fact, electronic states of singlet and triplet spin multiplicities were considered and we found that the $^1A_1$ state (C_{2v}) prevails.

We started with CASSCF calculations which included all 40 electrons of Pd_4 in the active space and 4d and 5s orbitals in the active space. Several possible geometries (tetrahedral, rhombus, square, triangular, linear, fork, etc.) were considered. Subsequent to the CASSCF we chose the two most important configurations in the CASSCF and allowed single + double excitations into the external space from all 40 electrons of Pd_4 (Pt_4). The results of our calculations are shown in Fig. 4. As evidenced from Fig. 4, the ground state of Pd_4 is of tetrahedral geometry with $^1A_1$ symmetry. The rhombus structure is 7 kcal/mole higher than the tetrahedron. The energy to convert the rhombus structure into the square structure (saddle point) is quite significant.

Our preliminary studies on Pt_4 have already revealed the dramatic difference between Pt_4 and Pd_4. Unlike Pd_4, Pt_4 appears to have a triplet ground state although with a tetrahedral structure. The M-M bond lengths for Pt_4 are shorter than Pd_4. Our RCI calculations which include the effects of both electron correlations and spin-orbit coupling have revealed that the spin-orbit coupling between triplet and singlet states for Pt_4 is quite significant while for Pd_4 this mixing is quite small. Note that the ground state of Pt is ^3D [$5d^9 6s^1$;^3D] while the ground state of Pd is ^1S [$4d^{10}$]. This difference in the atomic states itself arises from relativistic stabilization of the 6s outer orbital of the platinum atom.

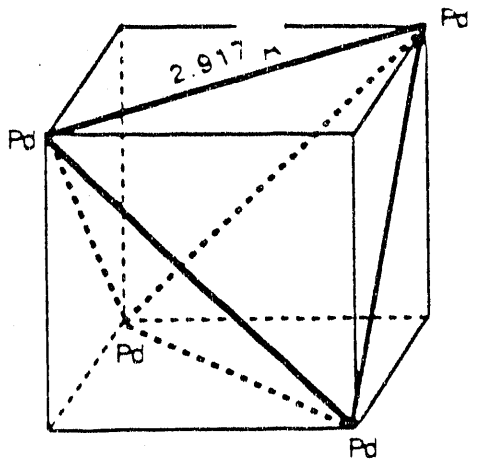
We propose to consider similar calculations on Ni_4 (tetrahedral, rhombus, etc.) and complete our preliminary studies on Pd_4. The Ni atom has a $3d^8 4s^2$ (^3F) ground state with a nearly-degenerate $3d^9 4s^1$ (^3D) [205 cm^{-1}] excited state. Of course the pure $3d^8 4s^2$ configuration of Ni would not lead to significant bonding and promotion of a 4s electron into 3d does not take much

energy. Hence a comparison study of all three clusters in this group would be very interesting.

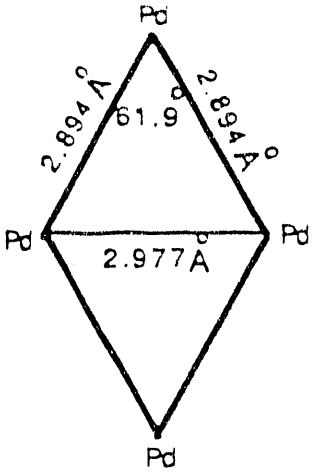
There are several possible isomers and topologies which need to be considered for larger clusters. The use of analytical gradient technique for geometry optimization at the CASSCF (MCSCF) stage will establish if the stationary points are minima or saddle points. However, at the MRCI level we will use a multi-dimensional cubic (quadratic) polynomial fitting procedure near the CASSCF optimized geometry for geometry optimization. For larger clusters, optimized geometries at the CASSCF level will have to be used with correction for electron correlation. For example, fully optimized CASSCF and MRCI computations on smaller clusters ($n \leq 4$) will be used to compute the differences in the CASSCF and MRCI geometries. These differences, usually 0.05-0.08 Å in bond lengths, can be applied as corrections if full geometry optimizations at the MRCI level become formidably difficult.

Figure 5 shows possible structures for pentamers and hexamers we propose to investigate for Ni_n, Pd_n, Pt_n (n = 5,6). All possible structures will be considered at the lower (CASSCF/Restricted-CASSCF) level of theory. Only feasible structures [structures with $T_e < 1$ eV] will be considered at the higher CI level of theory. Also for Pt_6, Pd_6 and Ni_6, no geometry optimization will be done at the CI stage. Corrections due to higher-order correlation effects will be applied on CASSCF geometries and only single point computations will be done for different feasible structures.

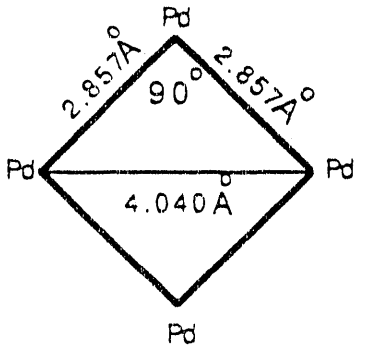
We propose to compute in addition to geometries, ionization potentials and binding energies for the ground state structures. The binding energies will be computed by removing one atom from the cluster and then adding the dissociation energy for $M_n \rightarrow M_{n-1}+M$ with the atomization energy of M_{n-1} already computed before. This procedure would be more practical since the MRCI computation for $M_n \rightarrow M_{n-1}+M$ generally contains fewer reference



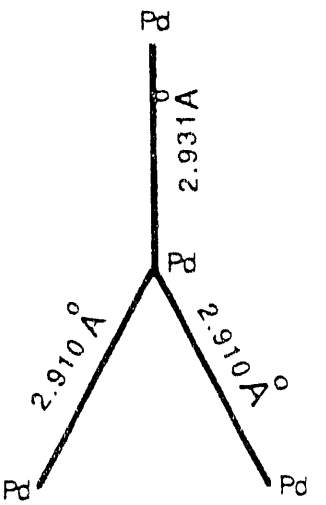
Tetrahedron 0 Kcal/mol



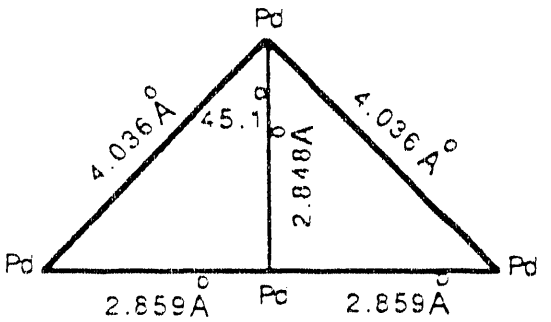
Rhombus 6.6 Kcal/mol



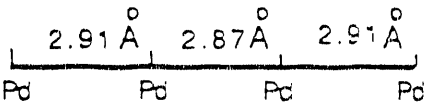
Square 9.5 Kcal/mol



Fork 15.2 Kcal/mol

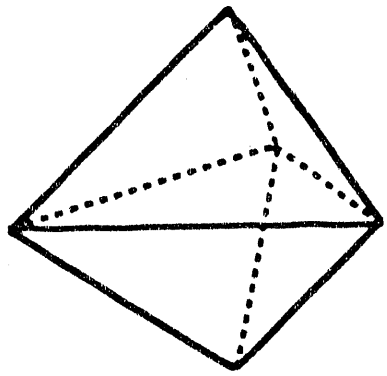


Triangle 19.3 Kcal/mol

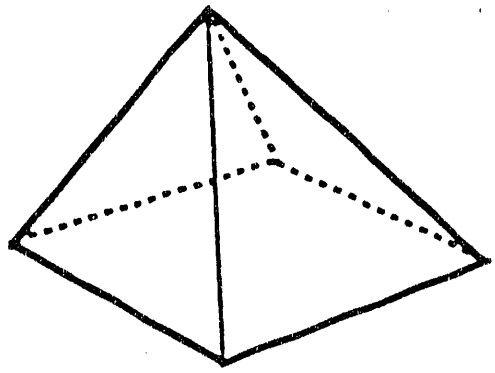


Linear 24.5 Kcal/mol

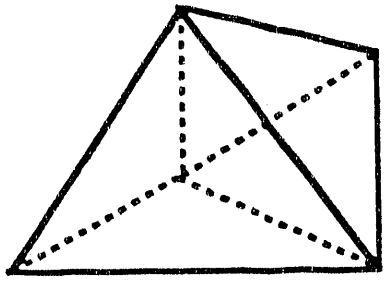
Fig. 4. Geometries and energy separations of electronic states of Pd_4.



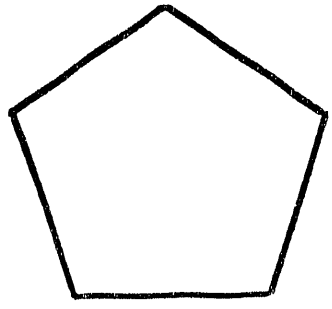
Trigonal bipyramid



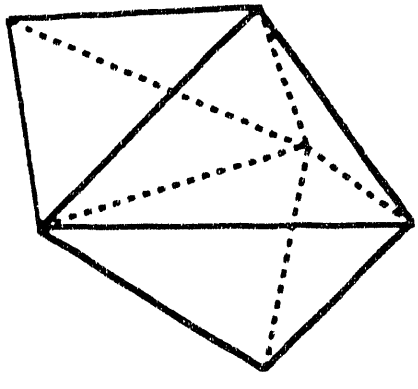
Capped-rhombus



Caapped-tetrahedrron



Pentagon



Bi-capped-tetrahedron

Fig. 5. Possible topologies for Ni_5, Pd_5, Pt_5 (see also Fig. 2 for other possibilities).

configurations compared to $M_n \rightarrow nM$. Also in general, AEs of smaller clusters are computed more accurately than larger clusters.

3.1.3. Rh_n, Ir_n, Ru_n, Os_n, Re_n, Y_n, Zr_n [n = 3-5].

Small clusters of the second row and third row transition metal atoms in the Rh-Ir group, the Ru-Os group and the early transition metal atoms (Y, Zr) are very interesting. First these clusters occur as substructures in numerous inorganic complexes. Second the iridium clusters are one of the most electron rich clusters as deomstrated by theory[162] and experiment[77,78]. Third numerous surface chemistry studies are focused on reactions of small molecules on Ir and Rh surfaces. Ru and Os clusters occur commonly as subunits in inorganic complexes.

Recent experimental study by Bruce et al.[46] has demonstrated the existence of Ru_5 cluster bound to triarylphosphine ligands. Two phases of $Ru_5(\mu_4\text{-PPh})(\mu_3\text{-PhC}_2\text{Ph})(\mu\text{PPh}_2)_2(CO)_{10}$ have been identified from x-ray studies. Masciocchi et al.[47] have reported in a recent communication to the editor a rare example of a square arrangement of Re atoms. They have synthesized compounds of the type $[HRe(CO)_4]_n$ n = 2, 3, 4. Anderson et al. (1991)[51] have reported single-crystal neutral diffraction study of (μ-η^1, $\eta^1C_2H_4)Os_2(CO_8)$ as a model for chemisorbed ethylene. They find that in this synthesized compound the Os_2C_2 ring is distorted away from planarity compared to the Os_4 ring in $Os_4(CO)_{16}$. The existence of Os_4 and Os_2C_2 rings is certainly interesting.

As demonstrated by our theoretical study on Rh_3[140] and the subsequent experimental ESR study by Van Zee and Weltner, such studies on small clusters can be extremely valuable. Van Zee and Weltner have communicated to the author that they have recorded the ESR spectra of Ir_3. Yet at present there are no theoretical studies on Ir_3. The mixing of high spin sextet electronic states of

Ir_3 with quartet states due to spin-orbit coupling is certainly expected to be significant. Hence Ir_3 is an interesting case for theoretical states. We will consider sextet, quartet and doublet electronic states at the CASSCF/MRCI levels of theory. Finally, spin-orbit coupling will be introduced using the relativistic CI (RCI) technique. Although in the past we considered the entire potential energy surfaces for trimers, the use of analytical gradient methods can facilitate faster geometry optimizations at the CASSCF level.

Our computations on the tetramers will include tetrahedron, rhombus (square), linear, fork and triangular structures at the CASSCF level. At the CI level we will consider among these only feasible structures. Likewise computations of the pentamer clusters will include structures in Fig. 5 at the restricted-CASSCF level and only feasible structures among these at the MRCI level. Another important difficulty that arises in dealing with clusters of open-shell d elements is the possibility of closely spaced electronic states of different spin multiplicities. However, if we find that some of these states are too far apart then they may be discarded. Also for the question of metal-metal multiple bonding low spin electronic states are more important than high spin states [for example, W_2 $^1\Sigma_g^+$].

We now illustrate the above points and show that these studies are indeed feasible. Let us consider Rh_4 (36 electrons). Our previous studies on YH-CdH[143] have shown that for elements Y-Ru and Hf-Os, the inner $(n-1)s^2$ $(n-1)p^6$ shells must be retained in the valence space (n = valence principal quantum number). We computed Rh_2 both ways (9e RECPs, 17e RECPs) and did not find any differences. A (3s3p3d) valence Gaussian basis set was employed for the Rh atom. All 36 electrons were included in the CASSCF of Rh_4. However, we had to try several alternative choices of active space and include an optimal set of selected orbitals to bring down the configuration counts in the CASSCF. We considered triplet, singlet and quintet electronic states of

several geometries for Rh_4. Our previous studies on Rh_3 and Rh_2 suggest that Rh-Rh bond lengths should be of the order of 2.6-2.8 Å. The results of the CASSCF calculations for the two lowest states are shown in Fig. 6. As seen from Fig. 6, at the CASSCF level the tetrahedral Rh_4 with $^1A_1$ state prevails although the rhombus structure is only 6 kcal/mole above the tetrahedron.

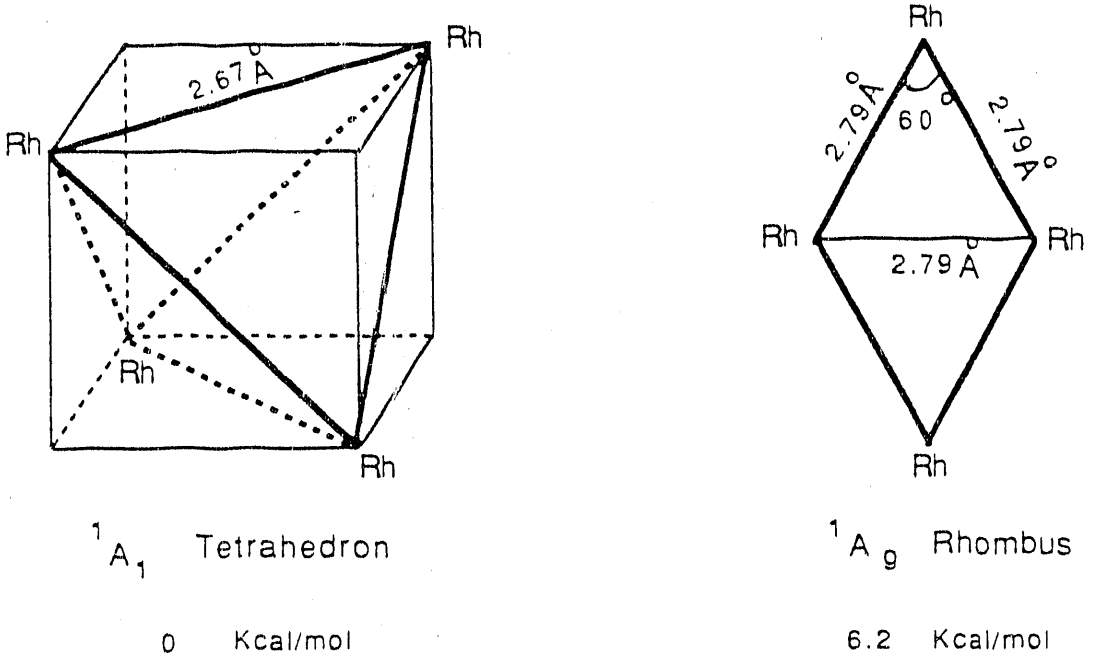


Fig. 6. Two low-lying structures and their energy separations for Rh_4.

We propose to compute geometries of different feasible structures, the IP of the ground state and binding energy of the ground state. We are somewhat more sure of computing Rh_n, Ir_n, Y_n, Zr_n compared to Ru_n, Os_n and Re_n. A previous study on Ru_2[151] has demonstrated that there are numerous possible electronic states although the high spin $^7\Delta_u$ state is the lowest at all levels of theory. If this trend were to continue for Ru_3 and Ru_4, we expect no real problem since only the highest spin states need to be considered. To the contrary if low spin states compete with the high spin states then several electronic states will have to be considered. Furthermore it is imperative that

the inner $4s^2 4p^6$ shells must be explicitly retained in the valence space for Y-Ru. This poses no special problem if one uses the generalized contraction scheme to contract the basis functions describing the inner 4s and 4p orbitals so that the basis set becomes effectively (4s4p3d) or slightly larger. To test this, we just carried out one set of pilot calculations on Zr_4. Indeed we find these calculations doable although time-consuming.

3.2. Transition metal ions. [Nb_n^+, Nb_n^{+2}, Ag_n^{+2}, Au_n^{+2} (n = 2-4), Cu_n^+ (n = 5,6)]

There are several spectroscopic studies on singly and multiply charged clusters.[52-57] Experimental studies on multiply-charged clusters to some extent are motivated by the so-called "coulomb explosion," a phenomenon attributed to the fast dissociation of multiply-charged clusters due to the strong repulsive coulomb forces. It was speculated that below a critical size multiply charged clusters could not be observed. However, recently Bowers and coworkers[52], Tsong, Saunders and Fredrigo have observed Nb_n^{2+}, Mo_2^{+2}, Au_2^{+2}, etc. The parent charge separation is estimated as 4.3 Å for Nb_2^{+2} and 5.7 Å for Nb_3^{+2}. This large charge separation for the trimer suggests that Nb_3^{+2} is linear. Nakamura[53], Kandler et al.[54] as well as Rabin et al.[55] have studied multiply charge silver and gold clusters. The reactivities of doubly charged TM ions with small molecules have been considered by Frieser and coworkers.[80,86]

Armentrout and coworkers[57] have studied the collision-induced dissociation of Nb_n^+ (n = 2-11) from which they have deduced the bond energies and dissociation pathways of Nb_n^+. The structures of even small Nb_n^+ clusters have not been established at the present time. Bond energies of Nb_n as a function of cluster size exhibit a sawtooth pattern which is quite interesting. Among small clusters, Nb_4 appears to be unusually stable compared to Nb_2 and Nb_3. It is not clear if this magic number of four for Nb_n is due to multiply-bonded closed shell ground state for Nb_4.

Jarrold and Creegan[56] have studied the photodissociation of Cu_n^+ (n = 3-8). As noted in our progress report, our computed results are in very good agreement with the experiment for Cu_4^+. The fragmentation pattern of Cu_n^+ is rather intriguing. While the main fragment obtained upon dissociation of Cu_5^+ is Cu_3^+ the corresponding daughter for Cu_6^+ is Cu_5^+. The fragmentation pattern of Cu_7^+ depended upon the wavelength of the light. Hence the photofragmentation of Cu_n^+ is very interesting and not fully understood.

The above survey of small cluster ions reveals the need for accurate *ab initio* calculations on the geometries, IPs and stabilities of these clusters. For the doubly charged cluster ions it is important to compute the charge separations and Mulliken populations from which the extent of charge delocalizations can be deduced.

3.3. Bimetallic clusters.

3.3.1. Mixed coinage metal clusters.

Morse and coworkers (Utah)[39-43] as well as Steimle and coworkers (Arizona State University) have been studying the spectroscopy of small coinage metal dimers and trimers such as PdNi, PtNi, PtPd, AuAg, AuCu, Cu_2Au, Cu_2Ag, etc. For example, the resonant two-photon ionization spectroscopy of jet-cooled NiPd and PdPt has revealed a dense spectrum for NiPd and a somewhat sparse spectrum for PdPt. Four vibrational progressions have been identified. These authors have also deduced the bond lengths, D_0^0 and IPs of these species. Spectroscopy of trimers such as Au_3, Cu_2Au and Cu_2Ag is considerably more complicated. Assignment of the observed systems is not definitive since theoretical studies especially on the excited electronic states of these species are not available.

At present there are no theoretical calculations on PdNi, PtNi or PtPd. Likewise excited electronic states of these species or mixed coinage metal

dimers and trimers have not been explained. We note that our previously computed spectroscopic constants and energy separations (T_e) for Au_2 were found to be in excellent agreement with the recent spectra of Au_2 obtained by Morse and coworkers.

Payne et al. (1991)[44] have recently synthesized mixed tetramer and pentamer cluster complexes, namely Pt_3Au and Pt_3Au_2 complexes. The structure and reactivity of these species were also explored by these authors. Multinuclear NMR has revealed that in these complexes Pt_3Au subunit has a triangular-pyramid structure in which the gold atom is at the apex. Likewise Pt_3Au_2 has a TPB structure. Existence of two different atoms could lead to isomers for Pt_3Au_2. Possible structures are in Fig. 7. Hence theoretical study of Pt_3Au and Pt_3Au_2 would certainly be interesting.

3.3.2. Pt_xRu_y ($x+y \leq 3$).

Del Angel et al. (1991)[37] inferred from the x-ray diffractograms that some Ru atoms insert into the Pt-network. They also detect metallic alloyed particles (Ru_xPt_y) of varied composition. The deactivation of Ru catalysts is found to diminish by alloying with Pt_n. The nature of bonding between Ru and Pt is poorly understood at present. Even the diatomic Pt-Ru has not been studied. It would also be interesting to study if Ru atom will insert into the Pt-Pt bond to form Pt $\overset{Ru}{}$ Pt cluster. Theoretical calculations on simple dimers and trimers such as Pt-Ru and Pt $\overset{Ru}{}$ Pt and comparison with Pt_2 and Pt_3 could provide valuable insight into this intriguing experimental phenomenon.

3.4. Transition metal carbide clusters (TaC_n^+, WC_n^+, Os_2C_2).

In an exciting experimental study on tantalum carbide clusters, Cassady and McElvany (1991)[49] find that the gas phase ion-molecule reactions of TaC_n^+ ($n = 0$-14) with D_2, CH_4 and C_2H_4 exhibit dramatic contrast in the reactivity of

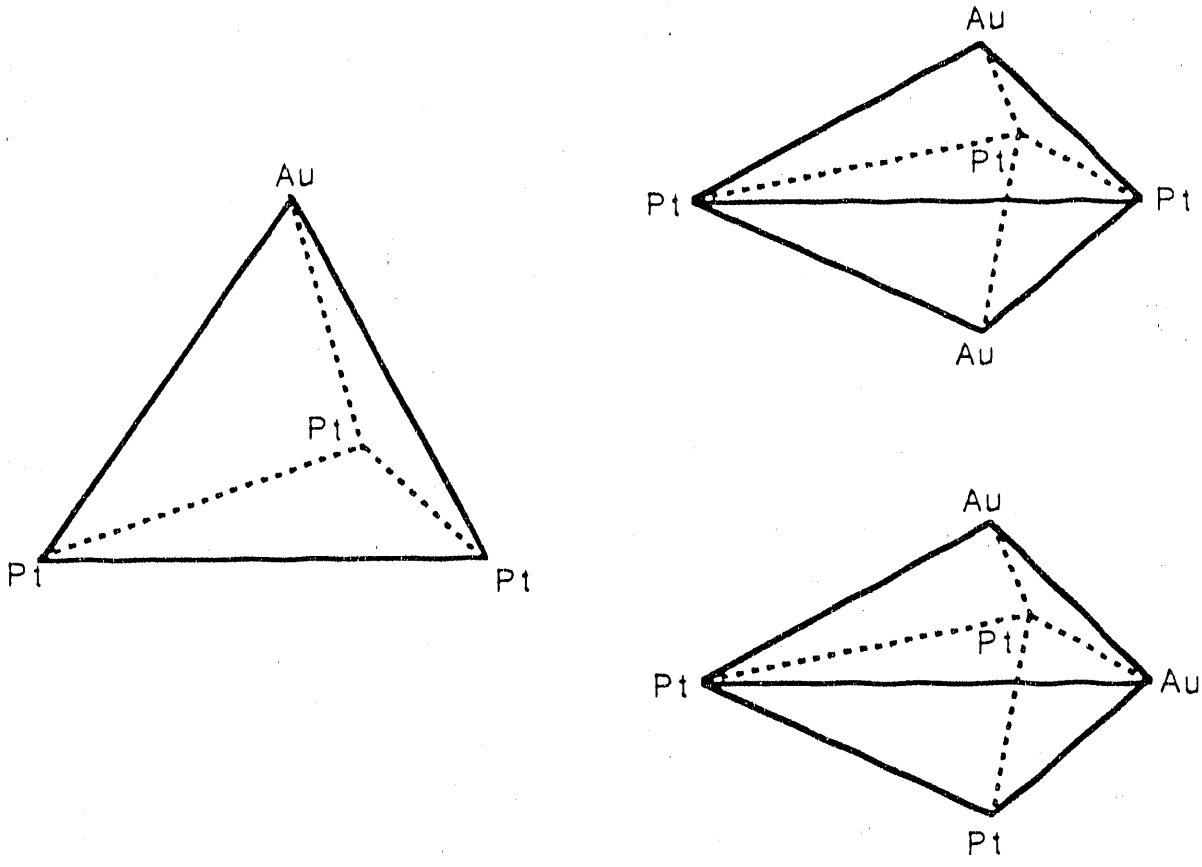


Fig. 7. Possible structures for Pt_3Au and Pt_3Au_2.

isomers with a given constitution. The addition of the Ta atom to C_n^+ clusters was found to dramatically alter the reactivity. These authors found evidences for two structural isomers of TaC_7^+, TaC_8^+ and TaC_9^+. The exact structures of TaC_n^+ are unknown at this time. There are practically no theoretical calculations on TaC_n^+ even for n = 1. The possibility of isomers for TaC_n^+ is intriguing.

In another single-crystal neutral diffraction study, Anderson and coworkers[51] as well as Larson and coworkers at Los Alamos National Laboratory found evidences for a non-planar Os_2C_2 ring in complexes as

models for the chemisorbed ethylene. The structure and the nature of bonding in Os_2C_2 are not fully understood at present.

Our proposed theoretical studies on TaC_n^+, WC_n^+ and Os_2C_2 are aimed at seeking answers to these fundamental and intriguing questions pertaining to the structures of these species. To illustrate, plausible structures proposed by Cassady and McElvany[49] for TaC_7^+ are shown in Fig. 8. Theoretical calculations on the structures of the type in Fig. 8 for different values of n could provide valuable insight into the nature of bonding in these species and relative energy separations of possible isomers.

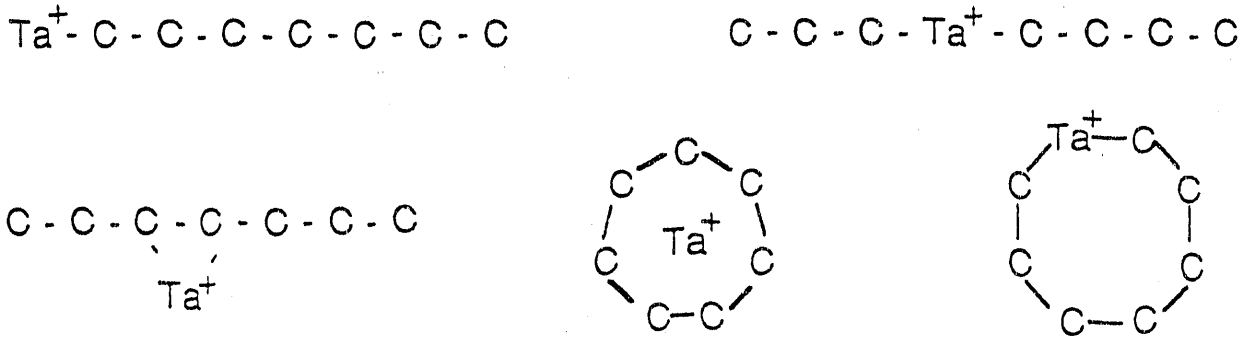


Fig. 8. Possible Structures for TaC_7^+

The reactivity of TaC_n^+ with D_2 has also revealed some fascinating trends. TaC_n^+ (n = 5-14) with even number of carbon atoms were found to react faster in contrast with C_n^+ for which odd clusters react faster. Hence the addition of Ta to C_n^+ changes the reactivity trends dramatically. This needs explanation.

There are experimental studies on tungsten carbide clusters too, based on direct laser vaporization of metal powder/carbon mixtures in a Fourier transform mass spectrometer.[50] Hence comparable theoretical studies on WC_n^+ would also be interesting.

At the present time among Os-carbide clusters, Os_2C_2 appears to be the most interesting candidate since it occurs as a non-planar subunit in complexes. Hence we propose theoretical studies on TaC_n^+, WC_n^+ and Os_2C_2. Theoretical studies on TaC_n^+, and WC_n^+ would be made using RECPs for Ta and W. For carbon both all-electron basis sets and ECP basis sets ($1s^2$ in core) will be compared. We will start with calculations on TaC and WC for which experimental D_0^0 values are available. Subsequently, larger TaC_n^+ and WC_n^+ ($n \geq 2$) will be computed. Transition point from the linear to cyclic structures will be obtained from theoretical calculations. For the Ta and W atoms, (5s5p3d) valence Gaussian basis sets together with $5s^25p^65d^n6s^1$ valence shell RECPs will be employed. Note that $5s^25p^6$ shells will be explictly retained in these computations since for Ta and W our previous studies have shown that it is necessary to retain these shells in the valence space for non-hydride compounds.

4. Reactivity Studies on Transition Metal Clusters

4.1. Reactivity with H_2: Pt_n+H_2, Pd_n+H_2, Ni_n+H_2 [n = 3-4].

As indicated in our progress reported all PES for $M+H_2$, $M^+ + H_2$ for the second and third row transition metal atoms have now been computed. In addition, theoretical studies on Pt_2+H_2, Pt_n+H, Pd_n+H, Pd_n+H, Ni_n+H [n = 2-3] have revealed significant insight into the reactivities with H and H_2. Hence the present proposal is mainly focused on the potential energy surfaces (PES) for Pt_n+H_2, Pd_n+H_2 and Ni_n+H_2 [n = 3-4]. Our previous study on Pt_2+H_2 has revealed that although the ground state of Pt_2 is a triplet state, the ground state

of Pt_2H_2 is a singlet electronic state which suggests an avoided crossing between triplet and singlet surfaces induced by spin-orbit coupling. It is clear that near the equilibrium geometries, singlet A_1 states will be favored for Pd_3H_2 and Pt_3H_2 although for Ni_3H_2 this is not unambiguously established yet.

To demonstrate the feasibility of such studies, we have initiated preliminary calculations on the Pt_3+H_2 system. We retained the outermost $5d^96s^1$ (10 electrons) in the valence space for Pt replacing the rest of the electrons in the core. Our previous studies on Pt_2[189] and Pt_3 have proven these RECPs to be accurate and effective. A valence (3s3p3d) Gaussian basis set was employed for the Pt atom. All CASSCF calculations were done in C_s symmetry for convenience. Since the ground state of Pt_3 is not too far distorted away from an equilateral triangle geometry we assume Pt_3 to be an equilateral triangle.

The inclusion of all Pt(5d), Pt(6s) and H(1s) orbitals in the active space leads to 20 orbitals, which is too large for our CASSCF studies. However, fortunately only some of the Pt(5d) orbitals are symmetry-compatible with H_2 $1\sigma_g$ and $1\sigma_u$ orbitals. That is, the other Pt(5d) orbitals are non-bonding relative to H(1s) although they are bonding with respect to other Pt(5d). At the CASSCF stage it is not necessary to allow excitations from such Pt(5d) orbitals. We found an optimal active space of seven a′ orbitals and five a″ orbitals in C_s symmetry. We used the C_s point group for all our computations.

Figure 9 shows our computed PES for the $^1A_1$ state of Pt_3+H_2 for the orientation of H_2 in Fig. 9. As seen from Fig. 9, there are two types of PES, one arises from Pt_3+H+H and the other arises from Pt_3+H_2. The barrier for dissociation of H_2 arises from the crossing of these two surfaces. Subsequent to the crossing point Pt_3H_2 molecule is formed. For each distance R between Pt_3 and H_2, Pt-Pt and H-H bond lengths were optimized. At the equilibrium geometry one H atom is bound between two Pt atoms above the plane in a

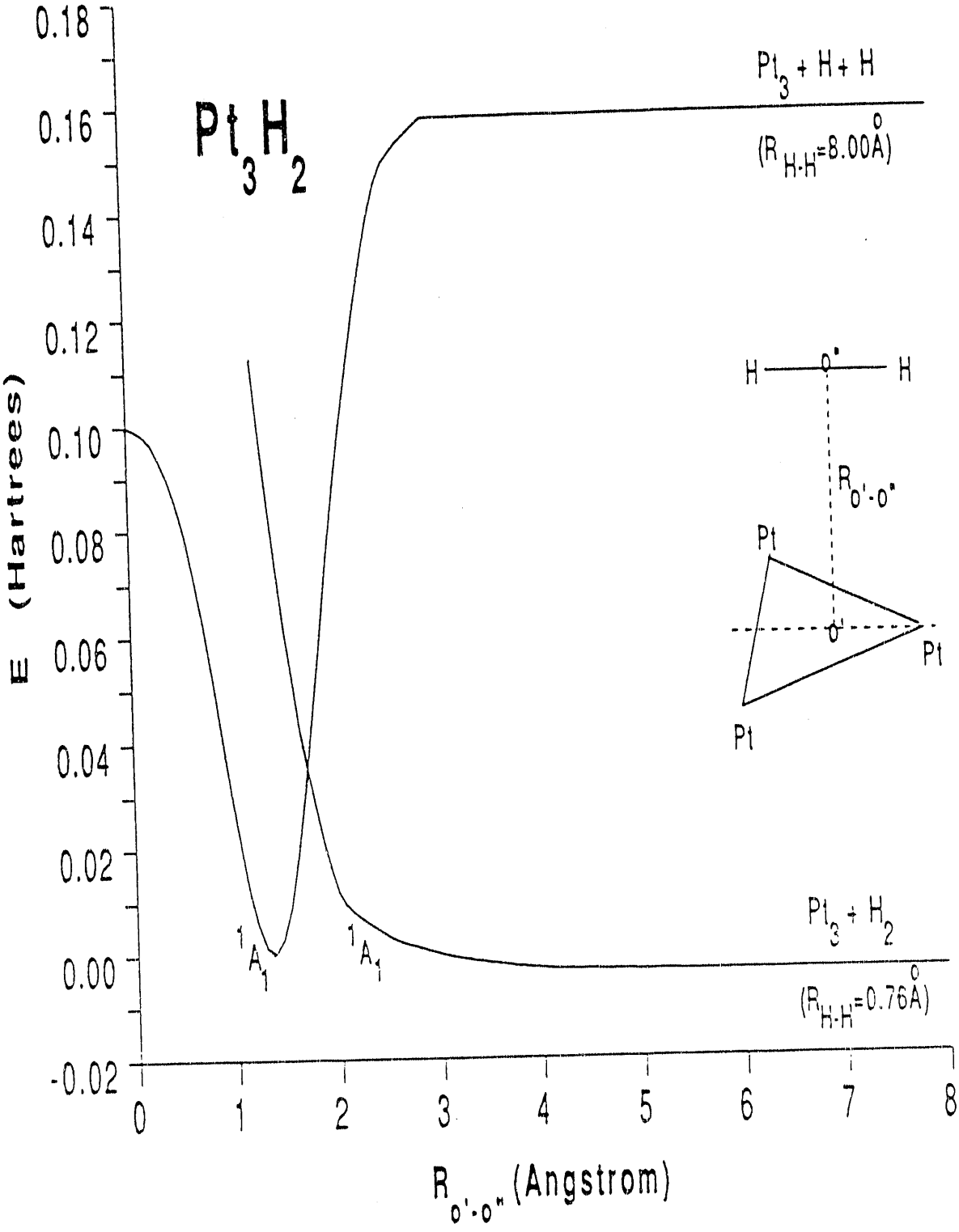


Fig. 9 PES for $Pt_3 + H_2$, H_2 approaching perpendicular to Pt_3

bridged position while the other H is bound to the third Pt atom such that both H atoms are above the plane. The direct Pt-H bond length is ~1.48 Å while in the Pt-H-Pt bridge, Pt-H bond lengths are longer (1.9 Å), as expected.

The question is whether the mode shown in Fig. 9 is the most stable one or if the in-plane mode (Fig. 10) in which the H-H bond is parallel to a Pt-Pt bond is more stable. For the Pt_2+H_2 reaction[144] the parallel mode was not only found to be favorable but also the resulting Pt_2H_2 (cis) structure is considerably more stable than Pt_2+H_2. Consequently study of the mode in Fig. 10 would facilitate comparison of the out of plane vs. the in plane modes of collision. We have not yet started computations on the in plane parallel mode in Fig. 10. The objective of this proposal is to carry out such computations for both the modes for Ni_3+H_2, Pd_3+H_2 and Pt_3+H_2 reactions. For Pt_3+H_2 the avoided crossing induced by the spin-orbit coupling will also be studied. This will provide significant insight into the impact of spin-orbit coupling on reactivity.

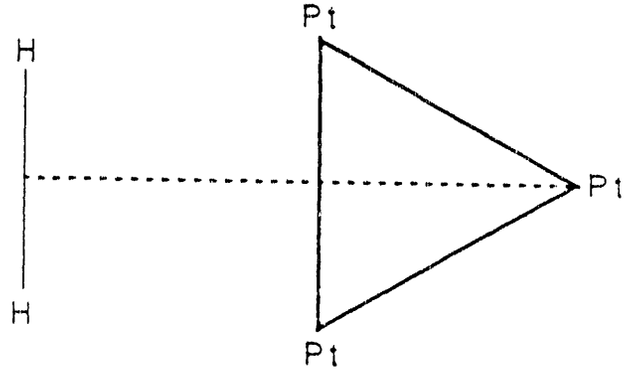


Fig. 10. H_2 approaching in plane parallel to one Pt-Pt bond.

Subsequent to the CASSCF calculations, we propose CI studies on selected regions (crossing, minima and dissociation) of the potential energy

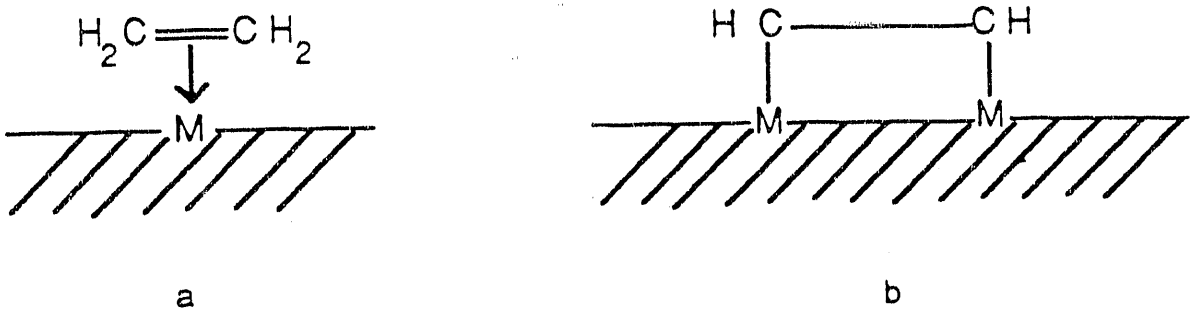
surfaces. We have McLean's localized orbital transformation codes. The use of localized orbitals on the two fragments (Pt_3,H_2) can control the configurations and lead to a more size-consistent treatment of the electron correlation effects. We will certainly take advantage of the 'correlated-fragment' approach based on localized orbitals.

Once the computations on M_3+H_2 are completed, we would gain considerable insight into the question of orientational selectivity. This will in turn help us to study Pt_4+H_2 and Pd_4+H_2. For these PES only tetrahedral M_4 geometries will be considered. Only singlet electronic states will be considered for $Pd_4 + H_2$. Our aim in these studies is to (i) find the crossing point of M_4+H_2 and M_4+H+H surfaces, (ii) estimate the most stable geometry of M_4H_2 and its stability relative to M_4+H_2, and (iii) find the most favorable orientation for H_2 approach.

4.2. Reactivity with ethylene and hydrocarbons.

4.2.1. Reactivity with ethylene: $M_2+C_2H_4$ vs. $M+C_2H_4$ as models for two modes of chemisorption.

Numerous experimental studies have examined the ethylene chemisorption on metal surfaces (see for example Ref. 51). Two alternative structures are proposed for the adsorbed species (Fig. 11). In the first mode (Fig. 11a) the bonding takes place between one metal atom on the surface and ethylene through the interaction of π-electrons of C_2H_4 and the metal atom. In the second structure (Fig. 11b), two M-C σ bonds are formed. Most of the conventional complexes are of type a (Fig. 11a). However, a recent neutron diffraction study by Anderson et al.[51] (1991) has shown the existence of structure b (Fig. 11b) for the Os atoms. Ethylene chemisorbed on Pt(111) surface at low temperatures also shows evidence of structure b. Dipalladium adduct of C_2F_4 is known (see Ref. 51 for other references).



a b

Fig. 11 Two Modes of Adsorption of Ethylene

In view of the above experiments it would indeed be interesting to explore $M+C_2H_4$ (π-bonded) vs. $M_2+C_2H_4$ (di-σ bonded) adducts for M = Pt, Pd and Os. The nature of bonding and relative stabilities of the two species relative to dissociated species will be investigated.

4.2.2. Pt_n+CH_4 ($n \leq 2$).

Trevor et al.[82] have studied methane activation on unsupported platinum clusters recently. They find that small clusters react readily with CH_4. A factor of four drop in the reactivity was observed in going from Pt_5 to Pt_6. At the present time, there are no theoretical studies on Pt_n+CH_4 reactions, although in our group we have studied $Pt+H_2$ and Pt_2+H_2 reactions. Trevor et al. found the following prominent products for Pt_n+CH_4 reactions for small n:

$$Pt + CH_4 \rightarrow PtC \text{ (major)}$$

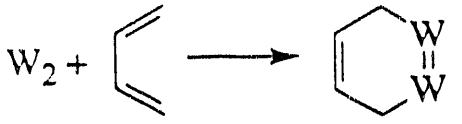
$$Pt_2 + CH_4 \rightarrow Pt_2C \text{ (major)}$$

For the Pt atom + CH_4 the only major product is PtC while for Pt_2, the major product is Pt_2C. As the cluster size increases the number of hydrogens retained increases. This finding is quite intriguing. We propose to study $Pt+CH_4$ and

Pt_2+CH_4 reactions with the objective of seeking answers to these mind-boggling questions.

4.2.3. W_2 + 

Chrisholm et al. (1991)[90] very recently reported Diels-Alder type of ring-closing reactions for Mo_2 and W_2 + 1,3-butadiene reaction (below):



The ability of a multiply bonded dimer such as W_2 and Mo_2 to bring about ring closure is very intriguing. The exact nature of the M-C orbital interactions which induce ring closure is certainly important to comprehend.

Our proposed study on this system will be restricted to the $^1\Sigma_g^+$ state of W_2 to yield the $^1A_1$ state with the ring structure. We will use a valence (4s4p3d) basis set for the W atom in conjunction with $5s^25p^65d^56s^1$ RECPs. For carbon the $1s^2$ shell will be replaced by ECPs. Restricted CASSCF calculations will be carried out. Our objective is to comprehend the orbital interactions leading to ring closure and the nature of bonding in the six-membered ring product.

4.3. Model calculations for NO and CO chemisorption on surfaces.

Yates and coworkers (1990)[96] have found evidences for anisotropic vibrations of NO and CO-chemisorbed on stepped Pt(112) surfaces. The amplitude of motions perpendicular to the plane are 2-3 times larger than in plane motions suggesting two possible structures for adsorbed NO, namely terminally bound (Pt-NO) versus bridge-bound  . Ho and coworkers[99]

have made similar experimental studies on Cu, Ag and Au surfaces. The adsorption of NO on noble metals is more complicated as noted by Ho and coworkers in that it could lead to desorption, dissociation, bridge-site rearrangement or synthesis of new species. There is also a question as to whether a bridged NO is more strongly bound to the surface compared to the atop-bound NO.

Reactions of CO on oxidized surfaces have also revealed interesting trends. For example, the exact mechanism for the observed production of CO_2 on oxidized surfaces is not fully understood. There are other studies by Riley and coworkers on Cu_n+O_2 as well as oxygen adsorption as oxidized Ir(110) surfaces. Sibener and coworkers[101] have studied the librations of CO adsorbed on Rh-surfaces.

In a recent study, Yates and coworkers[95] have examined alternative surface reaction channels involving CO-dissociation and inhibition of dissociation on Mo(110) surface. CO species with unusually low stretching frequency (ν(CO) = 1345 cm^{-1}) was observed as Mo(110). The schematic view of these channels presented by Yates and coworkers is reproduced (Fig. 12).

These experimental studies will constitute a basis for our theoretical studies for M+CO(NO) versus M_2+CO(NO). There are a few theoretical studies on M+CO (for M = Pt and Pd) especially by Hay and coworkers[109] and others. However at present there are practically no theoretical studies on M_2+CO(NO). We will focus our studies on a critical comparison of stability and bonding in M+CO versus M_2+CO in which CO is bound by the bridge bonding (Fig. 13).

Our computations will be focused on M = Pd, Pt, Ag, Au, Mo and W. Similar studies will also be made on M+NOand M_2+NO to compare and contrast NO-adsorption with CO-adsorption. We will also compute the vibrational frequencies for the stretching mode for adsorbed CO(NO) in the two structures (atop vs. bridge-bound).

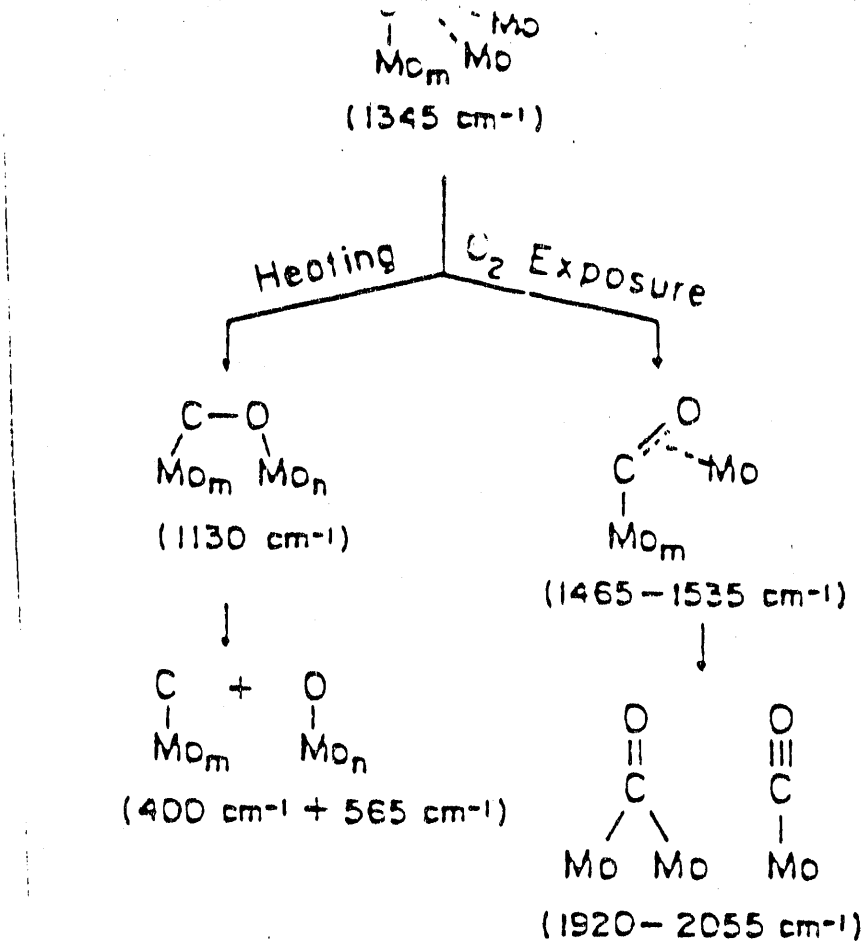


Fig. 12. A schematic view of two channels for CO adsorption on Mo(110). Left: dissociation channel; right: inhibition channel by adsorbed oxygen.

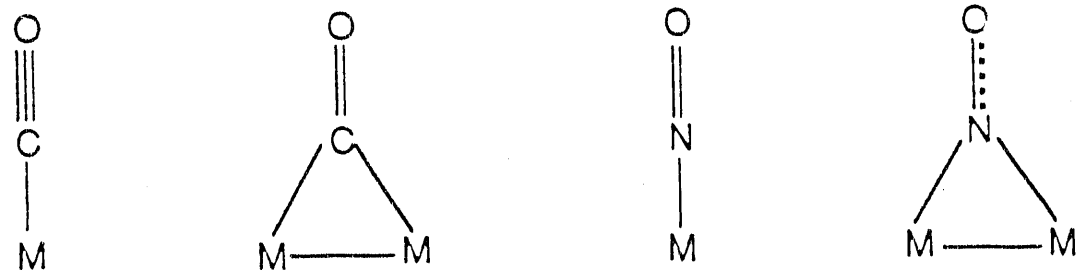


Fig. 13. Bridged vs. atop chemisorption

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6. Appendix

Supporting Information

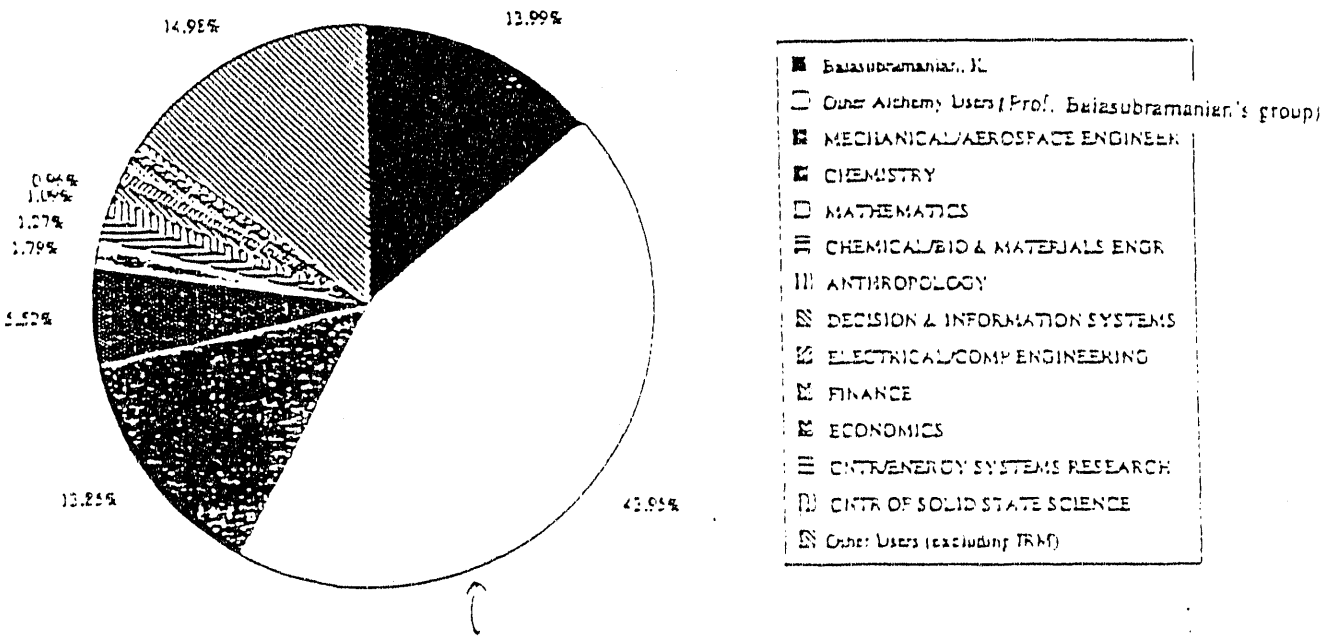
6.1. Computational Facilities for This Project

Hardware.

The PIs' dedicated research facility for cluster research is described in the diagrams on the next two pages. In a nut shell, the PI and his coworkers will be the sole users of four IBM RISC/6000-530 systems (each with 2.5 Gigabyte disk, fast tape drive) and five microvaxes which serve as work station links to other systems. In addition, the PI's group will have access to ASU's IBM 3090/600, ASU's Cray XMP, San Diego Super Computer Center's Cray YMP and Colorado's Atmospheric Research Center's Cray YMP. Below is a summary of total available CPU hours. We propose to upgrade two of the 530 systems to 550E models each with 64 M memory in the next two years.

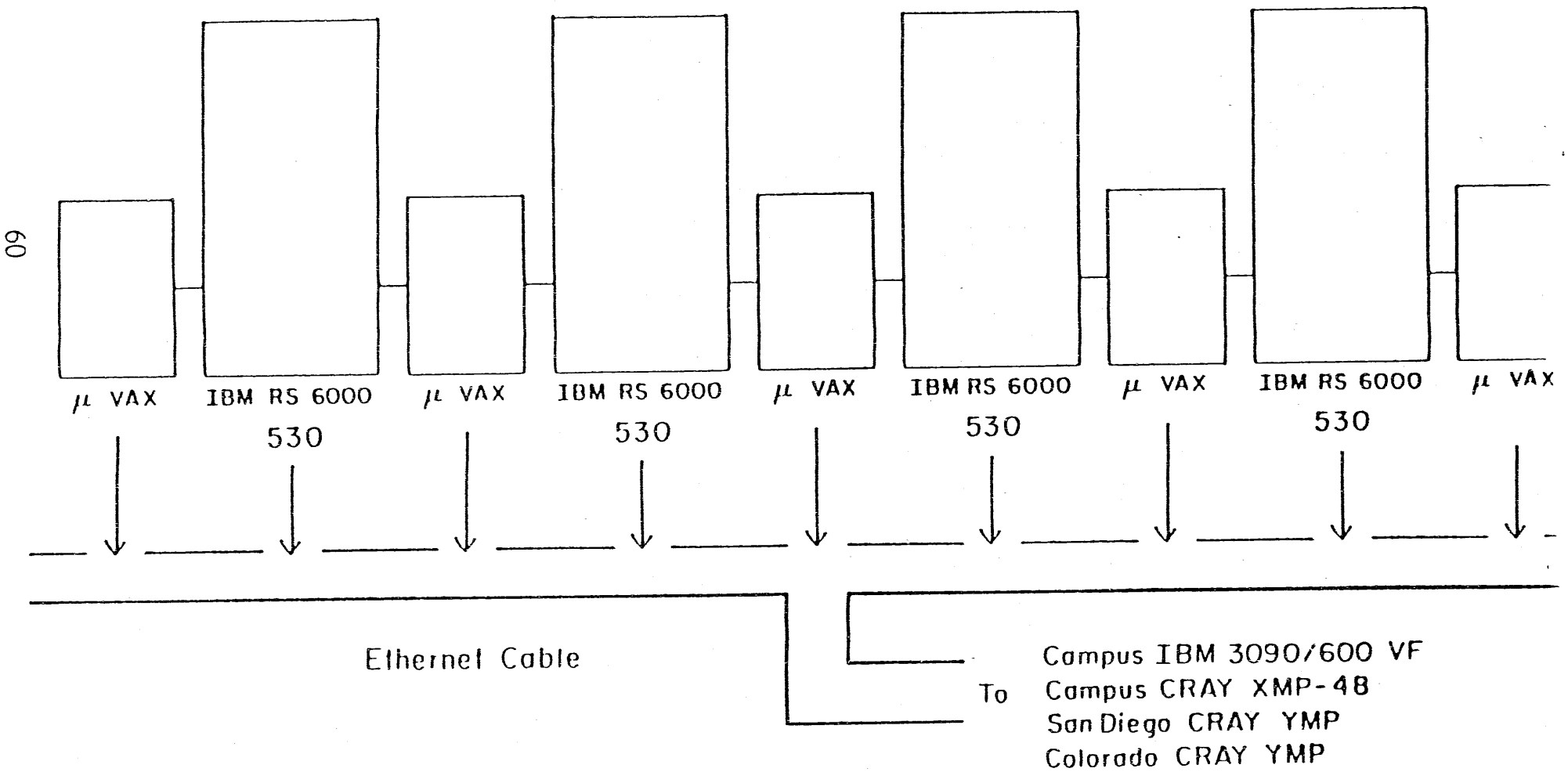
- 33,600 CPU hours on four IBM RS 6000-530
- 7,300 CPU hours on IBM 3090/600 (see the PI chart below)
- 1,200 CPU hours on SDSC Cray YMP; • 300 CPU hours on Colorado Cray YMP

ASU Academic MVS FY 1990 CPU Usage
Non-Reimbursible Accounts by Department/User



Prof. Balasubramanian's Group (other ALCHEMY Users)

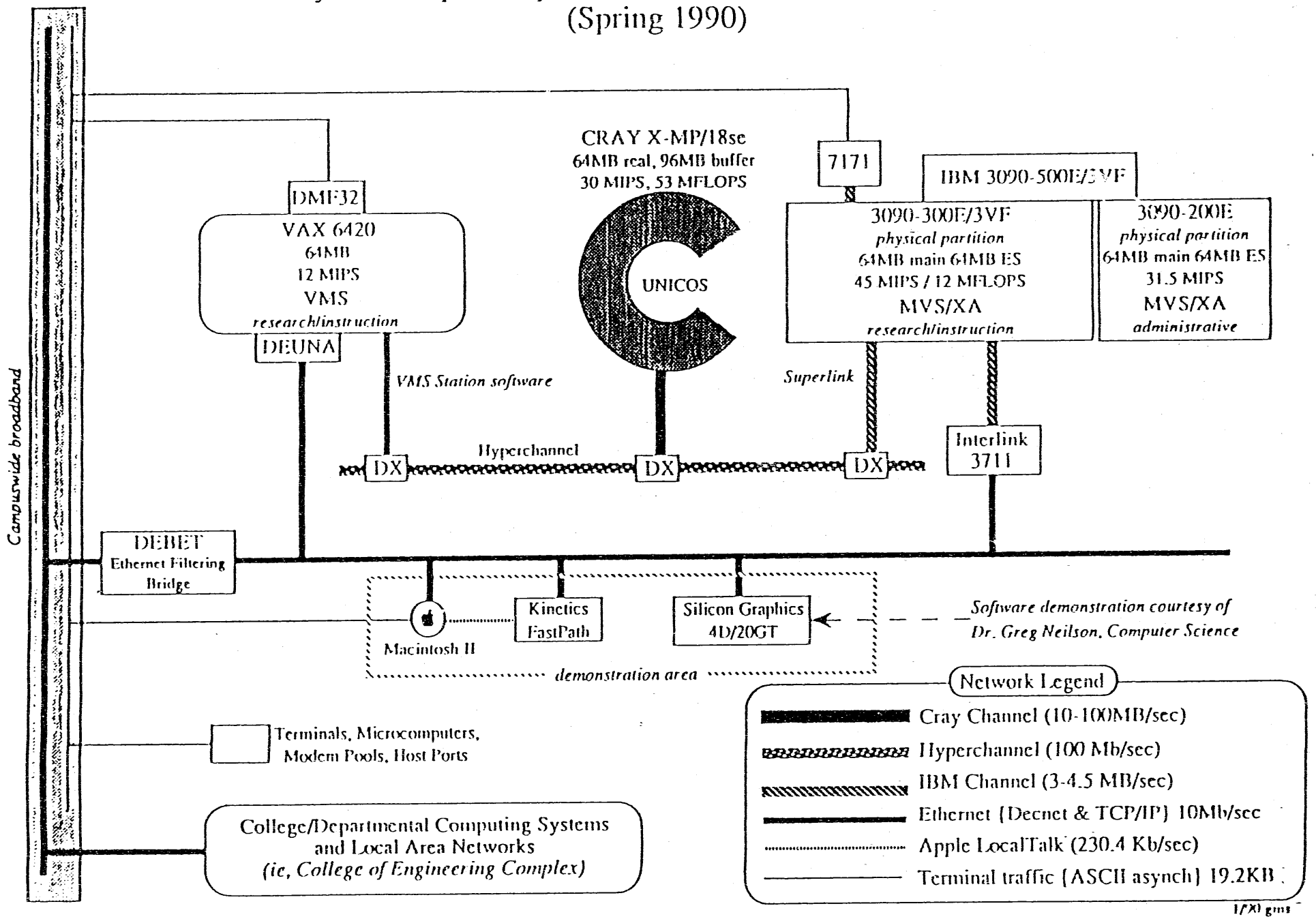
Computational Facility dedicated to Prof. Balasubramanian's Group for Cluster Research



ARIZONA STATE UNIVERSITY - INFORMATION RESOURCES MANAGEMENT

Cray/IBM Supercomputer Network Configuration Overview

(Spring 1990)



6.2. Software.

The PI and his coworkers have access to a variety of software packages developed both locally and elsewhere. These include the PI's modified version of ALCHEMY II package of codes to include relativistic ECPs. The ALCHEMY II is a package of programs that have the capabilities to do large-scale CASSCF (MCSCF)/direct CI. At present we are set up to carry out CI calculations which include up to 4 million on IBM RS-6000-530 (64 meg), 6 million on the San Diego Cray YMP. Larger CIs are locally possible (up to 8 million) once we upgrade IBM RS 6000-530 to 550E with 128 meg memory. The PI has also developed/interfaced relativistic CI codes which use the CI natural orbitals generated by ALCHEMY II. We have the latest version of ALCHEMY II which can handle up to i functions in the basis set and which is capable of retaining only the spherical harmonic components of the higher-angular momentum gaussian functions. The PI and his coworkers have access to modified version of GAMESS to include RECPs, MCSCF/CI programs for Slater-type orbitals (STOs), HONDO, relativistic DHF codes, codes to generate RECPs, codes for geometry-dependent transition moments for diatomics and a variety of other group theoretical and combinatorial packages locally developed for various applications.

6.3. Personnel and Related Information

At present the PI's group is comprised of two graduate students (one more to join in the summer of 1992), two post-doctoral researchers and three visiting scholars. The PI is required to teach one course per semester. Normally the PI teaches graduate courses such as computers and chemistry, quantum chemistry. The PI expects to devote 40% of his time during the regular semesters in this project and 100% of the time in the two months during the summer.

For this proposal during the academic year, three graduate students 67% time and two post-docs and a visiting scholar would each be putting in 50% time efforts. During the summer, these persons will devote 100% time for this proposal.

Past students, post-doctoral associates, visiting scholars and visiting professors.

1. Profesor Muzhen Liao
2. Dr. Douglas Chapman
3. Professor Jinqing Li
4. Professor PingYi Feng
5. Dr. Dai-wei Liao
6. Dr. Ch. Ravimohan
7. Professor Jia-zhen Wang
8. Dr. Ziaoyu Liu
9. Mr. Guyon-Bum Kim
10. Dr. Kalyan K. Das
11. Professor Haruo Hosoya
12. Dr. Ming Han
13. Dr. K. Sumathi
14. Ms. A. Huang

15. Ms. V. Nannegari
16. Dr. Dingguo Dai
17. Dr. W. Cheng
18. Professor J. X. Tao
19. Dr. ZhangXing Ma
20. Dr. Hongxing Zhang
21. Dr. M. Vijayakumar

VITA

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EDUCATION:	Birla Institute of Technology and Science, India	1977 MSc (Hons)
	The Johns Hopkins University	1980 M.A.
	The Johns Hopkins University	1980 Ph.D.
AREA OF SPECIALIZATION:	Theoretical studies of molecules and clusters containing very heavy atoms, chemical applications of group and graph theory, chemical applications of artificial intelligence.	
PROFESSIONAL EXPERIENCE:	Arizona State University Department of Chemistry	
	Professor	1990 -
	Associate Professor	1987 - 1989
	Assistant Professor	1983 - 1986
	Visiting Lecturer, Department of Chemistry, University of California, Berkeley	Spring 1983
	Postdoctoral Research Associate Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley	1980 - 1983
	The Johns Hopkins University, Department of Chemistry Teaching Assistant	1978 - 1979
	Birla Institute of Technology and Science, Pilani, India Instructor	1976
PROFESSIONAL ORGANIZATIONS AND HONORARY SOCIETIES:	American Chemical Society	
	American Association for Advancement of Science	
	New York Academy of Sciences	
	American Physical Society	
	Arizona-Nevada Academy of Sciences	
	Phi Kappa Phi	
	The International Academy for Mathematical Chemistry	
	World Association of Theoretical Organic Chemists (WATOC)	

Elected Member of The Mathematical Association of America

HONORS AND AWARDS:

The Camille and Henry Dreyfus Teacher-Scholar Award	1985 - 1990
Alfred P. Sloan Fellow	1984 - 1988
Birla Institute of Technology & Science Distinguished Lecturer and Alumnus Award	1989
Award for Distinction in Graduate Teaching	1991
Phi Kappa Phi	
National Science Talent Scholar, India	1973

LISTING IN BIOGRAPHICAL BOOKS:

The International Who's Who of Intellectuals, International Biographical Centre, Cambridge, England	
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Who's Who in Technology Today, Fifth Edition	1984
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American Men and Women of Science 17th and Succeeding Editions	1989

JOURNAL REFEREE:

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International J. Quantum Chem
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K. BALASUBRAMANIAN

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