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PROPERTIES AND CHEMISORPTIVE REACTIVITY OF TRANSITION METAL CLUSTERS

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Emily A. Carter, Principal Investigator

Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue
Los Angeles, California 90024-1569

During the tenure of this grant, we have examined the properties and chemisorptive reactivity of metal clusters by concentrating on issues related either to purely metallic bonding or to metal-ligand interactions. We have extended the concept of cluster to also examine metallic interactions in two-dimensional islands and thin films. We have used both quantum mechanical approaches and classical Monte Carlo/Molecular Dynamics simulations. In addition, we have developed a new first principles dynamics scheme specifically designed with atomic clusters in mind. The projects we have completed include: (i) the electronic structure and metal-metal bonding in low-lying states of Pt_2 and Pt_3;[5] (ii) the electronic structure and metal-metal bonding in mixed early/late transition metal clusters,[8] (iii) contrasting the interaction of NO versus CO with Pd and Pt atoms;[2] (iv) quantifying the influence of ancillary ligands on the preferred spin state of metal atoms in organometallic complexes and clusters, as evidenced by spin-induced changes in bond energies in $Mn(CO)_x^+$;[10] (v) structure and growth mechanisms of Pd islands and thin films on bcc(110) substrates as a function of coverage and temperature;[1,3,4] (vi) structure, growth, and interdiffusion of Ni films on Ag(100);[7] and (vii) first principles dynamics and simulated annealing of localized wavefunctions (Gaussian-based) to predict structures and dynamics of atomic clusters.[6,9] (The footnotes refer to the list of publications at the end of the final report section.) Progress made in each of the areas are summarized briefly below.

A. Quantum mechanical studies of metallic bonding

For most metallic materials, the interactions are poorly understood at this point. This prompted us to initiate a series of projects starting from the simplest metals, alkali metals, all the way up to mixtures of transition metals (TM's), in order to begin understanding metallic bonding from first principles. The goal is to use the quantum mechanical information to characterize the nature of various types of metallic interactions. Ultimately, we plan to design first principles-based interaction potentials for metals, for use in molecular dynamics and Monte Carlo simulations of bulk, surface, and interfacial phases. In particular, there is a dearth of potentials for describing alloys involving mixtures

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of fcc and bcc metals, because the character of such interactions is poorly understood. We believe that by studying small aggregates or clusters of these metals with quantum mechanics, we will be able to develop a detailed understanding of metallic bonding. So far, we have studied Pt, ZrPt, and Na clusters. We are interested in studying TM's, not only because of their technological importance, but also because of the fundamental complexity introduced by the presence of partially-filled d-shells.

The major result of the work on pure Pt clusters,[5] which was somewhat surprising, is that the s-electrons play the dominant role in metallic bonding for the noble metals. We had initially expected more d-electron participation since the d-shell is not filled, but the s-electrons appear to dominate, even for Pt. Employing both generalized valence bond (GVB) and configuration interaction (CI) methods combined with a relativistic effective core potential and a more than double-ζ quality valence basis set, we calculated the equilibrium structures of all low-lying states of Pt dimer and trimer. Our preliminary work assumed equilateral triangle geometries with bulk M-M distances for Pt_3. We find a very dense Pt_3 electronic state spectrum, with all nine states that were close in energy when the bulk geometry was imposed still staying close in energy for the optimized structures (within 7 kcal/mol of the ground state). In addition, we find a linear $^5\Delta_g$ state that is also very low-lying (6.3 kcal/mol up from the ground $^3A_1$ state). The physical reason for the high density of states of different spin lying so close to the ground state is that all of these low-lying states have only one strong ($\cong$50 kcal/mol) 6s-6s bond holding the cluster together. By contrast, d-d bonds are essentially worthless, as evidenced by the near degeneracy (within 0.002 eV) of the $^3A_1$ (s-s plus d-d bonding) and $^5B_2$ (s-s bonding only) states and the negligible orbital overlap in the d-d bond ($S_{d\text{-}d} = 0.03$ vs. $S_{s\text{-}s} = 0.78$). We find that the equilibrium geometries of the cluster in all these low-lying states have bond lengths greater than or equal to the bulk metal, but greater by no more than 0.21 Å. The structures we calculated are in good agreement with scanning tunneling microscopy determinations of the Pt dimer and trimer structures on graphite.[5] Most of the structures are within ±5 degrees of an equilateral triangle configuration, dictated by the predominance of the s-s bond. The linear state is obviously an exception, with the bonding consisting of a three-center two-electron bond involving s-electrons on the outer Pt's and a dz^2-electron on the central Pt, making this linear state competetive with the triangular states. Our calculations offer a simple explanation for the photoelectron spectrum of Pt_3^-, where transitions are observed within a 0.2-0.3 eV window. We believe these transitions, previously unassignable because it was unclear as to whether these were vibronic transitions or transitions to a dense electronic manifold of neutral Pt_3, have a strong component of the latter type. The nearly filled d-shell on Pt makes it impossible for the metal-metal bonds to shorten, because of interatomic repulsive interactions. This makes d-d coupling energies very small, leading to the dense manifold of states.

Our work on $ZrPt_x$ clusters[8] was prompted by a desire to understand metal-metal interactions between early and late TM's in these so-called Engel-Brewer intermetallic compounds. The only theory that has attempted to explain the high thermal stability of early-late transition metal alloys is an empirical theory due to Engel and Brewer. In particular, Engel-Brewer theory is a semiempirical theory designed to help predict crystal structures and stabilities of intermetallics. A fundamental assumption of this theory is that charge transfer occurs from the late TM to the early TM. We have carried out highly correlated first principles electronic structure calculations which clearly indicate the charge transfer in these intermetallics proceeds in the opposite direction to that assumed by the semiempirical theory! Indeed, the charge transfer follows exactly the direction one would have predicted based only on ionization potentials or work functions of the pure metals. So what is responsible for high stability of these compounds? We also find that these intermetallics are very strongly bound, and that the bonding is primarily ionic in nature. Charge transfer, in the correct direction, is enough to result in extremely high thermal stability. Thus, we are developing a new understanding of intermetallic bonding, based on these first principles calculations. Ultimately, we hope that the mixed metal clusters research will help us understand how alloys form and how to predict a priori which alloys will exhibit desired properties (e.g., thermal stability or enhanced catalytic reactivity).

B. Interactions of small molecules with transition metals

This area is of fundamental importance for understanding heterogeneous and homogeneous catalysis and for learning how to design materials that are chemically inert (e.g., corrosion-resistant, oxidation-resistant, etc.) yet possess other desirable properties (e.g., high thermal and electrical conductivities).

We have used first principles quantum mechanics to examine the interaction of NO and CO with Pd and Pt,[2] which is directly related to automobile exhaust catalysis whereby CO is oxidized to CO_2 and NO_x is reduced to N_2. We find that the interaction of NO and CO with Pd and Pt atoms involves two extremely different modes of bonding, which can be rationalized in a simple way by consideration of the ground electronic states of the metal atom and ligand. NO prefers a bent configuration while CO is linearly bonded to the metal center. CO bonds to both Pt and Pd in the expected fashion, involving σ-donation and π-backbonding, which favors a linear configuration. The affinities of Pt and Pd for CO are very different, however, with Pd binding CO $\cong$10 kcal/mol more strongly than Pt. This is due to the differences in ground electronic states of Pd (d^{10}) and Pt (s^1d^9). The ground state of MCO in both cases is $^1\Sigma^+$, which means that Pt, unlike Pd, must be promoted into its first excited state (d^{10}) to bond effectively to CO. This costs Pt some energy, leading to a weaker M-CO bond. The unpaired $2p\pi$ electron on NO allows a strong ($\cong$20 kcal/mol) covalent metal-N bond to form, forcing a bent configuration. The linear configurations are higher because of N 2s - metal $sd\sigma$ orbital repulsions. This is in contrast to what is found on a metal surface, where the metal electrons can polarize away from the N2s lone pair, allowing the linear configuration to compete. Again, Pt and Pd behave differently toward NO. Since Pd has no unpaired electrons in its ground electronic configuration, it must be promoted to its first excited state (s^1d^9) to form a covalent bond to NO. This costs energy, weakening the M-NO bond. Since Pt already has unpaired electrons in its ground state, it forms an M-NO bond that is $\cong 16$ kcal/mol stronger than for Pd. These differences in affinities for NO and CO by Pd and Pt, in which NO binds strongly to Pt but weakly to Pd, while CO has the opposite affinity, are due to the preference for closed shell species to bind more strongly to other closed shell species (e.g., CO to Pd) and for radicals to bind more strongly to other radicals (e.g., NO to Pt).

We have also studied how multiple carbonyl (CO) ligands, as a prototype small molecule, can induce electronic spin state changes in transition metals.[10] This is of both fundamental interest, from the point of view of developing theories for predicting electronic structure of metal complexes that go beyond ligand field theory ideas, and of practical importance, in that it is crucial to understand how magnetic properties of metals or metal-containing materials may change on exposure to air or other gases. In the case of Mn^+, we find that up to two CO's may bind without inducing any change in the electronic structure of Mn^+, but the third CO may be just enough to induce a spin flip to a lower spin state. The driving force for such a spin flip is to reduce electron-electron repulsions between the Mn^+ 4s electron and the CO 5σ (C 2s) electrons. By inducing a spin flip, the 4s electron on Mn^+ is placed in a d-orbital, leaving Mn^+ in a high spin d^6 configuration (^5D). This has lower metal-ligand electron-electron repulsion, because the d-orbitals are less diffuse than the valence s-orbitals. The number of CO's required to induce a spin flip is directly correlated with the intraatomic exchange interactions on the metal (i.e., with the metal's promotional energies). For instance, Mn^+ has a large promotional energy ($\Delta E(^7S \rightarrow {}^5D)$ = 42 kcal/mol), while Pt has a much smaller promotional energy ($\Delta E(^3D \rightarrow {}^1S)$ = 16.6 kcal/mol). While we find that it takes three CO's to induce a spin flip in Mn^+ because the promotional cost is so high, one CO is enough to favor a spin flip in Pt because the promotional cost is moderate. As in the cases of Pd and Pt, whether a spin flips or not affects dramatically the CO binding energies to Mn^+.

C. Structure and growth mechanisms of thin metal films

Isothermal (NVT) Monte Carlo simulations[1,3,4,7] have been used to characterize the structure and growth mechanisms of ultrathin transition metal films on transition metal substrates, as a function of substrate structure, interfacial strain, temperature, and coverage. Such films have promising technological applications in such areas as magnetic recording media (because of unusual magnetic properties of Fe, Co, and Ni in 2-D films) and heterogeneous catalysis (because of dramatically altered chemisorption properties), and as high temperature coatings (for mechanical properties, e.g., engine design).

We have carried out simulations of the temperature-dependent growth of a face-centered cubic (fcc) metal, Pd, on a body-centered cubic (bcc(110)) substrate.[1,3] Empirical embedded atom potentials were used for these studies, where the interactions were fit to such properties as the cohesive energies and elastic constants of the bulk crystal. At high temperatures (500 K), we find that a phase transition occurs within the first monolayer of deposited Pd atoms at a critical coverage of adatoms. At low coverages, Pd adsorbs pseudomorphically (i.e., in bcc lattice sites), indicating that the Pd-substrate interaction dominates Pd-Pd attractive forces. This overlayer is strained, because the bcc nearest neighbor (nn) distance is ≅19% larger than the equilibrium nn distance in bulk Pd. Once all bcc lattice sites are occupied, additional atoms deposited on the film could adsorb into second layer bcc sites. Instead, a phase transition occurs, in which these additional atoms are incorporated directly into the first layer of adatoms, resulting in domains of close-packed fcc regions, until the first layer has fully converted into an fcc overlayer. These results are in close agreement with some experiments and have important implications for understanding the behavior of two-dimensional metals.

In further comparisons with experiment, we have discovered the origin of a controversial and puzzling beat pattern feature in the LEED patterns observed for Pd grown on Ta(110) or Nb(110). It turns out that the interfacial layer relieves misfit dislocations by forming two-dimensional wavelike distortions in the adlayer. These "waves" give rise to the same beat pattern in our simulated LEED pattern as is seen in the experiment. Indeed, we can watch, as the film grows, the beat pattern disappearing, slowly but surely replaced with an fcc(111) pattern, just as is observed with LEED. The disappearance of the beat pattern directly correlates with a disappearance of these waves in the second and third layers (these upper layers grow essentiallly as fcc(111) sheets).

Finally, we find that if the film is grown at low temperature (75K), we can kinetically stabilize a pseudomorphic bcc phase of Pd. This has interesting implications for low-temperature deposition of fcc metals, since stabilizing a bcc phase of such metals should exhibit altered properties. In stark contrast to the high temperature growth mechanism, we find that Pd can be grown in a bcc structure for at least three layers. This prediction has stimulated the experimentalists in this field to look for such a structure at low temperature and to examine the properties of such a novel material. Thus, the new contributions from theory in this area of thin film growth include the prediction of a dramatic temperature dependence in the morphology of the film and an explanation of the beat patterns observed experimentally by LEED.

We have also examined[4] the structures of submonolayer coverages of Pd on a bcc(110) substrate, as function of both coverage and temperature, to understand when two-dimensional islands or three-dimensional crystallites may dominate dispersive structures. We find that large two-dimensional islands growing anisotropically along the [001] direction are preferred over any other structure. We have calculated barriers to diffusion of adatoms within the context of the EAM potential and find low barriers for reshaping the island to propagate along the preferred direction. The growth along the [001] direction can be rationalized in terms of maximizing the number of nearest neighbor and next nearest neighbor interactions within the adlayer. These channels of Pd should be visible using ion scattering spectroscopy.

We have also examined the adsorption of an fcc metal on an fcc substrate, in order to determine the conditions under which alloys are formed versus stable metal overlayers (i.e., stable phase separation). In particular, we have simulated the adsorption of Ni on Ag(100), which is of particular interest because of the potential for unusual magnetic properties in low-dimensional films. We find that Ni grows in a layer-by-layer, pseudomorphic fashion at room temperature up to at least 3.2 ML. This film has a tetragonal structure, consisting of a compressive interlayer stress that compensates for the expansive intralayer strain (Ni/Ag has a 13.9% lattice mismatch). Interdiffusion of Ag atoms to form a capping Ag monolayer on top of the Ni film is found to be thermodynamically favorable. Consistent with the fact that bulk Ni is immiscible in bulk Ag, no stable alloy formation is observed nor is a commensurate-incommensurate transition ever seen.

In sum, we are able to predict real space structures as a function of growth conditions that will aid the interpretation of both ion scattering and electron diffraction data, as they become available. The structures we calculate may help guide the design of thin films on certain substrates, based on the surface free energies, the interfacial strain, and the temperature at which the film is grown and is expected to operate.

D. Ab initio molecular dynamics

We have developed the first ab initio molecular dynamics/simulated annealing theory for both Hartree-Fock and Generalized Valence Bond (GVB) molecular wave functions.[6,9] Prior to this development, such theories were limited to density functional theory (DFT) dynamics. This method has two advantages over DFT approaches: (i) it incurs no large errors in the energy for molecular systems, unlike DFT, which was originally designed to model 3-dimensionally infinite systems rather than finite systems, where the gradient of the electron density changes drastically and (ii) it can be used to study excited electronic states. Electronically excited states would be accessible via spin-polarized DFT, but such wave functions are not eigenfunctions of spin. Our approach, which includes electron correlation at the GVB level, can be used to study the dynamics and structures of ground and excited spin eigenstates.

This method will be extraordinarily useful in our study of metal clusters, where we have an aggregate of atoms that are all identical or very similar. These similarities cause nightmares for traditional quantum chemical approaches for optimizing structures of such clusters, since normally one calculates the gradient of the energy given some initial configuration of the atoms and moves toward the nearest minimum. Such an approach is almost guaranteed to fail because of the many local minima bound to be present in such a situation. Our method utilizes a "simulated annealing" algorithm, which allows us to heat up the nuclei and then slowly cool them down to find the minimum energy structure (i.e., the global minimum). By using simulated annealing, we can search for global minima in an unbiased manner with ab initio forces. We will be able to predict structures of ground and excited states of these aggregates and see how they change with temperature. The electronic and vibrational structure can also be examined as a function of temperature. We have already demonstrated the power of this method in a preliminary manner, by looking the short-time dynamics of a distorted, stretched Na_4 cluster.[6] We observe completely different behavior for the singlet and triplet states, starting from exactly the same geometrical configuration and velocities. In particular, we observe spin-eigenstate dependent dynamics, in which the singlet, with two bonding pairs of electrons tend to pull the nuclei closer together, while in the triplet, the two high spin electrons repel each other, forcing a pair of nuclei to repel each other (the bond stretches further). Such dynamics would never be seen in a classical simulation and are a beautiful illustration of the Pauli Principle in action.

In sum, we have completed a number of projects during the past three years, many of which we intend to continue to work on. We have learned about metallic bonding in small pure and mixed metal clusters, about metal-ligand interactions, about some metallic thin films and interfaces, and we are beginning to learn about spin eigenstate-dependent cluster dynamics with our new theoretical technique of ab initio molecular dynamics.

E. Publications Acknowledging Current ONR Grant

1. B. C. Bolding and E. A. Carter, "Simulation of Lattice-Strain Driven Bcc→Fcc Phase Transitions in Pd Thin Films," *Phys. Rev. B*, **42**, 11380 (1990).

2. G. W. Smith and E. A. Carter, "Interactions of NO and CO with Pd and Pt Atoms," *J. Phys. Chem.*, **95**, 2327 (1991).

3. B. C. Bolding and E. A. Carter, "Temperature Dependence of the Morphology of Strained Overlayers: Deposition of Pd on a bcc(110) Substrate," *Phys. Rev. B*, **44**, 3251 (1991).

4. B. C. Bolding and E. A. Carter, "Two-dimensional Metallic Adlayers: Dispersion versus Island Formation," P. J. Reynolds, ed.; in the series "Random Processes and Materials," (North Holland, Amsterdam, 1991), in press.

5. H. Wang and E. A. Carter, "Metal-Metal Bonding in Transition Metal Clusters with Open d-Shells: Pt_3,"*J. Phys. Chem.*, in press (1991).

6. B. Hartke and E. A. Carter, "Spin Eigenstate-Dependent Hartree-Fock Molecular Dynamics," *J. Chem. Phys.*, submitted (1991).

7. B. C. Bolding and E. A. Carter, "Effect of Strain on Thin Film Growth: Deposition of Ni on Ag(100)," *Surface Sci.*, submitted (1991).

8. H. Wang and E. A. Carter, "Metal-Metal Bonding in Engel-Brewer Intermetallics: Anomalous Charge Transfer in $ZrPt_3$," *J. Am. Chem. Soc.*, to be submitted (1991).

9. B. Hartke, D. A. Gibson, and E. A. Carter, "Electron Correlation in Ab initio Molecular Dynamics: Generalized Valence Bond Simulated Annealing," *J. Chem. Phys.*, to be submitted (1991).

10. Y. Qin and E. A. Carter, "Electronic Structure and Thermochemistry of $Mn(CO)_x^+$ ($x=1-3$)," *J. Am. Chem. Soc.*, to be submitted (1991).

F. Seminars Presented Acknowledging Current ONR Grant

A. Invited Lectures

January 22, 1990	"Metal-Metal and Metal-Ligand Cluster Interactions," ONR Conference on the Physics, Chemistry, and Materials Science of Clusters, Lake Arrowhead, California.
May 17, 1990	"Theoretical Structure and Chemistry of Thin Films and Solid Surfaces," Union Carbide Innovation Recognition Award Symposium, South Charleston, West Virginia.
August 2, 1990	"Classical and Quantal Simlulations of Metallic and Semiconductor Surface Chemistry," American Conference on Theoretical Chemistry, San Diego, California.

March 7, 1991	"Spin-Induced Changes in Transition Metal Ion Chemistry," at the first Gordon Research Conference on Structures, Energetics, and Reaction Dynamics of Gaseous Ions, Ventura, California.
June 26, 1991	"Simulated Annealing: from Potential Fits to Ab Initio Molecular Dynamics," at a Workshop on Computer Simulations in Chemical Physics: Recent Advances and New Directions, Irvine, California.

B. Seminars

April 24, 1989	"Theoretical Studies of Semiconductor and Metallic Surface Chemistry." Chemical Physics Seminar, University of Southern California, Los Angeles, California.
September 5, 1989	"Classical and Quantal Simulations of Metallic and Semiconductor Surface Chemistry." Chemical Engineering Colloquium, Cornell University, Ithaca, New York.
December 8, 1989	"Simulations of Metallic and Semiconductor Surface Chemistry," Olin Research Center, Cheshire, Connecticutt.
December 11, 1989	"Simulations of Metallic and Semiconductor Surface Chemistry," IBM Thomas J. Watson Research Center, Yorktown Heights, New York.
February 26, 1990	"Simulation of Metallic and Semiconductor Surface Chemistry," Physical Chemistry Seminar, University of California, Riverside, California.
March 30, 1990	"Theoretical Chemistry of Transition Metals: Complexes, Clusters, and Surfaces," Chemistry Departmental Seminar, Wesleyan University, Middletown, Connecticut.
August 20, 1990	"Structure and Chemistry at Metal and Semiconductor Surfaces from Theory," IBM Almaden Research Center, San Jose, California.
September 19, 1990	"Structure and Chemistry of Transition Metal and Semiconductor Surfaces," Physical Chemistry Seminar, University of Illinois, Urbana-Champaign, Illinois.
September 24, 1990	"Metallic and Semiconductor Surface Chemistry from Theory," Chemistry Department Colloquium, Smith College, Northampton, Massachusetts.
September 25, 1990	"Structure and Growth Mechanisms of Thin Films of Transition Metals," Olin Metals Research Laboratories, New Haven, Connecticut.
November 6, 1990	"Growth Mechanisms and Morphology of Ultrathin Metal Films," Physical Chemistry Seminar, UC Irvine, Irvine, California.
November 8, 1990	"Structure and Chemistry of Palladium and Silicon Surfaces," Physical Chemistry Seminar, Stanford University, Palo Alto, California.

November 26, 1990	"Structure and Chemistry of Transition Metal and Semiconductor Surfaces from Theory," Chemical Physics Seminar, University of California, Los Angeles, California.
November 27, 1990	"Structure and Chemistry of Metallic and Semiconductor Surfaces," Physical Chemistry Seminar, University of California, San Diego, California.
September 6, 1991	"Sequential and Simultaneous Ab Initio Molecular Dynamics for Clusters and Surfaces," Chemical Physics Colloquium, University of Colorado, Boulder, Colorado.
September 12, 1991	"Sequential and Simultaneous Ab Initio Molecular Dynamics for Clusters and Surfaces," Chemistry Department Colloquium, Columbia University, New York City, New York.

C. Contributed Talks and Presentations

May 10, 1989	"Adsorption of NO and CO on Pd: Contrasts in Bonding," poster at the West Coast Theoretical Chemistry Conference, San Jose, California (with Greg Smith).
October 18, 1989	"Metal-metal Bonding in Intermetallic Compounds," talk at the Pacific Conference on Chemistry and Spectroscopy, Pasadena, California (with Hua Wang).
October 18, 1989	"Adsorption of NO and CO on Pd_x and Pt_x: Contrasts in Bonding," talk at the Pacific Conference on Chemistry and Spectroscopy, Pasadena, California (with Greg Smith).
December 20, 1989	"Adsorption of NO_x and CO_x on Pd and Pt Clusters," poster at the Pacifichem Conference, Honolulu, Hawaii (with Greg Smith).
March 24, 1990	"Metal-NO and Metal-CO Interactions for Pd and Pt," talk at the West Coast Theoretical Chemistry Conference, Salt Lake City, Utah (with Greg Smith).
March 24, 1990	"The Modelling of Pd Thin Film Growth on a Bcc Substrate," talk at the West Coast Theoretical Chemistry Conference, Salt Lake City, Utah (with Barry Bolding).
March 24, 1990	"Metal-metal Bonding in Intermetallic Compounds," poster at the West Coast Theoretical Chemistry Conference, Salt Lake City, Utah (with Hua Wang).
August 2, 1990	"Simulations of Crystal and Thin Film Growth of Metals on Metals," poster at the American Conference on Theoretical Chemistry, San Diego, California (with Barry Bolding).
October 26, 1990	"Coverage and Temperature Dependence of the Morphology of Strained Overlayers: Deposition of Pd on a bcc(110) Substrate", talk at the California Catalysis Society Fall Meeting, Pasadena, California (with Barry Bolding).

March 27, 1991	"Electronic Structure and Thermochemistry of $Mn(CO)_x^+$ (x=1-6)," poster at the West Coast Theoretical Chemistry Conference, Moffett Field, California (with Yi Qin).
March 28, 1991	"Structure and Energetics of Metallic Thin Films," talk at the West Coast Theoretical Chemistry Conference, Moffett Field, California (with Barry Bolding).
July 8, 1991	"Comparative Study of Structure of Strained Metal Thin Films," poster at the Gordon Conference on the Inorganic Thin Films, Plymouth College, Plymouth, New Hampshire (with Barry Bolding).