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Theoretical Research Program to Study Transition Metal Trimers
and Embedded Clusters

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16. Abstract

The results of ob-initio calculations are reported for (i) small transition metal clusters and (ii) potential energy surfaces for chemical reactions important in hydrogen combustion and high temperature air chemistry.

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TRANSITION METAL TRIMERS AND EMBEDDED CLUSTERS

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The original proposal for this grant was to study transition metal triatomics and embedded clusters. The interest in this problem arose from two areas. The first was an interest in the hydrogen embrittlement problem and the desire to extend previous studies of the interaction of H atoms with Fe clusters, which had been carried out with explicit inclusion of only the Fe 4s electrons, by including within the cluster several Fe atoms with the 4s and 3d electrons present. In addition to the materials science applications, the small clusters are also of direct interest, since experimental studies of these molecules are being carried out both in matrices and in the gas phase. The work on transition metal triatomics was an extension of work which had been carried out on transition metal dimers and on Fe clusters under an earlier NASA grant (NCC2-148). During the course of this work it became important to respond to agency needs in the area of reacting flows. Since the author had had considerable experience in computing potential energy surfaces for chemical reactions, the research effort was gradually redirected toward potential energy surfaces and for the last year of the grant the primary effort has been in that area. Thus, this report will describe work in two different areas. The first half of the report will concentrate on the transition metal triatomics, while the second half of the report will concentrate on chemical reactions. Since much of this work has been published this report will be mainly a summary.

Under NCC2-148, calculations had been carried out on the bonding in the transition metal dimers including studies on Sc_2, Ti_2, V_2, Cr_2, TiV, Cu_2, Y_2, Nb_2, and Mo_2. A summary of this work has been given in an invited paper[1] which was written during this grant. An important feature of the bonding in the transition metal dimers is that metal-metal d bonding is important for the elements with half filled or lower occupancy d shells, but the bonding mainly involves the s electrons for those elements with full or nearly full 3d shells (e.g. Cu and Ag). As we shall

2

see these trends also carry over to the transition metal trimers.

In order to understand the d bonding in the transition metal trimers studies were carried out for Ca_3, Sc_3, Sc_3^+, and Ti_3^+[2] and for Y_3[3]. The Sc_3 and Y_3 molecules were selected for study because matrix ESR experiments had been carried out by Weltner and coworkers which established that the ground state of Sc_3 is of doublet spin. The latter result indicates that the 3d electrons must be paired into bonding orbitals, since three ground state $4s^2 3d^1$ Sc atoms lead to a quartet spin if the 3d electrons are not paired. From the calculations, it was found that the bonding in Ca_3 arises by $4s \rightarrow 4p$ promotion and leads to a well depth of about 0.5 eV for R(Ca-Ca) = 7.5 a_0. For Sc_3 the 4s bonding is similiar to that in Ca_3, but the 3d electrons are also strongly bonding leading to a $^2A_2''$ ground state with a well depth of about 1.0 eV and R(Sc-Sc) = 5.75 a_0. The good 3d bonding orbitals (bonding between all three atoms) are $3da_2''$ derived from atomic $3d\pi''$ and $3da_1'$ derived from atomic $3d\sigma$, while $3d\pi'$ atomic orbitals lead to $3de'$ orbitals which are bonding between pairs of atoms, and the $3d\delta'$ and $3d\delta''$ derived levels are non-bonding. (Here the atomic symmetry is given with respect to an axis connecting the atom to the center of the molecule.) Based on the Sc_3 calculations and calculations on Ti_3^+, the bonding in V_3^+ and Cr_3^+ was also discussed[2].

Similar calculations were carried out for Y_3[3]. Comparison of the wave functions for Y_3 and Sc_3 indicates substantial 4d-5p hybridization in Y_3, but little 3d-4p hybridization in Sc_3. The increased 4d-5p hybridization leads to stabilization of $4d\pi$ bonding with respect to $4d\sigma$ bonding for equilateral triangle Y_3, and also leads to 4d-5p bonding for linear geometries. These effects lead to a different ordering of states for equilateral triangle geometries and a smaller excitation energy to the linear configuration for Y_3 as compared to Sc_3.

The ground state surface and several excited states of Cu_3 were studied at the

3

single configuration SCF plus singles doubles CI level[4]. Here the bonding mainly involves the 4s orbitals but correlation of the 3d electrons leads to significant bond contraction effects and 33 electrons were correlated in these studies. These studies neglected relativistic effects and also are not size consistent, which presents significant problems for Cu_3 which has three closed shell $3d^{10}$ configurations. In spite of these difficulties, which were recognized at the time, this study provided a more accurate ground state surface than had previously been available and provided information on the excited states which aided in understanding the R2PI spectrum of Cu_3 which had been studied by Morse and Smalley.

The work on Cu_3 generated some controversy, since the computed results were not in accord with the interpretations of the experimental results which were accepted at the time. The upper state in the Morse and Smalley R2PI spectrum had been analyzed in terms of a weakly Jahn-Teller distorted upper state of $^2E''$ symmetry, but the calculations favored a 3s Rydberg upper state of $^2A_1'$ symmetry. This assignment was supported by the computed upper state geometries, vibrational frequencies, and oscillator strengths. Since then Morse has reanalyzed his spectrum along with new spectral results from the dispersion fluorescence spectrum of Rohlfing and Valentini and concludes that the upper state is indeed $^2A_1'$.

An additional area of controversy was the computed symmetric stretch frequency for the ground state of Cu_3. Theory[4] obtained 224 cm^{-1}, while Moskovits and coworkers observed a progression in 350 cm^{-1} in the resonance Raman spectrum, which they assigned as the symmetric stretch frequency. Since the computations neglected relativistic effects and higher excitation effects, it was expected that this frequency might be somewhat too low, but by comparison of the computed and experimental vibrational frequency for Cu_2, it was concluded that the symmetric stretch frequency of Cu_3 could not be as large as 350 cm^{-1}. Since then Truhlar and

coworkers have combined the computed potential surface for Cu_3 and the observed ground state vibrational levels of Cu_3 as obtained by Moskovits and by Rohlfing and Valentini to obtain an adjusted surface (lower barrier to pseudorotation) which gave Jahn-Teller levels in agreement with the levels observed by Rohlfing and Valentini. From this analysis it was concluded that the progression in 350 cm^{-1} observed by Moskovits et al. is a progression in Jahn-Teller levels and the symmetric stretch frequency is about 270 cm^{-1} in much better agreement with the results of calculations. New calculations by Langhoff, Bauschlicher, Walch, and Laskowski[5] which incorporate the effects of relativity and higher excitations lead to 268 cm^{-1} in good agreement with the new interpretation of experiment.

Selected portions of the ground state potential energy surfaces of the Cu_3, Ag_3, $AgCu_2$, and $AuCu_2$ trimers were studied at the single-reference singles plus doubles configuration interaction and coupled pair functional(CPF) levels correlating 33 electrons[6]. The CPF method incorporates the effects of higher excitations, while relativistic effects are incorporated using relativistic effective core potentials.

The bonding in Cu_3, Ag_3, $AgCu_2$, and $AuCu_2$ molecules is found to arise basically from the $(n+1)s^1nd^{10}$ ground states of the atoms as had been found for Cu_3[4,5]. The ground state surface of Ag_3 is found to be similar to that of Cu_3. For $AgCu_2$ and $AuCu_2$, since the atoms are inequivalent, there are several possible isomers. Here the lowest energy structure has the unique atom in the center. Since the Cu-Cu bond length is shorter than the Ag-Cu or Au-Cu bond length, these molecules have acute angle structures which leads to $^2A_1$ ground states. For $AuCu_2$ the acute angle C_{2v} structure is a true minimum, but for $AgCu_2$ the potential is very flat with respect to distortions leading to C_s symmetry. These differences between $AgCu_2$ and $AuCu_2$ are related to the larger bond strength for an AuCu bond as compared to an AgCu bond.

For the Cu atom the $4s^2 3d^9$ state is at 1.49 eV, while for Ag the $5s^2 4d^9$ state is at 3.74 eV, and for Au the $6s^2 5d^9$ state is at 1.74 eV. For Cu_3 there is significant admixture of $4s^2 3d^9$ character leading to a 3d population of 29.47 at the CPF level. As has also been found for the transition metal hydrides, SCF does not allow for a proper mixing of atomic configurations and this defect is not corrected completely by singles and doubles CI. Higher excitations are therefore important for Cu_3 and CPF leads to significant differences as compared to SDCI. Ag_3 on the other hand is mostly $5s^1 4d^{10}$ because of the larger excitation energy to the excited state. This leads to a larger d population, 29.76 at the CPF level, and higher excitations are less important for Ag_3 than for Cu_3. Thus SDCI and CPF give similar results for this molecule. For Au on the other hand, the excitation energy decreases again and this is reflected in a low d population in $AuCu_2$ of 29.39 electrons at the CPF level. From this result we predict that higher excitations would be important for Au_3.

Calculations were also carried out for the Ni_3 molecule. Here the the results of experiment and of existing calculations were still ambiguous. Resonance Raman experiments had been interpreted in terms of a bent molecule with an apical angle of about 100 degrees. This structure was thought to arise from a Δ_u state of unspecified multiplicity via either matrix effects or Renner-Teller distortion.

If only $4s^1 3d^9$ states of Ni atom are involved in Ni_3, we expect that Ni_3 will be a near equilateral triangle Jahn-Teller distorted system much like Cu_3. However, there is another possibility which was first suggested by Walch and Goddard. For the linear configuration if the center Ni atom is promoted to the nearly degenerate $4s^2 3d^8$ state then it is possible to form two bonds to adjacent $4s^1 3d^9$ Ni atoms. We expect the latter state to be low-lying and the calculations show that for linear geometries the $4s^2 3d^8$ center atom state is slightly (less than 0.1 eV) below the all $4s^1 3d^9$ structure for near equilateral triangle geometries. From comparison of

6

the computed and observed vibrational frequencies it is concluded that the bent structure is the ground state in the matrix, but the linear structure may be the ground state in the gas phase. Note that this conclusion is different from the speculation above that the lowest state of Ni_3 arises by distortion from a linear structure.

An important problem in this area has been the difficulty in doing spectroscopy on these molecules. These difficulties arise because the small binding energies of these molecules lead to predisociation in most of the excited states. As for Cu_3, Ni_3 is found to have a 3s Rydberg upper state. Here the transition is predicted to be in the range 2.7-3.5 eV which is consistent with the work of Gole who finds a strong transition in Ni_3 at 2.8 eV. In addition, Gole has measured the symmetric stretch and bending frequencies of the ground state of Ni_3 and these frequencies are found to be in good agreement with the calculated values for the lowest computed state of Ni_3. As an extension of this work calculations were carried out of the the excited states of the Ag_3 molecule[8].

The work on transition metal trimers[9] and transition metal dimers and other systems[10] was presented at a NATO workshop on transition metal bonding.

In collaboration with other members of the research group calculations were carried out for dipole moment of NiH[11]. This work provided experimental conformation of the importance of admixture of atomic states in transition metal bonding. These effects had been discussed for example for Cu_3 above. NiH provides a more dramatic example in that the ground state of the molecule has about equal parts of $4s^2 3d^8$ and $4s^1 3d^9$ atomic character. It turns out that the dipole moment is a very sensitive function of the mixture of atomic states and the experimentally determined dipole moment by Field and coworkers confirms the mixed state model of the bonding in this molecule. These studies were later extended to other hydrides

7

of the first transition row[12].

During the second half of the funding period much of the research effort was redirected toward the calculation of potential energy surfaces for chemical reactions. This new emphasis reflected the importance of being able to compute, from first principles, reaction rate constants for applications related to the design of the National Aerospace Plane (NASP) and Aeroassisted Orbital Transfer Vehicles (AOTV's). Two groups of reactions were considered.

The first set of reactions is a subset of the reactions important in H_2 combustion. These reactions are important in the design of the Supersonic Combustion RAM (SCRAM) jet engine for the NASP. Among reactions which are being studied here are:

$$H + O_2 \rightarrow HO_2 \rightarrow OH + O \tag{1}$$

$$O(^3P) + H_2 \rightarrow OH + H \tag{2}$$

$$OH + H_2 \rightarrow H_2O + H \tag{3}$$

The combustion of H_2 in the SCRAM jet engine involves three steps. Initiation requires production of H or O atoms. Radical propagation then occurs for H atoms via reaction (1) or for O atoms via reaction (2). OH radicals produced by reactions (1) or (2) react further via reaction (3). These reactions lead to the production of radicals in the combustor region of the SCRAM jet engine. The third step, which occurs in the nozzle region of the SCRAM jet engine, is radical recombination. Among reactions which are important here are:

$$OH + H + M \rightarrow H_2O + M \tag{4}$$

$$H + H + M \rightarrow H_2 + M \tag{5}$$

8

Since these reactions evolve a considerable amount of heat, the rates are critical to computation of the net thrust production of the engine. The rates of these recombination reactions are slow compared to the residence time in the nozzle region, and the rates are not well known; thus, the computated rates for these reactions are crucial to the design of the SCRAM jet engine.

Calculations have been completed for reaction (2) and are currently underway for reaction (1). The work on reaction (2) is described in detail elsewhere[13]. The calculations on reaction (2) focused on the problem of obtaining an accurate barrier height. Previous work by Walch et al. on reaction (2) using the POL-CI method had given a barrier height of 12.5 kcal/mole, but attempts to improve upon this result by simple multi-reference singles and doubles CI methods lead to a barrier height of 16.0 kcal/mole. From comparison of computed and experimental thermal rates using the POL-CI surface, it was concluded that the 12.5 kcal/mole POL-CI barrier height is accurate. Similar results are seen for $F + H_2$ where first order CI gave a barrier height of 1.66 kcal/mole, but multi-reference singles and doubles CI leads to barrier heights greater than 3.2 kcal/mole.

The problem of computing the barrier height for these reactions is found to be related to the problem of computing the electron affinity of the O and F atoms. Ionic character is important in the saddle point and products regions but not in the reactants regions for these reactions. In these calculations, the convergence of the barrier height was studied as a function of expanding the active space in the CASSCF calculation as well as expanding the basis set. It was found that inclusion of $2p \rightarrow 2p'$ terms, which improve the description of the electron affinity of the O and F atoms, lowers the barrier height for the $O + H_2$ and $F + H_2$ reactions. It was also found that the good barrier height obtained using POL-CI results from a cancellation of opposing effects; the neglect of angular correlation in the POL-CI

9

favors the saddle point region over reactants while the neglect of ionic terms in the POL-CI favors the reactants over the saddle point region. The calculation on $O + H_2$ serves as an important benchmark for reactions involving O atoms.

For reaction (1) multi-reference singles and doubles CI calculations have been carried out along the minimum energy path for the addition of H atom to O_2 determined in the POL-CI studies of Dunning et al. The barrier to H atom addition is found to be less than 0.3 kcal/mole, in agreement with the earlier POL-CI work. Calculations are also being carried out for the process of dissociating HO_2 to OH + O. In collaboration with C. F. Melius and C. Rohlfing of Sandia laboratories it is planned to generate a global potential surface for this reaction.

The second set of reactions which are being studied are the reactions:

$$O + N_2 \rightarrow NO + N \tag{6}$$

$$N + O_2 \rightarrow NO + O \tag{7}$$
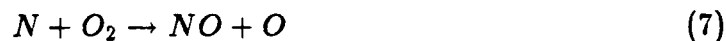
These reactions are important in high temperature air chemistry. Two areas where these reactions are expected to be important are i) the computation of the composition of the gas at the inlet to the SCRAM jet for the NASP and ii) the chemistry occuring in the shock layer in front of the AOTV. The details of this work are described elsewhere[14]. Calculations for these reactions are essentially complete. There has been some difficulty in obtaining a satisfactory fit to the computed points. An approximate fit has been obtained by M. Pattengill and R. L. Jaffe and trajectory calculations on this surface give good agreement with experiment in the high temperature region. This surface will subsequently be used to compute rates under non-equilibrium conditions such as occur in AOTV applications.

In addition to the work described here, several collaborative projects have been undertaken with other members of the Ames computational chemistry group. One

10

such project was the calculation of the potential curves for the low-lying $^3\Pi_u$ and $^3\Sigma_g^-$ states of Al_2[15]. Another related project involved computing the electronic structure of the lowest few states of linear and T shaped $CuAl_2$[16].

Finally, the POL-CI surface for reaction(2), which the author generated while working for the Department of Energy is still being used in dynamics studies[17].

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