analysis of the temperature dependence of the intervalence band moments.

The model will also clearly be applicable to other systems as new data accumulate. For example, Collman et al.\(^\text{19}\) have recently reported the presence of both an intervalence band and a CTIIR absorption in a partially oxidized sample of [Os(OEP)(pz)]\(_2\) (OEP is octaethylporphyrin), and Boekelheide and co-workers\(^\text{20,21}\) have reported the synthesis of mixed-valence dimers with a two-electron difference in oxidation state of the metal atom.

It would also be possible to extend our approach to more complicated cases, for example a many-mode treatment of the three-center model\(^\text{7,8}\) or a many-mode system in which one of the modes must be treated exactly.

Acknowledgment. This work was supported in part by the National Science Foundation (P.N.S.) under Grants CHE8400423 and CHE8700754. We also acknowledge receipt of a NATO travel grant (RG0146/87).

Appendix A1

Second-Order Terms in Eq 26. Second-order contributions to the dipole strength arise for three cases as follows \((D \approx \text{[TM]}^2)\):

(i) \(\Delta n_\alpha = 0:\)

\[
\text{(TM)} = -(c_i^{-1})^3 M \left[ \lambda^2 \left( \frac{\kappa_\alpha}{\kappa_\alpha + e_\alpha'} - 1 \right) + \frac{\kappa_\alpha + e_\alpha'}{(\kappa_\alpha + e_\alpha')^2 - 1} \right] + \frac{(n_\alpha + 1)(n_\alpha + e_\alpha + 1)}{(\kappa_\alpha + e_\alpha')^2 - 1} \left( \sigma_\alpha + \sigma_\alpha' + 1 \right)
\]

\[\text{(A1)}\]


Appendix A2

Second-Order Terms in Eq 44. Second-order contributions arise as follows \((D \approx \text{[TM]}^2)\):

(i) \(\Delta n_\alpha = \pm 2, \Delta n_\beta = 0:\)

\[
\text{(TM)}_{\alpha_2} = -\frac{1}{2}(c_i^{-1})^3 \lambda^2 M \left( \frac{(n_\alpha + 1)(n_\alpha + e_\alpha + 1)}{(\kappa_\alpha + e_\alpha')^2 - 1} \right) \left( \sigma_\alpha + \sigma_\alpha' + 1 \right)
\]

\[\text{(A2)}\]

(ii) \(\Delta n_\alpha = \pm 1, \Delta n_\beta = \pm 1:\)

\[
\text{(TM)}_{\alpha_1,\alpha_1} = -\frac{1}{2}(c_i^{-1})^3 \lambda^2 M \left( \frac{(2n_\alpha + 1)(2n_\alpha + e_\alpha + 1)}{(\kappa_\alpha + e_\alpha')^2 - 1} \right) \left( \sigma_\alpha + \sigma_\alpha' + 1 \right)
\]

\[\text{(A3)}\]

Electronic States and Potential Energy Surfaces of AgH\(_2\): Comparison with AuH\(_2\)

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(Received: February 8, 1988)

Complete active space MCSCF (CASSCF) followed by second-order configuration interaction (SOCI) and multireference single plus double configuration interaction (MRSDCI) which include excitations from the d shells are carried out on the two low-lying states of AgH\(_2\) \((^2\text{B}_3\text{g} \text{ and } ^2\text{A}_1\text{g})\). The bending potential energy curves of the two states with bond lengths optimized for all angles are presented. The \(^2\text{B}_3\text{g}\) surface contains a double minimum with acute and obtuse Ag-H-Ag angles. The \(^2\text{A}_1\text{g}\) state with obtuse bending angle. The d shell correlation lowers the potential energy surfaces and electronic states of AgH\(_2\) are compared with those of AuH\(_2\). Relativistic mass-velocity effects are significant for AuH\(_2\) in comparison to AgH\(_2\), while d correlation effects are more significant for AgH\(_2\) in comparison to AuH\(_2\). The Mulliken population analyses of the electronic states of AgH\(_2\) reveal considerable 5p participation. The bending potential energy surfaces of the \(^1\text{E}_{2u}\) and \(^2\text{A}_1\text{g}\) states of both the molecules cross, which would lead to avoided crossing of the \(^1\text{E}_{2u}\) components if the spin-orbit term is included. The effect of f-type polarization functions is also investigated by carrying out MRSDCI calculations which included the ten-component f functions in the basis sets.

1. Introduction

The electronic properties, geometries and reactivities of transition-metal clusters are topics of intense activity in recent years. The investigation of metal atom insertion into hydrogen bonds could provide considerable insight into the reactivities of small clusters with H\(_2\). Further, such calculations could also provide...
TABLE I: Valence Basis Sets for Gaussian-Type Functions for Ag (3s3p4d1f/3s2p3d1f)*

<table>
<thead>
<tr>
<th>shell</th>
<th>exponential factor</th>
<th>contract coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0.4981</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.1584</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.0471</td>
<td>1.0</td>
</tr>
<tr>
<td>p</td>
<td>0.7589</td>
<td>-0.0287</td>
</tr>
<tr>
<td></td>
<td>0.0908</td>
<td>0.2979</td>
</tr>
<tr>
<td></td>
<td>0.0283</td>
<td>1.0</td>
</tr>
<tr>
<td>d</td>
<td>2.4127</td>
<td>0.308853</td>
</tr>
<tr>
<td></td>
<td>1.0153</td>
<td>0.450434</td>
</tr>
<tr>
<td></td>
<td>0.4093</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.1503</td>
<td>1.0</td>
</tr>
<tr>
<td>f</td>
<td>0.45</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Reference 27. The exponent of f function from this work.

models for our understanding of the reactivity of metal with hydrocarbons due to the similarity of the C-H σ bond with the H₂ bond and photochemical processes.⁵

Theoretical studies of molecules containing gold and silver atoms such as AgH₂, AuH₂, Ag₅, Au₅, etc., are of considerable interest.⁶-¹³ These species are fundamentally interesting due to large relativistic effects. The relativistic mass-velocity contraction of the outer s orbital of the gold atom is the primary reason for the chemical and spectroscopic difference of gold-containing molecules in comparison to silver compounds. For example, the binding energy of Au₂ is larger than Ag₂ primarily due to this mass-velocity contraction.

The electronic states of AgH₂ and their potential energy surfaces could be quite valuable since these surfaces can reveal the differences in the reactivities of different states of the silver atom. Further, comparison of these states and the nature of the electronic states of AgH₂ with AuH₂ could provide valuable insights into the contrast and similarities of the two systems. The only theoretical calculation to date is that of Novaro et al.,¹⁴ who employed a model potential SCF procedure followed by perturbation CI calculation on AgH₂. There are no experimental studies such as AgH₂ or AuH₂, although the related AuH₅⁺ ion has been studied by using the field-induced surface-catalyzed reactions.¹⁵,¹⁶

The objective of the present investigation is to carry out ab initio complete active space MCSCF (CASSCF) calculations followed by configuration interaction calculations on AgH₂ with and without corre- lating the d electrons and including relativistic effects. We investigate the binding potential energy surfaces of the B² and A² states using the CASSCF method. The B² surface contains a double minimum (acute and obtuse angles) which is investigated further through configuration interaction methods which include excitations from the d shells. In addition, the linear B₂⁺ and C₂⁺ electronic states are investigated. These results are compared with similar calculations on AuH₂. Theoretical studies of electronic structure of molecules containing heavy atoms are topics of current interest.¹⁷-²⁶

Section 2 consists of results and discussions.

2. Method of Investigation

We carry out multiconfiguration self-consistent field (MCSCF) calculations followed by configuration interaction calculations with and without correlating the d shell of the silver atom. All calculations reported here were carried out using relativistic effective core potentials with the 4d¹⁵5s⁶ outer shell of the silver atom explicitly retained in the valence space. Lee et al.²⁷ have recently generated analytical Gaussian fits of relativistic effective potentials for the silver atom suitable for molecular calculations. We employ these potentials together with the (3s3p4d) valence Gaussian basis set optimized by these authors for the 5s and 5p ground states of the silver atom. The three p functions were contracted to a 2p set, and the four d functions were contracted to a set of three functions with the coefficients shown in Table I. The resulting basis set for the silver atom can be described as (3s3p4d/3s2p3d). To this set, a set of ten-component f-type polarization functions was added with the exponent shown in Table I with the objective of studying the effect of f functions. McLean²⁸ has shown that inclusion of f-type functions can lead to a bond contraction of about 0.07 Å in both AgH₂ and AuH₂. However, it should be noted that if one includes extensive d correlation, the shifts in bond lengths due to the f-type function are small.²⁹ The calculations that included f-type functions carried the f prefix. We employ van Duijneveldt's²⁸ (5s/3s) basis set augmented by a set of p-type polarization functions for the hydrogen atom. The αₚ for the hydrogen atom is 0.9. The hydrogen exponents were multiplied by a scaling factor of 1.44.

MCSCF calculations were made using the complete active space MCSCF (CASSCF) method. In this method, the outer electrons are distributed in all possible ways in a chosen set of internal space of the strongest occupied orbitals of the separated atoms. All calculations reported here were carried out in C₂ᵥ symmetry with the x axis being perpendicular to the plane of the AgH₂ molecule. Two sets of CASSCF calculations were carried out, one which did not include the d shells in the active space while the other, which we label d-CASSCF, included the d shell in the active space. The internal space of AgH₂ in C₂ᵥ symmetry without the d orbitals spans two a₁ and one b₂ representations. These orbitals correspond to the 5s atomic orbital of the silver atom and the 1s orbitals of hydrogens at infinite separation. Distribution of the three outer electrons of AgH₂ among the complete space of orbitals generates four CASSCF's in the C₂ᵥ group. In this CASSCF, no excitations from the d shells were allowed but the coefficients of the d orbitals were allowed to relax for all geometries.

The d-CASSCF included 13 electrons in the active space. The internal space of this CASSCF included five a₁, two b₂, one b₁, and one a₁ orbitals. The ALCHEMY II codes²⁹ were used to generate CASSCF orbitals. There is one more a₁ orbital than necessary in the d-CASSCF. Note that although for the ground state the four a₁, two b₂, one b₁, and one a₁ orbitals correspond to the 4d and 5s orbitals of the Ag atom and 1s orbitals of hydrogens, for the excited B₂ state the active space would contain the 5p orbital since this state dissociates into Ag(2P) + H₂. Thus, the exact nature of the orbitals in the active space would actually depend on the electronic state and geometry.

Three types of configuration interaction (CI) calculations were performed following CASSCF: The first type of CI calculations

(26) Balasubramanian, K. J. Mol. Spectrosc. 1987, 123, 228.
(29) The major authors of ALCHEMY II codes are B. Liu, B. Lengsfield, and M. Yoshimine.
TABLE II: Geometries and Energies of Electronic States of AgH₂

<table>
<thead>
<tr>
<th>system</th>
<th>state</th>
<th>r, Å</th>
<th>θ, deg</th>
<th>E⁺</th>
<th>r, Å</th>
<th>θ, deg</th>
<th>E⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgH₂</td>
<td>¹B₂</td>
<td>1.81</td>
<td>108</td>
<td>2.47</td>
<td>1.79</td>
<td>104</td>
<td>2.41</td>
</tr>
<tr>
<td>AgH₂</td>
<td>²Σ⁺</td>
<td>1.85</td>
<td>180</td>
<td>2.59</td>
<td>1.85</td>
<td>180</td>
<td>2.61</td>
</tr>
<tr>
<td>AgH₂</td>
<td>²B₂⁺</td>
<td>2.05</td>
<td>22</td>
<td>2.98</td>
<td>2.01</td>
<td>23.6</td>
<td>2.60</td>
</tr>
<tr>
<td>AgH₂</td>
<td>²Σ⁺</td>
<td>1.67</td>
<td>182</td>
<td>2.96</td>
<td>1.68</td>
<td>180</td>
<td>2.96</td>
</tr>
<tr>
<td>Ag(S) + H₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ag(P) + H₂</td>
<td>3.75</td>
<td>3.35</td>
<td>3.98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag(S) + 2H</td>
<td>4.16</td>
<td>4.55</td>
<td>5.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All energies in electronvolts with respect to Ag(S) + H₂ (E = -38.413216 hartrees). With respect to SOCI energy of Ag(S) + H₂ (-38.429936 hartrees). With respect to d-MRSDCI energy of Ag(S) + H₂ (-38.529703 hartrees). Second minimum in the ²B₂ surface (see Figure 1).*

Figure 1. Bending potential energy curves of ²B₂ and ²A₁ states of AgH₂.

carried out were second-order CI (SOCI) calculations and were done following the CASSCF without the d shell. The other type was multireference single and double CI including d electrons labeled d-MRSDCI calculations. The SOCI calculations did not allow excitations from the d shell. The SOCI calculations included all configurations in the CASSCF and first-order and second-order excited CI configurations. The first-order configurations were generated by distributing two electrons in the CASSCF internal space and one electron in the orthogonal MCSCF external space in all possible ways. The second-order configurations were generated by distributing one electron in the internal space and two electrons in the external space in all possible ways.

The d-MRSDCI calculations, which allow excitations from the d shells, included all configurations in the d-CASSCF with coefficients 10.07 for a given state as reference configurations. Single and double excitations were allowed from these reference configurations. The d-MRSDCI calculations were carried out using the orbitals generated by d-CASSCF which included the d shells in the active space. The SOCI calculations included about 1000 configurations. The d-MRSDCI which included excitations from the d shell contained 27000-50000 configurations depending on the electronic state and geometry. All the calculations reported here were carried out using one of the author's modified version of ALCHEMY ²⁹ of codes to include relativistic effective core potentials. Similar methods of CASSCF, SOCI, and MRSDCI calculations were employed on AuH₂ in an earlier investigation. The results on AuH₂ are compared here with the present results on AgH₂.

Another set of MRSDCI calculations which we label f-MRSDCI included the ten-component f-type functions in the basis set. The basis set employed in the f-MRSDCI is (3s3p4d1f/3s2p3d1f). Thus, f-MRSDCI calculations are more accurate than the d-MRSDCI calculations. The inclusion of the ten f functions increased the configuration count in the CI for the ²B₂ state to 84979 and for the ²A₁ state to 60180.

The ground-state spin–orbit splitting of the ²S silver atom is zero. The contributions from spin–orbit interaction can arise only through mixing of the ⁵p and ⁴d orbitals of the silver atom in the molecular states of AgH₂. We find that the ⁴d shell is nearly full in most of the electronic states of AgH₂ although the ⁴p configuration is nonnegligible. The spin–orbit contributions to the low-lying electronic states of both AgH₂ and AuH₂ are discussed in a qualitative manner using the atomic ⁵p/⁴d-⁵p/⁴d and ⁶p/⁵d-⁶p/⁵d splittings of Ag and Au, respectively.

### Table III: Effect of f-Type Functions on the Geometries and Energy Separations of Electronic States of AgH₂

<table>
<thead>
<tr>
<th>state</th>
<th>with f functions</th>
<th>without f functions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r, Å</td>
<td>θ, deg</td>
</tr>
<tr>
<td>²B₂</td>
<td>1.672</td>
<td>113</td>
</tr>
<tr>
<td>²Σ⁺</td>
<td>1.736</td>
<td>180.0</td>
</tr>
<tr>
<td>²B₂⁺</td>
<td>1.660</td>
<td>180.0</td>
</tr>
<tr>
<td>Ag(S) + H₂</td>
<td>0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*Absolute MRSDCI energy of Ag(S) + H₂ with f-type functions is -38.664714 hartrees. Absolute MRSDCI energy of Ag(S) + H₂ without f-type functions is -38.529703 hartrees.

### 3. Results and Discussion

In Table II, we show the calculated geometries and their energies for various electronic states of AgH₂ and the Ag(S)⁺ + H₂, Ag(P)⁺ + H₂ dissociation energies. Figure 1 shows the bending potential energy surfaces of the ²A₁ and ²B₂ electronic states of AgH₂.

The ground state of the AgH₂ molecule is found to be the ²B₂ electronic state with an obtuse bending angle at all levels of theory (CASSCF, SOCI, and MRSDCI). The Ag–H bond lengths and the bending angle are, however, sensitive to electron correlation and especially d correlation. The d-MRSDCI calculations which include single and double excitations from the d shells shorten the Ag–H bond length by almost 0.13 Å in comparison to SOCI calculations which included excitations from the s shells of silver and hydrogen atoms but not from the d shell. Thus, d correlation effects are quite significant for AgH₂. The separation of the ²B₂ ground state with respect to Ag(S)⁺ + H₂ is also consistently lowered as one includes correlation corrections and d correlations.

The ²Σ⁺ linear state is the state above the ²B₂ obtuse angle minimum. The SOCI calculation does not change the Ag–H bond lengths in this state, while excitations from the d shell bring about a bond contraction of 0.09 Å for this state. The linear ²Σ⁺ electronic state has the shortest Ag–H bond length (1.65 Å). The
As one can see from Table I, the second angle minimum before dissociation. As one can see from Table II, this minimum occurs at a H–Ag–H bond angle of 27.5° at the MRSDCI level of theory. The d correlations shorten the Ag–H bond length accompanied by an increase in the bond angle; thus, d correlations stabilize the complex. The second minimum in AgH₂ arises from the formation of a complex of Ag(2P) with H₂. The Ag(2P) linear 2Σ⁺ state which dissociates into Ag(2S) + H₂ is 2.26 eV less stable in comparison to the Ag(2S) + H₂ dissociation. The atomization energy of the 2Σ⁺ obtuse minimum (i.e., the energy required for the process AgH₂(2Σ⁺) → Ag(2S) + 2H₂(S)) is calculated to be about 75 kcal/mol.

Table III compares the MRSDCI geometries and energies of electronic states of AgH₂ obtained with and without the f-type functions in the basis sets. As one can see from that table, the Ag–H bond length changes by only 0.01 Å for the 2Σ⁺ and 2Σ⁺ states. For the 2Σ⁺ state the Ag–H bond lengths contract by 0.02 Å. Thus, the effect of f-type functions on the MRSDCI geometries is not large.

The energy separations with respect to the Ag(2S) + H₂ dissociation limit are a bit more sensitive to the addition of f-type functions. As one can see from Table III, the 2Σ⁺ linear state is lowered by 0.17 eV with respect to the Ag(2S) + H₂ dissociation due to the addition of f-type polarizability functions. The 2Σ⁺ state, on the other hand, goes up by 0.23 eV in comparison to the separation obtained without the f-type functions. The energy separation of the 2Σ⁺ ground state changes by only 0.02 eV due to the addition of f functions. Thus, the energy separations of the linear 2Σ⁺ and 2Σ⁺ states are influenced more by f functions.

Table IV shows the results of a similar calculation on AuH₂ carried out earlier by Balasubramanian and Liao. For AuH₂ also, the ground state is a 2Σ⁺ state with an obtuse angle geometry. The obtuse angle of 127° is somewhat larger than the corresponding angle for AgH₂. The metal–H bond lengths are shorter for AuH₂ for most of the states except for the linear 2Σ⁺ state for which Au–H bond length is 0.01 Å longer. Usually, the bond lengths increase for isoelectronic heavier systems in comparison to the lighter systems of the same group. In contrast, we find that the Au–H bond is shorter than the Ag–H bond. This shortening is largest for the linear 2Σ⁺ state (0.07 Å). This is attributed to relativistic mass–velocity corrections which shrink the inner s orbitals of the core. This is, in turn, manifested in the valence s due to core–valence orthogonality. The shrinking of the outer 6s orbital of the gold results in a shorter Au–H bond in comparison to the Ag–H bond.

The other striking contrast between AgH₂ and AuH₂ is the relative stabilities of the electronic states. The separations of the electronic states of AuH₂ with respect to AgH₂ + H₂ are substantially in comparison to the corresponding separations for AgH₂. For example, the ground state of AuH₂(2Σ⁺) is 0.85 eV above AgH₂, while the 2Σ⁺ state of AgH₂ is 1.89 eV above AgH₂ + H₂. Similar behavior is found for the linear 2Σ⁺ and 2Σ⁺ states. This implies that AuH₂ electronic states are more stable than the corresponding states of AgH₂. This is further justified by the fact that the atomization energy of AuH₂ is 85 kcal/mol while the corresponding value for AgH₂ is 75 kcal/mol.

The Ag(2P) atom forms a weak acute angle complex with H₂. A corresponding minimum for AuH₂ in the 2B₂ electronic state which dissociates into Au(2S) + H₂ + H₂ is 137 kcal/mol for AuH₂ while the corresponding value for AgH₂ is 75 kcal/mol.

The bending potential energy curves of the 2Σ⁺ and 2Σ⁺ states are influenced more by f functions. The energy separations of the linear 2Σ⁺ and 2Σ⁺ states are influenced more by f functions. The energy separation of the 2Σ⁺ ground state changes by only 0.02 eV due to the addition of f functions. Thus, the energy separations of the linear 2Σ⁺ and 2Σ⁺ states are influenced more by f functions.

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from the s shell. As noted before, the d correlation effects are quite high for AgH₂ and thus the barrier could be lowered. In any event, a CASSCF calculation of the same level gave a barrier height of 92 kcal/mol for AuH₂. While the difference in the barrier heights of the two molecules (45 kcal/mol) would certainly be lowered by d correlations, it is noted that the barrier for the insertion of Au₂⁺ into H₂ would be smaller than the corresponding barrier for the insertion of Ag₂⁺ into H₂.

The separation of the ₂B₂₉ minima with obtuse angle geometry for AgH₂ is much smaller with respect to Ag(₂P) + H₂ in comparison to the corresponding separation for AuH₂. This separation is 2.09 eV for AgH₂ in comparison to 4.4 eV for AuH₂.

The ₂B₂ surface of AuH₂ has no barrier, implying that the Au(₂P) atom would insert spontaneously into H₂ to form the bent ₂B₂ AuH₂ molecule (obtuse angle geometry). For AgH₂ (Figure 1), the insertion of Ag(₂P) into H₂ is again spontaneous but it forms a weak complex and a AgH₂ molecule with an obtuse angle geometry separated by a small barrier. Thus, in both cases the metal atom in the ₂P state inserts spontaneously into H₂ while the ₂S state has to surmount a large barrier.

The ₂B₂ and ₂A_1 bending surfaces of both AgH₂ and AuH₂ cross. This crossing occurs at θ = 47° for AgH₂ and θ = 60° for AuH₂. In the presence of the spin–orbit term, the ₂A_1 and ₂B₂ states correlate into the same ₂E₁₂ state in the C₂v double group. This would imply an avoided crossing of the two states, the first component designated as ₂E₁₂(I) and the second component designated as ₂E₁₂(II). The magnitude of the coupling of the two components would depend on the amount of spin–orbit mixing. The spin–orbit effects are larger for gold than for silver. If one looks at the two surfaces in the double group, the barrier in the ₂E₁₂(I) surface would occur at θ = 47° for AgH₂ and θ = 60° for AuH₂ and would be much smaller. Conversely, the ₂E₁₂(II) component would have a large barrier.

Next, we discuss the effect of spin–orbit interaction on the electronic states of AgH₂ and AuH₂. First, the separation of the ₂A_1 and ₂B₂ states at long distances should correspond to the metal (₂P) atomic splitting. This splitting is calculated to be 30 245 cm⁻¹ at the CASSCF level for AgH₂ and 38 553 cm⁻¹ at the same level for AuH₂. The CI separations are somewhat higher primarily due to higher order correlations could be quite significant.

Table VI shows the Mulliken population analysis of the various electronic states of AgH₂ and AuH₂ using the recently developed relativistic CI method for polyatomics would be the topic of a future investigation.

Next, we consider the nature of bonding in the low-lying states of AgH₂ and compare with AuH₂. First, we compare the CASSCF-CI wave functions of the ₂B₂ and ₂A_1 states of AgH₂ and AuH₂ for various geometries in Table V. As seen from Table V, the leading configuration has a consistently larger coefficient for AuH₂ in comparison to AgH₂, implying that correlation effects are much larger for AgH₂ in comparison to AuH₂. The worst case is near the saddle point of the ₂A_1 state which is a mixture of four configurations for AgH₂ while it is still predominantly described by one configuration for AuH₂. This would imply that the calculated barrier height for AgH₂ is only an estimate since higher order correlations could be quite significant.

Table VI shows the Mulliken population analysis of the various electronic states of AgH₂ and AuH₂. The ALCHEMY II codes which we use carry out Mulliken population analysis on a basis set of six-component d functions. Thus, the ₂E₁₂,₂P₉ component which corresponds to the s component is included in the d. A code was developed by one of the authors (K.B.) to extract the x² + y² + z² population from the d and add it to the s. Table VI shows the corrected d and s populations. The population analysis of AgH₂ reveals that the gross metal population is largest for the ₂E₁₂ state and smallest for the ₂E₁₂ state. The reduced metal populations for the ₂B₂ and ₂S₂⁺ states imply ionic character of the M–H bond with the polarity (M+H⁻). For AgH₂, the d population is nearly 10.0 except for the ₂E₁₂ state for which the d population is considerably smaller. The p population of all the states of AgH₂ is quite large, indicating that the participation of the 5p orbital is quite significant. For the ₂B₂ acute minimum, the population is, in fact, larger than the s population primarily because this corresponds to a weak complex of Ag(₂P) with H₂.

A striking contrast between the Mulliken populations of AgH₂ and AuH₂ is that the p population is considerably larger for AgH₂ while the s population is considerably larger for AuH₂. The d populations of the electronic states of AuH₂ are also somewhat smaller than 10.0. The overall gross populations of the two molecules indicate that the Au–H bond is much more ionic with the polarity (Au⁺H⁻) in comparison to the Ag–H bond since the gross metal population is much smaller in AgH₂.

The calculated dipole moments of the two bent ₂B₂ minima are 2.4317 and 1.568 D with the obtuse minimum having a larger dipole moment than the acute minima. The dipole moment of the ₂B₂ (obtuse minimum) of AuH₂ is calculated to be 1.250 D. The smaller dipole moment in AuH₂ is primarily because the

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Au–H bond is shorter than the corresponding bond length in AgH2.

4. Conclusion
In this investigation, we carried out complete active space MCSCF followed by second-order CI and MRSDCI calculations which included d correlation for 2B2 and 2A1 states of AgH2. For the 2B2 state of AgH2, two minima were found one with a short bond angle and the other with a large angle. The bending potential energy curves of 2B2 and 2A1 states of AgH2 were obtained and compared with AuH2. The 2A1 surface has a large barrier to the insertion of the metal 2S state into H2 while the excited 2P state of the metal atom inserts into H2 almost spontaneously. The barrier to the insertion of M(2S) into H2 was found to be larger for Ag than Au. The AuH2 electronic states were found to be more stable than AgH2 mainly due to the relativistic mass–velocity contraction of the outer s orbital of the gold atom. The same effect resulted in shorter M–H bonds in AuH2. The 2B2 and 2A1 surfaces cross at θ = 47° and θ = 60° for AgH2 and AuH2, respectively, implying an avoided crossing of the 2B2 states when spin–orbit coupling is included. The metal–hydrogen bonding was found to be more ionic for AuH2 than AgH2. The Mulliken population analysis of both the molecules revealed that the p population is considerably higher for AgH2 while the s population was found to be higher for AuH2.

Acknowledgment. This research was supported by the U.S. Department of Energy under Grant No. DEFG02-86ER13558. The authors thank the two referees for their invaluable comments.

Registry No. AgH2, 102502-37-4.

Resonant Two-Photon Ionization Spectroscopy of Jet-Cooled p-Dichlorobenzene

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This paper reports resonant two-photon ionization (R2PI) with reflectron time-of-flight mass spectrometry on jet-cooled p-dichlorobenzene (p-DCB) performed to study both the mechanism of multiphoton ionization/dissociation (MPID) at high laser intensities and the 1B2u–1A1g excitation spectrum at low laser intensities. Ionization via the 5S band at 274.10 nm under MPID conditions produces almost no C6H4Cl+. This observation demonstrates that dissociation of the parent ion at the three-photon level is too slow to compete with the higher energy processes that produce small fragments via additional photon absorption. However, absorption of one visible photon (548.20 nm) from the three-UV-photon level dramatically increases the rate of dissociation of the parent ion to form C6H4Cl+. A comparison of one- and two-color R2PI spectra (where the second color is 266 nm) allows us to bracket the adiabatic ionization potential (IP) for p-DCB as 8.90 eV ≤ IP ≤ 8.95 eV, in good agreement with previous measurements. High mass selectivity enables us to measure chlorine isotope shifts for 26 C6H4Cl+ and ionization steps or two-color R2PI in which a second laser provides both an optical spectrum and a mass spectrum, and this procedure allows a straightforward assignment of almost all of the observed vibrational bands and gives vibrational frequencies for 11 modes in the excited state.

I. Introduction
The trace detection of chlorinated aromatics is currently a topic of great interest because of the widespread presence of these species in the environment and their potential toxic and/or carcinogenic effects on man. Recently we have examined the use of resonantly enhanced multiphoton ionization (REMPI) in conjunction with time-of-flight mass spectrometry (TOF MS) to achieve sensitive and isomerically selective detection of jet-cooled chlorinated aromatics such as the mono- and dichlorinated naphthalenes and the dichlorobenzenes.1 Free-jet expansion cooling is necessary to achieve species and isomer selectivity for these polyatomic molecules via their S1–S0 absorption spectra. Mass-selective REMPI has some decided advantages over fluorescence detection. First, the quantum yield of fluorescence for highly chlorinated aromatics is very small because of facile intersystem crossing from S1 to low-lying triplet states. REMPI can be used effectively in such systems because the ionization rate can be made comparable to the rate of intersystem crossing. Second, REMPI/TOF MS provides both an optical spectrum and a mass spectrum, and this two-dimensional aspect greatly enhances species selectivity in complex mixtures.

In this paper we present results obtained as part of our investigation into the applicability of REMPI/TOF MS to chlorinated aromatics. The molecule under study is p-dichlorobenzene (p-DCB), which serves as a prototypical example of chlorinated aromatics while remaining simple enough to make detailed spectroscopic assignments and also to understand the mechanisms of multiphoton ionization/dissociation (MPID). It is known that the quantum yield and lifetime of fluorescence from p-DCB at the S1–S0 origin are 0.042 and 1.7 ns, respectively.3 Thus, p-DCB is a good test of the effectiveness of REMPI on a molecule that undergoes fairly rapid intersystem crossing. The specific REMPI ionization scheme that we employ is resonant two-photon ionization (R2PI also known as 1+1 REMPI) that is implemented either as one-color R2PI in which one laser performs both the excitation and ionization steps or two-color R2PI in which a second laser ionizes the electronically excited molecule. A high-resolution TOF MS of the reflectron type6–8 is used to provide mass analysis of...