The Gold Dihydride Molecule, AuH₂: Calculations of Structure, Stability, and Frequencies, and the Infrared Spectrum in Solid Hydrogen†

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The novel AuH₂ molecule has been formed in solid hydrogen by reactions of excited gold atoms from laser ablation and irradiation after thermal evaporation. The X²B₂ ground state of the AuH₂ molecule is separated by a 53 kcal/mol barrier from the Au(2D) + H₂ decomposition products and it is 27 kcal/mol more stable than Au(2D) + H₂. The bending modes of AuH₂, AuHD, and AuD₂ have been observed at 638.1, 570.6, and 457.0 cm⁻¹. These frequencies and the lack of infrared intensity in the stretching modes are in agreement with the results of relativistic ECP DFT, MP2, and CCD calculations. The computed bending potential energy surfaces of three electronic states of AuH₂ using CASCCF/MRSDCI methods reveal that there is a barrier for decomposition of the X²B₂ ground state to Au(2S) + H₂.

Introduction

Although gold is noble, excited gold is reactive; however, gold is the least reactive of the coinage metals. Despite this, AuH is the most stable of Group 11 monohydrides because of relativistic effects. The next gold hydride AuH₂ is computed to be a physically stable molecule and to have two unusual properties: AuH₂ is higher in energy than Au + H₂ and the Au-H stretching modes have low but the H-Au-H bending mode high infrared intensities. Gold trihydride was first predicted to be T-shaped, but two groups have calculated AuH₃ to be a transition state and stable as (H₂)AuH, which is the dihydrogen complex of AuH. In this laboratory, we have observed the (H₂)AuH complex in solid argon, neon, and hydrogen and found AuH₂ to be trapped as the (H₂)AuH₃ complex.

Gold(II) is an unusual oxidation state. Such compounds are rare, and many formally divalent gold complexes are in fact mixed valence Au(I)/Au(III) compounds. Most Au(II) compounds contain Au−Au bonds. However, the AuO molecule has been observed in two matrix isolation studies and the AuCl₂ molecule has been characterized by photodetachment of AuCl₂⁻ in a recent mass and photoelectron spectroscopic and theoretical investigation. The AuCl₂ molecule and AuCl₂⁻ anion are both stable to dissociation and the 4.60 ± 0.07 eV electron affinity measured for AuCl₂ attests the stability of AuCl₂⁻.

We report here another example of the close working relationship between quantum chemistry and matrix isolation spectroscopy, namely, AuH₂, a molecule formed in the excited Au(2P) and H₂ reaction, stabilized by relativistic effects, and separated by an energy barrier from its lower energy Au + H₂ decomposition products.

Schaefer was among the first theorists to address important experimental molecular subjects such as methylene using modern quantum chemistry. In particular, the Schaefer group established an effective working relationship with matrix isolation spectroscopy both in supporting earlier reports and in describing new molecular species for future experimental investigation.

Experimental and Theoretical Methods

Two experimental approaches were used to generate gold atoms for reaction with pure hydrogen, namely, laser ablation and thermal evaporation. The former employs 1064 nm from a YAG laser (10−20 mJ per 10-ns pulse at 10 Hz) focused onto a rotating gold target and the latter uses a shielded tungsten filament to evaporate gold at approximately 1900 °C. Both methods condense gold atoms with 2−3 millimoles of pure normal H₂ on substrates cooled to near 3.5 K by closed-cycle refrigerators. Infrared spectra are recorded, samples are subjected to filtered mercury arc radiation, annealing cycles, and more spectra are recorded.

Complementary density functional theory (DFT) calculations were performed using the Gaussian 98 program, the BPW91 and B3LYP density functionals, the 6-311++G(d,p) and

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6-311++G(3df, 3dp) basis sets\textsuperscript{29} for H and SDD and LANL2DZ effective core potentials and basis sets for gold as given in Gaussian 98.\textsuperscript{3,29} Vibrational frequencies were computed analytically from the potential energy surface in the harmonic approximation at the optimized structures: the calculated frequencies reported here are not scaled. The B3LYP functional and LANL2DZ pseudopotential have been recommended for Group 11 metal-containing molecules after comparison of results using several methods although the B3LYP functional works almost as well.\textsuperscript{36} The LANL2DZ basis is only of double-$\zeta$ quality and without 4f functions, and thus it is less accurate than the treatment described in the ensuing paragraph.

We have also computed both the potential energy surfaces and the vibrational frequencies using higher level methods. Recognizing that both relativistic effects\textsuperscript{31,32} and multireference techniques are important particularly for the study of the potential energy surfaces, we have employed a complete active space multiconfiguration self-consistent field method as a starting point. We used the relativistic effective core potential methods\textsuperscript{31} to represent the gold atom with 5d\textsuperscript{10}6s\textsuperscript{1} shells as the valence space replacing the remaining 68 electrons by RECPs of Ermler and co-workers. Since the first excited state of the gold atom arises from the 5d\textsuperscript{6}s\textsuperscript{2} configuration and the second excited state arises from the 5d\textsuperscript{10}6s\textsuperscript{2} configuration, it is important to include all 5d, 6s, and 6p orbitals in the active space of the CASSCF. Thus, our active space included five a\textsubscript{1} orbitals, three b\textsubscript{2} orbitals, two b\textsubscript{1} orbitals, and one a\textsubscript{2} orbital and all 13 valence electrons of AuH\textsubscript{2}. These 13 electrons were distributed in all possible ways among the active orbitals. We employed an extended (3s3p4d1f) basis set for the gold atom and a triple-$\zeta$ + polarization basis set for the hydrides.

We carried out multireference singles + doubles configuration interaction (MRSDCI) computations following the CASSCF. The MRSDCI computations again correlated all 13 electrons and included all configurations in the CASSCF with absolute coefficients more than or equal to 0.01. Thus, the MRSDCI typically included single + double excitations from 65 reference configurations which resulted in up to 3.4 million configurations. The MRSDCI thus included dynamical electron correlation effects. Since MRSDCI method is not size consistent, dissociation energies were computed carefully using a supermolecular computation in which the Au--H distances were set to 10 Å.

The vibrational frequencies were computed using the coupled cluster (CCD) method as well as the MP2 method in the same gold basis set and H aug-cc-pvtz basis sets. These frequencies together with the IR intensities were compared with both experiment and DFT levels of theory. All the CASSCF/MRSDCI computations were made using Balasubramanian\textsuperscript{31,32} modified version of ALCHEMY II codes,\textsuperscript{33} while the MP2 and CCD computations were made using the Gaussian package.\textsuperscript{25}

Results and Discussion

Gold and pure hydrogen reaction products will be reported using two methods of generating gold atoms. Gold dihydride calculations will be presented at the DFT/ECP and relativistic MP2, CCD, and CASSCF/MRSDCI levels of theory to support the identification of the novel AuH\textsubscript{2} molecule.

Laser Ablation. Experiments were first done with normal D\textsubscript{2} because it forms a more robust solid (FP 14.0 K)\textsuperscript{36} at the 3.5 K substrate temperature. The amount of gas deposited is 2.0–2.5 mmol, and the fraction actually condensed is less than for D\textsubscript{2} in these experiments. The major product absorptions are assigned to (H\textsubscript{2})AuH at 1198.6 cm\textsuperscript{-1} in the upper region\textsuperscript{5,10} and to AuD\textsubscript{2} at 457.0 cm\textsuperscript{-1} and (D\textsubscript{2})AuD at 434.8 cm\textsuperscript{-1} in the lower region. The lower region of the infrared spectrum is shown in Figure 1. Note that ultraviolet $\lambda > 240$ nm irradiation using a mercury arc lamp (Philips, 175 W) increased (D\textsubscript{2})AuD and AuD\textsubscript{2} absorptions. Final annealing to 9 K increased the 457.0 cm\textsuperscript{-1} band, which was first assigned\textsuperscript{5,10} to the b\textsubscript{1} D-Au-D bending mode of (D\textsubscript{2})AuD\textsubscript{3}, but is reassigned here to the bending mode of AuD\textsubscript{2}.

Investigations were subsequently done with normal H\textsubscript{2}, which forms a softer, more volatile solid (FP 14.5 K)\textsuperscript{46} at 3.5 K for 25 min. (a) Au + H\textsubscript{2}, (b) after $\lambda > 240$ nm photolysis, (c) after annealing to 6.4 K, (d) Au + HD, (e) after $\lambda > 240$ nm photolysis, (f) after annealing to 7.5 K, (g) Au + D\textsubscript{2}, (h) after $\lambda > 240$ nm photolysis, and (i) after annealing to 9.0 K.

![Figure 1. Infrared spectra in the 660–420 cm\textsuperscript{-1} region for laser-ablated Au co-deposited with pure hydrogen isotopic samples at 3.5 K for 25 min. (a) Au + H\textsubscript{2}, (b) after $\lambda > 240$ nm photolysis, (c) after annealing to 6.4 K, (d) Au + HD, (e) after $\lambda > 240$ nm photolysis, (f) after annealing to 7.5 K, (g) Au + D\textsubscript{2}, (h) after $\lambda > 240$ nm photolysis, and (i) after annealing to 9.0 K.](image)

Experimental. After several experiments, it became obvious from the brown-tan sample color that a higher gold deposition rate as measured by microbalance could be used for D\textsubscript{2} than for H\textsubscript{2} because of the greater condensation efficiency of D\textsubscript{2} compared to H\textsubscript{2}. Typically, co-deposited samples showed no reaction products in the infrared spectra.\textsuperscript{38} Because of the fortunate coincidence between the strong mercury emission line at 265 nm and the P\textsubscript{1/2} absorption of gold atoms measured in solid deuterium at 263 nm and solid hydrogen at 265 nm,\textsuperscript{38,39} selective resonance excitation of Au could be done using a dielectric notch filter and the simple Au(P\textsubscript{1/2}) + H\textsubscript{2} (solid, 3.5 K) reaction products could be observed and characterized. New infrared bands include strong 2164.2 cm\textsuperscript{-1} (H\textsubscript{2})AuH absorption in the upper region\textsuperscript{37} and weaker 638.1 cm\textsuperscript{-1} (H\textsubscript{2})AuH absorptions in the lower region for hydrogen.
The including of the first 4f function elongates the Au–H bond by 0.02 Å at the MP2 level and by 0.002–0.003 Å for the second 4f function at MP2 and CCD level. The vibrational frequencies are a bit more sensitive to the level of theory, and we consider the CCD method with gold (3s3p4d2f) basis set: the b1 frequency goes down as the level of theory goes up. The AuH2 bending mode is the only observable frequency and accurate prediction requires the f function.

CASSCF/MRSDCI Calculations of the Bending Potential Energy Surfaces. Figure 3 shows our computed potential energy surfaces of three AuH2 electronic states together with various dissociation limits. The X2B2 ground state diabatically dissociates into Au(2D) + H2 and forms a bent obtuse minimum with a bond angle near 129°. The 2S ground state of Au, on the other hand, has to surpass a huge barrier and forms only a linear 2Σ+ state that is considerably higher energy than its dissociation products. Thus, the ground state of Au is unreactive toward H2 as expected. In contrast to the silver atom, the first excited state of gold is 2P while it is 2D for Ag arising from the 4d95p1 configuration. The corresponding state of Au is 4.9 eV higher than the ground state, while the 2P state of Au is considerably lower than its dissociation products. This is a consequence of relativistic mass-velocity stabilization of the 6s orbital of Au and the corresponding destabilization of the 5d orbital. Thus, relativistic effects are important for gold.

The barrier to insert the Au(2D) atom into H2 is 53 kcal/mol as seen from Figure 3. However, the 2P state of Au is considerably higher than this barrier. When the Au atom is excited to the 2P state, it is very reactive because 2P Au also yields a 2Σ+ state, which undergoes avoided crossing with the 2B2 state arising from the 2D state of Au. The barrier in Figure 3 appears to arise from this avoided crossing. Moreover, the 2P state of Au also results in other states such as 2A1, which would cross the 2B2 curve. At the crossing point, spin–orbit coupling will
provide a strong channel for the formation of the X^2B_2 state. The barrier for the formation of the lowest 2A_1 state from 2S Au^+ + H_2 is 95 kcal/mol.

As seen from Figure 3, once the X^2B_2 state is formed through excitation of the gold atom to the 2P state, it will stay in the potential well as it has to surpass a large barrier to dissociate back to Au(2D)^+ + H_2. On the other hand, the crossing of the 2B_2 state with the 2A_1 state occurs at 65 deg. The crossing point is about 25 kcal/mol higher than the X^2B_2 minimum. Even if spin-orbit coupling between the two states is significant, the resulting barrier of 25 kcal/mol must be overcome before decomposition to Au(2S) and H_2. The spin-orbit effect between the two states cannot be large since the 2A_1 state has predominantly Au(5d_{10} 6s_1) character, and thus the spin-orbit effect must be small for the 2A_1 state. Although the 2B_2 state should be negligible because of the closed 5d_{10} shell of Au in the 2A_1 state. We thus conclude that X^2B_2 is quite a long-lived ground state: it is 27 kcal/mol more stable than Au(2D)^+ + H_2.

While the computed bending potential energy surface of the 2A_1 state here is close to the previous study, the 2B_2 surface differs especially near the dissociation and the minimum. This is primarily because the previous work did not include excitations from the 5d_{10} electrons of Au, and thus the surface in the previous study dissociates into Au(2D)^+ + H_2. While this is true for Ag, the AuH_2 2B_2 state dissociates differently when excitations from 5d_{10} are included at the CASSCF level.

Table 3 shows our computed MRSDCI geometries and energy separations of several electronic states of AuH_2. The MRSDCI geometries differ slightly from the MP2, CCSD, and DFT methods mainly because of the inclusion of multireferences in the MRSDCI while all other methods included only single

TABLE 3: The MRSDCI Properties of Electronic States of AuH_2

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<th>state</th>
<th>R_e (Å)</th>
<th>(\theta_e) (deg)</th>
<th>E(eV)</th>
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<tr>
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<td>4.75 (c)</td>
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reaction Mechanisms. The important reaction observed here is the insertion of Au(2P) into dihydrogen. The excess energy
Figure 5. Electron density contour plot of the AuH₃ ground state. The plot is consistent with a dative electron-transfer mechanism of dissociation, where Au transfers electronic charge to the hydrogen atoms and there is back transfer from the H₂₁s orbital to the Au(5d)⁵ orbital. Calculation at MP2 level with 3-21g(d) basis for gold and 6-31G(d) for hydrogen. The H₂Au molecule is located by lines intersecting at the Au center.

Finally, AuH₃ has a significant electron affinity (estimated as 68 kcal/mol by DFT), and the AuH₃⁻ anion has been observed in laser-ablation experiments.⁶

Conclusions

The novel AuH₃ molecule has been formed in solid hydrogen by reactions of excited gold atoms from laser ablation and thermal evaporation. The AuH₂ molecule is separated by a 53 kcal/mol barrier from Au(2D) + H₂ decomposition products. The bending modes of AuH₂, AuHD, and AuD₂ have been observed at 638.1, 570.6, and 457.0 cm⁻¹. These frequencies and the lack of infrared intensity in the stretching modes are in agreement with the results of relativistic ECP, DFT, MP2, and CCDD calculations. We find that the X2B₁ state of AuH₂ has a stability of 27 kcal/mol relative to Au(2D) + H₂ and is expected to be long-lived in this state because of a large barrier to dissociation. Unlike the X₂B₁ state of AgH₂ which dissociates into Ag(2P) + H₂, the corresponding state of AuH₂ dissociates into Au(2D) + H₂. This is a consequence of the fact that the first excited state of Au atom is 2D, while it is 2P for silver, which is attributed to relativistic stabilization of the 6s orbital of Au and destabilization of the 5d orbital.

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References and Notes


(34) The major authors of ALCHEMY II are B. Liu and M. Yoshimine.


