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Communications to the Editor

Gold Hydrides AuH and $(H_2)AuH$ and the AuH_3 Transition State Stabilized in $(H_2)AuH_3$: Infrared Spectra and DFT Calculations

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Gold hydride is a stable diatomic molecule which has been characterized by electronic band spectroscopy in the gas phase,[1] but there is no evidence for stable, solid gold hydrides.[2] The hypothetical AuH_3 molecule has been the subject of several recent theoretical investigations.[3−6] The AuH_3 species can be T-shaped or form the Y-shaped $(H_2)AuH$ complex. Very recent calculations show that the former is a transition state and the latter is a stable complex.[5,6] Hence, it should be possible to prepare $(H_2)AuH$ from AuH in a solid matrix, and accordingly, we report the first experimental evidence for higher gold hydrides. Gold is also interesting because it forms unusually strong chemical bonds due to relativistic effects,[3,7] such that Au^+ is predicted to bind noble gas atoms.[8]

Laser-ablated gold atoms were reacted with H_2, D_2, and HD in excess argon and neon and with pure deuterium during condensation at 3.5 K using methods described previously for hafnium, platinum, and palladium hydrides and gold carbonyls.[9−13] Infrared spectra were recorded, samples were annealed and irradiated, and more spectra were recorded. Complementary DFT calculations were performed using the Gaussian 98 program, BPW91 and B3LYP density functionals, 6-311++G(d,p) basis, and SDD pseudopotential.[14−18]

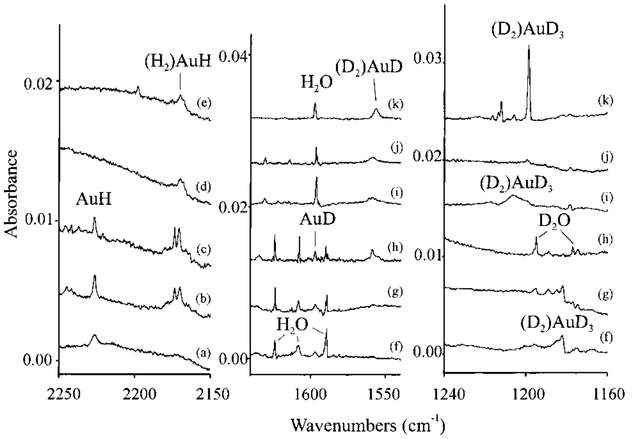

Figure 1. Infrared spectra in the 2250−2150, 1640−1540, and 1240−1160 cm^{-1} regions for laser-ablated gold atoms co-deposited with hydrogen and deuterium at 3.5 K: (a) 5% H_2 in argon deposited for 70 min, (b) after annealing to 15 K, (c) after annealing to 25 K, (d) 5% H_2 in neon deposited for 60 min, (e) after annealing to 7 K, (f) 5% D_2 in argon deposited for 60 min, (g) after annealing to 15 K, (h) after annealing to 25 K, (i) 2% D_2 in neon deposited for 60 min, (j) after 10 K annealing and broadband photolysis, (k) pure deuterium deposited for 25 min.

Co-deposition of laser-ablated gold atoms with H_2 in excess argon at 3.5 K produces a weak 2226.6 cm^{-1} band that increases on annealing to 15 K and then decreases on 25 K annealing while a 2173.6, 2170.6 cm^{-1} doublet appears and increases (Figure 1, Table 1). These bands shift to 1597.2 and 1559.3 cm^{-1} with D_2. The 2226.6 and 1597.2 cm^{-1} bands are invariant with the HD reagent, which shows that one H(D) is involved, and their 1.394 H/D frequency ratio is appropriate for a heavy metal hydride vibration. These bands, slightly blue shifted from the 2218.8 and 1591.7 cm^{-1} fundamentals deduced for AuH and AuD from electronic spectra,[1] are assigned to AuH and AuD in solid argon.

For calibration, our BPW91/6-311++G(d,p)/SDD calculation predicts a 2250 cm^{-1} fundamental and a 1.542 Å bond length for AuH, which are in excellent agreement with the observed values (1.524 Å).[1]

Using $H_2 + D_2$ mixtures, the 2226.6 and 1597.2 cm^{-1} bands for AuH and AuD are unchanged, but new bands appear at 2166.2 and 1564.0 cm^{-1}, which demonstrate a small secondary isotope effect for the 2173.6, 2170.6, and 1559.3 cm^{-1} bands and show that more than one hydrogen is involved in the latter absorptions. This species increases at the expense of AuH on annealing to allow diffusion of H_2, and hence, the $(H_2)AuH$ complex must be considered. In neon AuH is not trapped, but weak 2170.1, 2167.9 cm^{-1} H_2 and 1559.0 cm^{-1} D_2 counterparts of the above bands are produced. A stronger 1556.5 cm^{-1} band is observed in pure deuterium at 3.5 K (Figure 1k) where this band and associated 1361.6, 939.6, 434.8 cm^{-1} absorptions double on broadband photolysis.

DFT calculations were performed for $(H_2)AuH$ to determine the frequencies and intensities relative to AuH and the corresponding isotopic and mixed isotopic frequencies. Our calculation (Table 2) predicts the strongest (Au−H) mode 56.8 cm^{-1} below

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Table 1. Infrared Absorptions (cm^{-1}) Observed from Reactions of Gold Atoms and Dihydrogen in Excess Argon, Neon, and Deuterium

argon		neon		deuterium	
H_2	D_2	H_2	D_2	D_2	identification
2226.6					AuH
	1597.2				AuD
2173.6,		2170.1,			$(H_2)AuH$
2170.6		2167.9			
	1559.3		1559.0	1556.5	$(D_2)AuD$
2076	1485	2083	1498		Au_xH, Au_xD
2037.7	2037.7	2053.2	2053.2	2051	AuCO
		2025.5	2025.5		Au_3
1642		1684			$(H_2)AuH_3$
	1182		1207	1198.6	$(D_2)AuD_3$
				1361.6	$(D_2)AuD$
				939.6	$(D_2)AuD$
				457.0	$(D_2)AuD_3$
				434.8	$(D_2)AuD$

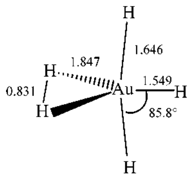
Table 2. Structures and Frequencies Calculated at the BPW91/6-311++G(d,p)/SDD Level for Gold Hydrides[a]

species	state	structure (Å, deg)	frequencies, cm^{-1} (intensities, km/mol)
AuH	$^1\Sigma^+$	1.542	2250.5 (4)
AuH_2	$^2B_2$	1.619, 129.1	2003.8 (a_1, 1), 1758.0 (b_1, 1), 666.5 (a_1, 25)
AuH_3	$^1A_1$	1.519,[b] 91.9, 1.650, 176.2	2405.5 (a_1, 23), 2066.8 (a_1, 0), 1846.1 (b_1, 634), 897.1 (a_1, 5), 854.3 (b_2, 6), 414.2 i (b_1, 247)
$(H_2)AuH$	$^1A_1$	1.576, 0.807, 1.863	3531.2 (a_1, 0), 2192.4 (a_1, 16),[c] 1268.9 (b_1, 12),[c] 786.1 (a_1, 2), 627.2 (b_2, 2), 568.8 (b_1, 6)[c]
$(H_2)AuH_3$	$^1A_1$	0.831, 1.847, 1.549,[b] 85.8, 1.646, 94.2[d]	3215.1 (a_1, 6), 2348.4 (a_1, 1), 2080.0 (a_1, 0), 1865.1 (b_1, 485),[e] 1440.8 (b_1, 16), 910.2 (a_1, 10), 824.3 (b_2, 3), 765.2 (a_1, 2), 696.3 (b_1, 139),[e] 673.1 (b_2, 3), 564.3 (a_2, 0), 491.9 (b_1, 13)

[a] All C_{2v} symmetry but AuH. [b] Unique shorter Au−H bond. [c] Deuterium counterparts are 1553.9, 898.5, 404.6 cm^{-1}, respectively. [d] Airplane structure with $(H_2)Au$ perpendicular to AuH_3 plane. [e] Deuterium counterparts are 1325.6 and 493.7 cm^{-1}.

AuH and with greater infrared intensity. The 2173.6 and 2170.6 cm^{-1} bands 53.0−56.0 cm^{-1} below AuH in solid argon are assigned accordingly. The increased yield of $(D_2)AuD$ in pure deuterium allows assignment of new 1556.5, 939.6, and 434.8 cm^{-1} bands to the strongest a_1, b_1, and b_1 fundamentals, respectively. The weaker 1361.6 cm^{-1} absorption is due to a combination band (939.6 + 434.8 = 1374.4 cm^{-1}), and its observation supports these vibrational assignments. Given that $(H_2)AuH$ is a dihydrogen−metal hydride complex, the BPW91 calculations predict the frequencies and relative band intensities very well. In addition, the strongest absorptions of $(D_2)AuH$ and $(H_2)AuD$ are calculated 6.5 cm^{-1} lower than $(H_2)AuH$ and 5.4 cm^{-1} higher than $(D_2)AuD$, respectively, in excellent agreement with our observed values.

The strongest band calculated for AuH_3 at 1846 cm^{-1} (1756 cm^{-1} at the MP2 level)[5] shifts to 1317 cm^{-1} for AuD_3 (1253 cm^{-1} at the MP2 level).[5] The weaker 1642 and 1182 cm^{-1} argon, 1684 and 1207 cm^{-1} neon, and very strong 1198.6 cm^{-1} deuterium matrix bands match these predictions reasonably well, considering the anticipated accuracy of such frequency calculations. However, AuH_3 is a transition state with an imaginary b_1 bending frequency though which AuH_3 can rearrange to the more stable $(H_2)AuH$ structure.[6] Computations were done to locate a stable complex without an imaginary b_1 frequency: Ne_2AuH_3 dissociated but $(H_2)AuH_3$ is stable and retains essentially the same structure and strong characteristic antisymmetric b_1 Au−H stretching fundamental as AuH_3 (Table 2). Accordingly, the above bands can be assigned to the $(H_2)AuH_3$ and $(D_2)AuD_3$ complexes. In addition, the $(D_2)AuD_3$ complex has a real b_1 bending frequency computed at 493.7 cm^{-1} and observed here at 457.0 cm^{-1}, which are in very good agreement. This complex is bound by 8−9 kcal/mol (BPW91 and B3LYP). Hence, H_2 effectively stabilizes AuH_3 by changing its b_1 bending potential in the $(H_2)AuH_3$ complex. The $(H_2)AuH_3$ species is similar to the $(H_2)RhH_3$ complex calculated and observed for rhodium.[4,19] We find no evidence for Au_2D_6 based on its computed spectrum.[5]



Laser-ablated gold atoms have sufficient excess energy[20] to promote the endothermic (29.0 kcal/mol)[1] reaction 1. The small growth of AuH on first annealing is due to atom combination as H(D) atoms are manifested in trace quantities of other species.[21] The $(H_2)AuH$ complex is formed spontaneously in exothermic (−13 kcal/mol at CCSD(T) level)[5] reaction 2 on annealing the argon matrix to allow diffusion of H_2 (Figure 1).

$$Au(^2S) + H_2(^1\Sigma_g^{\ +}) \rightarrow AuH(^1\Sigma^+) + H(^2S) \qquad (1)$$

$$H_2 + AuH \rightarrow (H_2)AuH \qquad (2)$$

$$AuH^* + H_2 \rightarrow (AuH_3)^* \rightarrow (H_2)AuH \qquad (3)$$

$$H_2 + (AuH_3)^* \rightarrow (H_2)AuH_3 \qquad (4)$$

Collision of energetic AuH molecules from reaction 1 and H_2 during sample deposition can form the AuH_3 transition state (26−28 kcal/mol higher than $(H_2)AuH$ at the CCSD(T) level),[5,6] reaction 3,which would rearrange to $(H_2)AuH$ if not stabilized by an additional dihydrogen in the trihydride complex, reaction 4. It is therefore clear why the yield of $(D_2)AuD_3$ is relatively high on deposition in the pure deuterium matrix experiments. The contrasting yields of the three gold hydride species in argon, neon, and deuterium matrix experiments depend on the condensation rate at 3.5 K and the effective concentration of the $H_2(D_2)$ reagent. In argon AuH is isolated from H_2 on deposition but not in the more slowly condensing neon medium. Deuterium serves as both a reactive and an inert matrix to produce and stabilize gold deuteride complexes with little perturbation.[22]

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