Group 11 Hydrides

Gold Is Noble but Gold Hydride Anions Are Stable**

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Gold is the classic noble metal as shown by its use for valued ornaments through the ages. Gold does not oxidize nor adsorb most molecules from the gas phase.[1] However, nanometer-sized gold particles on oxide supports function as catalysts.[2–5] One reason offered for making these clusters of gold atoms catalytically active is partial electron transfer from the support surface to the gold cluster.[3] This suggests that extra electron density might lead to greater stability for small gold-containing molecules in general and gold hydrides in particular. Hence, hydrogen on gold clusters will enhance the charge transfer and may enable gold clusters to function as hydrogenation catalysts.

In the course of a matrix-isolation investigation of gold, silver, and copper (Group 11) hydrides,[6] we discovered the coinage metal dihydride anions, which have unique properties. Our density functional theory (DFT) calculations show that these MH_2^- ions are very stable, but the corresponding neutral MH_2 molecules, which have also been computed by others,[7–11] are unstable relative to M and H_2. Four late first-row transition metal dihydride anions (MnH_2^- through NiH_2^-) have been characterized by photoelectron spectroscopy (PES), but the neutral molecules are stable[12] in contrast to CuH_2. Although there are many examples of homoleptic transition metal hydride anions, the only known Group 11 hydride anion is CuH_4^{3-} in solid Ba/Cu alloys under H_2 pressure.[13]

In contrast, the chemistry of copper(I), silver(I), and gold(I) halide complexes is well-known.[14] The $CuCl_2^-$ and $CuBr_2^-$ ions have been characterized recently by PES in the gas phase and by electronic structure calculations.[15] The $AgCl_2^-$ ion has been prepared, and the linear structure determined by X-ray diffraction.[16] A very recent investigation of gas-phase AuX_2^- ($X = Cl$, Br) and AuX_4^- ions from electrospray mass spectrometry of AuX solutions has determined electron-detachment energies.[17] In addition, Au^{III} compounds are stable, and Au^{I} complexes disproportionate to Au^{III} compounds and gold. Accordingly, the AuX_2^- ions can be photooxidized to AuX_4^- in the presence of electron acceptors.[18] Finally, the trend in observed vibrational force constants $k(Au{-}X^-) > k(Cu{-}X^-) > k(Ag{-}X^-)$ and the stability of Au^{III} compounds have been explained by relativistic effects for heavy metals.[11,19]

In spite of extensive chemistry for the Group 11 metal dihalide complexes, the corresponding metal dihydrides are unknown. A theoretical study, however, predicted that AuH will add H^- to form AuH_2^-.[11] This is mechanistically significant as the neutral MH_2 dihydrides are higher in energy than M + H_2,[9,10] and are thus unstable, in contrast to the corresponding MX_2 dihalides.[15,17] Calculations have been performed for CuH_2, AgH_2, and AuH_2 and the energies for these bent $^2B_2$ ground state molecules range from 6 to 43 to 20 kcal mol^{-1}, respectively higher than the corresponding M + H_2 reagents although dissociation barriers are found.[9,10] Hence, preparation of the MH_2^- ions will be experimentally difficult as formation of the MH_2 molecules requires excited metal atom reactions.

Our investigation of Group 11 hydrides involves the reaction of energetic laser-ablated metal atoms and H_2 in excess argon, neon, and hydrogen. All of the Group 11 metal hydrides, MH, and dihydrogen complexes, $(H_2)MH$, have been observed by matrix infrared spectroscopy and confirmed by comparison to DFT calculated frequencies.[6,20] We report here the first observation of the stable linear coinage metal MH_2^- ion complexes and the square-planar AuH_4^- ion, and supporting DFT calculations of their structures and vibrational frequencies. Earlier calculations show that both AuH_2^- and AuH_4^- are stabilized by relativistic effects.[11,19]

Laser-ablated gold, silver, and copper atoms were allowed to react with H_2, D_2, and HD in excess argon and neon, and with pure H_2, HD, and D_2 during condensation at 3.5 K using methods described previously for gold carbonyls and chromium hydrides.[21–23] IR spectra were recorded, samples were

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annealed, irradiated, and more spectra were recorded. Complementary DFT calculations were performed by using the Gaussian 98 program, the BPW91 density functional, 6-311++G(d,p) and 6-311G(3df,3pd) basis sets for hydrogen, and SDD pseudopotentials for the metal atoms.[24] The BPW91 functional has been recommended for copper, silver, and gold compounds.[25]

Laser-ablated gold experiments used as low laser energy as possible to trap charged species in addition to neutral hydride products. Energized gold atom reactions with pure hydrogen gave several new IR product absorptions including a strong 2164.0 cm^{-1} $(H_2)AuH$ band (not shown) and the 1661.5 cm^{-1} $(H_2)AuH_3$ band[6] and weaker 1676.4 (AuH_4^-) and 1636.0 cm^{-1} (AuH_2^-) absorptions (Figure 1). Although the latter bands are weak, they are reproduced in several experiments (the graphics program does not do justice to the original spectra). Annealing to 5.3 K decreased the band at 1676.4 cm^{-1} and destroyed the peak at 1636.0 cm^{-1}. Irradiation ($\lambda > 290$ nm) produced a new matrix site absorption at 1678.8 cm^{-1}, increased the $(H_2)AuH_3$ absorption at 1661.5 cm^{-1}, and formed a weaker photochemical site at 1666.8 cm^{-1}.

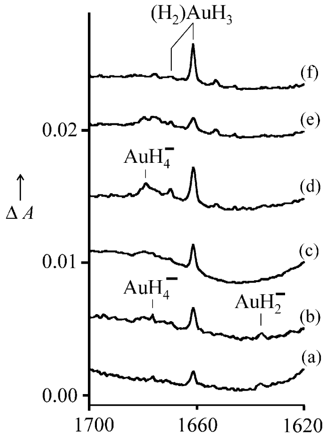

Figure 1. IR spectra of gold hydrides. a) Au + H_2 deposited for 12 min, b) Au + H_2 deposited for 12 min more, c) after annealing to 5.3 K, d) after photolysis at $\lambda > 290$ nm, e) after photolysis at $\lambda > 240$ nm, and f) after annealing to 6.0 K.

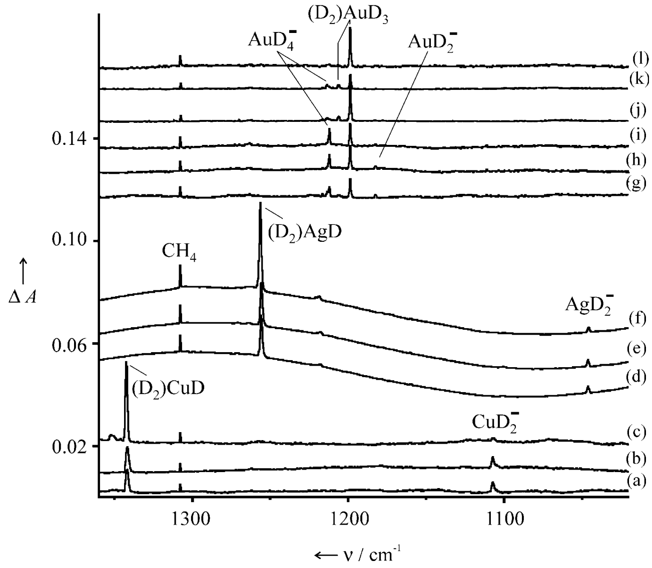

Figure 2. IR spectra of laser-ablated Cu, Ag, and Au codeposited with pure deuterium at 3.5 K for 30 min. a) Cu + D_2, b) after annealing to 7.0 K, c) after photolysis at $\lambda > 240$ nm, d) Ag + D_2, e) after annealing to 7.0 K, f) after photolysis at $\lambda > 240$ nm, g) Au + D_2, h) after annealing to 7.3 K, i) after photolysis at $\lambda > 530$ nm, j) after photolysis at $\lambda > 290$ nm, k) after photolysis at $\lambda > 240$ nm, and l) after annealing to 8.0 K.

A pure deuterium experiment with gold is illustrated in Figure 2 in which AgD_2^- and CuD_2^- spectra are also compared. The strong 1556.5 cm^{-1} $(D_2)AuD$ absorption (not shown) and 1198.6 cm^{-1} $(D_2)AuD_3$ complex band are observed as before,[20] but the weaker bands at 1212.2 (AuD_4^-) and 1182.3 cm^{-1} (AuD_2^-) identified here for the first time are enhanced by using lower laser energy. Note that the AuD_2^- and AuD_4^- bands are three times stronger than the hydrogen counterparts, and they validate the hydrogen matrix observations with proper H/D isotopic frequency ratios. This larger deuteride yield is due to the greater photochemical stability of the gold deuteride anions as well as the thermal stability of solid D_2 itself (F.P. 18.6 K) as compared to solid H_2 (F.P. 14.0 K). Photolysis ($\lambda > 530$ nm) decreased the weaker band at 1182.3 cm^{-1} and increased the band at 1212.2 cm^{-1} (Figure 2i). The weakest hydrogen and deuterium matrix bands at 1636.0 and 1182.3 cm^{-1}, respectively, are isotopic counterparts: their frequency ratio of 1.384 indicates a primarily H(D) atomic mass vibration. For example the $(H_2)AuH/(D_2)AuD$ isotopic Au-H/Au-D frequency ratio is 1.390, which also includes the effect of anharmonicity.[6] Subsequent irradiation ($\lambda > 290$ nm) increased the major 1198.6 cm^{-1} and minor 1205.9 cm^{-1} $(D_2)AuD_3$ absorptions and produced AuD_4^- at 1213.7 cm^{-1}, and full arc photolysis ($\lambda > 240$ nm) decreased the $(D_2)AuD_3$ bands and increased the 1213.7 cm^{-1} AuD_4^- absorption (Figure 2j,k). Finally, mixed isotopic experiments provide diagnostic information for the stronger bands at 1676.4 and 1212.2 cm^{-1} with an Au–H/Au–D ratio of 1.383. Two experiments with pure H_2 + D_2 gave essentially the same positions for the new band, 1681.3 and 1211.3 cm^{-1} (*trans*-$AuH_2D_2^-$), but pure HD produced distinctly different 1840.4 and 1280.4 cm^{-1} absorptions (*cis*-$AuH_2D_2^-$) that showed the same photolysis behavior as the 1676.4 and 1212.2 cm^{-1} bands (Figure 3), hence they are isotopic counterparts. Stronger bands were observed for neutral (HD)AuH, (HD)AuD, (HD)AuHDH, and (HD)AuHDD species. Table 1 summarizes the observed absorptions.

Very recent resonance photoexcitation (265 nm) of Au to the ^2P state in solid hydrogen (and deuterium) gave strong $(H_2)AuH[(D_2)AuD]$ absorptions with weak 1666.8 (1205.9) cm^{-1} photochemical $(H_2)AuH_3[(D_2)AuD_3]$ site bands, and no anion absorptions.[6] This complementary experiment produced only the neutral species observed with laser-ablated gold atoms.

Our BPW91 calculation predicts a linear centrosymmetric AuH_2^- anion, in agreement with the results obtained by

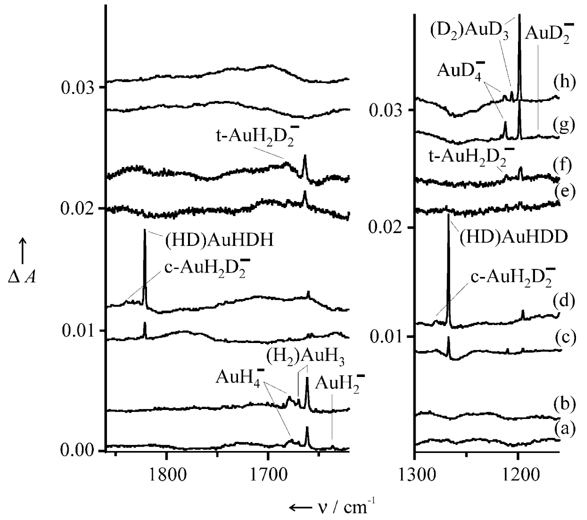

Figure 3. IR spectra in the 1860–1620 and 1300–1160 cm^{-1} regions for laser-ablated Au co-deposited with pure hydrogen isotopic samples at 3.5 K and after photolysis. a) Au + H_2, b) photolysis at $\lambda > 290$ nm, c) Au + HD, d) photolysis at $\lambda > 290$ nm, e) Au + 50% H_2 + 50% D_2, f) photolysis at $\lambda > 290$ nm, g) Au + D_2, and h) photolysis at $\lambda > 290$ nm.

Table 2: Comparison of frequencies [cm^{-1}] observed (solid H_2, HD, D_2 or H_2 + D_2) and calculated (BPW91/6-311++G(d,p)/SDD) for coinage metal hydride anions.

Observed	Calculated	Anion
1586.7	1601 (1611)[c]	$HCuD^-$
1517.8	1501 (1507)	CuH_2^-
1137.6	1122 (1128)	$HCuD^-$
1107.3	1078 (1083)	CuD_2^-
1442.4	1445 (1440)	AgH_2^-
1045.9	1031 (1027)	AgD_2^-
1636.0	1642 (1640)	AuH_2^-
1182.3	1167 (1166)	AuD_2^-
1840.4	1906 (1904)	*cis*-$AuH_2D_2^-$
1681.3[a]	1724 (1714)	*trans*-$AuH_2D_2^-$
1676.4	1724 (1714)	AuH_4^-
1280.4	1303 (1297)	*cis*-$AuH_2D_2^-$
1212.0	1226 (1219)	AuD_4^-
1211.3[b]	1227 (1220)	*trans*-$AuH_2D_2^-$

[a] In mixed H_2 + D_2 experiments, this product absorption represents AuH_4^- and *trans*-$AuH_2D_2^-$. [b] In mixed H_2 + D_2 experiments, this product absorption represents AuD_4^- and *trans*-$AuH_2D_2^-$. [c] Calculated by using a larger 6-311++G(3df, 3pd) basis set for H.

Schwerdtfeger et al.,[11] with a very strong antisymmetric (σ_u) mode at 1642 cm^{-1} and AuD_2^- counterpart at 1167 cm^{-1}. Table 2 compares the calculated and observed frequencies: it is perhaps amazing how close DFT in the harmonic approximation predicts the observed anharmonic frequencies of gold dihydride anions. (The AuH_2^- frequency is calculated 0.3% high and the AuD_2^- mode 1.3% low). These small deviations between calculated and observed AuH_2^- and AuD_2^- frequencies are different because we are comparing calculated harmonic and observed anharmonic frequencies, and hydrogen vibrations are more anharmonic than deuterium motions. On the basis of this excellent agreement between calculated and observed frequencies, the band at 1636.0 cm^{-1} is assigned

Table 1: IR absorptions [cm^{-1}] observed from laser-ablated copper, silver, and gold atom reactions with dihydrogen in excess argon, neon, and hydrogen.

Argon			Neon			Hydrogen			Identification
H_2	HD	D_2	H_2	HD	D_2	H_2	HD	D_2	
1879.8	1879.8		1889.9	1889.9					CuH
	1354.9	1354.9		1362.2	1362.2				CuD
1862.5	1862.7		1869.1	1869.1		1861.4	1865.5		$(H_2)CuH$
	1343.0	1343.2		1346.4	1344.9		1345.4	1341.6	$(D_2)CuD$
1497.2	1566.9		1529.5			1517.8	1586.7		CuH_2^-
	1122.7	1089.4		1158.3	1116.5		1137.6	1107.3	CuD_2^-
1717.0	1717.0					1691.8			AgH
	1233.8	1233.8							AgD
1746.5	1748.2		1750.8			1742.6	1748.6		$(H_2)AgH$
	1256.9	1257.6			1264.3		1255.4	1255.7	$(D_2)AgD$
1427.5	1496.8		1460			1442.4			AgH_2^-
	1068.9	1032.3			1053			1045.9	AgD_2^-
2226.6									AuH
		1597.2							AuD
2173.6, 2170.6			2170.1, 2167.9			2164.0			$(H_2)AuH$
		1559.3			1559.0			1556.5	$(D_2)AuD$
						1678.8			AuH_4^- site
						1676.4	1840.4		AuH_4^-
						1666.8			$(H_2)AuH_3$ site
1642				1831		1661.5	1821		$(H_2)AuH_3$
			1638.6			1636.0			AuH_2^-
								1213.7	AuD_4^- site
							1280.4	1212.2	AuD_4^-
								1205.9	$(D_2)AuD_3$ site
		1182		1275	1207		1257	1198.6	$(D_2)AuD_3$
								1182.3	AuD_2^-

to AuH_2^- in solid hydrogen, and the band at 1182.3 cm^{-1} to AuD_2^- in solid deuterium.

The $Au^IH_2^-$ ion is a very photosensitive species in solid hydrogen in part because Au^{III} compounds are more stable for gold.[19] Accordingly laser-ablated gold with pure H_2 and pure D_2 favor the bands at 1676.4 and 1212.2 cm^{-1} (frequency ratio 1.383), which are assigned to AuH_4^- and AuD_4^- formed during deposition: the photogenerated counterparts at 1678.8 and 1213.6 cm^{-1} (ratio 1.383) are due to AuH_4^- and AuD_4^- in a slightly different solid hydrogen matrix environment created by a different mechanism (see below). Photolysis (530 nm) appears to convert AuD_2^- into AuD_4^- in solid D_2. Our BPW91 calculation predicts very strong 1724 and 1226 cm^{-1} antisymmetric stretching (e_u) modes for the square-planar species (Figure 4), which are 2.9% and 1.2% higher than the observed absorptions and in the range of agreement found for DFT frequency calculations.[25] When the larger basis set with more polarization functions is employed the calculated frequencies, 1714 and 1219 cm^{-1}, are closer to the observed absorptions. Our DFT bond length (1.653 Å) is nearly the same (1.652 Å) as computed previously[19] for AuH_4^-. However, confirmation comes from H_2 + D_2 and HD isotopic substitution. Unlike the case for a tetrahedral product, such as the Group 3 and 13 MH_4^- ions[26,27] where the same $MH_2D_2^-$ species are produced from H_2 + D_2 and 2HD, the square-planar AuH_4^- ion has *cis* and *trans* dideuterio isomers. Hence, H_2 must add across linear H-Au-H$^-$ *without* going through a tetrahedral intermediate. Our calculations show the *trans* product to be spectroscopically similar to the pure isotopic species because the observed vibration is an antisymmetric stretching mode of a linear (H-Au-H) linkage and the bonding of an orthogonal (crossed) D-Au-D linkage makes little difference. However, the *cis* product with linear H-Au-D vibrations is substantially different, as is observed for the HD reaction. We calculate the strong *cis*-$AuH_2D_2^-$ ion absorptions at 1906 and 1303 cm^{-1}, which are higher than the strong AuH_4^- and AuD_4^- modes, respectively, and we observe these bands at 1840.4 and 1280.4 cm^{-1}, which are in very good agreement (calculated 3.6% and 1.8% high).

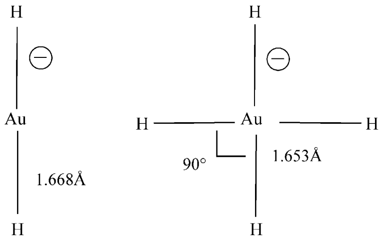

Figure 4. Structures calculated (with BPW91/6-311++G(d,p)/SDD) for AuH_2^- and AuH_4^-.

As will be discussed later, the HD reaction proceeds first to give the HAuD molecule, then electron capture occurs to give the linear (H-Au-D)$^-$ ion, which adds another HD across the gold center. Hence, the reactions of 2HD and H_2 + D_2 give different *cis*-$AuH_2D_2^-$ and *trans*-$AuH_2D_2^-$ ions, respectively.

Analogous weaker bands were observed with laser-ablated silver at 1460 and 1050 cm^{-1} in excess neon, at 1442.4 and 1045.9 cm^{-1} in pure solid H_2 and solid D_2 (Figure 2), and at 1427.5 and 1032.3 cm^{-1} in excess argon. These pairs exhibit H/D ratios of 1.383 ± 0.004 and destruction by $\lambda > 240$ nm irradiation. For comparison the $(H_2)AgH$/$(D_2)AgD$ ratio is 1.388.[6] A very strong σ_u mode is computed for AgH_2^- at 1445 cm^{-1}. Similar agreement is found for $AgHD^-$ in argon, in which the calculated Ag–H and Ag–D absorptions at 1543.2 and 1076.9 cm^{-1} are 6.8 and 4.4% higher than the calculated σ_u modes of AgH_2^- and AgD_2^-, and the observed bands are 4.9 and 3.5% higher (Table 1). These differences between calculated and observed frequencies of 1.9 and 0.9% strongly support our identification of AgH_2^-.

IR spectra for laser-ablated Cu reaction products with H_2 and D_2 in excess argon give new bands at 1879.8, 1862.8, and 1497.2 cm^{-1} in the Cu–H stretching region and at 1354.9, 1343.2, and 1089.4 cm^{-1} in the Cu–D region. Annealing to 15 K slightly increases all of these absorptions, but photolysis at $\lambda > 240$ nm increases the first, decreases the second, and destroys the third band in each region. A subsequent annealing to 20 K sharpens the first, increases the second, and has no regenerative effect on the third band. The use of HD as the reagent reveals important diagnostic information. First, the bands at 1879.8 and 1354.9 cm^{-1} are unchanged, but the bands at 1862.5 and 1343.2 cm^{-1} are each shifted by 0.2 cm^{-1}, and the absorptions at 1497.2 and 1089.4 cm^{-1} are observed along with new stronger bands at 1566.9 and 1122.7 cm^{-1} (Table 1).

The unshifted bands at 1879.8 and 1354.9 cm^{-1} are due to CuH and CuD in solid argon[6] and are blue shifted 13.5 and 8.2 cm^{-1} from the gas-phase values[28] owing to matrix repulsion as observed for AuH and AuD.[20] The slightly shifted bands at 1862.8 1343.2 cm^{-1} exhibit the same H/D ratio of 1.387 as CuH/CuD and are assigned to the $(H_2)CuH$ and $(D_2)CuD$ complexes. In pure solid H_2 and D_2, the CuH and CuD molecules are not observed, but the $(H_2)CuH$ and $(D_2)CuD$ complex bands are stronger at 1861.4 and 1341.6 cm^{-1}, and weaker associated H–H and D–D stretching modes occur at 3566.6 and 2582.0 cm^{-1}. The Cu–H/Cu–D ratio in these complexes is 1.387. The Cu and pure D_2 spectrum is illustrated in Figure 2. The photosensitive bands at 1497.2 and 1089.4 cm^{-1} are observed at 1517.8 and 1107.3 cm^{-1} in solid H_2 and D_2, and at 1529.5 and 1116.5 cm^{-1} in excess neon (Table 1). These band pairs exhibit H/D ratios of 1.372 ± 0.002 and are too low in frequency for a neutral hydride. The CuH_2 molecule stretching frequencies are computed in the 1600–1800 cm^{-1} region,[6] and since this molecule is higher in energy than Cu + H_2, it is not expected to survive the photochemical conditions required for formation.[29]

Therefore, the simple CuH_2^- ion comes to mind. Our DFT calculations produce a very intense antisymmetric stretching (σ_u) mode at 1501.0 cm^{-1} for the linear CuH_2^- ion, which is in excellent agreement with the present observations. Since the unobserved symmetric stretching (σ_g) mode is higher in frequency than the σ_u mode, the $HCuD^-$ ion is calculated to have Cu–H and Cu–D stretching absorptions at 1600.7 and 1121.9 cm^{-1}, which are 6.6 and 4.1 % higher than the σ_u modes calculated for CuH_2^- and CuD_2^-. The observed $HCuD^-$ bands are 4.7 and 3.1 % higher (argon matrix). The differences, 1.9 % and 1.0 %, show close agreement between calculated and observed frequencies for CuH_2^-, $CuHD^-$, and CuD_2^- and confirm our identification of CuH_2^-. The Ar_nH^+ and Ar_nD^+ ions provide for charge balance in the argon matrix.[30]

It is interesting to compare the new Group 11 dihydride anions with the isoelectronic Group 12 dihydrides, which have been observed by matrix isolation spectroscopy.[31,32] The strong antisymmetric H-M-H stretching fundamentals (1870, 1753, and 1896 cm^{-1} for M = Zn, Cd, and Hg, respectively, in solid argon), are considerably higher than those for this mode for the MH_2^- ions (1518, 1442, and 1636 cm^{-1} for M = Cu, Ag, and Au in solid hydrogen), but both data sets follow the same vertical family relationship in the periodic table. Finally, the results for our AuH_4^- ion isolated in solid hydrogen may be compared with recent computations for the square-planar isoelectronic HgH_4 molecule,[33] which finds the strong mode at 1959 cm^{-1}, and with the known square-planar PtH_4^{2-} dianion combined with sodium cations in the solid compound, which has a comparable bond length of 1.639 Å.[34]

The straightforward reaction mechanism includes the formation of MH molecules in endothermic[28] reaction (1)

$$M(^2S) + H_2(^1\Sigma_g^+) \rightarrow MH(^1\Sigma^+) + H(^2S) \quad (\Delta E = 38,\ 52,\ 32\,\text{kcal mol}^{-1})^{[36]} \tag{1}$$

driven by the excess electronic/kinetic energy in the laser-ablated metal atoms.[35] Electrons produced in the ablation process[21,22] are captured by hydrogen to form hydride anions for exothermic reaction with the MH molecules to make the stable linear $M^IH_2^-$ ions, reactions (2) and (3). Our computed

$$H(^2S) + e^- \rightarrow H^-\ (^1S) \quad (\Delta E = -17\,\text{kcal mol}^{-1})^{[37]} \tag{2}$$

$$MH\ (^1\Sigma^+) + H^-\ (^1S) \rightarrow MH_2^-\ (^1\Sigma_g^+) \quad (\Delta E = -68,\ -68,\ -77\,\text{kcal mol}^{-1})^{[36]} \tag{3}$$

electron-detachment energies for CuH_2^-, AgH_2^-, and AuH_2^-, of 55, 62 and 65 kcal mol^{-1}, respectively,[36] attest the stability of these coinage metal dihydride anions. The latter may be compared with the relativistic value of 64 kcal mol^{-1} computed by Schwerdtfeger et al.[11]

The sequential reaction (4), to make the stable square-planar $M^{III}H_4^-$ ions, is too endothermic for the Cu and Ag

$$MH_2^- + H_2 \rightarrow MH_4^-\ (^1A_{1g})\ \ \Delta E = 16,\ 23,\ 9\,\text{kcal mol}^{-1}) \tag{4}$$

matrix reactions; however, the greater stability of Au^{III} is revealed by the reaction energetics, and the solid hydrogen and deuterium environments apparently help to form the AuH_4^- and AuD_4^- ions. Reaction (4) likely proceeds during sample deposition for gold before the AuH_2^- product of reaction (3) is completely relaxed, and the overall energy change for reactions (3) and (4) for gold is computed as −68 kcal mol^{-1}, which is very favorable for the formation of AuH_4^-. Furthermore, atomic gold can also capture an electron during deposition, reaction (5), and the Au^- ion is particularly stable.[38] The photochemical formation of AuH_4^-

$$Au\ (^2S) + e^- \rightarrow Au^-\ (^1S) \quad (\Delta E = -53\,\text{kcal mol}^{-1})^{[38]} \tag{5}$$

in solid hydrogen probably involves the excited Au^- (^3P) state in reaction (6), which is analogous to the reaction of Hg (^3P)

$$Au^-\ (^1S) + 2\,H_2 \xrightarrow{290\,\text{nm}} Au^-\ (^3P) + 2\,H_2 \rightarrow AuH_4^-\ (^1A_{1g}) \tag{6}$$

with H_2,[32] and produces AuH_4^- in a slightly different matrix environment. Reaction (7) is observed in pure HD, in which

$$Au\ (^2P) + HD \rightarrow HAuD \tag{7}$$

following electron capture, $HAuD^-$ reacts with HD to give *cis*-$AuH_2D_2^-$. Finally, a relativistic computational investigation concluded that AuH_4^- is quite stable,[19] and the present observation of AuH_4^- suggests that this anion may be stable in solid-state compounds.

The basic science reported here shows that negative charge stabilizes coinage metal hydrides. This further suggests that the presence of hydrogen may augment charge transfer to Group 11 metal clusters,[3] and that these clusters, gold, silver, and copper included, may be effective for the industrially important catalytic hydrogenation process. It would therefore be interesting to reexamine the catalytic oxidation of carbon monoxide on gold clusters[2] with hydrogen present to foster charge transfer to the gold cluster.

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