Infrared spectrum and structure of the gold dihydroxide molecule

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Reactions of laser-ablated gold atoms with H_2O_2 and $H_2 + O_2$ mixtures give four new infrared absorptions, which match the four most intense vibrational frequencies calculated for $Au(OH)_2$ using density functional theory; the calculations find a C_{2h} structure and substantial covalent bonding character for the $Au(OH)_2$ molecule, which is probably due to the high electron affinity of gold.

Gold is noble owing to its lack of reactivity, but gold reacts with strong chemical oxidizing agents such as chlorine or aqua regia.[1] Although the most stable binary gold compounds are halides, gold hydrides have been prepared in spectroscopic quantities.[2–4] Gold hydroxide is unknown as an isolated molecule, and evidence for pure gold hydroxide solid compounds is limited. Gold hydroxide or aquoxide materials have been prepared by electrochemical oxidation of gold anode surfaces in solutions.[5] The formation of $AuOH{\cdot}H_2O$ and $Au(OH)_2^-$ was proposed from solubility measurements of gold(I) in NaOH solutions.[6] A solid produced by cooling annealed gold films in H_2 and then O_2 was characterized as having $Au(OH)_2$ stoichiometry from early electron diffraction measurements,[7] but this observation has not been confirmed. Neutralization of aqueous gold chloride solutions ($HAuCl_4$) by Na_2CO_3 gives an amorphous brown gold(III) aquoxide precipitate, $Au_2O_3{\cdot}nH_2O$, which is also called $Au(OH)_3$.[8] The dimethyl gold(III) hydroxide compound has a tetrameric ring structure.[9] The tetrahydroxoaurate(III) anion $[AuO_2{\cdot}2H_2O]^-$ is present in aqueous alkaline solutions,[5] and the structure for this anion in solid $Sr[Au(OH)_4]_2$ has been determined.[10]

Metallic gold does not react with the chemical oxidizing agent hydrogen peroxide,[11] but excited gold atoms are likely to react with H_2O_2 molecules, as we have found for H_2 in matrix isolation experiments.[3,4] Although calculations have been performed for AuOH[12,13] this molecule has not been observed experimentally.[12,14] Pure simple monomeric gold(II) compounds are not common,[14] but AuH_2 and AuO molecules have been prepared in solid matrixes,[15,16] and AuO has been observed recently in the gas phase.[17] Here we report the discovery of gold dihydroxide molecules through the reaction of excited gold atoms and hydrogen peroxide molecules in excess argon and comparison to frequencies computed by density functional theory.

Experimentally laser-ablated Au atoms were reacted with H_2O_2 molecules in excess argon during condensation onto an infrared transparent window at 10 K as reported previously.[4,18] Urea–hydrogen peroxide (Aldrich) at room temperature provided H_2O_2 molecules to the flowing argon reaction medium, and deuteriated urea–D_2O_2 was prepared using methods described previously.[19] Infrared spectra were recorded on a Nicolet 750 spectrometer after sample deposition, after annealing, and after irradiation by a common mercury arc street lamp. Complementary experiments were performed with H_2 and O_2 mixtures so that $^{18}O_2$ can be incorporated into the product molecules.[20,21] Theoretically, the structure and vibrational frequencies of the $Au(OH)_2$ molecule were calculated using methods employed for gold hydrides.[4,22] Relativistic effects were included in the SDD pseudopotential for gold.[23]

Infrared spectra of the Au and H_2O_2 reaction products are illustrated in Fig. 1. Sharp new absorptions are observed at 3565.9, 884.9, 676.6, and 532.5 cm^{-1} (labeled **d**) along with H_2O_2 reagent at 3586.2 and 1270.8 cm^{-1}, and common water absorptions.[19,24] Annealing the sample to 20 K has no effect on the **d** bands. Near ultraviolet (240–380 nm) and full arc ($\lambda > 220$ nm) irradiation markedly increased the **d** absorptions, and slightly increased a weak OAuO band at 817.9 cm^{-1}, and a weak AuH absorption at 2226.6 cm^{-1}.[3,16]

Investigations were also done with $H_2 + O_2$ as the reagent. Deposition with laser-ablated Au atoms gave weak product bands including OAuO, but UV irradiation increased these absorptions at essentially the same wavenumbers observed with H_2O_2. The major product absorptions labeled **d** were about 4 times stronger with H_2O_2. All product bands were shifted with $^{18}O_2$ substitution. A $H_2 + {}^{16}O_2 + {}^{18}O_2$ reagent mixture gave the same bands observed with each oxygen isotopic precursor. Spectra with the $H_2 + {}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$ reagent mixture gave multiplet absorptions near 3560, 880, and 660 cm^{-1}. The observed frequencies are listed in Table 1. IR absorptions were also observed for the HO_2 and OH radicals.[25–27]

The gold atom reaction was investigated with D_2O_2 and with $D_2 + O_2$ mixtures, and shifted product absorptions were observed in each case at the same wavenumbers. Fig. 1 also illustrates the Au + D_2O_2 reaction product spectrum. Experiments with HD and O_2 gave the unique mixed H, D product.

The **d** product absorptions at 3565.9, 884.9, 676.6, and 532.5 cm^{-1} are associated by common behavior on photolysis and annealing, production from both the H_2O_2 and $H_2 + O_2$ reagents, and they are assigned to the same new molecule. The IR band positions and isotopic shifts characterize O–H stretching, Au–O–H bending, O–Au–O stretching, and Au–O–H deformation modes. The strong 3565.9 cm^{-1} absorption shifts to 3555.1 cm^{-1} with $^{18}O_2$ (16/18 ratio 1.00304) and to 2632.3 cm^{-1} with D_2O_2 (H/D ratio 1.3547), which are appropriate for an O–H stretching fundamental.[20,21] The spectrum with H_2 and $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$ shows four bands; namely the $^{16}O_2$ band at 3565.9 cm^{-1}, the $^{18}O_2$ band at 3555.1 cm^{-1}, and new 3570.8 and 3557.5 cm^{-1} bands in a

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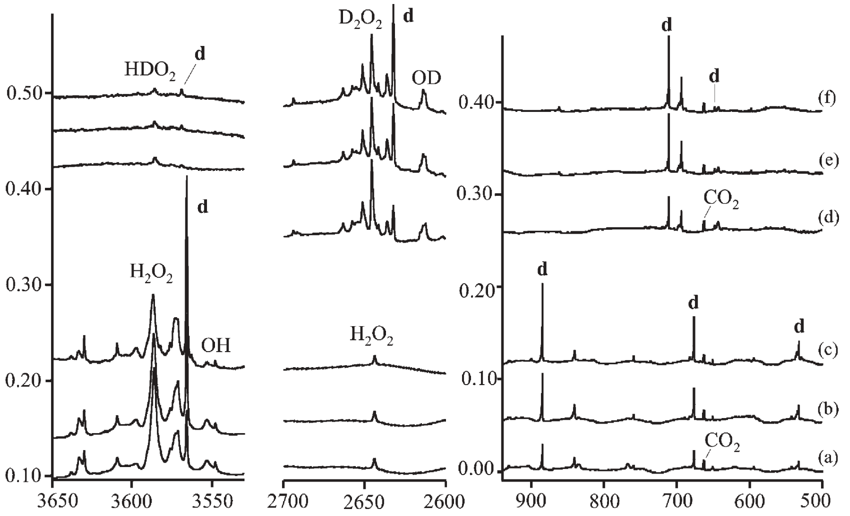

Fig. 1 Infrared spectra in the 3650–3530, 2700–2600, and 940–500 cm^{-1} regions for laser-ablated Au atom reactions with H_2O_2 and D_2O_2 in excess argon. (a) Au + H_2O_2, (b) after 240–380 nm irradiation, (c) after $\lambda > 220$ nm irradiation, (d) Au + D_2O_2, (e) after 240–380 nm irradiation, and (f) after $\lambda > 220$ nm irradiation.

Table 1 Observed and calculated frequencies (cm^{-1}) for $Au(OH)_2$ in the C_{2h} structure

	$Au(OH)_2$		$Au(OH)(OD)$		$Au(OD)_2$		$Au(^{18}OH)_2$	
Mode	Obs.[a]	Calc.[b]	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
O–H stretch		3783.0 (a_g, 0)[c,d]	3569.1	3779.7 (167)		2753.9 (0)		3770.5
O–H stretch	3565.9	3776.4 (b_u, 335)[c]	2635.5	2751.4 (94)	2632.3	2748.9 (187)	3555.1	3764.0
Au–O–H bend	884.9	906.5 (b_u, 218)	862.1	888.3 (127)	711.3	708.6 (170)	879.0	900.3
Au–O–H bend		865.9 (a_g, 0)	692.6	682.8 (82)		651.1 (0)		862.6
O–Au–O stretch	676.6	641.2 (b_u, 39)		619.7 (5)	648.1	601.7 (1)	645.7	611.7
O–Au–O stretch		590.4 (a_g, 0)		573.9 (1)		563.8 (0)		557.7
Au–O–H deform	532.5	555.5 (a_u, 158)	474.4	491.5 (123)		417.6 (87)	530.7	551.7
O–Au–O bend, in		194.7 (b_u, 6)		189.3 (6)		184.0 (6)		186.3
O–Au–O bend, out		121.0 (a_u, 0)		119.0 (0)		114.4 (0)		115.9

[a] Observed in solid argon. [b] Calculated at B3LYP/6-311++G(3df, 3pd)/SDD level of theory. [c] Mode symmetry in C_{2h}, infrared intensity, km/mol. [d] Strong absorptions calculated for $Au(^{16}OH)(^{18}OH)$ are 3780.5 (89), 3766.5 (244), 903.5 (213), 630.7 (36), 553.6 cm^{-1} (158 km/mol).

1 : 3 ratio. The last two are due to coupled ^{16}OH and ^{18}OH stretching modes in the same molecule, which demonstrates that our new molecule is a dihydroxide. This point is further confirmed through the use of the HD + O_2 reagent, which gives two similar new absorptions at 3569.1 and 2635.5 cm^{-1} for O–H and O–D stretching modes in the same molecule. The strong 884.9 cm^{-1} band shifts to 879.0 cm^{-1} with $^{18}O_2$ (16/18 ratio 1.00671) and to 711.3 cm^{-1} with D_2O_2 (H/D ratio 1.2441), which are appropriate for a Au–O–H bending mode. It is important that the spectrum with statistical $^{16,18}O_2$ revealed a triplet absorption at 884.9, 882.0, 879.0 cm^{-1}, which verifies the participation of two equivalent oxygen atoms. Finally, the 676.6 cm^{-1} absorption shifts to 645.7 cm^{-1} with $^{18}O_2$ (16/18 ratio 1.0478), and the band becomes an asymmetric triplet at 676.6, 666.2, 645.7 cm^{-1} with statistical $^{16,18}O_2$. Such a triplet was also observed for the antisymmetric stretching mode at 817.9 cm^{-1} for the linear O–Au–O molecule (16/18 ratio 1.0506).[16] We conclude that our new molecule contains an O–Au–O subunit. Similar experiments with copper give a natural copper isotopic doublet for the analogous 773.5, 769.4 cm^{-1} band, which is due to the antisymmetric O–Cu–O stretching mode for the $Cu(OH)_2$ molecule and demonstrates the participation of a single metal atom. From the above isotopic vibrational spectroscopic observations, we have definitively identified the new molecule $Au(OH)_2$. This is the first experimental evidence for any gold hydroxide molecule.

These experimental assignments to $Au(OH)_2$ are confirmed by the excellent agreement between theoretical and observed isotopic frequencies, and this agreement in turn confirms that the converged C_{2h} structure is the ground state configuration of $Au(OH)_2$. The $Au(OH)_2$ molecule has the computed C_{2h} structure illustrated in Fig. 2 and frequencies listed in Table 1. Our calculated 1.937 Å Au–O bond length is slightly longer than the recently determined 1.849 Å value for the AuO diatomic molecule[17] and slightly shorter than that measured as 1.980(8) Å for the $Au(OH)_4^-$ anion in solid $Sr[Au(OH)_4]_2$.[10] Notice that the

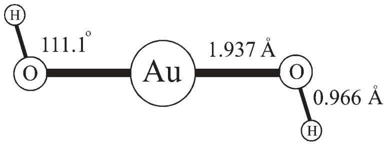

Fig. 2 The C_{2h} structure of $Au(OH)_2$ calculated at the B3LYP/6-311++G(3df, 3pd)/SDD level of theory.

three modes involving O–H stretching and bending are predicted 5.9, 2.4, and 4.3% too high by the B3LYP calculation, which is the expected relationship between harmonic calculated and anharmonic observed frequencies.[28] However, the O–Au–O stretching mode is predicted 5.2% too low: apparently the SDD pseudopotential and B3LYP density functional do not model the gold–oxygen bond perfectly.

The O–H and O–Au–O stretching frequencies for the isolated $Au(OH)_2$ molecule at 3566 and 677 cm^{-1} may be compared to those observed for $[(CH_3)_2AuOH]_4$ in $CHCl_3$ solution at 3602 and 466 cm^{-1}.[9] The latter O–Au–O stretching mode is lower because it involves a tetrameric ring structure.

Reactions (1) and (2) are the primary mechanism for the gold dihydroxide molecules formed here. Gold atoms in the ground ^2S state do not react with H_2O_2 even on annealing, but we observe a substantial increase in product absorptions on UV irradiation, which promotes the $^2S \rightarrow {}^2P$ excitation for gold.[3,4,29] Gold atoms can also be excited in the laser-ablation process.[3,4] The condensing matrix relaxes the energized intermediate and stabilizes the $Au(OH)_2$ product. The $Au(OH)_2$ molecule is 54 kcal/mol lower in energy than Au (^2S) and H_2O_2. The gold reaction with $O_2 + H_2$ proceeds first through OAuO, also observed here, which we believe inserts into molecular hydrogen, based on observation of pure isotopic Au(OH)(OD) from the Au reaction with O_2 + HD.

$$Au\ (^2P) + H_2O_2 \rightarrow [HOAuOH]^* \rightarrow Au(OH)_2 \qquad (1)$$

$$Au\ (^2P) + O_2 + H_2 \rightarrow [OAuO]^* + H_2 \rightarrow Au(OH)_2 \qquad (2)$$

Several interesting comparisons can be made between the heavy metal dihydroxides of Ba, Hg, and Au.[20,30,31] First, the strong antisymmetric O–H stretching frequencies decrease in this order 3724.2 to 3629.4 to 3565.9 cm^{-1} almost reaching the 3555.6 cm^{-1} value for gaseous OH^-.[32] However, the neutral OH radical fundamental (3568 cm^{-1}) also falls in this region,[2] and the O–H stretching frequency is not a measure of ionic character. It is important to note that the computed structures of $Ba(OH)_2$, $Hg(OH)_2$, and $Au(OH)_2$ are quite different: $Ba(OH)_2$ is bent at the metal center (127.3°) with essentially linear Ba–O–H subunits[30] in this largely ionic molecule, but $Hg(OH)_2$ is linear at the metal center with Hg–O–H angles 109.1° and dihedral angle 85.8° in C_2 symmetry, and $Au(OH)_2$ is also linear at the metal center with Au–O–H angles 111.1° with C_{2h} symmetry. The computed O–H bond length increases in this series (0.956, 0.963, 0.966 Å), being longest for gold. Clearly the gold dihydroxide molecule exhibits a strong Au–O interaction and has substantial covalent bonding character. This is supported by the decreasing Mulliken charges at the metal centers (Ba, 1.51; Hg, 1.41; Au, 0.75) and is probably due to the high electron affinity of the gold atom, which is an effect of relativity.[14] We find the $Au(OH)_2$ ground state to be ^2B_g and postulate that the unpaired electron[33] may exhibit sufficient repulsion with terminal H to force the molecule to be planar whereas closed shell $Hg(OH)_2$ is a dihedral molecule like H_2O_2. We conclude that solid $Au(OH)_2$ will not be a strong base like $Ba(OH)_2$.

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