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Infrared Spectrum of $Hg(OH)_2$ in Solid Neon and Argon

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Mercury(II) hydroxide molecules have been prepared upon mercury arc lamp irradiation of Hg, H_2, and O_2 mixtures in solid neon and argon. The strongest three infrared absorptions are identified through isotopic substitution (D_2, HD, $^{18}O_2$, $^{16}O^{18}O$) and comparison to frequencies from DFT calculations. The isolated $Hg(OH)_2$ molecule is stable and has a linear O–Hg–O linkage in a C_2 structure with an 86° dihedral angle. However, in aqueous solution Hg^{2+} and $2OH^-$ may form an $Hg(OH)_2$ intermediate, which eliminates water and precipitates solid HgO: The solid $Hg(OH)_2$ compound is not known.

Introduction

Mercury is an exotic element. Divalent mercury forms a number of binary compounds, and many of these are toxic.[1−3] The common $HgCl_2$ compound, calomel, is a volatile covalent molecular solid stabilized by "metallophilic" attraction, which gives a linear molecule in the vapor.[4−7] The addition of OH^- to Hg^{2+} in aqueous solution precipitates the yellow solid HgO, which consists of zigzag −O−Hg−O−Hg− chains with linear O−Hg−O units, and it is possible that $Hg(OH)_2$ is a transient intermediate in this precipitation reaction.[1,8] The $Hg(OH)_2$ molecule has been computed,[9] but there is no evidence for the gaseous molecule nor the solid compound[1,2,8] although $Hg(OH)_2$ is thought to coprecipitate with $Fe(OH)_3$.[10] The presence of mercury in industrial wastes is a significant environmental problem, and precipitation reactions provide a means of recovery. Furthermore, gas phase elemental mercury is rapidly oxidized to Hg(II) compounds in the arctic regions,[11] and $Hg(OH)_2$ may play an intermediate role in this process.[12]

The most closely related compound HgH_2 is reported to be an unstable solid, which decomposes at −125 °C.[13] The HgH_2 molecule has been formed by 247 nm laser irradiation of Hg, H_2 samples in excess argon, hydrogen, and nitrogen[14,15] and by mercury arc lamp irradiation of Hg atoms in solid hydrogen.[16] Recent work has shown that irradiation of mercury/water mixtures in excess argon gives the HHgOH molecule.[17] Here we employ a mercury arc street lamp to form $Hg(OH)_2$ molecules from mixtures of Hg, H_2, and O_2 in excess neon and argon and report the first experimental evidence for the $Hg(OH)_2$ molecule. In addition, we compare the infrared spectrum with vibrational frequencies calculated by density functional theory for the stable isolated $Hg(OH)_2$ molecule.

Experimental and Computational Methods

The technique for reactions of metal atoms with hydrogen during condensation in excess hydrogen and neon has been described in detail previously.[18,19] Mercury atoms were evaporated from the liquid at 50 °C in a stainless steel, valved system. Mercury atoms were thus codeposited with hydrogen (2 to 8%) and oxygen (0.2−2.0%) in excess neon, argon, or pure deuterium onto a 5 K CsI cryogenic window at 2−4 mmol/h (Ne, Ar for 1 h and pure D_2 for

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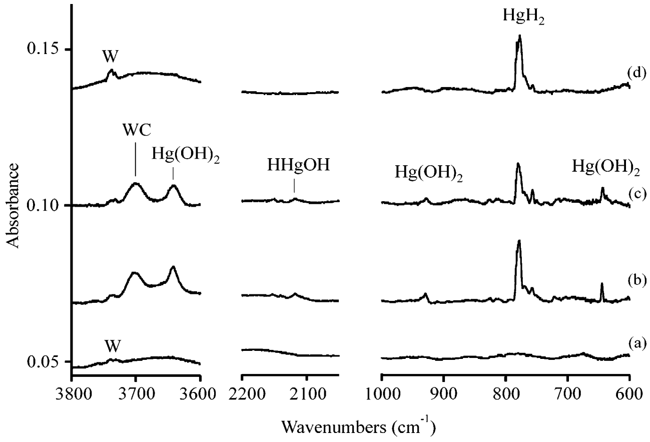

Figure 1. Infrared spectra of neon matrix samples codeposited at 5 K with mercury vapor: (a) Ne and Hg with 2% H_2 and 0.2% O_2, (b) after $\lambda > 220$ nm mercury arc irradiation for 25 min, (c) after annealing to 12 K, and (d) Ne and Hg with 4% H_2 after irradiation. W denotes water, and WC identifies water complex absorptions.

30 min). The D_2, HD (Cambridge Isotopic Laboratories), $^{18}O_2$, and $^{16,18}O_2$ (Yeda) reagents were used in different experiments. FTIR spectra were recorded at 0.5 cm^{-1} resolution with 0.1 cm^{-1} accuracy on a Nicolet 750 using an HgCdTe detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband photolysis by a medium-pressure mercury arc street lamp (Philips, 175W) with globe removed.

Density functional theoretical calculations of mercury hydroxide are given for comparison. The Gaussian 98 program[20] was employed to calculate the structures and frequencies of expected product molecules using the B3LYP functional. The 6-311++G(3df,3pd) basis set for O and H atoms and SDD pseudopotential for Hg were used. All the geometrical parameters were fully optimized, and the harmonic vibrational frequencies were obtained analytically at the optimized structures.

Results

Infrared spectra and density functional calculations will be presented for the major products in the photochemical reaction of mercury with hydrogen and oxygen.

Neon. Figure 1 illustrates infrared spectra of the products formed by the reaction of mercury with hydrogen and oxygen in excess neon. The first sample with 2% H_2, 0.2% O_2, and Hg vapor (0.1−0.2%) codeposited at 5 K has no infrared absorption except for the usual trace impurities (H_2O, CO_2, CO, CH_4). Full mercury arc irradiation ($\lambda > 220$ nm) for 25 min produces strong HgH_2 absorptions[16] at 1918.1 and 781.7 cm^{-1} and new absorptions at 3702, 3642.3, 2118.2, 1612 (not shown), 928.8, and 644.2 cm^{-1}. Note that the weak 3737.5 cm^{-1} water band does not grow on irradiation. Annealing to 12 K slightly increased the 3702 and 1612 cm^{-1} bands but decreased the other bands by 20−30%. Without oxygen the spectrum shows only the HgH_2 reaction product (Figure 1d). A similar experiment with Ne, Hg, O_2, and no H_2 gave no observable product absorptions.

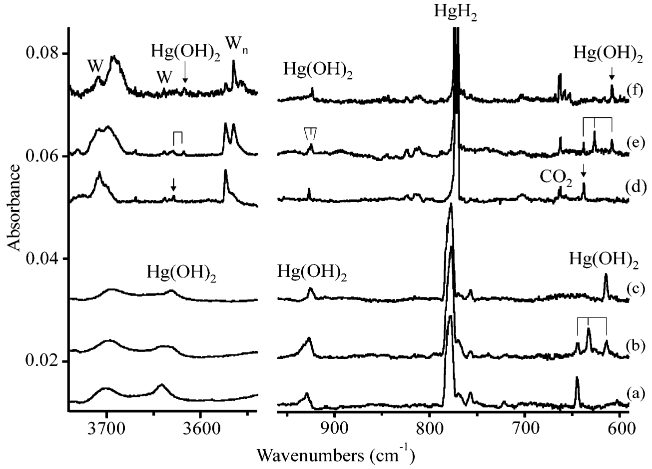

Figure 2. Infrared spectra of neon and argon matrix samples codeposited with mercury vapor, hydrogen, and isotopic oxygen molecules, and irradiated at $\lambda > 220$ nm: (a) Ne, 2% H_2, 0.2% $^{16}O_2$, (b) Ne, 3% H_2, 0.4% $^{16,18}O_2$, (c) Ne, 2% H_2, 0.3% $^{18}O_2$, (d) Ar, 8% H_2, 0.8% $^{16}O_2$, (e) Ar, 10% H_2, 1% $^{16,18}O_2$, and (f) 8% H_2, 0.8% $^{18}O_2$. W denotes water.

Similar investigations with $^{18}O_2$ substitution shifted the new absorptions to 3695, 3631.7, 925.2 and 614.1 cm^{-1}. The weak 2118.2 cm^{-1} band was not shifted. A scrambled $^{16,18}O_2$ sample gave doublet absorptions at 3702, 3695 cm^{-1} and 3642, 3672 cm^{-1}, a partially resolved triplet at 929, 927.1, 925 cm^{-1}, and a triplet at 644.0, 632.3, 614.0 cm^{-1}. Spectra showing the effect of oxygen isotopic substitution are compared in Figure 2, and the product absorptions are listed in Table 1.

Experiments with D_2 and $^{16}O_2$ gave strong HgD_2 absorptions at 1378 and 562 cm^{-1} and new product absorptions at 2733, 2685.0, 1519.2, 711.5, and 619.9 cm^{-1}. The new product bands again shifted with $^{18}O_2$ as listed in Table 1, and $^{16,18}O_2$ also gave doublet absorptions in the upper region and partially resolved triplet absorptions in the lower region, which are illustrated in Figure 3.

An investigation with $^{16}O_2$ and HD was particularly productive: Strong absorptions were observed for HgHD at 1968, 1407, and 683 cm^{-1}. New absorptions were observed at 3697, 3643.1, 2687.5, 934.3, 701.8, and 632.4 cm^{-1}. The latter, lower frequency bands are also shown in Figure 3. Although no absorption was observed at 2118 cm^{-1}, a weak deuterium counterpart was observed at 1520.6 cm^{-1}.

Argon. Analogous experiments were done with higher reagent gas concentrations and Hg vapor in excess argon codeposited at 8 K. The samples were irradiated by the full mercury arc for 15 min, and HgH_2 absorptions[14,21] at 1895 and 773 cm^{-1} and new product absorptions at 3629.4, 927.1, and 637.3 cm^{-1} were produced along with water and water dimer bands. Argon matrix bands were weaker and sharper

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Table 1. Infrared Absorptions (cm^{-1}) Produced by Mercury Arc Irradiation of Solid Neon or Argon Containing Hydrogen, Oxygen, and Mercury

H_2, $^{16}O_2$	H_2, $^{18}O_2$	H_2, $^{16,18}O_2$	HD, $^{16}O_2$	D_2, $^{16}O_2$	D_2, $^{18}O_2$	D_2, $^{16,18}O_2$	identity
			Neon Matrix				
3702	3695	3702, 3695	3697 br	2733	2717	2732, 2717	HOH···X
3642.3	3631.7	3642, 3632	3643.1, 2687.5	2684.0	2668.7	2685, 2668	$Hg(OH)_2$
2118.2	2118.2	2118.2	1520.6	1519.2	1519.2	1519.2	HHgOH
1918	1918	1918	1968, 1407	1368	1368	1368	HgH_2
1612	1605	1612, 1605		1180	1171	1180, 1171	HOH···X
928.8	925.2	929, 927.1, 925	934.3	711.5	688.4	712, 704, 689	$Hg(OH)_2$
782	782	782	683	562	562	562	HgH_2
644.2	614.1	644.0, 632.3, 614.0	701.8, 632.4	619.9	598.2	620, 612, 599	$Hg(OH)_2$
551	524				512		$[Hg(OH)_2]_2$
			Argon Matrix				
3629.4	3618.6	3629.5, 3618.4	3629.7, 2677.9	2677.7			$Hg(OH)_2$
1896	1896	1986	1948, 1392	1363			HgH_2
927.1	923.7	927, 924.9, 924	932.1	704.5			$Hg(OH)_2$
773	773	773	675	555			HgH_2
637.3	607.8	637.3, 626.2, 607.8	698.9, 626.9				$Hg(OH)_2$

Table 2. Infrared Absorptions (cm^{-1}) Produced by Mercury Arc Irradiation of Solid Deuterium Containing O_2 and Hg

$^{16}O_2$	identity	$^{18}O_2$
2782	D_2O	2762
2773.9	D_2O	2754.0
2690.6	DHgOD	2674.3
2679.6	DOHgOD	2663.4
2661.5	D_2O	2650.8
2611	$(D_2O)_2$	2599
2531.1	DO_2	2515.3
1523.9	DHgOD	1523.8
1368.9	HgD_2	1368.9
1178.3	D_2O	1169.9
1124.2	DO_2	
1024.6	DO_2	1002.9
709.4	DOHgOD	691.2
652	DHgOD	644
617.9	DOHgOD	596.5
569.1	DHgOD	544.7
556.0	HgD_2	556.0
554.7	HgD_2	554.7

than neon matrix counterparts. The samples were annealed to 12 K and photolyzed for another 20 min: The product absorptions doubled their intensity. The samples were annealed to 14 K and photolyzed again, and the product absorptions increased another 50%. The new product absorptions in solid argon are illustrated in Figure 2. Isotopic precursor molecules were reacted in a like manner; infrared spectra are compared in Figure 2, and band positions are listed in Table 1.

Deuterium. Mercury and O_2 were subjected to irradiation in two solid deuterium samples, and the spectra revealed a different distribution of analogous product absorptions. Strong HgD_2 bands at 1398 and 555 cm^{-1} and D_2O absorptions at 2782, 2773.9, 2661.5, and 1178.3 cm^{-1} and $(D_2O)_2$ at 2611 cm^{-1} were observed along with DO_2 at 2531.1, 1124.2, and 1024.6 cm^{-1}.[22-24] Additional weak bands were observed at 2690.6, 2679.6, 1523.9, 709.4, 652, 617.9, and 569.1 cm^{-1}. Continued irradiation substantially increased the HgD_2, D_2O, 2690.6, 1523.9, 652, and 569.1 cm^{-1} absorptions and slightly increased the 2679.6, 709.4, and 617.9 cm^{-1} bands as shown in Figure 4. A similar irradiation of solid D_2 containing O_2 without Hg failed to produce D_2O.

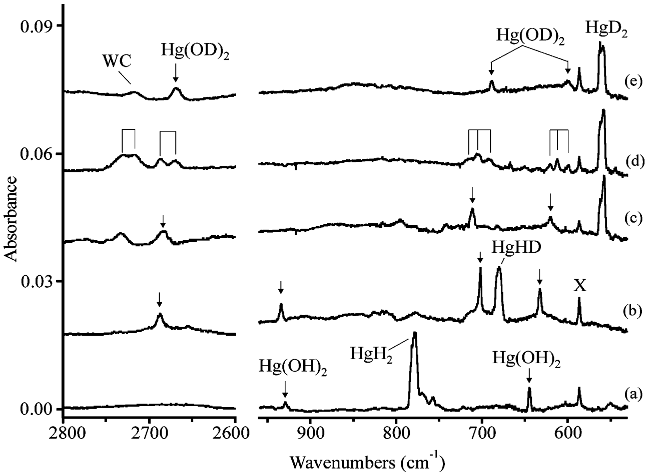

Figure 3. Infrared spectra of neon matrix samples codeposited at 5 K with mercury vapor and irradiated at $\lambda > 220$ nm: (a) Ne and Hg with 2% H_2 and 0.2% O_2, (b) Ne and Hg with 3% HD and 0.3% O_2, (c) Ne and Hg with 4% D_2 and 0.4% $^{16}O_2$, (d) Ne and Hg with 3% D_2 and 0.4% $^{16,18}O_2$, and (e) Ne and Hg with 2% and 0.2% $^{18}O_2$. WC indicates water complex.

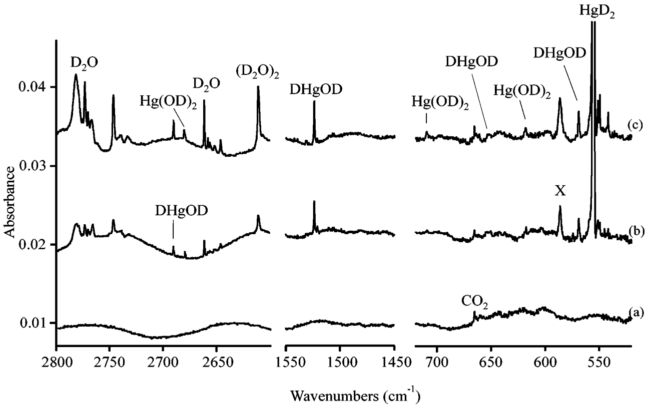

Figure 4. Infrared spectra of deuterium matrix sample codeposited at 5 K with mercury vapor: (a) D_2 and 0.1% O_2, (b) after $\lambda > 220$ nm irradiation for 22 min, and (c) after $\lambda > 220$ nm irradiation for 20 additional min. X denotes common unknown photolysis product.

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Table 3. Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) of $Hg(OH)_2$ and HHgOH Calculated at the B3LYP/6-311++G(3df,3pd)/SDD Level

$Hg(OH)_2$[a]

mode	HOHgOH	DOHgOD	HOHgOD	$H^{18}OHg^{18}OH$	$H^{16}OHg^{18}OH$	$D^{18}OHg^{18}OD$	$D^{16}OHg^{18}OD$
O−H str	3828.0(13)	2787.0(8)	3827.4(57)	3815.3(12)	3827.4(53)	2769.5(8)	2786.4(34)
O−H str	3826.8(101)	2785.8(65)	2786.4(36)	3814.2(98)	3814.8(59)	2768.4(61)	2768.8(36)
Hg−O−H bend	957.2(10)	706.2(99)	951.6(44)	953.6(9)	955.7(11)	698.0(6)	705.4(49)
Hg−O−H bend	946.1(81)	705.0(6)	705.7(56)	942.0(75)	943.7(76)	695.5(78)	697.0(46)
Hg−O str	606.9(112)[b]	588.7(67)	598.4(87)	578.2(104)	595.7(104)	566.0(74)	580.0(68)

HHgOH[c]

mode	HHgOH	DHgOD	HHgOD	DHgOH	$HHg^{18}OH$	$DHg^{18}OD$
O−H str	3846.3(42)	2800.1(29)	2800.1(29)	3846.2(42)	3833.6(41)	2782.6(27)
Hg−H str	2126.0(123)	1507.7(64)	2125.8(122)	1508.1(66)	2126.0(122)	1507.7(64)
Hg−O−H bend	871.8(40)	647.5(45)	688.9(30)	860.2(40)	868.1(38)	639.3(36)
H−Hg−O bend	584.7(5)	543.9(53)	583.2(7)	556.2(70)	583.8(4)	519.2(54)
H−Hg−O bend	579.2(11)	422.0(4)	557.8(7)	424.8(9)	578.8(12)	420.9(4)
Hg−O str	556.2(74)	414.2(7)	525.1(2)	424.2(2)	527.5(67)	413.8(7)

[a] Structure given in Figure 5 for ^1A ground state. [b] Four lower frequencies: 541.2(0), 167.0(5), 152.1(3), and 123.2(78) cm^{-1} (km/mol). [c] Planar $^1A'$ ground state. H−Hg, 1.601 Å; Hg−O, 2.021 Å; O−H, 0.962 Å; ∠HHgO, 176.7°; ∠HgOH, 111.3°.

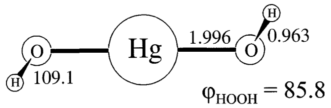

Figure 5. Structure of $Hg(OH)_2$ calculated at the B3LYP/6-311++G-(3df,3pd)/SDD level. Bond lengths in angstroms and angles in degrees.

A like investigation of Hg and $^{18}O_2$ in solid D_2 gave the same HgD_2 bands, $D_2{}^{18}O$, and $D^{18}O_2$: Additional weak bands are listed in Table 2. Continued irradiation behaved as described above.

Calculations. DFT calculations were performed on the two anticipated product species HHgOH and $Hg(OH)_2$, and the results are given in Table 3. Our structures are similar to those computed previously.[9,17] The ^1A $Hg(OH)_2$ molecule has C_2 symmetry, a linear O−Hg−O linkage, and a 85.8° dihedral angle as illustrated in Figure 5. The high energy OHgO molecule is calculated to be stable in a $^3\Sigma_g{}^-$ state.[25]

Discussion

The new absorptions will be assigned on the basis of observed isotopic shifts and splittings and comparison with isotopic frequencies computed by density functional theory.

$Hg(OH)_2$. The major product requires three elements, Hg, H_2, and O_2, and the transient molecule $Hg(OH)_2$ is identified from the mixed isotopic spectra shown in Figure 2. The 644.0, 632.3, 614.0 cm^{-1} triplet in neon and the corresponding 637.3, 626.2, 607.8 cm^{-1} triplet in argon using scrambled isotopic oxygen ($^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$) clearly demonstrate that two equivalent oxygen atoms are involved in this vibrational mode. The large $^{16}O_2$ to $^{18}O_2$ shift (16/18 ratio 1.0489 (neon) and 1.0485 (argon)) identifies this predominately antisymmetric HO−Hg−OH motion. The weaker 928.8 cm^{-1} absorption also gives a triplet band contour, and the small $^{16}O_2$ to $^{18}O_2$ shift and large H_2 to D_2 shift characterize an Hg−O−H bending mode. The associated band at 3642.3 cm^{-1} shifts to 2684.0 cm^{-1} with D_2 in neon, and the corresponding argon matrix counterparts are 3629.4 and 2677.7 cm^{-1}: These bands exhibit large H/D ratios (1.357 and 1.355) that are characteristic of O−H stretching modes. Crucial information is obtained with the HD reagent, which gives new bands at 3643.1 and 2687.5 cm^{-1} in neon and at 3629.7 and 2677.9 cm^{-1} in argon in the upper region, and at 701.8 and 632.4 cm^{-1} in neon and at 698.9 and 626.9 cm^{-1} in argon in the lower region. Thus, with HD we observe two slightly different O−H and O−D stretching modes and Hg−O−H and Hg−O−D bending modes, and the $Hg(OH)_2$ molecule is thereby identified. There is precedent for dihydroxide molecules: the $Be(OH)_2$ molecule is a major product of the laser-ablated Be atom and H_2O reaction,[26] and the $Ca(OH)_2$ molecule is formed by photolysis of Ca and H_2O in excess argon.[27]

Assignment of the 3642.3, 928.8, and 644.2 cm^{-1} absorptions to the $Hg(OH)_2$ molecule is confirmed by B3LYP harmonic frequency calculations, which predict the strongest three infrared absorptions at 3826.8, 946.1, and 606.9 cm^{-1}. These predictions, 5.0% high, 1.9% high, 5.8% low, respectively, deviate more than previous results for first row transition metals,[28] but the Hg−O stretching mode is difficult to model. The ^{18}O shifts, however, are predicted accurately for these modes (calculated/observed: 12.6/10.6 cm^{-1}, 3.6/3.6 cm^{-1}, 28.7/28.1 cm^{-1}), respectively.

DHgOD. The solid deuterium experiment was performed for the ultimate high concentration, and similar bands were observed at 2679.6, 709.4, and 617.9 cm^{-1}, which are between the above neon and argon matrix observations for $Hg(OD)_2$. Three additional strong, sharp bands at 2690.6, 1523.9, and 569.1 cm^{-1} and a weaker, broad band at 652 cm^{-1} can be assigned to the related DHgOD molecule. First, the 1523.9, 652, and 569.1 cm^{-1} bands are slightly higher than 1519.2, 646.7, and 565.6 cm^{-1} argon matrix counterparts for the DHgOD product of the photochemical Hg + D_2O reaction where the 2700 cm^{-1} region was drowned in excess D_2O.[17] Our B3LYP calculation predicts the O−D stretch 14.3 cm^{-1} higher than that for $Hg(OD)_2$, and our new associated

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(25) The OHgO ($^3\Sigma_g{}^-$) molecule has computed 1.894 Å Hg−O length and frequencies (intensities) 698 cm^{-1} (15 km/mol), 625 (0), 184 (12 × 2).

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band at 2690.6 cm^{-1} is 11.0 cm^{-1} higher. The 16.3 cm^{-1} observed ^{18}O shift is in good agreement with the 17.5 cm^{-1} calculated value, which for a single O−D bond is necessarily less than the 19.7 cm^{-1} ^{18}O shift observed for the sharp 2772.2 cm^{-1} antisymmetric D_2O stretching mode. The DHg−OD stretching mode observed here at 569.1 cm^{-1} shifts to 544.7 cm^{-1} with ^{18}O substitution, in excellent agreement with the calculated 24.7 cm^{-1} shift. Unfortunately, interaction with the D_2 matrix broadened the 652 cm^{-1} DHgOD bending mode.

Our B3LYP calculation predicts harmonic frequencies in good agreement with observed values for DHgOD as does a previous BP calculation.[17] The O−D stretch is predicted 4.0% high, which is in the range for this functional, but the Hg-D stretch and Hg−O stretch are predicted 1.0% and 4.4% too low. Our density functional calculations for mercury compounds are only approximate, but they support the recent argon matrix assignments.[17]

The strongest band, the Hg−H stretching mode, was observed for HHgOH at 2118.2 cm^{-1} in solid neon, just 1.7 cm^{-1} higher than the recent argon matrix observation,[17] and the DHgOD counterpart was observed at 1519.2 cm^{-1}. We note that with Hg, HD, and O_2 in neon only the DHgOH isotopomer is formed. We provide additional information on the DHgOD transient species, namely the O−D stretching mode and ^{18}O shift for the Hg−O stretching mode, and its photochemical synthesis by a different route, which substantiates its recent identification.[17]

The HHgOH molecule may be compared with HXeOH formed in the 193 nm induced reaction of H_2O in pure xenon.[29] The most interesting mode observed here for DHgOD in solid deuterium, the O−D stretching mode, was not observed for DXeOD, but the calculated O−D stretching frequency and bond length for these two species are nearly the same.

Other Absorptions. Two broad absorptions are produced at 3702 and 1612 cm^{-1} on irradiation in neon experiments. Their position near water absorptions invites our consideration of water, and their shift down from isolated water at 3737.5 cm^{-1} and up from H_2O at 1596.3 cm^{-1} shows that hydrogen bonding is involved.[30] Hence, the 3702 and 1612 cm^{-1} bands are due to a water complex HOH···X where H_2O and X are photolysis products. The isotopic shifts are in agreement with this assignment. As expected, the photochemical yield of water is highest in the solid D_2 experiments. In addition, DO_2 radicals[22,23] are observed in the higher yield pure D_2 investigations, which shows that D atoms are formed in the photochemical reactions with Hg atoms.

Finally, a weak 551 cm^{-1} band shifts to 524 cm^{-1} with ^{18}O and exhibits a 1.052 ^{16}O/^{18}O ratio, and the latter band has a 1.023 H/D ratio, which are comparable to the values observed for $Hg(OH)_2$. This suggests that the 551 cm^{-1} band is due to a Hg−O vibration, coupled with H, and the $Hg(OH)_2$ dimer is a likely carrier for this band.

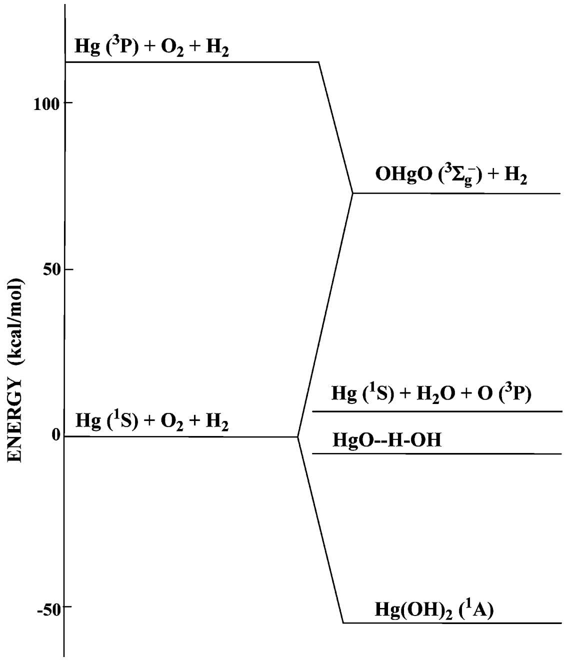

Figure 6. Relative energies computed at the B3LYP/6-311++G(3df,3pd)/SDD level for important Hg, O_2, H_2 species.

Reaction Mechanisms. The mercury dihydroxide molecule is prepared here by the reaction of excited Hg with O_2 and H_2, reaction 1, in the matrix cage. The excited Hg(^{3}P) state (+112.6 kcal/mol)[31] is formed directly by mercury arc resonance radiation (254 nm) to activate this reaction. The stable ^{1}A $Hg(OH)_2$ molecule is calculated to be 54 kcal/mol lower in energy than Hg(^{2}S) + O_2 + H_2 at the B3LYP level. In addition, we have evidence for H_2O and HHgOH formation, which are likely products of reaction 2 with more dihydrogen. Molecular oxygen is not photodissociated at 254 nm,[32] and full arc irradiation of solid H_2 containing O_2 gives no photolysis products, but when Hg is added, HgH_2 is formed and O_2 can react with both H_2 and HgH_2 to give H_2O and HHgOH. Reaction 2 can, of course, give Hg and $2H_2O$ as well. Water and water dimer (Figures 2d and 4c) are also produced on full arc irradiation.

On the other hand, HXeOH is formed by a different mechanism in the 193 nm induced reaction of Xe and H_2O, which involves H and OH radicals.[29] We do not detect OH radicals[33] in this work, and OH is not a likely reagent in our 254 nm excited photochemical reactions.

$$\mathrm{Hg(^3P)} + \mathrm{O_2} + \mathrm{H_2} \rightarrow \mathrm{(OHgO)^*} + \mathrm{H_2} \rightarrow \mathrm{HOHgOH} \quad (1)$$

$$\mathrm{Hg(^3P)} + \mathrm{O_2} + 2\mathrm{H_2} \rightarrow \mathrm{HHgOH} + \mathrm{H_2O} \quad (2)$$

An interesting question is the mechanism of reaction 1. The reaction of Hg (^{3}P) and H_2 proceeds directly to HgH_2, as shown in previous work[14−16] and in Figure 1d. It is counterintuitive to suggest that reaction 1 proceeds through

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HgH_2 although HgO is very weakly bound[34] and evidence for HgO_2 is tenuous.[35] Following the preparation of stable $^3\Sigma_g^-$ states for the OZnO and OCdO molecules,[36] and the recent formation of stable $Zn(OH)_2$ and $Cd(OH)_2$ molecules in this laboratory, we have calculated a physically stable $^3\Sigma_g^-$ state for OHgO, which is 72.5 kcal/mol higher in energy than $Hg(^1S) + O_2$, but this does not preclude OHgO ($^3\Sigma_g^-$) as a reactive intermediate in reaction 1. The relative computed energies of important Hg, O_2, and H_2 species are given in Figure 6: Note that OHgO is 40 kcal/mol more stable than $Hg(^3P) + O_2$. We suggest that OHgO produced in the initial reaction then inserts into dihydrogen to form HOHgOH. Recall that no mercury oxides are observed when Hg and O_2 are irradiated in excess neon. Hence, H_2 chemically "traps" the OHgO subunit as the stable HOHgOH molecule. The strongest $Hg(OH)_2$ absorption at 637.3 cm^{-1} was also observed but not assigned in recent photochemical studies of Hg and H_2O in solid argon.[17] Therefore, the $Hg(OH)_2$ molecule is stable enough to result from the reaction of excited Hg and two water molecules.

Even though $Hg(OH)_2$ is a very stable molecule, solid $Hg(OH)_2$ does not precipitate from aqueous solution.[1] The HgO molecule is computed to be bound by about 4 kcal/mol,[34] and the total energy of HgO and H_2O molecules is approximately 57 kcal/mol above that for the $Hg(OH)_2$ molecule. Hence, the thermodynamic driving force for the precipitation of HgO from solution must arise mainly from the stability of the solid covalent chain zigzag HgO compound.[37]

Conclusions

We have prepared the stable $Hg(OH)_2$ molecule by mercury arc irradiation of Hg, H_2, and O_2 mixtures in solid neon and argon. The strongest three infrared absorptions are identified through isotopic substitution (D_2, HD, $^{18}O_2$, $^{16}O^{18}O$) and comparison to frequencies from DFT calculations. The isolated $Hg(OH)_2$ molecule is stable and has a linear O−Hg−O linkage in a C_2 structure with a 85.8° dihedral angle. A like irradiation of pure D_2 doped with Hg and O_2 formed $Hg(OD)_2$ and DHgOD. The photochemical reaction is believed to proceed through a linear OHgO intermediate to the stable HOHgOH molecule. In aqueous solution, Hg^{2+} and $2OH^-$ may form the $Hg(OH)_2$ intermediate molecule, which eliminates H_2O and precipitates solid HgO; hence, solid $Hg(OH)_2$ is not known.[1,2,8]

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