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Calculation of the Structures, Stabilities, and Properties of Mercury Sulfide Species in Aqueous Solution

J. A. Tossell

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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Quantum mechanical methods are used to determine the structures, stabilities, and properties of a number of different mercury(II) sulfide, bisulfide, and hydroxide species in aqueous solution. Relativistic effective core potential bases and methods ranging in rigor from Hartree−Fock to quadratic configuration interaction with single and double substitutions are used for the gas-phase calculations while explicit solvation with small numbers of water molecules, SCRF, and IPCM methods are used to describe hydration. We find that the species with molecular composition HgS is unstable in water solution and that it probably exists as Hg(SH)(OH), hydrated strongly by four waters. Its isomer $HgS(H_2O)$ is unstable, spontaneously rearranging to Hg(SH)(OH). By comparing the dissociation energetics of Hg(SH)(OH) with that of other compounds containing a −SH group, we have determined that Hg(SH)(OH) has a pK_a of 7 or larger, so that it is not significantly deprotonated near neutral pH. The HgS and $HgS(H_2O)$ species are also unstable to photolysis by sunlight since their lowest energy allowed spectral transitions occur in the visible or near UV. By contrast, Hg(SH)(OH) does not photolyze in sunlight. When the SH^- concentration is increased, Hg(SH)(OH) becomes unstable with respect to $Hg(SH)_2(OH)^{-1}$. Therefore, the species which is observed to partition into organic solvents under conditions of low SH^- concentration is actually Hg(SH)(OH) and the species produced at higher SH^- concentrations, which does not partition into organic solvents, is $Hg(SH)_2(OH)^{-1}$.

Introduction

An inverse relationship has been observed between dissolved sulfide concentration and the production of methylmercury (MeHg) in sediments from aquatic ecosystems.[1−3] Benoit and co-workers have hypothesized that uptake of inorganic Hg by methylating bacteria is diffusive and that the observed sulfide inhibition arises from a decreasing fraction of neutral Hg complexes with increasing sulfide concentration.[4,5] It has been shown that at least some neutral complexes of inorganic Hg, such as $HgCl_2$, are lipid soluble and that their uptake by phytoplankton occurs by passive diffusion.[6] By contrast, the crossing of the blood-brain barrier by methylmercury appears to involve one of the amino acid transport systems.[7]

Recently, Benoit and co-workers have shown that the percentage of Hg compounds partitioned into 1-octanol decreases sharply when the sulfide concentration is increased.[8] They identified the neutral Hg-containing species which is partitioned into the organic solvent as HgS(aq), using one of the values for the intrinsic solubility of cinnabar, HgS, given by Dyrssen and Wedborg.[9] However, studies by Paquette and Helz[10] on the solubility on HgS, cinnnabar, in sulfidic solutions did not find that a HgS(aq) species was needed to fit the solubility data. As noted in ref 9, it is impossible to distinguish by solubility studies (in water) between an actual HgS molecule and species with additional water molecules, such as $HgS(H_2O)_n$ or isomers such as Hg(SH)(OH). We were skeptical of the existence of an actual molecule of formula HgS in water since isolated molecules with Hg in one-coordination are not known in crystalline solids. Also, our previous calculations on various HgS[11a] and CH_3HgL[11b] species had indicated that a one-coordinate species like CH_3Hg^+ or HgS would strongly bond a water molecule to give a discrete molecule with two-coordinate Hg. In addition, our studies[11b] of the photochemistry of $CH_3Hg(H_2O)$ species indicated that the two-coordinate aquo species would by photolyzed by visible light.

While a species designated HgS(aq) is perhaps meant to be ambiguous in terms of its atomistic composition, we believe it is still important to constrain it atomistically, if possible. Only from the atomistic composition can we determine what the properties of the species will be, whether we consider structural properties like bond distances (determinable by EXAFS), spectral properties like IR/Raman or NMR, or energetics. Thus, to identify the species by matching measured spectral properties to their calculated values, we must first characterize its composition atomistically. To more completely characterize the neutral HgS(aq) species and those formed under higher sulfide concentrations, we have carried out quantum mechanical calculations on a number of the species involved. These studies are similar to our recent studies of Cu and Zn group thioarsenites,[11c,d] utilizing high-level quantum mechanical methods for the gas-phase part of the computations and for some of the spectral properties.

Computational Methods

We use mainly the techniques of Hartree−Fock theory and many-body perturbation theory. The theoretical foundations and capabilities of these techniques are discussed in ref 12a,b. Recent studies[13] have established that accurate calculation of reaction energies requires consideration of the instantaneous correlations between electron motions, using the techniques of many-body perturbation theory, configuration interaction, coupled cluster theory, or density functional theory. This is particularly important for transition metal compounds, for which even structural properties are sensitive to electron correlation. We

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have calculated energy-optimized structures for all molecules considered using the simplest version of Moller−Plesset many-body perturbation theory (second order or MP2[14a]). The MP2 method is now routinely used for calculations on both main-group and transition-metal organometallic compounds.[14b] It is very efficient and reliable, failing to give a better description than the Hartree−Fock only for some pathological open-shell systems.[14c] However, recent studies have shown that it can give poor results for some transition metal systems, producing substantial overbonding, i.e., bonds which are too short and too strong, which can be corrected[14d] by going to higher levels of theory, such as coupled cluster[15] or quadratic configuration interaction[16] approaches. For the complexes HgS, HgS(H_2O), and Hg(SH)(OH), we have therefore also carried out geometry optimizations using quadratic configuration interaction with single and double substitutions (QCISD), a considerably more demanding approach which recovers a very large fraction of the energy arising from electron correlation. In addition, we have done some calculations on these complexes using the density functional methods BLYP and B3LYP[17] to establish that our calculated geometries and energetics are stable toward changes in the quantum mechanical method.

The basis sets used for the calculations were of the relativistic effective core potential type, as implemented by Stevens, Basch, and Krauss (which we designate SBK, ref 18). These basis sets neglect core electrons but properly describe their effects upon the valence electrons, with relativistic effects incorporated. In some cases we also obtained results using the LANL2DZ bases[19] which have larger cores than the SBK (i.e., the $(n - 1)$ s and p orbitals are part of the core). Additional basis functions of d type (polarization functions) are added to each of the non-H atoms to better account for the polarization of the electron density during bond formation. For the studies on the −SH acids and arsenic acids, we also utilized polarized SBK basis sets. For comparison of one acid with another these should be adequate, although larger basis sets with diffuse functions and polarization functions on the H's would be needed to obtain accurate absolute deprotonation energies,[20] Our method for obtaining pK_a's from calculated gas-phase and solution deprotonation energetics is presented in more detail in our recent work on silicate pK_a's.[21] Basically, we calculate gas-phase deprotonation energies at a fairly high level (in this case MP2), evaluate the difference between the hydration (free) energy of the acid and its anion using the IPCM method and then correlate the calculated aqueous deprotonation energy with known experimental pK_a's. Then from this correlation we estimate the pK_a's for other species, for which experimental values are not available. We employed the programs GAMESS[22] and GAUSSIAN.[23]

The calculation of hydration effects upon chemical reactions is currently a very active area within quantum chemistry, with a number of different approaches being employed by various researchers.[24,25] To evaluate hydration enthalpies, we use a multipart approach. For common small polyatomics, such as OH^- or SH^-, we can either use "experimental" hydration energies from the tables of Rashin and Honig[26] or evaluate them using the isodensity polarized continuum method, (IPCM, ref 24), implemented in GAUSSIAN. For the other polyatomic molecules, we employ the IPCM method to calculate hydration energies for *both* the neutral molecules and their corresponding anions. The IPCM avoids an empirical estimate of the Born radius by employing an electron density criterion for defining a surface enclosing the species. For the supermolecules such as Hg(SH)(OH)·6H_2O we employ the Onsager spherical cavity version of the SCRF method,[24] both because the supermolecules are better approximated by a spherical cavity and because they converge very poorly or not at all using the IPCM method.

TABLE 1: Calculated Internal Energies (in kcal/mol) for Reactions of Neutral Molecules in the Gas Phase, Evaluated at the MP2 Level Using the Polarized SBK Basis (Energies in kcal/mol)

reaction	energy change
(1) $HgS + H_2O \rightarrow HgS(H_2O)$	−19.6
(2) $HgS(H_2O) \rightarrow Hg(SH)(OH)$	−24.0
(3) $2HgS \rightarrow Hg_2S_2$	−67.1
(4) $2HgS(H_2O) \rightarrow Hg_2S_2(H_2O)_2$	−55.7
(5) $2Hg(SH)(OH) \rightarrow Hg_2(SH)_2(OH)_2$	+15.4
(6) $Hg(SH)(OH) + H_2S \rightarrow Hg(SH)_2 + H_2O$	−20.3
(7) $HgS + H_2S \rightarrow Hg(SH)_2$	−64.0

It is useful to consider what accuracy we might expect to attain in evaluating the energetics of the Hg complexes. As described in ref 13, even an extremely accurate method such as the composite G2 approach of Pople and co-workers, which incorporates electron correlation at a very high level and effectively extrapolates to the infinite basis set limit, cannot obtain reaction energies to better average accuracy than about 1.5 kcal/mol, resulting in equilibrium constant errors at room temperature of about a factor of 10. G2 is a considerably more accurate theory than the polarized SBK MP2 or even QCISD approaches we employ for the gas-phase calculations. In addition, we must add hydration energies using methods which are clearly approximate (polarizable contintuum models) and parameter dependent. Nonetheless, we have found that *relative* complex formation enthalpies, within a series of related compounds, can be evaluated with meaningful accuracy, even at our lower level of theory. It is important that the method be simple enough computationally that we can apply it to a wide range of metal complexes, so as to identify stable species for further more detailed theoretical or experimental study.

To estimate spectral transition energies we use the configuration interaction singles (CIS) method,[27] sometimes augmented with MP2 corrections, which is implemented within GAUSSIAN. More accurate methods are available using multiconfigurational SCF plus MP*n* methods[28] but CIS is extremely simple and efficient and has yielded good results for Hg compounds such as $HgCl_2$ in our previous work.[10] To estimate XANES energies we use the equivalent ionic-core virtual orbital method pioneered by Schwarz.[29] The implementation is very simple—we replace the Hg by the core-equivalent species Tl^+, perform a Hartree−Fock calculation, and take differences of core and virtual orbital energies to simulate the XANES. In our calculations of supermolecule, e.g., Hg(SH)(OH)·6H_2O, the interaction energies are corrected for basis set superposition error using the counterpoise method.[30]

There have been a few previous quantum mechanical calculations on some of the molecules considered her. The study by Stromberg et al.[31a] was the most extensive, evaluating structures, energetics, and optical excitation spectra using CASSCF theory for HgS and $Hg(SH)_2$. Akesson et al.[31b] examined the hydration of $HgCl_2$, establishing the importance of including four water molecules coordinated to the central Hg. They also calculated XANES energies. Raptis et al.[31c] calculated the bond distance in HgS at higher quantum mechanical levels (CCSD(T)), finding good agreement with the CASSCF results of ref 31a.

Results

Stabilities of Complexes. In Table 1 we present the energies calculated at the polarized SBK MP2 level for a number of

TABLE 2: Contributions to the Energy Difference for $Hg(SH)(OH) - HgS(H_2O)$ (in kcal/mol), at Various Levels of Theory and Using Various Models for Hydration

gas-phase molecules	energy difference
HF	−21.6
MP2	−24.0
QCISD	−22.7
BLYP	−19.7
B3LYP	−19.8
zero-point energy at MP2 level	−1.7
supermolecule with four H_2O molecules at HF level (with BSSE correction)	+5.6
supermolecule with six H_2O molecules at HF level (with BSSE correction)	+5.4
SCRF for six H_2O supermolecule at HF level	+4.1
IPCM on bare molecules	+19.8
gas-phase QCISD plus ZPE plus supermolecule with six H_2O plus SCRF	−14.9
gas-phase QCISD plus ZPE plus IPCM	−4.6

reactions involving only neutral species. On the basis of these gas-phase energies we find that HgS exothermically adds a water to form $HgS(H_2O)$ (reaction 1) and that this species exothermically isomerizes to Hg(SH)(OH) (reaction 2). The HgS and $HgS(H_2O)$ species exothermically dimerize (reactions 3 and 4) but Hg(SH)(OH) is stable with respect to dimerization (reaction 5). The species which has the lowest energy per Hg of all those considered is $Hg_2S_2(H_2O)_2$, but we would not expect to encounter this under natural conditions with very small total Hg concentrations. The most stable monomeric species is Hg(SH)(OH). This Hg(SH)(OH) species is calculated to transform with modest exothermicity to $Hg(SH)_2$ in the presence of H_2S (reaction 6, −20.3 kcal/mol). The transformation of HgS to $Hg(SH)_2$ in the presence of H_2S is much more strongly exothermic (reaction 7, −64.0 kcal/mol). On the basis of the equilibrium constants given in the Appendix of ref 8 and a pK_{a1} of 7.0 for H_2S, we calculate an equilbrium constant of 10^4 for reaction 7 in aqueous solution, corresponding to a free energy change of only about −5.4 kcal/mol. We cannot evaluate the change in entropy for this reaction in solution, but since all the species are neutral, we anticipate that it is small (on the order of a few kcal/mol). Thus our calculated energetics is apparently in strong disagreement with experiment. However, we believe that the species characterized by Benoit et al.[8] is in fact not HgS, but rather Hg(SH)(OH), and that the equilibrium they have observed is described by reaction 6 rather than reaction 7. Our calculated energetics for reaction 6 are in much better agreement with their observed reaction energetics.

For all the monomeric species (e.g., those with only one Hg) we have also calculated the zero-point vibrational energy contributions to the reaction energies. These zero-point contributions are typically less than 2 kcal/mol, e.g., +1.1 kcal/mol for reaction 1 and −1.7 kcal/mol for reaction 2 and so we have not included them in Table 1. The effect of hydration on the energies for these reactions involving neutrals is expected to be small, but may be difficult to assess. For example, should we include a hydration energy for H_2O in reaction 1? The experimental hydration energy of water (essentially the enthalpy of vaporization) is about 9 kcal/mol, while the value obtained from our IPCM calculations (vide infra) is 8.7 kcal/mol. Similarly, we can calculate hydration energies for both HgS and $HgS(H_2O)$ using the IPCM method, but as previously noted HgS is not stable by itself in the presence of a real H_2O solvent.

In Table 2 we present the energy difference between Hg(SH)(OH) and $HgS(H_2O)$, obtained at a number of different levels of theory for the free molecules and with explicit water hydration, IPCM hydration, and SCRF hydration of the supermolecules. We find that the level of theory causes relatively little change in the $Hg(SH)(OH) - HgS(H_2O)$ energy difference for the gas-phase molecules. For each type of calculation the Hg(SH)(OH) form is more stable by about 20 kcal/mol. The MP2 results do show some tendency toward overbonding, as expected. For example, for gas-phase Hg(SH)(OH)) we obtain Hg−S bond distances of 2.373, 2.350, 2.365, 2.409, and 2.379 Å at the HF, MP2, QCISD, BLYP, and B3LYP levels of theory, respectively (using the polarized SBK basis). In fact, for each species considered MP2 always gives the shortest bonds. Calculations using a polarized LANL2DZ basis set (an effective core potential basis with a larger number of electrons in the core) show the same *trends* in energies and bond distances, although the calculated bond distances are systematically about 0.03 Å longer. In Figure 1 we show the structures calculated for $HgS(H_2O)$ and Hg(SH)(OH) at the polarized SBK QCISD level, with bond distances obtained at HF, MP2, and QCISD levels indicated. The qualitative trends are as expected: the bond from Hg to −SH is longer than that to −S and the bond from Hg to −OH is shorter than that to $-OH_2$.

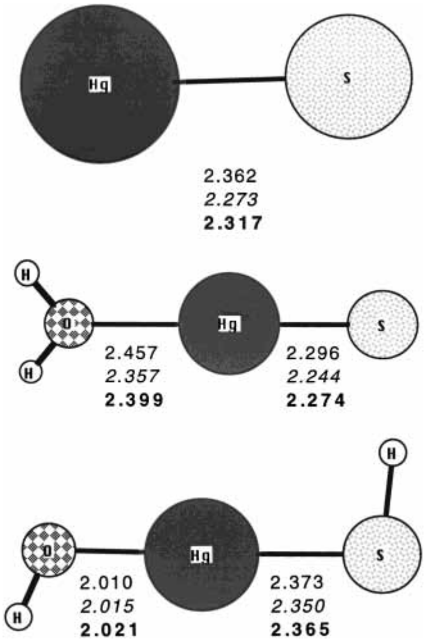


Figure 1. Calculated structures obtain at the Hartree−Fock, MP2, and QCISD levels for HgS, $HgS(H_2O)$, and Hg(SH)(OH) using the polarized SBK basis. MP2 distances in italics, QCISD in bold.

The energy difference between Hg(SH)(OH) and $HgS(H_2O)$ is reduced significantly by hydration, as shown by the other entries in Table 2. This effect appears both in calculations using four or six explicit water molecules and in those using the IPCM approach. All the explict water hydration studies were done at the polarized SBK HF level while the IPCM calculations were done at the Hartree−Fock level with MP2 geometries. Qualitatively, the Hg in Hg(SH)(OH) is more strongly bonded than in $HgS(H_2O)$ and so has lesser capacity to form additional bonds with water. At the same time, Hg(SH)(OH) is much less polar than $HgS(H_2O)$ (the calculated dipole moments are actually 0.6 and 11.6 D, respectively) and so interacts less strongly with a polarizable continuum solvent model. We have separated the hydration sphere of the solute into two parts, a set of four waters arranged around the central Hg to create the highly distorted 2+4 octahedral geometry typically found for Hg(II) species in solution and a set of six H_2O molecules, with the last two coordinated to the peripheral ligands (−SH and −OH) or (−S

TABLE 3: Hydration Energies (in kcal/mol) Calculated Using the IPCM Method with a Polarized SBK Basis for the Hg-Containing Compounds and a 6-31G* Basis for the Others

molecule	hydration energy	molecule	hydration energy
H_2O	−8.7	$Hg(SH)_2$	−6.2
OH^-	−92.6	$HgS(OH)^-$	−61.9
H_2S	−2.6	$Hg(SH)_2OH^-$	−57.3
SH^-	−71.1	$Hg(SH)_3^-$	−43.9
HgS	−27.6	$HgCl_2$	−9.0
$HgS(H_2O)$	−37.3	$HgS(SH)^-$	−54.2
Hg(SH)(OH)	−17.4		

and $-OH_2$). The interaction energies for Hg(SH)(OH) and $HgS(H_2O)$ with the six water molecules were −19.0 and −24.4 kcal/mol (the basis set superposition energy correction evaluated by a counterpoise calculation at the HF level has been included, reducing the interaction energies by about 3%). The IPCM calculations give hydration energies of −17.4 and −37.3 kcal/mol for Hg(SH)(OH) and $HgS(H_2O)$, respectively. We have also calculated hydration energies for the supermolecules, i.e., $Hg(SH)(OH)\cdot 6H_2O$ and $HgS(H_2O)\cdot 6H_2O$, using the SCRF method. These SCRF calculations enhance the relative stability of the $HgS(H_2O)$ species by about 4.1 kcal. Thus, explicit solvation by six waters plus SCRF for the supermolecule favors the $HgS(H_2O)$ species by a total of about 9.5 kcal/mol, while IPCM on the bare solute favors it by 19.8 kcal/mol. It is clear that the explicit water solvation calculations plus supermolecule SCRF and the IPCM calculations on the bare solutes are giving similar, but certainly not identical, results. Although there is substantial uncertainty in results from the SCRF and IPCM methods because of the effects of fairly abitrary choices of density contours and basis sets, the difference between these two results may arise mostly from the difference in physical picture. When we use the IPCM method on the bare solutes the difference in polarity between those solutes is the dominant effect. The explicit hydration calculation reduces this polarity difference (the calculated dipole moments for the supermolecules are now 3.6 and 9.1 D, respectively). Thus, the flexibility of explicit hydration creates a more realistic local environment for the solute.

Our results therefore indicate that the Hg(SH)(OH) species will still be more stable than $HgS(H_2O)$, even in aqueous solution, although the difference will be considerably smaller than in the gas phase. Using the IPCM hydration energies for Hg(SH)(OH) and $HgS(H_2O)$, this difference is fairly small (−4.6 kcal/mol) and using the explicit 6 water molecule hydration plus the SCRF energies for the supermolecules it is much larger (−14.9 kcal/mol). However, even the smaller difference would indicate an equilibrium constant at room temperature on the order of 10^3 for conversion of $HgS(H_2O)$ to Hg(SH)(OH).

We collect in Table 3 the hydration energies calculated using the IPCM method for all the species of interest. In these calculations we have used either a polarized SBK basis (for the Hg-containing species) or a 6-31G* basis (for the others), without polarization functions and using a dielectric constant of 80.0 for water and an isodensity contour of 0.001 e/au^3. Certainly the results are sensitive to the basis set, particularly to our neglect of diffuse functions, and to the electron density contour chosen but we have not experimented with these or tried to adjust them to match any particular experimental value. The values calculated for OH^- and SH^- are probably about 10% too small compared to the experimental values of Rashin and Honig.[26] Nonetheless, the trends and approximate magnitudes should be correct. We see a number of expected trends in these hydration enthalpies:[1] values for the anions are all large in magnitude and decrease as the size of the anion increases,[2] and values for neutral molecules are smaller but are highly variable, with the more symmetrical species showing small hydration enthalpies. Experiment indicates that $HgCl_2$ is readily partitioned into organic solvents,[6] which may be connected with its lower calculated hydration energy. On the basis of the calculated hydration energies, we might expect $Hg(SH)_2$ to also partition into organic solvents. By contrast, the anions and the highly polar neutrals, like $HgS(H_2O)$, have higher calculated hydration energies. The calculated hydration energy of Hg(SH)(OH) is somewhere in the middle. Note that the larger calculated hydration energy of Hg(SH)(OH) compared to $Hg(SH)_2$ would make reaction 6 in Table 1 less favorable by about 11 kcal/mol, reducing its exothermicity of about −20 kcal/mol to around −9 kcal/mol. Vibrational, rotational, and translational contributions (at 298 K) evaluated for the gas-phase reaction reduce the free energy difference in reaction 6 by another 1.4 kcal/mol, yielding a calculated free energy change in solution around −8 kcal/mol. This is now approaching the experimental result of around −5 kcal/mol. Clearly, there are many serious approximations involved, particularly in the calculation of hydration effects, so better agreement cannot be expected.

TABLE 4: Calculated Gas-Phase Deprotonation Energies, Hydration Free Energy Differences of Neutral and Anion, Total Estimated Solution Deprotonation Energies, and Experimental pK_a's[a]

molecule	ΔE(gas)	$\Delta\Delta G_{\text{hydration}}$	ΔE(gas) − $\Delta\Delta G_{\text{hydration}}$	exp pK_a
C_2H_5SH	360.0	−64.8	295.3	9.4
H_2S	359.2	−68.6	290.6	7.0
$As(OH)_3$	343.9	−52.8	291.1	9.2
C_6H_5SH	342.7	−59.0	283.7	6.5
Hg(SH)(OH)	335.7	−44.5	291.2	-
$Hg(SH)_2$	332.6	−48.0	284.6	-
$AsO(OH)_3$	326.6	−49.4	277.2	2.2
$HgS(H_2O)$	309.5	−24.6	284.9	-

[a] Gas-phase deprotonation energies from polarized SBK MP2 calculations, hydration free energies from Hartree−Fock IPCM calculations.

Acidities of Complexes. It is desirable to also determine the acidities of the different Hg-containing species, so as to anticipate their protonation state and charge under various conditions of pH. In Table 4 we collect calculated gas-phase deprotonation energies, differential hydration free energies of neutral acid and anion, the sum of these two contributions, and the experimental pK_a's (where known) for a number of different bisulfides, as well as for two oxyacids, $As(OH)_3$ and $AsO(OH)_3$, which have pK_a's bracketing those of the sulfides. The experimental pK_a's were obtained from ref 32a,b. In recent work on silicates,[21] we have shown that if the gas-phase deprotonation energy is calculated at a high correlated level and if the hydration energy difference between acid and anion is then included at a reasonable level such as SCRF or IPCM, the corrected solution deprotonation enthalpy correlates very well with the experimental pK_a for a series of oxyacids. Employing the same approach and the data from Table 4, we see a good correlation of the estimated aqueous deprotonation energy with experimental pK_a,for three nonmetal sulfides and the arsenic oxyacids, as shown in Figure 2, with a correlation coefficient of about 0.86. Using the correlation line given in Figure 2 and the gas-phase deprotonation energies and differential hydration energies of Hg(SH)(OH), $HgS(H_2O)$, and $Hg(SH)_2$ in Table 4, we project pK_a's of 8.1, 5.7, and 5.6 for these three molecules, respectively. The experimental value of pK_a for $Hg(SH)_2$ has been reported

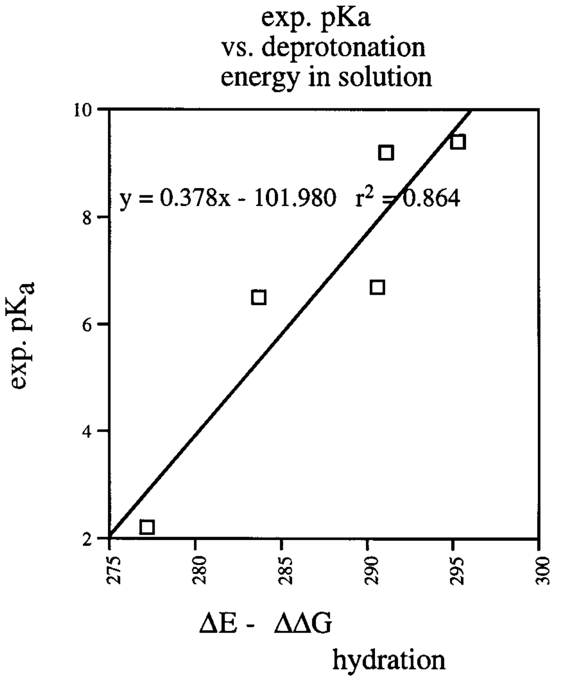


Figure 2. Correlation of experimental pK_a's with sum of calculated gas-phase deprotonation energies plus differential hydration free energies (of neutral and anion) obtained from IPCM calculations.

TABLE 5: Calculated Hg−S and Hg−O Stretching Frequencies (in cm^{-1}) in Hg Hydroxybisulfides, from Polarized SBK MP2 Calculations

molecule	ν(Hg−S)	ν(Hg−O)
Hg(SH)(OH)	356	580
HgS(H_2O)	414	238
HgS(OH)$^{-1}$	396	505
Hg(SH)$_2$(OH)$^{-1}$	259, 281	464

as 6.7 by Paquette and Helz[10b] and as 6.2 by Dyrssen and Wedborg.[9] Certainly our calculated values are uncertain by at least ±1 pK_a units, but they gives us rough information on relative acidity. We find that Hg(SH)(OH) is considerably less acidic than HgS(H_2O) or Hg(SH)$_2$. In the near-neutral pH conditions employed by Benoit et al.,[8] Hg(SH)(OH) will thus exist mainly as the neutral molecule, and so will have a greater tendency to partition into organic solvents. By contrast, HgS(H_2O) would exist primarily in the anionic form at neutral pH. It is important to establish that Hg(SH)(OH) would exist in the neutral form near neutral pH since one virtue of the Benoit et al. identification[8] of the species as HgS(aq) was its apparent neutrality and lack of ionizable H's.

Spectral Properties of Complexes. The concentrations of mercury sulfide species in aqueous solution are usually very small, so that their characterization by spectroscopy will be difficult—no spectroscopic data is presently available for systems such as that studied by Benoit, Gilmour, and co-workers. Nonetheless, it may be possible to concentrate such species, for example using partitioning into organic solvents, and in such a case characterization by spectroscopy such as IR/Raman, optical/UV absorption, EXAFS, or XANES may be possible. We have therefore calculated a range of spectral properties for the species considered. Calculated Hg−S and Hg−O stretching frequencies, obtained at the polarized SBK MP2 level, are given in Table 5. The trends are as expected: (1) Hg−O frequencies increase when H_2O is changed to OH and decrease when the coordination number increases or the bonding strength of the other ligand to Hg increases, (2) Hg−S frequencies increase when −SH is changed to −S and decrease as the coordination number of Hg increases. HgS(H_2O) would thus be identifiable by a high-frequency Hg−S stretching frequency. For comparison the calculated frequencies at the MP2 level for gas-phase $HgCl_2$ are 88, 348, and 402 cm^{-1} for the Π, Σ^+, and Σ^+ normal modes compared to experimental values of 107, 348, and 405 cm^{-1} .[33] Of course, hydration will somewhat alter these frequencies and we are presently calculating vibrational frequencies for some of the supermolecule species to test this effect.

We have also calculated the energies for optical transitions in the Hg species, using the CIS method, which we have applied before to methyl-Hg species,[10] and in a few cases CIS with MP2 corrections. We found in the CH_3HgL study[11b] that the lowest energy transitions were invariably from the HOMO's (nonbonding p orbitals on the ligands such as Cl 3p in CH_3HgCl) to the LUMO's (Hg-L σ^* orbitals), and that the energy of this transition increased as the strength of bonding to the Hg increased. Thus, the transition energy was systematically smaller for 1-coordinate than for 2-coordinate Hg complexes. We find the same trend for the present molecules, as shown in Table 6: HgS shows the lowest transition energies, those for HgS(H_2O) are somewhat higher, and those for Hg(SH)(OH) (or $HgCl_2$) are higher still. Plots of the HOMO and LUMO of HgS(H_2O) and Hg(SH)(OH) are given in Figure 3. For each molecule the lowest energy transition is mainly a HOMO to LUMO excitation. The lowest energy calculated singlet ⇒ singlet optical excitation for $HgCl_2$ are 6.2 eV (singlet to singlet) which compare fortuitously well with the experimental values of 6.2 in the gas phase and 6.1 in cyclohexane solution.[34a,b] Incorporation of MP2 corrections for the ground state and lowest energy singlet changes the transition energies by only a few tenths of an eV, as shown in Table 6. As expected, the singlet ⇒ triplet transition energies are smaller than the singlet ⇒ singlet energies by around 1 eV.

These results indicate that solar radiation, with a maximum energy of about 4.4 eV imposed by the ozone layer, will provide sufficient energy for absorption by HgS or HgS(H_2O) but not by Hg(SH)(OH). Using the CIS method, it is also possible to optimize the geometries of excited states and we find that in the lowest excited singlet state HgS(H_2O) dissociates its water molecule. Thus, such a species is photochemically unstable, at least in the gas phase and probably also in solution. Experimental studies indicate that the optical absorption spectra of Hg halides are only slightly different between the gas phase and cyclohexane solution, but results are not available for water. Our calculations indicate that the optical transition energies are systematically higher in the supermolecule with four waters, by around 1 eV.

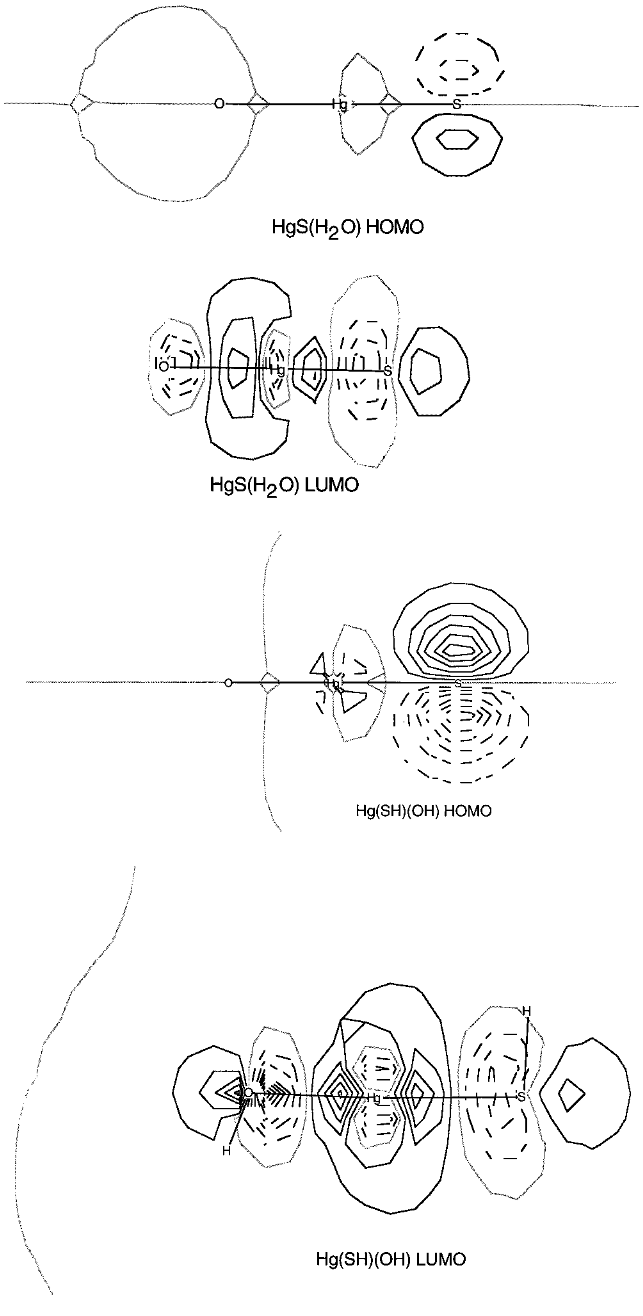
Just as the optical transition energies of HgS and HgS(H_2O) are low because of the weak destabilization of the σ^* MO, the XANES energies of these species are also expected to be low compared to those of more strongly bonded species like Hg(SH)(OH) or $HgCl_2$. Using the effective ionic-core virtual orbital model of Schwarz,[29] we obtain the results in Table 6, Our calculated Hg 5p to σ^* transition in $HgCl_2$ corresponds to a term energy of 6.5 eV, i.e., 6.5 eV below the Hg 5p ionization potential, which is close to the value of 7.3 eV obtained by Akeesson et al. using a better method (a modified coupled pair functional method with an effective core potential reoptimized for an ionized Hg atom). As expected, the Hg 5p XANES energies are indeed lower for HgS and HgS(H_2O), providing a method for characterizing them.

It is important to also establish how the Hg(SH)(OH) complex will react in the presence of additional SH$^-$ (as in the experiments of Benoit et al.). In Table 7 we present energetics

TABLE 6: Lowest Optical Transition Energies and Lowest XANES Transitions (in eV) Calculated for Hg Hydroxybisulfides and $HgCl_2$ Using the CIS Method for the Optical Excitations and the Equivalent Ionic Core Virtual Orbital Method for the XANES Transitions, with the Polarized SBK Basis, at Polarized SBK MP2 Geometries[a]

molecule	$\Delta E(S \rightarrow T)$	$\Delta E(S \rightarrow S)$[b]	ΔE(Hg5p →HardReturnLUMO)
HgS	0.1, 0.1, 1.6	1.0 (*1.1*), 1.0, 4.0	94.0
$HgS(H_2O)$ gas-phase geometry	1.6, 1.6, 3.0	2.4 (*2.7*), 2.4, 4.6	95.3
in 4 H_2O supermolecule	3.1, 3.2, 4.2	3.9, 3.9, 5.6	96.1
Hg(SH)(OH) gas-phase geometry	4.9, 5.3, 5.8	5.6 (*5.9*), 6.6, 6.8	96.9
in 4 H_2O supermolecule	5.5, 5.9, 6.0	6.1, 7.0, 7.1	96.7
$Hg(SH)_2(OH)^{-1}$ gas-phase geometry	4.9, 5.0, 5.5	5.9 (*6.2*), 6.2, 6.4	96.0
$HgCl_2$ gas-phase geometry	5.5, 5.5, 5.7	6.1, (*6.1*) 6.1, 6.6	96.6
in 4 H_2O supermolecule	6.4, 6.8, 6.8	7.4, 7.4, 7.9	96.4
		exp **6.2** gas, **6.1** cyclohexane	

[a] Both triplet and singlet optical excitation energies are given for the optical transitions. [b] Values in italics from CIS-MP2 calculations for lowest singlet−singlet transition, values in bold from experiment for lowest singlet−singlet transitions.



HgS(H2O) HOMO

HgS(H2O) LUMO

Hg(SH)(OH) HOMO

Hg(SH)(OH) LUMO

Figure 3. Plots of HOMO and LUMO for $HgS(H_2O)$ and Hg(SH)(OH), obtained from Hartree−Fock calculations at polarized SBK MP2 geometries. Positive contours are solid black, zero contours are gray, and negative contours are dashed.

TABLE 7: Calculated Energies for Reactions Involving Ions in Aqueous Solution[a]

reaction	ΔE(gas)	$\Delta G_{\text{hydation}}$	ΔG(total)
$Hg(SH)(OH) + SH^- \rightarrow$	+29.6	−10.3	19.3
$Hg(SH)_2 + OH^-$		(−16.4)	(13.2)
$Hg(SH)(OH) + SH^- \rightarrow$	−44.8	31.2	−13.6
$Hg(SH)_2(OH)^-$		(43.4)	(−1.4)

[a] Gas-phase eneergies are from polarized SBK MP2 calculations, hydration energies from HF IPCM calculations. When experimental values from ref 20 are used for the hydration energies of OH^- and SH^- the values in parentheses result.

for two possible reactions between Hg(SH)(OH) and SH^-, one leading to exchange of OH^- by SH^- and the second leading to addition of SH^- to form a complex with three-coordinate Hg (of course complexes like $HgCl_4^{-2}$, with four-coordinate Hg, are well characterized in solutions of high Cl^- concentration). We have evaluated the contribution to the hydration energetics both using the IPCM values for all species and using experimental values for the small anions with large hydration energies, SH^- and OH^-. Using either set of values, we find that the exchange reaction is unfavorable while the addition reaction is favorable. Note that the gas-phase energy for the first reaction in Table 7 differs from that for reaction 6 in Table 1 (involving neutral H_2S and H_2O) because of the great difference in gas-phase deprotonation energies between H_2S and H_2O (that of H_2O is about 50 kcal/mol larger at the polarized SBK MP2 level). This difference is somewhat reduced by hydration but is not eliminated. These results indicate that the species existing in solutions with high SH^- concentration is $Hg(SH)_2(OH)^{-1}$. Its apparently strong preference from water over organic solvents is consistent with its large calculated hydration energy.

Conclusions

HgS is unstable in the presence of H_2O, reacting to form $HgS(H_2O)$ which subsequently isomerizes to Hg(SH)(OH). Hg(SH)(OH) is more stable than $HgS(H_2O)$ for all levels of theory, in both gas phase and solution. The pK_a of Hg(SH)(OH) is estimated to be 7 or higher, so it exists as the neutral molecule near neutral pH and, due to its small hydration energy, it can partition into organic solvents. When the SH^- concentration is increased, $Hg(SH)_2(OH)^{-1}$ becomes the stable species. This anion has a large hydration energy and is thus confined to aqueous solution. These qualitative conclusions are well established, but quantitatively there is enormous room for improvement in the calculated energetics, particularly in the incorporation of hydration effects.

The various species considered differ substantially in their calculated vibrational spectra, visible, and UV absorption spectra and XANES. In particular, HgS and $HgS(H_2O)$ have singlet ⟹ singlet absorptions in the visible or near-UV, indicating that they would be decomposed by sunlight.

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