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Mercury Monoxide: A Systematic Investigation of Its Ground Electronic State

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One of the possible key products in the oxidation and transport of atmospheric mercury is mercury monoxide, HgO. In the present work, large-scale multireference configuration interaction, as well as coupled cluster, wave functions have been used in conjunction with a series of correlation consistent basis sets to calculate the near-equilibrium potential energy functions of the first two electronic states of HgO. In the absence of spin−orbit coupling, the lowest $^1\Sigma^+$ and $^3\Pi$ states are nearly isoenergetic with a binding energy with respect to ground-state atoms of only 2−3 kcal/mol at the estimated complete basis set limit. After spin−orbit coupling effects are accurately included, the resulting $X0^+$ state has a D_0 of just 4.0 kcal/mol, leading to a $\Delta H_f(0\ K)$ of 70.4 kcal/mol. These values are in stark contrast to the currently accepted experimental values. The implications of these results to atmospheric mercury chemistry are briefly discussed.

I. Introduction

Recent studies in both the Arctic and Antarctic during polar springtime have revealed episodic depletions in the concentration of tropospheric mercury.[1−6] Mercury, which prior to polar sunrise exists primarily as gaseous elemental mercury, is believed to be converted to some form of reactive gaseous mercury (RGM) or particulate mercury [Hg(p)] that is then deposited on the snowpack. It has been suggested that these mercury depletion events (MDEs) are a significant source of mercury introduction to the biosphere during this sensitive time of year and an important global sink for atmospheric mercury.[3−5] The MDEs are strongly correlated with tropospheric ozone depletions that occur at the same time of year.[1−3,5,6] The ozone depletion events are known to be caused by reactions of ozone with reactive halogen species,[7−10] and it has been suggested that reactive halogen species are also responsible for the mercury depletion events.[1−6] In particular, the reaction Hg + BrO → HgO + Br has been proposed to be a major path for the depletion of mercury in the troposphere and a major source of RGM.[2,5,8]

While HgO is well-known as a solid, it is poorly characterized in the gas phase. Mercury monoxide has been tentatively identified in argon matrixes[11] with a fundamental IR vibrational frequency of 676 cm^{-1}. An earlier mass spectrometric measurement reported a dissociation energy for HgO of 53 ± 8 kcal/mol,[12] while JANAF cites a value of 64 ± 15 kcal/mol.[13] The latter of these is apparently based on comparisons to lead compounds and other mercury species. Heats of formation based on these values yield a reaction enthalpy for the Hg + BrO reaction that is either slightly endothermic (2.2 kcal/mol) or slightly exothermic (−8.8 kcal/mol), respectively. Theoretical calculations of the dissociation energy of mercury monoxide, however, show even more significant variations. In particular, while the 4-component Dirac Hartree−Fock (DHF) calculations of Hu et al.[14] yielded an equilibrium dissociation energy of ∼40 kcal/mol, two previous calculations[15,16] based on relativistic effective core potentials (RECPs) resulted in HgO being *unbound* with respect to dissociation to ground-state atoms by more than 14 kcal/mol. All of these previous ab initio calculations utilized relatively small basis sets with little or no electron correlation.

To unambiguously determine the reaction enthalpy of the Hg + BrO reaction, large scale ab initio calculations have been carried out on HgO involving highly correlated wave functions and sequences of basis sets approaching the complete basis set (CBS) limit. Both RECP and all-electron calculations have been used in the calculation of the potential energy function of HgO. In the absence of spin−orbit coupling, the electronic ground state is predicted to be a $^3\Pi$ state with a $^1\Sigma^+$ state lying above by only 0.6 kcal/mol. The inclusion of spin−orbit coupling results in an $\Omega = 0^+$ ground state that is bound with respect to $Hg(^1S_0) + O(^3P_2)$ products by only 4.0 kcal/mol (D_0). This results in a Hg + BrO → HgO + Br reaction enthalpy that is strongly endothermic.

II. Methodology

Both singles and doubles coupled cluster with perturbative triples,[17] CCSD(T), and internally contracted multireference singles and doubles configuration interaction[18,19] (MRCI) calculations were carried out in this work. For the open-shell calculations, a variant of CCSD(T), denoted R/UCCSD(T),[20−22] was used which employs restricted open-shell Hartree−Fock (ROHF) orbitals but where some spin contamination is allowed to enter into the solution of the CCSD equations. In the present calculations the resulting spin contamination was always very small (≤0.01). The MRCI calculations included the multireference Davidson correction[23−25] for approximately including the effects of higher excitations (MRCI + Q). To obtain accurate dissociation energies for HgO at the MRCI level of theory, it was found to be very important to include the Hg 6*p* orbitals in the reference function. For example, MRCI + Q calculations with standard valence (i.e., Hg 5*d*6*s* and O 2*s*2*p*) complete active space (CAS) reference functions underestimated the dissociation energy by over 3 kcal/mol for the $^1\Sigma^+$ state. The final reference

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function was formed from a CAS in the valence orbitals (16 electrons in 9 orbitals, i.e., Hg 5*d*6*s* and O 2*s*2*p*, with the O 2*s* orbital constrained to be doubly occupied) plus additional configurations involving a maximum of two electrons in the next higher orbitals of a_1, b_1, and b_2 symmetry (in C_{2v}), which were primarily of Hg 6*p* character. This yielded 799 reference configurations for the $^1\Sigma^+$ state (742 for the $^3\Pi$ state), and the resulting internally contracted MRCI expansions involved a total number of variational parameters of just over 13 million for the $^1\Sigma^+$ and 22 million for the $^3\Pi$ state when basis sets of 5Z+diffuse quality were used (see below). The orbitals for these large MRCI calculations were taken from the CI natural orbitals of CAS(6,4)-MRCI calculations in order to obtain well-defined Hg 6*p* orbitals across both potential curves. Those for the $^3\Pi$ state were derived from the average density matrixes of analogous $^3\Pi_x$ and $^3\Pi_y$ MRCI calculations ($^3B_1$ and $^3B_2$ in C_{2v}, respectively). Unless otherwise noted, the frozen core approximation was employed throughout, i.e., only the 2*s* and 2*p* electrons of O and the 5*d* and 6*s* electrons of Hg were correlated.

The basis sets used in the present work corresponded to the standard cc-pV*n*Z sets for oxygen[26] augmented with extra diffuse functions,[27] denoted aug-cc-pV*n*Z, where *n* ranged from D, T, Q, and 5. New correlation consistent basis sets for mercury, denoted cc-pRV*n*Z and aug-cc-pRVnZ, have recently been developed in our laboratory and were used in the present work. These will be discussed in more detail in a separate publication.[28] The Hg basis sets incorporate the 60 electron relativistic effective core potential (RECP) of Häussermann et al.,[29] which leaves 20 electrons (5*s*5*p*5*d*6*s*) to be explicitly treated in the ab initio calculations. The cc-pRV*n*Z basis sets range in size from (7*s*7*p*6*d*1*f*)/[4*s*4*p*3*d*1*f*] for the cc-pRVDZ to (14*s*14*p*11*d*4*f*3*g*2*h*1*i*)/[8*s*8*p*7*d*4*f*3*g*2*h*1*i*] for the cc-pRV5Z. The diffuse augmented variations were obtained by adding one additional even-tempered function in each angular symmetry. The combination of an aug-cc-pRV*n*Z basis set on Hg and an aug-cc-pV*n*Z on O is denoted AV*n*Z (*n* = D, T, Q, 5). To test the accuracy of the pseudopotential (PP) approximation and the effects of scalar relativity, all-electron calculations were also carried out. In these cases, two different series of basis sets were developed for mercury, one in which the exponents were optimized in calculations using the Douglas-Kroll-Hess (DK) approximation[30,31] for scalar relativity and one series in which the exponents were optimized without relativistic effects. The former will be denoted by cc-pV*n*Z-DK (*n* = D, T, Q, 5) and the latter by cc-pV*n*Z-NR (*n* = D, T, Q, 5). Similar shells of correlating functions were included in these sets as for the previously described cc-pRV*n*Z ones, but the underlying Hartree−Fock sets consisted of (32*s*26*p*19*d*13*f*) and (29*s*24*p*19*d*13*f*) base sets for -DK and -NR, respectively, which were of valence triple-ζ quality. In the DK calculations, the *sp* parts of the oxygen basis sets were recontracted based on atomic SCF-DK calculations. In all cases only the pure spherical harmonic components of the *d* through *i* polarization functions were included.

The systematic convergence behavior of the basis sets used in this work was exploited by extrapolating to the estimated complete basis set (CBS) limit. Two different extrapolation formulas were used:

$$E(n) = E_{\mathrm{CBS}} + Be^{-(n-1)} + Ce^{-(n-1)^2} \quad (1)$$

$$E(n) = E_{\mathrm{CBS}} + B/n^3 \quad (2)$$

eq 1[32,33] was used with basis sets from TZ through 5Z (*n* = 3−5), while eq 2[34,35] was only used for the two largest sets, QZ and 5Z. In this work the average of these two values will be taken as the best estimate of the true CBS limit.

To investigate the effects of correlating the Hg 5*s*5*p* and O 1*s* electrons on the dissociation energies and spectroscopic constants, CCSD(T) calculations were also carried out with aug-cc-pwCV*n*Z (oxygen)[36] and cc-pRwCV*n*Z (mercury) basis sets (*n* = T and Q) both with and without correlating the core electrons. The weighted core-valence basis sets for mercury were derived in an analogous manner as recently described[36] for the first- and second-row atoms and consisted of additional 2*s*2*p*2*d*1*f* functions for TZ and 2*s*2*p*2*d*1*f*1*g* for the QZ set.

Spectroscopic constants were obtained via the usual Dunham analysis[37] using polynomial fits to 7 near-equilibrium bond lengths ($-0.3\ a_o \le r - r_e \le +0.5\ a_o$). Dissociation energies at the MRCI level were calculated relative to the energy of the $^3\Pi$ state at $r = 50$ bohr. Those at the CCSD(T) level of theory were obtained relative to ground-state atoms, where the O(^{3}P) calculations employed partially symmetry equivalenced (*x* and *y* components only) Hartree−Fock orbitals.

The effects of spin−orbit coupling on the potential energy functions employed the effective 1-electron SO operator on Hg from the RECP within the interacting states method, whereby the spin−orbit coupled eigenstates were obtained by diagonalizing a matrix of $H_{\mathrm{el}} + H_{\mathrm{SO}}$ in a basis of pure Λ-S states. The spin−orbit matrix elements were calculated at the MRCI/aug-cc-pVQZ level of theory[38] (aug-cc-pRVQZ for Hg) with an active space similar to the large MRCI described above, but the Hg 5*d* electrons were not correlated. The orbitals used in these calculations corresponded to state-averaged CASSCF orbitals with an active space that included the Hg 6*p* orbitals. A total of 16 electronic states were used in the construction of $H_{\mathrm{el}} + H_{\mathrm{SO}}$, which included all singlets and triplets that correlate with Hg(^{1}S) + O(^{3}P), Hg(^{1}S) + O(^{1}D), Hg(^{1}S) + O(^{1}S), and Hg(^{3}P) + O(^{3}P). Neither the repulsive quintets nor the two highest-lying $^{1,3}\Sigma^-$ states were included. The diagonal elements of $H_{\mathrm{el}} + H_{\mathrm{SO}}$ were replaced by MRCI+Q/CBS energies for the $1^1\Sigma^+$ and $1^3\Pi$ states (Hg 5*d* electrons correlated), while the higher states were shifted by the difference of MRCI+Q/CBS (Hg 5*d* correlated) and MRCI+Q/aug-cc-pVQZ (Hg 5*d* not correlated) calculations on the $^1\Sigma^+$ state. Since a spin−orbit RECP was not included on oxygen, the asymptotic atomic energy of O was corrected by the experimental SO splitting of the O(^{3}P) state, i.e., $E(^3P_2 - {}^3P_{\mathrm{avg}}) = -0.22$ kcal/mol.[39]

All of the ab initio calculations in this work were carried out with the MOLPRO suite of programs.[40]

III. Results

Among the low-lying electronic states of HgO, two of these, the $1^1\Sigma^+$ and $1^3\Pi$, are candidates for the electronic ground state when spin−orbit coupling is neglected. The $1^3\Pi$ state is one of two states correlating asymptotically to ground-state atoms, i.e., Hg(^{1}S) + O(^{3}P). The other state correlating to this asymptote, the $1^3\Sigma^-$ state, is purely repulsive. The $1^1\Sigma^+$ is one of 3 states (the others are the higher-lying $1^1\Pi$ and the $1^1\Delta$ states) that correlates to Hg(^{1}S) + O(^{1}D). Near their equilibrium geometries, however, both the $1^1\Sigma^+$ and $1^3\Pi$ states correlate with Hg$^+$(^{2}S) + O$^-$(^{2}P). As discussed previously by Bauschlicher and Langhoff for ZnO,[41] these two states differ in the orientation of the *p* hole on O$^-$. The $p\sigma$ hole is favored by Pauli repulsion interactions, while the $p\pi$ hole is favored by the electrostatic interaction. In the case of the $^3\Pi$ state, the wave function changes from an ionic to a covalent charge distribution at bond distances only slightly longer than its equilibrium separation.

TABLE 1: Calculated Spectroscopic Constants of $1^1\Sigma^+$ and $1^3\Pi$ HgO Neglecting Spin−Orbit Coupling

method	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (kcal/mol)[a]	ΔE_e (kcal/mol)[b]
			$1^1\Sigma^+$		
CCSD(T)/					
AVDZ	1.9468	566.8	3.2	−5.75	
AVTZ	1.9195	593.9	3.6	0.04	
AVQZ	1.9145	596.7	3.4	1.59	
AV5Z	1.9124	599.2	3.5	2.17	
CBS(1)				2.52	
CBS(2)				2.79	
MRCI+Q/					
AVDZ	1.9440	572.7	3.8	−5.42	6.52
AVTZ	1.9186	594.6	3.7	−0.03	2.04
AVQZ	1.9145	596.3	3.6	1.33	1.20
AV5Z	1.9125	598.8	3.8	1.84	0.84
CBS(1)				2.14	0.44
CBS(2)				2.38	0.46
			$1^3\Pi$		
MRCI+Q/					
AVDZ	2.2979	305.1	(*c*)	0.77	
AVTZ	2.2410	294.9	(*c*)	2.01	
AVQZ	2.2284	293.9	(*c*)	2.53	
AV5Z	2.2214	287.8	(*c*)	2.68	
CBS(1)				2.77	
CBS(2)				2.84	

[a] Calculated with respect to ground-state Hg(^{1}S) and O(^{3}P). [b] $E(1^1\Sigma^+) - E(1^3\Pi)$, i.e., a positive value indicates the $^3\Pi$ is lower in energy. [c] A reliable value was not obtained due to the flatness of the potential.

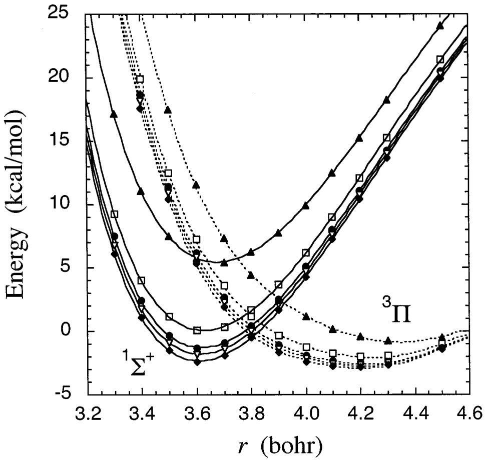

Figure 1. Potential energy curves for the lowest two electronic states of HgO calculated as a function of basis set [AVDZ (▲), AVTZ (□), AVQZ (●), AV5Z (▽), and CBS (◆)] at the MRCI+Q level of theory (neglecting spin−orbit coupling).

This is essentially an avoided crossing and results in discontinuous potential energy curves at the R/UCCSD(T) level of theory. Table 1 shows the calculated spectroscopic constants for CCSD(T) and MRCI+Q as a function of basis set for the $1^1\Sigma^+$ and $1^3\Pi$ states. The R/UCCSD(T) results for the $1^3\Pi$ state were deemed unreliable and are not shown. Potential energy curves at the MRCI+Q level of theory are plotted for both states in Figure 1 as a function of basis set. The stronger basis set dependence of the $1^1\Sigma^+$ state is clearly observed. As shown in Table 1, CCSD(T) and MRCI+Q yield essentially identical spectroscopic constants for the $^1\Sigma^+$ state and the equilibrium dissociation energies differ by only a few tenths of a kilocalorie per mole. At the CBS limit (without including SO coupling in the molecule or atoms), this state is predicted to be bound with respect to ground-state atoms by just 2.4 kcal/mol (only 1.5 kcal/mol after zero-point vibrational effects are included). The $^1\Sigma^+$ state is unbound with the DZ basis set by over 5 kcal/mol, which is consistent with earlier RECP calculations.[15,16] In the case of the $1^3\Pi$ state, the equilibrium bond length is longer than that of the $1^1\Sigma^+$ by nearly 0.3 Å with a much shallower well ($\omega_e \sim 290$ cm^{-1}). Relative to ground-state atoms, the $^3\Pi$ state is bound by 2.8 kcal/mol at the MRCI+Q/CBS level of theory (2.4 kcal/mol with ZPE corrections). Hence, before the inclusion of spin−orbit coupling, the ground state of HgO would correspond to the $1^3\Pi$ state, albeit by only a small margin (∼0.4 kcal/mol without ZPE, and ∼0.9 kcal/mol with ZPE corrections).

TABLE 2: Effects of Scalar Relativity on the Spectroscopic Constants of $1^1\Sigma^+$ HgO at the CCSD(T) Level of Theory in All-Electron Calculations[a]

method	r_e (Å)	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (kcal/mol)
NR				
DZ	2.0628	512.2	2.2	17.56
TZ	2.0360	538.6	2.8	21.56
QZ	2.0291	547.0	3.0	22.88
5Z	2.0268	548.9	3.0	23.15
DK				
DZ	1.9425	566.1	2.9	−3.20
TZ	1.9201	593.0	3.4	1.07
QZ	1.9143	599.5	3.4	2.40
5Z	1.9124	601.4	3.5	2.69

[a] NR=nonrelativistic, DK=Douglas-Kroll with cc-pV*n*Z-NR or cc-pV*n*Z-DK on Hg and aug-cc-pV*n*Z or aug-cc-pV*n*Z-DK on O. See the text. All electrons are explicitly treated in these calculations, but only the valence electrons were correlated.

Table 2 shows the effects of scalar relativity on the spectroscopic constants of the $^1\Sigma^+$ state from all-electron calculations (note that these are implicitly included via the RECP in the results described above). Scalar relativistic effects as obtained at the CCSD(T)-DK level of theory are calculated to decrease the bond length by 0.11 Å with a concomitant increase in the harmonic frequency of 52 cm^{-1}. An even larger effect is observed for the dissociation energy, which is strongly decreased by scalar relativity from 23.2 to just 2.7 kcal/mol. Both of these effects are presumably due to the relativistic contraction of the 6*s* orbital of Hg, which shortens the bond length but strongly destabilizes the resulting σ bond. Comparison of the cc-pV5Z-DK results of Table 2 with the 5Z RECP values of Table 1 reveals an estimate of the accuracy of the relativistic PP approximation near the CBS limit for HgO. In the present case, the differences between the DK and PP calculations are found to be negligible for the spectroscopic constants and only ∼0.5 kcal/mol for D_e. It should be noted, however, that the Douglas-Kroll calculations used in this work are only correct to second order, so the DK scalar relativistic effects may be slightly underestimated for an element as heavy as Hg.[42]

Last, the effects of correlating the core electrons at the CCSD(T) level of theory using the RECPs are much more modest and result in a bond shortening of −0.009 Å, an increase in ω_e by 9 cm^{-1}, and nearly no change in D_e (+0.02 kcal/mol) for the $^1\Sigma^+$ state. Similar calculations on the $^3\Pi$ state yielded core-valence correlation effects of just +0.0015 Å on r_e and −0.25 kcal/mol on D_e.

Figure 2 shows the potential energy functions that were used (before adjustment) in the construction of the spin−orbit matrix within the interacting states method as described previously. In addition to the $1^1\Sigma^+$ and $1^3\Pi$ states, several other states are calculated to be clearly bound before including the effects of spin−orbit coupling, namely the low-lying $^1\Pi$ state that dissociates to Hg(^{1}S) + O(^{1}D), the $^3\Sigma^+$, $^3\Pi$, and $^1\Pi$ states that dissociate to Hg(^{3}P) + O(^{3}P), and the $^1\Sigma^+$ state that leads to Hg(^{1}S) + O(^{1}S). Figure 3 depicts the lowest spin−orbit coupled

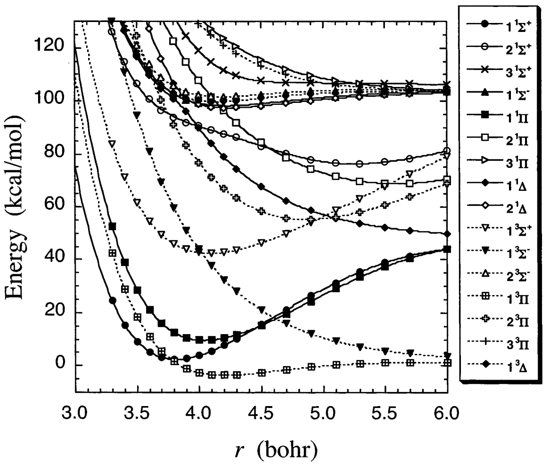

Figure 2. Potential energy curves at the MRCI+Q/AVQZ level of theory for the low-lying electronic states of HgO used in the calculation of spin−orbit coupling effects. The Hg 5*d* electrons were not correlated in these calculations.

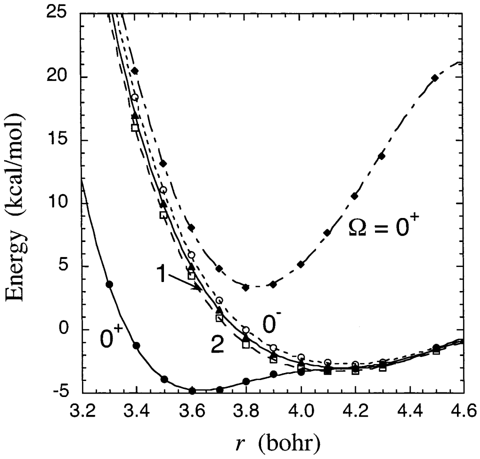

Figure 3. Potential energy curves for the lowest spin−orbit coupled electronic states of HgO calculated at the MRCI+Q/CBS level of theory. The states are labeled by their Ω quantum numbers.

eigenstates of HgO. With spin−orbit effects included, the $\Omega = 0^+$ state arising from the $^1\Sigma^+$ exhibits a spin−orbit-induced avoided crossing with the $\Omega = 0^+$ component of the $^3\Pi$ state and dissociates to ground-state atomic products. The inclusion of spin−orbit coupling results in a 0^+ state that is lower than the previous $^1\Sigma^+$ state by 2.4 kcal/mol. Thus, the equilibrium dissociation energy of the 0^+ ground state is calculated to be 4.7 kcal/mol (relative to Hg $^1S_0$ + O $^3P_2$). This result cannot be reconciled with the previous DHF result of Hu et al.[14] of nearly +40 kcal/mol. The result of ref 14 is presumably in error, possibly due to extensive BSSE, since at the RHF level of theory both the $^1\Sigma^+$ and $^3\Pi$ states are calculated in this work to be *unbound* with respect to ground-state atoms by more than 50 and 20 kcal/mol, respectively. At this uncorrelated level of theory, the lowest 0^+ state as calculated in ref 14 would correspond to the $^3\Pi$ state in the absence of spin−orbit coupling. Thus the inclusion of spin−orbit coupling would have to contribute 60 kcal/mol to the binding energy, which is more than an order of magnitude larger effect than obtained in this work. It should also be mentioned that HgO is a challenging case for all-electron, 4-component methods due to the strong effects of both basis set completeness and electron correlation.

The equilibrium bond length (calculated using polynomial fits near the minimum) and $v = 0-1$ fundamental vibrational frequency (calculated using the program LEVEL[43]) of the X0^+ state are predicted in this work to be 1.922 Å and 361 cm^{-1}, respectively. These values do not include the effects of core-valence correlation reported above, which are expected to decrease this equilibrium bond distance by approximately 0.009 Å and only slightly increase the vibrational frequency. The vibrational frequency calculated for the final SO-coupled potential (361 cm^{-1}) is in strong disagreement with the tentative vibrational assignment of Butler et al.[11] in rare gas matrixes, 676 cm^{-1}, and leads one to believe that HgO was not actually observed in their experiments. (The experimental value is also in disagreement with the calculated $^1\Sigma^+$ vibrational frequency of ~590 cm^{-1}.) Combining the calculated zero-point vibrational energy of 225 cm^{-1} with a D_e value of 4.7 kcal/mol yields a predicted D_0 for HgO of just 4.0 kcal/mol. This value cannot be reconciled with the current experimental values of 64 ± 15 (ref 13) and 53 ± 8 (ref 12) kcal/mol. The former of these was obtained only by comparison with various Pb compounds and can be safely discounted. The discrepancy with the latter experiment is more difficult to explain. Certainly there is a need for further experimental studies of this species.

IV. Discussion

Accurate electronic structure methods have been used to determine the energetics and spectroscopic constants of the ground electronic state of HgO. After accounting for basis set truncation errors, electron correlation, scalar relativity, spin−orbit coupling, and vibrational zero-point energy, the X0^+ ground state of HgO is predicted to be bound by only 4.0 kcal/mol with respect to ground-state atoms. This is in stark contrast to the JANAF value[13] of 64 ± 15 kcal/mol and a more recent mass spectrometric value[12] of 53 ± 10 kcal/mol. The much lower value for the dissociation energy of HgO has a strong impact on the predicted reactivity of Hg with BrO leading to HgO. Using the best available heats of formation[13,44] for Hg, BrO, and Br together with a $\Delta H_f(0\ K)$ of 70.4 kcal/mol derived from the above D_0, the reaction Hg + BrO → HgO + Br is now calculated to be very endothermic, $\Delta H_r(0\ K) = 51.2$ kcal/mol. Hence it appears unlikely that gas-phase mercury monoxide will be directly formed from the oxidation of Hg by BrO.

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