THE JOURNAL OF CHEMICAL PHYSICS **133**, 144309 (2010)

# Spin-orbit density functional and *ab initio* study of $HgX_n$ ($X=F$, Cl, Br, and I; $n=1$, 2, and 4)

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(Received 30 June 2010; accepted 15 September 2010; published online 11 October 2010)

Quantum chemical calculations of $HgX_n$ ($X=F$, Cl, Br, and I; $n=1$, 2, and 4) in the gas phase are performed using the density functional theory (DFT), two-component spin-orbit (SO) DFT, and high-level *ab initio* method with relativistic effective core potentials (RECPs). Molecular geometries, vibrational frequencies, and various thermochemical energies are calculated and compared with available experimental results. We assess the performances of DFT functionals for calculating various molecular properties. The PBE0 functional is generally reasonable for the molecular geometries and the vibrational frequencies, but the M06 functional is more appropriate for estimating thermochemical energies. Both shape-consistent and energy-consistent RECPs correctly describe the SO effect. © *2010 American Institute of Physics*. [doi:10.1063/1.3497189]

## I. INTRODUCTION

Metal halides have become growingly important not only for fundamental interest but also for industrial applications such as halogen metallurgy and etching semiconductor devices.[1,2] In particular, mercury halides have been studied both experimentally[1,3–7] and theoretically[8–13] due to their interesting molecular properties. For example, the oxidation state of mercury has been under controversy. Mercury possesses the oxidation state of +I or +II in most molecules, but the existence of $HgF_4$, where the oxidation state of mercury is +IV, has been suggested.[9–12] The +IV oxidation state means that mercury is not a post-transition metal but a transition metal that uses d electrons for making chemical bonds. Although quantum chemical calculations have suggested the existence of $HgF_4$ in gas phase since 1993,[9–12] its experimental evidence has been found only recently.[7]

In most quantum chemical calculations of mercury halide made thus far,[8–13] only compounds containing one or two halogen atoms have been studied, while a systematic study including, for example, halogen atoms varying from F to I, is lacking. In addition, despite the importance of relativistic effect in the calculation of molecular properties of mercury halides containing heavy mercury atom, most of the previous calculations were made only at a scalar relativistic level, with the spin-orbit (SO) effect of mercury halides often being ignored. Shepler *et al.* investigated HgI, HgBr, HgCl, and $HgI_2$ using very high-level *ab initio* method with accurate relativistic corrections including the SO effect, thus providing the results in a good agreement with experimental results.[13] However, they did not provide the performance of density functional theory (DFT) (Ref. 14) calculation. Using the high-level *ab initio* method such as coupled-cluster singles and doubles with perturbative triples [CCSD(T)] is expected to produce accurate results, but the computation is quite demanding. The DFT method combined with a proper functional can serve as an alternative for CCSD(T), but the type of DFT functional considerably affects the reliability of the calculated results. Riedel *et al.* studied the performance of several DFT functional, but only $HgX_4$ ($X=F$, Cl, and H) was considered.[12] Rather than for a specific system, the performance test of DFT for general $HgX_n$ ($X=F$, Cl, Br, and I; $n=1$, 2, and 4) is highly required in view of that numerous experimental results for $HgX_n$ ($X=F$, Cl, Br, and I; $n=1$, 2, and 4) are readily available. Thus, these molecules are appropriate for the assessment of DFT functionals as well as RECPs, which include the SO potential for the two-component SO calculations.

In this study, we have applied the DFT and two-component spin-orbit DFT (SODFT) (Ref. 15) to $HgX_n$ ($X=F$, Cl, Br, and I; $n=1$, 2, and 4). The spin-orbit coupling (SOC) is explicitly considered using two sets of relativistic effective core potential (RECP). The performance of the RECP in treating the SOC is tested through comparison with all-electron SO *ab initio* calculations. In addition, we have assessed the performance of newly developed DFT exchange-correlation functionals in calculations of molecular properties of $HgX_n$.

## II. COMPUTATIONAL DETAILS

The DFT and SODFT calculations were carried out using the NWCHEM5.1 program.[16] We used PBE0 (hybrid),[17] M06 (hybrid-meta),[18] and M06-L [meta-generalized gradient approximation (GGA)] (Ref. 19) for the exchange-correlation functional. Recent investigation of 5d transition metal complexes showed that PBE0 functional provides good results for the molecular geometries.[20] Moreover, the performance of M06 family functional for mercury halides has not been assessed. For these reasons, we chose these DFT functionals. Two types of RECP were used for Hg. The first one is the CRENBL (Christiansen, Ross, Ermler, Nash,

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TABLE I. Optimized Hg–F distances (in angstrom) of HgF, $HgF_2$, and $HgF_4$. Values in parentheses are calculated using aug-cc-pVQZ for F.

| | RECP | PBE0 | SO-PBE0 | M06 | SO-M06 | M06-L | SO-M06-L | CCSD(T) | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| HgF | CRENBL | 2.055 | 2.049 | 2.091 | 2.085 | 2.102 | 2.096 | 2.003 | ⋯ |
| | AVTZ-PP | 2.044 (2.042) | 2.036 | 2.083 | 2.075 | 2.089 | 2.085 | 2.028 | |
| $HgF_2$ | CRENBL | 1.928 | 1.926 | 1.941 | 1.940 | 1.952 | 1.951 | 1.918 | 1.94(2)[a] |
| | AVTZ-PP | 1.915 (1.914) | 1.912 | 1.930 | 1.927 | 1.942 | 1.939 | 1.914 | |
| $HgF_4$ | CRENBL | 1.900 | 1.899 | 1.912 | 1.911 | 1.934 | 1.934 | 1.885 | ⋯ |
| | AVTZ-PP | 1.885 (1.885) | 1.884 | 1.899 | 1.897 | 1.921 | 1.919 | 1.889 | |

[a] $L_3$-edge EXAFS data, Ref. 4.

Bursten, and Large-valence-shape-consistent)[21] RECP, and the second one is the aug-cc-pVTZ-PP (AVTZ-PP, energy-consistent), which denotes the combination of energy-consistent pseudopotential (PP) and the aug-cc-pVTZ basis set for the valence space.[22] These two RECPs have the same core size of 60 electrons, that is, the 20 valence electrons for Hg. In addition, both RECPs have the SO potential for the two-component SO calculation. For F and Cl, we used all-electron aug-cc-pVTZ basis sets. The all-electron aug-cc-pVQZ basis set was used only for F with PBE0 functional to check the dependence of the basis set. In the calculations for $HgBr_n$ and $HgI_n$, we used the RECPs for all atoms. The CRENBL RECPs and the aug-cc-pVTZ-PPs for both Br (Ref. 23) and I (Ref. 24) were used in conjunction with the CRENBL and the aug-cc-pVTZ-PP for Hg. In summary, we divide the RECPs used in this work into the CRENBL (shape-consistent) and AVTZ-PP (energy-consistent) sets. We used the uncontracted AVTZ basis sets instead of the contracted one for SODFT calculations because the contracted AVTZ basis set with the SO potential cannot reasonably describe the SO effect. In addition, we made the modified CRENBL basis set for Hg and I by adding the diffuse functions of AVTZ-PP into the original CRENBL. The geometry optimizations and calculations of vibrational frequencies for HgI and $HgI_2$ were performed using the modified CRENBL with PBE0 and SO-PBE0.

We also performed *ab initio* calculations to check the validity of the DFT calculations. The reference *ab initio* calculation is at the CCSD(T) level.[25] In the CCSD(T) calculations, only scalar relativistic effect was considered using the RECPs. All CCSD(T) calculations were performed using the Gaussian03 program.[26] Using the CCSD(T)/AVTZ-PP, we only performed geometry optimizations without doing the vibrational frequency calculations for both $HgBr_4$ and $HgI_4$ because of the expensive computational time. To calculate thermochemical energies for these molecules, we used zero-point energy (ZPE) of the PBE0/AVTZ-PP for the ZPE corrections.

We also calculated $HgF_4$ using the complete active space self-consistent field (CASSCF) (Ref. 27) and multiconfigurational second-order perturbation theory (CASPT2).[28] Eighteen electrons were distributed in 12 active orbitals [CAS(18,12)], which is composed of one 6s orbital, five 5d orbitals, and their counterpart of antibonding orbitals; thus, a total of 12 active orbitals was selected. In the CASSCF and CASPT2 calculations, we used the atomic natural orbital-relativistic semicore correlation (ANO-RCC) (Ref. 29) all-electron basis sets for all atoms {Hg, (25s22p16d12f4g)/[8s8p7d4f2g] and F, (14s9p4d)/[4s3p2d]}, and the scalar relativistic effect was considered using the Douglas–Kroll–Hess second order method (DKH2).[30] The spin-orbit coupling (SOC) was considered using the restricted active space state interaction with spin-orbit coupling[31] method with the atomic mean field integral approximation.[32] All multiconfigurational *ab initio* calculations (CASSCF and CASPT2) were performed using the MOLCAS6.4 program.[33] The basis set superposition error (BSSE) was corrected in CCSD(T) and PBE0 (only the $HgI_n$ cases) calculations using the counterpoise (CP) method.[34]

## III. RESULTS AND DISCUSSION

### A. $HgF_n$ ($n$=1, 2, and 4)

The molecular structures of HgX, $HgX_2$, and $HgX_4$ are linear ($C_{\infty v}$), linear ($D_{\infty h}$), square planar ($D_{4h}$), respectively. The optimized geometries of $HgF_n$ are summarized in Table I. The PBE0 generally gives shorter bond lengths than other functionals, M06 and M06-L. This trend is universal on other Hg–X distances. The M06-L provides longer Hg–F distances than those of other methods. The results of the PBE0/AVTZ-PP are quite close to those of the CCSD(T)/AVTZ-PP at the scalar relativistic level. The PBE0/CRENBL results also match well with those of CCSD(T)/CRENBL, except the Hg–F distance of HgF. In the DFT calculations, all the Hg–F distances using the CRENBL are longer than those using the AVTZ-PP. These may be attributed to the size of the valence basis sets because the size of the valence basis sets of the CRENBL is smaller than those of the AVTZ-PP. This trend continues in other Hg–X distances of $HgX_n$. As can be seen in Table I, the F atom basis set dependence is negligible in the molecular geometries (see values in parentheses in Table I).

The SO effect on the molecular geometry of $HgX_n$ can be seen by comparing the results between DFT and SODFT. As shown in Table I, the SOC shortens the Hg–F bond lengths, and the degree of shortening is negligible in closed shell molecules, $HgF_2$ and $HgF_4$. Both CRENBL and AVTZ-PP give similar degree of shortening by the SO effect. A recent EXAFS experiment[4] has provided the value of 1.94(2) Å for the Hg–F bond length in $HgF_2$. However, its error range is rather large; most of DFT calculation results of $HgF_2$ fall in this range so that the DFT performance test for the Hg–F bond length in $HgF_2$ is not conclusive.

The calculated harmonic vibrational frequencies of $HgF_n$ are summarized in Table SI in the supplementary material.[35] All DFT methods underestimate the vibrational frequency

TABLE II. Thermochemical energies (in kcal/mol) of HgF, $HgF_2$, and $HgF_4$. Values in parentheses are calculated using aug-cc-pVQZ for F. Values in italic are the BSSE corrected values using CP method.

| | RECP | PBE0 | SO-PBE0 | M06 | SO-M06 | M06-L | SO-M06-L | CCSD(T) | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| (1) $HgF \rightarrow Hg + F$ | CRENBL | 33.2 | 33.7 | 31.8 | 32.3 | 36.1 | 36.6 | 41.1, *32.7* | 32.9[a] |
| | AVTZ-PP | 33.6 (33.7) | 34.4 | 31.8 | 31.6 | 35.9 | 36.6 | 29.1, *27.5* | |
| (2) $HgF_2 \rightarrow HgF + F$ | CRENBL | 87.8 | 88.3 | 90.4 | 90.9 | 90.3 | 90.8 | 97.4, *92.1* | 89.9[a] |
| | AVTZ-PP | 89.5 (89.7) | 90.4 | 91.4 | 92.2 | 91.5 | 92.3 | 91.9, *89.8* | |
| (3) $HgF_2 \rightarrow Hg + F_2$ | CRENBL | 87.3 | 88.2 | 89.4 | 90.4 | 90.6 | 91.5 | 103.3, *87.5* | 84.9[a] |
| | AVTZ-PP | 89.4 (89.7) | 91.1 | 89.7 | 91.0 | 91.6 | 93.1 | 85.9, *82.1* | |
| (4) $HgF_4 \rightarrow HgF_2 + F_2$ | CRENBL | 5.4 | 7.4 | 2.9 | 5.2 | 15.2 | 17.1 | 14.1 | ⋯ |
| | AVTZ-PP | 10.7 (11.2) | 13.9 | 7.1 | 9.8 | 19.2 | 21.4 | 5.8 | |
| (5) $HgF_4 \rightarrow Hg + 4F$ | CRENBL | 165.4 | 168.3 | 163.0 | 166.3 | 182.1 | 184.9 | 192.7 | ⋯ |
| | AVTZ-PP | 172.9 (173.7) | 172.4 | 167.6 | 166.4 | 187.2 | 186.1 | 167.2 | |

[a] Reference 37.

for the $\Sigma$ mode of HgF, but only the CCSD(T)/AVTZ-PP gives reasonable results. Both M06 and M06-L seriously underestimate, which correlates with the overestimation of the Hg–F distance. The SO effect on the $\Sigma$ mode of HgF increases the vibrational frequency, but the discrepancy still remains. For $HgF_2$, in contrast to HgF, the M06 functional provides good results. The PBE0 functional slightly overestimates $\Pi_u$ and $\Sigma_g$ modes of $HgF_2$ but provides good results for the $\Sigma_u$ mode. In DFT calculations, all frequencies calculated by AVTZ-PP are larger than those of CRENBL because all DFT functionals with AVTZ-PP give shorter bond length than with CRENBL. The calculated frequencies of the $E_u$ mode of $HgF_4$ by PBE0 ($688.7\ \mathrm{cm}^{-1}$) and CCSD(T) ($687.6\ \mathrm{cm}^{-1}$) with AVTZ-PP agree well with the experimental value ($682\ \mathrm{cm}^{-1}$) in solid argon matrices. On the other hand, M06 family functionals underestimate the value of the $E_u$ mode. The SO effect increases the vibrational frequency on the $E_u$ mode. If we assume that the gas-phase value of the $E_u$ mode lies between neon and argon matrices value,[7,36] the SO-PBE0/AVTZ-PP gives the most reasonable result. We note that the results for the vibrational frequencies calculated by the PEB0 at the scalar relativistic level are in good agreement with those of the CCSD(T) as in the case of bond length. Therefore, we conclude that in calculations of molecular geometry and vibrational frequency, PBE0 results are in good agreement with CCSD(T) ones. The dependence on the F atom basis set is also insignificant for the calculations of vibrational frequency (see values in parentheses in Table SI in the supplementary material).[35]

Various thermochemical energies of $HgF_n$ have been calculated, and the results are summarized in Table II. In CCSD(T) calculations, the BSSE corrections are performed for comparison with the experimental ones. In DFT calculations, the BSSEs are expected to be negligible, and indeed the BSSEs of PBE0 in thermochemical energies of $HgI_n$ are less than 0.2 kcal/mol. Both PBE0 and M06 provide good results for the energy of case 1 (i.e., bond dissociation energy of HgF, see Table II), and the results of M06 are closer to the experimental value. The M06-L functional overestimates the energy of case 1. CCSD(T)/CRENBL provides reasonable result for the energy of case 1 (32.7 kcal/mol), while CCSD(T)/AVTZ-PP underestimates (27.5 kcal/mol). For case 2, all methods provide good results, and especially, the result of CCSD(T)/AVTZ-PP is in excellent agreement with the experimental value. In contrast, for the energy of case 3, all methods except CCSD(T)/AVTZ-PP overestimate the energy. PBE0/CRENBL and CCSD(T) with both RECPs give result close to the experimental value. As shown in these three cases, the BSSE corrections of CCSD(T)/CRENBL are much larger than those of CCSD(T)/AVTZ-PP, which also indicates the deficiency of valence basis sets of CRENBL. As can be seen in Table II, all methods yield the positive values of the energy for case 4, indicating that $HgF_4$ is thermodynamically stable. Since the BSSE of CCSD(T)/CRENBL is large in these three cases, we can expect that this 14.1 kcal/mol of the energy value for the energy of case 4 may be larger than the real value. CCSD(T)/AVTZ-PP gives 5.8 kcal/mol for the energy of case 4, which is similar to the previous CCSD(T) investigation (6.5 kcal/mol).[7] Both PBE0 and M06-L with AVTZ-PP describe $HgF_4$ as a very stable molecule, and in contrast, the M06/AVTZ-PP gives 7.1 kcal/mol of the energy, which is close to that of CCSD(T)/AVTZ-PP. In addition, the atomization energy of $HgF_4$ (case 5) calculated by M06/AVTZ-PP is in excellent agreement with that of CCSD(T)/AVTZ-PP, while other methods with AVTZ-PP overestimate. Overall, M06/AVTZ-PP gives the results that are similar to those of CCSD(T)/AVTZ-PP. Therefore, M06 seems to yield good results for estimating the thermochemical energy values of $HgF_n$. When the basis set of F increases from aug-cc-pVTZ to aug-cc-PVQZ, the energies slightly increase, but the effect is negligible (see values in parentheses in Table II). As can be seen in Table II, the SO effect increases the stability of $HgF_4$ by about 2–3 kcal/mol, which is similar to the stabilization energy by SO effect in a previous study (2.7 kcal/mol).[9] Therefore, we expect that the real value of case 4 is larger than 5.8 kcal/mol calculated by CCSD(T)/AVTZ-PP due to the SO effect. However, the BSSE correction will reduce the energy of case 4, and the degree of reduction may be slightly larger than the degree of stabilization by the SOC. Therefore, we expect that the real value of case 4 is slightly smaller than 5.8 kcal/mol. Both CRENBL and AVTZ-PP give a similar trend of SO effect for the energy of case 4. The SO effect with CRENBL increases the atomization energy of $HgF_4$ (case 5), but the opposite result is observed using AVTZ-PP.

We have performed all-electron SO calculations of $HgF_4$ based on a multiconfigurational wave function approach to compare the results with those calculated by the RECPs. If $HgF_4$ is assumed to have $D_{4h}$ symmetry, Hg–F distance is the only degree of freedom to be optimized. On the basis of this assumption, we have calculated the potential energy surface (PES) of $HgF_4$ using the $D_{2h}$ symmetry for electronic structure calculations. Although the atomization energy of $HgF_4$ may be the better metric to check the SO effect than the molecular geometry of $HgF_4$, the calculation of the atomization energy is impossible due to the lack of adequate active space for $HgF_4$. We have calculated the energy of $HgF_4$ along the Hg–F distance, but the calculations have failed at the longer distance of the Hg–F. A total of 18 active orbitals (for Hg, one s and five d orbitals; for four F, 12 p orbitals) is needed to calculate PES near the dissociation limit, but the present computational facility is limited to 15 active orbitals. The optimized Hg–F distance at the CAS(18,12) level is 1.859 Å, and the consideration of the dynamic electron correlation elongates the Hg–F distance. Accordingly, the optimized Hg–F distance at the CASPT2 level is 1.889 Å, which is in excellent agreement with that of the CCSD(T)/AVTZ-PP (see Table I). This result partially supports that the selection of active orbitals and all-electron basis sets is appropriate for the CASSCF and CASPT2 calculations. The SOC calculations have been performed both for CASSCF and CASPT2, and the results are depicted as a graph in the supplementary material.[35] The minimum point of $HgF_4$ obtained from CASPT2-SO is 1.886 Å where the state composition is 95.8% of $^1A_g$ and 3.1% of $^3B_{1g}$ state. Therefore, the contraction of the bond length caused by the SO effect is correct, but the degree of shortening is insignificant; the magnitude of contraction is just 0.003 Å, which is similar to the results of both CRENBL and AVTZ-PP.

### B. $HgCl_n$ ($n$=1, 2, and 4)

The optimized Hg–Cl distances and vibrational frequencies of $HgCl_n$ are shown in Tables SII and SIII in the supplementary material, respectively.[35] The overall trend in the molecular geometries and the vibrational frequencies is similar to that of $HgF_n$. In $HgCl_2$, all methods overestimate the Hg–Cl distance compared with the experimental value. Nevertheless, the results of PBE0 and CCSD(T) with the AVTZ-PP are closer to the experimental value. Especially, PBE0 without considering the SOC is quite close to those of the CCSD(T), except in HgCl using CRENBL. The same trend also occurs in the calculations of the vibrational frequencies. The SO effect on the bond length of $HgCl_2$ leads toward the correct direction. SO-PBE0/AVTZ-PP provides good result closer to the experimental value of Hg–Cl distance in $HgCl_2$.

Both PBE0 and CCSD(T) give reasonable results for the vibrational frequency of HgCl. On the other hand, other methods seriously underestimate it. PBE0 and CCSD(T) also provide good results for the vibrational frequencies of $HgCl_2$, except for the $\Pi_u$ mode. The deviation between the two experimental values for the $\Pi_u$ mode of $HgCl_2$ is large, but if we consider the real value to be 107 $cm^{-1}$, both PBE0 and CCSD(T) give good results. All other methods underestimate the vibrational frequencies of $HgCl_2$. For the vibrational frequencies of $HgCl_4$, however, M06 gives values closer to those of CCSD(T) than PBE0. As can be seen in Tables SII and SIII in the supplementary material,[35] although the SO effect on the molecular geometries and vibrational frequencies of $HgCl_n$ is small, all results get closer to experimental values by considering the SO effect.

Various thermochemical energies of $HgCl_n$ have been calculated, and the results are summarized in Table SIV in the supplementary material.[35] The RECP dependence is negligible in the DFT calculations. The M06 functional gives very close results to the experimental values except for case 3. It seems that PBE0 gives better result (CRENBL, 50.1 kcal/mol, and AVTZ-PP, 50.9 kcal/mol) than M06 (CRENBL, 47.4 kcal/mol, and AVTZ-PP, 46.7 kcal/mol) for the energy of case 3. However, when we take the SO effect into account, SO-M06 provides a result (CRENBL, 48.4 kcal/mol, and AVTZ-PP, 47.9 kcal/mol) closer to the experimental value (49.6 kcal/mol) than SO-PBE0 (CRENBL, 51.0 kcal/mol, and AVTZ-PP, 52.4 kcal/mol) because of the increment of bond strength induced by SO effect. Including the SOC makes the results of SO-M06 correct and closer to the experimental values. The M06 functional effectively works for the calculations of the thermochemical energies as in the case of $HgF_n$. As shown in the energy of case 4, although the SO effect further stabilizes $HgCl_4$, the molecule is still thermodynamically unstable. Similar results are found in previous theoretical studies.[11,12]

### C. $HgBr_n$ ($n$=1, 2, and 4)

The optimized Hg–Br distances and calculated vibrational frequencies of $HgBr_n$ are summarized in Tables SV and SVI in the supplementary material, respectively.[35] Overall, the trend in the Hg–Br distances and the vibrational frequencies of $HgBr_n$ among different methods is similar to those of $HgF_n$ and $HgCl_n$; thus, similar discussions can be applied. CCSD(T)/AVTZ-PP quite closely reproduces the experiments for the Hg–Br distance of $HgBr_2$ and vibrational frequencies of HgBr and $HgBr_2$. Among the DFT methods, only PBE0/AVTZ-PP gives result closer to the experimental value of the Hg–Br distance in $HgBr_2$. Because the SO effect slightly reduces the Hg–Br distance of $HgBr_2$, the Hg–Br distance calculated by SO-PBE0/AVTZ-PP agrees with the upper limit of the corresponding experimental value. In addition, both $\Sigma_g$ and $\Pi_u$ modes of $HgBr_2$ calculated by SO-PBE0/AVTZ-PP perfectly match the experimental values. As can be seen in Table SV in the supplementary material,[35] the SO effect slightly elongates the Hg–Br distance in $HgBr_4$, unlike in $HgF_4$ and $HgCl_4$. A similar situation also occurs in $HgI_4$, and the discrepancy is more significant (see next section).

Various thermochemical energies of $HgBr_n$ have been calculated, and the calculated results are summarized in Table SVII in the supplementary material.[35] In the energy of case 1 (i.e., BDE of HgBr), the SO effect calculated consistently reduces the BDE of HgBr, and similar results can be found in the calculation of the energy of case 5 (i.e., the

TABLE III. Optimized Hg–I distances (in angstrom) of HgI, $HgI_2$, and $HgI_4$.

| | RECP | PBE0 | SO-PBE0 | M06 | SO-M06 | M06-L | SO-M06-L | CCSD(T) | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| HgI | CRENBL | 2.813 (2.767)[a] | 2.831 (2.776)[a] | 2.949 | 3.014 | 2.929 | 2.954 | 2.793 | |
| | AVTZ-PP | 2.745 | 2.753 | 2.888 | 2.949 | 2.852 | 2.873 | 2.744 | |
| $HgI_2$ | CRENBL | 2.621 (2.600)[a] | 2.623 (2.601)[a] | 2.657 | 2.660 | 2.665 | 2.668 | 2.614 | 2.558(7),[b] 2.554 ± 0.003[c] |
| | AVTZ-PP | 2.578 | 2.578 | 2.616 | 2.619 | 2.622 | 2.623 | 2.568 | |
| $HgI_4$ | CRENBL | 2.728 | 2.748 | 2.775 | 2.797 | 2.802 | 2.862 | 2.748 | |
| | AVTZ-PP | 2.683 | 2.700 | 2.734 | 2.752 | 2.756 | 2.806 | 2.683 | |

[a] Values in parentheses are calculated using CRENBL with additional diffuse functions.
[b] Experimental equilibrium bond length is estimated from measured thermal average values (Ref. 1).
[c] Reference 6.

atomization energy of $HgBr_4$). In the dissociation limit of $HgX_4$, where X stands for the halogen atom, the SOC of X atom is dominant, and thus the energy of the X atom is stabilized by the SOC of X. However, at the equilibrium geometry of $HgX_4$, the SOC of Hg may be dominant. If the halogen atom of $HgX_4$ has a large electronegativity value, Hg has a significant $d^8$ character so that the SOC stabilizes the equilibrium point of $HgX_4$. These two stabilizations compete with each other. Since Br does not have sufficiently large electronegativity, the Br atom at the dissociation limit is much more stabilized by the SOC. Accordingly, the atomization energy of $HgBr_4$ is reduced by the SOC. In the case of $HgF_4$ and $HgCl_4$, the opposite occurs because F and Cl have large electronegativity values with small SO splitting. The same discussion can be applied to BDE of HgX. SO-PBE0/CRENBL is reasonable for the energy of the case 1, but SO-M06 underestimates. The SO effect reduces the energy of case 1 by 2.5 kcal/mol when SO-M06/CRENBL is used. This value coincide with that (2.26 kcal/mol) calculated by the SO configuration interaction (SOCI) method.[13] Although CRENBL cannot give accurate results for the molecular geometry and vibrational frequency, CRENBL well reproduces thermochemical energy changes induced by the SOC. All SODFT methods underestimate the energy of case 2. For case 3, SO-PBE0/AVTZ-PP gives reasonable results. From the negative value of the energy for case 4, $HgBr_4$ is also thermodynamically unstable. As shown in Table SVII in the Supplementary Material, the SO-M06-L only slightly reduces the atomization energy of $HgBr_4$ compared with the results of other SODFT. Thus, one should be careful in calculating the thermochemical value with SO-M06-L.

### D. $HgI_n$ ($n$=1, 2, and 4)

The optimized Hg–I distances and calculated vibrational frequencies of $HgI_n$ are summarized in Table III and Table SVIII in the supplementary material, respectively.[35] PBE0 and CCSD(T) with the AVTZ-PP provide good results for the bond length of $HgI_2$. PBE0 also yields the bond length of HgI similar to that of CCSD(T). Other DFT methods seriously overestimate the bond length of HgI and underestimate the vibrational frequency of the $\Sigma$ mode of HgI as in the case of HgX (X=F, Cl, and Br). Therefore, both M06 and M06-L are inadequate functionals for calculations of the molecular geometry and the vibrational frequency of HgX. As can be seen in the results of SODFT, the SO effect elongates all bond lengths of $HgI_n$. These results are different from those of other $HgX_n$ (X=F, Cl, and Br). Since the SOC of I is large, the $p_{3/2}$ spinor of I dominates the chemical bonding. Therefore, the bond lengths are elongated by the SO effect. For vibrational frequencies, both PBE0 and CCSD(T) produce good results, especially for $HgI_2$. From the result of the vibrational frequency of HgI calculated by SO-PBE0/CRENBL, it appears that the SO effect make the frequency deviate further from the experimental value. However, this may be attributable to the deficiency of basis sets for valence space (a detailed discussion is in the last paragraph of this section).

Various thermochemical values of $HgI_n$ have been calculated, and the calculated results are summarized in Table IV. The result of the energy of case 1 calculated by SO-M06/CRENBL is in excellent agreement with the experimental values. The SO effect reduces the energy of case 1 due to the reason already explained in the previous section. The reduction by the SO effect is 5.0 kcal/mol when using SO-M06/CRENBL, and this value coincide with that (5.07 kcal/mol) calculated by the SOCI method.[13] The SO-M06/CRENBL calculated energy is also reasonable for case 3, being in good agreement with the experimental value. According to these results, SO-M06 is an appropriate functional for the calculation of the thermochemical energies for the molecules involving heavy atoms. $HgI_4$ is also thermodynamically unstable, such as $HgCl_4$ and $HgBr_4$.

In the calculations of thermochemical energy using DFT at the scalar relativistic level, the RECP dependence is generally not significant. In contrast, for the calculations of the molecular geometries and vibrational frequencies, CRENBL provides longer bond lengths and smaller vibrational frequencies than those calculated by AVTZ-PP because the size of basis sets of valence space is insufficient. Thus, the direct comparison of the results calculated by the CRENBL with the experimental values is difficult. However, CRENBL with additional diffuse functions substantially improves the agreement when calculating the molecular geometries and vibrational frequencies (see values in parenthesis in Table III and Table SVIII in the supplementary material).[35] In addition, the vibrational frequency of HgI calculated by SO-PBE0 with CRENBL and the modified basis set is in excellent agreement with the experimental value. The inclusion of the SOC produces results closer to the experimental value than ignoring the SOC. Because the SO potentials of the CRENBL work well for calculating the SOC, SO-PBE0 with the modi-

TABLE IV. Thermochemical energies (in kcal/mol) of HgI, $HgI_2$, and $HgI_4$. Values in italic are the BSSE corrected values using CP method.

| | RECP | PBE0 | SO-PBE0 | M06 | SO-M06 | M06-L | SO-M06-L | CCSD(T) | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| (1) $HgI \rightarrow Hg + I$ | CRENBL | 14.2 | 9.9 | 12.1 | 7.1 | 13.1 | 11.2 | 8.6, *3.6* | 8.2[a] |
| | AVTZ-PP | 16.0, *15.9* | 11.6 | 12.2 | 5.1 | 14.5 | 10.7 | 11.9, *9.2* | $7.83 \pm 0.11$[b] |
| (2) $HgI_2 \rightarrow HgI + I$ | CRENBL | 61.8 | 56.5 | 58.0 | 50.9 | 57.7 | 54.9 | 60.8, *52.4* | ⋯ |
| | AVTZ-PP | 64.3, *64.2* | 59.0 | 59.1 | 49.9 | 62.0 | 57.1 | 65.6, *59.0* | |
| (3) $HgI_2 \rightarrow Hg + I_2$ | CRENBL | 39.4 | 39.7 | 33.1 | 33.5 | 33.8 | 34.0 | 41.4, *28.8* | $33.4 \pm 0.5$[c] |
| | AVTZ-PP | 34.1, *33.9* | 35.2 | 24.9 | 26.1 | 28.8 | 29.6 | 32.9, *26.3* | |
| (4) $HgI_4 \rightarrow HgI_2 + I_2$ | CRENBL | −26.3 | −22.8 | −23.2 | −19.4 | −22.2 | −14.8 | −25.2 | ⋯ |
| | AVTZ-PP | −35.4 | −31.5 | −33.0 | −29.0 | −29.4 | −23.9 | (−28.6)[d] | |
| (5) $HgI_4 \rightarrow Hg + 4I$ | CRENBL | 86.1 | 70.3 | 83.8 | 63.1 | 85.7 | 83.4 | 72.0 | ⋯ |
| | AVTZ-PP | 91.1 | 74.5 | 84.5 | 54.9 | 94.9 | 82.1 | (93.6)[d] | |

[a] Reference 38.
[b] Reference 5.
[c] Reference 39.
[d] Values in parentheses are calculated using the ZPE of PBE0.

fied CRENBL will work well in predicting the molecular geometries and the vibrational frequencies where the SOC plays crucial roles.

## IV. CONCLUSIONS

Various molecular properties of $HgX_n$ (X=F, Cl, Br, and I; $n$=1, 2, and 4) are calculated by DFT and SODFT, and the performances of RECP are tested. Both CRENBL (shape-consistent) and AVTZ-PP (energy-consistent) RECPs reasonably describe the SOC effect. The SOC further stabilizes $HgX_4$, but only $HgF_4$ is thermodynamically stable. The SOC should be considered for the calculations of molecular properties of HgI, in particular, the reaction energies involving HgI.

The PBE0 functionals are generally reasonable and comparable to CCSD(T) method for the molecular geometries and the vibrational frequencies. Especially, the molecular geometries calculated by PBE0/AVTZ-PP are in excellent agreement with those of CCSD(T)/AVTZ-PP. However, M06 is more appropriate for the estimate of thermochemical energies. M06-L (meta-GGA) is inferior to PBE0 (hybrid) and M06 (hybrid-meta) for calculating the molecular properties. Especially, for calculations of the bond length and the vibrational frequency of HgX, M06 family functionals are inadequate. In order to calculate the molecular structures of large complex systems involving both mercury and halogen atoms, PBE0 functional is recommended. On the basis of optimized structures by PBE0, M06 functional provides reasonable relative energy values. We hope that this systematic quantum chemical study of $HgX_n$ will be helpful for further experimental studies and choosing proper DFT functional for calculations of similar and larger system.

## ACKNOWLEDGMENTS

This work was supported by grants (Grant Nos. 2009-0084918 and 2010-0001632) from National Research Foundation and the Creative Research Initiatives (Center for Time-Resolved Diffraction) of MEST/NRF. We acknowledge the support from the WCU program. Computational resources were provided by the supercomputing center of the Korea Institute of Science and Technology Information (Grant No. KSC-2009-S02-0015)

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