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Research paper

Relativistic effect on enthalpy of formation for transition-metal complexes

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ABSTRACT

This Letter examines the enthalpy of formation for 12 transition metal diatomic molecules and 23 transition metal complexes from the viewpoint of effect of the relativistic effect by using the infinite-order Douglas–Kroll–Hess method with the local unitary transformation and three types of pseudopotentials for several levels of theory. The spin-orbit effect contribution to the enthalpy of formation is more than 10 kcal/mol for third transition metal complexes. Frozen orbital approximation at the outermost orbitals in pseudopotential methods shows a contribution to the enthalpy of formation that is more than two times larger than those of inner core orbitals.

1. Introduction

Relativistic effects play an essential role in the accurate description of chemical phenomena in molecules containing transition metals. The relativistic effects are mainly divided into spin-free (SF) and spin-dependent (SD) relativistic effects. In general, the SF relativistic effect contracts and expands s/p and d/f orbitals, respectively. The SD relativistic effect splits orbitals according to their angular momentum numbers such as $p_{1/2}$ and $p_{3/2}$ and $d_{5/2}$ and $d_{7/2}$. These changes affect geometries and reactivities of molecules. For describing the SF relativistic effect efficiently, pseudopotential (PP) methods are widely utilized for transition metal calculations because PPs decrease the computational cost of electronic state calculations because of introduced core potentials. Core potentials replace the effect of core orbitals in molecules with potentials fitted to both of all-electron atomic valence orbitals and energies or all-electron (AE) atomic transitions in valence space [1]. Several effective core potentials (ECPs) have been proposed such as LANL2DZ [2–4], SBKJC [5], and SDD [6–9]. The model core potential and the ab initio model potential are alternatives to core potentials because the basic equation for constructing the potential is different from that of ECPs [10]. The frozen core potential (FCP) [11] method is another method that directly uses atomic orbitals for describing core potentials; the computational cost is still higher than that for other PPs but less than AE treatments.

The thermochemical properties are difficult to precisely determine experimentally at the equivalent accuracy among all transition metal complexes. Many computational studies have been performed on this topic using the density functional theory (DFT) and post-Hartree–Fock (HF) methods [12–28], time-dependent DFT [29,30], Gaussian-4 method [31], and the correlation consistent composite method [32–38]. A theoretically accurate calculation is accomplished for first and second transition metal complexes. The mean absolute error (MAE) is less than 3 kcal/mol. However, realizing the sufficient accuracy in thermochemical properties for the third transition metal complexes is difficult by means of theoretical calculations owing to many effects and phenomena such as low-lying excited states, the spin-orbit interaction, and the electron correlation. While relativistic effects are considered in these transition metal calculations, the accuracy depends on the PPs. The reasons for the accuracy differences between PPs are varied: a reference relativistic method for constructing potentials, optimized geometry of molecules, and need to be relativistic effects taken into account in calculations. Note that PPs give reliable and accurate results compared with AE relativistic methods when a core size is carefully chosen [39–41].

Our group has developed and employed an accurate and efficient relativistic method based on the infinite-order Douglas–Kroll–Hess (DKH) method with the local unitary transformation (LUT) since 2010 not only for energy calculations [42,43] but also molecular properties such as geometry optimizations [44,45]. These methods consider enough relativistic effect to calculate all the element at the same accuracy. In addition, FCP fixes the core orbitals arbitrarily, meaning that individual core orbital

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contributions to a target property can be examined. This Letter focuses on the relativistic effect on the enthalpy of formation for transition metal molecules using the AE, ECP, and FCP methods. Section 2 provides computational details. In Section 3, the accuracy of the wave function theory (WFT) and relativistic effect for the enthalpy of formation of transition metal complexes are discussed. Finally, concluding remarks are provided in Section 4.

2. Computational details

Twelve diatomic molecules including those composed of first to third transition metals were investigated to assess the accuracy of the AE method: TiO, VO, NiF, YO, ZrO, ZrF_2, MoO, AgH, TaO, WO, WF, and HgH, which are assigned the code numbers, S1 to S12, respectively. The spin multiplicities of these diatomic molecules set to the most stable state: singlet for ZrO, AgH, and WO, doublet for NiF, YO, TaO, WF, and HgH, triplet for TiO, ZrF_2, and MoO, and quartet for VO. 23 transition-metal complexes were investigated, which are in the subset of transition-metal complexes used in previous assessments by Cundari et al. [46] and Mori et al. [47]: TiF_4, $TiOCl_2$, $VO(OEt)_3$, $Cr(CO)_6$, $Mn(CO)_5Br$, $Fe(CO)_5$, Ferrocene, $Co(CO)_4H$, $Ni(CO)_4$, $ZnMe_2$, $ZrBr_4$, ZrF_4, $NbCl_5$, $Mo(CO)_5py$, $MoBr_4$, RuO_4, *cis*-$PdCl_2(NCMe)_2$, $CdEt_2$, $TaCl_5$, $WOCl_4$, OsO_4, *cis*-Platin, and $HgMe_2$, which are assigned the code numbers, C1 to C23, respectively.

The gas-phase enthalpies of formation ΔH were calculated as follows:

$$\Delta H = \Delta E^{\mathrm{elec}} + \Delta E^{\mathrm{vib+rot+trans}} + \Delta E^{\mathrm{ZPE}}, \tag{1}$$

where ΔE^{elec} is electronic energy, $\Delta E^{\mathrm{vib+rot+trans}}$ is sum of the vibrational, rotational, and translational energies, and ΔE^{ZPE} is the zero-point energy. Experimental atomization enthalpy was adopted. ΔE^{elec} was obtained at WFT for HF, second-order møller-plesset (MP2), coupled-cluster singles and doubles (CCSD), and CCSD and perturbative triples (CCSD(T)). A composite approach (CA) was employed for estimating electronic energies of transition-metal molecules using the formula as follows:

$$E^{\mathrm{CA}} = E[\mathrm{MP2/QZ\text{-}QZ}] + (E[\mathrm{CCSD(T)}/X_1\mathrm{Z} - X_2\mathrm{Z}] - E[\mathrm{MP2}/X_1\mathrm{Z}\text{-}X_2\mathrm{Z}]), \tag{2}$$

where $E[\mathrm{MP2/QZ\text{-}QZ}]$ is the total energy at MP2 with quadruple-ζ basis sets for transition metals (shown in former QZ) and quadruple-ζ basis sets for other elements (shown in later QZ), $\mathrm{E[CCSD(T)}/X_1\mathrm{Z}\text{-}X_2\mathrm{Z}]$ and $\mathrm{E[MP2}/X_1\mathrm{Z}\text{-}X_2\mathrm{Z}]$ are the total energy at CCSD(T) and at MP2, respectively. Here, X_1 and X_2 mean a cardinal number of the basis sets, D for 2, T for 3, and Q for 4. Furthermore, in order to examine the functional dependence on DFT, five types of the DFT functional were employed with quadruple-ζ quality of basis sets for all elements: BLYP, B3LYP, M06, ωB97XD, and LC-ωPBE.

The effect of spin-orbit interaction ΔE^{SO} was calculated as the difference in the total energy of SD and SF methods at the MP2 level using triple-ζ quality of basis sets,

$$\Delta E^{\mathrm{SO}} = \Delta E[\mathrm{MP2(SD\text{-}IODKH)/uTZ\text{-}TZ}] - \Delta E[\mathrm{MP2(SF} - \mathrm{IODKH)/uTZ\text{-}TZ}]. \tag{3}$$

Here, uTZ denotes that a triple-ζ quality basis set in uncontracted form was used.

The geometry was optimized with the DFT with B3LYP-D functional using DKH3-Gen-TK-NOSeC-V-TZP for transition metals and cc-pVDZ-DK for other elements. The thermal corrections and zero-point energy at 298.15 K were taken into account for the gas-phase enthalpy of formation. All of the AE energies were obtained by the fourth-order DKH Hamiltonian with spin-orbit corrections using a quadruple-ζ quality of the same basis set family as used in the geometry optimization unless otherwise stated.

The different levels of relativistic Hamiltonians were utilized for evaluating the higher-order relativistic effect in the enthalpy of formation: non-relativistic (NR), relativistic elimination of small components (RESC), and first-, second-, and third-order DKH (DKH1, DKH2, and DKH3) Hamiltonians. Three types of pseudopotentials were adopted for comparison with AE: LANL2DZ, SBKJC, and SDD. The standard accompanying basis sets were adopted for LANL2DZ and SBKJC; cc-pVTZ-PP basis sets were adopted for SDD. The contribution of frozen-core orbitals to the enthalpy of formation was estimated by the FCP method.

3. Results and discussion

3.1. Accuracy of WFT

This subsection examines the accuracy of WFT for determining the enthalpy of formation of transition metal diatomic molecules. The left panel of Fig. 1 shows the deviation of enthalpy of formation in transition metal diatomic molecules from experimental values at the MP2, CCSD, and CCSD(T) levels of theory. The horizontal axis indicates the code number. The vertical axis indicates the deviation from the experimental values.

The deviation from experimental value in MP2 was larger that those in CCSD and CCSD(T); the MAEs were 9.65, 7.46, and 3.21 kcal/mol, respectively. CCSD overestimated the enthalpy of formation in all cases except for AgH and HgH. The largest deviation was 24.50 kcal/mol in MoO. Furthermore in the case of CCSD (T), the largest deviation is less than 10 kcal/mol, which is in good agreement with experimental values among the three methods. These results indicate that the electronic correlation energy beyond doubles is important for accurate estimation of the enthalpy of formation.

The right panel of Fig. 1 shows the basis set dependence of the enthalpy of formation at the composite approach. The horizontal axis indicates the code number while the vertical axis indicates the deviation from the experimental values. The difference in CA (TZ-DZ), CA(QZ-DZ), and CA(QZ-TZ) is the basis set for transition metals and other elements. TZ-DZ means triple-ζ quality of the basis set for transition metals and double-ζ quality of the basis set for other elements. Similarly, QZ-DZ and QZ-TZ respectively denote quadruple- and double-ζ quality of the basis set and quadruple- and triple-ζ quality of the basis set for transition metals and other elements. For comparison, CCSD(T) result with QZ-QZ basis sets is shown in the right panel of Fig. 1.

The basis set dependence is small in the CA method. MAEs are 4.36, 3.81, and 3.41 kcal/mol for CA(TZ-DZ), CA(QA-DZ), and CA (QZ-TZ), respectively. Considering the balance of accuracy and efficiency, CA(TZ-DZ) is the most reasonable method.

Table 1 shows the maximum error (MaxE) and MAE of enthalpy of formation for 23 transition metal complexes at the HF, MP2, and CA levels. Both of MaxE and MAE were improved as the electron correlation effect is taken into account: 630.6 and 247.4 kcal/mol for HF, 213.9 and 82.5 kcal/mol for MP2, and 33.1 and 14.9 kcal/mol for CA. Similar to the transition metal diatomic molecules, the electron correlation effect from a perturbation triple excitation, (T), was significant in the enthalpy of formation.

3.2. Functional dependence

This subsection investigates the functional dependence of the enthalpy of formation for the transition metal molecules. Table 2 shows the MaxE and MAE of six functionals of the enthalpy of formation for transition metal molecules at DFT with BLYP, B3LYP,