

## Spin-Orbit Density Functional Theory Calculations for TlAt with Relativistic Effective Core Potentials

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Bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt are calculated at *ab initio* molecular orbital and density functional theory using effective spin-orbit operator and relativistic effective core potentials. Spin-orbit effects estimated from density functional theory are in good agreement with those from *ab initio* calculations, implying that density functional theory with effective core potentials can be an efficient and reliable methods for spin-orbit interactions. The estimated  $R_e$ ,  $\omega_e$  and  $D_e$  values are 2.937 Å, 120 cm<sup>-1</sup>, 1.96 eV for TlAt. Spin-orbit effects generally cause the bond contraction in Group 13 elements and the bond elongation in the Group 17 elements, and spin-orbit effects on  $R_e$  of TlAt are almost cancelled out. The spin-orbit effects on  $D_e$  of TlAt are roughly the sum of spin-orbit effects on  $D_e$  of the corresponding element hydrides. Electron correlations and spin-orbit effects are almost additive in the TlAt molecule.

**Key Words** : Spin-orbit effect, Density functional theory, *Ab initio* calculation, Relativistic effective core potentials

### Introduction

It is widely known that inclusion of spin-orbit interactions is necessary for the calculations of molecules of heavy atoms. Despite the difficulty that electron correlations and the relativity should be taken into consideration to obtain reliable results, *ab initio* calculations for molecules have been progressing rapidly in the field of heavy element chemistry. It is possible to perform a variety of correlated relativistic calculations based on four-component Dirac-Hartree-Fock (DHF) wave functions obtained for the Dirac-Coulomb Hamiltonian or some other variants of the relativistic Hamiltonian. These straightforward all-electron approaches are, however, computationally too demanding at the present time for molecules with so many electrons. Instead, high-level correlated calculations may be performed by including proper relativistic effects using the relativistic effective core potentials (RECP). An economic alternative is the use of density functional theory (DFT) for the electron correlation. Recently, the method of using RECP with spin-orbit terms in DFT (SO-DFT) has been reported for the NWChem suite of programs.<sup>1</sup> Since we have been interested in spin-orbit RECP calculations, we decide to compare SO-DFT calculations with *ab initio* molecular orbital calculations, selecting TlAt molecule as the test case.

In the present work, we calculate bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt molecule with various methods using one- and two-component shape-consistent RECPs. We have shown that our two-component Hartree-Fock (HF), Møller-Plesset Second-order perturbation theory (MP2), coupled-cluster singles and doubles (CCSD), and CCSD with perturbative triples [CCSD(T)]

calculations mimic all-electron DHF, DHF-MP2, DHF-CCSD, and DHF-CCSD(T) calculations, respectively, for valence states.<sup>2,3</sup> We compare our one- and two-component HF results with Fægri and Saue's Spin-Free, MVD and four-component DHF results.<sup>4</sup> To the best of our knowledge, there is no experimental results for TlAt. With various two-component correlation calculations, the electron correlation and spin-orbit effects on bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt are studied.

### Computational Details

We performed SO-DFT, HF, MP2, CCSD, and CCSD(T) calculations with spin-orbit averaged RECPs (AREPs) and RECPs with spin-orbit terms (REPs) for TlAt molecule and obtained bond lengths, harmonic vibrational frequencies and dissociation energies. Dissociation energies were evaluated using results of separate calculations of atoms. All bond lengths and harmonic vibrational frequencies were obtained from Dunham analysis.

The shape-consistent *spdsp*-type 21 valence electrons (VE) RECP for Tl with corresponding *8s8p5d* basis sets, and shape-consistent *spdsp*-type 25VE RECP for At with corresponding *9s9p6d* basis sets generated by Christiansen<sup>5</sup> are employed. The additional 1f polarization function for each atom is optimized and added. The core *sp* orbitals were excluded and valence *dsp* orbitals and all virtual orbitals were correlated at all post-HF correlated levels of theory employed here. The applied functionals at DFT level are ACM<sup>6</sup> and PBE0<sup>7</sup> functionals. For our approaches, spin-orbit effects are defined as the difference between AREP and REP results calculated with the same basis set at a given level of theory. AREP calculations were carried out with

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GAUSSIAN98<sup>8</sup> and MOLPRO2000<sup>9</sup> and REP calculations with our two-component packages and NWChem.<sup>1</sup>

### Results and Discussion

The optimized bond lengths ( $R_e$ ), harmonic vibrational frequencies ( $\omega_e$ ) and dissociation energies ( $D_e$ ) for TlAt evaluated by one- and two-component HF, MP2, CCSD, CCSD(T) and SO-DFT methods using RECPs are listed in Table 1. Fægri and Saue's Spin-Free, MVD and DHF results<sup>4</sup> are also included for comparison. The REP values of bond lengths and harmonic vibrational frequencies at the HF level are in very good agreement with the four-component DHF results. Spin-Free method takes scalar relativistic effects into account to generate orbitals, whereas the MVD method treats scalar relativistic effects in a perturbed way using NRHF molecular orbitals. There has been no report of experimental and correlation calculations for TlAt. Electron correlation effects on TlAt in AREP- and REP-CCSD(T) calculations decrease  $R_e$  and increase  $\omega_e$  and  $D_e$  of TlAt. Electron correlation effects on TlAt estimated at the REP-CCSD(T) level are  $-0.045 \text{ \AA}$ ,  $+4 \text{ cm}^{-1}$ ,  $+0.76 \text{ eV}$  for  $R_e$ ,  $\omega_e$  and  $D_e$ , respectively and those estimated by SO-DFT with ACM functional are  $-0.041 \text{ \AA}$ ,  $+6 \text{ cm}^{-1}$ ,  $+0.99 \text{ eV}$  for  $R_e$ ,  $\omega_e$  and  $D_e$ , respectively. At the highest level of theory, *i.e.*, REP-CCSD(T),  $R_e$ ,  $\omega_e$  and  $D_e$  values of TlAt are  $2.937 \text{ \AA}$ ,  $120 \text{ cm}^{-1}$ ,  $1.96 \text{ eV}$ , respectively. Using pseudopotentials and various levels of electron correlation Schwerdtfeger and Ischtwan calculated on thallium halides up to TlI and reported results in good agreement with experiment.<sup>10</sup> In order to examine the reliability of the calculated spectroscopic properties, experimental bond lengths, vibrational frequencies and dissociation energies for the whole series from TlF to TlI are listed in Table 2 with those of TlAt calculated at the REP-CCSD(T) level of theory. The general trend in the experimental bond lengths is the elongation of equilibrium bond length with increasing atomic number. The dissociation energies of TlX (X = F, Cl, Br, I and At) decrease with increasing atomic number. The near-linear increase in bond

**Table 1.** Calculated bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt at the various levels of theory using AREP and REP

	$R_e$ (Å)		$\omega_e$ (cm <sup>-1</sup> )		$D_e$ (eV)	
	AREP	REP	AREP	REP	AREP	REP
TlAt						
HF	2.990	2.982	115	116	2.45	2.20
MP2	2.910	2.907	122	124	3.27	2.05
CCSD	2.941	2.938	121	120	3.04	1.84
CCSD(T)	2.937	2.937	122	120	3.16	1.96
ACM	2.939	2.940	123	122	3.30	2.19
PBE0	2.931	2.931	124	124	3.35	2.23
DHF <sup>a</sup>		2.977		116		
S-F <sup>a</sup>	2.990		115			
MVD <sup>a</sup>	2.995		113			

<sup>a</sup>All-electron Spin-free, MVD and DHF results by Fægri and Saue from Ref. 4.

**Table 2.** Calculated bond length, harmonic vibrational frequency and dissociation energy of TlAt at the REP-CCSD(T) level of theory with experimental results of TlX (X = F, Cl, Br, I)<sup>b</sup>

Molecule	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
TlF	2.084	477	4.57
TlCl	2.485	284	3.82
TlBr	2.618	192	3.42
TlI	2.814	150	2.76
TlAt <sup>a</sup>	2.937	120	1.96

<sup>a</sup>This work. <sup>b</sup>All other experimental results are from Ref. 11.

lengths with atomic number is matched by a near-linear decrease in bond dissociation energies for TlX (X = F, Cl, Br, I and At). The vibrational frequencies decrease for lower period as expected from smaller  $D_e$  and heavier mass.

Electron correlation seems less important for bond lengths and harmonic vibrational frequencies but necessary for dissociation energies. In order to examine the spectroscopic properties of hetero diatomic molecules between Group 13 and Group 17 elements with increasing period number, the calculated  $R_e$ ,  $\omega_e$  and  $D_e$  values of TlAt at the REP-CCSD(T) level of theory are compared with experimental ones of their congeners from BF to InI in Table 3. Except for BF, there are near-linear increase in bond lengths and near-linear decrease in bond dissociation energies with increasing period number for AlCl, GaBr, InI, TlAt. The vibrational frequencies decrease in reverse pattern with increasing period number.

Spin-orbit effects are defined as the difference between AREP and REP results calculated with the same basis set at a given level of theory. Spin-orbit effects on bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt at the various levels of theory are summarized in Table 4. Spin-orbit effects from the all-electron calculations, which are defined as the difference between Fægri and Saue's Spin-Free and DHF results, are also listed in Table 4. Our spin-orbit effects at the HF level are very similar to those from the all-electron calculations. Spin-orbit effects from DFT calculations are in good agreement with CCSD(T) implying that spin-orbit effects may be reliably estimated from DFT and RECP combinations. For the TlAt molecule at the HF level,  $R_e$  and  $D_e$  decrease due to spin-orbit effects by about  $-0.008 \text{ \AA}$  and  $-1.25 \text{ eV}$ , respectively. Although the nonadditivity between electron correlations and spin-orbit effects in the TlAt molecule is not significant, spin-orbit effects on  $R_e$  are zero at the CCSD(T) level of theory. Due to

**Table 3.** Calculated bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt at the REP-CCSD(T) level of theory with experimental results of their lighter congeners<sup>b</sup>

Molecule	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
BF	1.210		7.81
AlCl	2.130	481	5.12
GaBr	2.352	263	4.31
InI	2.754	177	3.43
TlAt <sup>a</sup>	2.937	120	1.96

<sup>a</sup>This Work. <sup>b</sup>All other experimental results are from Ref. 11.

**Table 4.** Spin-orbit effects on bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt at the various levels of theory<sup>a</sup>

	$R_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$D_e$ (eV)
TlAt			
HF	-0.008	1	-1.25
MP2	-0.003	2	-1.22
CCSD	-0.003	-1	-1.20
CCSD(T)	0.000	-2	-1.20
ACM	0.001	-1	-1.11
PBE0	0.000	0	-1.12
S-F/DHF <sup>b</sup>	-0.013	1	

<sup>a</sup>The spin-orbit effects are defined by (REP value - AREP value). <sup>b</sup>The spin-orbit effects for all-electron calculations are obtained from the differences between Spin-Free and DHF results-Ref. 4.

spin-orbit effects,  $R_e$  of TlH decreases by -0.022 Å and that of AtH increases by +0.031 Å at the CCSD(T) level.<sup>12</sup> The variations of bond lengths due to spin-orbit effects may be explained by the radial contraction and energetic stabilization of the valence  $6p_{1/2}$  spinors compared to the  $6p$  orbitals of Tl and the radial expansion and energetic destabilization of valence  $6p_{3/2}$  spinors compared to the  $6p$  orbitals of At. In the TlAt molecule the variations of bond lengths due to spin-orbit effects on two atoms almost cancel each other. The  $D_e$  of TlAt at the AREP-CCSD(T) is 3.16 eV, which decreases to 1.96 eV upon inclusion of spin-orbit interactions. The TlAt bond calculated with spin-orbit interactions is roughly two-thirds as strong as that in the absence of spin-orbit coupling. The spin-orbit effects (-1.20 eV) on  $D_e$  of TlAt are about equal to the sum of the spin-orbit effects on  $D_e$  of TlH(-0.52 eV) and AtH(-0.68 eV).<sup>12</sup> The changes of  $\omega_e$  due to spin-orbit effects are negligibly small.

### Conclusions

We have calculated bond lengths, harmonic vibrational frequencies and dissociation energies of TlAt at the DFT, HF, MP2, CCSD and CCSD(T) levels of theory using one- and two-component shape-consistent RECPs. Our two-component HF calculations are in excellent agreement with four-component DHF calculations, and SO-DFT calculations are in reasonable agreement with REP-CCSD(T) calculations. It appears that SO-DFT can be a useful tool in studying systems with large spin-orbit and correlation effects. Correlation calculations starting from the spinors of the two-component HF calculation are expected to yield reasonable spectroscopic properties of TlAt. At the REP-CCSD(T) level of theory,  $R_e$ ,  $\omega_e$  and  $D_e$  values are 2.937 Å, 120 cm<sup>-1</sup>, and 1.96 eV for TlAt, respectively. Spin-orbit effects generally cause the bond contraction in Group 13 elements and the

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