

All-electron segmented contraction basis sets of triple zeta valence quality for the fifth-row elements

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INTRODUCTION

Segmented all-electron contracted triple zeta valence plus polarization function (TZP) basis sets for the elements Cs, Ba, La, and from Hf to Rn are constructed¹ for using in conjunction with the non-relativistic and Douglas-Kroll-Hess (DKH) Hamiltonians. Using the B3LYP hybrid functional, the performance of the TZP-DKH basis set is assessed for predicting atomic ionization energy as well as spectroscopy constants of fifteen compounds. Here, we will discuss only one of them.

METHODS

The Hartree-Fock (HF) and restricted open-shell Møller-Plesset perturbation theory (ROMP2) methods were used to construct the non-relativistic TZP basis set, namely: [9s5p4d1f] for Cs and Ba; [9s5p5d2f1g] for La; [9s6p5d3f1g] for Hf, Ta, Os, Au, and Hg; [9s5p5d3f1g] for W, Re, Ir, and Pt; and [9s8p5d3f1g] for Tl to Rn. The relativistic set was obtained from the TZP set by re-optimizing the values of the contraction coefficients using the second-order DKH Hamiltonian.

RESULTS AND DISCUSSION

Spectroscopic constant results obtained at the DKH2-B3LYP level of theory are listed in Table 1. For comparison, experimental² and other theoretical results are also included.

For TiCl, our results are very similar to the previously published theoretical data by other authors. For example, Metz *et al.*³, using the 21-valence-electron relativistic pseudo potential (RPP)-CCSD(T)/[6s6p4d3f2g] procedure, found excellent agreement with us. Their SO effect estimates on r_e , ω_e , and D_e were -0.011 Å, 1 cm⁻¹, and -0.684 eV. One can verify that the DKH2-B3LYP/TZPDKH + SO results (2.462 Å, 286.5

cm⁻¹, and 3.917 eV) give excellent accordance with the experiment².

Table 1. Theoretical and experimental bond length (r_e in Å), harmonic vibrational frequency (ω_e in cm⁻¹), and bond energy (D_e in eV) for the ground state.

		TZP-DKH ^a	Previous theoretical results ³	Expt. ²
TiCl (¹ Σ ⁺)	r_e	2.473	2.497	2.48483
	ω_e	285.5	282	283.75
	D_e	4.601	4.448	3.835

^a DKH2-B3LYP calculation. Basis set generated in [4,5] and in this work (fifth-row elements).

CONCLUSIONS

In general, the DKH2-B3LYP/TZP-DKH spectroscopic constants compare well with those obtained from higher level of theory.

For compounds containing main group elements, the addition of the SO corrections to the DKH2-B3LYP/TZP-DKH results always improve the agreement with experiment.

With few exceptions, the accordance between the theory and the experiment is good.

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