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 constructed for use 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, experimental results 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., using the 21-valence-electron relativistic pseudo potential (RPP)-CCSD(T)/[6s6p4d3f2g] procedure, found excellent agreement with us. Their SO effect estimates on $r_e$, $\omega_e$, 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 experiment.

Table 1. Theoretical and experimental bond length ($r_e$ in Å), harmonic vibrational frequency ($\omega_e$ in cm$^{-1}$), and bond energy ($D_e$ in eV) for the ground state.

<table>
<thead>
<tr>
<th></th>
<th>TZP-DKH$^a$</th>
<th>Previous theoretical results$^3$</th>
<th>Expt.$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCl ($^1\Sigma^+$)</td>
<td>2.473</td>
<td>2.497</td>
<td>2.48483</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>285.5</td>
<td>282</td>
<td>283.75</td>
</tr>
<tr>
<td>$D_e$</td>
<td>4.601</td>
<td>4.448</td>
<td>3.835</td>
</tr>
</tbody>
</table>

$^a$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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