

Towards accurate ab initio thermochemistry and spectroscopy of lanthanide compounds: Quantifying basis set, electron correlation, and spin-orbit coupling effects in lanthanide species

V.G. Solomonik, A.N. Smirnov, O.A. Vasiliev

Ivanovo State University of Chemistry and Technology, Russia

sol@isuct.ru

The importance of theoretical electronic structure investigations for the study of lanthanide compounds is well known, however, accurate quantum chemical calculations are still a quite difficult task for these systems. There are at least three reasons for that. First, the electron correlation problem in such a system is extremely demanding. Second, the resulting accuracy of any correlated electronic structure calculation can be highly dependent on the quality of 1-particle basis set used to represent the underlying molecular orbitals. Third, a proper account of both scalar relativity and spin-orbit coupling (SOC) can be very important.

All these issues are addressed in the study on a 26-molecules test set containing 17 diatomic LnX (Ln = La, Ce, Eu, Yb, Lu; X = O, F, Cl, Br, I) and 9 polyatomic species YbX₂, CeX₃ (X = F, Cl, Br, I), LaF₃. Bond lengths r_e , bond angles, vibrational frequencies ω_e , barriers to linearity in YbX₂, inversion barriers in LnX₃, and atomization energies D_0 have been calculated at sophisticated levels of theory including coupled cluster CCSD, CCSD(T), EOM-, FS-CCSD, configuration interaction MRCI, and perturbation theory MRPT2. Using the sequences of systematically convergent correlation consistent triple- ζ , quadruple- ζ , and quintuple- ζ basis sets the complete basis set (CBS) limit has been accurately estimated. Core-valence (CV) electron correlation effects involving the Ln outer-core 4s,4p,4d electrons and the X atom outer-core (n-1)s,(n-1)p,(n-1)d electrons were evaluated separately. The Douglas-Kroll-Hess Hamiltonian and the Breit-Pauli spin-orbit operator, or the 2-component methods with relativistic core pseudopotentials were used to account for and to separate the scalar relativistic and SOC effects.

The molecular properties of diatomics for which the experimental values are well established, have been reproduced at the CCSD(T)(CV)/CBS level with mean absolute deviation of 2.0 kcal mol⁻¹ for D_0 (7 comparisons), 0.0048 Å for r_e (13 comparisons), 5.3 cm⁻¹ for ω_e (16 comparisons). The capability of T1 and D1 diagnostics of a multireference character of wave function to give indication of the quality of results to be expected from the single-reference CCSD(T) calculation has been verified. A composite scheme for accurate calculation of thermochemical and spectroscopic properties of lanthanide compounds is proposed.

The authors acknowledge support from the Russian Foundation for Basic Research, Grant No. 13-03-01051.