Abstract

The focus of present work is the study of various properties of atomic and molecular systems, using relativistic many-body methods. Recently, ¹¹³Cd⁺ has been proposed for better frequency standard in microwave regime and quantum computing. We have computed the hyperfine energy separation (including ground state) and lifetime of low-lying excited states of ¹¹³Cd⁺ and ⁶⁷Zn⁺, using relativistic CCSD(T) method, which are in excellent agreement with the recent experimental results. On the basis of ground state hyperfine energy separation, ⁶⁷Zn⁺ is proposed as a suitable candidate for better frequency standard, where there is no experimental measurement till date. The strength of E1, E2, and M1 transitions of ⁶⁷Zn⁺, important for astrophysics, have been calculated with high accuracy. The distinct order of lifetime of $5d_{5/2}$ and $5d_{3/2}$ states, obtained in recent experiments; have been supported theoretically for the first time by our calculation. For both the atomic systems, the detailed many-body analysis of core-correlation, pair-correlation, and core-polarization for various atomic properties have been carried out.

A module for calculating the infrared intensities of molecules in relativistic density functional program PARAGAUSS have been implemented. After verifying the implemented schemes, the structure and vibrational spectra of uranium methylidene complexes: $CH_2=UHX$ (X = F, Cl, Br) have been determined. Understanding the nature of bond formation between uranium and unsaturated hydrocarbons is an interesting subject due to agostic interactions and may be expected to leave a unique fingerprint in the vibrational spectra from the methylidene related modes. We have shown that the earlier assignment of the vibrational modes as simple local modes can be improved in line with experimental and calculated isotope shifts. The overall very good agreement of calculated and measured isotope shifts corroborates our assignments of the vibrational modes.

Key words: frequency standard, hyperfine interaction, vibrational spectra, infrared absorption intensities, CCSD(T), relativistic DFT, electron correlation.