Density functional study on Keggin heteropolyanions containing fifth period main group heteroatoms

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In this article, a serie of density functional theory (DFT) calculations were carried out on Keggin heteropolyanions[XM12O40]n-(X = Sn(IV), Sb(V) and Te(VI); M = Mo and W; n = 2,3,4) to analyze their molecular structure, vibrational spectra and electronic structure. The energy and composition of the frontier orbitals resemble those containing internal heteroatoms of preceding periods. We found that the diameter of the encapsulated internal{XO4}subunit varies as X does, while{M12O36}size and distances remain almost constant along the series. Vibrational modes calculations show that exist a dependency of the frequency and the anionic charge, nature of the heteroatom X and calculation methodology. Energy decomposition analysis of the{XO4}?{M12O36}interaction shows a predominant ionic character due to the high charge of the{XO4}anionic subunit. COSMO solvation model enabled us to compare heteropolyanions with different total charges. Our results suggest the possibility that these Keggin anions should be stable, being a new challenge for synthetic inorganic chemists. © 2016 Elsevier Ltd

DFT

Heteroplyanions

Keggin

Polyoxometalates

Vibrational spectra