Relativistic Effects in Chemistry

K. Balasubramanian

Department of Chemistry & Biochemistry
Arizona State University
Tempe, AZ 85287-1604

The objective of this talk is to discuss relativistic effects in the chemistry of very heavy molecules. We would be considering the electronic structure and properties of transition metal and heavy main group clusters, transition metal carbides and the interaction of transition metal clusters with hydrocarbons such as ethylene, butadiene, benzene, etc. Our studies on transition metal clusters included the ground and excited states of Hf₃, W₃, Nbₙ, Rhₙ, Ptₙ, Pdₙ, etc. These computations were carried out using high level relativistic ab initio computations and included both relativistic and electron correlation effects. The atomization and dissociation energies have also been computed and the results are compared with the smaller clusters. The results of such computations will be discussed with available spectroscopic data on these species. The electronic structural and thermodynamic properties of transition metal carbides and very heavy main group clusters would also be discussed. This obviates high level ab initio computations of not only the structures but also the vibrational frequencies so that the partition functions could be computed. The experimental thermodynamic properties were corrected in most of the cases for the assumed incorrect structures. Comparison
with recent experimental studies on the interaction of transition metal clusters such as Pt\textsubscript{n} and Nb\textsubscript{n} will be made.