PREDICTIONS OF STRUCTURES AND PROPERTIES OF NOVEL MOLECULAR SPECIES USING AB INITIO QUANTUM CHEMICAL TECHNIQUES

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Abstract
First-principles based quantum chemical methods can be employed to design new molecular system and to characterize them through prediction of their structure and various physico-chemical properties. Here an overview of some of our ongoing work is presented. Particularly, the prediction of chemical compounds formed by rare gas atoms is discussed. Excellent correlation between the calculated electric dipole polarizability of hydrogen-bonded molecular assemblies with aggregation number has also been demonstrated to exist. Finally, the scope of computational techniques in rationalizing the experimentally observed results described briefly, with a special emphasis to lanthanide and actinide chemistry.

Keywords: Computational Chemistry, Density Functional Theory, Rare-gas Compounds, Hydrogen-Bonded Clusters, Lanthanides

Introduction
In recent years computational chemistry continues to play a central role in the prediction of structure and various physico-chemical properties of atoms, molecules and clusters with the results obtained through quantum chemical calculations using various levels of theory. With the award of the 1998 Nobel Prize in chemistry to Walter Kohn and John Pople jointly, the potential role of quantum chemistry has been recognized. With the advancement of high-speed computers and efficient algorithms, in principle \textit{ab initio} quantum chemistry\(^1\) now allows the investigation of molecular species containing atoms of any element in the periodic table. With the inclusion of density functional theory (DFT)\(^2\) based methods into the quantum chemistry softwares, it has been possible to obtain the structures and energies accurately with DFT methods. It is also important to note that computations using DFT is much less expensive as compared to that using Hartree-Fock theory based correlated methods such as Møller-Plesset perturbation theory, configuration interaction or multi-configuration approaches\(^3\). The properties that are most commonly calculated include molecular geometry in ground and excited states, charge and spin density distributions, potential energy surfaces, spectroscopic properties, reaction rate constants, thermodynamic properties, details of the dynamics of a process etc. Computational quantum chemical methods can also be employed for the prediction of the novel chemical species. Particularly, computational chemistry is very useful in investigating potentially hazardous compounds that are difficult to handle in laboratory or inaccessible experimentally. It can also be used in combination with experiment to corroborate or complement experimental results. In the following sections we discuss some of our ongoing research activities along these lines.
Theoretical Prediction of New Noble Gas Chemical Compounds

It is well known that the noble gas elements helium, neon, argon, krypton, and xenon are chemically inert due to their closed shell stable electronic configurations in the ground state. However, search for the rare-gas compounds started way back in the late thirties envisioned by Pauling, and subsequently became a reality through the synthesis of the first rare-gas compound, xenon hexafluoro-platinate (Xe' (PtF₆)) by Bartlet in 1962. In recent years, several novel rare-gas compounds are predicted theoretically as well as prepared and identified experimentally. The most notable development among them is the preparation and characterization of the molecules of the type HNgX, where Ng is a rare-gas atom such as Ar, Kr, and Xe, and X is an electronegative atom or group. We now consider altogether a new class of rare gas compounds containing noble gas-noble metal bond where a noble gas atom (Ng) is inserted into a noble metal molecule (AuX) resulting into the formation of Au-Ng-X species. The origin of this development has been the behavior of a gold atom as a hydrogen atom in various gold compounds and thus we have been motivated to investigate the bonding between a noble gas atom and a noble metal atom in the insertion compounds, Au-Ng-X (Ng=noble gas atom and X= electronegative atom or group), e.g. AuKrF and AuXeF. Our objective has been to investigate the structure and properties of the Au-Ng-F compounds with the aid of quantum chemical calculations and to explore whether they are stable or not with reference to their corresponding dissociated products on the respective potential energy surface. We have also considered Cu-Ng-F and Ag-Ng-F compounds for the purpose of comparison with the corresponding Au-Ng-F species (with Ng=Ar, Kr and Xe). The optimized geometries reveal that the structures of all the MNgF species are linear with short M-Ng bond. The computed results indicate that the M-Ng bond length in MNgF species are always shorter than that in NgMF systems published in the literature. Some of the M-Ng bond distances are found to be slightly above the corresponding triple bond covalent radii sum, implying a partial triple bond and covalent nature in the noble metal atom and the noble gas atom bonding. It is imperative to note that some of the calculated values of the M-Ng bond dissociation energies are remarkably larger in MNgF species than that in NgMF systems, e.g., Cu-Xe bond energy in CuXeF (139.1 kJ/mol) is 2 times larger than the same in XeCuF (67.9 kJ/mol) species. Similarly, the Ag-Xe bond energy in AgXeF (101.1 kJ/mol) is ~2.7 times larger than the same in XeAgF (38.1 kJ/mol) species. The calculated barrier heights indicate that most of the species should be kinetically stable with respect to the bending reaction coordinate corresponding to the dissociated products MF and Ng. Recently, we have predicted the existence of several other rare gas compounds.

Correlation between Electric Dipole Polarizability and Size of Hydrogen-Bonded Clusters

Behavior of molecular systems in Excited states is an important area of research in chemistry for the understanding of several chemical processes that occur at different time scale. Here we are interested to investigate the effect of excitation on the electric response properties of hydrogen-bonded clusters such as water and methanol clusters. The static electric dipole polarizability is one of the most important physico-chemical properties of molecular assemblies because it measures the distortion of the electron density distribution under the effect of an external static electric field, which in turn dictates the intermolecular interaction parameters. Simultaneously, an excited state may be considered as a perturbed ground state as far as the electron density distribution is concerned. Thus, two different kinds of perturbations are in operation in the calculation of polarizability for an excited state of a molecular assembly. Therefore, it is interesting to investigate the variation of excited states polarizabilities of hydrogen-bonded molecular clusters with the cluster size (n). Variation of excited state polarizabilities of water and methanol clusters are given in Fig. 1. It is clearly evident that variation of excited state polarizability of methanol clusters is linear with size, however, for water clusters a non-monotonic variation is observed. This trend indicates that perturbation due to excitation for water cluster is significantly higher than that in methanol cluster. Consequently, perturbation due to electric field, which in turn dictates the variation of polarizability from one water cluster to another cluster, is strongly influenced by the excitation process. On the other hand, excellent linear
correlation has been demonstrated\textsuperscript{15} for the variation of ground state polarizabilities of water clusters with size (Fig. 2). It is true for ground state methanol clusters as well. However, alkali metal clusters show a completely different trend where the variation of ground state polarizability has been found to be zigzag in nature with respect to cluster size\textsuperscript{16-18}.

**Structure of Lanthanide Complexes**

Coordination chemistry of trivalent lanthanides (Ln) and actinides is an important area of research because of its significance in the management of nuclear spent fuel. Transmutation of the trivalent actinides will only be possible after separation of the minor actinides from the trivalent lanthanides that are present in large excess. This separation is often difficult because of the great chemical similarity of these two series of f-block elements with similar charge and size. Nevertheless, it is possible to discriminate between the two series of ions because of a small difference in their affinities for a comparatively softer donor ligands containing N or S as donor atoms, e.g., viz. Cyanex-301 (Bis (2,4,4-trimethyl pentyl) dithiophosphinic acid). Depending on the experimental conditions, the structure and the composition of the ion-ligand complexes have been reported to differ drastically\textsuperscript{19}. Therefore, our objective\textsuperscript{20,21} has been to find out the ion-ligand complexes (extracted species) for various lanthanide ions in presence of Cyanex-301 and nitrate ion as ligands, through the calculation of the energy of complex formation using ab initio molecular orbital theory. We have considered the following equation to determine the composition of the complex for different ions.

\[
\text{Ln(NO}_3\text{)}_3 + n\text{Me}_2\text{PS}_2\text{H} \rightarrow \text{Ln(Me}_2\text{PS}_2)_n\text{NO}_3\text{)}_{3-n} + n\text{HNO}_3
\]

The calculated complex formation energies indicate that the formation of the species with two Me\(_2\)PS\(_2\)- and one nitrate ion [Ln(Me\(_2\)PS\(_2\))\(_2\)(NO\(_3\))] is the most preferred one for all the three lanthanides. However, at higher Me\(_2\)PS\(_2\)H concentration the formation of La(Me\(_2\)PS\(_2\))\(_3\) species is more probable because of almost the same complex formation energy for the Ln(Me\(_2\)PS\(_2\))\(_2\)NO\(_3\) and Ln(Me\(_2\)PS\(_2\))\(_3\) complexes. The calculated results also indicate that Lu(III) is likely to be extracted as Lu(Me\(_2\)PS\(_2\))NO\(_3\) irrespective of the Me\(_2\)PS\(_2\)H concentration. It is indeed interesting to note that similar kind of behavior has been observed experimentally through solvent extraction experiments with varying Cyanex-301 concentration. Recently, we have also rationalized\textsuperscript{22} the unusual transport behavior of Americium(III) ion across a composite polymer membrane containing Cyanex-301 and TBP through calculations of the possible hydrogen-bonded complexes involved in the transport process.

**Conclusion**

In this article we have briefly discussed the potential role of computational chemistry in the prediction and rationalization of structure and properties of three different types of chemical systems. The investigation of noble gas compounds proves the unusual examples of chemical bonding; therefore their exploration unravels new bonding mechanism and expands our understanding of a chemical bond. Through calculated results we have rationalized the experimental observations obtained from solvent extraction.
experiments, viz., different extractable species corresponding to different trivalent lanthanides in presence of Cyanex-301 and NO$_3^-$ ligands. We have also discussed the computed results on the ground and excited states polarizabilities of the water and methanol clusters, and the difference in the trend in the excited state polarizabilities of water and methanol clusters has been ascribed to the dissimilarity in the nature of hydrogen bonding in the two sets of clusters. Demonstration of an excellent linear correlation between the ground state polarizability of water clusters and the aggregation number may be very useful to obtain the polarizability of larger cluster from the cluster size. All the work discussed here demonstrates the predictive ability of first-principles based computational techniques to design new molecular systems and rationalize the experimentally observed results.

Acknowledgements

I am greatly indebted to Dr. Swapan K. Ghosh, Head, Theoretical Chemistry section for his excellent guidance, help and support since the beginning of my research carrier at BARC. I am very much thankful to Dr. Arunasis Bhattacharyya, Radiochemistry Division and Dr. T. Jayasekharan, Applied Spectroscopy Division for many helpful discussions. It is a pleasure to thank Dr. Tulsi Mukherjee, Director Chemistry Group for his kind interest, help and constant encouragement. Computer Division, BARC, is gratefully acknowledged for providing computational facilities and support.

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