Superatoms

Brad Zeiger Literature Seminar 28 October 2008

The design of new materials with novel or tunable properties is a topic of compelling current interest. One frontier of this field is the assembly of extended materials in which the elementary building block is a cluster of atoms rather than a single atom.[1] This field has been bolstered by rapid gains in the manipulation and construction of clusters on a very small scale, but significant technical challenges persist.

Clusters on the scale of interest (where physical properties are intermediate between atomic and bulk) are metastable towards coalescence into bulk solid. While this problem can to some degree be ameliorated by embedding the clusters in matrices such as zeolites, rare-gas solids, or other substrates, these approaches add another level of complexity and may have deleterious effects on the properties of the material.[2]

An alternative approach is to increase the stability of the constituent clusters and significantly lower their tendency to aggregate. Clusters that exhibit such enhanced stability are frequently called "superatoms." The origins of superatom stability are electronic, and the term is sometimes used broadly to encompass well-known molecules such as buckminsterfullerene[3] or Zintl phases.[4] It is, perhaps, better applied to a subclass of these materials in which the electronic structures of the clusters parallel the electronic structures of atoms.

The "jellium" model of atomic clusters is often able to rationalize and predict the stability of clusters. This model is rooted in nuclear physics and was first applied to clusters by Knight and Clemenger to explain the size distribution of ionized clusters of sodium in the gas-phase.[5] In the jellium model, the nuclear charge experienced by the valence electrons of the cluster nuclei is assumed to be distributed evenly over the cluster.[6] This spherically-symmetric charge distribution gives rise to a potential surface different from, but analogous to, an atomic charge (which is invariably modeled as a single point charge). The jellium model is typically considered valid for clusters composed of atoms that have weakly bound valence electrons.[7]

The stabilities of superatoms are rationalized by the closing of electronic shells and the existence of large HOMO-LUMO gaps, in the same way that noble gases are rendered stable. The "magic" numbers that lead to stability are slightly dependent on the model used for the potential, but are mostly consistent for smaller clusters. Closed-shell electron counts include 2, 8, 18, 20, 34, and 40 electrons.[7] Among the most prominent examples of superatomic behavior is the Al_{13} cluster. The icosohedral structure of Al_{13}[8] and its electron count[2] are shown in Figure 1 (also the ordering of cluster orbitals by the jellium model).

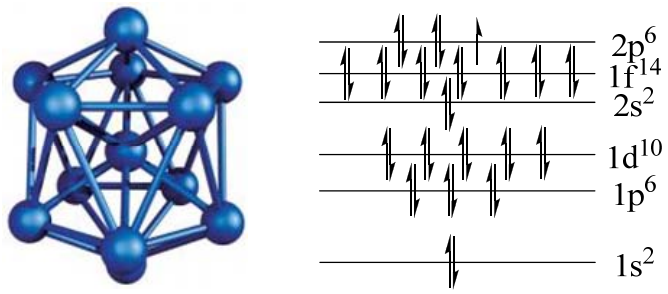

Figure 1

As can be seen above, the Al_{13} cluster is a 39-electron species; one electron short of a stable magic number. As a result, similarities between Al_{13} and the halogens are observed. The electron affinity of Al_{13} is 3.6 eV, essentially the same as that of a chlorine atom.[9] The ready reduction of Al_{13} to its exceptionally stable[10] anion led to the prediction that it should form a metastable ionic solid when combined with potassium counter-ions. Such a solid would have an unprecedented stoichiometry, as potassium and aluminum are immiscible substances according to the conventional Al/K phase diagram.[11] Recent work has successfully produced ionic KAl_{13} in the gas phase, although isolating a pure substance has still not been achieved.[9]

Superatom chemistry is typically investigated by means of mass-spectrometry coupled with computational tools. The chemistry of aluminum clusters in particular has been studied in great detail and has advanced the understanding of superatoms through observations such as the ability of Al clusters to form covalent bonds to make "jellium compounds,"[12] the ability of Al_{13} to serve as a "superhalogen,"[13] and the ability of Al_{14} to act as a pseudoalkaline earth metal.[1]

These recent advances in the understanding of superatoms, coupled with improved computational models and synthetic techniques, are important steps towards the fabrication of cluster-assembled materials. A great deal of work remains to be done, however, before superatoms can find real-world applications.

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