Clusters: A bridge across the disciplines of environment, materials science, and biology

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Clusters in Environmental/Atmospheric Science

The formation of finite particles and dust grains in interstellar media, heterogeneous reactions occurring in the stratosphere, and unidentified infrared bands in interstellar gas clouds have been suggested to have a cluster origin. In the following, we provide examples where clusters have played a role in describing and accounting for phenomena in atmospheric science.

Aerosols and Fine Particles. Fine particles are ubiquitous throughout the universe; they are present in interstellar media (e.g., in dense clouds where ion clustering reactions have been invoked in mechanisms responsible for the formation of molecules); they are ultimately responsible for the rings around Saturn; and, in some theories of planetary evolution, they are used to explain the origin of planets themselves. The fascinating issue of interstellar dust, which could serve as a supply of biotic raw material on earth, is also relevant for astrobiology. In high altitudes of our own planet, there are layers of meteoritic ablation where dust layers are known and nocluetic clouds form, possibly enhanced by ion-induced nucleation processes. For more “down-to-earth” reasons, fine particles are of interest to environmental scientists who must contend with them in ways more germane to our everyday life in terms of visibility and health (1–6). Clustering and related nucleation phenomena are, in part, responsible for their formation (7–13).

For many years, the community of atmospheric scientists was divided into two groups: those dealing with problems of visibility effects, clouds, and condensation processes and those interested in chemical transformations. Many atmospheric chemists considered heterogeneous processes to be of secondary importance and of third-order interest; they usually attempted to account for most observed phenomena considering only gas-phase reactions. However, one need only realize that gas-phase molecules in the troposphere end up in particles and precipitation or consider the discrepancies in homogeneous model predictions having to do with the ozone hole to appreciate that all phases of the atmosphere are intimately coupled.

In addition to influencing solvation processes and chemical reactions, aerosols also play an important role as cloud droplet nucleation centers; in some cases they are formed by nucleation. One such proposed mechanism involves ion-induced nucleation, which has recently become a topic of significant interest because of a number of computational and experimental findings that implicate direct ion nucleation as well as ion–ion recombination as potentially significant sources of aerosol particles (14–18). Interestingly, the energy barriers to ion-induced nucleation involve thermodynamic considerations similar to ones mentioned in the section on solvation effects on reactions.

Heterogeneous Reactions and Gas-To-Particle Conversion. Interest in the uptake of atmospheric molecules by ice and aqueous surfaces has increased dramatically in recent years, as more attention is devoted to the potential importance of heterogeneous chemical reactions. Particular interest in these processes has been derived from findings of the significance of heterogeneous reactions occurring in the stratosphere of the Arctic and Antarctic, particularly with regard to reactions on polar stratospheric clouds of species including chlorine nitrate and N2O5. Before an intense field program and modeling effort was devoted to unraveling the origin of the ozone hole, comparatively little attention had been paid to heterogeneous processes in the stratosphere other than in the context of their possible role in governing the sulfate aerosol layer known since the late 1950s (1–13, 19). Attention to possible heterogeneous processes in the troposphere, of course, has been much more extensive over the years because of recognition of the extensive surface area provided by both background aerosols and particles existing in polluted environments, as well as the availability of condensed media in the presence of cloud droplets and ice crystals under various weather conditions. Despite extensive studies of aerosols using reactive smog or cloud chambers, it is not unfair to say that much of the interest in interpreting basic reaction phenomena in heterogeneous systems has been motivated in large measure by findings in the field of upper atmospheric chemistry.

Field investigations (20–30), as well as numerous model studies (31–33), gave particularly important insight into the probable significance of heterogeneous reactions that can take place on ice surfaces, including those doped with acid molecules such as HCl, HNO3, and H2SO4. In particular, laboratory findings have provided important evidence for the potential role that polar stratospheric clouds may have in effecting catalytic reactions between species whose reactions are otherwise too slow to account for observed transformations. A notable example is the reaction between ClO2 and HCl. Although the connections have been more to surface science than cluster studies, the interplay has been quite substantial. Among the many studies in this area, new insights have been derived from computer simulations (34) and related experimental findings. The findings have been particularly thought-provoking in bringing to the attention of the atmospheric community that the formation of H2O+ and Cl− upon HCl interaction with the surface of stratospheric ice particles can provide the prerequisites for potentially important ion catalyzed reactions of ClO2. Theoretical studies (35) have yielded further evidence for the important role that ion-catalyzed reactions may have in the chemistry of Cl− interacting with ClO2 on surfaces. Calculations point to the existence of large energy barriers in the neutral reactions, whereas involvement of an anion (e.g., NO3−) via an attachment/detachment

Conflict of interest statement: No conflicts declared.

This paper was submitted directly (Track II) to the PNAS office.

Abbreviations: BNCT, boron neutron capture therapy; MetCar, metallocarbonylhexayne.
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The stability of NO$_3$ has been made of the thermodynamic pathways to the production of the gas-phase acid loading of the atmosphere (42, 43). Laboratory studies have been observed throughout the lower atmosphere (42, 43). The central question is how to design and synthesize stable clusters. The criteria depend on the nature of bonding that exists within a cluster. In clusters of simple metals, as outlined previously, the stability is governed by the electronic shell structure. In covalently bonded clusters such as those of C and Si, the atomic arrangements are important for stability. It is also possible to form stable compound clusters by using suitable alloying techniques. In the following, we discuss these cases through illustrative examples.

**Covalently Bonded Clusters.** The discovery of C$_{60}$ in the gas phase (48) as an unusually stable cluster and its synthesis in macroscopic quantities following chemical routes (49) has given rise to a new field called fullerene chemistry. The ability to introduce metal atoms inside C$_{60}$ also has provided the hope that new cluster-assembled materials with unique properties can be synthesized. Applications of these materials range from superconductivity to medicine, and there is a vast body of literature on this subject. Instead, we briefly discuss Si clusters, which behave very differently from those of C, although both elements belong to the same column in the periodic table. Numerous attempts to synthesize Si$_{60}$ in the fullerene form have failed, and it has been suggested (50) that the only way to confine Si$_{60}$ to a cage structure is to have it encapsulate a metal cluster such as Al$_2$Si$_2$. However, a recent experiment on Si$_{12}$W (51) suggested that it may be possible to confine Si atoms in a planar structure by using appropriate metal atoms as dopants. The authors suggested that the structure of Si$_{12}$W is that of a W atom sandwiched between two hexagonal arrangements of Si atoms (Fig. 1). The stability of this cluster was attributed to the 18-electron rule where each Si atom is assumed to contribute one electron. This idea was later pursued in the design and synthesis of the Si$_{12}$Cr (52) cluster. The validity of the structure of this cluster was established by comparing the predicted electron affinity with that of the measured value (53). Recently, experiments have shown that stable metal-doped Si clusters also can be synthesized based on the 20-electron rule (54).

Fig. 1. Structure of the Si$_{12}$W cluster. The W atom is sandwiched between two planar Si$_6$ clusters.

**Metallocarbohedrynes (Met-Cars).** Among the magic numbers frequently seen in cluster systems, another class in which there has been particular interest is the Met-Car family. The first member of the Met-Car class to be discovered was comprised of 8 titanium atoms bound with 12 carbons (Ti$_8$C$_{12}$) and assembled into a cage-like structure (56–58). A wide range of Met-Cars have been observed to form from metals including Ti, Zr, Hf, V, and Nb, and also Cr and Mo, and there are some indications for Fe as well (59). It has been found that binary Met-Cars can be prepared from the above metals. Furthermore, other metals that do not apparently form the pure Met-Car can be substituted into at least the titanium member of the class; these include Y, Ta, W, Mn, Th, and even Si, which interestingly replace a metal rather than a carbon position. To date, all of the indications of mechanisms of formation are that the Met-Car assembles from species comprised of metal–C$_3$ units, which ultimately undergo carbon loss at the point of cage closure to the 8–12 structure. These species, together with the Buckminsterfullerene family, offer the prospect that molecular clusters in general, and the related field of cluster-assembled materials, may be expected to have a significant impact in materials science. Determining the exact geometry through conventional structural characterization techniques and developing purification methods for use in producing bulk quantities represents an active area of current study.

Among the more interesting findings is that the Met-Cars display unique behavior after laser photoexcitation (60).
In addition to delayed ionization, the building blocks of Met-Cars have been observed to undergo delayed atomic ion emission. Also, although comprised of atoms having relatively high ionization potentials, Met-Cars are found to have rather low values in the vicinity of 4 eV (1 eV = 1.602 × 10^-19 J) for the Ti- and Zr-containing species (61). This unexpected unique behavior is seen in Fig. 2. Because of these factors, extensive interest has arisen in the electron relaxation dynamics of the Met-Car class of clusters. Femtosecond pump–probe techniques have been applied to a study of the vanadium Met-Car system, allowing a detailed study of the electronic to vibrational relaxation processes in this class of molecular cluster systems that display an appreciable free electron behavior. The onset of behavior that leads to thermionic emission is evident from ionization potentials of Met-Cars and their partial cage building-block structures.

**Metal Clusters.** The idea of Khanna and Jena (47) regarding the use of clusters as building blocks arose from a consideration of some surprising findings coming from various laboratories; these include ones related to the observation of magic numbers in metallic clusters and influences on their reactive properties (62, 63). The connection of magic numbers in alkali metal clusters to the jellium model has been discussed earlier in this work. Another finding related to the magic numbers in clusters containing more than a few dozen atoms was that the most stable species correspond to sizes that have complete geometric shells in icosahedral or cuboctahedral atomic arrangements. It was realized that an ideal situation would arise if the geometric close packing as well as electronic shell closure could be simultaneously achieved to enhance the stability of a cluster. Another study revealed that even the chemical behavior and associated stability of clusters also could be predicted by the shell model. In particular, it was found that Al_{13} clusters etched with oxygen-produced species that exhibited a marked peak at Al_{13}, as well as at Al_{13} and Al_{13}. Because Al_{13} has 40 valence electrons, its inertness could be understood in terms of a closed electronic shell, as could the 23- and 37-atom-containing systems, which also have closed electronic configurations (62). These and other observations began to suggest that the jellium picture, although extremely simplistic and marked by indisputable limitations, is amazingly successful in describing many of the global observed electronic features in a variety of systems and that certain metallic clusters could be described as superatoms (63, 64). The prospect of using clusters as building blocks thereby arose.

More recently, these interesting findings prompted a new and extensive series of undertakings that produced very promising and totally unexpected results, namely that selected aluminum compounds and intermetallics can even take on electronic properties associated with some elements of the periodic table (63–66).

Consider an Al_{13} cluster that has a slightly distorted icosahedral structure and possesses 39 electrons, one short of filling a complete electronic shell. The chemistry of this cluster is analogous to that of Cl and indeed has a large electron affinity, ~3.6 eV. Thus, when an electron is attached to the Al_{13} cluster, the resulting Al_{13} cluster becomes perfectly icosahedral and stable. Thus, the cluster KAl_{13} behaves very much like a salt, KCl. Several experiments (63) recently confirmed this unique chemistry, and the possibility of synthesizing cluster-assembled materials rests on our ability to produce macroscopic quantities of stable clusters. For example, reactivity studies revealed that Al_{13}, in reactions with hydrogen iodide and iodine, exhibited behavior associated with a superhalogen, while retaining the intact aluminum geometric and electronic structure. As an isolated ion, Al_{13} takes on a rare gas-like electronic character. Even more revealing were findings that Al_{13} could undergo somewhat similar reactions and function as an alkaline earth. Subsequently, both of these aluminum cluster species were identified to form classes of polyfluorides and to develop a unique chemistry after the formation of active sites on the cluster structure (64). These concepts, if they can be extended to other systems, offer the possibility of using clusters to accomplish unique synthetic chemistry and to form various classes of superatoms that would be analogues to elements of the periodic table. If these new ideas are borne out, there is the very promising and exciting concept that new materials using atomic or compound clusters of selected electronic properties and geometries may be formed through the self-assembly of superatoms that mimic selected elements of the periodic table.

**Clusters in Biology and Medicine**

Biology is the ultimate expression of molecular engineering where nature has perfected the science and technology of organic and metalloorganic complex matter at the nanoscale. Considerable amount of research on the properties of nanoscale inorganic materials in the past 2 decades has formed a bridge between biology and physical sciences, leading to the emergence of a new class known as biomaterials (67). These are designed and synthesized not only to imitate, monitor, and repair biology but also to learn from it in making new materials. Clusters have been playing a fundamental role in this endeavor in allowing one
ties where this noble goal may someday have the same length scales as those of healthy cells. Nanoscale particles that selectively destroyed without damaging find ways by which cancer cells can be sired goal in cancer therapy has been to tissues as well as cancerous ones. A de- procedures that wreck havoc in healthy and surgery. All these are invasive pro- ago, namely chemotherapy, radiation, primarily the same as it was 30 years cer, its conventional treatment today is the progress made in understanding can- ter, ‘noninvasive treatment of tumors’ has been a label used to describe several approaches in the last decade that have been shown to be effective in laboratory tests in animals and test tubes.

Halas and her group (68) have pioneered a technique in which they target tumors with gold-coated silica nanoparticles, which absorb infrared light and create enough heat to potentially kill the cancer cells. However, a fundamental understanding of how gold attaches to the silica nanoparticle and how the amount of coating affects its optical properties was not available. Recently, Sun et al. (69) showed that small silica clusters containing as few as three molecular units can also absorb infrared light when coated with one or two gold atoms. The gold atoms attach to the dangling bonds of silicon atoms in the silica nanoparticle and modify the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMOLUMO) gap such that even a tiny cluster can absorb infrared light. The advantage of having a small cluster with similar functionality as the large nanoparticles is that it can penetrate the crowded environments such as biological milieu of cells and live tissues for effective drug delivery.

The above technique, however, is not suitable for tumors such as anaplastic astrocytomas or glioblastomas that are buried in the human body. For such tumors, magnetic fluid hyperthermia (70) provides an alternative method where a magnetic nanoparticle can be heated by absorbing radio frequency, and the resulting heat can destroy the tumor. In addition, the magnetic nanoparticle can be manipulated externally by a gradient magnetic field for targeted drug delivery. The conventional magnetic nanoparticles that are widely used in experiments and animal testing involve iron oxides. These particles can be functionalized by coating with gold and can be targeted to attack specific cells. For example, in a recent experiment, gold-coated iron oxide particles were interacted with 13 different amino acids (71). It was found that only two sulfur-containing amino acids (cystine and methionine) are adsorbed onto the gold-coated iron oxide particles. Sun et al. (Q. Sun, Q. Wang, P.J., B. V. Reddy, C. Gonzalez, and M. Marquez, unpublished data) recently studied the interaction of a model gold-coated iron oxide cluster, namely, Au6Fe13O8 with the above three amino acids. From their total energy calculations, they found that whereas both cystine and methionine bind to the gold atom in the Au6Fe13O8 cluster, taurine was not bound. The geometries of these amino acids illustrate the reason; whereas both cystine and methionine have exposed S atoms, the S atom in taurine is bonded to three O atoms and one C atom. Thus, the strong bonding between exposed S and Au atoms is the key to functionalizing these nanoparticles for effective drug delivery.

**Boron Neutron Capture Therapy (BNCT).** In the elemental form, boron exhibits a variety of complex isomorphic phases. In these solidified solids, boron occurs mainly as B12 icosahedra. However, the structure and energetics of boron clusters are very different. Recent theoretical and experimental studies have shown that B12 clusters (n ≤ 20) occur in several distinct shapes (convex, spherical, and quasiplanar), and for n > 20, tubular structures are preferred (72). These 2D structures have extended π-delocalization and exhibit different chemical, physical, and structural properties compared with the bulk. Passivated boron clusters also occur in diverse shapes and

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**Fig. 3.** Mass spectra of Al cluster anions (A) reacted with I2 vapor (B) and etched with O2 (C). Peaks shaded green fall into the Al13I5 family, whereas peaks shaded blue fall into the Al14I5 family (64). In A–C, the y-axis is peak intensity (in arbitrary units). [Reproduced with permission from ref. 64 (Copyright 2005, AAAS, www.sciencemag.org).]
sizes, and application of polyhedral boranes range from designing boron-based materials to medicine.

Of all of the applications of boron and the passivated clusters, BNCT is a very selective and special one (73, 74). For certain types of cancer where conventional approaches fail, as in case of malignant melanoma, BNCT is the only alternative. BNCT involves the capture of thermal neutrons by boron-10 ($^{10}$B) nuclei because of the property of the boron nuclei. However, the delivery of the boron to the tumor is administered by a variety of boron compounds. Initial screening for BNCT compounds concentrated on the derivatives of boric acid [B(OH)$_3$] such as p-carboxyphenoxyboronic acid and the salts of polyhedral boranes (see Fig. 4 and ref. 75). Recently, new generations of boron compounds have been designed to achieve higher tumor cell selectivity than the previous BNCT agents. Boron containing amino acids, related peptides, porphyrins, DNA binders, and other tumor-targeting anchor agents are being attached to a polyhedral borane skeleton for better tumor-cell recognition (75, 76).

It is evident that there are numerous reasons for the extensive activity and continuing growth of the field of cluster science. From the examples given in this work, as well as the new advances presented in the seven accompanying articles of this Special Feature, it is clear that studies of clusters do indeed have an impact on many fields and, in many cases, provide unifying concepts. Elucidating the properties and reactivity of matter of small sizes that often display quantum confinement on the properties for further study. Unraveling the role of quantum confinement on the properties of matter in the nanoscale and sub-nanoscale size regime is a topic of considerable fundamental importance.

The prospect of using clusters for building blocks for nanoscale materials with tailored properties abounds. We may expect many developments that lead to new, highly selective and efficient catalytic materials on the one hand or ones with unique electronic or magnetic properties on the other hand. Of equal excitement and promise are the developments arising from cluster research in areas spanning studies of the origins of interstellar molecules to planetary formation mechanisms, as well as factors influencing climate and environmental conditions. The same is true of solar cells and especially Dr. Michele Kimble for discussions and valuable suggestions during the course of preparing the manuscript and for careful editing. This work was supported by U.S. Air Force Office of Scientific Research Grant FA 9550-04-1-0066; National Science Foundation Atmospheric Sciences and Experimental Physical Chemistry Divisions Grant NSF-ATM-0089233; and Department of Energy Grants DE-FG02-02ER46009, DE-FG02-92ER4258, DE-FG02-96ER45579, and DE-FG02-96ER45579.

We thank K. Boggavarapu for discussions, Q. Sun for discussions and help in the design of the cover, and especially Dr. Michele Kimble for discussions and valuable suggestions during the course of preparing the manuscript and for careful editing. We thank K. Boggavarapu for discussions, Q. Sun for discussions and help in the design of the cover, and especially Dr. Michele Kimble for discussions and valuable suggestions during the course of preparing the manuscript and for careful editing.


