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Pulsed Arc Cluster Ion Source

N.Suganya[1], R. Kiruthika[2], P.Sutha[3], S.Lavanya[4], S.Reegala Mary[5]
[1, 2,3,4,5] UG Scholar, PG and Research Department of Physics,
Thanthai Hans Roever College, Perambalur, India

Abstract: Clusters belong to a new class of systems and are studied to understand several aspects related to the science of nanomaterials. Nanoparticles are nucleated at the cluster stage and it is important to understand these systems in the naked state using mass spectrometry in order to know the origin of molecular and electronics structure in bulk system. Almost everything forms clusters and the diversity in cluster system is vast. The methods of preparation of clusters and their diverse variety are discussed in this chapter. While exploring clusters, scientists have discovered new molecules such as C_{60}. The chemistry of clusters in the gas phase still constitutes an active area of investigation.

Key words: Nanomaterials, Nanoparticles, C_{60}

I. INTRODUCTION

Clusters belong to a new category of materials; in size they fall between bulk materials and their atomic or molecular constituents. Sometimes they are considered to constitute a new form of matter, as their properties are fundamentally different from those of discrete molecules and bulk solids. They are systems of bound atoms are molecules, existing as an intermediate form of matter, with properties that lie between those of atoms (or molecules) and bulk materials. Depending on the kind of constituent units, they are called either atomic or molecular clusters. The term, 'molecular clusters' also implies clusters which behave like super molecules. Clusters include species existing only in the gas phase or in the condensed phase or in both. Clusters identified first in the gas phase have been synthesized later in the condensed phase and vice versa. They can have a net charge (ironic clusters) or no charge (neutral clusters) at all. The finite aggregates of atoms or molecules constituting clusters are bounded by forces which may be metallic,, covalent, ironic, hydrogen bonded or Vander Waals in character and can contain up to a few thousand atoms (called the *Nuclearity* of cluster). As a result, they have regular shapes (such as icosahedra). However, they also exist in a spherical shape.

II. HISTORY OF CLUSTER SCIENCE

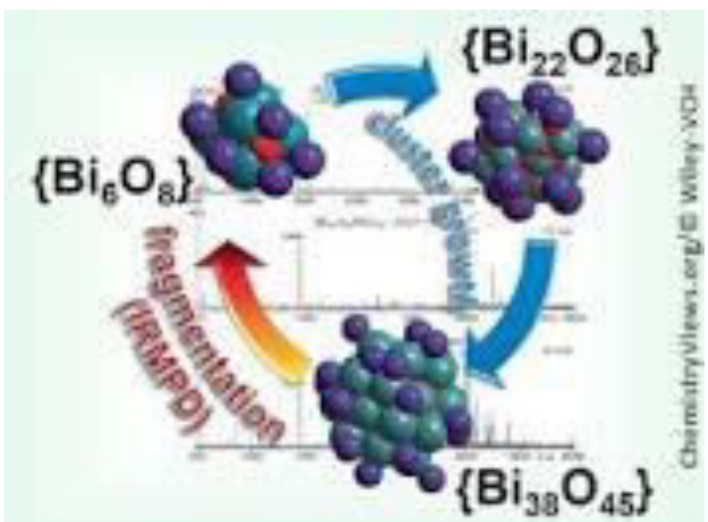
The importance of clusters was first proposed by the Irish-born chemist Robert Boyle in his book, The *Skeptical Chemist* published in 1661. In it Boyle was critical of Aristotle's four element theory of matter and proposed that it exists in the form of 'corpuscles'. He thought about it, "minute masses or clusters that were not easily dissipable into such particles that composed them." 'Clusters' for him were not collections of atoms or molecules as both were unknown then. During the last several decades, cluster science has grown to become a field of interdisciplinary study. Improvement in experimental techniques such as mass spectrometry and advancement in computational power (and methods) have increased the interest in cluster science. The use of clusters goes back to several centuries.

III. GAS PHASE CLUSTERS

Gas phase clusters are generated in cluster sources. There are many kinds of cluster sources. Some of them are listed below.

- Laser vaporization-flow condensation source
- Pulsed arc cluster ion source
- Laser ablation cluster source
- Supersonic (free jet) nozzle source
- Knudsen cell (effusive sources)
- Ion sputtering source
- Magnetron sputtering source
- Gas aggregation/Smoke source
- Liquid metal ion source

Some of the more common methods are described below.



IV. LASER VAPORIZATION

The vaporization sources is a pulsed cluster source which is used to produced small-and medium-size clusters. The resultant cluster may be formed from any element or compound. This method typically combines laser ablation and supersonic jet expansion. In the laser vaporization source, vapor is generated by pulsed laser ablation of a rod the starting material. An intense

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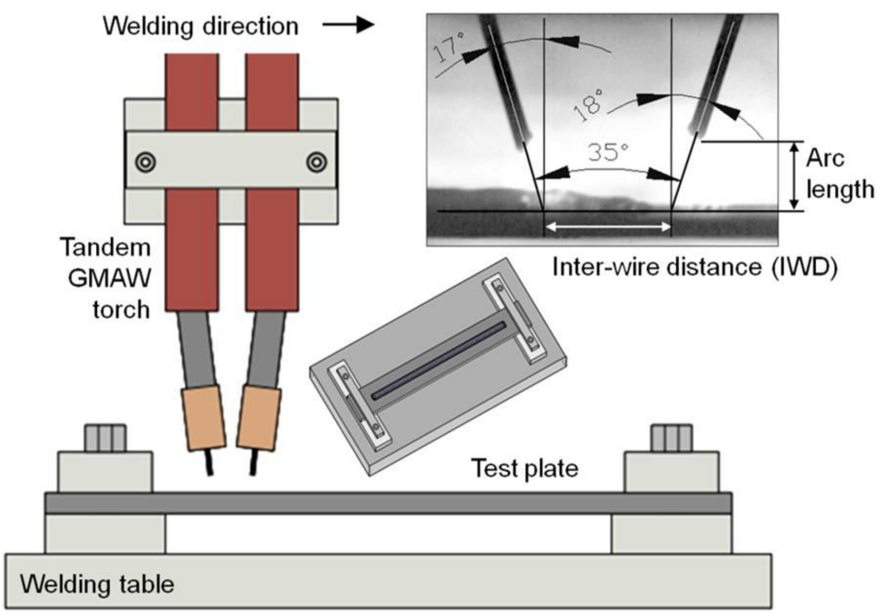
pulsed *UV* laser is used here (typically third or fourth harmonic of *Nd: YAG*). Each 10 ns pulse 10^{14}-10^{15} atoms per mm^2 of the target. Since the use of lasers for cluster generation also leads to ionization, this source also generates neutral, cationic and anionic clusters which can be investigated directly by mass spectrometry, without post ionization. In fact what is produced by laser evaporation is a plasma.

V. PULSED ARC CLUSTER ION SOURCE

Pulsed arc cluster ion sources (PACIS) are related to laser vaporization sources. Instead of the laser here the cluster precursor is vaporized by an intense electrical discharge. Cluster beams generated in this way are significantly more intense in comparison to laser vaporization. Nearly 10 per cent of the clusters formed by using this technique are charged and again, post ionization is not necessary for mass analysis.



VI. SUPERSONIC (FREEJET) NOZZLE SOURCES

Supersonic nozzle sources are of two main types.

- Unseeded and
- Seeded

In the first type, clusters of inert gases, molecules and low boiling metals (e.g. Hg) are formed. In the other type, the metal is vaporized (with a vapor pressure of 10-100 mbar) in an oven and the vapor is mixed with (seeded) an inert carrier gas at a pressure of several atmospheres (10^5-10^6 pa) at a temperature of 77-1500 K. The metal/carrier gas mixture is then expanded through a nozzle (with diameter of 0.03-0.1 mm) into high vacuum (10^{-1}-10^{-3} pa), which create a supersonic beam. Nozzles with rectangular opening have been used to generate two-dimensional cluster beams (normally they have a disk-like cross section), which are necessary for certain studies.

VII. GAS-AGGREGATION OR SMOKE SOURCES

The source utilizes the property of aggregation of atoms in inert media. The vapors generated by one of the several means are introduced into a cold inert gas at a high pressure of the order of 1 torr. The species, originally at a high temperature, are thermalized. The gas phase is supersaturated with the species and they aggregate. These sources produce continuous beams of clusters of low-to-medium boiling (<2000 K) metals. By controlling the kinetics of quenching and aggregation, various cluster sizes can be produced.

VIII. KNUDSEN CELL

The Knudsen cell produces a continuous, low flex beam of clusters. The velocity of the species is low (subsonic). In the cell having a small aperture, a volatile solid or liquid is heated; the cell itself is held in a vacuum vessel. In design, this is similar to a smoke source. At the low vapor pressures produced, their mean free path is greater than the collision diameter of the aperture, as a result of which there are very few collisions before particles leave the cell. The energy resolution of the cluster beam formed in the effusive sources is poor. The angular spread is also larger. In these sources, as the aperture is small, the solid gas mixture is nearly at equilibrium. The cluster intensity (I) falls exponentially with an increase in the cluster nuclearity (N) according to the equation, $I(N)= ae^{-b/N}$, where a and b are parameters. The intensities in a smaller window of masses are related to the stability of the cluster. For example, in antimony, Sb_4 dominates than Sb_3 or Sb_5.

IX. LIQUID METAL ION SOURCE

These sources are primarily used to produce clusters of multiple charges, with low-melting metals. A needle held above the melting point of the metal to be studied. The tip of it is

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wetted with the metal and it is held at a potential. Very high electric fields at the tip of the needle (due to smaller dimension) cause the emission of a spray of tiny droplets from it. Similar sources are used as ion sources. Hot, multiply charged droplets undergo evaporative cooling and fission to smaller sizes. Fission occurs as Coulomb repulsion between the charges become larger than the binding energy of the drop itself. In addition to the above source sputter sources are used in which a high energy ion beam is used to sputter atoms, ions and clusters from a surface.

X. CLUSTER GROWTH

Cluster growth occurs in two stages.

- Nucleation
- Growth

Nucleation:

The nucleation can be homogeneous or heterogeneous. Heterogeneous implies the nucleation occurs on foreign objects, dust particles, etc. In it, collision between like or unlike atoms occurs such that the thermal energy is lower than the binding energy of the species formed. Dimer formation occurs when the third body involved in the collision removes the excess internal energy as kinetic energy.

Growth:

Initial growth occurs by the aggregation of atoms or molecules one at a time. Coalescence of clusters results in the formation of larger clusters.

XI. DETECTION AND ANALYSIS OF GAS PHASE CLUSTERS

The formed clusters can exist as neutrals or ions (both positively and negatively charged). Various mass spectrometers are used to detect the ionic clusters. The clusters which exist in solid or in liquid state can be analyzed by several spectroscopic, microscopic or diffraction techniques. Here we will discuss the mass spectrometric studies on clusters, because we are focusing only on gas phase clusters. Mass spectrometers are unique devices used to study the exact constitution of the clusters which exist in the gas phase. From the mass we can easily calculate the empirical formula of the cluster. Wien filter, time of flight (TOF), quadrupole mass filter (QMF), and ion cyclotron resonance (ICR) are the normal kinds of mass spectrometric techniques used to study clusters (although magnetic sector instruments can also be used). These techniques are briefly discussed below.

XII. TYPES OF CLUSTERS

Most of the elements in the periodic table form clusters. Alkali metal, coinage metal and rare atoms of which they are made and the nature of the bonding in these clusters. We can classify the clusters by their composition; for example, if the clusters are formed metallic elements they are called metallic clusters. Types of cluster:

- Ionic clusters
- Covalent clusters
- Metal clusters
- Molecular clusters
- Vander Waals clusters

XIII. METAL CLUSTERS

Metal clusters are formed from alkali metals, alkaline earth metals and transition metals. Metal clusters may be formed from single metallic element or from more than one metal, giving rise to inter metallic or nano-alloy clusters. Some of the metal clusters are discussed below. Neutral sodium clusters are produced in a gas aggregation source. Metallic sodium is heated in an oven to a temperature of about 400^0C. The hot sodium vapor (partial pressure~ 0.1 mbar) expands into a low vacuum He-atmosphere (several mbar, T~77K) where it condenses due to super-saturation. Clusters are formed and they are directed into a differentially pumped section followed by an interaction region, with additional differential pumping. The cluster velocity is related to the sources conditions and ranges from 200 to 400 m/s. Various kinds of clusters such as silver, aluminum, copper and nickel are known.

XIV. SEMICONDUCTOR CLUSTERS

Semiconductor clusters are generated from elements which are semiconductors in nature such as silicon, carbon and germanium. The discovery of the fullerene, C_{60} a carbon cluster, stimulated form a greater variety of clusters as compared to other elements. The bonding in these clusters is covalent in nature. The earlier carbon clusters were produced by using an electric discharge between graphite electrodes. The generated carbon clusters were detected by mass spectrometers. C_{60} was discovered in such experiments in an FT-ICR, with laser desorption ionization. Fullerenes, discovered in the gas phase were later made in the condensed phase. Next to carbon, silicon clusters have been studied widely. The first reported silicon clusters were generated by laser flash evaporation, quenched in a carrier gas and then cooler by supersonic expansion. Photo fragmentation studies on mass selected silicon clusters were conducted. The reactivity of mass selected silicon clusters has been studied widely by using ion trap mass analyzers. Apart from carbon and silicon, other semiconductor elements such as germanium also form clusters. Both silicon and germanium also form nanoparticles, which are interesting today in view of their luminescence which can be tuned across a large window of wave length. These are, however, investigated in the condensed phase.

XV. IONIC CLUSTERS

The term 'ionic clusters' signifies those clusters derived from ionic solids having large differences in electro negativity, such as NaCl, CsCl,etc. Ionic clusters may exist with positive or negative charge. Ionic clusters can be generated by methods like heating or laser vaporization of ionic compounds in a stream of cold inert gas. The studies on ionic clusters have made it possible to determine the size at which ionic clusters begin to acquire the properties of solids.

XVI. PROPERTIES OF CLUSTERS

The properties of clusters explain the transition from single atoms to the solid state. This transition can be carefully examined with clusters. For example, one can ask the question when cluster of a metal indeed become a metal. One can systematically increase the cluster size and find out when specific features emerge in certain spectroscopic techniques. It is important to remember that such studies can also be done in the condensed phase with techniques such as

STM. There are numerous properties which make clusters interesting. We will list a few examples. Mercury clusters show very interesting properties with respect to the size of clusters. They show a transition from Vander Waals to metallic clusters. We note that such changes are expected in a number of clusters but only a few are investigated in a large size range.

XVII. MERCURY CLUSTERS

The clusters are generated by a molecular cluster beam source. A monochromatized radiation (typically from a synchrotron) is used to photo ionize the neutral cluster beam. The light coming out from the undulator (one of the insertion devices in a synchrotron, used for enhanced light intensity) provides more than 10^{13} photons/sec/m rad. The photo ionization efficiency (PLE) curve of each mass selected cluster ion is monitored by the variation of the photon energy. The PIE curve of the atom is recorded between the ionization corresponding to the ejection of one *s* electron or *d* electron. For small clusters with Hg_n ($n<12$), the two auto ionization lines are well resolved and appear to shift with respect to the corresponding atomic transition. For cluster size n=13, the 1/n dependence is no longer observed in PIE. The gradually increasing shift for both lines illustrates the deviation from Vander Waals bonding in larger cluster size (in which isolated atomic features are expected).

XVIII. OPTICAL PROPERTIES

Optical properties of isolated clusters in the gas phase are rarely investigated. One can obtain electron removable of negatively charged species is investigated. From this one learns about the properties. It is also possible to do spectroscopy of isolated clusters (such as fluorescence) to obtain information on optical transition. However, most of the optical studies are done in the condensed phase. For metals, the optical absorption gives beautiful colors, which has been the subject of investigation for a long time. In a metal cluster, in the metallic regime, there are free electrons which distribute throughout the cluster. As a result they are susceptible for external electric field. When a cluster is irradiated by light, which has a wavelength much larger than the cluster size, the electrical field is uniform as far as the cluster is concerned. The field induces collective oscillations of the electrons in the clusters.

XIX. CONCLUSION

A simpler model, the Liquid Drop model (LDM) has also been developed for metal clusters. This is an electrostatic model, in which the metal cluster is represented as a uniform conducting sphere. Variations of properties with size can be predicted by developing scaling laws using this model. According to the LDM, the IP should decrease as the cluster size gets larger (i.e. it requires less energy to remove an electron from a larger cluster than from a smaller one).

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AUTHOR(S) BIOGRAPHY

She is N.Suganya. She has studied in UG Student, PG and Research Department of Physics, Thanthai Hans Roever College, Perambalur. She as presented in 3 National level paper presentation. She has published one International Online Journal (with high impact factor). She has participated in Many National level conferences and Workshop.

She is R. Kiruthika. She studied UG Student, PG and Research Department of Physics, Thanthai Hans Roever College, Perambalur. She has presented in One National level Paper Presentation.

She is P. Sutha. She studied in UG Student, PG and Research Department Of Physics, Thanthai Hans Roever College, Perambalur. She has Participate in Many National Conferences.

She is s. Lavanya. She studied in UG Student, PG and Research Department of Physics, Thanthai Hans Roever College, Perambalur. She has Presented One National level Paper Presentation. She has Participate Many National level Conferences.

She is S. Reegala Mary. She Studied in UG Student, PG and Research Department Of Physics, Thanthai Hans Roever College, Perambalur. She has presented One National level Paper presentation