

# **Cryochemistry of Metal Atoms and Nanoparticles**

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**ABSTRACT:** The whole set of modern theoretical simulation methods are actively used for interpretation of properties and chemical reactivity of molecular systems of interest for nanochemistry. Of paramount importance is the information on the potentials of interactions between particles in a system, according to which the calculation methods are divided into semiempirical and nonempirical (ab initio).

In the former methods, the potentials are written in the analytical form based on the known theoretical expressions, and the parameters of these expressions are fitted to a sampling of experimental data. The most popular expressions are those used in molecular mechanics, classical molecular dynamics, as well as the potentials applied in solid-state physics. Such an approach is employed to simulate the properties of atomic clusters both homogeneous and heterogeneous. In the first stage, the equilibrium geometrical configurations of clusters are calculated as the points in minima on the multidimensional potential-energy surfaces. Here, it should be borne in mind that a nanosystem has a great number of such minima and, correspondingly, a wide range of structural modifications. As a rule, local minima are separated by the potential barriers, which are so low that the transitions between structures can occur even at moderate temperatures. Hence, it is necessary to enumerate quite a number of minima, which is, however, a cumbersome task. Next, from the points determined, the energy characteristics are calculated and the thermodynamic stability of a system is forecasted. A great body of information is provided by the molecular dynamic calculations of the paths of particles within a cluster, which are carried out at a fixed temperature. Analyzing the trajectories and building different functions of distribution and autocorrelation functions allow one to characterize a cluster, observe how far its properties deviate from those of the condensed medium built of the same atoms, and analyze the dependence of the cluster properties on its size. The most significant limitation on the simulations based on the analytical potentials is the fact that they cannot be used for analyzing the chemical reactions involving clusters: the parameters of potentials are not calibrated for describing the changes in the electronic structures of the particles.

**KEYWORDS:** cryochemistry, nanosystem, molecular dynamic, potentials, cluster, homogeneous, heterogeneous

## **I. INTRODUCTION**

The interaction potentials derived by ab initio methods of quantum chemistry are naturally more universal and make it possible to solve in principle all the problems concerned with the structure and chemical reactions in molecular systems. Here, the major limitations are associated with the size of the system. [1,2] However, modern quantum-chemical methods can provide sufficiently reliable results for particles comprising up to 10 atoms. Moreover, they allow one to find the coordinates of steady-state points on the potential-energy surfaces constructed for the ground electron states of clusters (i.e. the points that correspond to local minima and the potential barriers hindering rearrangements), estimate relative energies in these points, calculate energy profiles of chemical reactions in the system, predict vibrational and electronic spectra, and analyze in detail the electron density distributions. Such calculations are rather expensive, because they require using methods that take into account the electron correlation effects (first of all, the theory of electron density functional), but are technically feasible. For systems comprising 20–30 atoms, ab initio calculations are also technically possible but at the cost of the accuracy of the results obtained. Equilibrium geometrical configurations of low minima in potential-energy surfaces can be determined with sufficient accuracy, and the thermodynamic stability of the clusters can be assessed. However, the prognosis of spectra and the reactivity of the cluster particles are given with lower accuracy, although the qualitative trends are reproduced quite correctly.[3,4]

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The so-called hybrid methods that combine quantum mechanics and molecular mechanics (QM/MM) are actively developed and are very promising for simulating properties of large molecular systems. The main idea of such approaches consists in applying the quantum description only to that part of a subsystem that is assumed to be most important and take into account the structure of the peripheral part of the total system and its effect on the central region by employing empirical and ab initio potentials. In many cases, the size of the central part can be chosen within 20–30 atoms, and ab initio methods of quantum chemistry would ensure a good quantitative description of both the structure and the reactions in the chosen subsystem. Although certain fundamental problems of the QM/MM theory are still far from their final solution, such an approach is finding increasing use in simulating the processes in biosystems and material science.[5,6]

Nanochemistry is an emerging new field of chemistry, in particular of solid-state chemistry, which emphasizes the study and development of preparation methods of useful materials with nanometer-size dimensions (1–100 nm), as defined by Geoffry Ozin, a pioneer in the field. The direct synthesis of metal complexes and organometallic compounds from zerovalent metals is a known methodology that was well developed during the past 165 years, since the first preparation of  $Zn(CH_2CH_3)_2$  by Frankland from the direct reaction of metallic zinc powder and ethyl iodide. Although comparatively, the dimensions of the simplest and smaller nanoparticles are a thousand times larger than the most common coordination or organometallic compounds,[7,8] there are several interesting characteristics that may serve as bridges to extrapolate several of the synthetic tools developed around the direct synthesis of metal complexes toward the preparation of inorganic nanomaterials. First of all, the surface of inorganic nanomaterials (metallic, metal oxides, or metal chalcogenides, among several others) is very reactive and unstable, unless a coordinating surfactant is used to coat the surface. It is relatively easy to understand that the surfactant behaves as a coordination ligand and that it may play an important role not only on stabilization, but also on the control of the structure and properties of the resulting nanomaterial. Here, we discuss several bridging concepts among coordination compounds and nanochemistry, and present direct synthesis as a novel and useful synthetic tool for the preparation of several useful and interesting inorganic nanomaterials.[9,10]

## II. DISCUSSION

Cryochemistry is the study of chemical interactions at temperatures below  $-150\text{ }^\circ\text{C}$  ( $-238\text{ }^\circ\text{F}$ ; 123 K). It is derived from the Greek word cryos, meaning 'cold'. It overlaps with many other sciences, including chemistry,[11,12] cryobiology, condensed matter physics, and even astrochemistry.

Cryochemistry has been a topic of interest since liquid nitrogen, which freezes at  $-210\text{ }^\circ\text{C}$ , became commonly available. Cryogenic-temperature chemical interactions are an important mechanism for studying the detailed pathways of chemical reactions by reducing the confusion introduced by thermal fluctuations. Cryochemistry forms the foundation for cryobiology, which uses slowed or stopped biological processes for medical and research purposes. As a material cools, the relative motion of its component molecules/atoms decreases - its temperature decreases. Cooling can continue until all motion ceases, and its kinetic energy, or energy of motion, disappears. This condition is known as absolute zero and it forms the basis for the Kelvin temperature scale, which measures the temperature above absolute zero. Zero degrees Celsius ( $^\circ\text{C}$ ) coincides with 273 Kelvin.[13,14]

At absolute zero most elements become a solid, but not all behave as predictably as this; for instance, helium becomes a highly unusual liquid. The chemistry between substances, however, does not disappear, even near absolute zero temperatures, since separated molecules/atom can always combine to lower their total energy. Almost every molecule or element will show different properties at different temperatures; if cold enough, some functions are lost entirely. Cryogenic chemistry can lead to very different results compared with standard chemistry, and new chemical routes to substances may be available at cryogenic temperatures, such as the formation of argon fluorohydride, which is only a stable compound at or below 17 K ( $-256.1\text{ }^\circ\text{C}$ ). One method that used to cool molecules to temperatures near absolute zero is laser cooling. In the Doppler cooling process, lasers are used to remove energy from electrons of a given molecule to slow or cool the molecule down. This method has applications in quantum mechanics and is related to particle traps and the Bose–Einstein condensate. All of these methods use a "trap" consisting of lasers pointed at opposite equatorial angles on a specific point in space. The wavelengths from the laser beams eventually hit the gaseous atoms and their outer spinning electrons. This clash of wavelengths decreases the kinetic energy state fraction

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by fraction to slow or cool the molecules down. Laser cooling has also been used to help improve atomic clocks and atom optics. Ultracold studies are not usually focused on chemical interactions, but rather on fundamental chemical properties. Because of the extremely low temperatures, diagnosing the chemical status is a major issue when studying low temperature physics and chemistry. The primary techniques in use today are optical - many types of spectroscopy are available, but these require special apparatus with vacuum windows that provide room temperature access to cryogenic processes.[15,16]

The measurement of heat changes is performed using calorimetry, usually an enclosed chamber within which the change to be examined occurs. The temperature of the chamber is monitored either using a thermometer or thermocouple, and the temperature plotted against time to give a graph from which fundamental quantities can be calculated. Modern calorimeters are frequently supplied with automatic devices to provide a quick read-out of information, one example being the differential scanning calorimeter.

Several thermodynamic definitions are very useful in thermochemistry. A system is the specific portion of the universe that is being studied. Everything outside the system is considered the surroundings or environment. A system may be:

- a (completely) isolated system which can exchange neither energy nor matter with the surroundings, such as an insulated bomb calorimeter
- a thermally isolated system which can exchange mechanical work but not heat or matter, such as an insulated closed piston or balloon
- a mechanically isolated system which can exchange heat but not mechanical work or matter, such as an uninsulated bomb calorimeter
- a closed system which can exchange energy but not matter, such as an uninsulated closed piston or balloon
- an open system which it can exchange both matter and energy with the surroundings, such as a pot of boiling water

Liquefied gases, such as liquid nitrogen and liquid helium, are used in many cryogenic applications. Liquid nitrogen is the most commonly used element in cryogenics and is legally purchasable around the world. Liquid helium is also commonly used and allows for the lowest attainable temperatures to be reached.[17]

These liquids may be stored in Dewar flasks, which are double-walled containers with a high vacuum between the walls to reduce heat transfer into the liquid. Typical laboratory Dewar flasks are spherical, made of glass and protected in a metal outer container. Dewar flasks for extremely cold liquids such as liquid helium have another double-walled container filled with liquid nitrogen. Dewar flasks are named after their inventor, James Dewar, the man who first liquefied hydrogen. Thermos bottles are smaller vacuum flasks fitted in a protective casing.

Cryogenic barcode labels are used to mark Dewar flasks containing these liquids, and will not frost over down to  $-195$  degrees Celsius

- Nuclear magnetic resonance (NMR) is one of the most common methods to determine the physical and chemical properties of atoms by detecting the radio frequency absorbed and subsequent relaxation of nuclei in a magnetic field. This is one of the most commonly used characterization techniques and has applications in numerous fields. Primarily, the strong magnetic fields are generated by supercooling electromagnets, although there are spectrometers that do not require cryogenics. In traditional superconducting solenoids, liquid helium is used to cool the inner coils because it has a boiling point of around 4 K at ambient pressure. Cheap metallic superconductors can be used for the coil wiring. So-called high-temperature superconducting compounds can be made to superconduct with the use of liquid nitrogen, which boils at around 77 K.
- Magnetic resonance imaging (MRI) is a complex application of NMR where the geometry of the resonances is deconvoluted and used to image objects by detecting the relaxation of protons that have been perturbed by a radio-frequency pulse in the strong magnetic field. This is most commonly used in health applications.

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- In large cities, it is difficult to transmit power by overhead cables, so underground cables are used. But underground cables get heated and the resistance of the wire increases, leading to waste of power. Superconductors could be used to increase power throughput, although they would require cryogenic liquids such as nitrogen or helium to cool special alloy-containing cables to increase power transmission. Several feasibility studies have been performed and the field is the subject of an agreement within the International Energy Agency.[18]



Cryogenic gases delivery truck at a supermarket, Ypsilanti, Michigan

- Cryogenic gases are used in transportation and storage of large masses of frozen food. When very large quantities of food must be transported to regions like war zones, earthquake hit regions, etc., they must be stored for a long time, so cryogenic food freezing is used. Cryogenic food freezing is also helpful for large scale food processing industries.
- Many infrared (forward looking infrared) cameras require their detectors to be cryogenically cooled.
- Certain rare blood groups are stored at low temperatures, such as  $-165\text{ }^{\circ}\text{C}$ , at blood banks.
- Cryogenics technology using liquid nitrogen and  $\text{CO}_2$  has been built into nightclub effect systems to create a chilling effect and white fog that can be illuminated with colored lights.
- Cryogenic cooling is used to cool the tool tip at the time of machining in manufacturing process. It increases the tool life. Oxygen is used to perform several important functions in the steel manufacturing process.
- Many rockets use cryogenic gases as propellants. These include liquid oxygen, liquid hydrogen, and liquid methane.
- By freezing the automobile or truck tire in liquid nitrogen, the rubber is made brittle and can be crushed into small particles. These particles can be used again for other items.
- Experimental research on certain physics phenomena, such as spintronics and magnetotransport properties, requires cryogenic temperatures for the effects to be observed.
- Certain vaccines must be stored at cryogenic temperatures. For example, the Pfizer–BioNTech COVID-19 vaccine must be stored at temperatures of  $-90$  to  $-60\text{ }^{\circ}\text{C}$  ( $-130$  to  $-76\text{ }^{\circ}\text{F}$ ).[16]

### III. RESULTS

It is counterintuitive that chemical reactions can be accelerated by freezing, but this amazing phenomenon was discovered as early as the 1960s. In frozen systems, the increase in reaction rate is caused by various mechanisms and the freeze concentration effect is the main reason for the observed acceleration. Some accelerated reactions have great application value in the chemistry synthesis and environmental fields; at the same time, certain reactions accelerated at low temperature during the storage of food, medicine, and biological products should cause concern. The study of reactions accelerated by freezing will overturn common sense and provide a new strategy for researchers in the chemistry field. In this review, we mainly introduce various mechanisms for accelerating reactions induced by freezing and summarize a variety of accelerated cryochemical reactions and their applications.

The main objectives of cryochemistry include studying the mechanism of elementary chemical reactions at low temperatures; studying the effect of intermolecular interactions on the reactivity and its connection with physical and chemical properties of substances; obtaining chemical compounds and particles that are unstable or highly reactive at normal temperatures; identifying the low-temperature limit of chemical activity of substances.[17]

Chemical reactions at low temperatures were observed for the first time by J. Dewar in the early 20th century (fluorination of hydrocarbons at 90 K; reaction of alkali metals,  $\text{H}_2\text{S}$  and other compounds with liquid oxygen). Systematic studies in the field of cryochemistry have been conducted since 1950s; they were contributed by the

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emergence of new experimental techniques, especially methods of radio spectroscopy and matrix isolation. In liquid-phase reactions (for example, halogen with olefins) at low temperatures an important role is played by the relatively weak intermolecular interaction of reagents with each other and with molecules of the medium, which at ordinary temperatures is not significant due to thermal motion. Various features can be observed in cryochemical reactions. Thus, instead of the Arrhenius dependence of the rate constant on the temperature, the constant increases with the decreasing temperature, reaches its maximum and then decreases. In addition, the reaction mechanism, order and direction are often changed. Solid-state reactions at ultra-low temperatures usually require external initiating action (e.g. photolysis, UV radiation, mechanochemical effect) or the participation of high-activity reagents, such as atomic metals. Cryochemistry offers unique opportunities for obtaining and stabilizing chemically unstable particles and compounds. The particles are isolated in inert matrices (usually solid noble gases - Ar, Kr, Xe, Ne) at temperatures that exclude the possibility of thermal diffusion, usually below the boiling point of liquid nitrogen (method of matrix isolation). Matrix isolation can be used to obtain high-energy fuels, whose energy content exceeds the energy of the most performant modern fuels. New methods of cryochemical synthesis are based on low-temperature co-condensation of reagents. [17] In the chemical industry low temperatures are used for ammonia synthesis, for catalytic conversion of methane and for cationic polymerisation of isobutylene, for obtaining amorphous and fine-grained metals, etc. Cryochemical processes based on physical and chemical conversions of aqueous solutions at low temperatures (cryocrystallisation, freeze-drying, extraction and dispersion), in combination with subsequent dehydration, thermal decomposition, sintering, etc., at temperatures above 70 K are promising for the production of ferrites, solid electrolytes, piezoceramics, catalysts, and adsorbents. [18]

## IV. CONCLUSIONS

The methods of cryochemistry and cryonanochemistry make it possible to carry out and control self-assembling processes of metal atoms to form subnano- and nanosized aggregates, perform competitive chemical interactions of atoms, small clusters and nanosized metal particles with different organic and inorganic substances. At present time the effective approaches of cryochemistry are being developed aimed on stabilization of metal atoms, dimmers, trimmers and higher clusters and metal particles in inert gas matrices and polymer films and by certain organic substances layers at different substrates. The use of low temperatures and controlled condensation of reagent vapors allowed us to obtain and stabilized metal particles of 1 nm and less in size. Such hybrid organic-inorganic film materials can find their applications in catalysis and as highly sensitive chemical sensors. The accumulation of data on the reactions of the variety of different metals for a wide range of temperatures in condensed systems, including solid co-condensate films, will allow one to reveal the fundamental peculiarities of nanochemistry, and at first the manifestation of size effects and clearing its nature for the competitive reactions of metal species. [19]

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