Properties of cluster ions

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Usp. Fiz. Nauk 159, 45-81 (September 1989)

Recent studies of cluster ions are reviewed. Experimental methods of studying cluster ions are discussed, and the parameters of large cluster ions are presented. Physical processes occurring with the participation of cluster ions are investigated.

1. INTRODUCTION

A cluster ion is defined as an ion consisting of an atomic or molecular ion and gas molecules attached to it. Such ions are present in low-temperature plasmas at moderate temperatures and intermediate and high pressures. Examples of such plasma are the *D*-layer of the atmosphere (at 80–90 km above ground),¹⁻³ the stratosphere (at 30–50 km),³⁻⁷ and the gas discharge in CO₂ and CO lasers.⁸ In all these cases, the electrical properties of the plasma are modified by the presence of cluster ions. When cluster ions are present in low-temperature plasmas, they usually contain a small number of gas atoms or molecules. Most of the information available on cluster ions refers to such cases. ^{3,9–12}

There are also situations in which we have to deal with large cluster ions, e.g., in condensation processes in the Wilson cloud chamber that has played a major part in the history of nuclear physics. This instrument relies on the fact that condensation in a slightly supersaturated homogeneous vapor takes a very long time to occur. The critical drop radius above which the drop begins to grow (rather than evaporate) in the supersaturated vapor is then so large that the probability of a random formation of a drop of this type is statistically small. The consequence of this is that condensation takes a very long time in this case, and is almost always incipient rather than actual. When ions acting as condensation nuclei are introduced into this type of system, the critical drop size is reduced, and condensation occurs on the ions. Analysis shows that the critical radius is usually not much greater than the atomic dimensions, i.e., a drop of critical radius is a cluster ion that usually consists of several or several tens of molecules.

This example illustrates the importance of cluster ions with a small number of impurity atoms or molecules, but it also leads us to the following fundamental question: what is the difference between a charged drop and a cluster ion? This problem becomes even more acute for neutral clusters that contain a large number of atoms or molecules. It is then important to know the number of atoms or molecules in a cluster beyond which the system must be looked upon as a macroscopic system. In this review, we shall consider that a system is macroscopic if the addition of one atom or molecule to the cluster produces a monotonic change in its properties. General considerations suggest that the transition from a cluster to a macroscopic particle occurs when the system contains a large number of atoms and the phrase "large number" refers to, say, ten or, at any rate, a few tens of atoms per cluster. However, experience shows that the situation is actually more complex. Thus, first, different parameters of a cluster ion behave differently as its dimensions increase, and the macroscopic characteristics of a charged drop are established for different ion dimensions. Second,

the transition to macroscopic properties occurs for much greater cluster dimensions than one might expect. For example, the nonmonotonic behavior of the structural parameters of a cluster can be seen for clusters containing a few hundred atoms.

All this complicates the true picture of processes that occur with the participation of cluster ions and requires additional information about the properties of the ions. For example, let us suppose that we wish to describe condensation in supersaturated water vapor containing ions. We describe this process as the result of the successive attachment of water molecules to a cluster ion and the detachment of these molecules from the ion. To implement this scheme we must have data on the rate of attachment of water molecules to the cluster ion, and on the enthalpy and entropy of cluster ions with a given number of water molecules. If the cluster ion can be looked upon as a macroscopic particle, all we need do is introduce into this scheme the dependence of these parameters on the drop dimensions. Clearly, the simplified scheme of calculation becomes unsatisfactory when the cluster ion does not exhibit macroscopic properties. The correct description of the process then involves not only a more complicated scheme of calculation, but also requires additional data on the properties of the cluster ion, which necessarily involves special measurements.

Significant advances have been made in recent years in the investigation of cluster ions containing a substantial number of atoms or molecules. This has been due, in the first instance, to the development of techniques capable of selecting and then investigating cluster ions with a given number of atoms. These techniques rely on the use of modern lasers and mass spectrometers. Our review is devoted to an analysis of the data obtained in this way, and also to theoretical studies of cluster ions with intermediate and large dimensions.

2. METHODS OF PRODUCING AND DETECTING LARGE CLUSTER IONS

The notable advances achieved during the last few years in studies of the physical properties of large cluster ions¹² have largely been due to advances in experimental methods of producing and detecting high-mass cluster ions. This means that it is now possible to select and reliably identify cluster ions with masses up to 10^4 a.u. and up to several hundred particles or more. It is also possible to subject such ions to external agencies (electromagnetic radiation, fast particles, chemically active particles, surfaces, etc.) and to determine reliably the consequences of the elementary interaction. The popularity of these techniques has led to extensive data on the stability and structure of cluster ions of different type and size, and also on the processes in which they participate.

The difficulties encountered in producing cluster ions and in investigating processes in which they participate are due to the following factors. The binding energy of particles in clusters is usually very low (a few eV or less), so that large clusters have appreciable lifetimes only at low enough temperatures. Clusters can be produced in ternary collisions in a gas, which means that relatively high gas pressures are necessary for this to happen. On the other hand, the detection of clusters of a given type, and especially, the detection of elementary processes with the participation of these clusters, require low gas pressures. These apparently conflicting requirements presented a complex technical problem whose solution had to await the advent of modern high-resolution mass spectrometers during the last decade. The necessary techniques used to solve this problem are based either on the condensation of atoms or molecules in a gas or on the fragmentation of condensed-state matter by some external agency. We now turn to a review of the most commonly employed method of producing and detecting large cluster ions.

2.1. Ion sputtering

Cluster ions of metals can be produced by the well tried method in which a metal surface is bombarded by a beam of ions.¹³ Cluster ions of the metal, which are produced together with neutral clusters, are then mass and charge selected by electric and magnetic fields, and are finally detected by a mass spectrometer. The basic advantage of this method is that it enables us to investigate cluster ions under high-vacuum conditions, which means that the method yields information on the characteristics of elementary processes occurring with the participation of cluster ions of different charge and size.

A typical example of the successful application of this method is reported in Ref. 13 where cluster ions of a metal were produced by bombarding a flat metal target with noblegas ions with energies up to 22 keV at current densities of about $100 \,\mu\text{A/cm}^2$. The ion beam was focused down to a 2mm diameter spot. A residual pressure of about 10 - 7 torr was maintained in the experimental chamber. Cluster ions of a particular mass and charge that passed through the mass separator were directed into a collision chamber where interactions with gas particles produced the dissociation of the clusters, which was in fact the process under investigation in these particular experiments. The cluster dissociation products were investigated using a time-of-flight mass spectrometer (the reflectron). This method enabled the authors of Ref. 13 to produce collimated beams of clusters of the form $\operatorname{Cu}_{n}^{+}(n \leq 20), \operatorname{Al}_{n}^{+}(n \leq 20), \operatorname{Mo}_{n}^{+}(n \leq 20) \operatorname{Pb}_{n}^{+}(n \leq 30),$ and W_n^+ ($n \leq 10$) and to measure the typical collisionless dissociation time of these clusters as a function of the size of the initial clusters and fragments, and also the rate of dissociation of such clusters in collisions with Ar atoms and oxygen molecules as a function of the size of the resulting fragments.

An interesting variant of the ion sputtering method, based on the use of a beam of high-energy neutral atoms, was developed and used in Ref. 14 to produce cluster ions of different metals. The experimental setup described in Ref. 14 is reproduced in Fig.1. A plasma gun capable of producing 20-keV ions with a beam current of 2 kA and beam diameter of about 1 cm was located at 50 cm from the target and was held at an acute angle to its surface. A beam of atoms of the



FIG. 1. Experimental setup for the investigation of the photodissociation products and chemical transformations of metal cluster ions: ¹⁴ 1—source of inert-gas ions, 2—diaphragms, 3—neutralization chamber, 4—electro-static ion filter, 5—target, 6—furnace, 7—energy analyzer, 8—diaphragm, 9—quadrupole mass spectrometer, 10—drift tube, 11—quadrupole mass spectrometer, 12—diaphragms, 13—deflecting system, 14—mirrors, 15—laser, 16—laser beam chopper, 17—electron multiplier.

same species as the target was incident on the surface at the same angle but on the other side of the normal. This arrangement favored the formation of negative cluster ions. Fast ions were neutralized in a special chamber and the resulting beam of fast atoms was allowed to strike the target surface after ions were removed by an electrostatic filter. This produced free atoms and also neutral and charged clusters of the metal. Charged clusters were mass, energy, and charge selected by a time-of-flight energy analyzer and quadrupole mass spectrometers. Photodissociation byproducts were investigated using an argon laser (working wavelength 488 nm). The experiment was based on the comparison of the mass spectra of cluster ions before and after the drift tube, and also before and after exposure to laser radiation. These measurements produced data on the photodissociation byproducts of Ag_n^+ ($n \le 16$) ions, and also on the byproducts of chemical reactions between Ni_n^+ ions and CO molecules.

2.2. Laser evaporation

In this method, clusters are produced by illuminating a solid surface with high intensity laser radiation.^{15,16} A typical example of the successful application of the laser evaporation method as a means of producing charged metal clusters is reported in Ref. 17. Figure 2 illustrates the apparatus employed. The target was a copper plate mounted on a rotating disk (see Ref. 18 for previous publications). The plate was exposed to pulses of radiation from a frequency-doubling neodymium laser($\lambda = 532$ nm), which produced an



FIG. 2. Experimental setup for the investigation of the photoionization spectra of negatively-charged copper clusters:¹⁷ 1—laser beam, 2—target in the form of a copper plate fixed on a rotating disk, 3—tube for introducing the carrier gas, 4—ionization chamber, 5—ionizing laser beam.

outflow of material from the surface, some of which was in the form of clusters. The surface was located in a stream of a carrier gas (helium) at 14 atm. This produced rapid cooling and stabilization of the clusters, which were then carried by the helium gas through a 15° conical nozzle. The supersonic jet formed in this way was illuminated by pulses from an excimer laser ($\lambda = 193$ nm) at an energy density of 5 which produced mJ/cm^2 , negatively charged Cu_n^- (6 < n < 41) clusters. Selection and detection were performed by a time-of-flight mass spectrometer. The aim of the experiment was to measure the spectra of electrons produced by the photoionization of charged clusters and hence determine the electron affinity as a function of cluster size.

An interesting variant of the method of producing charged metal clusters by illuminating a metal surface with laser radiation was used in Ref. 19 in which the illuminated target was placed in a magnetic field. This design is essentially a mass spectrometer with laser evaporation. The strength of the magnetic field, which was either parallel or perpendicular to the laser beam, was up to 3 T. The target was illuminated by light pulses from a frequency-doubling neodymium laser ($\lambda = 532$ nm). The pulse energy was 1–10 mJ and the laser beam spot had a diameter of about 100 μ m. Singlycharged positive and negative gold, silver, and copper cluster ions with up to six atoms per cluster were produced.

2.3. Gas-dynamic methods of producing cluster ions

These methods have been traditionally used to produce clusters from the gas phase. They are based on gas condensation by expansion and cooling in a gas-dynamic nozzle. For certain nozzle parameters, and high enough initial gas pressures at entry to the nozzle, practically any gas can be cooled down to temperatures below the melting point. Cluster formation is then thermodynamically convenient, and the lower the initial gas temperature and higher the initial pressure, the larger the clusters that can be produced for given nozzle configuration. Charged clusters are produced by exposing the supersonic gas flow containing neutral clusters of any size to a beam of electrons or ultraviolet radiation, which give rise to photodissociation of the neutrals. The resulting clusters of different size and charge are then identified by a mass spectrometer. Much of the data available on the properties and behavior of ion clusters consisting of atoms or molecules that are normally in the gas phase has been obtained by gas-dynamic methods.

A typical example of the application of gas-dynamic methods of producing and studying charged clusters from gas molecules is reported in Ref. 20, which is an extension of previous publications by these authors (see, for example, Refs. 11, 12, and 21). Clusters of the form $(N_2)_n$ with $n \leq 190$ were produced by expanding nitrogen gas at 700–800 torr and temperatures just above the liquid nitrogen temperature, using a nozzle with a critical cross section of 20 μ m. Much more favorable conditions for producing large clusters were achieved by adding neon gas at 2.5 atm to the nitrogen. The supersonic gas jet produced in this way contained large nitrogen clusters and was bombarded with electrons of energy up to 180 eV at 1 mA. The electron beam was perpendicular to the jet. Cluster ions produced by ionization were extracted from the jet by an electric field perpendicular to it, and were accelerated up to 3 keV. This meant that ions with particular values of charge and mass could be selected



FIG. 3. Setup used to produce and investigate charged metal clusters:^{22,23} 1—furnace, 2—nozzle, 3—ionization chamber, 4—drift tube, 5—detector, 6—to pump.

by a transverse magnetic field. Ions with a given mass-tocharge ratio were counted by a semiconductor detector working in conjunction with a multichannel electron multiplier. This high-resolution experiment succeeded in establishing the spectrum of nitrogen cluster ions produced when the gas was expanded, and to determine the minimum size of the multiply-charged nitrogen clusters.

The gas-dynamic method is convenient not only for producing charged clusters of gas molecules, but also for generating metal clusters. Such clusters are readily formed by the gas-dynamic expansion of the metal vapor in a buffergas atmosphere. The function of the buffer gas is to remove energy released when metal atoms are converted into clusters. As a rule, ionized clusters are produced by illuminating the supersonic jet with ultraviolet radiation. Examples of this technique can be found in Refs. 22 and 23 which report the ionization and dissociation of metal clusters and cluster ions on interaction with radiation. The experimental setup is illustrated in Fig. 3. Neutral clusters are produced by expanding the metal vapor at a pressure of a few hundred or a few thousand torr in a gas-dynamic nozzle. The clusters are then ionized by the second harmonic of a tunable liquid laser producing 15-ns pulses at a repetition rate of 15 Hz. The required cluster ions are selected by a time-of-flight mass spectrometer.

2.4. Ion cyclotron resonance

In this method, ions are selectively accelerated in a constant magnetic field by a high-frequency electric field whose frequency ω_c is equal to the cyclotron frequency, ω_c = ZeH /Mc, where Ze is the ion charge, M its mass, H the magnetic field strength, and c the velocity of light. This can be used to select ion clusters with given Z/M ratio in order to investigate their properties or to obtain information on the mass spectrum of ions formed in a particular way.

An interesting example of the application of ion cyclotron resonance to the investigation of cluster ions is reported in Refs. 24 and 25 where this technique was used to investigate the dissociative chemisorption of hydrogen molecules on positively-charged Nb_n⁺ ($n \le 19$) clusters. The experimental setup is illustrated in Fig. 4. The gas jet containing metal clusters of different charge and mass is produced by illuminating a metal surface with high-intensity laser beam and then expanding the heated vapor through a nozzle in a buffer-gas atmosphere. The cluster ions are separated from the jet by deflecting plates and are focused by ion-optical devices into a narrow collimated beam. The ions are then slowed down from about 700 eV down to 0–50 eV and are let into the ion cyclotron resonance chamber. The cylindrical chamber is 50 cm long and has an internal diameter of 4.8

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FIG. 4. Setup used to investigate cluster ions by the ion cyclotron resonance method.^{24,25} 1—vapor jet containing clusters, 2—deflecting and accelerating plates, 3—ion-optical focusing devices, 4—retarding electrode, 5—ion-cyclotron resonance chamber, 6—superconducting magnet.

cm. The high-frequency voltage necessary for the resonant interaction with cluster ions of a particular mass is applied to two opposite sectors of the cylinder. Ion cyclotron resonance is recorded by another pair of opposite sectors.

Ion cyclotron resonance can be used to record ions captured in an ion trap.²⁶ The principle of this trap is illustrated in Fig. 5. A uniform magnetic field **B** points along the z axis and forces the ions into cyclic motion around the axis with a frequency $\omega_c = eZB / Mc$. This motion is controlled by the potential difference U between the parabolic electrodes placed at the ends of the trap and a ring electrode with minimum radius r_0 . In this field configuration, the motion of the ions can be looked upon as a superposition of oscillations of frequency

$$\omega_z := \left(\frac{2eE}{mr_0^2}\right)^{1/2}$$

along the z axis and cyclotron oscillations of frequency

$$\omega_{\pm} = \frac{\omega_{\mathrm{c}}}{2} \pm \left(\frac{\omega_{\mathrm{c}}^{2}}{4} - \frac{\omega_{\mathrm{z}}^{2}}{2}\right)^{1/2}.$$

Ion detection in this trap relies on the ion cyclotron resonance and is accomplished by applying to the ring electrode a pulse of an alternating electric field at the cyclotron frequency. Ions of mass satisfying the resonance condition rapidly acquire kinetic energy from this pulse, and reach the detector.

2.5. Gas discharge

An effective method of producing cluster ions consisting of gas atoms or molecules is based on the use of a gas discharge. The method is very convenient for the simulation of atmospheric electrical processes in which cluster ions are formed. The main distinguishing feature of the gas-discharge method of producing cluster ions is that complex cluster ions are produced from simpler ions as a result of ternary collisions, for example,

$$A_n^+ + 2A \rightarrow A_{n+1}^+ + A$$
,

so that the binding energy released when the complex cluster



FIG. 5. Penning ion trap used to store and investigate cluster ions²⁶.

ion is formed is removed by the third particle. Cluster ions produced in this way are usually stable, which cannot always be achieved by ionization of neutral clusters by optical radiation or by fast electrons. The most common method of producing cluster ions in a gas discharge employs the corona discharge²⁷⁻³¹ which is distinguished by low temperature and high gas pressure. This facilitates the efficient formation of large clusters.

A successful example of the corona discharge as a source of hydrogen cluster ions of the form \mathbf{H}^+ $(\mathbf{H}_2)_n$ can be found in Ref. 32 where ionization of neutral clusters $(H_2)_n$ by electron impact was used alongside the corona discharge. The experimental setup is illustrated schematically in Fig. 6. The copper discharge chamber could be cooled either by liquid nitrogen or by freon, and the needleshaped nickel-coated steel electrode could be displaced in the longitudinal direction. The potential difference between the needle and the body was 350 eV. The discharge occupied a cylindrical region 1 mm in diameter and 1.7 mm long. The discharge current was 30 μ A at a hydrogen gas pressure of 100-200 torr at entry to the nozzle. The gas jet containing the clusters was formed as a result of expansion in the 75- μ m in diameter nozzle. After interaction with the skimmer, the jet entered the magnetic deflecting system from which the cluster ions of a particular type were directed into the octupole magnetic trap³³ in which experiments on the infrared spectroscopy of cluster ions were carried out.

It is important to note that gas-discharge methods are of limited utility as a means of producing large cluster ions (as compared with gas-dynamic methods) because of the relatively small amount of large ions that are produced in this way. For example, only the H_s^+ ions could be reliably recorded in Ref. 32, and the intensity of larger cluster ions of hydrogen was found to be significantly lower as compared with the method employing the ionization of clusters produced by gas-dynamic expansion or electron impact.

3. THE STRUCTURE OF CLUSTERS AND CLUSTER IONS

As already noted, we shall refer to a system of bound atoms or molecules as a macroscopic particle when different parameters of the system vary monotonically with the number of particles in the system. When this is not so, we have a



FIG. 6. Schematic diagram of apparatus used to produce hydrogen cluster ions in a corona discharge: ³² 1—sharp cathode of the corona discharge, 2—75 μ m diameter nozzle, 3—cathode holder, 4—gas inlet, 5—skimmer.

cluster. We have noted that a cluster can contain tens or even hundreds of atoms or molecules. We shall illustrate this below by investigations that have already been carried out.¹⁾

There is now a considerable range of experimental techniques that can be used to determine particular parameters of a cluster containing a known number of atomic particles. The simplest approach is to determine the mass distribution of charged clusters. Analysis of such distributions can be used to select clusters containing enough atoms or molecules to ensure maximum stability. The number of clusters in which the number of atoms (or molecules) is greater or smaller by one is then less than the number of clusters of the given type. The number of atoms or molecules in this type of stable cluster is often referred to as the magic number. By definition, clusters with the maximum number of atoms or molecules have the largest magic number.

Magic numbers can be determined by a number of methods. One of them^{11,34} is based on the mass spectrometry of charged clusters produced in the gas jet issuing from a nozzle. The charged clusters are produced by ionization of neutral clusters by electron impact. Another method³⁵⁻³⁸ relies on the bombardment of a surface with ions in the keV energy range. In addition to simple atomic particles, the incident ions eject fragments containing a large number of atoms or molecules. Mass spectrometry of the resulting charged clusters can then be used to determine their magic numbers. The particular feature of this process is the formation of metastable fragment ions which can dissociate into smaller ions as they pass through the mass spectrometer. Charged clusters can also be produced by illuminating a solid surface with laser radiation of sufficient intensity.

All these methods are convenient for the identification of atoms or molecules in a cluster. The first is used to analyze clusters containing gas atoms or molecules, the second relies on ionic crystals as the source of clusters, and the third employs metal atoms. In each case, the experimental data must be augmented by calculations capable of elucidating the cluster structure. We now turn to the information that is now available on many different cluster species.

The experimental and theoretical studies reported in Refs. 29, 30, 39, and 45 refer to cluster ions of water of the form $H^+ \cdot (H_2O)_n$ and $D^+ \cdot (D_2O)_n$. They demonstrate the existence of the magic number n = 21. The stable configuration corresponds to the clathrate with the H_3O^+ ion at the center and twenty water molecules around it.

The helium clusters He_n^+ have magic numbers n = 7, 10, 14, and 30 (Ref. 46) for both isotopes and n = 23 for the isotope ⁴He. The magic numbers for neon clusters are n = 13, 21, 55, and 75 (Ref. 47), for argon clusters n = 14, 16, 19, 21, 23, and 27 (Ref. 48), for krypton clusters n = 14, 16, 19, 22, 27, 29, 75, and 87 (Ref. 48), and for xenon clusters n = 13, 16, 19, 25, 55, 71, 87, and 147 (Refs. 48–51).

Calculations⁵² show that in the case of the van der Waals interaction, the magic numbers are n = 7, 13, and 16, which explains some of the inert-gas clusters. It seems that the most suitable structure for a cluster consisting of inertgas atoms is the icosahedron which corresponds to a shortrange interaction between the component particles. The first magic number for the icosahedron is n = 13, and is found to occur not only in the cluster consisting of inert-gas atoms, but also in molecular clusters containing molecules with a closed electron shell. For example, for clusters of the form $(SF_6)_n$, the magic number is n = 13 (Ref. 50), whereas for $(C_2F_2Cl_2)_n$ clusters the magic numbers are 13 and 19 (Ref. 50), which fits into the above scheme.

We note that the icosahedron is an analog of a closepacked crystal system with the structure of a face centered cubic lattice. Inert-gas crystals usually have this structure. Hence the icosahedron structure is the most acceptable for inert gas clusters. The icosahedron can be looked upon as a system with a shell structure in which magic numbers correspond to the filling of the successive shells and are given by ¹²

$$n=\frac{1}{3}(10N^3-15N^2+11N-3),$$

where N is the shell number. This formula gives the following magic numbers: n = 1, 13, 55, 147, 309, and 567.

Another close-packed structure that is observed for inert-gas crystals under certain conditions is the body-centered cubic lattice. Its analog is the dodecahedron for which the magic numbers are given by¹²

$$n=\frac{1}{2}N(15N-1).$$

This formula gives n = 7, 29, 66, 118, and 185.

It is readily seen that simple and maximally stable structures can explain some of the data on magic numbers of inert-gas clusters. However, more careful analysis shows that the set of magic numbers contains more extensive information on the interaction between atoms in a cluster. Actually, in the first approximation, the interaction potential between two identical inert-gas atoms has the same form for different inert gases. However, differences between the magic numbers of different inert gases show that the numbers are sensitive to the details of the interaction potential between atoms in a cluster.

Analysis of the magic numbers of clusters provides information on the extent to which a system of bound atoms can be regarded as a cluster rather than a macroscopic particle. The parameters of a macroscopic particle vary monotonically with the number of atoms contained by it, so that a particle is a cluster so long as it has magic numbers of atoms that ensure higher stability. Measurements⁵³ show that a system of bound argon atoms has magic numbers for up to about 500 atoms per particle. Hence a cluster can contain up to a few hundred atoms.

The stability of clusters of the form $M^+ \cdot (MX)_n^+$ and $(MX)_n^+$, was investigated in Refs. 54–58 where M is an alkali-metal atom and X is a halogen. The magic numbers of $M^+ \cdot (MX)_n$ are 13, 22 and 31, and confirm the presence of ion-ion bonding in such clusters (as an ionic crystal). The first magic number corresponds to the $3 \times 3 \times 3$ cubic lattice with the ion at the center, and the second and third cases correspond to parallelepipeds containing $3 \times 3 \times 5$ and $3 \times 3 \times 7$ atoms. The magic numbers 37 and 62 have also been observed and correspond to parallelepipeds containing $3 \times 5 \times 5$ atoms, respectively.

The structure of a large cluster is determined in the first instance by nearest-neighbor interactions. Taking this as the starting point, we see that, in the case of interaction between atoms with a closed electron shell (inert-gas atoms), the structure with close-packed atoms has the highest stability, whereas in the above case of ion-ion coupling between nearest neighbors, the atoms form a cubic lattice. Other cases of

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TABLE I. Stable configurations C_n .

Magic number	Geometric structure	Diameter of sphere
24 48 60 (footbolino) 120 (archimedino)	Truncated octahedron Truncated cubic octahedron Truncated icosahedron Truncated dodecahedron	$\begin{array}{r} 3.162 \\ 4.635 \\ 4.956 \\ 7.605 \end{array}$
*'In units of the sep	aration between nearest neighbors.	F

interaction can give rise to a great variety of other structures. Cluster structures consisting of carbon atoms have been investigated in some detail. The stable structure of this type of cluster corresponds to the saturation of bonds between the s^2p^2 valence electrons of the separate atoms. This gives rise to a structure in which all or most of the carbon atoms lie on a sphere, and each of them is strongly coupled to four nearest neighbors. Table I shows the corresponding configurations of atoms in a cluster.⁵⁹ It is important to note that the most stable carbon cluster is C_{60} . It has been observed in many experiments as an enhanced-stability cluster.⁶⁰⁻⁶⁶

Many of the structural properties of cluster ions consisting of the atoms of semiconducting materials (C, Si, Ge, etc.) have similar features. For example, for all the above clusters, the stability of a cluster ion and its parameters are oscillating functions of the number of particles per cluster.⁶⁷ This is explained by the abrupt change in the structure of cluster ions from the line to the ring configuration as the number of valence electrons changes from even to odd.^{67,68}

By analyzing the nature of the magic numbers of clusters it is possible to identify two different models of interaction between particles in clusters, which lead to different geometric cluster structures, and, as a consequence, to different sets of magic numbers. One of these models, sometimes referred to as the soft sphere model,⁶⁹ describes a cluster that consists of close-packed atoms, which in turn corresponds to the maximum stability of the above icosahedral shell configurations with magic numbers n = 1, 13, 55, 147, 309, 561 The other model, called the hard sphere model, describes a cluster with a fixed equilibrium internuclear separation and describes stable polyhedral shell structures with magic numbers n = 2, 8, 20, 40, 58, 90... Analysis of the experimental magic numbers shows that the soft sphere model can be used for the crude description of clusters consisting of gas atoms or molecules, whereas the hard sphere model is more suitable for metal clusters. Thus, the magic numbers established for the Na_n clusters are n = 2, 8, 20, 40, 58, and 92 (Ref. 70) and are in good agreement with the magic numbers predicted by the hard sphere model. An analogous set of magic numbers has been observed for Cu_n^+ (Ref.60) It is important to remember that the structure of real clusters often exhibits some of the features of both models at the same time. This happens for the more complex structures and leads to sets of magic numbers that are significantly different from those given above, and characterize particular model situations in pure form. For example, clusters consisting of atoms of semiconducting materials have magic numbers that are different from the above model sets, e.g., the clusters C_3 , Si_6^+ , Si_{10}^+ , and Si_{10}^- have enhanced stability.67

Analysis of the most stable cluster-ion structures is complicated by the fact that the corresponding experimental data depend significantly on the conditions under which the cluster ions are formed. For example, the mass spectra of metal and semicondcutor cluster ions produced by the gasdynamic and by the laser methods are very different.¹⁶¹ The stability of large cluster ions produced as a result of the gasdynamic expansion of the vapor is significantly lower as compared with laser evaporation. This is so because cluster ions produced by the gas-dynamic expansion of a vapor are not in equilibrium, and their vibrational temperature is much higher than the equilibrium temperature. The energy concentrated in the vibrational degrees of freedom then facilitates the dissociation of the cluster ions, so that the maximum number of atoms observed for positive singly-charged cluster ions of Ge, Ag, Al, Te, Se, Zn, and Mn, formed by the gas-dynamic expansion of the vapor, is low and amounts to 8, 9, 2, 5, 8, 2, and 2, respectively.¹⁶¹

A further source of uncertainty in the interpretation of the mass spectra of cluster ions is encountered when these ions are formed from neutral clusters ionized by electron impact or by ultraviolet radiation. Several experimental studies (see, for example, Refs. 162-164) have shown that the degree of stability of a cluster ion depends both on the method used to ionize the neutral clusters and on the energy of electrons or photons used to ionize them. This is explained by the fact that the ionization of a neutral cluster can result in cluster ions in vibrationally excited states, and the vibrational energy excess depends significantly on the method of ionization and the ionization energy of the particles. Moreover, since the stability of a cluster depends significantly on its vibrational energy excess (over and above the equilibrium value), the character of the observed mass spectra is determined by the conditions under which the cluster ions are produced. This type of dependence of the mass spectrum of the cluster ions Pb_n^+ and Sn_n^+ on the conditions of ionization of neutral clusters was observed in Ref. 164 in which ionization by 157-nm radiation produced magic numbers n = 7 and 10 (for both elements), and n = 13 (for lead), whereas ionization by 193-nm radiation gave rise to n = 13(for lead). These results are somewhat different from the data obtained by ionizing neutral clusters by electron impact.^{162,163} According to these data, the magic numbers of lead are n = 7, 10, and 13, whereas no magic numbers were observed at all for Sn_n^+ with $n \leq 16$.

To summarize, we note that studies of the stability of systems containing a large number of bound atoms or molecules show that such systems are clusters if they contain up to ~ 100 atoms or molecules. The systems are then characterized by magic numbers that reflect the enhanced stability of such clusters. In clusters containing a large number of atoms and molecules, the magic numbers correspond to a closed-shell cluster structure or a structure containing a certain number of bound stable elements.

4. PARAMETERS OF CLUSTER IONS

Whether or not a cluster ion is a macroscopic or a quantum-mechanical system can be established by examining its parameters as functions of the number of atoms or molecules per cluster. For example, Fig. 7 shows the energy needed to remove an atom of sodium from a singly-charged sodium cluster ion.⁷¹⁻⁷³ It is clear that, for these relatively low numbers of atoms per cluster, the separation energy is a nonmonotonic function that does not tend to a limiting value as the number *n* of atoms per cluster increases.

Let us now consider another parameter, namely, the ionization potential of a neutral cluster. We shall confine our attention to spherical clusters and cluster ions. It is clear that if the cluster is infinitely large, its ionization potential must be equal to the work function φ of the material in bulk. When the cluster radius is finite, the difference between the ionization potential J_n and the work function of the material is proportional to e^2/R , i.e.,

$$J_{i:} - \varphi = C \, \frac{e^a}{R} \,. \tag{1}$$

Actually, to remove an electron, we must overcome the Coulomb potential representing the interaction with the resulting cluster ion. Thus, if the cluster is simulated by a metal drop, the coefficient C in (1) is found⁷⁴ to be C = 3/8. The Coulomb interaction between the electron and the ion then ensures that the ionization potential of the cluster exceeds the work function of the material by the amount e^2/R , and the interaction between the electron and its image reduces this difference by the amount $5e^2/8R$.

Bearing in mind the relation between the number of atoms per cluster and its radius $(n \sim R^3)$, we find from (1) that

$$J_n = \varphi + \frac{\varphi_0}{n^{1/a}} , \qquad (2)$$

where φ_0 is a constant. If we suppose that (2) can be used for all values of *n*, the parameter φ_0 can be determined by introducing the atomic ionization potential *J* into (2). Actually, under the above assumptions, we have $J_n = \varphi + \varphi_0$ for



FIG. 7. Detachment energy of a sodium atom in the cluster ion Na_n^+ measured for different values of *n* (Refs. 71–73).

n = 1, i.e., (2) assumes the form

$$J_n = \varphi + \frac{J - \varphi}{n^{1/s}} \,. \tag{3}$$

Figure 8 shows the ionization potential of the xenon cluster ion.⁷⁵ It is clear that (3) does not provide a satisfactory approximation to the ionization potential of the cluster for this particular range of values of n. Although the discrepancy between the model relation (3) and the experimental data decreases with increasing n, the above comparison shows that the cluster is not a macroscopic particle in this range of values of n. The same conclusion may be drawn from an analysis of the electron affinity energy of copper⁷⁶ based on (3) and illustrated in Fig. 9. The binding energy of an electron in neutral and charged clusters cannot therefore be described by a simple monotonic function of the number of atoms per cluster for $n \leq 20$.

Measurements show that practically the same situation arises for larger values of n amounting to a few tens. Figure 10 shows the ionization potential of the potassium cluster as a function of the number of atoms per cluster for $n \leq 100$ (Ref. 77). This demonstrates, once again, that the cluster ion is not a macroscopic particle for these values of n. Thus, first, for values of n up to ~ 100 , the cluster ionization potential differs from the work function of potassium (2.4 eV). Second, the graph shows that the ionization potential is approximately constant as the successive cluster shells are filled, but there is an abrupt change each time a shell is completed. The last fact confirms the shell structure of these clusters.

We conclude that data on any given cluster ion or cluster parameter as a function of the number of atoms per clus-



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FIG. 8. Ionization potential of the neutral cluster Xe_n , as a function of the number of atoms in the cluster.⁷⁵ Solid line—calculated from (3).



FIG. 9. Electron affinity of the cluster Cu_n as a function of the cluster size⁷⁰.

ter cannot be approximated by simple functions of n, and must be described by a set of values for each n up to $n \sim 100$. For example, Table IIa shows the enthalpy ΔH_T and the binding energy D_0 of the system $H_{n-2}^+ - H_2$, obtained classically by measuring the ratio of ion currents for different nand different gas temperatures. Another example of this kind is provided by recent measurements of the electron binding energy in the negative cluster ion $(CO_2)_n^-$ as a function of the cluster size n (Ref. 83). These results are shown in Table IIb. The break observed at n = 6 suggests that there are two cluster ion structures, one of which is the negative ion CO_2^- , dressed in a "cloak" of CO_2 , molecules, whereas the core of the other structure is the complex $(CO_2)_2^-$. The first of these structures occurs for $n \leq 6$ and the other for

FIG. 10. Ionization potential of the cluster K_n as a function of the cluster size⁷⁷.

 $n \ge 6$. The transition from one structure to the other occurs at n = 6 and is accompanied by an abrupt change in the electron binding energy.

5. MULTIPLY-CHARGED CLUSTER IONS

5.1. Cluster ion consisting of gas molecules

The multiply-charged cluster ion is of interest as a special physical object. The first problem that arises when an attempt is made to analyze its properties is its stability. If the cluster ion contains a small number of atoms or molecules, it is unstable because of the Coulomb repulsion between its fragments, and the ion breaks up into its component parts. There is therefore a critical number n_c of atoms or molecules in the cluster ion above which the multiply-charged cluster ion is stable. Table III lists the critical numbers n_c of cluster ions with 2, 3, and 4 charges per ion and containing gas atoms or molecules.

The critical number n_c of a doubly or multiply charged

	n							
Parameter	5	7	9	11	13			
ΔH_T^0	6.6±0.3	3.1			-	31		
ΔH_T^0	5.8±1.1	3.1	-	-	-	[78		
ΔH_T^0	5.8 <u>+</u> 1.1	-	-	-		[79		
ΔH_T^0	8.1±0.7	-	-	-	_	180		
ΔH_T^0	9,6	4.1	3.8	2.4] _	[81		
ΔH_T^0	9.7 <u>+</u> 0.2	1.8 0.1	-	-	_	182		
ΔH_T^0	5.1 <u>+</u> 0.6	-	-	_	_	183		
$D_0(D_e)$	5.4 (8.2)	_	-		-	[84		
$D_0(D_e)$	4.0 (6.9)	2.6 (3.4)	1.8 (3.2)	-		[85		
De	6.4	3.8	3.2	1.4	-	[[86		
D _e	4.5	3.0	2.6	0.8	0.7	86		
D	5.7	3.8	3.0	1.2	1.2	[87		

TABLE II. (a) Energy parameters of the cluster ion $H_{n-2}^+ - H_2$ measured and calculated by different workers.

(b)Binding energy of an electron in cluster ion $(CO_2)_n^-$ as as a function of the cluster size n (Ref. 88).

n	2	3	4	5	6	6	7	8	9	10	11	12	13
Binding energy, eV Uncertain- ty, eV	2.79 0.02	2.94 0.02	2.96 0.04	3 .25 0.02	3.40 0.06	2.49 0.10	2.57 0.02	2.73 0.005	2,80 0.02	2.84 0.02	2.89 0.03	2, 90 0.03	2.95 0.03

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TABLE III. Limit of	existence of clu	uster ions of	different charge.
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Ion	Z=1	Z=2	Z=-3	Ref.
$Ar^+ \cdot Ar^{+Z}_{n-1}$	91	225	_	[91]
$Kr^+ \cdot Kr_{n-1}^{+Z}$	70	156		[48, 9 0]
$Xe^+ \cdot Xe_{n-1}^{+Z}$	53	114	208	[90, 92]
$N_{a}^{+} \cdot (N_{2})_{n-1}^{+Z}$	99	215	_	[20]
$\operatorname{CO}_{2}^{+} \cdot (\operatorname{CO}_{2})_{n-1}^{+Z}$	44	108	215	[90, 93]
$CO^+ \cdot (CO)_{n-1}^{+Z}$	98	_		[90]
$O^+ \cdot (O_2)_{n=1}^{+Z}$	92		_	[20, 94]
NH_{4}^{+} (NH ₃) _{n-1} ^{+Z}	51	121	_	[20, 95]
$H_{Z+1}^{Z+1}(H_2O)_n$	35	84		[89]
$H_{2}O^{+}(H_{2}O)_{n-1}^{+Z}$	33	_		[96]
$H_2S^+(H_2S)_{n-1}^{+Z}$	38	84	_	[90, 97]
$C_2 H_4^+ (C_2 H_4)_{n-1}^{+Z}$	51	108	192	[90]
$N_2O^+ (N_2O)_{n-1}^{+Z}$	51	105	184	[90, 97]
$CHF_{3}^{+}(CHF_{3})_{n=1}^{+Z}$	41	90	168	[90]
$CF_{3}Cl^{+}(CF_{3}Cl)_{n-1}^{+Z}$	43	87		[90]
$C_2H_4F_2^+(C_2H_4F_2)_{n-1}^{+Z}$	33	69		[90]
$C_2H_6O^+(C_2H_6O)_{n-1}^{+Z}$	35	72		[90]
$C_{3}H_{6}^{+}(C_{3}H_{6})_{n-1}^{+Z}$	39	78		[90]
$c - C_4 H_8^+ (c - C_4 H_8)_{n-1}^{+Z}$	31	66		[90]
$C_5H_{12}^+$ $(C_5H_{12})_{n-1}^{+Z}$	30	_		[90]
$C_{6}H_{6}^{+}(C_{6}H_{6})_{n-1}^{+Z}$	23	52	92	[90]
$n - C_4 H_{10}^+ (n - C_4 H_{10})_{n-1}^{+Z}$	31	78	-	[90]

cluster ion can be determined from the condition that the binding energy of a simple ion corresponding to this number must be equal to the energy of the Coulomb interaction with the other simple ions in the cluster. This is the basis for models in which the cluster is regarded as a macroscopic drop of permittivity ε , in which stability is maintained by surface tension. Such models have often been used with different charge distributions in the drop to determine the limiting values of the cluster ion parameters (see, for example, Refs. 98 and 99), but the instability of the multiply charged ions can assume a variety of forms. One type of instability is related to the removal of a simple ion and leads to a reduction in the cluster charge by one and a reduction in the number of atoms in the cluster by one. Another type of instability corresponds to the partition of the cluster and of its charge into almost equal parts.

If the multiply-charged cluster can be modeled by a macroscopic drop, its stability is determined by the second instability mechanism in which the drop divides into two almost equal parts. If the charge is high enough, and is distributed uniformly over the drop surface, we have the Rayleigh instability of a charged drop. The energy of a drop of radius R is then given by

$$U = \frac{q^2}{2R} + 4\pi R^2 \alpha, \tag{4}$$

where q is its charge and α the surface tension. Symmetry considerations then show that the drop is unstable if it conveniently divides into two equal parts. The energy of the two drops produced in this way with radii $R' = R/2^{1/3}$ and charges q/2 is

$$U'=2\left(\frac{q^2}{2R'}+4\pi R'^2\alpha\right).$$

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The condition U' < U is the condition for the instability of the drop with respect to a large deformation. This so-called Rayleigh condition is (see Ref. 100)

$$q^{2} \ge 16\pi R^{3} \alpha [2^{1/3} (2^{1/3} + 1)]^{-1} = 0.708\pi R^{3} \alpha.$$
 (5)

It is clear that the Rayleigh condition does not involve the polarization parameter of the drop. This is readily understood. If we suppose that the charge is uniformly distributed over the drop, we find that the electric field strength inside the drop is zero. The situation that we have considered corresponds to a large drop charge (and, correspondingly large radius), and also high permittivity of the drop material. The Rayleigh condition therefore applies to a macroscopic metal drop.

Expression (5) is the condition for the stability of the drop with respect to a large deformation. The drop can also have a high charge if it is in a metastable state. Let us derive the stability condition for a drop subjected to a small deformation. We shall consider an elastic drop in which deformation in one direction does not produce deformation in any other (i.e., Poisson's ratio is zero). These conditions are satisfied by a cluster consisting of gas atoms or molecules coupled by a weak two-body interaction between the particles. The stability condition for this type of drop is that the pressure due to surface tension, $2\alpha/R$, must be greater than the electrostatic pressure $Eq/(4\pi R^2)$ due to the effect of the electric field acting on the surface charge. As soon as the electrostatic pressure exceeds the pressure due to surface tension, the drop breaks up and the corresponding instability condition is

$$q^2 \geqslant 8\pi R^3 \alpha. \tag{6}$$

Naturally, instability with respect to a small drop deforma-

tion, as described by (6), occurs for a larger drop charge than the instability with respect to a large deformation, governed by (5). Moreover, for other elastic properties of the drop, the right-hand side of (2) must be modified. In particular, for an incompressible drop, the latter condition assumes the form (see Ref. 100)

$$q^2 \ge 16\pi R^3 \alpha. \tag{7}$$

These results refer to the case of a macroscopic cluster with ions situated on the surface. The interaction between the ions and the cluster atoms does not then play a fundamental part. This model therefore describes a metallic macroscopic drop with a big charge and is methodologically interesting for us. Let us consider how the result is affected by a change in the charge distribution in the interior of the cluster. We shall examine the case where the charge is uniformly distributed throughout the volume. The energy (4) of the drop is given by

$$U = \frac{q^2}{2R} \left(1 + \frac{1}{5e} \right) + 4\pi R^2 \alpha.$$
 (8)

It is clear that since, in practice, $\varepsilon \gtrsim 1$, the condition for the stability of a cluster with respect to a large deformation, as given by (5), must be only slightly modified. All that needs to be done is to replace q^2 in (5) with $q^2[1 + (1/5\varepsilon)]$. However, in the condition for instability with respect to a small deformation, given by (6), we now have the permittivity ε because the interaction between the charges in the cluster must involve this parameter. Actually, the electrostatic pressure on the surface is given in this case by⁹⁹

$$\rho = \frac{3q^{\mathbf{x}}}{16\pi R^{\mathbf{4}}e}$$
 ,

and the condition for instability with respect to a small oscillation becomes

$$q^2 \geqslant \frac{32\pi}{3} R^3 \alpha \varepsilon. \tag{9}$$

Let us now consider the results obtained for one further model in which the charges are localized at diametrically opposite points in the drop, a distance R apart. The condition for instability with respect to the partition of the drop into two parts as a result of a small deformation is⁹⁹

$$q^2 \geqslant 8\pi R^3 \alpha \epsilon. \tag{10}$$

This differs from (9) by the small change in the numerical factor.

The above analysis of macroscopic models enables us to estimate the precision of these models and their sensitivity to the charge distribution in the cluster. It can be used to determine the dependence of the critical number on the parameters of the problem. For the critical number corresponding to instability with respect to a large deformation, we have from (5)

$$n_{\rm c} = \frac{0.24q^2\rho}{m\alpha} , \qquad (11)$$

where ρ is the mass density of the cluster material and *m* is the mass of an individual atom or molecule in the cluster. The critical number corresponding to stability with respect to a small deformation can be found using (10):

$$n_{\rm c} = \frac{q^2 \rho}{6\alpha \varepsilon m} \ . \tag{12}$$

In particular, for a doubly-charged xenon ion, we find from (11) that $n_c = 180$, where (12) gives $n_c = 66$ and measurements show that $n_c = 53$ (see Table III).

The above results are valid for clusters consisting of gas atoms or molecules. The interaction between atoms or molecules in the cluster is then relatively weak, so that the critical number of atoms or molecules in the cluster is large, i.e., the cluster can be modeled by a macroscopic particle. The macroscopic model is unsuitable for clusters consisting of metal atoms that contain a small number of such atoms. However, even in the case of clusters consisting of gas atoms or molecules, the model is relatively crude because it ignores the interaction between ions and atoms in the cluster, and also the change in the shape of the cluster due to the interaction. i.e., it does not take into account the cluster structure. The true situation cannot be described even at the price of complicating the model. There is very little point in expecting it to provide any numerical results, and it is best used simply to estimate the dependence of the results on the parameters of the problem.

Let us therefore examine a cluster consisting of gas atoms or molecules. Assuming that the two-body interaction between nearest neighbors plays the dominant part, we shall determine the dependence on the parameters of this interaction, i.e., the depth \mathcal{D} of the well in the interaction potential and the equilibrium separation r_0 corresponding to the minimum interaction potential between two atoms or molecules. The quantities in (11) and (12) that appreciably depend on these interaction parameters are the density of the cluster material $\rho \sim mr_0^{-2}$ and the surface tension $\alpha \sim \mathcal{D} r_0^{-2}$. In view of this, we have

$$n_{\rm c} \sim \frac{1}{\mathscr{D}r_0}$$

Figure 11 shows the data of Table III for clusters consisting of gas molecules, fitted by the formula

$$n_{\rm c} = A + \frac{B}{\mathcal{D}r_0} \,. \tag{13}$$

The resulting empirical dependence includes the interaction between ions and atoms in the cluster, and also the influence of the structure of the cluster on its critical parameters.

FIG. 11. Critical size n_c of a doubly-charged cluster ion as function of $(\mathscr{D}r_0)^{-1}$ where \mathscr{D} is the depth of the potential well for the interaction between the two neutral particles making up the cluster; r_0 is the equilibrium separation in the well.

We note one further feature of these results. According to (11) and (12), the critical number of atoms in a multiplycharged cluster ion is proportional to the square of the charge. Hence n_c for a triply-charged cluster ion is greater by the factor of 2.25 than for the doubly-charged cluster ion. According to the data of Table III, this ratio is 2.2 ± 0.2 . The ratio of values of n_c calculated using the data of Table III for ions with four and two charges, is 4.0 ± 0.2 and is also in agreement with the model similarity relations formulated above.

5.2. Multiply-charged metal cluster ion

In a multiply-charged cluster ion containing metal atoms or ions, the exchange interaction between the atoms and ions is much stronger than for gas atoms or molecules. Hence the value of the critical number n_c for multiplycharged metal ions is significantly lower than for gas ions. On the other hand, for small cluster ions, we have typically the above departure from the spherical structure, which means that the basic assumptions adopted in the derivation of the critical number n_c are no longer valid. Hence, for doubly-charged metal cluster ions we have the relatively typical situation in which experiment confirms the presence of clusters with dimensions much smaller than the values of n_c calculated from the above models. These experimental facts suggest that there are significant departures from the spherical shape of the cluster. Similar facts were found in Ref. 101 where charged clusters Pb_n^{2+} were produced by gas-dynamic cooling of lead vapor in a helium atmosphere, followed by ionization of neutral clusters by electron impact. Doubly-charged clusters Pb_7^{2+} , Pb_9^{2+} , Pb_{11}^{2+} , and Pb_{13}^{2+} , were observed, whereas the minimum size of the spherically symmetric doubly-charged lead cluster corresponds to n_c = 31 (Ref. 102).²⁾ This suggests that the smaller doublycharged lead clusters have an extended structure. Thus, assuming that (1) the clusters have the structure of a onedimensional chain with ions at the opposite ends, (2) that the binding energy U_0 of the atoms in the chain is equal to the binding energy of the Pb_2 molecule (0.84 eV), and (3) the nuclear separation R_0 in the cluster is equal to the nuclear separation in this molecule Pb_{13}^{2+} , we find that the minimum number of atoms that ensures the stability of the onedimensional chain is $n_{\min} = 1 + (e^2/U_0R_0) \approx 6$. This agrees with the experimental results reported in Ref. 101 and cited above.

The surprising result is that stable multiply-charged metal ions M_3^{+} exist in many cases. Such ions have a line structure, and the exchange interaction potential between the extreme ions and the central atom must exceed the Coulomb repulsion energy e^2/R between the atoms, where *e* is the electron charge and *R* the separation between nearest-neighbor nuclei in the cluster ion. Stable cluster ions M_3^+ are actually observed in the case of Ni (Ref. 103), Sn (Ref. 104), W (Ref. 103), Ge (Ref. 110), Au (Refs. 103, 105, and 106), Bi (Refs. 107 and 108), Sb (Ref. 108), As (Ref.165), and Si (Ref. 166). Such ions were not observed in the case of Ga (Refs. 94, 107, and 109) and In (Refs. 102 and 107).

To analyze the possibility that the doubly-charged ion M_3^{++} may be formed, let us examine a simple model of such an ion in which it is assumed that it has the structure $M^{+}-M-M^{+}$, i.e., atomic ions linked by the exchange inter-

action with the central atom are located at the edges of the cluster ion. We shall take the interaction potential between the atomic ion and the atom in the form

$$U(\mathbf{r}) = -\mathcal{D}\left[2\left(\frac{R_0}{r}\right)^4 - \left(\frac{R_0}{r}\right)^8\right],\tag{14}$$

where r is the separation between the ion and the atom, R_0 is the equilibrium separation in the case of the two-body interaction, and \mathscr{D} is the depth of the well in the two-body interaction potential. Neglecting the short-range interaction between the extreme ions, we find that the interaction potential in the system is given by

$$U(r_1, r_2) = -\mathcal{D}\left[2\left(\frac{R_0}{r_1}\right)^4 - \left(\frac{R_0}{r_1}\right)^8\right] - \mathcal{D}\left[2\left(\frac{R_0}{r_2}\right)^4 - \left(\frac{R_0}{r_2}\right)^8\right] + \frac{e^2}{r_1 + r_2},$$
(15)

where r_1 is the separation between the atom and the first atomic ion and r_2 is the corresponding separation for the second atomic ion.

Let us first establish the relationship between the parameters of this potential that corresponds to a stable state of the doubly-charged triatomic ion. We note that, in its stable state, the cluster ion executes two types of oscillation along the ion axis. In the case of the symmetric oscillation, $r_1 = r_2$, whereas for the antisymmetric oscillation, $r_1 + r_2 = \text{const}$ (we assume that the three nuclei have equal masses). It is readily seen that the Coulomb interaction between the atomic ions does not affect the second type of oscillation, so that the stability of the cluster ion can be established by analyzing the symmetric oscillations. Substituting ($R = r_1 = r_2$), we find that the interaction potential takes the form

$$U(R) = -2\mathcal{D}\left[2\left(\frac{R_0}{R}\right)^4 - \left(\frac{R_0}{R}\right)^8\right] + \frac{e^2}{2R}.$$
 (16)

It is clear that the separation R between the atom and the atomic ion is a generalized coordinate corresponding to the symmetric oscillations. The equilibrium separation R_m can be determined from the condition

$$U'(R_m) = 0.$$
 (17)

The magnitude of the vibrational quantum for this type of oscillation can be expressed in terms of the second derivative of the interaction potential. In the classical case, these oscillations exist if

$$U''(R_m) \ge 0. \tag{18}$$

Conditions (17) and (18) for the interaction potential (16) lead to the following inequality for the parameters of the interaction potential:

$$R_0 \mathcal{D} > 0, 10e^2. \tag{19}$$

We note that the numerical factor on the right-hand side depends significantly on the rate of change of the shortrange interaction potential. In general, if we describe the interaction between the atom and the ion by the potential

$$U(r) = \mathscr{D}\left[\left(\frac{R_0}{r}\right)^{n/2} - \frac{n}{4}\left(\frac{R_0}{r}\right)^n\right],$$

we obtain instead of (19)

TABLE IV. Critical number n_c for multiply-charged metal cluster ions M_n^{+Z}

		Ζ							
M	2	3	4	Ref.	м	2	3	4	Ref.
Hg Ag Ag Pb Pb	30 5 9 19 31			[92] [112] [111] [113] [102]	Pb Sn Bi Bi Cs	30 28 26 9 18	45 38 	72 — — —	[9] [101] [101] [9] [58]

$$\frac{R_0\mathscr{D}}{e^2} > \frac{(n-1)^{(n-1)/(n-4)}}{4n(n-4)\,3^{3/(n-4)}} \,. \tag{20}$$

In particular, when n = 10, the numerical factor on the right-hand side of (20) is 0.065, whereas for n = 12 it is 0.047.

We shall now use the above model to perform some numerical estimates for the cluster ion (Ni_3^{++}) Assuming that the equilibrium separation between the atomic ion and the atom in this system is equal to the equilibrium separation between the nuclei in the diatomic molecule of nickel (0.22 nm), we find that $\mathcal{D} \ge 0.45$) eV for n = 10. Since the exchange interaction potential between the ion and atom is of the order of 1 eV, this condition can be satisfied. Our model thus demonstrates that the diatomic cluster ion (M_3^{++}) can exist. We note that the parameter \mathscr{D} in the interaction potential (14) between the atomic ion and the atom corresponds to the exchange interaction that occurs without the transition of the electron from the field of one of the ions to the field of the other. Hence the parameter \mathcal{D} is not the dissociation energy of the diatomic ion and, being less than this, is determined by the exchange interaction between the electrons. The parameter \mathscr{D} is therefore small for atoms with one valence electron, i.e., it is highly doubtful whether doubly-charged cluster ions of the form Cs_3^{+} + can exist. Conversely, in atoms with an unfilled d-shell, the exchange interaction due to the inner electrons determines the dissociation energy of the diatomic ion. We may expect that the stable cluster ion M_3^{++} will exist in such cases.

It is possible that some of the observed doubly-charged metal trimers are in metastable states. There is an even greater likelihood of a metastable state in the case of the doubly-charged metal clusters containing a large number of atoms.

Whether or not a multiply-charged cluster ion can then be observed depends on the method by which the ion is produced, because this determines its structure. This is apparently the reason for the discrepancy between different experimental data on the critical number of multiply-charged metal cluster ions. Table IV summarizes some of these results.

6. PROCESSES INVOLVING CLUSTER IONS

6.1. Spontaneous dissociation

Since the binding energy of atoms in a cluster is relatively low (between a fraction of an electron volt and a few electron volts), cluster ions can spontaneously dissociate under laboratory conditions. The nature of this process must be known in all studies of cluster ions because the possibility of dissociation must be taken into account in the analysis of experimental data obtained with a view to determining other

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characteristics of the cluster ion. The main parameters of the spontaneous dissociation of the cluster ion are the characteristic dissociation time as a function of the cluster size, the size and charge distributions of the decay products (the latter in the case of multiply-charged ions), and the temperature dependence of the characteristic dissociation time for clusters of different size and charge.

Figure 12 shows the temperature dependence of the equilibrium rate constant for the attachment of the ammonia molecule to the cluster ion Na⁺ (NH₃)_n (Ref. 73)

$$Na^+ \cdot (NH_3)_n + NH_3 \rightarrow Na^+ \cdot (NH_3)_{n+1}$$
.

It is clear that the temperature dependence is satisfactorily described by the Arrhenius function $\exp(-D_n/T)$ where the activation energy D_n is a measure of the binding energy of the molecule in the cluster. Since the temperature dependence of the equilibrium constant is exponential, the same function can be used to describe spontaneous dissociation of the cluster with the detachment of one NH₃ molecule. Similar features can be seen on the temperature dependence of the equilibrium rate constants for the following reactions, investigated in Ref. 114

$$N_{2}^{+} \cdot (N_{2})_{n-1} + N_{2} \rightarrow N_{2}^{+} \cdot (N_{2})_{n},$$

$$O_{2}^{+} \cdot (N_{2})_{n-1} + N_{2} \rightarrow O_{2}^{+} \cdot (N_{2})_{n},$$

FIG. 12. Temperature dependence of the equilibrium rate constant for the reactions $Na^+ \times (NH_3)_{n+1} + NH_3 \Rightarrow Na^+ \times (NH_3)_n$ (Ref. 73). Numbers against curves show values of the activation energy for these reactions (eV) determined from these results.

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FIG. 13. Temperature dependence of the rate constant for the reactions $N_2^+ \times (N_2)_{n-1} + N_2 \boxminus N_2^+ \times (N_2)_n$ (a) and $O_2^+ \times (N_2)_{n-1} + N_2 \leftrightharpoons O_2^+ \times (N_2)_n$ (b) (Ref. 114). Numbers below graphs show values of the activation energy (kcal/mol) for these data.

These functions are plotted in Fig. 13.

The appreciable reduction in the binding energy of a molecule in a cluster ion with increasing ion size suggests that the principal cluster dissociation channel involves the removal of one molecule. Such a situation is relatively typical for large cluster ions. For example, Table V lists the neutral dissociation products of cluster ions of alkali metals. A similar conclusion is reported in Ref. 167 where it is shown that the main spontaneous dissociation channel of the cluster ion $(NH_3)_n NH_4^+$ (n < 10) is the detachment of an NH_3 molecule.

Analysis performed in Ref. 115 shows that this type of dissociation process can be explained completely in terms of energy considerations whereby the preferential dissociation channel corresponds to the minimum energy required to break the bonding. The preferential separation of one or two atoms has been confirmed for the clusters Al_n^+ , Cu_n^+ , Mo_n^+ , W_n^+ and Pb_n^+ ($n \ge 30$) (Ref. 13) and Sb_n^+ , Bi_n^+ ($n \le 14$) (Ref. 169).

The special features of the spontaneous dissociation of a cluster ion and its other properties depend significantly on the above structural regularities that, in turn, are related to the existence of stable structures and magic numbers. This is reflected in the nonmonotonic dependence of the spontaneous dissociation rate of a cluster ion on the number of particles it contains. For example, measurements performed on the ion Ar_n^+ ($30 \le n \le 200$) (Ref. 168) show that the most stable structures correspond to n = 81, 87, 96, 105, 11, 117, and 120. The rate at which these ions dissociate is much smaller than the corresponding rate for ions with an intermediate number of atoms.

Interesting properties appear in the decay of doublycharged ammonia cluster ions.⁹⁵ As noted above, ions of this type can exist only above a certain critical size which is n_c = 51 in the case of ammonia. The effective dissociation mechanism in the case of these ions should involve the Coulomb repulsion of positive ions in the cluster. However, experiments⁹⁵ suggest that the dissociation channel involving the detachment of a single NH₃ molecule is the preferred mode. The process accompanied by the separation of two NH_3 molecules simultaneously is less probable by a factor ten. In contrast to the doubly-charged ammonia cluster ions, triply-charged clusters dissociate into two charged fragments, and about 90% of the mass of the original ion is taken up by the doubly-charged fragment. A similar situation is observed in the dissociation of the triply-charged ions $(CO_2)3_n^+$ (Refs. 90 and 116). This is not in agreement with the above analysis of the mechanism of instability of multiply-charged ions whereby dissociation into two roughly equal parts is the energetically most convenient mode. This discrepancy suggests that the macroscopic drop model of clusters containing ≤ 100 particles is of limited utility. However, this conclusion is not general because it has been reported²⁰ that the main channel for the dissociation of doubly-charged ions $(O_2)_n^{2+}$ is dissociation into two fragments of similar mass.

6.2. Photodissociation of cluster ions

Since the binding energy of atoms in cluster ions is relatively low, the absorption of a relatively low-energy photon tends to intensify cluster ion processes. The main mechanism for this dissociation is probably the statistical mecha-

Cluster ion	Neutral decay product	Cluster ion	Neutral decay product	Cluster Ion	Neutral decay product	Cluster Ion	Neutral decay product
Na_{4}^{+} Na_{5}^{+} Na_{6}^{+} Na_{7}^{+} Na_{8}^{+} K_{4}^{+} K_{5}^{+}	Na Na Na Na Na K K	Na₃K+ Na₄K+ Na₅K+ Na₅K+ Na₅K+ NaK+ NaK4	Na Na2 Na Na2 Na Na Na	$\begin{array}{c} K_{a}^{+} \\ K_{7}^{+} \\ K_{8}^{+} \\ K_{9}^{+} \\ K_{10}^{+} \\ K_{11}^{+} \end{array}$	K K K K₂	NaK ⁺ NaK ⁺ NaK ⁺ NaK ⁺ NaK ⁺ NaK ⁺ NaK ⁺	K K K K K K c

TABLE V. Neutral decay products of alkali-metal cluster ions¹¹⁵.

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TABLE VI. Distribution of the relative probabilities of appearance of fragments in the photodissociation of Ag_n^+ clusters by 488-nm laser radiation (*n'* is the number of atoms in a large fragment)¹¹⁷.

.							S	ize of	initial	ion <i>n</i>					
n'	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1 2 3 4 5 6 7 8 9 10 11 12 13 14		43.3 56.7	20.9 38.8 40.3 	0.9 0.9 89.8 8.3 	0 91.3 4,3 4.3 	0 0 38.9 2.0 55.7 3.4 - - - - - - - - - - - -	0 0 21.7 1.1 30.0 3.7 43.4 	0 0 3.7 0 9.8 0 52.8 25.6 - - - - -	0 6.3 3.1 13.8 0 35.2 12.6 28.9 	0 0 5.6 0,6 10.4 0.7 25.0 14.9 42.8 0 	$\begin{array}{c} 0 \\ 0 \\ 5.7 \\ 0 \\ 10.1 \\ 20.6 \\ 16.6 \\ 46.6 \\ 0 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ -$	0 0 0 0 0 1.3 30.3 0 55.3 13.2	0 0 0 0 0 12.8 0 19.1 8.5 59.6	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 11.6 10.9 57.4 20.2	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
15	-	-	-	-	-	-	_	-		-			_		40

nism whereby the absorbed energy is statistically shared between all the degrees of freedom of a cluster ion, and the probability that a particular bond will be broken is determined by the bond energy. The relationship between different cluster-ion photodissociation channels is therefore a reflection of the relationship between the binding energies of different fragments of the ion. For example, Table VI shows the probability distribution for the appearance of different fragments in the photodissociation of Ag_n^+ by argon laser radiation¹⁷ (488 nm).

As can be seen, the most probable photodissociation channel is the detachment of between one and three silver atoms from the cluster ion. A similar conclusion was reported for the photodissociation of $(Bi_n^+ \text{ and } Sb^+ (n \leq 8) \text{ in Ref.})$ 124.

The statistical photodissociation mechanism manifests itself in the dependence of the number of atoms detached from the ion on the energy of the absorbed photon, as reported, for example, in Refs. 22 and 118–120. Figure 14 shows typical photodissociation data for K_n^+ ions and laser radiation of different wavelength. The linear relationship, which has also been established for the photodissociation of $(CO_2)_n^+$ (Ref. 118), $(CO_2)_n^-$ (Ref. 119), and Ar_n^+ (Ref. 120), suggests that the absorbed energy is almost completely shared between all the degrees of freedom of the cluster ion.

The photodissociation properties of large cluster ions reflect the structure of these objects. For example, the photodissociation fragments of C_n^+ (n < 80) were investigated in Ref. 65, using laser radiation of 193, 249, 353, and 266 nm. It was shown that the dissociation products of ions with n < 32

FIG. 14. Mean number of detached atoms as a function of photon energy in the dissociation of the clusters $(8 \le n \le 41)$ (Ref. 22).

and n > 32 were very different. In particular, the dissociation of ions with n > 32 was accompanied by the detachment of the C_3 fragments,³ whereas the dissociation of ions with n < 32 was accompanied by the detachment of a carbon atom (in the case of odd n) or a C_2 molecule (in the case of even n). The C_{32}^+ ions dissociate into two fragments of similar mass. This suggests that there is a difference between the structures of large and small clusters, which has been frequently noted in the literature.^{61,121} According to Refs. 61 and 121, small carbon cluster ions have a line structure or a closed ring structure, whereas large ions typically have a spheroidal structure.

The dissociation of cluster ions on absorption of a laser photon has been used as a basis for the investigation of the structure of $H_3^+ \times (H_2)_n$, by the method developed in Refs. 32, 122, 123. In the so-called predissociative vibrational spectroscopy, the cluster ions are illuminated by infrared laser radiation corresponding to vibrational energy of the bound H₂ molecules. The absorption of this energy by weakly-bound molecules produces the predissociation of the cluster ion, and is detected by recording the fragments produced in this process. The change in the vibrational frequency of the bound H₂ molecule relative to the frequency of an isolated molecule provides information on the structure of hydrogen cluster ions. This approach has also been used to investigate the structure of methyl alcohol clusters dissociating as a result of the absorption of laser photons with energies of about 1020–1050 cm⁻¹, which corresponds to the vibration-al frequency of the C-O bond.¹²⁵ It has also been used to investigate the dissociation of the clusters $(NH_3)_n$ $(n \le 5)$ (Ref. 125) in which nonequilibrium vibrational excitation was produced by the absorption of radiation from a tunable CO₂ laser.

When the photodissociation of negative cluster ions is analyzed, it must be remembered that the effects of optical radiation on such ions can give rise not only to photodissociation, but also to photodetachment of an outer electron. The relationship between these two photodissociation channels of a negative cluster ion depend significantly both on the wavelength of the optical radiation and on the size of the cluster ion. In particular, measurements show¹⁷⁰ that the cluster ions $(H_2O)_n^ (15 \le n \le 40)$ are dissociated or their outer electrons are photodetached by 1064 nm radiation,

FIG. 15. Cross section for the dissociation of Cu_n^+ by impact as a function of the number of particles¹³ (relative units). Dashed line shows the gas-kinetic cross section.

and the relative contribution of photodissociation rises from 4 to 60% as *n* increases from 15 to 40.

6.3. Collision-induced dissociation

Optical illumination is not the only cause of the dissociation of a cluster ion. Any other external agency, for example, collisions with atoms or molecules, can have the same result. In general, the result depends on the size and type of cluster, the collision energy, and the type of particle producing the cluster dissociation. Figure 15 shows the cross section for the dissociation of the cluster ion Cu $^+$ (in relative units) in collisions with Ar atoms and O_2 molecules (the collision energy was 1.8 keV) as a function of the cluster size n (Ref. 13). The nonmonotonic character of this dependence is a reflection of the nonmonotonic character of the stability of the cluster as a function of its size, which was discussed above. Measurements of the energy dependence of the dissociation cross section of the cluster ions Nb_4^+ and Fe_4^+ in collisions with Xe atoms at energies up to 75 eV (Ref. 171) have been used to determine the binding energy of these ions.

6.4. Attachment of electrons to clusters

A collision between an electron and a cluster can result in the formation of a negative ion. The most effective mechanism for this in the case of electronegative atoms and molecules involves the subsequent dissociation of the cluster (dissociative attachment). Dissociative attachment process produces a great variety of byproducts. For example, the attachment of electrons to $(SO_2)_n$ $(n \le \infty)$ results in the formation of not only the cluster ions $(SO_2)_{n-k}^{-}$, but also the ions $O^- \times (SO_2)_{n-k}$, $SO^- \times (SO_2)_{n-k}$ (Ref. 127). This is in agreement with studies of the dissociative attachment of electrons to SO_2 molecules, ¹²⁸ which show that the ions S⁻, O⁻ and SO⁻ can be the attachment byproducts. The dissociative attachment of an electron to the clusters (HCl), $(\text{Ref. 172}), (\text{CO}_2)_n$ (Ref. 129 and 130), and $(\text{N}_2\text{O})_n$ (Ref. 131) is usually accompanied by cluster dissociation with the retention of the component molecules. This difference in the character of dissociative attachment is due to the difference between the process energetics.

Studies of the dissociative attachment of an electron to the cluster $(CCl_4)_n$ $(n \le 9)$ (Ref. 132) have revealed an interesting property. It was found that the probability of formation of negative ions of different type in this process has a distribution that is not very different from that observed for the process of charge transfer between the Rydberg atom Kr^{**} and the cluster $(CCl_4)_n$. In other words, the free electron interacts with the cluster $(CCl^4)_n$ in the same way as a weakly-bound electron of a Rydberg atom. It is important to note that this property of Rydberg atoms is also observed in the case of charged transfer between a Rydberg atom and an SF_6 molecule;¹³³ this property is exploited in the detection of Rydberg atoms.

6.5. Chemical processes involving cluster ions

Many of the properties of cluster ions are due to the fact that a considerable fraction of the atoms or molecules in clusters is located on their surface or in the immediate neighborhood of the surface. One of the important characteristics of a cluster ion is therefore its ability to sorb chemicallyactive particles (atoms or molecules).

This property is very sensitive both to the size of the cluster ion and to its chemical composition.¹³⁴⁻¹⁴³ This is confirmed, in particular, by measurements¹³⁴ of the size of the activation barrier for chemisorbtion of the molecule D_2 by the surface of the cluster ion $Al_nO_k^+$ ($10 \le n \le 27$, $0 \le k \le 2$)

$$Al_nO_k^+ + D_2 \rightarrow Al_nO_kD_2^+$$
.

The cluster ions were produced by laser illumination of the surface of an aluminum target in a helium atmosphere containing a small amount of oxygen, followed by the ionization of the neutral clusters by fast electrons. The cluster ions $Al_n O_k^+$ were first mass selected in a quadrupole mass spectrometer and then passed through a chamber filled with deuterium at a pressure of 0.25-1 mtorr. The size of the activation barrier for chemisorption was estimated by measuring the threshold energy of ions for chemisorption. The results are listed in Table VII. These data show that the activation barrier is determined both by the size (n) of the cluster ion and by the number (k) of oxygen atoms adsorbed by the ion. The maximum sensitivity of the barrier height to these parameters is observed for small cluster ions for which the addition of one aluminum or oxygen atom to the cluster ion can give rise to a 30-40% change in the activation energy for chemisorption. The fact that the addition of one or two oxygen atoms to a cluster ion usually gives rise to an increase in the size of the activation barrier suggests that this produces a change in the electron structure of the cluster as a whole and not merely of the region in which the oxygen is localized. Actually, if this were to give rise to a change in the sorption properties of only a portion of the surface on which the oxygen was sorbed, the threshold energy for chemisorption would remain the same on account of the areas from which the oxygen is absent.

The interaction between cluster ions Al_n^+ and molecular oxygen can lead not only to chemisorption by the cluster surface, but also (if the collision energy is high enough) to a chemical reaction accompanied by the partial dissociation of the cluster ion.^{143,173} Measurements ¹⁴³ show that, for collision energies between Al_n^+ (5 < n < 26) and O_2 of either 1.2 or 4.2 eV, the main reaction channel involves the production of Al_{n-4}^+ and Al_2O molecules. The reaction cross section corresponds, roughly speaking, to the geometric size of the cluster ion. Analysis of experimental results based on the statistical theory of chemical reactions suggests the presence of the statistical mechanism for this reaction.

The sorbtive power of the cluster reflects its structural properties, as noted above. For example, measurements on

TABLE VII. Size of activation barrier for the chemisorption of D_2 molecules on the surface of the clusters $Al_n O_k^+$ (eV) (Ref. 114).

-		k	
n	0	1	2
10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27	$\begin{array}{c} 1.32 \pm 0.30 \\ 1.26 \pm 0.30 \\ 1.26 \pm 0.25 \\ 0.25 \\ \bullet \end{array}$	*) **) 1.71 ± 0.30 1.69 ± 0.25 1.68 ± 0.25 2.21 ± 0.20 1.32 ± 0.30 1.50 ± 0.25 1.66 ± 0.25 1.66 ± 0.25 1.72 ± 0.25 1.86 ± 0.20 1.99 ± 0.20 1.99 ± 0.20 1.99 ± 0.20 1.99 ± 0.20 1.95 ± 0.15 2.18 ± 0.15 1.75 ± 0.15 1.93 ± 0.15	$\begin{array}{c} 1.55\pm0.30\\ \bullet\\ \bullet\\$
*) No ch **'Weak	emisorption observed chemisorption signal		
***)Ion n	nass outside the sensitivity	range of mass spectromet	er

the chemisorption of hydrogen molecules by the surface of the clusters Nb_n^+ ($n \le 25$) (Ref. 24) have established a strong nonmonotonic dependence of reactivity and limiting relative amount of sorbed material on the cluster size. The clusters were produced by illuminating the surface of a solid niobium target with 5-ns second-harmonic pulses from a neodynium laser (532 nm) producing 25 mJ per pulse. The chemisorption kinetics was examined by the ion cyclotron resonance method. Figure 16 shows the rate constant for the chemisorption reaction

$$Nb_n^+ + H_2 \rightarrow Nb_n H_2^+$$

as a function of the cluster size *n*. As can be seen, the addition of only one atom to the cluster can alter its reactivity by several orders of magnitude. It is noticeable that there are two very different rate constants for chemisorption by the cluster Nb_{19}^+ . This means that there are probably two different structural forms of the cluster.

Analysis of the measured²⁴ dependence of the maximum number of sorbed hydrogen atoms on the cluster size also leads to some intersting conclusions with regard to the part played by the structure of the cluster ion in its behavior. This dependence is also nonmontonic and is shown in Fig. 17. The points at n = 11 and n = 19 suggest that there are two different structural modifications of the cluster ions Nb_{11}^+ and Nb_{19}^+ . This conclusion is in agreement with an analysis of the reactivity of the cluster Nb_{19}^+ . Generally, data on the rate of chemisorption are in reasonable agreement with measurements of the limiting number of sorbed hydrogen atoms.

Chemical reactions involving cluster ions can be accompanied not only by the dissociation of the clusters, but also by the dissociation of the particles interacting with the cluster. An interesting mechanism of this dissociation process has been suggested and analyzed in Ref. 144 in which a study was made of the reaction between the cluster Ar_n (n > 100) and the ion $C_2H_4^+$ This analysis suggests that the interaction between the ion and the neutral cluster is accompanied by the transition of an electron from the cluster to the ion, followed by the dissociative recombination of the ion with the electron. One of the recombination fragments (the H_2 molecule or H atom) leaves the system, whereas the other is sorbed by the surface of the cluster ion Ar_n^+ , produced in this process, and the latter, in turn, dissociates into fragments of different size.

FIG. 16. Chemisorption rate constant of hydrogen molecules on the surface of the cluster ion Nb_n^+ as a function of the cluster size²⁴.

FIG. 17. Limiting number of hydrogen atoms sorbed by the surface of Nb_n^+ of different size²⁴

TABLE VIII. Composition of negative ions in the atmosphere (rounded-off data).

Mass of observed		Relative concent	tration, %	
ion, a.u.	lon	Ref. 145, 36 km	Ref. 146, 32–34 km	
62 ± 2	NO	_	0.6	
125 <u>+</u> 1	NO ₃ ·HNO ₃	3	6.5	
143 <u>+</u> 2	$NO_{3} \cdot HNO_{3} \cdot H_{2}O$	—	0.9	
160 <u>+</u> 1	HSO, HNO3	5	14	
178 <u>+</u> 2	HSO₄ · HNO₃ · H₂O	—	2	
188 <u>+</u> 1	NO_3 (HNO ₃) ₂	65	19	
195 <u>+</u> 3	HSO ₄ · H₂SO ₄	7	10	
223±1	$HSO_4 \cdot (HNO_3)_2$	14	1.4	
251 <u>+</u> 1	$NO_3 \cdot (HNO_3)_3$	-	0.3	
276±3	HSO ₄ ·H ₂ SO ₄ ·HNO ₃	3	1.0	
293 <u>+</u> 1	$HSO_4 \cdot (H_2SO_4)_2$	3	1.2	
311 <u>+</u> 3	$HSO_{4} \cdot (H_2SO_4)_2 \cdot H_2O$		0.3	
374 <u>+</u> 3	$HSO_4 \cdot (H_2SO_4)_2 \cdot HNO_3$	_	0.3	
391 ± 2	$HSO_{4} \cdot (H_2SO_{4})_3$	_	14	
409 <u>+</u> 3	$HSO_4 \cdot (H_2SO_4)_3 \cdot H_2O$	-	13	
427 <u>+</u> 3	HSO_{4}^{-} (H ₂ SO ₄) ₃ ·(H ₂ O) ₂		2.2	
454 <u>+</u> 2	HSO ₄ (H ₂ SO ₄) ₃ · HNO ₃	1 -	1.5	
472 <u>+</u> 3	$HSO_4 \cdot (H_2SO_4)_3 \cdot HNO_3 \cdot H_2O$	_	0.4	
489±3	$HSO_4 \cdot (H_2SO_4)_4$	-	1.2	
507±3	$HSO_{4} \cdot (H_2SO_{4})_{4} \cdot H_2O$	—	1.5	
587 <u>+</u> 3	$HSO_{4}^{-} \cdot (H_2SO_4)_5$	-	0.4	

7. CLUSTER IONS IN THE EARTH'S ATMOSPHERE

The Earth's atmosphere is a multicomponent gas system whose parameters vary within very wide limits. Different USP 159(1), 45-81 (September 1981) 57 mechanisms of cluster ion production and dissociation predominate at different altitudes and this, in turn, is reflected in the ion composition of the atmosphere. For example, the D-layer that lies at a height of 80–100 km contains cluster ions of the form $H^+ \times (H_2O)_n$ with $H^+ \times (H_2O)_3$ being the most common positive ion.²⁻⁶

General considerations suggest that cluster ions are formed with higher efficiency at lower gas temperatures and higher densities. This means that the most favorable conditions for the formation of cluster ions occur at altitudes of up to 100 km in the atmosphere. The variation in these parameters with height gives rise to a great variety of cluster ions at different heights and under different conditions. Table VIII lists the negative ion species present in the stratosphere at altitudes of 33-36 km. It is important to note that the formation of cluster ions in the atmosphere occurs on the H₂O, H₂SO₄, HNO₃ impurity molecules whose concentrations are relatively low. At these altitudes, the density of air molecules is of the order of 10^{17} cm⁻³, the density of sulphuric acid molecules is 10^5-10^6 cm⁻³, and the density of nitric acid molecules is 10^7-10^8 cm⁻³. Estimates¹⁴⁷ show that the stratospheric concentration of impurities (H₂SO₄, HNO₃) that is necessary for the formation of large cluster ions is 2×10^{-12} at 30 km and 5×10^{-13} at 42 km. According to Bates,¹⁴⁸ this critical concentration of impurities is 5×10^{-13} at 42 km.

The composition of positive ions produced in the stratosphere has been under extensive discussion ⁴⁻⁶ ^{149–152}This has been forced by measurements of the mass spectra of positive

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cluster ions, which can only be interpreted in a logically consistent way by including an unknown impurity molecule in the composition of the cluster ions. Analysis¹⁵⁰ shows that the most probable unknown component is acetonitrile CH_3CN . Table IX lists the concentrations of cluster ions in the stratosphere with such identification of the unknown component.

Cluster ions affect the electric properties of the atmosphere at altitudes at which simple ions are absent. Moreover, cluster ions act as condensation centers for impurity molecules at these altitudes, and thus participate in the formation of sulphate and nitrate aerosols in the stratosphere.⁷

The role of cluster ions in the terrestrial atmosphere is not always related to the fact that they carry a charge. Cluster ions can sometimes act as catalysts of chemical processes in the atmosphere. The low density of the ions is then offset by their high reactivity. For example, the transformation of N_2O_5 into nitric acid in the stratosphere (at 15–20 km) oc-

TABLE IX. Positive cluster ions in the stratosphere at 36 km.

Mass of ob-	Proposed ion	Relative concentration, %			
served ion, a.u.	$(X = CH_3CN)$	[151]	[152]		
$55737891101114119\pm1136\pm1141\pm1$	$\begin{array}{c} H^+ \cdot (H_2O)_3 \\ H^+ \cdot (H_2O)_4 \\ H^+ \cdot X \cdot (H_2O)_2 \\ H^+ \cdot (H_2O)_5 \\ H^+ \cdot X \cdot (H_2O)_3 \\ H^+ \cdot X_2 \cdot H_2O \\ H^+ \cdot X_2 \cdot (H_2O)_4 \\ H^+ \cdot X_2 \cdot (H_2O)_2 \\ H^+ \cdot X_3 \cdot (H_2O)_8 \\ H^+ \cdot X_3 \cdot H_2O \end{array}$	3.426.87.28.919.610.716.14.42.9	5.5 29.6 8.4 2.8 44 3.5 0.9 4.9 —		

curs in accordance with the scheme¹⁵³⁻¹⁵⁵

$$\begin{split} &N_2O_5 + H^+ (H_2O)_n \rightarrow HNO_5 + H^+ \cdot (H_2O)_{n-1} \cdot HNO_3; \\ &H^+ (H_2O)_{n-1} \cdot HNO_5 + H_2O \rightarrow HNO_5 + H^+ \cdot (H_2O)_n, \\ &N_2O_5 + H_2O + H^+ (H_2O)_n \rightarrow 2HNO_5 + H^+ \cdot (H_2O)_n. \end{split}$$

There is particular interest in processes involving cluster ions near the Earth's surface. Studies of this kind are complicated by the possible contamination of the nearground layer of the atmosphere by large amounts of anthropogenic and natural impurities that determine the composition of the cluster ions. This is responsible for the considerable uncertainty in the ionic composition of the atmosphere, as indicated by traditional mass-spectrometric methods. Considerable advances in this direction have been achieved by research carried out at the Tartu University,¹⁵⁶⁻¹⁵⁹ using measurements of the mobility spectrum of charged particles in the atmosphere. These measurements are performed in two variants. In the first variant, the ion mobility spectrum in the atmosphere is measured at a given point for a long period of time. In the other variant, atmospheric air is ionized and the "aging" of ions during the recombination of charges is investigated, i.e., the evolution of the ion mobility spectrum in the course of ion recombination is determined.

This is an integrating method that cannot provide detailed information about atmospheric impurities forming cluster ions. Nevertheless, the approach is of considerable practical importance because it relies on a relatively simple experimental technique. Studies of the ion mobility spectrum in the atmosphere show that the stratosphere can be subdivided into two parts. Relatively light cluster ions are formed from simple ions as a result of ion-molecule reactions, whereas large cluster ions are formed by the attachment of simple ions to aerosol particles. By studying the mobility spectrum of charged particles in the atmosphere containing different impurities, and also by investigating the evolution of the mobility spectra in the course of the recombination of charged particles in the atmosphere, it is possible to consider the inverse problem as well, i.e., determine the degree of atmospheric contamination from the mobility spectra of charged particles in the atmosphere.

8. CONCLUSION

Cluster ions have been the subject of scientific research for several decades. Large cluster ions have attracted particular attention during the last decade. This was facilitated by new experimental techniques that can be used in selective studies of cluster ions with a given number of atoms or molecules. Such studies have resulted not only in extensive quantitative data, but have also led to the formulation of new fundamental questions in cluster-ion physics. One of the most significant conclusions is that a cluster ion is not a macroscopic particle even if it contains up to several hundred atoms or molecules. This means that the individual parameters of the cluster ion are nonmonotonic functions of the number of component atoms or molecules. In fact, the atoms in a cluster ion form a definite structure and the ion has enchanced stability in the case of a closed structure.

The difference between a cluster ion and a macroscopic particle requires a more careful approach to computational models of the properties of cluster ions and processes in which they participate. Hence, it follows, among other things, that the drop model of condensation, which decribes the behavior of a cluster ion as a condensation center will have to be revised.

New data on the properties of large cluster ions and processes in which they participate should stimulate the development of new applications of these particles. One of these could be the implementation of particular chemical processes. Cluster ions are usually chemically highly reactive, and their properties can be exploited in two ways. First, a cluster ion has a developed surface and is a chemically active particle, so that it can be used as a catalyst. One example of this kind, which occurs in the Earth's atmosphere, was mentioned in Section 7. Second, since a cluster ion differs from a macroscopic particle, its participation in chemical processes can result in the formation of chemical products that are different from the products of reactions involving condensed media or their surfaces. This may well be of particular interest in nonequilibrium chemistry.

Thus, the cluster ion traditionally attracts the attention of reseachers both as a charged particle participating in different processese in gas and plasma systems and as a physical object occupying an intermediate position between an atomic particle (atom or molecule) and a condensed state of matter. At present, the rate of advance in studies of cluster ions is unusually high, and new results that will be of interest from both scientific and applied points of view may confidently be expected.

- ¹¹For large clusters, we do not distinguish between clusters and cluster ions. Thus, first, when the neutral cluster is detected, it is ionized so that we do in fact deal with a cluster ion. Second, when the number of atoms or molecules is large, the structure properties of clusters and cluster ions are the same. Third, some properties such as the ionization potential and the affinity energy can just as well be treated as the properties of clusters as those of cluster ions.
- ²⁾An analogous situation occurs in the case of Ag_n^{2+} . These ions were observed for cluster sizes well below the critical value.¹¹¹

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Translated by S. Chomet