Cluster ions in gases

B. M. Smirnov

I. V. Kurchatov Institute of Atomic Energy
Usp. Fiz. Nauk **121**, 231–258 (February 1977)

The properties of cluster ions and the processes in which they participate are examined. Information is given on the bond-dissociation energies of cluster ions. Processes that give rise to compound and cluster ions in ternary collisions, dissociative recombination of a cluster ion and an electron, and ion-molecule reactions involving cluster ions are studied, and the experimental rate constants are given for these processes. The processes that involve cluster ions in the upper atmosphere of the Earth are analyzed.

CONTENTS

1. INTRODUCTION

The compounds of ions are richer and more varied than those of atoms, since the interaction of an ion with an atom or with a molecule is stronger than the interaction of neutral particles. Therefore we are faced with a large number of types of ions, even in the gas phase of a single element. For example, the fundamental types of ions in helium under normal conditions are He^+ and He_2^+,[1] with the ions He_3^+ and He_4^+ added at liquid-nitrogen temperature.[2] The fundamental types of ions in nitrogen under normal conditions are N^+, N_2^+, N_3^+, and N_4^+,[3] while N_5^+, N_6^+, N_7^+, N_8^+, and N_9^+,[4-6] etc., are added at low temperature. Thus a large number of types of ions can be realized in a weakly ionized gas.

We shall divide the compounds of ions into two classes. We shall term as compound ions the compounds involving ions in which the bonding involves valence forces. These compounds resemble chemical compounds in binding energy. Among the cited ions, the compound ions include He_2^+, N_2^+, and N_3^+. The other type of compounds of ions with atoms and molecules, in which the bonding arises from long-range interaction of ions with atoms and molecules, is termed the cluster ions. The bond-dissociation energies of cluster ions are considerably smaller than those of chemical compounds, and they amount to something of the order of tenths of an electron volt. Hence a change in the parameters of a weakly ionized gas (temperature and pressure) affects the type of ions that exist in it.

The properties of a weakly ionized gas depend on the type of ions that arise therein under the studied conditions. As an example, let us treat a gas discharge in an inert gas. If the gas is dense enough, while its temperature is not very high, then molecular ions of the type Ar_2^+ are formed in it. These ions efficiently recombine with electrons. If we raise the temperature of the gas, then the fundamental ions in the gas become simple ions like Ar^+, whose rate of recombination with electrons is several orders of magnitude smaller than that of the molecular ions.

Formation of compound and cluster ions in a gas affects both the parameters of the weakly ionized gas, the processes that involve them, and the reaction products that arise. Cluster ions are formed rather efficiently at low temperatures and not very low pressures, so that their study is primarily of interest for a low-temperature, weakly ionized gas. In particular, the fundamental types of positive ions in the D layer of the Earth's atmosphere[1)] are the ions $H^+ \cdot H_2O$ and $H^+ \cdot (H_2O)_2$.[7,8] There are also the ions $H^+ \cdot (H_2O)_3$,[7,8] $Na^+ \cdot H_2O$, $NO^+ \cdot H_2O$,[8] $NO_3^- \cdot HNO_3$,[9] etc. Cluster ions are formed even more efficiently under non-equilibrium conditions at low temperatures. In particular, ions of the type $K^+ \cdot (H_2)_n$ up to $n = 32$ have been observed in[10] upon bombarding the surface of solid hydrogen with potassium ions.

Cluster ions, being complicated and weakly bound structures, manifest their specifics in various processes and phenomena that arise in a weakly ionized low-temperature gas. The aim of this review is to give briefly a picture of the nature and peculiarities of the

---

1)The height of the D layer is 80 km, its temperature is about 190 °K, and the air pressure is of the order of 10^{-5} atm.

processes that involve cluster ions, and also to collect the information on the parameters of cluster ions and on the rate constants of the processes in which they participate.[2]

2. BOND-DISSOCIATION ENERGY OF CLUSTER IONS

One of the fundamental parameters of cluster ions that characterize their possible existence under studied equilibrium conditions is the dissociation energy of the cluster ions. Let a compound or cluster ion AB^+ exist in which A^+ is an atomic or molecular ion and B is an atom or molecule. In a gas that consists of atoms or molecules of the type M, the studied cluster ion is produced and destroyed via the following processes:

$$A^+ + B + M \xrightarrow[k_{\text{dissoc}}]{\mathscr{K}} AB^+ + M. \qquad (1)$$

The rate constant of the corresponding process is indicated above each arrow.

If the ions stay long enough within the given volume, and the processes (1) run faster than other possible processes that involve a change in the type of ions (e.g., recombination processes, interaction with the wall, emission processes, etc.), then thermodynamic equilibrium is established between the studied types of ions. Then the relationship between the densities of the compound and simple ions is determined by a formula analogous to that of Saha:

$$\frac{[AB^+]}{[A^+][B]} = \frac{\mathscr{K}}{k_{\text{dissoc}}} \equiv K(T) = f(T)\, e^{D/T}.$$

Here $[AB^+]$ and $[A^+]$ are the densities of the corresponding ions, $[B]$ is the density of particles of type B, $K(T)$ is the equilibrium constant for process (1), T is the temperature of the gas, D is the dissociation energy of the cluster ion, i.e., the energy for breaking the A^+–B bond, and $f(T)$ is some function of the temperature that varies more slowly than exponentially with varying temperature.

Under equilibrium conditions, in which the relationship between the densities of the ions is determined by the presented equation, a maximum density of cluster ions is reached under certain fixed conditions (total density of ions, temperature, and pressure of the gas). This relationship serves as the basis of the very widespread method of determining the dissociation energy of a cluster ion. If we apply a small electric field to the studied volume of gas, this will give rise to ion currents. The ratio of current strengths for the ions of different types is practically proportional to the ratio of densities of the studied ions in the volume.

Thus, measuring the ratio of ion currents makes it possible to determine the ratio of densities of the cluster and simple ions. This ratio depends exponentially on the temperature, so that a measurement of the ratio

of currents for the cluster and simple ions permits one to recover the dissociation energy of the cluster ion. From (2) we get the following expression for the equilibrium constant:

$$\ln K = \text{const} + \frac{D}{T}.$$

This relationship is the basis of the studied method of determining the dissociation energy of a cluster ion. The equilibrium constant $K(T)$ is proportional to the ratio of ion currents, and the constant on the right-hand side of this relationship depends weakly on the temperature. Yet this dependence limits the accuracy of determining the dissociation energy by the studied method, which is recovered from the derived relationships to an accuracy of the thermal energy.

A cruder method of determining the dissociation energy of cluster ions is based on studying ion-molecule reactions. If the process

$$A^+ - B + C \to A^+ - C + B$$
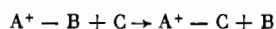
takes place, then we can conclude that the dissociation energy of the ion A^+–B is no higher than that of the ion A^+–C. If one studies this process in single collisions and measures the energies of the ions before and after reaction, then one can get the difference of dissociation energies for the studied ions. Of course, we must assume here that the ions before and after reaction are in the ground state.

Tables I–III give values of the bond-dissociation energy for a set of compound and cluster ions as obtained by the described methods. Let us call attention to one idea that we can gather by analyzing these tables. The dissociation energy of the bonds $A^+ \cdot (H_2O)_n$–H_2O, $A^- \cdot (H_2O)_n$–H_2O declines with increasing number of water molecules in the complex ion, and it approaches the value 0.42 eV, which is the energy of removal of a water molecule from the surface of a water droplet. The amount of this type of cluster ions for which the dissociation energy does not strongly differ from the given value of 0.42 eV is small. In the studied system, it is always thermodynamically more favorable either to form simpler ions (at high temperature) or for the water vapor to condense into a drop (at lower tempera-

TABLE I. Bond–dissociation energy of compound and cluster ions.

Ion	Bond-dissociation energy	Reference	Ion	Bond-dissociation energy	Reference
$N^+ - N_2$	2.6 *	12, 13	$NO^+ - CO_2$	0.4	30
$N_2^+ - N_2$	0.8	14–16	$H_3^+ - H_2$	0.25	31–33
$O_2^+ - O_2$	0.44	17–21	$Cs^+ - CO_2$	0.27	34
$O_2^+ - N_2$	0.24	22	$Cs^+ - SO_2$	0.5	34
$O_2^+ - H_2$	<0.2	23	$He_2^+ - He$	0.17	35
$O_2^+ - O_2$	0.28	19, 21	$O^- - O_2$	1.4	36
$O_4^+ - O_2$	0.13	19, 24	$O_2^- - O_2$	0.09	37, 38
$O_4^+ - O_2$	0.12	19, 24	$O^- - CO_2$	2.0	39
$O_6^+ - O_2$	0.11	19, 24	$O_2^- - CO_2$	0.6	27, 40
$O_4^+ - H_2O$	0.7	23, 25, 26	$OH^- - CO_2$	2.5	39
$O_2^+ - N_2O$	0.56	27	$SF_5^- - F$	1.4	41
$NO^+ - N_2$	0.18	28	$NO_3^- - H_2O$	0.5	42, 43
$NO^+ - H_2O$	0.8	29	$NO_3^- - HNO_3$	0.9	42

*Here and in the following tables, the boldface numbers are averaged results of the several cited studies.

[2]Much information on the properties of cluster ions that contain nuclei of a single type is contained in the review by Kulik, Norman, and Polak.[22]

TABLE II. Proton-affinity energies of atoms and molecules.*

Atom, molecule	Proton-binding energy, eV	Reference	Atom, molecule	Proton-binding energy, eV	Reference
H	2.65	44	CO	5.6	45, 55, 56
O	4.9	44	NO	5.5	57
He	2.0	45	H_2O	7.0	58
Ne	2.3	45	H_2S	7.4	59, 60
Ar	3.7	46–48	N_2O	5.8	47
Kr	4.4	45	CO_2	5.3	49, 60
Xe	6.7	45	NH_3	8.9	60
F	4.5	44	HNO_2	8.1	42
Cl	4.6	44	HNO_3	7.7	42
H_2	4.3	49–52	CH_4	5.5	61
N_2	4.8	47, 49, 53	CF_4	5.2	47
O_2	4.1	54	SF_6	3.7	49

*By definition, the proton-affinity energy of the particle A is the dissociation energy of the bond H^+-A.

ture), whereby the ion can serve as the condensation center. Thus an analysis of Table III implies that the probability of finding cluster ions in the system with a number $n > 4$ of water molecules is small.

This conclusion can be extended to other ions. Thus, Table I gives the dissociation energies of the cluster ions $O_{2n}^+-O_2$. They decline with increasing number of oxygen molecules in the cluster ion to approach the value 0.07 eV, which is the binding energy of an oxygen molecule with the surface of liquid or solid oxygen. Hence the probability of finding in oxygen an ion O_{2n}^+ having $n > 3$ is small at any temperature and oxygen pressure.

Thus, we arrive at the conclusion that the relative number of cluster ions in a system having a large number of molecules is small under all conditions. Mass-spectrometric measurements permit one to detect exotic cluster ions, such as O_{2n}^+, $n \leq 9$, [19] Ar_n^+, $n \leq 33$, [69] $K^+ \cdot (H_2)_n$, $n \leq 32$, [10,11] and Ag_n^-, $n \leq 30$. [70] However, we must remember that the fraction of ions having a large number of atoms and molecules in the gas phase under equilibrium conditions is very small.

3. FORMATION OF COMPOUND AND CLUSTER IONS IN TERNARY COLLISIONS

Compound and cluster ions are produced in a gas by ternary collisions according to the scheme:

$$A^+ + B + M \rightarrow AB^+ + M. \qquad (2)$$

Here A^+ is an atomic or molecular ion, and B and M are atoms or molecules. Here the excess energy from creation of the bound state of the particles A^+ and B is imparted to the particle M. The process (2) is characterized by a rate constant $\mathscr{K}$, so that the equation of balance for the densities of the produced ions when only process (2) occurs has the form

$$\frac{d[AB^+]}{dt} = \mathscr{K}[A^+][B][M]. \qquad (3)$$

Here [X] is the density of the particles of the studied type. The rate constant $\mathscr{K}$ for the ternary process has the dimensions of cm^6/sec.

The size of the formation rate constant of a compound or cluster ion depends on the nature of the interaction of the particles A^+ and B and the possible formation of a long-lived complex when they collide. If a long-lived

complex is not formed when the particles A^+ and B collide, then the formation rate constant of the ion AB^+ can be estimated by the theory of Thomson. While Thomson's theory was first used for estimating ternary recombination of a positive and a negative ion, [71,72] its results are easily extended to any other ternary process in which a bound state of two classical particles is created in a simultaneous collision with a third particle. We shall take up this theory further.

The essence of Thomson's theory is as follows. In order for the particles A^+ and B to yield a bound state, one of them must collide with a third particle M at the instant when they are interacting strongly. This particle removes the excess energy so that A^+ and B end up in a bound state.

We shall assume that the masses of the particles A^+ and M are of the same order of magnitude, of the order of m. Following Thomson, we shall introduce the critical radius b on the basis of the relationship

$$U(b) \sim T, \qquad (4)$$

where $U(R)$ is the interaction potential of the recombining particles A^+ and B. The formation of the bound state of the particles A^+ and B occurs as follows. In the collision of the particles, when the energy of attraction of the particles A^+ and B proves to be of the order of the thermal energy T, the particles A^+ and M collide in such a way that an energy of the order of the thermal energy T is imparted to M. Consequently, the particles A^+ and B end up in the bound state.

The rate of conversion of A^+ ions into AB^+ ions resulting from the process (2) is the product of the rate $[M]\bar{v}\sigma$ of collisions of the particles A^+ with M in which the energy exchange between them is of the order of the thermal energy, times the probability $[B]b^3$ that the distance from A^+ to the nearest B particle will prove to be less than the critical radius. We get from this the equation of balance for the density of the produced ions

$$\frac{d[AB^+]}{dt} \sim [A^+][M]\bar{v}\sigma[B]b^3.$$

Comparing it with Eq. (3), we get the following estimate for the formation rate constant of the ion AB^+:

$$\mathscr{K} \sim \bar{v}\sigma b^3. \qquad (5)$$

Here $\bar{v}$ is the characteristic velocity of the particles A^+ and M, and σ is the characteristic collision cross-sec-

TABLE III. Bond–dissociation energies of $A^+ \cdot (H_2O)_n-H_2O$ and $A^- \cdot (H_2O)_n-H_2O$ (in eV).*

n	Ion												
	Li+	Na+	K+	Rb+	Cs+	Pb+	Bi+	F-	Cl-	Br-	I-	OH-	O_2^-
0	1.50	1.04	0.78	0.69	0.56	0.97	0.99	1.01	0.57	0.55	0.44	0.98	0.80
1	1.12	0.86	0.70	0.59	0.52	0.73	0.77	0.72	0.55	0.53	0.42	0.71	0.75
2	0.90	0.68	0.57	0.53	0.45	0.53	0.61	0.59	0.51	0.50	0.41	0.65	0.67
3	0.71	0.60	0.51	0.48	0.46	0.47	0.52	0.58	0.48	0.47	—	0.62	—
4	0.60	0.52	0.46	0.45	—	0.43	0.46	0.57	—	—	—	0.61	—
5	0.52	0.46	0.43	—	—	0.42	0.42	—	—	—	—	—	—

* Results of [62–68,212,213].

tion of these particles that corresponds to an energy transfer of the order of T. Under the studied conditions, it coincides with the large-angle elastic scattering cross-section of A^+ and M.
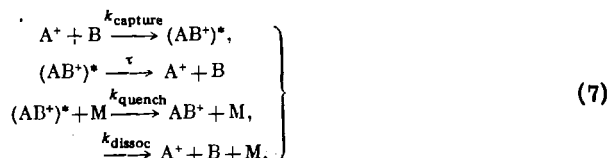
The obtained estimate (5) for the rate constant of the ternary process is valid at low densities of the particles of the third type, when the free flight path of the ions in the gas of particles of the third type is large in comparison with the critical radius:

$$[M]\, \sigma b \ll 1. \tag{6}$$

Then three-particle collisions occur considerably more rarely than pair collisions, and the studied process is third-order in type.

Let us discuss another mechanism of production of compound and cluster ions, in which a long-lived complex is formed in the collision of the recombining particles. The lifetime of the long-lived complex is considerably longer than the time of collision of the recombining particles, which is of the order of magnitude of 10^{-13}–10^{-12} sec. Hence the rate constant for formation of compound and cluster ions when a long-lived complex exists is considerably greater than when this reaction follows the direct mechanism.

Let us write a scheme of the processes that occur in the formation of a compound or cluster ion via an intermediate long-lived state. Here the process occurs in two stages. The first is the formation of the long-lived complex, and the second is the transition of the long-lived complex to a stable state. The equations of the processes that occur here have the form:

$$\left. \begin{array}{l} A^+ + B \xrightarrow{k_{capture}} (AB^+)^*, \\ (AB^+)^* \xrightarrow{\tau} A^+ + B \\ (AB^+)^* + M \xrightarrow{k_{quench}} AB^+ + M, \\ \qquad \xrightarrow{k_{dissoc}} A^+ + B + M. \end{array} \right\} \tag{7}$$

Here $(AB^+)^*$ is the long-lived complex that is formed upon collision of the recombining particles A^+ and B, the rate constants of the corresponding processes are indicated above the arrows, and τ is the lifetime of the long-lived process.

When we have accounted for the processes (7), the equation of balance for the ion densities in the autoionizing state and that of the ions being produced have the form

$$\frac{d[(AB^+)^*]}{dt} = [A^+][B]k_{capture} - [(AB^+)^*]\left\{ \frac{1}{\tau} + (k_{quench} + k_{dissoc})[M] \right\}$$

$$\frac{d[AB^+]}{dt} = [(AB^+)^*][M]k_{quench}.$$

We shall assume that the density of the third type of particles is small, so that we are dealing with a ternary process:

$$[M]\,(k_{quench} + k_{dissoc})\,\tau \ll 1. \tag{8}$$

Upon assuming that the characteristic times under study are much longer than the lifetime of the long-lived com-

plex, we get $d[(AB^+)^*]/dt = 0$. Let us determine therefrom the density of the ions in the autoionizing state. Upon accounting for Eq. (8), we get

$$[(AB^+)^*] = [A^+][B]k_{capture}\tau. \tag{9}$$

When we substitute this relationship into the equation of balance for the density of the ions being created, and compare this equation with Eq. (3), we get the following expression for the rate constant of the ternary process:

$$\mathscr{K} = k_{capture}k_{quench}\tau. \tag{10}$$

The derived formula acquires a simple form if we use the rate constants for capture of the ion by polarization of the neutral particles as the capture and quenching rate constants. Polarization capture leads to strong approach, and hence to strong interaction of the colliding particles, so that polarization capture must precede both the formation of the long-lived complex and the transition of the ion to the stable state. Correspondingly, the capture and quenching rate constants are less than or equal to the rate constants for polarization capture. Therefore, if we replace $k_{capture}$ and k_{quench} in (10) by the polarization-capture rate constants, we get an upper bound for the rate constant for ternary cluster-ion formation.

The rate constant for polarization capture of an ion by a molecule is[73]

$$k_{pol} = 2\pi \sqrt{\frac{\beta e^2}{\mu}}. \tag{11}$$

Here β is the polarizability of the molecule, and μ is the reduced mass of the colliding ion and molecule. Upon substituting such expressions for the capture and quenching rate constants in Eq. (10), we convert it into the form[74]:

$$\mathscr{K} = 4\pi e^2 \sqrt{\beta_B \beta_M} \sqrt{\frac{m_1 + m_2 + m_3}{m_1 m_2 m_3}}\,\tau. \tag{12}$$
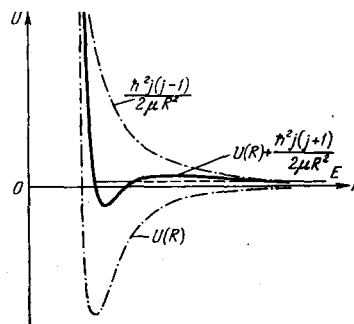
Besides the two discussed mechanisms for formation

FIG. 1. Interaction potential of an ion and an atom as a function of the distance R between them for a given angular momentum j. Since the centrifugal energy corresponds to repulsion, a hump appears in the overall effective potential that involves the existence of autoionizing states. One of these having energy E is indicated in the diagram.

of a compound or cluster ion in ternary collisions, one of which involves elastic collision of three particles, and is described by Thomson's theory, while the other is accompanied by formation of a long-lived complex, there is an intermediate case. Namely, the elastic collision of two particles whose interaction potential contains no barrier can give rise to autoionizing bound states of these particles owing to the centrifugal interaction potential (Fig. 1). Then tunneling upon collision of the particles A^+ and B gives rise to quasibound states of these particles with a lifetime longer than the time of collision. Thus, even when the recombining particles A^+ and B lack internal degrees of freedom and have a simple form of interaction potential, a long-lived complex of the colliding particles can be produced that will give rise to a stable bound state. [75-78]

Let us elucidate the role of tunneling transitions in the recombination of a simple ion with an atom and a molecule. We shall establish the relation between the lifetime of the individual autoionizing state and the other parameters of the problem. Let us substitute into (9) the Saha distribution that gives the relationship between the density of ions, molecules, and cluster ions in the given autoionizing state:

$$\frac{[A^+][B]}{[(AB^+)^*]} = \frac{g_A \cdot g_B}{g_{AB^+}} \left(\frac{\mu T}{2\pi\hbar^2} \right)^{3/2} e^{E/T}.$$

Here g_{A^+}, g_B, and g_{AB^+} are the statistical weights that correspond to the electronic state of the corresponding particle, μ is the reduced mass of the colliding particles A^+ and B, and E is the excitation energy of the studied autoionizing level as measured from the edge of the continuous spectrum. Hence we get

$$k_{capture}\tau = \frac{g_{AB^+}}{g_A + g_B} \left(\frac{2\pi\hbar^2}{\mu T} \right)^{3/2} e^{-E/T}.$$

Upon substituting this expression into the formula (10) for the third-order formation rate constant of the compound or cluster ion and summing over all the autoionizing levels, we get

$$\mathscr{K} = \frac{g_{AB^+}}{g_A + g_B} \left(\frac{2\pi\hbar^2}{\mu T} \right)^{3/2} \sum_{j,\,v} (2j+1) k_{quench}(j,v) e^{-E_{j,\,v}/T}. \qquad (13)$$

Here the indices v and j characterize the vibrational and rotational state for the studied level, and $2j+1$ is the statistical weight of the rotational state.

Let us estimate the value of the third-order formation rate constant of a compound when the process occurs via formation of an autoionizing state of the colliding ion and molecule. Here we shall start with the idea that the fundamental contribution to (13) comes from the autoionizing states whose excitation energy is of the order of the thermal energy. The characteristic distance R_0 between the particles in the region where their motion is classical in the bound state can be estimated from the relationship $U(R_0) \sim T$. According to (4), it and they migrate toward the cathode where one measures with a mass spectrometer the time-dependence of the current for ions of a given type. By varying the density of the gas or the distance between the electrodes,

one can establish from the measured current the rate constants of the ion-molecule reactions that occur in the gas, including the formation rate constant for compound and cluster ions. In addition, one can measure the rate proves to be of the order of the critical radius. Taking this into account, we find from Bohr's quantization condition that the number of vibrational levels that contribute to the summation in (13) is equal in order of magnitude to $v \sim (1/\hbar)\sqrt{\mu Tb}$. The fundamental contribution to the summation of (13) comes from rotational states having a centrifugal energy of the order of the thermal energy: $\hbar^2 j^2/\mu b^2 \sim T$.

Upon using the characteristic values of the rotational and vibrational quantum numbers that determine the value of the summation of (13), we get the following estimate for the rate constant of the ternary process in the studied mechanism:

$$\mathscr{K} \sim k_{quench} b^3.$$

Quenching of the autoionizing state in the studied case amounts to collision of the generated ion in the autoionizing state with a particle of the third type, whereupon an energy of the order of T is imparted to the particle of the third type. Thus the quenching constant k_{quench} in the derived formula plays the same role as the quantity $\bar{v}\sigma$ does in Thomson's formula (5). Thus the studied mechanism leads to a value of the formation rate constant of the compound ion that is of the same order of magnitude as is given by Thomson's formula. Therefore we shall not henceforth treat this mechanism as being independent, but shall include it in Thomson's formula (5).

In addition to the studied mechanisms for formation of compound and cluster ions in ternary collisions, other channels for this process can arise that mainly involve transition between different electronic-energy surfaces, i.e., between different electronic states of the system of colliding particles. These problems have been presented in the monograph[79] so that we shall not spend further time on them.

Let us proceed to the experimental methods of studying the process of formation of compound and cluster ions. There methods have been presented in detail in the monograph,[80] and their fundamental idea is as follows. Ions are injected into a drift tube filled with gas, constant for formation of molecular ions by studying the parameters of a decaying plasma or the parameters of the positive column of a gas discharge.

Table IV gives the experimental values of rate constants for formation of compound ions in atomic gases in ternary collisions. Let us take up in greater detail the process

$$A^+ + 2A \rightarrow A_2^+ + A, \qquad (14)$$

where A is an atom. Here the formation rate constant of the molecular ion is determined by Thomson's formula (5):

$$\mathscr{K} = C \sqrt{\frac{T}{M}} b^5, \qquad (15)$$

TABLE IV. Formation rate constants of compound and cluster ions in atomic gases at thermal energies* (in units of 10^{-31} cm^6/sec).

Process	Rate constant of the process, 10^{-31} cm^6/sec[a]	Reference
He$^+$ + 2He → He$_2^+$ + He	1.0	81–92
Ne$^+$ + 2Ne → Ne$_2^+$ + Ne	0.60 (0,62)	84, 87, 91, 93–98
Ar$^+$ + 2Ar → Ar$_2^+$ + Ar	2.2 (2,0)	82, 95, 96, 99–103
Kr$^+$ + 2Kr → Kr$_2^+$ + Kr	2.3 (2.2)	104, 105
Xe$^+$ + 2Xe → Xe$_2^+$ + Xe	2.8 (3.1)	105–106
Cs$^+$ + 2Cs → Cs$_2^+$ + Cs	150 (130)	107
Hg$^+$ + 2Hg → Hg$_2^+$ + Hg	1, $T = 700$ °K (3,1)	108
He$_2^+$ + 2He → He$_3^+$ + He	1.7, $T = 77$ °K	35
Ar$_2^+$ + 2Ar → Ar$_3^+$ + Ar	32, $T = 77$ °K	103
Ar$_2^+$ + Ar + He → Ar$_3^+$ + He	5.5, $T = 80$ °K	11
Cs$_2^+$ + 2Cs → Cs$_3^+$ + Cs	300	107
Ne$^+$ + Ne + He → Ne$_2^+$ + He	3.0	89, 109
Ar$^+$ + Ar + He → Ar$_2^+$ + He	1.0, 16, $T = 82$ °K	74, 89, 110
Kr$^+$ + Kr + He → Kr$_2^+$ + He	0.6	111
Xe$^+$ + Xe + He → Xe$_2^+$ + He	1.3	111
Hg$^+$ + Hg + He → Hg$_2^+$ + He	1.7, $T = 700$ °K	108
Ne$^+$ + 2He → (NeHe)$^+$ + He	0.21	109
Ar$^+$ + Ar + Ne → Ar$_2^+$ + Ne	3	89
HeH$^+$ + 2He → He$_3$H$^+$ + He	0.4, $T = 200$ °K	112
H$_3^+$ + 2Ar → H$_3^+$·Ar + Ar	1	114
Li$^+$ + 2Ar → Li$^+$·Ar + Ar	1.8	226

* The gas temperature is noted whenever differing appreciably from room temperature.

FIG. 3. Rate constant of the process Ar$^+$ + 2Ar → Ar$_2^+$ + Ar as a function of the temperature. 1—[103], 2—the set experiments of Table IV, 3—calculation by Eqs. (15) and (16).

FIG. 4. Rate constant of the process Kr$^+$ + 2Kr → Kr$_2^+$ + Kr as a function of the temperature. 1—experiment,[105] 2—calculation by Eqs. (15) and (16).

where C is a constant coefficient, M is the mass of the atom, and b is the critical radius of (4). Let us write the interaction potential of the ion and the atom in the form of the sum of polarization and exchange interactions, so that the relationship (4) for the critical radius has the form

$$|U(b)| = \frac{\beta e^2}{2b^4} + \Delta(b) = T. \tag{16}$$

Here β is the polarizability of the atom, and $\Delta(b)$ is the exchange-interaction potential of the ion and the atom,[115] which declines exponentially at great distances between them.

If we can neglect the exchange interaction of the ion and the atom in comparison with the polarization interaction, then, according to Eqs. (15) and (16), the rate constant of the process (14) depends as follows on the parameters of the problem[116]:

$$\mathscr{K} \sim (\beta e^2)^{3/4} M^{-1/2} T^{-3/4}. \tag{17}$$

We note that one can derive this relationship from considerations of dimensionality. Actually, one can make only one combination of the parameters βe^2, M, and T that has the dimensions of cm^6/sec, and it corresponds to Eq. (17).

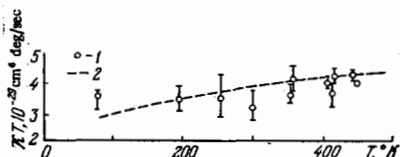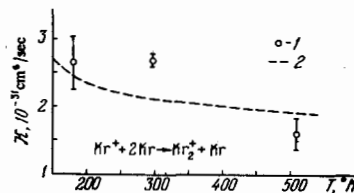Table IV gives in parentheses the values of the rate constant of the process (14) as calculated by Eqs. (15)
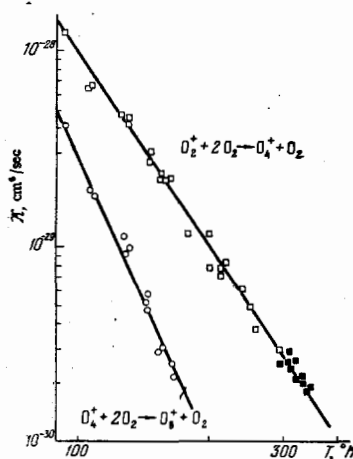

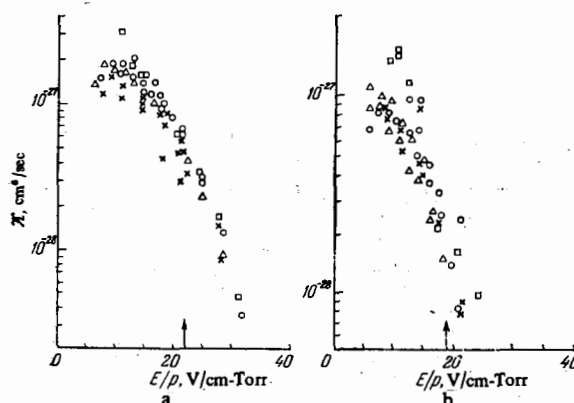FIG. 5. Temperature-dependence of the formation rate constants of the molecular ions O$_4^+$ and O$_6^+$.[131]

FIG. 6. Formation rate constant of complex ions[127] as a function of the electric field intensity in ternary collisions: a) H$^+$·(H$_2$O)$_2$ + H$_2$O + O$_2$ → H$^+$·(H$_2$O)$_3$ + O$_2$; b) H$^+$·(H$_2$O)$_3$ + H$_2$O + O$_2$ → H$^+$·(H$_2$O)$_4$ + O$_2$. The arrows indicate the field intensity values at which the mean energy of the ions exceeds the thermal energy by a factor of two.

FIG. 2. Temperature-dependence of $\mathscr{K}T$ (where $\mathscr{K}$ is the rate constant of the process He$^+$ + 2He → He$_2^+$ + He). 1—Experiment,[35] 2—theory.[116]

and (16). Here the parameters of the exchange-interaction potential of the ion and atom in Eq. (16) were taken from the monograph,[115] while the constant coefficient in Eq. (15) ($C = 13$) was chosen from the condition that the value of the formation rate constant of the molecular helium ion as calculated by this formula should agree with the data of Table IV. The molecular ions of the inert gases, except for helium, can exist in three electronic states that correspond to different exchange-interaction potentials. The mean exchange-interaction potential of the ion with the particular atom for which this interaction is larger is used in Eq. (16).

According to (17), the temperature-dependence of the formation rate constant of molecular ions has the form $\mathcal{K} \sim T^{-3/4}$ when the interaction of the ion with the atom obeys a polarization law. Exchange interaction of the ion with the atom makes this relationship smoother. Figures 2–4 show the temperature-dependence of the formation rate constant of the molecular ions He_2^+, Ar_2^+, and Kr_2^+ in the corresponding gases.

Table V gives the experimental values of the formation rate constant of compound and cluster positive ions in molecular gases. Table VI gives the formation constant of positive cluster ions that include a water molecule, and Table VII gives the measured values of the formation rate constants of compound and complex negative ions. The formation of the cluster ions occur via an intermediate long-lived complex. Therefore the formation rate constant of the cluster ions considerably exceeds that of the compound ions. Moreover, the lifetime of the long-lived complex declines sharply with increasing gas temperature, since a large amount of energy must be transferred here to the internal degrees of freedom. Hence the formation rate constants of the cluster ions decline sharply with increasing gas temperatures. Figures 5–7 show the temperature-dependence of the formation constants of the ions O_4^+, O_6^+, $H^+ \cdot (H_2O)_3$, and $H^+ \cdot (H_2O)_4$ in oxygen, and of the cluster ion $NO^+ \cdot N_2$ in nitrogen.

We arrive at the following conclusions from the set of theoretical and experimental results that pertain to the formation of compound and cluster ions in ternary collisions. There are two fundamental mechanisms for formation of compound and cluster ions. One of them involves elastic collision of three particles, and it is described by Thomson's theory. The other one involves formation of an intermediate long-lived complex of two colliding particles, whereupon the internal excitation of this complex is transferred to a third particle. The rate constant for formation of cluster ions when an intermediate long-lived complex exists exceeds in order of magnitude the value of this quantity that characterizes elastic collision of particles. Here the intermediate complex ion has a lifetime that increases with greater complexity of the ion that is formed, and with lower gas temperature.

4. DISSOCIATIVE RECOMBINATION OF A CLUSTER ION AND AN ELECTRON

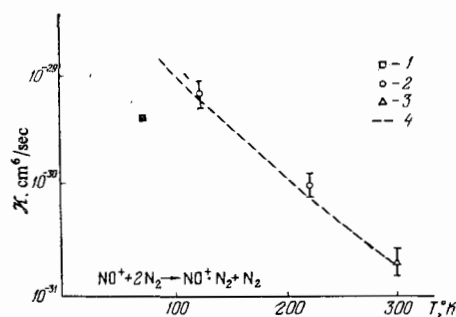The efficient destruction of cluster ions in a weakly ionized gas arises from their recombination with elec-

FIG. 7. Temperature-dependence of the rate constant of the process $NO^+ + 2N_2 \rightarrow NO^+ \cdot N_2 + N_2$. 1—[148], 2—[28], 3—[144], 4—the relationship 2×10^{-31} cm^6/sec $\cdot (300/T)$,[4,2] where T is the temperature of the gas in K.

trons. Dissociative recombination of an electron and a molecular ion occurs via formation of an autoionizing state of the molecules. Figure 8 shows the nature of the dissociative recombination of an electron and the

TABLE V. Formation rate constants of positive compound and cluster ions in molecular gases at room temperature.

Process	Rate constant, 10^{-30} cm^6/sec	Reference
$H^+ - 2H_2 \rightarrow H_3^+ + H_2$	30	117–120
$D^+ + 2D_2 \rightarrow D_3^+ + D_2$	30	117, 120
$H_3^+ + 2H_2 \rightarrow H_5^+ + H_2$	0.65	31, 33, 118
$D_3^+ + 2D_2 \rightarrow D_5^+ + D_2$	0.45	31
$N^+ + 2N_2 \rightarrow N_3^+ + N_2$	30	121–123
$N^+ + N_2 + He \rightarrow N_3^+ + He$	30; 70, $T = 80$ °K	74, 124
$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$	85	121–123, 125, 126
$N_2^+ + N_2 + He \rightarrow N_4^+ + He$	36; 120, $T = 80$ °K	74, 124
$O_2^+ + 2O_2 \rightarrow O_4^+ + O_2$	2.5; 10, $T = 200$ °K; 160, $T = 80$ °K	13, 127–131
$O_2^+ + O_2 + He \rightarrow O_4^+ + He$	1.5; 2.4, $T = 200$ °K; 31, $T = 82$ °K	74, 128, 132
$O_2^+ + O_2 + Kr \rightarrow O_4^+ + Kr$	8, $T = 180$ °K	133
$O_2^+ + O_2 + H_2O \rightarrow O_4^+ + H_2O$	1.5	129
$O_2^+ + 2N_2 \rightarrow O_2^+ \cdot N_2 + N_2$	0.8	128
$O_2^+ + N_2 + He \rightarrow O_2^+ \cdot N_2 + He$	19, $T = 80$ °K	132
$O_2^+ + H_2 + He \rightarrow O_2^+ \cdot H_2 + He$	0.74, $T = 80$ °K	132
$O_2^+ + O_3 + He \rightarrow O_2^+ \cdot O_3 + He$	100, $T = 200$ °K	30
$O^+ + N_2 + He \rightarrow O^+ \cdot N_2 + He$	54, $T = 80$ °K	74
$NO^+ + 2NO \rightarrow NO^+ \cdot NO + NO$	5	134
$CO^+ + 2CO \rightarrow CO^+ \cdot CO + CO$	140	130, 135, 136
$CO_2^+ + 2CO_2 \rightarrow CO_2^+ CO_2 + CO_2$	320	130, 137
$C_2H_4^+ + 2C_2H_4 \rightarrow C_2H_4^+ \cdot C_2H_4 + C_2H_4$	2000	138
$O_2^+ + CO_2 + He \rightarrow O_2^+ \cdot CO_2 \cdot He$	23	132
$O_2^+ + N_2O + He \rightarrow O_2^+ \cdot N_2O + He$	52 $\}$ $T = 200$ °K	132
$O_2^+ + SO_2 + He \rightarrow O_2^+ \cdot SO_2 + He$	600	
$Mg^+ + O_2 + Ar \rightarrow Mg^+ \cdot O_2 + Ar$	2.5	139
$Ca^+ + O_2 + Ar \rightarrow Ca^+ \cdot O_2 + Ar$	6.6	139
$Fe^+ + O_2 + Ar \rightarrow Fe^+ \cdot O_2 + Ar$	1.0	139
$Na^+ + O_2 + Ar \rightarrow Na^+ \cdot O_2 + Ar$	0.2	140
$K^+ + O_2 + Ar \rightarrow K^+ \cdot O_2 + Ar$	< 0.2	140
$Li^+ + 2N_2 \rightarrow Li^+ \cdot N_2 + N_2$	2.0	141
$Li^+ + 2O_2 \rightarrow Li^+ \cdot O_2 + O_2$	1.1	225
$Na^+ + 2O_2 \rightarrow Na^+ \cdot O_2 + O_2$	0.1, $T = 193$ °K	142
$Li^+ \cdot N_2 + 2N_2 \rightarrow Li^+ \cdot (N_2)_2 + N_2$	2.2	141
$O_2^+ \cdot N_2 + N_2 + He \rightarrow O_2^+ \cdot (N_2)_2 + He$	10, $T = 80$ °K	132
$O_2^+ + O_2 + He \rightarrow O_4^+ + He$	5, $T = 80$ °K	132, 143
$O_2^+ + N_2 + He \rightarrow O_2^+ \cdot N_2 + He$	10, $T = 80$ °K	132
$O_4^+ + 2O_2 \rightarrow O_6^+ + O_2$	0.07; 1, $T = 200$ °K; 50, $T = 80$ °K	131
$O_4^+ + 2O_2 \rightarrow O_6^+ + O_2$	25, $T = 90$ °K	131
$NO^+ + 2N_2 \rightarrow NO^+ \cdot N_2 + N_2$	0.2	144
$NO^+ + 2O_2 \rightarrow NO^+ \cdot O_2 + O_2$	0.09	144
$NO^+ + 2CO_2 \rightarrow NO^+ \cdot CO_2 + CO_2$	24	144
$NO^+ + CO_2 + He \rightarrow NO^+ \cdot CO_2 + He$	4; 10, $T = 200$ K	143
$NO^+ + CO_2 + Ar \rightarrow NO^+ \cdot CO_2 + Ar$	25, $T = 200$ °K	143
$NO^+ + CO_2 + N_2 \rightarrow NO^+ \cdot CO_2 + N_2$	30, $T = 200$ °K	142
$NO^+ + 2NH_3 \rightarrow NO^+ \cdot NH_3 + NH_3$	54	145
$NH_4^+ + NH_3 + O_2 \rightarrow NH_4^+ \cdot NH_3 + O_2$	1800	146
$Na^+ + 2CO_2 \rightarrow Na^+ \cdot CO_2 + CO_2$	50	142
$Na^+ \cdot CO_2 + 2CO_2 \rightarrow Na^+ \cdot (CO_2)_2 + CO_2$	0.05	142
$Cs^+ + SO_2 + N_2 \rightarrow Cs^+ \cdot SO_2 + N_2$	30	34

TABLE VI. Rate constants of the process $A^+ + H_2O + M \rightarrow A^+ \cdot H_2O + M$.

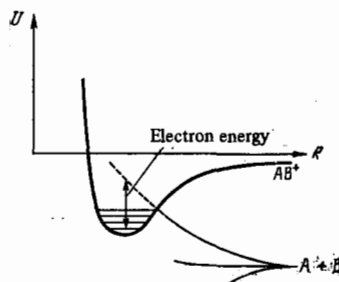| A^+	M	Rate constant, 10^{-29} cm^6/sec	Reference	A^+	M	Rate constant, 10^{-29} cm^6/sec	Reference
Na^+	He	0.47	147	Xe^+	He	1.5	148
Na^+	H_2O	10	147	NO^+	He	3.4	149, 150
K^+	He	0.26	147	NO^+	Ar	8.2	149, 150
K^+	H_2O	4.5	147	NO^+	N_2	15	149, 150, 214, 223
Cs^+	N_2	0.9	34	NO^+	O_2	8.6	149, 150
NO^+	NO	15	150–152	$H^+ \cdot H_2O$	Ar	4	154, 155
NO^+	H_2O	15	152, 153	$H^+ \cdot H_2O$	N_2	34	123, 127
$NO^+ \cdot H_2O$	He	30	149, 150	$H^+ \cdot H_2O$	O_2	27	127, 129
$NO^+ \cdot H_2O$	Ar	90	149, 150	$H^+ \cdot (H_2O)_2$	Ar	3.4	154, 155
$NO^+ \cdot H_2O$	N_2	110	25, 149, 150, 223, 214	$H^+ \cdot (H_2O)_2$	N_2	23	123
$NO^+ \cdot H_2O$	O_2	80	150	$H^+ \cdot (H_2O)_2$	O_2	15	127, 129
$NO^+ \cdot H_2O$	NO	110	150	$H^+ \cdot (H_2O)_3$	Ar	1.6	154, 155
$NO^+ \cdot (H_2O)_2$	He	36	149, 150	$H^+ \cdot (H_2O)_3$	N_2	24	123
$NO^+ \cdot (H_2O)_2$	Ar	140	149, 150	$H^+ \cdot (H_2O)_3$	O_2	20	127
$NO^+ \cdot (H_2O)_2$	N_2	180	25, 149, 150, 214, 223	$H^+ \cdot (H_2O)_4$	Ar	0.07	155
$NO^+ \cdot (H_2O)_2$	O_2	90	150	$H^+ \cdot (H_2O)_4$	O_2	9	127
$NO^+ \cdot (H_2O)_2$	NO	190	150	NO_2^+	N_2	50	42
$NO^+ \cdot (H_2O)_3$	He	28	149, 150	$NO_2^+ \cdot H_2O$	N_2	200	42
$NO^+ \cdot (H_2O)_3$	Ar	90	149, 150	O_2^+			25, 128, 132
$NO^+ \cdot (H_2O)_3$	N_2	140	149, 150	O_2^+	He	8.7	25, 128
$NO^+ \cdot (H_2O)_3$	O_2	80	150		N_2	27	127, 128
$NO^+ \cdot (H_2O)_3$	NO	190	150	O_2^+	O_2	20	133, 154
$H^+ \cdot H_2O$	He	12	128	O_2^+	Ar	17	25, 128, 154
				$O_2^+ \cdot H_2O$	O_2	13	127

FIG. 8. Terms of the excited molecule $A^* = + B$ and the molecular AB^+ in dissociative recombination. Upon colliding with the molecular ion, the electron is captured into an autoionizing state that breaks down into two atoms as the nuclei separate.

ion of a diatomic molecule. A peculiarity of recombination involving a cluster ion is that a system consisting of an electron and a cluster ion possesses many autoionizing states. Then we shall study the process of recombination of an electron and a cluster ion with very simple models that account for the complex nature of the ion and the effect that this has on the recombination process.

Let us estimate the dissociative-recombination coefficient α of an electron and a cluster ion, which is introduced via the relationship

$$\frac{dN_i}{dt} = -\alpha N_e N_i. \tag{18}$$

Here N_i is the density of ions, and N_e is the density of electrons. Upon entering the region where the cluster ion lies, the electron interacts strongly with it, with

TABLE VII. Formation rate constants of negative compound and cluster ions at thermal energies.

Process	Rate constant, 10^{-30} cm^6/sec	Reference
$O^- + 2O_2 \rightarrow O_3^- + O_2$	0.9	156–163
$O_3^- - 2O_2 \rightarrow O_4^- + O_2$	0.4	163–166
$O_3^- + O_2 + He \rightarrow O_4^- + He$	0.34, $T=200\,°K$	132
$O^- + CO_2 + He \rightarrow CO_3^- + He$	150; 260, $T=200\,°K$	44, 132
$O^- + 2CO_2 \rightarrow CO_3^- + CO_2$	90	161
$O_3^- + CO_2 + He \rightarrow CO_4^- + He$	47, $T=200\,°K$	132
$O_3^- + 2CC_2 \rightarrow CO_4^- + CO_2$	9	161
$O_3^- + CO_2 + O_2 \rightarrow CO_4^- + O_2$	20	161
$O^- + N_2 + He \rightarrow O^- \cdot N_2 + He$	1.3, $T=82\,°K$; 0.04, $T=200\,°K$	167, 132
$O_2^- + N_2 + He \rightarrow O_2^- \cdot N_2 + He$	0.04, $T=200\,°K$	132
$O^- + H_2O + O_2 \rightarrow O^- \cdot H_2O + O_2$	100	166
$O_2^- + H_2O + O_2 \rightarrow O_2^- \cdot H_2O + O_2$	160	163
$O_3^- + H_2O + O_2 \rightarrow O_3^- \cdot H_2O + O_2$	210	166
$O_3^- \cdot H_2O + H_2O + O_2 \rightarrow O_3^- \cdot (H_2O)_2 + O_2$	540	163
$NO^- + CO_2 + Ar \rightarrow NO^- \cdot CO_2 + Ar$	56	168, 169
$NO^- + N_2O + Ar \rightarrow NO^- \cdot N_2O + Ar$	7.8	168, 169
$NO_2^- + H_2O + NO \rightarrow NO_2^- \cdot H_2O + NO$	150	151
$NO_3^- + HNO_3 + N_2 \rightarrow NO_3^- \cdot HNO_3 + N_2$	$\geqslant 10^4$	42
$Br^- + 2Br_2 \rightarrow Br_3^- + Br_2$	29	170
$Cl^- + H_2O + NO \rightarrow Cl^- \cdot H_2O + NO$	120	151
$WO_3^- + O_2 + Ar \rightarrow WO_4^- + Ar$	10^3	171

consequent recombination. While accounting for this, we introduce the following model for the recombination of an electron and a cluster ion. Let us introduce the size R_0 of the cluster ion. We shall assume that recombination occurs as soon as the electron enters the region of radius R_0.

Upon using the classical law of motion of the electron, we get the following relationship between the distance of least approach r_{min} of the electron and the ion and the impact parameter ρ of the collision with account taken of the nucleonic interaction between them[73]:

$$\frac{\rho^2}{r_{min}^2} = 1 + \frac{e^2}{r_{min}\varepsilon},$$

Here ε is the energy of the electron. We find from this the cross-section of the studied process, which includes all collisions having a distance of closest approach that doesn't exceed R_0:

$$\sigma = \pi\rho^2 = \pi R_0^2 \left(1 + \frac{e^2}{R_0\varepsilon}\right). \tag{19}$$

We have defined the cross-section for collisions of an electron and an ion in which the distance of closest approach is less than R_0. According to the studied model, it is the recombination cross-section of the electron and the cluster ion.

In the low-energy limit where $\varepsilon \ll e^2/R_0$, we find from this the dissociative-recombination coefficient of the electron and the cluster ion, which is[79]

$$\alpha = \overline{v\sigma} = \frac{2\sqrt{2\pi}\,R_0 e^2}{\sqrt{mT}}. \tag{20}$$

Here the bar denotes averaging over the velocities of electrons having a Maxwellian velocity distribution function, and T is the temperature of the electrons.

Now we shall determine the validity of the classical law of motion of the electron that we have used for this estimate. Using the classical law of motion is warranted if the fundamental contribution to the recombination cross-section comes from collisions that have large values of the collision moment l. In the studied case, the characteristic values of the collision moment are

$$l \sim \frac{m\rho v}{\hbar} \sim \frac{m\sqrt{\sigma(\varepsilon/m)}}{\hbar} \sim \sqrt{\frac{R_0}{a_0}}.$$

Here $a_0 = \hbar^2/me^2$ is the Bohr radius. The characteristic

size R_0 of the cluster ion considerably exceeds the Bohr radius. Therefore, although the characteristic collision moment l amounts to several units, we do not arrive at a contradiction if we treat the derived expression for the recombination coefficient as an estimate.

Let us approach the studied process from somewhat different standpoints. We shall treat the dissociative recombination of the electron and the cluster ion as resulting from capture of the electron by the cluster ion to form an autoionizing state of the interacting system. This autoionizing state has a long lifetime, in line with the large number of degrees of freedom, and its decomposition gives rise to neutral particles since their statistical weight is greater than that of the electron and the cluster ion. Then the recombination cross-section is determined by the Breit–Wigner formula,[172] which we can represent in this case in the form

$$\sigma_{rec} = \frac{\pi \hbar^2}{2m\varepsilon} \sum_h \left\langle \frac{\Gamma_{ih}\Gamma_{eh}}{(\varepsilon - \varepsilon_h)^2 + (\Gamma_h^2/4)} \right\rangle. \tag{21}$$

Here ε is the energy of the electron, Γ_k and ε_k are the width of the k-th autoionizing level and its excitation energy, Γ_{ek} is the width corresponding to elastic scattering, and Γ_{ik} is the width of the autoionizing level that corresponds to the inelastic decomposition process. The given quantities depend on the configuration of nuclei in the cluster ion, the angle brackets denote averaging over the configuration of the nuclei in the cluster ion, and the summation is performed over all possible reaction channels.

Let us write Eq. (21) in the form

$$\sigma_{rec} = \frac{2\pi \hbar^2}{m\varepsilon} n(\varepsilon), \tag{22}$$

where

$$n(\varepsilon) = \frac{1}{4} \sum_h \left\langle \frac{\Gamma_{eh}\Gamma_{ih}}{(\varepsilon - \varepsilon_h)^2 + (1/4)\,\Gamma_h^2} \right\rangle.$$

Whenever the width Γ_k of the autoionizing level is large enough, the value of n does not depend on the energy of the autoionizing state. When the width of the inelastic channel is small ($\Gamma_{ik} \ll \Gamma_{ek}$), the total width Γ_k of the autoionizing level coincides with the elastic width Γ_{ek}. Then the quantity

$$\frac{1}{4} \left\langle \frac{\Gamma_{eh}\Gamma_{ih}}{(\varepsilon - \varepsilon_h)^2 + (1/4)\,\Gamma_h^2} \right\rangle = \left\langle \frac{\Gamma_{ih}}{\Gamma_h} \right\rangle$$

coincides with the probability of recombination of the electron via the given channel, while the quantity

$$n(\varepsilon) = \sum_h \left\langle \frac{\Gamma_{ih}}{\Gamma_h} \right\rangle$$

is the sum of these probabilities, or the effective number of autoionizing states that lead to recombination.

Thus we have used two approaches in estimating the dissociative-recombination cross-section of a cluster ion and an electron. We assumed in the first of these approaches that some region exists within the cluster ion in which the electron and the cluster ion interact

strongly. Entry of an electron into it leads to recombination of the electron and the ion. We assumed in the second case that a certain number of autoionizing states of the electron and the cluster ion have a large width of the autoionizing levels. These autoionizing states make possible the strong interaction of the electron and the ion in recombination. A comparison of the dissociative-recombination cross-sections obtained from these models under the assumption that the energy of the electron is small and that the electron and the ion interact strongly in certain autoionizing states shows the analogy of the formulas for the dissociative-recombination cross-sections in the given cases. Hence we can conclude that the dissociative-recombination cross-section is inversely proportional to the energy of the incident electron when the electron and the cluster ion interact strongly. Here the quantity R_0 in the first model is equivalent to the quantity $2a_0 n$ in the second model.

We get from Eq. (22) the following expression for the dissociative-recombination coefficient:

$$\alpha = \frac{4\sqrt{2\pi}\,\hbar^2 \bar{n}}{m\sqrt{mT}}. \tag{23}$$

Here the superior bar denotes averaging over the electron energies. When the electron and the cluster ion interact strongly, the quantity $\bar{n}$ does not depend on the temperature of the electrons,[3] so that the dissociative-recombination coefficient of the electron and the cluster ion is inversely proportional to the square root of the temperature. At room temperature Eq. (23) gives

$$\alpha \approx 2\cdot 10^{-6}(\text{cm}^3/\text{sec})\,\bar{n}. \tag{24}$$

Since $\bar{n} \sim 1$, the dissociative-recombination coefficient of the electron and the cluster ion is of the order of magnitude of 10^{-6} cm^3/sec.

Let us proceed to analyzing the experimental data on the dissociative recombination of an electron and a cluster ion. We shall not take up the methods of measuring dissociative-recombination coefficients, which have been discussed in sufficient detail in the reviews.[79,173,174] We note only that the beam method of measuring dissociative-recombination cross-sections,[175–184] in which recombination is studied in interacting beams of ions and electrons, has become widespread in recent years. For simple ions such as O_2^+ and NO^+, the measured dissociative-recombination cross-section[184] has a resonance structure. The dissociative-recombination cross-section[183] for the cluster ion H_3^+ smoothly varies with the energy of the electron, and in the studied energy region from 0.38 to 4

---

[3] We note that when the electron and the cluster ion interact weakly, and the width of the autoionizing level is small in comparison with its characteristic excitation energy, the quantity $\bar{n}$ depends on the temperature as $\bar{n} \sim 1/T$, or more weakly. However, in this case, the dissociative-recombination coefficient is appreciably smaller, so that if there is a single autoionizing level, $\bar{n} \ll 1$. In particular, if ε_i and $\Gamma_i \ll T$, we get from Eqs. (21) and (22) for a single autoionizing level: $\bar{n} = \pi \Gamma/2T$.

TABLE VIII. Dissociative-recombination coefficient for electrons and cluster ions at thermal energies.

Cluster ion	O_2^+	N_2^+	$NO^+ \cdot NO$	He_2^+	H_2^+	H_3^+	NH_4^+
Dissociative-recombination coefficient, 10^{-6} cm³/sec	2.0, $T=200$ °K	2.0	1.7	3.4, $T=80$ °K	0.23	3.6, $T=205$°K	1.8
$\bar{n}$ Reference	0.8 [133, 185]	1 [185-188]	0.8 [189]	0.9 [190]	0.12 [191]	1.5 [191]	0.9 [192]

Cluster ion	$Na^+ \cdot O_2$	$Na^+ \cdot CO_2$	$H^+ \cdot H_2O$	$H^+ \cdot (H_2O)_2$	$H^+ \cdot (H_2O)_3$	$H^+ \cdot (H_2O)_4$	$H^+ \cdot (H_2O)_5$	$H^+ \cdot (H_2O)_6$
Dissociative-recombination coefficient, 10^{-6} cm³/sec	5	5	1.2	2.2	3.8	4.9	6, $T=205$°K	10, $T=205$°K
$\bar{n}$ Reference	2.5 [193]	2.5 [193]	0.6 [194, 195]	1.1 [194]	1.9 [194]	2.4 [194]	2.5 [194]	4.1 [194]

FIG. 10. Dependence of the dissociative-recombination coefficient of an electron with an He_3^+ ion on the electron temperature when the gas temperature is 80 °K. [190]

the given process based thereon yield a recombination cross-section σ_{rec} inversely proportional to the electron energy ε ($\sigma_{rec} \sim 1/\varepsilon$) and a recombination coefficient α that depends on the temperature T as $\alpha \sim T^{-1/2}$. Here the dissociative-recombination cross-section of an electron and a complex ion acquires a value of the order of magnitude of $\alpha \sim 10^{-6}$ cm³/sec at thermal energies. On the average, these rules are confirmed by experiment.

5. ION-MOLECULE REACTIONS INVOLVING CLUSTER IONS

The processes in which cluster ions participate involve formation of an intermediate long-lived complex. Correspondingly, the ion-molecule exchange reaction follows the scheme:

$$A^+ - B + C \rightarrow (B - A^+ - C)^* \rightarrow B + A^+ - C. \qquad (25)$$
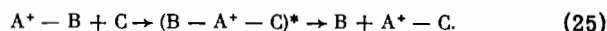
Here the lifetime of the intermediate long-lived complex is long in comparison with the time of collision of the particles. Upon accounting for the mechanism of the ion-molecule reactions that involve a cluster ion, we get the following expression for the rate constant of the process (25):

$$k = k_{capture} \zeta. \qquad (26)$$

Here $k_{capture}$ is the rate constant for capture of the molecule C by the cluster ion, and ζ is the probability that the intermediate long-lived complex will decay via the studied channel.

The capture rate constant $k_{capture}$ in Eq. (26) is of the order of the polarization-capture rate constant of the molecule C with the cluster ion, though differing from this quantity because the cluster ion is rather large, and its interaction with the incident molecule differs from a polarization interaction. If we assume that $\zeta \sim 1$, we find that an endothermic reaction involving a cluster ion is characterized by a rate constant of the order of the rate constant for polarization capture of the complex ion by the molecule, which is about 10^{-10}–10^{-9} cm³/sec.

eV, it is well approximated by the formula $\sigma_{rec} = 10$ Å² $\varepsilon^{-0.87}$, where the electron energy ε is given in electron-volts. Processing of this relationship by Eq. (22) gives the value $n = 0.19$ at the lower energy value $\varepsilon = 0.38$ eV. According to beam measurements, [224] the recombination cross-section of an electron with the cluster ion $H^+ \cdot H_2O$ at low energies is well approximated by $\sigma = 60$ Å² $\cdot \varepsilon^{-1}$. (The electron energy ε is in electron-volts.) This agrees with Eqs. (19) and (22). The mean number of autoionizing states that participate in recombination as calculated from (22) is $n = 1.2$ according to this relationship.

Table VIII gives the experimental values of the dissociative-recombination coefficients for an electron and a set of cluster ions. Analysis of these results shows that the effective number $\bar{n}$ of autoionizing states that take part in the studied process in a system that consists of a cluster ion and an electron is of the order of unity. Figures 9–11 show the temperature-dependence of dissociative-recombination coefficients involving ions.

Analysis of the obtained results on dissociative recombination of an electron and a cluster ion that are given in Table VIII and in Figs. 9–11 yields the following conclusions concerning this process. Dissociative recombination results from strong interaction of the electron and the cluster ion. The different models of
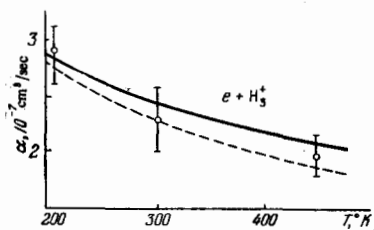

FIG. 9. Dissociative recombination of an electron with the H_3^+ ion. Circles—experiments[191]: the solid curve is obtained from the extrapolation relationship for the dissociative-recombination cross section $\sigma \sim \varepsilon^{-0.87}$, as extracted from processing the data of beam experiments[183]: the dotted curve corresponds to the relationship $\sigma \sim T^{-1/2}$.
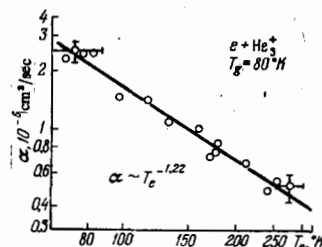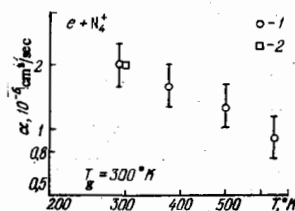

FIG. 11. Dependence of the dissociative-recombination coefficient of an electron with an N_4^+ ion on the electron temperature when the gas temperature is 300 °K. 1—[187], 2—[188].

Process	Polarization-capture rate constant, 10^{-10} cm^3/sec	Rate constant of the process, 10^{-10} cm^3/sec	Reference
$O_4^+ \cdot N_2 + O_2 \rightarrow O_4^+ \cdot O_2 + N_2$	6.4	0.5, $T = 80$ °K	23
$O_4^+ \cdot O_2 + N_2O \rightarrow O_4^+ \cdot N_2O + O_2$	7.8	2.5, $T = 200$ °K	23
$O_4^+ \cdot O_2 + SO_2 \rightarrow O_4^+ \cdot SO_2 + O_2$	8.0	4.2; 8.2, $T = 200$ °K	23
$O_4^+ \cdot N_2O + SO_2 \rightarrow O_4^+ \cdot SO_2 + N_2O$	7.7	5.6, $T = 200$ °K	23
$O_4^+ \cdot N_2O + H_2O \rightarrow O_4^+ \cdot H_2O + N_2O$	7.4	$\Big\} > 1$	23
$O_4^+ \cdot SO_2 + H_2O \rightarrow O_4^+ \cdot H_2O + SO_2$	7.2		
$O_4^+ \cdot H_2O + H_2O \rightarrow O_4^+ \cdot H_2O + O_2$	7.5	18	25, 127
$O_4^+ \cdot H_2O + H_2O \rightarrow O_4^+ \cdot H_2O \cdot OH + O_2$	7.3	14	25, 127
$H^+ \cdot H_2O \cdot OH + H_2O \rightarrow H^+ \cdot (H_2O)_2 + OH$	8.1	21	25, 127
$H_3^+ + H_2O \rightarrow H^+ \cdot H_2O + H_2$	18	29	167
$NO^+ \cdot H_2O + NH_3 \rightarrow NH_4^+ + HNO_2$	10	10	29
$NO^+ \cdot (H_2O)_2 + NH_3 \rightarrow NH_4^+ \cdot H_2O + HNO_2$	9.6	10	29
$NO^+ \cdot (H_2O)_3 + NH_3 \rightarrow NH_4^+ \cdot (H_2O)_2 + HNO_2$	9.4	10	29
$NO^+ \cdot (H_2O)_3 + H_2O \rightarrow H^+ \cdot (H_2O)_3 + HNO_2$	7.3	0.7	25, 127, 153
$NO^+ \cdot N_2 + CO_2 \rightarrow NO^+ \cdot CO_2 + N_2$	7.6	10	143
$NO^+ \cdot CO_2 + H_2O \rightarrow NO^+ \cdot H_2O + CO_2$	7.4	10	144
$O_2^- \cdot O_2 + H_2O \rightarrow O_2^- \cdot H_2O + O_2$	7.5	1	23
$O^- \cdot O_2 + CO_2 \rightarrow O_3^- \cdot CO_2 + O_2$	7.4	4.3	196
$O_3^- \cdot O_2 + NO \rightarrow O_3^- \cdot NO + O_2$	6.8	2.5	196
$O_3^- \cdot O_2 + N_2 \rightarrow O_3^- \cdot N_2 + O_2$	7.0	< 0.1	23
$O_3^- \cdot O_2 + CO \rightarrow O_3^- \cdot CO + O_2$	7.4	< 0.2	23
$O_3^- \cdot O_2 + N_2O \rightarrow O_3^- \cdot N_2O + O_2$	7.8	< 0.01	23
$O_3^- \cdot H_2O + CO_2 \rightarrow O_3^- \cdot CO_2 + H_2O$	7.8	5.8	23
$O_3^- \cdot H_2O + NO \rightarrow O_3^- \cdot NO + H_2O$	6.5	3.1	23
$O_3^- \cdot CO_2 + NO \rightarrow O_3^- \cdot NO + CO_2$	6.3	4.8	196

Table IX gives experimental values for the rate constants of ion-molecule reactions in which cluster ions participate. As we see, the order of magnitude of the rate constants for the endothermic reactions agrees with that of the given quantity. Moreover, Table IX gives for comparison the values for the polarization-capture rate constants of a cluster ion with a molecule:

$$k_{pol} = 2\pi \sqrt{\frac{\beta e^2}{\mu}}. \qquad (27)$$

Here β is the polarizability of the molecule, and μ is the reduced mass of the colliding particles. Upon analyzing the data of Table IX, we can conclude that the rate constant of ion-molecule reactions involving cluster ions proves in most of the studied cases to be of the order of magnitude of the polarization-capture rate constant, which is about 10^{-9} cm^3/sec. Thus any approach between a cluster ion and a molecule culminates in chemical reaction with a probability near unity, of course, if such a reaction is energetically favorable. This allows us to estimate the rate constant of an endothermic ion-molecule reaction that involves cluster ions as being of the order of 10^{-9} cm^3/sec.

6. CLUSTER IONS IN THE UPPER ATMOSPHERE OF THE EARTH

The upper atmosphere of the Earth at altitudes below 100 km is a suitable milieu for formation of cluster ions. The temperature in this region of the atmosphere is appreciably below room temperature. The ultraviolet radiation of the Sun is absorbed in the higher layers of the atmosphere, and the ions that are produced at higher altitudes penetrate into these layers of the atmosphere. Moreover, molecules like H_2O and CO_2, which easily combine into clusters, occur here in small

amount. Therefore, although the atmospheric pressure at these altitudes is small, cluster ions of various types are formed here after relatively long times.

The most favorable conditions for formation of cluster ions arise in the so-called D layer, where the temperature of the upper atmosphere is minimal, amounting to about 190 °K. The height of this layer above the Earth's surface is 80 km, and the air pressure is about 10^{-5} atm. An entire cycle of processes occurs in this region of the atmosphere whereby the simple ions that are formed in the higher layers of the atmosphere are converted into compound and cluster ions. The individual details of the overall pattern of this type of conversions can be reconstructed from laboratory measurements of the rate constants of the individual processes.

At altitudes above 100 km, the fundamental types of positive ions are NO^+ and O_2^+,[197-200] the concentration of O_2^+ ions being severalfold smaller than that of NO^+. As they migrate into lower layers of the atmosphere, these ions undergo a chain of transformations, so that the fundamental types of ions at 80 km altitude are $H^+ \cdot (H_2O)_2$ and $H^+ \cdot H_2O$.[7,199,215] Upon using the rate constants of the different processes as measured under laboratory conditions, we can draw up an overall pattern of the processes that occur at each altitude, and thus describe the chemistry of the ions at a given altitude. This approach has been undertaken repeatedly.[201-206] Figure 12 gives a diagram of the processes that occur in the D layer of the atmosphere involving positive ions, while Fig. 13 illustrates those in which negative ions participate. As measurements have shown,[9,207] the fundamental types of negative ions at an altitude near 80 km (the negative charge at this altitude involves negative ions) are CO_3^- and CO_4^-. The ions Cl^-, O_2^-, HCO_3^-, NO_3^-, $NO_3^- \cdot HNO_3$, and $O_2^- \cdot (H_2O)_2$ are observed in lesser amount.

More thorough laboratory studies of the processes that describe the chemistry of the ions in the upper atmosphere permit us, on the one hand, to alter somewhat the pattern of processes shown in Figs. 12 and 13, which is correct in general outline. On the other hand, they create contradictions that can lead to fundamental
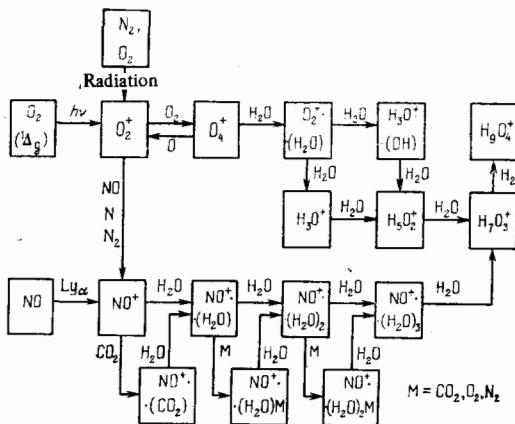

FIG. 12. Diagram of the processes that involve positive ions in the D layer of the upper atmosphere of the Earth.[201,202]
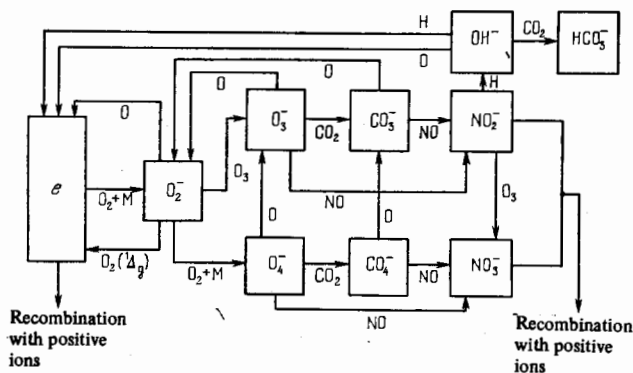
FIG. 13. Diagram of the processes that involve negative ions in the D layer of the upper atmosphere of the Earth. [201,202]

FIG. 15. Photolysis cross section of the negative ions $CO_3^- \cdot H_2O$ and CO_3^-.

changes. Let us take up the nature of the transformations of the positive ion NO^+. Analysis of the laboratory measurements[28] has shown that the cluster ions $NO^+ \cdot H_2O$ are formed from NO^+ ions in the D layer of the Earth's atmosphere via the cluster ion $NO^+ \cdot N_2$. Figure 14 shows the possible channels for formation of this ion and the times for the corresponding processes as calculated from laboratory measurements. This diagram implies that conversion of the NO^+ ion into the complex ion $NO^+ \cdot H_2O$ takes about a half a minute. Further conversion of the $NO^+ \cdot H_2O$ ions into the more complex ions $NO^+ \cdot (H_2O)_n$ in the D layer of the atmosphere takes a time of the order of 10^3 seconds, as can be found from the data of Table VI. It is hard to understand the next step, which consists in conversion from complex ions of the type $NO^+ \cdot (H_2O)_n$ into complex ions of the series $H^+ \cdot (H_2O)_m$, which are the fundamental types of positive ions in the D layer of the atmosphere. The trouble is that it is hard to choose reactions on the basis of laboratory measurements whereby a conversion to the studied types of ions can be realized in reasonable times.

Apparently this contradiction can be explained by the fact that the upper atmosphere of the Earth is not at equilibrium. The radiation of the Sun and the processes that occur in the upper atmosphere give rise to particles in vibrationally and electronically excited states.

For example, the density of vibrationally excited oxygen molecules $O_2(^1\Delta_g)$ at altitudes 50−80 km proves to be of the order of 10^{10} cm^{-3}. [198,208−210] That is, it is of the same order as the density of water molecules. Participation of excited particles in reactions can lead to
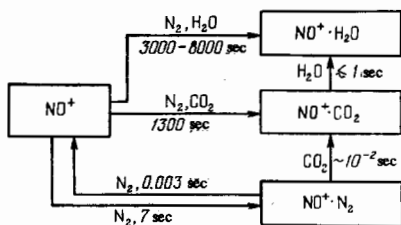
new channels for processes that differ from those that occur under laboratory conditions.

In addition to chemical reactions that involve participation of cluster ions, absorption of solar radiation by the cluster ions can play an important role in the upper atmosphere of the Earth. These processes have begun to be studied under laboratory conditions. There are measurements of the photolysis cross-sections of the negative cluster ions $O^- \cdot CO_2$, $OH^- \cdot CO_2$, and $O^- \cdot CO_2 \cdot H_2O$, [39,211,216,217] the cluster ions O_3^- and O_4^-, [216−220] and also the positive cluster ions N_4^+ [221] and $O_2^+ \cdot H_2O$. [222] For almost all of the studied cluster ions, the photolysis cross-section in the optical region of the spectrum is of the order of 10^{-18} cm^2. [4] Figure 15 shows as an example the photolysis cross-sections of the ions $O^- \cdot CO_2$ and $O^- \cdot CO_2 \cdot H_2O$. [217]

When the photolysis cross-section of cluster ions is of the order of 10^{-18} cm^2, their characteristic decay time in the upper atmosphere under the action of solar radiation proves to be of the order of 10 sec. This is several orders of magnitude smaller than the characteristic time of passage of ions through the D layer of the atmosphere. Thus the solar radiation is essentially included in the conversion processes among the types of ions, so that the type of cluster ions in the upper atmosphere can differ from day to night, i.e., with or without solar radiation in the atmosphere.

Cluster ions can also exist in the atmospheres of other planets of the solar system. The farther a planet lies from the Sun, the lower its temperature, and thus the greater the portion of the atmosphere of the planet where charged particles can be bound into cluster ions. However, the atmospheres of the other planets have not been studied fully enough to permit discussing their properties in connection with cluster ions.

Thus the upper atmosphere of the Earth is the most studied object where cluster ions are produced rather efficiently. Here the information on the cluster ions and on the processes that involve them that we possess from laboratory measurements permits us to explain the fundamental laws involving the cluster ions in the

FIG. 14. Conversions of the ion NO^+ and switching times in the D layer of the upper atmosphere of the Earth.

_____

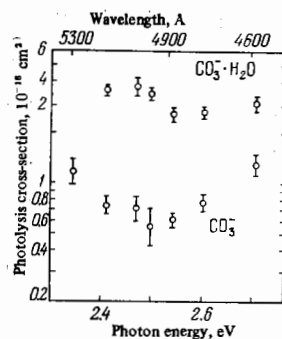[4] The N_4^+ ion is an exception in this respect among the studied ions. It is not destroyed by photons in the wavelength region around 6000 Å. [221] This can be explained by the large bond-dissociation energy for this ion (see Table I).

upper atmosphere. Yet the more detailed data of observations of cluster ions in the upper atmosphere cannot be explained on the basis of the currently existing information on cluster ions. Hence the problem involving the behavior of cluster ions in the upper atmosphere of the Earth requires more thorough studies.

7. CONCLUSION

As this review has implied, the cluster ions are a distinctive object whose study belongs to the boundary region between plasma physics and chemical physics. Enough information has been accumulated in this field to get a general picture of the properties of the cluster ions and of the processes in which they participate. We should note that the studies of cluster ions have been supported thus far mainly by the study of the upper atmosphere of the Earth. The bulk of the information presented in this review has been obtained from these studies. However, the current growth of physics of weakly-ionized gases at low temperatures may become a new impetus for expanding the studies on cluster ions, since cluster ions are formed rather efficiently under conditions of a low-temperature weakly ionized gas. This will require new information on the cluster ions, and will expand our concepts on their properties.

[1]J. A. Hornbeck, Phys. Rev. 84, 615 (1951).
[2]C. P. de Vries, H. J. Oskam, Phys. Lett. A29, 299 (1969).
[3]B. M. Smirnov, Atomnye stolknoveniya i élementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in a Plasma), Atomizdat, M., 1968.
[4]H. H. Brömer, K. Fette, Phys. Lett. A28, 127 (1968).
[5]R. N. Varney, Phys. Rev. 174, 165 (1968).
[6]D. K. Bohme et al., J. Chem. Phys. 51, 863 (1969).
[7]R. S. Narcisi and A. D. Bailey, J. Geophys. Res. 70, 3787 (1965).
[8]R. S. Narcisi and W. Roth, Adv. Electron. and Electr. Phys. 29, 79 (1970).
[9]F. Arnold et al., J. Atmos. and Terr. Phys. 33, 1169 (1971).
[10]R. Clampitt and D. K. Jefferies, Nature 226, 141 (1970).
[11]R. Clampitt, in: 10th of Intern. Conference on Ionization Phenomena in Gases. Survey papers, Oxford, 1971, p. 43.
[12]J. L. Franklin, V. H. Dibeler, R. M. Reese, and M. Krauss, J. Amer. Chem. Soc. 80, 298 (1958).
[13]M. Saporoschenko, Phys. Rev. A139, 352 (1965).
[14]R. N. Varney, Phys. Rev. 89, 708 (1953); J. Chem. Phys. 31, 1314 (1959).
[15]R. N. Varney, Phys. Rev. 174, 165 (1968).
[16]J. D. Payzant and P. Kebarle, J. Chem. Phys. 53, 4723 (1970).
[17]J. H. Yang and D. C. Conway, ibid. 40, 1729 (1964).
[18]D. A. Durden, P. Kebarle, and A. Good, J. Chem. Phys. 50, 805 (1969).
[19]D. C. Conway and G. S Janik, ibid. 53, 1859 (1970).
[20]J. Dutton and P. Howells, J. Phys. B1, 1160 (1968).
[21]B. M. Smirnov and S. G. Shchegol'kov, Teplofiz. Vys. Temp. 10, 512 (1976).
[22]G. S. Janik and D. C. Conway, J. Phys. Chem. 71, 823 (1967).
[23]N. G. Adams et al., J. Chem. Phys. 52, 3133 (1970).
[24]D. C. Conway, ibid., p. 2689.
[25]F. C. Fehsenfeld, M. Mosesman, and E. E. Ferguson, ibid. 55, 2115 (1971).
[26]J. C. Howard et al., ibid. 47, 5325 (1967)[sic!].
[27]N. G. Adams et al., Bull. Am. Phys. Soc. 15, 420 (1970).

[28]R. Johnsen, C. M. Huang, and M. A. Biondi, J. Chem. Phys. 63, 3374 (1975).
[29]F. C. Fehsenfeld and E. E. Ferguson, ibid. 54, 439 (1971).
[30]F. C. Fehsenfeld, ibid. 61, 1588 (1974).
[31]U. A. Arifov et al., Khimiya vys. énergii 5, 81 (1971).
[32]J. T. J. Huang, M. E. Schwartz, and G. V. Pfeiffer, J. Chem. Phys. 56, 755 (1972).
[33]M. T. Elford and H. B. Milloy, Austral. J. Phys. 27, 795 (1974).
[34]L. G. McKnight and J. M. Sawina, J. Chem. Phys. 57, 5156 (1973).
[35]P. L. Patterson, ibid. 48, 3625 (1968).
[36]R. H. Wood and L. A. D. Orazio, ibid. 69, 2562 (1965).
[37]D. C. Conway, ibid. 36, 2549 (1962).
[38]R. E. Voshall, J. L. Pack, and A. V. Phelps, ibid. 43, 1990 (1965).
[39]P. C. Cosby et al., in: 4th Int. Conference on Atomic Physics, Heidelberg, 1974.
[40]J. L. Pack and A. V. Phelps, J. Chem. Phys. 45, 4316 (1966).
[41]C. L. Chen and P. J. Chantry, Bull. Amer. Phys. Soc. 15, 418 (1970).
[42]F. C. Fehsenfeld et al., J. Chem. Phys. 63, 2835 (1975).
[43]J. D. Payzant, A. J. Cunningham, and P. Kebarle, Can. J. Chem. 50, 2230 (1972).
[44]V. I. Vedeneev et al., Énergii razyva khimicheskikh svyazeĭ (Dissociation Energies of Chemical Bonds). Handbook, Izdvo AN SSSR, M., 1962 (Engl. Transl., Bond Energies, Ionization Potentials, and Electron Affinities, St. Martin's Press, New York, 1966).
[45]H. U. Mittman et al., Zs. Naturforsch 26a, 1122 (1971).
[46]W. A. Chupka and M. E. Russel, J. Chem. Phys. 49, 5426 (1968).
[47]A. E. Rocke et al., ibid. 55, 5480 (1971).
[48]H. U. Mittman et al., Zs. Naturforsch 26a, 1112 (1971).
[49]H. U. Mittman et al., ibid., S. 1282.
[50]W. A. Chupka, M. E. Russel, and K. Refaey, J. Chem. Phys. 48, 1518 (1968).
[51]J. A. Burt et al., ibid. 52, 6062 (1970).
[52]M. E. Schwartz and L. J. Schaad, ibid. 47, 5325 (1967).
[53]T. W. Shannon and A. G. Harrison, ibid. 43, 4201 (1965).
[54]S. N. Foner and N. L. Hundson, ibid. 36, 268 (1962).
[55]A. G. Harrison, ibid. 50, 1043 (1969).
[56]C. S. Matthews and P. Warneck, ibid. 51, 854 (1969).
[57]F. S. Kohout and F. W. Lampe, ibid. 45, 1074 (1966).
[58]S.-L. Chong, R. A. Myers Jr., and J. L. Franklin, ibid. 56, 2427 (1972).
[59]J. L. Beauchamp and S. E. Buttrill Jr., ibid. 48, 1783 (1968).
[60]M. A. Haney and J. L. Franklin, ibid. 50, 2028 (1969).
[61]W. A. Chupka and J. Berkowitz, ibid. 54, 4257 (1971).
[62]I. Dzidic and P. Kebarle, J. Phys. Chem. 74, 1466 (1970).
[63]M. Arshadi, R. Yamdagni, and P. Kebarle, ibid., p. 1475.
[64]M. Arshadi and P. Kebarle, ibid., p. 1483.
[65]E. Clementi and H. Popkie, J. Chem. Phys. 57, 1077 (1972).
[66]L. G. McKnight and J. M. Sawina, ibid. 57, 5156 (1972).
[67]I. N. Tang and A. W. Castleman, ibid., p. 3638.
[68]I. N. Tang and A. W. Castleman, ibid. 60, 3981 (1974).
[69]I. Popescu and R. Von der Heide, Zs. Phys. 220, 337 (1969).
[70]G. Hortig and M. Muller, ibid. 221, 119.
[71]J. J. Thomson, Phil. Mag. 47, 334 (1924).
[72]L. B. Loeb, Basic Processes in Gaseous Electronics, Univ. of California Press, Berkeley, 1973.
[73]L. D. Landau and E. M. Lifshits, Mekhanika (Mechanics), Fizmatgiz, M., 1958. (Engl. Transl., Pergamon Press, Oxford, 1960).
[74]D. K. Bohme et al., J. Chem. Phys. 51, 863 (1969).
[75]D. L. Bunker, ibid. 32, 1001 (1960).
[76]J. Keck, ibid., p. 1035.
[77]R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, ibid. 50, 5163 (1969).
[78]P. A. Whitlock, J. J. Muckerman, and R. E. Roberts,

Chem. Phys. Lett. **16**, 460 (1972).

[79] B. M. Smirnov, Iony i vozbuzhdennye atomy v plazme (Ions and Excited Atoms in a Plasma), Atomizdat, M., 1942.

[80] E. W. McDaniel, V. Čermák, A. Dalgarno, E. E. Ferguson, and L. Friedman, Ion-Molecule Reactions, Wiley-Interscience, New York, 1970.

[81] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

[82] C. B. Kretschmer and H. L. Peterson, J. Appl. Phys. **34**, 3209 (1963).

[83] H. J. Oskam and V. L. Mittelstadt, Phys. Rev. **132**, 1435 (1963).

[84] R. Hackam and J. J. Lennon, Proc. Roy. Soc. **84**, 133 (1963).

[85] F. E. Niles and W. W. Robertson, J. Chem. Phys. **40**, 3568 (1964).

[86] E. C. Beaty and P. L. Patterson, Phys. Rev. **A137**, 346 (1965).

[87] G. F. Sauter, R. A. Gerber, and H. J. Oskam, Phys. Lett. **19**, 656 (1966).

[88] D. Smith and M. J. Copsey, J. Phys. **B1**, 650 (1968).

[89] H. J. Oskam, Phillips Res. Rept. **13**, 401 (1958).

[90] G. G. Morgan, F. Llewellyn Jones, and D. K. Davies, Proc. Phys. Soc. **86**, 403 (1965).

[91] G. G. Dolgov-Saveljev et al., in: Proc. of 9th Intern. Conference on Ionization Phenomena in Gases, Bucharest, 1969, p. 9.

[92] E. C. Beaty and P. L. Patterson, in: Proc. of 6th Intern. Conference on Ionization Phenomena in Gases, v. 1, Paris, 1964, p. 311.

[93] R. A. Gerber and M. A. Gusinov, Phys. Rev. **A4**, 2027 (1971).

[94] E. C. Beaty and P. L. Patterson, ibid. **170**, 116 (1968).

[95] D. Smith and P. R. Cromey, J. Phys. **B1**, 638 (1968).

[96] J. P. Gaur and L. M. Chanin, Phys. Rev. **182**, 167 (1969).

[97] A. P. Vitols and H. J. Oskam, ibid. **A5**, 2618 (1972).

[98] O. J. Orient, Chem. Phys. Lett. **23**, 579 (1973).

[99] J. C. Cronin and M. C. Sexton, Brit. J. Appl. Phys. **1**, 889 (1967).

[100] J. L. Gilkinson, H. Held, and L. M. Chanin, J. Appl. Phys. **40**, 2350 (1969).

[101] V. B. Brodskiĭ and N. B. Kolokolov, Zh. Tekh. Fiz. **40**, 496 (1970) [Sov. Phys. Tech. Phys. **15**, 383 (1970)].

[102] A. K. Bhattacharya, J. Appl. Phys. **41**, 1707 (1970).

[103] W. F. Liu and D. C. Conway, J. Chem. Phys. **62**, 3070 (1975).

[104] A. K. Bhattacharya, Phys. Rev. **A1**, 1196 (1970).

[105] D. Smith, A. G. Dean, and I. C. Plumb, J. Phys. **B5**, 2134 (1972).

[106] A. P. Vitols and H. J. Oskam, Phys. Rev. **A8**, 1860 (1973).

[107] R. S. Bergman and L. M. Chanin, in: Proc. of 10th Intern. Conference on Ionization Phenomena in Gases, Oxford, 1971, p. 6.

[108] M. A. Biondi, Phys. Rev. **90**, 730 (1953).

[109] G. E. Veatch and H. J. Oskam, ibid. **A2**, 1422 (1970).

[110] G. E. Veatch and H. J. Oskam, ibid. **A1**, 1498.

[111] C. L. Chen, ibid. **131**, 2550 (1963).

[112] N. G. Adams, D. K. Bohme, and E. E. Ferguson, J. Chem. Phys. **52**, 5101 (1970).

[113] F. C. Fehsenfeld and E. E. Ferguson, J. Geophys. Res. **74**, 2217 (1969).

[114] F. C. Fehsenfeld et al., J. Chem. Phys. **46**, 2802 (1967).

[115] B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh stolknovenii (Asymptotic Methods in the Theory of Atomic Collisions), Atomizdat, M., 1973.

[116] B. M. Smirnov, Zh. Eksp. Teor. Fiz. **51**, 1747 (1966) [Sov. Phys. JETP **24**, 1180 (1967)].

[117] T. M. Miller et al., Phys. Rev. **173**, 115 (1968).

[118] U. A. Arifov et al., see Ref. 107, p. 11.

[119] E. W. McDaniel et al., in: Proc. of 8th Intern. Conference on Physics of Electron and Atomic Collisions, Belgrade, 1973, p. 104.

[120] E. Graham et al., J. Chem. Phys. **59**, 4648 (1973).

[121] L. G. McKnight, K. B. McAfee, and D. P. Sipler, Phys. Rev. **164**, 62 (1967).

[122] J. T. Moseley, R. M. Snuggs, D. W. Martin, and E. W. McDaniel, ibid. **178**, 240 (1969).

[123] A. Good, D. A. Durden, and P. Kebarle, J. Chem. Phys. **52**, 212 (1970).

[124] T. D. Märk and H. J. Oskam, Phys. Rev. **A4**, 1445 (1971).

[125] P. Warneck, J. Chem. Phys. **46**, 502 (1967).

[126] S. B. Woo, ibid. **42**, 1251 (1965).

[127] A. Good, D. A. Durden, and P. Kebarle, ibid. **52**, 222 (1970).

[128] J. C. Howard et al., ibid. **57**, 3491 (1972).

[129] C. E. Young and W. E. Falconer, ibid., p. 918.

[130] L. W. Sieck and R. Gorden, J. Nat. Bur. Stand. **A78**, 315 (1974).

[131] J. D. Payzant et al., J. Chem. Phys. **59**, 5615 (1973).

[132] N. G. Adams et al., ibid. **52**, 3133 (1970).

[133] I. C. Plumb, D. Smith, and N. G. Adams, J. Phys. **B4**, 1762 (1972).

[134] W. C. Lineberger and L. J. Puckett, Phys. Rev. **186**, 116 (1969).

[135] J. H. Schummers et al., ibid. **A7**, 689 (1973).

[136] S. L. Chong and J. L. Franklin, J. Chem. Phys. **54**, 1487 (1971).

[137] J. F. Paulson, F. Dale, and R. L. Mosher, Nature **204**, 377 (1964).

[138] J. S. Dahler et al., J. Chem. Phys. **36**, 3332 (1962).

[139] F. C. Fehsenfeld et al., Bull. Am. Phys. Soc. **13**, 212 (1968).

[140] E. E. Ferguson and F. C. Fehsenfeld, J. Geophys. Res. **73**, 6215 (1968).

[141] I. R. Gatland et al., Phys. Rev. **A12**, 1885 (1975) [sic!].

[142] G. E. Keller and R. A. Beyer, J. Geophys. Res. **76**, 289 (1971).

[143] D. B. Dunkin et al., J. Chem. Phys. **54**, 3817 (1971).

[144] J. M. Heimerl and J. A. Vanderhoff, ibid. **60**, 4362 (1974).

[145] L. J. Puckett and M. W. Teague, ibid. **54**, 4860 (1971).

[146] D. K. Bohme and F. C. Fehsenfeld, ibid. **47**, 2715 (1969) [sic!].

[147] R. Johnsen, H. L. Brown, and M. A. Biondi, ibid. **55**, 186 (1971).

[148] F. C. Fehsenfeld et al., Compilation of Reaction Rate Constants, Colorado, Boulder 1969.

[149] F. C. Fehsenfeld et al., J. Chem. Phys. **55**, 2120 (1971).

[150] C. J. Howard, H. W. Rundle, and F. Kaufman, ibid., p. 4772.

[151] W. C. Lineberger and L. J. Puckett, Bull. Am. Phys. Soc. **14**, 261 (1969).

[152] M. J. McAdams and L. I. Bone, J. Chem. Phys. **57**, 2173 (1972).

[153] L. J. Puckett and M. W. Teague, ibid. **54**, 2564 (1971).

[154] C. E. Young, D. Edelson, and W. E. Falconer, ibid. **53**, 4295 (1970).

[155] U. A. Arifov, D. L. Pozharov, and I. G. Chernov, Khim. vys. énergii **5**, 3 (1971).

[156] D. S. Burch and R. Geballe, Phys. Rev. **106**, 183 (1957).

[157] E. C. Beaty et al., Bull. Am. Phys. Soc. **9**, 535 (1964).

[158] L. G. McKnight, Phys. Rev. **A2**, 762 (1970).

[159] J. H. Schummers et al., ibid. **A7**, 689 (1973).

[160] J. H. Whealton and S. B. Woo, Phys. Rev. Lett. **20**, 1137 (1968).

[161] J. L. Moruzzi and A. V. Phelps, J. Chem. Phys. **45**, 4617 (1966).

[162] R. M. Snuggs et al., Phys. Rev. **A3**, 487 (1971).

[163] J. D. Payzant and P. Kebarle, J. Chem. Phys. **56**, 3482 (1972).

[164] L. G. McKnight and J. M. Sawina, Bull. Amer. Phys. Soc. **15**, 434 (1970).

[165] L. G. McKnight and J. M. Sawina, Phys. Rev. **A4**, 1043 (1971).

132   Sov. Phys. Usp., Vol. 20, No. 2, February 1977

B. M. Smirnov   132

[166]J. L. Pack and A. V. Phelps, Bull. Amer. Phys. Soc. 16, 214 (1971).

[167]E. E. Ferguson et al., Adv. Atom. and Molec. Phys. 5, 1 (1969).

[168]D. A. Parkes, J. Chem. Soc. 68, 2103 (1972).

[169]R. Marx, G. Mauclaire, F. C. Fehsenfeld, D. B. Dunkin, and E. E. Ferguson, J. Chem. Phys. 58, 3267 (1973).

[170]F. K. Truby, Phys. Rev. A4, 114 (1971).

[171]R. E. Center, J. Chem. Phys. 56, 371 (1972).

[172]L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, M., 1974 (Engl. Transl. of 2nd ed., Addison—Wesley, Reading, Mass., 1965).

[173]J. N. Bardsley and M. A. Biondi, Adv. Atom. and Molec. Phys. 6, 1, (1970).

[174]A. V. Eletskiĭ and B. M. Smirnov, in Nizkotemperaturnaya plazma (Low-Temperature Plasma), ed. L. S. Polak, Nauka, M., 1974, p. 68.

[175]G. Hagen, in: Proc. of 5th Intern. Conference on Physics of Electron and Atomic Collisions, L., Nauka, 1967, p. 165.

[176]R. H. Neynaber, Adv. Atom. and Molec. Phys. 5, 57 (1969).

[177]L. P. Theard, in: Proc. of 6th Intern. Conference on Physics of Electron and Atomic Collisions, Massachusetts, 1969, p. 1042.

[178]L. P. Theard, Bull Amer. Phys. Soc. 14, 255 (1969).

[179]B. Peart and K. T. Dolder, see Ref. 119, p. 419.

[180]B. Peart and K. T. Dolder, J. Phys. B6, 2409 (1973).

[181]B. Peart and K. T. Dolder, ibid., p. L359.

[182]B. Peart and K. T. Dolder, ibid. B7, 236 (1974).

[183]B. Peart and K. T. Dolder, ibid. p. 1948.

[184]F. L. Walls and G. H. Dunn. J. Geophys. Res. 79, 1911 (1974).

[185]W. H. Kasner and M. A. Biondi, Phys. Rev. 174, 139 (1968).

[186]W. H. Kasner, W. A. Rogers, and M. A. Biondi, Phys. Rev. Lett. 7, 321 (1961).

[187]R. Hackam, Plante Space Sci. 13, 667 (1965).

[188]W. H. Kasner and M. A. Biondi, Phys. Rev. A137, 317 (1965).

[189]C. S. Weller and M. A. Biondi, ibid. 172, 198 (1968).

[190]J. B. Gerardo and M. A. Gusinow, ibid. A3, 255 (1971).

[191]M. T. Leu, M. A. Biondi, and R. Johnsen, ibid. A8, 413 (1973).

[192]M. C. Sauer, Jr. and W. A. Mulac, J. Chem. Phys. 55, 1982 (1971).

[193]G. E. Keller and R. A. Beyer, J. Geophys. Res. 76, 289 (1971).

[194]M. T. Leu, M. A. Biondi, and R. Johnsen, Phys. Rev. A7, 292 (1973).

[195]W. Lindinger, ibid., p. 328.

[196]F. C. Fehsenfeld et al., Planet. and Space Sci. 17, 1759 (1969).

[197]A. P. Mitra, Aeronomy Rept.; No. 32, 174 (1969).

[198]A. D. Danilov and M. N. Vlasov, Fotokhimiya ionizovannykh chastits v nizhneĭ atmosfere (Photochemisty of Ionized Particles in the Lower Atmosphere), Gidrometeoizdat, M., 1973.

[199]R. S. Narcisi et al., J. Geophys. Res. 79, 2843, 2849 (1974).

[200]Aéronomicheskie reaktsii v verkhneĭ atmosfere (Aeronomic Reactions in the Upper Atmosphere), (translations) ed. A. D. Danilov, Mir, M., 1968.

[201]E. E. Ferguson, Ann. Geophys. 25, 819 (1969).

[202]E. E. Ferguson, ibid. 26, 589 (1970).

[203]E. E. Ferguson, Rev. Geophys. and Space Phys. 9, 997 (1971).

[204]F. C. Fehsenfeld and E. E. Ferguson, Radio Sci. 7, 113 (1972).

[205]E. E. Ferguson, Rev. Geophys. and Space Phys. 12, 703 (1974).

[206]E. E. Ferguson, Ann. Phys. Chem. 26, 17 (1975).

[207]R. S. Narcisi et al., J. Atmos. and Terr. Phys. 33, 1147 (1971).

[208]J. C. Haslet et al., Can. J. Phys. 47, 2351 (1969).

[209]H. C. Wood et al., ibid. 48, 7, 1970.

[210]W. F. J. Evans and E. J. Llewellyn, Ann. Geophys. 26, 167 (1970).

[211]J. T. Moseley et al., J. Chem. Phys. 62, 4826 (1975).

[212]A. J. Cunningham et al., J. Am. Chem. Soc. 94, 7627 (1972).

[213]H. Kistenmacher et al., J. Chem. Phys. 61, 799 (1974).

[214]M. A. French, L. P. Hills, and P. Kebarle, Can. J. Chem. 51, 456 (1973).

[215]F. Arnold and D. Krankowsky, Geophys. Res. Lett. 1, 243 (1974).

[216]J. T. Moseley et al., Chem. Phys. Lett. 26, 288 (1974).

[217]J. T. Moseley et al., in: 9th Intern. Conference on Physics Electron and Atomic Collisions, Seattle, 1975, p. 3.

[218]G. Sinnott and E. C. Beaty, in: 7th Intern. Conference on Physics Electron and Atomic Collisions, Amsterdam, 1971, p. 176.

[219]S. F. Wong, T. V. Vorburger, and S. B. Woo, Phys. Rev. A5, 2598 (1972).

[220]J. R. Peterson et al., see Ref. 217, p. 5.

[221]T. M. Miller, J. L. Heidrish, and J. T. Moseley, ibid., p. 5.

[222]J. A. Vanderhoff and R. A. Beyer, Chem. Phys. Lett. 38, 537 (1976).

[223]J. C. Howard et al., Bull. Amer. Phys. Soc. 16, 213 (1971).

[224]R. A. Heppner et al., Phys. Rev. A13, 1000 (1976).

[225]L. M. Colonna-Romano and G. E. Keller, J. Chem. Phys. 64, 2684 (1976).

[226]G. E. Keller, R. A. Beyer, and L. M. Colonna-Romano, Phys. Rev. A8, 1446 (1973).

[227]P. P. Kulik, G. É. Norman, and L. S. Polak, Khim. vys. énergiĭ 10, 203 (1976).

Translated by M. V. King