

Dissociative recombination of electrons and molecular ions

A. V. Eletskiĭ and B. M. Smirnov

I. V. Kurchatov Institute of Atomic Energy
Usp. Fiz. Nauk **136**, 25–59 (January 1982)

The mechanisms of dissociative recombination of electrons and molecular ions are described. Methods for experimental study of this process are discussed. The results of measurements of the dissociative recombination cross section and coefficient for various systems are reported. Theoretical models of the process are analyzed. The role of dissociative recombination in the low-temperature plasma of the upper atmosphere, gas lasers, and the glow discharge is demonstrated.

PACS numbers: 34.80.Gs

CONTENTS

1. Introduction	13
2. Electron-molecular ion recombination mechanisms	13
3. Methods of measurement of dissociative recombination cross section, and basic results	15
a) The ion trap; b) The congruent-beam method; c) The crossed-beam method;	
d) Results of measurements	
4. Methods of measurement and temperature dependence of dissociative recombination coefficient	20
a) Decay of gas-discharge plasma; b) The spectroscopic method; c) The shock-wave method; d) Results of measurements. Temperature dependence of dissociative recombination coefficient	
5. Dissociative recombination with participation of a complex ion	22
6. Recombination of vibrationally excited ions and products of dissociative recombinations	25
7. Dissociative recombination in weakly ionized gases	27
8. Conclusion	28
References	28

1. INTRODUCTION

The recombination of electrons and ions is the process responsible for the disappearance of charged particles in weakly ionized gases and plasmas. This process therefore determines the charged-particle balance in various phenomena which occur in the gas discharge, the earth's atmosphere, and plasmas. When atomic ions participate in recombination, this process may take place with participation of a third particle or should be accompanied by emission of a photon. This third particle or photon removes the excess energy released on formation of a bound state of the electron and ion. In the presence of a molecular ion, recombination may proceed in a pair collision of particles. Then the energy excess is converted to kinetic energy of the nuclei and is accompanied by the breakup of the molecular ion. This process is known as dissociative recombination.

Naturally, the efficiency with which charges are neutralized by dissociative recombination as a pair process is with rare exceptions much higher than the efficiency with which charge vanishes on triple recombinations or on radiative recombination of electrons and ions in a gas or plasma. Under the conditions under which it is possible, therefore, dissociative recombination "forgets" all other recombination pathways and is the primary cause of the disappearance of charged particles in the volume. Since dissociative recombination proceeds with participation of molecular ions, it makes sense to investigate it at gas temperatures that are not very high. The highest gas temperatures of interest for this process amount to a few thousand degrees, and the

highest electron temperatures to a few electron-volts. The process is not of practical interest beyond these limits of the parameters.

Our purpose in the present review is to set forth present conceptions of the electron-molecular ion dissociative recombination process. This review is a natural extension of our earlier reviews of this subject.¹⁻³⁾ Significant changes have taken place in this area during the last decade. First of all, the beam method of measuring the cross sections of dissociative recombination has been developed extensively and yields detailed information on the process. Secondly, a major series of studies pertaining to atomic states formed on dissociative recombination has been carried out. Finally, our information on other aspects of this problem has been expanded significantly. All these topics are reflected in the review.

2. ELECTRON-MOLECULAR ION RECOMBINATION MECHANISMS

Let us investigate the possible mechanisms of these processes. The basic recombination mechanisms are illustrated in Fig. 1, which shows the electronic terms of the system in its initial and final states. In the case of the "direct" mechanism of dissociative recombination (d.r.), the electron is captured in an autoionized state (Fig. 1a), which corresponds to mutual repulsion of the nuclei. The subsequent fly-apart of the nuclei results in stabilization of this state, i.e., recombination. Another, "indirect," d.r. mechanism consists

¹⁾ See also the comprehensive review of Bardsley and Biondi.⁴

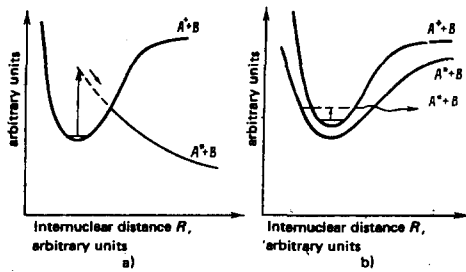


FIG. 1. Illustrating dissociative recombination (d. r.) mechanisms of electrons and molecular ions. a) Direct mechanism; b) indirect mechanism. The arrows mark transitions on recombination.

of two stages (Fig. 1b). The electron is first captured into an excited vibrational level of the electronically excited molecule or captured into an autoionization level of the molecule by another process, exciting internal degrees of freedom of the molecular ion. This is followed by predissociation of the excited molecule, accompanied by transition to another (lower) excited state of the atoms and fly-part of the nuclei (see Fig. 1b). As a result, the excess energy is converted into kinetic energy of the nuclei. However, since the coupling between the electronic and nuclear motions is weak, a second transition from the excited vibrational state of the electronically excited molecule is much less probable than decay of this molecule back into the electron and molecular ion. Therefore the "indirect" dissociative-recombination mechanism is less efficient. It can occur when the ion has a complex internal structure, so that many opportunities exist for excitation of internal degrees of freedom. Such a situation may be brought about on dissociative recombination involving a cluster ion. Dissociative recombination of simple molecular ions takes place by the direct mechanism.

The cross section of dissociative recombination $\sigma_{\text{rec}}(\varepsilon)$ in a pair collision of an electron with energy ε and an ion²⁾ and the coefficient of dissociative recombination $\alpha = \langle v\sigma_{\text{rec}} \rangle$, if the process occurs in the gaseous phase, are characteristics of the dissociative recombination process. Here v is the velocity of the electron and averaging is extended over the velocities of the electron in the gas. The coefficient of dissociative recombination appears in the balance equation for the electron density N_e in the gas:

$$\frac{dN_e}{dt} = -\alpha N_e N_i, \quad (1)$$

where N_i is the density of the molecular ions. Only dissociative recombination is taken into account in this balance equation.

The order of magnitude of the dissociative recombination coefficient at thermal energies can be estimated as follows. When the process is effective, the recombination cross section is of the order of magnitude of the cross section for elastic scattering of electrons by molecules: $\sigma_{\text{rec}} \sim 10^{-14} \text{ cm}^2$. Since the characteristic velocity of electrons at room temperature $v \sim 10^7 \text{ cm/}$

²⁾ The energy of the electron is the same as the energy of a particle in the center-of-inertia system.

sec, the order of magnitude of α is $\sim 10^{-7} \text{ cm}^3/\text{sec}$. Table I gives values of the dissociative recombination coefficient for simple molecular ions at room temperature. We see that the values basically confirm our rough estimate.

Since the atom has an infinite number of excited states, a large number of recombination channels and a large number of excited atomic states formed as a result of dissociative recombination are possible. We shall discuss this problem separately in Sec. 6. We note for the moment that given a wide choice of final channels, the process takes place efficiently via a limited number of optimum pathways.

Considering the nature of the process, we write an equation for the cross section of dissociative recombination. Assuming the motion of the nuclei to be quasiclassical, we have

$$\sigma_{\text{rec}}(\varepsilon) = \int \sigma_{\text{Capt}}(\varepsilon, R) |\Psi(R)|^2 dR \exp\left(-\int_R^{R_0} \frac{\Gamma dR}{R v_R}\right), \quad (2)$$

$$\sigma_{\text{Capt}}(\varepsilon, R) = \frac{\pi \hbar^2}{2m\varepsilon} \frac{\Gamma^2}{[\varepsilon - E_a(R)]^2 + (\Gamma^2/4)}; \quad (2a)$$

here $\sigma_{\text{Capt}}(\varepsilon, R)$ is the cross section for capture of an electron with energy ε into an autoionization level at a distance R between nuclei and $\Psi(R)$ is the nuclear wave function of the molecular ion, so that $|\Psi(R)|^2 dR$ is the probability that the nuclei will be in the range from R to $R + dR$. The exponential multiplier in (1) represents the probability of survival of the autoionized state until the nuclei fly apart, so that $\Gamma(R)$ is the width of the autoionization level, v_R is the radial velocity component of the relative motion of the nuclei, and R_0 is the intersection point of the repulsive term and the term of the molecular ion; when $R > R_0$, the repulsive state becomes stable. We have assumed for simplicity in the Breit-Wigner formula (2a) that there is only one autoionization state in which dissociative recombination proceeds efficiently; $E_a(R)$ is the difference between the energies of the autoionized state and the molecular ion at a distance R between nuclei. We note that the Breit-Wigner relation (2) holds if the width of the autoionization level $\Gamma(R)$ is small compared to the characteristic distance $E_a(R)$ between terms.

Equations (1) and (2) can be used to analyze the nature of dissociative recombination in specific cases and to establish the relations between the parameters of this

TABLE I. Dissociative recombination coefficients for simple ions at room temperature*

Ion	α , $10^{-7} \text{ cm}^3/\text{sec}$	Reference	Ion	α , $10^{-7} \text{ cm}^3/\text{sec}$	Reference
H_2^+	0.3	5	O_2^+	2.0	26, 38-50
Ne_2^+	1.8	6-17	N_2^+	3.3	41, 46, 48, 49, 51-56
Ar_2^+	6.9	8, 12, 18-29	NO^+	3.7	46, 48, 57-63
Kr_2^+	10.3	18, 30-35	CH^+	5 (**)	165
Xe_2^+	20	18, 31-33, 36	CO^+	6.8	64
HeNe^+	0.2	37	CO_2^+	3.6	46, 48
C_2^+	10 (**)	155	CH_2^+	8.7 (**)	166

*Values given are averages over the results of the studies cited.

** $T = 100 \text{ K}$.

process and those of the system. We present an integral relation that follows from (2) and (2a) and is convenient for use in the analysis:

$$\int_0^{\infty} \sigma_{\text{rec}}(\varepsilon) \varepsilon d\varepsilon = \frac{\pi \hbar^2}{m} \left\langle \Gamma(R) \exp \left(- \int_{\dot{R}}^{R_a} \frac{\Gamma dR}{\hbar v_R} \right) \right\rangle, \quad (3)$$

where the averaging takes into account the distribution of the relative distances separating the nuclei in the molecular ion. This relation is conveniently used to estimate the dissociative-recombination coefficient averaged over a Maxwellian electron distribution. In the case $\Gamma \ll T$ (T is the electron temperature), we have taking (3) into account

$$\alpha_{\text{rec}} = \int_0^{\infty} v \sigma_{\text{rec}} \frac{2e^{1/2}}{\sqrt{\pi T^{3/2}}} e^{-\varepsilon/T} d\varepsilon = \frac{2\sqrt{2\pi} \hbar^2}{(mT)^{3/2}} \left\langle \Gamma(R) \exp \left(- \frac{E_a(R)}{T} - \int_{\dot{R}}^{R_a} \frac{\Gamma dR}{\hbar v_R} \right) \right\rangle. \quad (4)$$

Relation (4) is convenient for estimation of the dissociative-recombination coefficient under optimum process conditions. In this case, the electronic terms intersect close to the bottom of the well, so that $\int_{\dot{R}}^{R_a} \Gamma dR / \hbar v_R \lesssim 1$, i.e., the survival probability of the repulsive state until it is stabilized as the nuclei fly apart is near unity. Then, using (4) in the optimum case $\Gamma \sim T$ and $E_a \sim T$, we obtain the following estimate for the dissociative-recombination coefficient under optimum conditions:

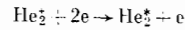
$$\alpha_{\text{rec}} \sim \frac{\hbar^2}{m^{3/2} T^{1/2}}, \quad T \gg \Gamma. \quad (5)$$

Using this estimate, we find that $\alpha_{\text{rec}} \sim 10^{-7}$ cm³/sec at room temperature. It is with these scales of the process rate constant that we shall work below.

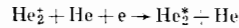
In those cases in which the conditions for recombination of a given molecular ion differ significantly from the conditions considered above, which are the optimum from the standpoint of the d.r. process, the recombination of molecular ions may proceed via a more complex path than that considered above, and the rate constant of the process may differ substantially from the results of the above estimates. Such a situation arises on recombination of the He₂⁺ molecular ion, which has been investigated experimentally in some detail.⁷¹⁻⁷⁷ The specifics of this system are determined by the manner of intersection of the terms of the He₂⁺ molecular ion and the quasimolecule, which is composed of helium atoms in the 1s²1S₀ ground and 2¹P excited states. The bottom of the molecular-ion potential well is ~1 eV below the intersection point of these terms, so that d.r. of a slow electron with the molecular ion is possible only if the molecular ion is in a vibrationally excited state (according to Ref. 71, $\nu \geq 2$ for this state). This circumstance is responsible for the anomalously low (10⁻⁹ to 10⁻⁸ cm³/sec) values of the d.r. coefficient of the molecular ion He₂⁺ at room temperature,⁷²⁻⁷⁶ as well as the experimentally observed⁷⁷ increase of this coefficient with the temperature of the gas.

Since the He₂⁺ molecular ion has a relatively small d.r. coefficient, other recombination processes that are of no particular importance for other gases may

compete with this process under the conditions of a weakly ionized plasma. For example, it has been established⁷²⁻⁷⁶ (see also Refs. 78, 79) that triple processes of the type



or



may be important in the neutralization of He₂⁺ molecular ions, leading to the formation of an electronically excited (excimeric) helium molecule. Here the effective recombination coefficient α_{rec} measured experimentally is found to depend on such parameters of the plasma as the electron and atom densities N_e and N , so that the results of measurements made by various authors differ by more than an order of magnitude. Another cause of these disagreements is found in the aforementioned dependence of the d.r. coefficient of He₂⁺ on the degree of vibrational excitation of this ion. Because of this dependence, the result of a measurement depends firstly on the manner of formation of the molecular ions and secondly on the relation between the characteristic times of dissociative recombination and vibrational relaxation of the molecular ion. In turn, the latter is determined by the degree of ionization of the plasma.

3. METHODS OF MEASUREMENT OF DISSOCIATIVE RECOMBINATION CROSS SECTION, AND BASIC RESULTS

The ability of theory to describe the d.r. process is extremely limited. This can be explained by two circumstances. On the one hand, analysis of the d.r. mechanism shows that the process results from simultaneous interaction of the incident electron with the inner electrons and nuclei of the atoms, i.e., the problem is essentially a many-particle problem. Fundamental difficulties are encountered in the attempt to solve such problems analytically. On the other hand, d.r. is an essentially multilevel process, i.e., it is generally characterized by a large number of possible intermediate and final channels. Proper allowance for the influence of all these channels, even within the framework of a numerical model, is not realistic in practice, since we lack the necessary detailed information on the relative positions of the terms of the molecular ion and the autoionization states involved in the process, on the widths of these states, etc. In such a situation, experiment is our basic source of information on the process.

The most complete available information on the specifics of recombination of an electron and a molecular ion is inherent in the cross section of this process, measured for all possible initial and final states of the system as a function of collision energy. In acquiring information of this kind, however, we encounter serious technical difficulties with the creation of highly monochromatic beams of electrons and molecular ions, and with fixing and identifying specific vibrational states of the molecular ions and excited states of the atoms. It is also difficult to create beams of weakly ionized molecular ions.

Because of these difficulties, the number of papers devoted to direct measurement of the d.r. cross sections of molecular ions has been relatively small compared to the number of papers that give estimates of the coefficients of recombination of electrons and molecular ions under specific conditions brought about in plasmas. Below we briefly discuss the methods used to measure d.r. cross sections and present results obtained from such measurements.

a) The ion trap

The first direct measurement of a d.r. cross section was made by Walls and Dunn,⁶³ who designed and executed an elegant experiment based on use of an ion trap. In this procedure, a certain number of ions ($\sim 10^4$ – 10^5) are admitted into a vacuum chamber, to which external electric and magnetic fields of special configuration are applied. The magnetic field, whose direction coincides with the initial velocity of the ion beam, is highly uniform in space and serves to keep the ions from moving in the radial direction. The electric field varies quadratically in the axial direction, so that the ions entering the chamber execute harmonic oscillations with a frequency that depends on the ratio Z/M (Z is the charge on the ion and M is its mass) under the action of this field.

By virtue of the thorough evacuation of the chamber (residual-gas pressures at the 10^{-10} mm Hg level) and the high-quality construction of the electrostatic and magnetic elements of the system, the characteristic existence time of the ions in this chamber is very long—depending on the species of ion, it ranges from tens of minutes to tens of hours).³⁾ These times are considerably longer than the characteristic times of optically allowed radiative vibrational-rotational transitions of molecular ions, so that the ions in the trap spend a very large part of the time in the ground vibrational and (all the more so) electronic states. The number of ions in the trap is determined by measuring the currents induced in the body of the chamber by the ionic vibrations.

When a monochromatic electron beam is passed through the trap, recombination occurs in the chamber and lowers the number of ions present in it. Knowing the density of the electrons in the beam, the percentage decrease of the number of ions as a result of recombination, and the time of interaction of the electron beam with the ions in the trap, we can easily calculate the recombination cross section. The basic source of error in this method is associated with the finite width of the electron energy distribution in the beam. This is indicated, for example, by comparison of data⁹² obtained using electron beams with varying degrees of monochromaticity (widths of distribution ≈ 0.15 and 0.04 eV) (see below, Fig. 9).

³⁾ The time of retention of the ion in the vacuum chamber is limited by the possible ion-molecular reactions that take place with participation of residual gases. This time ranges up to 24 hours for the ion NH_4^+ , which is not affected by such reactions.⁸⁰

The ion-trap method has been used successfully to measure the d.r. cross sections of such molecular ions as NO^+ , O_2^+ , H_3O^+ , NH_4^+ , N_2H^+ , and HCO^+ .

b) The congruent-beam method

Another effective method for direct measurement of the d.r. cross section is based on the use of beams of electrons and ions that intersect at a small (or zero) angle with their closing velocity much smaller than of either of the beams in laboratory coordinates.

This method has one advantage in the relatively long interaction time of the beams and another in the possibility of running experiments in which the energies of relative approach of the colliding particles are as small as desired. It can be shown⁸¹ that the relative collision-energy scatter $\Delta E_c/E_c$ is determined by the relative scatters of the electron energies ($\Delta E_e/E_e$) and of the ion energies ($\Delta E_i/E_i$) in the laboratory system, and by the scatter $\Delta\theta/\theta$ of the angles at which the electron and ion beams intersect, and does not depend on the collision energy in the center-of-mass system. Thus, the calculations of Ref. 81 indicate that when a beam of H_2^+ ions with energies of 443 keV and an energy scatter of ± 200 eV and a beam of electrons with energies ≈ 120 eV and energy scatter of ± 0.1 eV meet at a 1° angle accurate to $\Delta\theta = 1.0^\circ$, the maximum scatter of the relative energy of electrons and ions does not exceed 0.1 eV. Since the attainable relative energy scatter $\Delta E_i/E_i$ in the ion beam decreases with increasing beam energy E_i , switching to the use of fast beams to study slow collisions increases the accuracy of the measurements. This also makes it relatively easy to solve the problem of detecting the d.r. products, which is done with the traditional fast-particle detectors developed in nuclear physics.

The chief drawback to the congruent-beam method arises from the difficulty of identifying and fixing the initial state of the molecular ion in the beam. Usually, the vibrational-state distribution of the beam ions depends on the way in which the ions are formed and on the state of the plasma that serves as the ion source. This may give rise to an additional uncertainty in interpretation of the results of measurements and differences between results obtained by different authors. Nevertheless, the congruent-beam method is a highly productive source of information on the behavior of the d.r. cross section at low collision energies. Thus, Ref. 82 reports measurements of d.r. cross sections made for 25 ion species in the range of collision energies from 0.01 to 0.1 eV with an uncertainty of $\sim 15\%$.⁴⁾ No other method is capable of ensuring such measurement accuracy in this range of energy variation.

c) The crossed-beam method

This method, which is widely used in the physics of atomic collisions, is hardly suitable for investigation of d.r. One reason for this is the difficulty of producing monochromatic electron and ion beams with en-

⁴⁾ These measurements were continued in Refs. 134, 155, and 165.

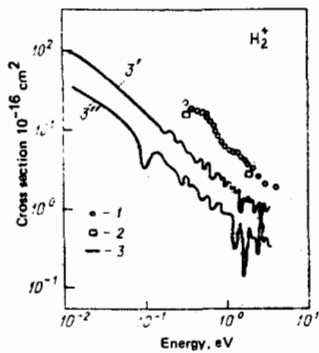
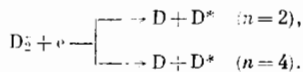


FIG. 2. Cross section for dissociative recombination of electrons and molecular hydrogen ions H_2^+ vs collision energy. 1) experiment,⁸⁵ vibrational states of H_2^+ molecular ions $0 \leq \nu \leq 15$, width of electron energy distribution 0.2 eV; 2) calculation⁸⁶; 3) experiment,^{81,87} width of electron energy distribution 0.04 eV; curve 3') states with $0 \leq \nu \leq 15$ participate in recombination; curve 3'') states with $\nu = 0-2$ participate in recombination.

ergies of a few electron volts, and another is the short time of interaction of the beam and the consequent difficulty of recording the d.r. products, which are formed in vanishingly small quantities. An opportunity to use the crossed-beam technique successfully arises when one of the atoms formed as a result of d.r. emits an easily registered quantum. This possibility was discovered and used by Dunn *et al.*,^{83,84} who measured the d.r. cross section of the molecular ion D_2^+ :



The relative efficiency of d.r. was recorded at various collision energies by measuring the intensities of the Lyman ($2p-1s$) and Balmer ($4p-2s$) lines of the deuterium atom. This method has an important advantage in that it enables us not only to estimate the energy dependence of the d.r. cross section, but also to form an idea of the relative contributions of the various process channels, which differ from one another in the final states of one of the atoms. However, the wide energy

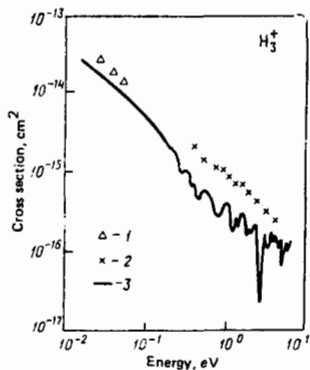


FIG. 3. Dissociative recombination cross section of electrons and H_3^+ molecular ions vs collision energy. 1) According to Ref. 88 (reconstructed from rate-constant measurements); 2) Ref. 89 (energy resolution 0.2 eV); 3) Ref. 81 (energy resolution 0.07 eV).

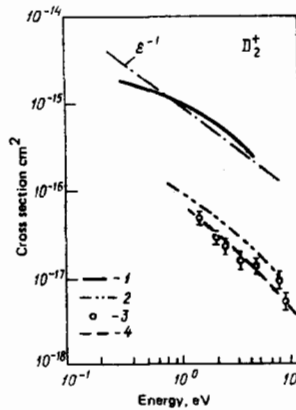


FIG. 4. Energy dependence of d. r. cross section of D_2^+ molecular ions. 1) Experiment⁸⁵ (total cross section of process); 2) experiment⁸⁴ [partial cross section of recombination with formation of $D(1s4p)$]; 3) partial cross section of recombination with formation of $D(1s2p)$ ⁸³; 4) result of statistical analysis of this experiment.⁸³

scatter of the colliding particles, which we mentioned above, has made it impossible to detect the subsequently established oscillation structure on the energy curve of the cross section. Because of this disadvantage, the crossed-beam method, which was developed for investigation of d.r. in 1975, has not been used further.

d) Results of measurements

Figures 2-9 show d.r. cross sections obtained in experiments by various authors as functions of energy. The data represented in these figures show that the measured curves are monotonically decreasing functions. Where the resolution (in energy) of the measuring system was high enough, fine structure appears on these curves.

Figure 9, which shows data obtained with resolutions of 0.04 eV (a) and 0.15 eV (b), clearly shows how sensitive the result of measurement of the energy dependence of the d.r. cross section is to the resolving power of the measurement apparatus. The considerable difference between these data indicates, first of all, that information on the fine structure in the energy dependence of the cross section was lost in most of the experiments

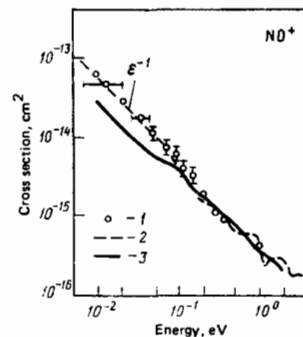


FIG. 5. Dissociative recombination cross section of NO^+ molecular ions as measured and calculated by various authors for various collision energies. 1) experiment⁴⁸; 2) experiment⁶³; 3) theory.⁹⁰

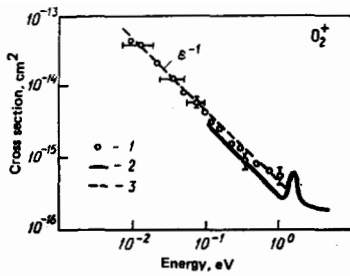


FIG. 6. Energy dependence of d. r. cross section of O_2^+ molecular ions. 1) experiment⁴⁸; 2) experiment⁶³; 3) $\sigma \sim \epsilon^{-1}$ relation.

made at resolutions poorer than 0.1 eV. We should expect such information to be acquired as experimental techniques are developed further.

In analyzing the experimental data, we shall proceed from the general expression (2) for the d.r. cross section. Let us consider the extreme case of small Γ . Here, substituting in (2)

$$\frac{\Gamma}{2\pi\{\epsilon - E_a(R)\}^2 + (\Gamma/4)} \rightarrow \delta[\epsilon - E_a(R)] = \left(\frac{dE_a}{dR}\right)^{-1} \delta(R - R_\epsilon),$$

where $E_a(R_\epsilon) = \epsilon$, we obtain for the dissociative recombination cross section

$$\sigma_{rec} = \frac{\pi h^2 \Gamma}{4m\epsilon} \frac{|\Psi(R_\epsilon)|^2}{|dE_a/dR|_{R_\epsilon}} \exp\left(-\int_{R_\epsilon}^{R_0} \frac{\Gamma dR}{\hbar v}\right), \quad (6)$$

$$\Gamma \ll \epsilon, \quad \left|\frac{dE_a}{dR}\right| a,$$

where a is the amplitude of the vibrations of the nuclei in the molecular ion.

This expression indicates that the nature of the energy dependence of the d.r. cross section is determined essentially by the vibrational state of the molecular ion. If there is a range of internuclear distances in which the energy of the molecular ion is larger than or of the order of magnitude of the energy of the autoionized state, d.r. is possible on capture of arbitrarily slow electrons. This case occurs either for vibrationally excited molecular ions or under conditions such that the intersection of the terms of the molecular ion and the autoionized state of the quasimolecule takes place near the bottom of the potential well of the molecular ion. In this case, relation (6) shows that in the limit

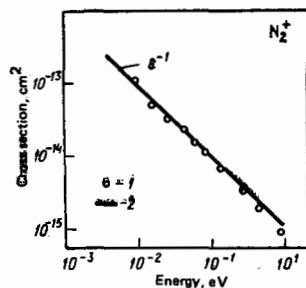


FIG. 7. Energy dependence of d. r. cross section of N_2^+ molecular ions. 1) experiment⁴⁸; 2) $\sigma \sim \epsilon^{-1}$ relation.

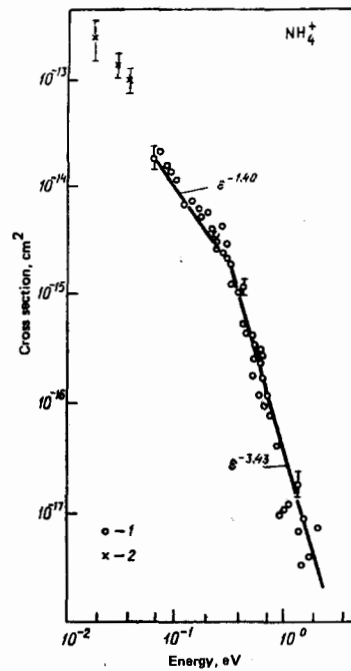


FIG. 8. Energy dependence of d. r. cross section of NH_4^+ molecular ions. 1) experiment⁸⁰ (energy resolution 0.05 to 0.15 eV, errors of single experiments indicated on the figure); 2) reconstructed from measurements of process rate constant.⁹¹

of low electron energies

$$\Gamma \ll \epsilon \ll \left|\frac{dE_a}{dR}\right| a;$$

the energy dependence of the d.r. cross section has the form

$$\sigma_{rec}(\epsilon) = \frac{\pi h^2 \Gamma_a |\Psi(R_a)|^2}{4m\epsilon dE_a/dR(R_a)} \sim \frac{1}{\epsilon}. \quad (7)$$

Let us now analyze the opposite limiting case, which corresponds to reversal of the inequalities (6).⁵⁾ Here we can easily verify that the integrand is practically independent of ϵ , so that we again have an inversely proportional dependence of cross section on energy. In this case, however, we may expect a strong dependence of the d.r. cross section on the number ν of the vibrational state of the molecular ion. In fact, as ν increases, so does the characteristic width ΔR of the nuclear wave function of the molecular ion. This makes possible the capture of an electron at large internuclear distances, when the value of $\exp(-\int_{R_0}^{R_a} \Gamma dR/\hbar v)$ is much larger than it is when the molecular ion is in the ground vibrational state.

Still another interesting extreme case corresponds to a negligibly small characteristic width ΔR of the nuclear wave function $\Psi(R)$. In this case, the range of internuclear distances that makes the basic contribution to the integral is concentrated near the point R_0 , and the d.r. cross section is found to be proportional to

$$\sigma(\epsilon) \sim \frac{1}{\epsilon} \frac{1}{[\epsilon - E_a(R_0)]^2 + (\Gamma^2/4)}. \quad (8)$$

⁵⁾ It must be remembered that the conditions for use of the Breit-Wigner formula (2a) are violated in this case; the result is therefore of qualitative nature.

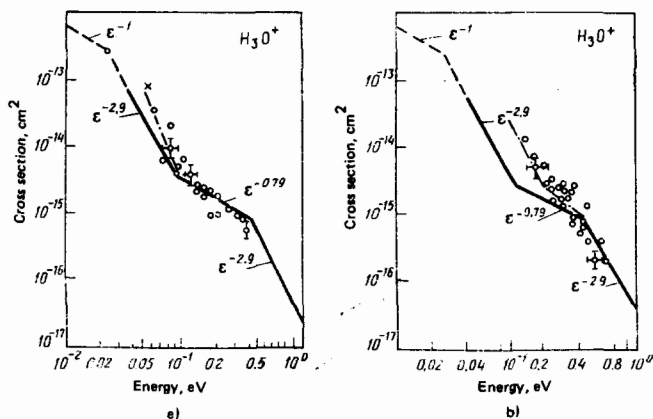


FIG. 9. Energy dependence of the d. r. cross section of H_3O^+ molecular ions. The circles represent experiment.⁸² a) Electron energy scatter 0.04 eV; b) electron energy scatter 0.15 eV; dashed line from reduction of process rate constant measurements.⁸³

The nature of the relationship described by (8) is determined by the energy $E_a(R_0)$ corresponding to the intersection point of the terms of the molecular ion and the autoionized state of the quasimolecule. If $E_a(R_0)$ is large compared to Γ and to the characteristic energy scatter of the electron beam, the $\sigma(E)$ relation exhibits a characteristic resonant structure. When intersection of the terms occurs near the bottom of the potential well of the molecular ion [$E_a(R_0)$ is small], expression (8) describes a $\sigma(\varepsilon)$ that decreases more sharply with energy than indicated by relation (7).

The energy relations (6)–(8) obtained on the basis of the general expression (2) for the d. r. cross section agree qualitatively with the experimental results in Figs. 2–9. For example, Table II gives results from measurements of d. r. cross sections at low collision energies ($0.01 < \varepsilon < 0.1$ eV).⁸² The electron energy above which the energy dependence of the d. r. cross section deviates from the inversely-proportional relation (7) is given in the last column of the table. Where this parameter is not indicated, small deviations from relation (7) that do not exceed the error of the experiment are observed over the entire range of electron energies. The slope of the energy curve $\sigma(\varepsilon)$ increases at electron energies exceeding ~ 0.1 eV. This behavior of $\sigma(\varepsilon)$ is consistent with expression (8), which follows from the general expression for the cross section in the case of an extremely small nuclear wave function width of the molecular ion. The increase in the sharpness of the cross section vs energy curve can also be seen in Figs. 4, 8, and 9, where the sharpest power-law dependence corresponds to expression (8) in the extreme case $\varepsilon \gg E_a(R_0)$, $\varepsilon \gg \Gamma$.⁶⁾

6) We note that the sharpest dependence of the d. r. cross section on electron energy according to (8) has the form $\sigma \sim \varepsilon^{-3}$, $\varepsilon \gg E_a \gg \Gamma$. However, relation (8) takes into account only one autoionized level of the quasimolecule. The contributions from the various autoionized states may prove to be comparable in the range of the parameters under consideration, and interference of contributions from these states may result in a sharper dependence of the cross section on energy.

TABLE II. Results of measurements of d. r. cross sections at low electron energies.⁸²

Molecular ion	D. r. cross section at $\varepsilon = 0.01$ eV, 10^{-13} cm ²	rate constant at $T_e = 120$ K, 10^{-7} cm ³ /sec	Energy beginning at which dependence of cross section on energy deviates from inverse proportionality
H_1^+ (all v)	0.6	4	0.07
H_2^+ ($v = 0 - 2$)	0.12	0.8	> 0.1
HD^+ (all v)	0.6	4	> 0.1
H_3^+ (all v)	0.4	2.7	> 0.1
CH^+ (exc)	1.1	7.4	> 0.1
CH^+ ($v = 0$)	0.6	4	> 0.1
NH^+	0.25	1.7	0.1
OH^+	0.2	1.3	> 0.1
C_2^+	1.4	9.4	> 0.1
N_2^+	1.85	5.7	> 0.1
NO^+	0.55	3.7	0.09
O_2^+	0.45	3	> 0.1
<hr/>			
H_2^+ ($v = 0$)	1.0	6.5	0.1
H_2^+	0.8	5.4	0.1
D_2^+	0.6	4	0.1
CH_2^+	1.2	8	> 0.1
CH_2^+	1.7	12	0.1
CH_2^+	1.3	9.5	0.07
CH_2^+	1.5	1.1	0.08
H_2O^+	1.8	1.2	0.1
H_3O^+	1.5	1.1	0.1
C_2H_2^+	1.4	9.4	0.1
C_2H_2^+	2.2	1.5	0.1
N_2H^+	1.8	1.2	0.06

The energy dependence of the d. r. cross section for the molecular ion O_2^+ in Fig. 6 shows a rather narrow resonance at $\varepsilon \approx 1.6$ eV. This structure of the cross section is described, as follows from the above analysis of the general expression (1) for the d. r. cross section, by relation (8) in the case when the width of the nuclear wave function of the molecular ion is small and the terms intersect in the high-energy range.⁹³ Since no such structure of the cross section was observed for the other systems, we may infer that the situation in which the intersection point is near the bottom of the potential well is the typical one.

Expression (6) qualitatively explains the oscillations observed on the energy curves of the d. r. cross sections for H_2^+ and H_3^+ when high-resolution apparatus is used (see Figs. 2 and 3). In these experiments, the molecular ions could have been in several different vibrational states, so that the measured cross section represents a sum of the type $\sum_i \sigma_i f_i$, where i is the number of the vibrational state, σ_i is the d. r. cross section for ions in that state, and f_i is the relative number of nuclear-ion molecules in that state. Since, as follows from (6), the energy dependence of the d. r. cross section of a vibrationally excited molecular ion reflects the oscillation structure of the nuclear wave function of this ion, we may state that the total cross section should exhibit a disordered oscillation structure.⁷⁾ The details of this structure are determined by the specific nature of the vibrational-state distribution of the molecular ions, which is very difficult⁶⁾ to establish experimentally.

7) O' Malley¹⁶⁷ makes an attempt at a qualitative explanation of this oscillation structure in terms of the influence of vibrationally excited Rydberg states of the molecules—an effect manifested in the form of narrow resonances superposed on the $\sigma \sim \varepsilon^{-1}$ relationship.

4. METHODS OF MEASUREMENT AND TEMPERATURE DEPENDENCE OF DISSOCIATIVE RECOMBINATION COEFFICIENT

The coefficient α , which is defined by relation (1), is the basic parameter determining the influence of charged-particle recombination on plasma properties. In this section we briefly describe methods for experimental study of the d.r. coefficient and discuss results of such studies.

a) Decay of gas-discharge plasma

The most natural method of measuring the d.r. coefficient is based on the use of relation (1). This method, which was elaborated in detail by M. A. Biondi *et al.*⁴ and has been used extensively by various authors, consists of measurement of the decrease in electron density with time in the afterglow of a gas-discharge plasma. This is usually done by a microwave procedure based on the dependence of the natural oscillation frequency of the microwave cavity on the density of the electrons filling the cavity. Excitation of electromagnetic vibrations in a microwave cavity enables us not only to measure the electron density, but also, if necessary, to heat the electron gas with the object of investigating the electron-temperature (average-energy) dependence of the d.r. coefficient.

In a decaying gas-discharge plasma, the continuity equation for the electron density N_e takes the form

$$\frac{\partial N_e}{\partial t} = D_a \Delta N_e - \alpha N_e^2, \quad (9)$$

where D_a is the coefficient of ambipolar diffusion. It was assumed in writing this relation first of all that there is only one molecular-ion species in the plasma, and, secondly, that no ionization of atomic particles occurs as a result, for example, of the Penning ionization mechanism, such as occurs when excited or metastable particles participate. The validity of the first assumption is tested by mass-spectral analysis to determine the ionic composition of the gas-discharge plasma, and that of the latter by optical measurements of metastable-atom density.

Since diffusion of the charged particles may be neglected at high gas densities, the solution of Eq. (9) with the initial condition $N_e(t=0) = N_0$ has the form.

$$\frac{1}{N_e(t)} = \frac{1}{N_0} + \alpha t. \quad (10)$$

The simple relation (10) is convenient for processing experimental data, and the very fact that the measured $N_e^{-1}(t)$ relation coincides with the straight line of (10) at high pressures confirms the validity of the assumptions made above. However, measurements indicate that at high gas pressures, $p \gg 10$ mm Hg, when the diffusion of charged particles is immaterial, complex molecular ions form rapidly in the plasma, with the result that its ionic composition becomes more complicated. Recombination-coefficient measurements are therefore usually made at intermediate gas pressures, at which diffusion and recombination make comparable contributions to the charged-particle balance. In such a situation, of course, the nature of the $N_e(t)$ relation is determined

by the geometry of the system containing the plasma. Equation (9) is solved numerically to determine the recombination coefficient from the measured $N_e(t)$ relation, with the diffusion coefficient D_a determined independently and the recombination coefficient α varied until the result of the numerical solution agrees with the measured relationship.

The above procedure is most convenient in investigation of the d.r. of molecular inert-gas ions, since the ionic composition of the plasma and the course of the processes that form and destroy the molecular ions are simplest in this case. The measurements are made both at thermodynamic equilibrium and under non-equilibrium conditions, with the electron temperature substantially above the temperature of the gas. In the latter case, as we have noted, the electrons are heated with an electromagnetic field set in oscillation in a microwave cavity. Here the nature of the electron energy distribution function, which, generally speaking, differs from Maxwellian, is determined by the ratio of the electromagnetic-field frequency ω to the frequency ν_{e1} of the elastic electron-atom collisions (see, for example, Ref. 94). If this ratio is large, the electron distribution function is Maxwellian and characterized by an average energy

$$\bar{\epsilon}_e = \frac{3}{2} T_e = \frac{M e^2 E^2}{4 m^2 \omega^2} + \frac{3}{2} T,$$

where m and M are the masses of the electron and the atom, respectively, E is the maximum electric field strength, and T is the temperature of the gas. If the frequency of electron-atom collisions is higher than or of the order of magnitude of the frequency of the external field, the distribution function differs significantly from Maxwellian. Here the average electron energy is expressed in terms of the collision cross section, and the accuracy with which this parameter is determined depends on the accuracy of the cross sections. The usual practical case is intermediate: the error in determination of $\bar{\epsilon}_e$ is small, but it influences the over-all accuracy of the experiment.

Another source of error in this method of measuring the d.r. coefficient is the fact that the microwave procedure of electron-density measurement yields volume-averaged values of N_e . Under conditions such that the characteristic diffusion and recombination times of the charged particles are of the same order of magnitude, the spatial electron-density distribution is known with an uncertainty that also influences the error in determination of α . In spite of these error sources, the method is characterized by rather high accuracy (which is estimated by the authors as being within 10–30%).

b) The spectroscopic method

Another method of measuring the d.r. coefficient is based on the fact that dissociative recombination results in the formation of excited atoms and molecules that emit light on transition to less highly excited states. The rate of decrease of the density of the emitting excited atoms can be established by measuring the intensity of the radiation as a function of time.^{18, 95–98} If the intensity of the radiation is propor-

tional to the squared charged-particle density measured or estimated in an auxiliary procedure, it is concluded that this radiation is of recombinational nature and the coefficient of recombination is established. The difficulties of this method stem, first of all, from the large number of possible d.r. channels and the correspondingly large number of lines emitted in a broad range of the spectrum. Since the measurements are usually made with spectral instruments that are sensitive over a limited region of the spectrum, this method cannot produce absolute values of the d.r. coefficient with the same accuracy as other experimental procedures.

Another problem that complicates use of this method arises when the d.r. coefficient is comparable to the rate constants of the other processes that take place in the afterglow and result in the formation of the same excited states of the atoms. In this case, new channels that populate excited states may appear during decay of the plasma, and since the rate of population of these levels may, by virtue of the variety of mechanisms, depend in different ways on the electron density, the relation of the time dependence of the radiation intensity to the d.r. coefficient may prove highly complex. This situation evidently arises in the case of recombination of He_2^+ . For this reason, the values of the d.r. coefficients obtained for He_2^+ by different authors⁷²⁻⁷⁶ disagree sharply with one another. The spectroscopic technique for investigation of d.r. is essentially our only source of information on the channels of the process and the final states of the products. This method is most effectively used in combination with study of the type of decay of the gas-discharge plasma,^{35,36,100} because the absolute value of the d.r. coefficient is established on the one hand, and, on the other, the dependence of the relative contributions of the various process channels on the electron and gas temperatures is investigated.

One variety of this method, which involves measurement of the radiation intensity as a function of time, is known as flash radiolysis (see, for example, Refs. 101 and 102). In this method, the d.r. coefficient is reconstructed from the variation of the plasma's radiation intensity over short time intervals ($\sim 10^{-7}$ sec), during which the plasma decays. The experiment is performed at atmospheric pressures, so that the plasma formed during short nanosecond flashes decays only as a result of recombination. The accuracy of the flash-radiolysis technique is limited, firstly by the aforementioned problems of establishing the correspondence between the emission of the plasma and specific recombination channels and secondly by the difficulties of measuring the electron density and ionic composition of a plasma that exists only for a few tens of nanoseconds.

c) The shock-wave method

This method enables us to investigate the temperature dependence of the d.r. coefficient over a broad range of gas temperatures. It is based on measurement of the characteristic dimension d of the region behind the shock front on which a significant change in charged-

particle density occurs as a result of recombination. This dimension is related to the characteristic recombination time τ_{rec} by the simple expression $d = c\tau_{\text{rec}}$, where c is the velocity of the shock front. The temperature of the gas behind the shock front is determined by its velocity. Charged particles are created by an external ionization source, and their concentration is measured by the usual probe methods. An important distinctive feature of this method arises out of the fact that the state of the gas behind the shock front is nearly that of thermodynamic equilibrium, so that the results of the measurements pertain to a situation in which the electron temperature T_e is close to the gas temperature T . Such conditions are not usually realized in the gas-discharge plasma.

The principal difficulty encountered in using this measurement procedure stems from the fact that the temperature of the gas and its pressure and ionic composition behind the shock front vary in rather complex fashion. Under certain conditions, therefore, determination of the d.r. coefficients requires a conversion that is often based on additional and not particularly sound assumptions. In particular, a plasma ionic composition is postulated and used unchanged behind the shock front. Since the temperature of the gas usually changes by more than an order of magnitude behind the front, this assumption is unjustified and may produce erroneous data. Thus, the sharp decrease in the d.r. coefficient with gas temperature that is in certain cases can be explained by an increase in the relative number of atomic ions, which recombine much less efficiently than molecular ions.¹⁰³ Since the species of the ions is not registered directly during the experiment, quantitative estimation of the resulting error is difficult.

Thus, the shock-wave method is significantly less accurate than methods based on study of plasma afterglow. In spite of these difficulties, the method and its various modifications have come into rather extensive use,^{13,50,28,67,104-109} because they make it possible to study the process over an extremely broad temperature range.

d) Results of measurements. Temperature dependence of dissociative recombination coefficient

Table III presents the results of measurements of the d.r. coefficient at room temperature ($T_e = T = 300$ K). These figures were obtained by averaging over the available experimental data. Figures 10-17 show values of the d.r. coefficient as functions of electron and gas temperatures that have been measured by various authors. The values of the parameters γ_e and γ_g that characterize this relationship and can be approximated by the power-law expression

$$\alpha = \alpha_0 \left(\frac{300}{T_e} \right)^{\gamma_e} \left(\frac{300}{T} \right)^{\gamma_g}, \quad (11)$$

appear in Table III.

We see from the data that the results of measurement of the temperature dependence of the d.r. coefficient depend strongly on the conditions of the experiment.

TABLE III. Dissociative recombination coefficient vs electron and gas temperatures from measurements by various authors.

Ion	T_e^* , 10^3 K	T_g , 10^3 K	α , 10^{-7} cm ³ /sec	γ_e	$\gamma_e + \gamma_d$	Method and conditions of measurement	Reference
Ne ₂ ⁺	3	3	—	1.5	—	Microwave cavity	88
	3-6	3	2-1.5	0.4	—	Same	10
	9-24	3	1.5-1	0.25	—	» »	10
	3-110	3	1.7-0.4	0.43	—	» »	9
	3-5	3-5	1.8-1.4	—	0.42	Microwave cavity, gas in furnace	11
	3-46	3	1.8-0.4	0.49	—	Microwave cavity, ions identified	—
Ar ₂ ⁺	4.5-9	4.5-9	1.4-1.2	—	0.5	double probe in shock tube	18
	9-35	9-35	1.2-0.15	—	1.5	Same	13
	3-70	3-5.6	2-0.5	0.42	1.12	Microwave cavity with furnace	17
	3-100	3	8-0.9	0.67	—	Same	28
	10-30	10-30	2.5-0.4	—	1.3	double probe in shock tube	28
	4.5-6.7	4.5-6.7	4.5-4	—	0.5	Same	13
Kr ₂ ⁺	6.7-30	6.7-30	4-0.4	—	1.5	» »	13
	3-100	3-5	8-0.8	0.64	1.5	Microwave cavity with furnace	29
	3-85	3	10-1	0.61	—	Microwave cavity	27
	9-27	9-27	42-9.6	—	1.5	double probe in shock tube	67
	3-190	3-5.2	10-1	0.53	1.5	Microwave cavity with furnace	34
	3-100	3	16-2.5	0.55	—	Microwave cavity	38
N ₂ ⁺	2-4.8	2-4.8	2.7	—	0.02	Microwave cavity with furnace	56
	35-72	35-72	1.2-0.4	—	1.5	Shock tube	68
	3-30	3	1.8-0.6	0.39	—	Microwave cavity, neon pressure 13 mm Hg	49
	7-27	7-27	1.3-0.8	—	0.37	Shock tube, neon pressure 2-6 mm Hg	49
NO ⁺	2-4.5	2-4.5	7-3	—	1	Microwave cavity with furnace, neon pressure 3 mm Hg	59
	2-3.6	2-3.6	10-4	—	1.2	Microwave cavity, neon pressure 132 mm Hg	57
	4-55	4	4-1.5	0.37	—	Microwave cavity, neon pressure 12 mm Hg	62
O ₂ ⁺	2-6.9	2-6.9	3-1	—	1	Microwave cavity, gas in furnace, neon pressure 20 mm Hg	44
	18-50	18-50	1-0.2	—	1.5	Shock tube	70
	3-50	3	2-0.3	0.56	—	Microwave cavity	49
	3-9	3-9	2-1.4	—	0.4	Microwave cavity, gas in furnace	38
CO ⁺	6-25	6-25	1.1-0.46	—	0.63	Shock tube	50
	3: 7.75	3	6.8-3.9	0.57	—	Microwave cavity	64

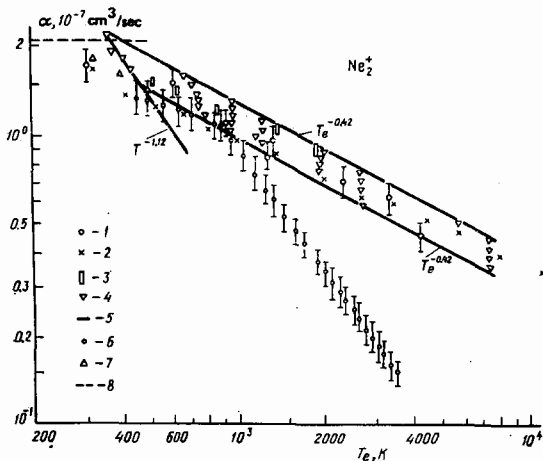


FIG. 10. Temperature dependence of d. r. coefficient of Ne₂⁺ molecular ions. $T = T_i = 300$ K: 1) from Ref. 12; 2) from Ref. 9; 3) from Ref. 10; 4) from Ref. 17; 5) from 17; $T = T_e = T_i$: 6) from Ref. 13; 7) from Ref. 11; 8) from Ref. 7.

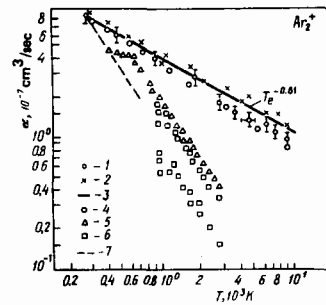


FIG. 11. Temperature dependence of d. r. coefficient of Ar₂⁺ molecular ions. $T = T_i = 300$ K: 1) from Ref. 22; 2) from Ref. 27; 3) from Ref. 27; 4) from Ref. 29; $T_e = T = T_i$: 5) from Ref. 13; 6) from Ref. 28; 7) from Ref. 29.

For example, when the measurements were made under nonequilibrium conditions, with the temperature of the gas remaining at room level while the electron temperature was varied over a broad range, the value of γ_e is about 0.5 ($\alpha \sim T_e^{-0.5}$). This agrees well with the previously described results of measurements of the dependence of the process cross section on electron energy, according to which the inverse proportionality $\sigma \sim 1/\epsilon$ is a good approximation for most of the systems studied over a broad range of electron energies. Using this relation, we easily obtain for the d.r. coefficient

$$\alpha = \langle \sigma v \rangle \sim T_e^{-0.5}. \quad (12)$$

5. DISSOCIATIVE RECOMBINATION WITH PARTICIPATION OF A COMPLEX ION

The d.r. coefficient increases with increasing complexity of the ion. Typical values of the dissociative recombination coefficient of electrons and cluster ions at room temperature are of the order of magnitude of 10^{-6} cm³/sec, or approximately an order of magnitude higher than the characteristic value of the dissociative recombination coefficient in the case of simple molecular ions. Thus, the appearance of composite and cluster ions in the gas accelerates the decay of the plasma.

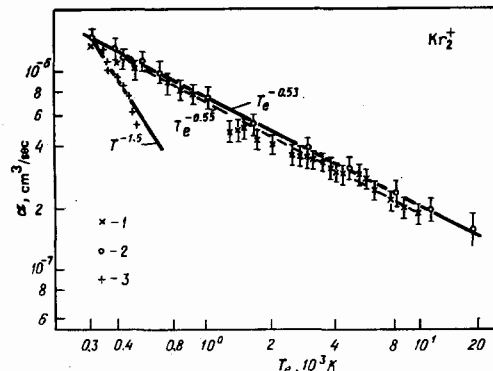


FIG. 12. Temperature dependence of d. r. coefficient of Kr₂⁺ molecular ions. $T_e = T = 300$ K: 1) from Ref. 35; 2) from Ref. 34; $T_i = T = T_e$: 3) from Ref. 34.

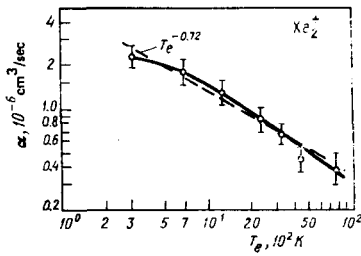


FIG. 13. Temperature dependence of d. r. coefficient of Xe_2^+ molecular ions.³⁶

An experimental technique for measurement of the coefficient of d.r. with participation of a cluster ion is based on investigation of the decay of a weakly ionized plasma in the afterglow. It employs the same microwave electron-heating procedure as in the simple case (see Sec. 3). The difference is that the recombination process usually involves several species of cluster ions. Therefore the investigation is performed at a constant gas temperature, since this ensures that the concentrations of the individual cluster-ion species remain constant during decay of the plasma. The concentrations of cluster ions of various species are determined at the corresponding temperature and pressure of the gas from the known equilibrium constants for cluster ions. A set of measurements made under different conditions can be used to establish the coefficient of d.r. with participation of a cluster ion of a given species as a function of electron temperature.

Dissociative recombination can proceed via many channels in the presence of complex and cluster ions. This circumstance can be used as a basis for simple models,^{3,113,114} that describes this process. Below we shall examine these dissociative-recombination models and use them as a basis for analysis of the results of existing experiments.

In the first of the models, treating the electron as a classical particle, we introduce the effective recombination radius R_0 . On entering the sphere of radius R_0 surrounding the complex ion, the electron recombines with probability ζ . The cross section of this process, which is equal to ζ times the cross section of penetration of the sphere R_0 by the electron with Coulomb interaction with the center, is given by¹¹⁵

$$\sigma_{\text{rec}} = \zeta \frac{\pi R_0 e^2}{\epsilon}, \quad \epsilon \ll \frac{e^2}{R_0}, \quad (13)$$

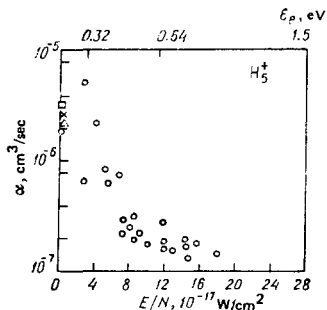


FIG. 14. Dependence of d. r. coefficient of H_5^+ molecular ions on E/N ratio and average energy of electrons in hydrogen in an electric field.¹¹⁰

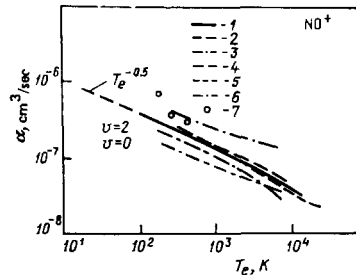


FIG. 15. Electron-temperature dependence of d. r. coefficient of NO^+ molecular ions. 1) from Ref. 48 (calculated from measured cross section) 2) from Ref. 48 (calculated from approximation of measured cross section); 3) from Ref. 62 (experiment); 4) from Ref. 111 (calculated); 5) from Ref. 63 (calculated from measured cross section); 6) from Ref. 90 (calculated); 7) from Ref. 65 (experiment).

where ϵ is the energy of the incident electron. For the coefficient of dissociative recombination with a Maxwellian electron velocity distribution, this gives

$$\alpha = \langle \nu \sigma_{\text{rec}} \rangle = \frac{2\sqrt{2\pi}}{\sqrt{mT_e}} \zeta R_0 e^2, \quad (14)$$

where m is the mass of the electron and T_e is the electron temperature.

Another model takes into account the fact that d.r. proceeds via the formation of autoionized states of the electron and the ion. It uses the presence of a large number of recombination channels, thus smoothing the characteristics of this process. According to the Breit-Wigner formula, the recombination cross section in this case is

$$\sigma_{\text{rec}} = \frac{2\pi\hbar^2}{m\epsilon} n(\epsilon), \quad n(\epsilon) = \sum_k \Gamma_k f_k; \quad (15)$$

here Γ_k is the width of the k -th autoionization level and $f_k(\epsilon) d\epsilon_k$ is the probability that the cluster ion has a configuration of the nuclei with which the energy of the autoionization level lies in the range from ϵ_k to $\epsilon_k + d\epsilon_k$. An assumption used within the framework of this model is that $n(\epsilon)$ is smooth. This is the case if the autoionization level is smeared out strongly by the motion of the nuclei or if the number of autoionization states is large.

For $n = \text{const}$, therefore, both models give the same dependence of the recombination cross section on in-

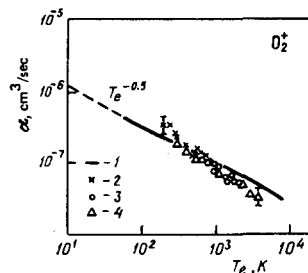


FIG. 16. Electron-temperature dependence of d. r. coefficient of O^+ molecular ions. 1) from Ref. 48 (calculated from measured cross section); 2) from Ref. 44; 3) from Ref. 50; from Ref. 49.

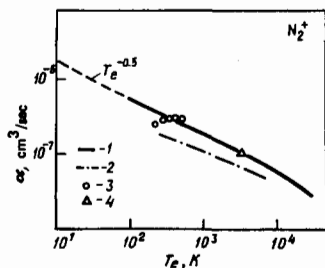


FIG. 17. Electron-temperature dependence of d. r. coefficient of N_2^+ molecular ions. 1) from Ref. 48 (calculated from measured cross section), 2) from Ref. 49 (experiment); 3) from Ref. 55; 4) from Ref. 112.

cident-electron energy [the quantity $(R_0/a_0)\xi$ in the first model is equivalent to $2n$ in the second; $a_0 = \hbar^2/me^2$ is the Bohr radius]. Therefore the consideration of many process channels gives the same result in the different models. This enhances the value of these approaches.

Using the parameter of the second model, relation (14) for the recombination coefficient is conveniently written in the form

$$\alpha = 2 \cdot 10^{-8} n \sqrt{\frac{300}{T_e}}, \quad (16)$$

where α is expressed in cm^3/sec and the electron temperature T_e in degrees. Since $n \sim 1$, the coefficient of recombination with participation of a composite ion at thermal energies is $\alpha \sim 10^{-8} \text{ cm}^3/\text{sec}$.

Table IV gives values of the parameters n deduced from experimental values of the recombination coefficient using relation (16). The experimental data pertain to room temperature unless another measurement temperature is indicated in parentheses. Statistical processing of the data in Table IV after elimination of

TABLE IV. Coefficient of recombination of electrons and cluster ions.

Cluster ion	Recombination coefficient, $10^{-6} \text{ m}^3/\text{sec}$	n	Reference
O_2^+	2.0 (200 K)	0.8	44, 118
N_2^+	1.6	0.8	14, 51, 149
$NO^+ \cdot NO$	1.7	0.8	53
He_2^+	3.4 (80 K)	0.9	117
H_2^+	0.23	0.12*	88
$CO^+ \cdot CO$	1.3	0.65	118
H_3^+	3.6 (205 K)	1.5	88
NH_4^+	1.6	0.8	101, 91
$Na^+ \cdot O_2$	5	2.5	119
$Na^+ \cdot CO_2$	5	2.5**)	119
H_3O^+	1.2	0.6	120, 121
$CO^+ \cdot (CO)_2$	1.9	1.0	116
$H_2O^+ \cdot H_2O$	2.4	1.2	120, 122
$H_2O^+ \cdot (H_2O)_2$	3.4	1.7	120, 122
$H_2O^+ \cdot (H_2O)_3$	3.6	1.8	120, 122
$H_2O^+ \cdot (H_2O)_4$	6 (205 K)	2.5	120
$H_2O^+ \cdot (H_2O)_5$	10 (205 K)	4.1	120
$NH_4^+ \cdot NH_3$	2.8	1.4	91
$NH_4^+ \cdot (NH_3)_2$	2.7	1.4	91
$NH_4^+ \cdot (NH_3)_3$	3 (200 K)	1.2	91
$NH_4^+ \cdot (NH_3)_4$	3 (200 K)	1.2	91

*Beam measurements⁸⁸ for an electron energy of 0.38 eV give $n = 0.19$.

**Beam measurements⁹² give $n = 1.2$.

TABLE V. Dissociative recombination coefficient α vs. electron temperature T_e , or dissociative recombination cross section σ_{rec} vs electron energy ϵ in the case of cluster ions.

Cluster ion	$-\frac{d \ln \alpha}{d \ln T_e}$	$-\frac{d \ln \sigma_{\text{rec}}}{d \ln \epsilon}$	Electron temperature range, K	Electron energy range, eV	Reference
He_2^+	1-1.6	—	80-250, $T = 80$ K	—	117
N_2^+	0.8-1.2*)	—	290-650	—	123
	0.41	—	300-5600	—	149
$CO^+ \cdot CO$	0.34	—	300-5000	—	118
H_3O^+	0.4-0.7**)	—	300-10 000	—	124
	—	2.9	—	0.38-0.110	
	—	0.79	—	0.110-0.42	92
	—	2.9	—	0.42-1.15	
D_2O^+	0.4-0.7**)	—	300-10 000	—	124
NH_4^+	1.0±0.3*)	—	200-410	—	101
	—	1.40	—	0.05-0.3	80
	—	3.43	—	0.3-2.0	80
$CO^+ \cdot (CO)_2$	0.33	—	200-5000	—	116
$H_2O^+ \cdot (H_2O)_2$	0.08***)	—	300-8000	—	91
$NH_4^+ \cdot NH_3$	0.147	—	300-3000	—	101
$H_2O^+ \cdot (H_2O)_3$	0.08***)	—	300-8000	—	91
$NH_4^+ \cdot (NH_3)_2$	0.050	—	300-3000	—	101
$H_3O^+ \cdot (H_2O)_3$	0.00***)	—	300-3000	—	91

*The electron temperature is equal to the gas temperature.

**Ion temperature varies in range 800-3500 K, γ_e increases with ion temperature.

***Ion and gas temperatures constant at 300-400 K.

the H_3^+ ion, which can hardly be regarded as composite, gives for the average value of the parameter n

$$\bar{n} = 1.4 \pm 0.5. \quad (17)$$

Table V gives the parameters of the dependence of the d.r. cross sections of cluster ions on electron energy or of the d.r. coefficient on electron temperature. We see that beam measurements produce either relation (13) or a sharper one.⁸¹ However, measurements made for more complex ions in a decaying plasma indicate that the dissociative recombination coefficient does not depend on temperature, i.e., that the recombination cross section is a smoother function of electron energy. This contradiction can be explained if we posit an indirect recombination mechanism for the complex cluster ions included in the table.⁷⁶ For a slow electron, the cross section of excitation of internal degrees of freedom of a cluster ion is proportional to $1/v$ (v is the electron velocity). If we assume that this transition results in capture of the electron into an autoionization level and that subsequent decay of the autoionization state is accompanied by dissociation, the d.r. coefficient will not depend on temperature in this mechanism.

Concluding the analysis, we can say that on the average, the models considered give the correct picture of the process. Relations (13) and (15) yield reliable estimates of the coefficients of d.r. of the electron and complex ion.

Let us consider the dependence of the d.r. coefficient for the electron and cluster ion as a function of the number of molecules present in the cluster ion. If we assume that the number of recombination channels (i.e., the number of autoionization states) of the elec-

⁸¹ We note that beam measurements⁸² give $\sigma_{\text{rec}} = 1/\epsilon$ for a whole list of complex ions if the electron energy is small enough ($\epsilon \leq 10^{-1} \text{ eV}$).

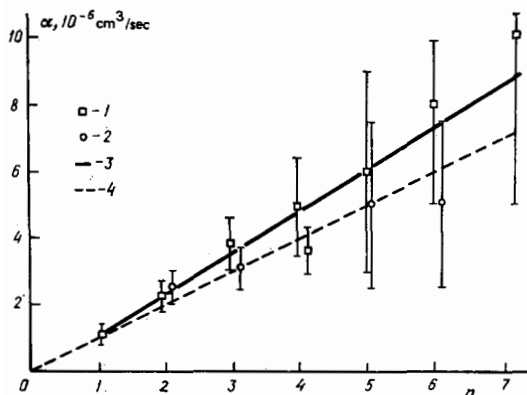


FIG. 18. Dependence of dissociative recombination coefficient of electrons and $H^+(H_2O)_n$ cluster ions on number of molecules n . Experiment: 1) from Ref. 120; 2) from Ref. 91; 3) from Botcher's formula¹²⁵: $\alpha_n = \alpha_1(1.3n - 0.3)$; 4) $\alpha_n = \alpha_1 n$ [α_n is the recombination coefficient for $H^+(H_2O)_n$ ions].

tron and cluster ion is proportional to the number of molecules in this ion, the recombination coefficient will be proportional to the number of molecules in the ion. Figure 18 shows plots of the coefficient of recombination of electrons and $H_3O^+(H_2O)_n$ cluster ions against the numbers of molecules in the ion. The experimental results of Ref. 34 were obtained by investigating the afterglow of a decaying plasma, and the theoretical expression of Ref. 44 makes use of these arguments.

6. RECOMBINATION OF VIBRATIONALLY EXCITED IONS AND PRODUCTS OF DISSOCIATIVE RECOMBINATION

We now discuss the dependence of the dissociative recombination coefficient on the vibrational temperature of the ions. It follows from general considerations that this dependence may vary. If decay proceeds via autoionization state 1 (Fig. 19) the term of which intersects the molecular-ion term near the bottom of the well, vibrational excitation of the molecular ion results in a certain decrease of the dissociative recombination coefficient. If recombination proceeds via the formation of autoionization state 2, it is more rapid from a vibrationally excited state of the ion than from the ground state.

Some information on the influence of vibrational excitation on the dissociative recombination coefficient can be obtained from its dependence on the temperature of the gas (see Table III). In fact, the dependence

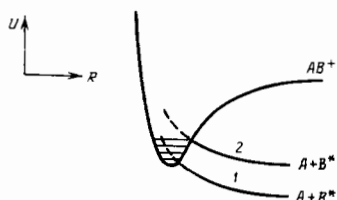


FIG. 19. Positions of terms of molecular ion and molecule in dissociative recombination.

of the dissociative recombination coefficient on gas temperature may be due solely to vibrational excitation of the gas. Analysis of the data in Table III shows that with the exception of helium, the term of the molecular ion intersects the autoionization term near the bottom of the well for inert-gas molecular ions, and that the recombination coefficient decreases with increasing vibrational excitation.

We shall assume that the influence of gas temperature reduces to the formation of vibrationally excited molecular ions, which recombine with a different efficiency. The over-all recombination coefficient can then be represented in the form¹²⁶

$$\alpha = (1 - X) \sum_v \alpha_v \left(\frac{300}{T_e} \right)^{\gamma_v} X^v, \quad (18)$$

$$X = \exp \left(- \frac{h\nu}{T_v} \right),$$

where T_v is the temperature corresponding to the vibrational levels of the ion, $h\nu$ is the energy of the vibrational quantum, α_v is the coefficient of recombination of the molecular ion from a given vibrational level, and T_e is the electron temperature. The main contribution comes from the first few vibrational levels at low vibrational temperatures. We may therefore introduce the approximation $\alpha_v/\alpha_0 = (\alpha_1/\alpha_0)^v$, which recognizes that high levels enter into the relation with low weights. Then, assuming that the exponent γ_v does not depend on vibrational level, we bring relation (18) to the form⁷⁰

$$\alpha = \frac{1 - X}{1 - (\alpha_1/\alpha_0) X} \alpha_0 \left(\frac{300}{T_e} \right)^{\gamma}. \quad (19)$$

Use of this relation in analyzing the experimental vibrational-temperature dependence of the dissociative recombination coefficient makes it possible to obtain the coefficient for a vibrationally excited ion. Results of this procedure as applied in Ref. 126 appear in Table VI. We see that the dissociative recombination coefficient drops off sharply with increasing vibrational excitation in the cases considered.

A procedure that permits measurement of the vibrational-level population of a molecular ion has been developed in recent years.^{127,128} It is based on tunable-laser electronic excitation of the molecular ion. The relative populations of molecular ions in various vibrational states and their time dependence are reconstructed from the fluorescence intensity of the electronically excited state of the ion. Ultimately, this makes it possible to determine the dropoff of ion density in the corresponding vibrational state with time. Vibrational relaxation is insignificant under the conditions of the experiment, since there are no transitions between vibrational states of the ion as a result of collisions

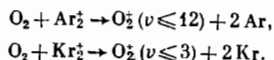
TABLE VI. Parameters of coefficient of dissociative recombination with participation of molecular ions of inert gases¹²⁶.

Ion	Ne ₂ ⁺	Ar ₂ ⁺	Kr ₂ ⁺
$\alpha_0, 10^{-7} \text{ cm}^3/\text{sec}$	1.8	10.4	24
$\alpha_1, 10^{-7} \text{ cm}^3/\text{sec}$	0.50	3.2	8.9
γ	0.43	0.67	0.55

with neutral particles of the gas. If it is assumed that these transitions are not caused by electrons, the measured time curves of the densities of the molecular ions in given vibrational states can be used to reconstruct the dissociative recombination coefficients for various vibrational states of the ion.

This procedure was applied in Refs. 127 and 128 for N_2^+ ions. Under the conditions of the experiment, the ion vibrational temperature was 1543 K, and the electron temperature and the rotational temperature of the ions were practically at room level. The measurements correspond to a weak dependence of the dissociative recombination coefficient on ion vibrational temperature. The dissociative recombination coefficients were $\alpha = 2.15 \cdot 10^{-7}$ cm³/sec for the ground vibrational state $v=0$, $\alpha = 2.42 \cdot 10^{-7}$ cm³/sec for $v=1$, and $\alpha = 2.70 \cdot 10^{-7}$ cm³/sec for $v=2$. We note that if quenching of the vibrational excitations of the ion proceeded more rapidly than recombination, the recombination coefficient reconstructed in this way for the vibrationally excited ion would have been considerably higher than the value for the unexcited ion.

Vibrational excitation of ions opens up new channels for dissociative recombination. This has been established experimentally in a study of the quantum yield of excited oxygen atoms $O(^1S)$ in the case of dissociative recombination of the molecular ion O_2^+ . In Ref. 129, O_2^+ ions were obtained by two methods, using different mixtures:



The quantum yield of metastable oxygen atoms $O(^1S)$ was 10% in the former case and 2% in the latter. These studies made it possible to clear up the contradictions between two earlier groups of measurements.¹³⁰ One group included the laboratory measurements of Ref. 131 and studies of the daytime skyglow and aurora¹³² at 5577 Å, which corresponds to the transition $O(^1S) - O(^1D) + \hbar\omega$. According to these studies, the quantum yield of the metastable oxygen atom $O(^1S)$ on recombination of O_2^+ was 8–10%. Another group of measurements^{135–139} pertained chiefly to investigation of the day and night skyglow and gave $O(^1S)$ quantum yields in the 2–5% range. Analysis of the vibrational state of O_2^+ for these cases¹³⁰ showed that the degree of vibrational excitation of the O_2^+ molecular ions was relatively high in the former, and low in the latter.

The formation of excited states of atoms in dissociative recombination of electrons and molecular ions is of interest as a mode of conversion of the energy of ionized particles to photon energy on deexcitation of excited ions that are dissociative-recombination products. Thus, dissociative recombination is responsible for the emission of the ionosphere in forbidden lines of atomic nitrogen and oxygen. According to Refs. 139–141, the quantum yield of the metastable nitrogen atom $N(^2P)$ in the dissociative recombination of NO^+ is near unity, and according to Ref. 141 it is 0.76 ± 0.06 ; the quantum yield of the metastable oxygen atom $O(^1S)$ in this process is 0.6 ± 0.2 .¹⁴²

A separate series of studies was devoted to the afterglow of excited inert-gas atoms formed by dissociative recombination with participation of molecular ions of inert gases.^{27, 35, 36, 100} Study of the emission spectra of atoms formed on dissociative recombination in neon,¹⁰⁰ argon,²⁷ krypton,³⁵ and xenon³⁶ yields qualitatively identical results: at thermal electron energies, the dissociative recombination products correspond to the same group of levels as the np state of the excited electron. The value of the principal quantum number n for the strongest of the lines observed is one higher than the principal quantum number of the unexcited electron. As the electron temperature rises, the number of observed spectral lines increases, i.e., dissociative recombination also produces excited atoms with higher excitation energies. To demonstrate this fact, Fig. 20 presents a diagram of the excited levels of the xenon-atom products of the dissociative recombination of Xe_2^+ and the electron at various electron temperatures.

The species of the atoms and molecules formed on dissociative recombinations of complex and cluster ions are a separate problem. Investigation of this problem is currently in its initial stage. A statistical theory of the dissociative recombination of complex ions was developed in Ref. 166. This theory has been used to calculate the d.r. product distribution of the molecular ions HCN^+ , H_3O^+ , CH_3^+ , and NH_4^+ at low tem-

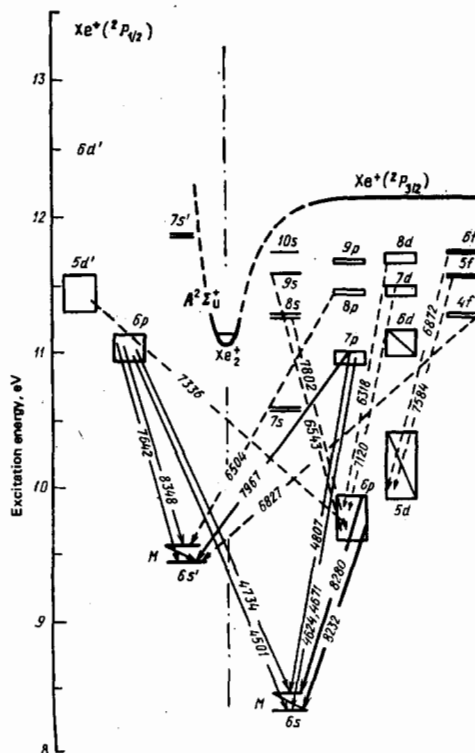


FIG. 20. Diagram of xenon energy levels that participate in dissociative recombination of Xe_2^+ with electrons.³⁶ The solid lines correspond to radiative transitions observed at $T_e = 300$ K. The dashed lines indicate transitions that are added at $T_e = 8000$ K. Ion and gas temperature 300 K. The diagonal lines indicate levels transitions from which could not be observed with the instrumentation used.

peratures. This information is of interest for the chemistry of interstellar clouds.

7. DISSOCIATIVE RECOMBINATION IN WEAKLY IONIZED GASES

As the fastest recombination process in volume, the dissociative recombination of electrons and ions often determines the parameters of the weakly ionized plasma and the phenomena that take place in it. Let us illustrate this with a few examples.

Dissociative recombination plays an important role in the charged-particle balance of the earth's ionosphere. It was research done in this area that led to the discovery of the dissociative recombination process itself. Analysis of photorecombination¹⁴³ in the earth's ionosphere has shown that this process is not capable of producing the observed rate of charge disappearance in the ionosphere.⁹⁾ And it was a further analysis of these phenomena that led to formulation of the dissociative recombination mechanism¹⁴⁴ and its experimental detection.¹⁴⁵

Let us estimate the densities of the electrons and ions in the earth's ionosphere (its *E* and *F* layers), recognizing that the formation of charged particles results from photoionization of atoms and molecules under the action of the sun's ultraviolet radiation and that their disintegration is determined by dissociative recombination. To estimate the electron-density scale, we shall assume that photoionization and recombination occur in a layer ≈ 100 km in thickness. Here the flux of photons, absorption of which results in ionization of oxygen atoms, as well as nitrogen and oxygen molecules and nitrogen oxides, is $j_p \sim 3 \cdot 10^{10}$ cm² sec⁻¹. From this we find with the balance equation $j_p/L \sim \alpha N_e^2$ that the electron density in the ionospheric region considered is of the order of magnitude $N_e \sim 10^5$ cm⁻³.

This estimate gives the correct order of magnitude for the electron density in the earth's ionosphere, but it is a rough one because it does not consider the nature of the processes in detail. It is in fact important that atoms and molecules of various species participate in photoionization, so that each of them absorbs a certain part of the solar spectrum and is responsible for photoionization at certain heights. If we were dealing with monochromatic radiation and a single ionized-particle species, absorption and photoionization would take place in a layer of thickness $L \sim 10$ km, since it is at this distance that the density of the ionosphere changes significantly. Owing to the presence of several species of ionized particles and the nonmonochromatic nature of the radiation, the thickness of the layer in which photoionization occurs is found to be an order of magnitude larger. But radiation at a given wavelength is absorbed in a layer of thickness $L \sim 10$ km, and the height of this layer is determined by the relation $N\sigma_p \times L \sim 1$ where σ_p is the cross section of photoionization

⁹⁾ The coefficient of the photorecombination $e + O^+ \rightarrow O + \hbar\omega$ at thermal electron energies is $5 \cdot 10^{-12}$ cm³/sec, which is several orders of magnitude below the value of the dissociative recombination coefficient.

by these photons and N is the density of the particles that absorb radiation most effectively at the particular wavelength. This relation corresponds to the condition that the photon path should be of the order of magnitude of the length over which the density of the atmosphere changes.

In addition to the above, ion-molecule reactions play an important role in the formation of the ionosphere, resulting in conversion of the atomic ion O^+ to the molecular ions NO^+ and O_2^+ , which recombine efficiently with electrons. Other factors of importance are the formation of atomic and molecular ions in excited states, downward transport of ions in the *F* layers of the ionosphere, and the variation of temperature with height in the atmosphere. Together with the characteristics of solar radiation, including the sun's zenith angle, these factors influence the density of the electrons in the ionosphere, its vertical profile, and the vertical distribution of the ion species. Since information on the basic processes is available, the parameters of the charged particle distribution in the ionosphere can be calculated with confidence (see, for example, Refs. 146–148). Moreover, measurements in the ionosphere are used to establish the parameters of the elementary processes, e.g., the contributions of dissociative recombination channels¹⁴⁹ and ion-molecular reactions.^{150, 151}

The characteristic time of recombination of electrons and ions in the daytime atmosphere is $(\alpha N_e)^{-1} \sim 10^2$ sec. Hence follows that the density of the charged particles in the ionosphere at night, when the flux of ionizing radiation from the sun is absent, is significantly lower than the daytime level. This quantity can be estimated from the electron balance equation $dN_e/dt = -\alpha N_e^2$, from which it follows that the characteristic density of the electrons in the night ionosphere $N_e \sim (\alpha t_n)^{-1} \sim 10^3$ cm⁻³, where $t_n \sim 10^4$ sec is the length of the night. This estimate explains the observed order of magnitude of the electron density in the night ionosphere, although careful analysis^{152, 153} indicates that the photoionizing radiation of the stars makes a significant contribution to the formation of the night ionosphere.

Another example of a situation in which d.r. significantly influences the macroscopic behavior of a weakly ionized gas is the contraction of positive gas-discharge columns. This phenomenon arises when a certain current or gas pressure is exceeded in the discharge, and consists of a sharp decrease in the transverse dimension of the region filled by the electrons—on contraction, the discharge moves away from the walls and continues to burn in the form of a bright glowing filament. It has been established by many years of experimental and theoretical study^{157, 158} that the most general mechanism of this contraction is as follows. At high specific energy inputs, the discharge acquires a radial temperature inhomogeneity, and this, because of the strong dependence of the rate constant of ionization of the gas molecules by electron impact on the ratio of the electric field strength to the gas density, causes the rapid formation of free electrons in a narrow axial region of the discharge tube. Contraction occurs when free elec-

trons formed near the tube axis recombine in the space before they reach the tube walls. Here the characteristic dimension r_e of the electron-filled region is estimated as the distance traveled by an electron in diffusion during the characteristic recombination time $\tau_{\text{rec}} \sim 1/\alpha_{\text{rec}} N_e$:

$$r_e \sim \sqrt{D_n \tau_{\text{rec}}} \sim \sqrt{\frac{D_n}{\alpha_{\text{rec}} N_e}}; \quad (20)$$

here N_e is the characteristic electron density in the discharge and D_n is the ambipolar diffusion coefficient.

We see that $r_e \ll R_0$ (the radius of the discharge tube) if

$$\frac{D_n}{R_0^2} \ll \alpha_{\text{rec}} N_e, \quad (21)$$

which is a necessary condition for contraction along with the requirement of sharp radial dependence of the rate constant of ionization of the molecules by electron impact.

In the gas-discharge plasma, dissociative recombination of electrons and molecular ions is practically the only charged-particle volume-neutralization process capable of competing with diffusion. In a molecular-gas discharge, where the basic ion species are generally molecular ions, condition (21) is satisfied over a broad range of variation of the discharge parameters; therefore the radial temperature nonuniformity requirement emerges as the basic condition for contraction.¹⁵⁸ In an inert-gas discharge, molecular ions predominate at high pressures (in the tens of mm Hg and higher) and relatively low gas temperatures (not above 1000 K); therefore the contracted-discharge range is limited in this case on both the high-current and low-current ends.^{154, 159}

Dissociative recombination plays an important role in the physics of gas lasers. Possibilities for the use of this process to create ultraviolet lasers were pointed out in Refs. 160 and 161. They have become realities during the last few years with the development of excimeric lasers. For example, this process is the basis of the mechanism creating inverse population in lasers that operate on the transitions between excited and ground (repulsive) terms of inert-gas dimers (Ar_2 , Kr_2 , Xe_2).¹⁶²⁻¹⁶⁴ The laser is excited as a result of passage of a strong electron beam through the dense inert gas. Most of the beam energy is expended on ionization of atoms and formation of free electrons. The subsequent processes



(R is the inert-gas atom), which take place very rapidly, result in efficient formation of excited inert-gas atoms R^* . The excimeric molecules R_2^* , which emit in the lasing process, are formed efficiently at high (above atmospheric) gas pressures:



If a certain amount of a halogen-containing gas (for example, F_2 or Cl_2) is added to the inert gas in the

situation described above, the process (24) may be accompanied by the chemical reaction¹⁶⁴



which results in the formation of excimeric molecules of the type RX^* (X is the halogen atom). The emission of these molecules, which occurs in the ultraviolet, can also be used to construct a laser. Excimeric lasers operating on transitions of dimers or inert-gas halides offer a unique source of coherent ultraviolet radiation with high energy properties.

8. CONCLUSION

Significant progress toward understanding of the details of the dissociative recombination process has been made during the last ten years. The advances have been due largely to the development of experimental beam techniques, which enable us to measure dissociative recombination cross sections. Studies of the earth's upper atmosphere and the development of excimeric lasers and other applied areas in the physics of weakly ionized plasma have also had more than minor roles. These investigations require detailed information on dissociative recombination and to some extent provide such data themselves. Together with the ongoing development of existing methods for measurement of the dissociative recombination coefficient, this has yielded a wealth of quantitative information on the process, and theoretical models that describe it have begun to appear as a result. On the whole, all this yields an updated conception of the dissociative recombination process, which is interesting in itself and manifests itself in a variety of phenomena in weakly ionized plasma. Further application of modern methods in investigation of the process will broaden our conception of it.

- ¹B. M. Smirnov, *Atomnye stolknoveniya i elementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in Plasmas)*, Atomizdat, Moscow, 1968, Chap. 10.
- ²A. V. Eletskii and B. M. Smirnov, In: *Modelirovanie i metody rascheta fiziko-khimicheskikh protsessov v nizkotemperaturnoi plazme (Modeling and Methods of Calculation of Physicochemical Processes in the Low-Temperature Plasma)*. L. S. Polak (ed.), Nauka, Moscow, 1974, p. 68.
- ³B. M. Smirnov, *Iony i vobuzhdennyye atomy v plazme (Ions and Excited Atoms in Plasmas)*, Atomizdat, Moscow, 1974, Chap. 8.
- ⁴J. N. Bardsley and M. A. Biondi, In: *Advances in Atomic and Molecular Physics*, Ed. D. R. Bates and I. Esterman, N.Y.: Academic Press 6, 1 (1970).
- ⁵K. B. Persson and S. C. Brown, *Phys. Rev.* 100, 729 (1955).
- ⁶M. A. Biondi and S. C. Brown, *ibid.* 76, 1697 (1949).
- ⁷R. B. Holt *et al.*, *ibid.* 77, 239 (1950).
- ⁸T. R. Connor and M. A. Biondi, *ibid.* Ser. A. 140, 778 (1965).
- ⁹L. Frommhold, M. A. Biondi, and F. J. Mehr, *ibid.* 165, 44 (1968).
- ¹⁰W. Hess, *Zs. Naturforsch.* 20a, 451 (1965).
- ¹¹W. H. Kasner, *Phys. Rev.* 167, 148 (1968).
- ¹²J. Philbrick, F. J. Mehr, and M. A. Biondi, *ibid.* 181, 270 (1969).
- ¹³A. J. Cunningham and R. M. Hobson, *ibid.* 185, 98 (1969).
- ¹⁴E. O. Gray and D. E. Kerr, *Ann. of Phys.* 17, 276 (1962).
- ¹⁵M. A. Biondi, *Phys. Rev.* 129, 1181 (1963).

- ¹⁶F. J. Mehr and M. A. Biondi, *Bull. Am. Phys. Soc.* **13**, 199 (1968).
- ¹⁷O. Mikus and P. Lukac, In: *Proc. of 4th ESCAMPIG. Essen*, Rept. C 37, 89 (1978).
- ¹⁸H. J. Oskam and V. R. Mittelstadt, *Phys. Rev.* **132**, 1445 (1963).
- ¹⁹M. S. Sexton, M. J. Mulcahy, and J. J. Lennon, In: *Proc. of 4th Intern. Conference on Phenomena in Ionized Gases. Upsala*, 1959.
- ²⁰S. Takeda, *J. Phys. Soc. Japan* **13**, 112 (1958).
- ²¹P. Lukac, In: *Proc. of 9th Intern. Conference of Phenomena in Ionized Gases. Bucharest*, 1961, p. 3.
- ²²F. J. Mehr and M. A. Biondi, *Phys. Rev.* **176**, 322 (1968).
- ²³A. Redfield and R. B. Holt, *ibid.* **82**, 874 (1951).
- ²⁴M. A. Biondi, *ibid.* **83**, 1078 (1951).
- ²⁵M. H. Mentzoni, *J. Appl. Phys.* **36**, 57 (1965).
- ²⁶D. Smith *et al.*, *J. Phys. Ser. B* **3**, 34 (1970).
- ²⁷Y. J. Shiu and M. A. Biondi, *Phys. Rev. Ser. A* **17**, 868 (1978).
- ²⁸J. N. Fox and R. M. Hobson, *Phys. Rev. Lett.* **17**, 161 (1966).
- ²⁹P. Lukac, O. Mikus, and Z. Zabudla, collection cited in Ref. 17, p. 90.
- ³⁰N. A. Popov and E. A. Afanas'ev, *Zh. Eksp. Teor. Fiz.* **29**, 846 (1959) [sic].
- ³¹J. M. Richardson, *Phys. Rev.* **82**, 318 (1951); **88**, 895 (1952).
- ³²M. S. Sexton and J. D. Craggs, *J. Electr. and Contr.* **4**, 493 (1958).
- ³³J. J. Lennon and M. C. Sexton, *ibid.* **7**, 123 (1959).
- ³⁴O. Mikus, *J. Phys. Ser. D* **11**, L 39 (1978); collection cited in Ref. 17, p. 91.
- ³⁵Y. J. Shiu, and M. A. Biondi, *Phys. Rev. Ser. A* **16**, 1817 (1977); *Bull. Am. Phys. Soc.* **23**, No. 2, Rept KB-6 (1978).
- ³⁶Y. J. Shiu, M. A. Biondi, and D. P. Sipler, *Phys. Rev. Ser. A* **15**, 494 (1977).
- ³⁷P. Lukas, I. Trnovec, and O. Mikus, In: *Proc. of 8th Intern. Conference of Physics of Electron and Atomic Collisions. Beograd*, 1973, p. 893.
- ³⁸M. H. Mentzoni, *J. Appl. Phys.* **36**, 57 (1965).
- ³⁹D. Smith and C. V. Goodall, *Planet and Space Sci.* **16**, 1177 (1968).
- ⁴⁰E. C. Zipf, *Bull. Am. Phys. Soc.*, **15**, 418 (1970).
- ⁴¹C. B. Kretschmer and H. L. Petersen, *J. Appl. Phys.* **34**, 3209 (1963).
- ⁴²R. C. Gunton, *Bull. Am. Phys. Soc.* **12**, 218 (1967).
- ⁴³M. Hirsch *et al.*, *ibid.* **11**, 495 (1966).
- ⁴⁴W. H. Kasner and M. A. Biondi, *Phys. Rev.* **174**, 139 (1968).
- ⁴⁵A. I. Anisimov, N. I. Vinogradov, and V. E. Golant, *Zh. Tekh. Fiz.* **33**, 1141 (1963) [*Sov. Phys. Tech. Phys.* **8**, 850 (1964)].
- ⁴⁶J. B. Hasted, M. R. Mahdavi, and G. L. Awad, In: *Proc. of 7th Intern. Conference on Physics of Electron and Atomic Collisions. Amsterdam*, 1971, p. 999.
- ⁴⁷E. H. Holt, *Bull. Am. Phys. Soc.* **4**, 112 (1959).
- ⁴⁸P. M. Mul and J. W. McGowan, *J. Phys. Ser. B* **12**, 1591 (1979).
- ⁴⁹F. J. Mehr and M. A. Biondi, *Phys. Rev.* **181**, 264 (1969).
- ⁵⁰A. J. Cunningham and R. M. Hobson, *J. Phys. Ser. B* **5**, 2320, 2328 (1972).
- ⁵¹W. H. Kasner M. A. Biondi, *Phys. Rev. Ser. A* **137A**, 137 (1965).
- ⁵²A. C. Faire and K. S. W. Champion, *ibid.* **113**, 1 (1959).
- ⁵³W. H. Kasner, W. A. Rogers, and M. A. Biondi, *Phys. Rev. Lett.* **7**, 321 (1961).
- ⁵⁴J. J. Gibbons, In: *Abstracts of DASA Reaction Rate Conference, Boulder, Colorado*, 1961.
- ⁵⁵W. H. Kasner, *Phys. Rev.* **164**, 194 (1967).
- ⁵⁶E. S. Zipf, *Geophys. Res. Lett.* **7**, 645 (1980); *Bull. Am. Phys. Soc.* **24**, 2, (1979).
- ⁵⁷R. C. Gunton and T. M. Shaw, *Phys. Rev.* **140**, 44 (1965).
- ⁵⁸R. A. Young and G. St. John, *ibid.* **152**, 25 (1966).
- ⁵⁹C. S. Weller and M. A. Biondi, *ibid.* **172**, 198 (1968).
- ⁶⁰R. C. Gunton, *Bull. Am. Phys. Soc.* **15**, 418 (1970).
- ⁶¹W. B. Kunkel and A. L. Gardner, *J. Chem. Phys.* **37**, 1785 (1962).
- ⁶²C. M. Huang, M. A. Biondi, and R. Johnsen, *Phys. Rev. Ser. A* **11**, 901 (1975).
- ⁶³C. S. Walls and G. H. Dunn, *J. Geophys. Res.* **79**, 1911 (1974).
- ⁶⁴M. H. Mentzoni and J. Donohoe, *J. Phys. Lett. Ser. A* **26**, 1911 (1968).
- ⁶⁵C. S. Weller and M. A. Biondi, *Phys. Rev. Lett.* **19**, 59 (1967).
- ⁶⁶N. A. Nesterko and É. N. Taran, *Teplofiz. Vys. Temp.* **10**, 961 (1972) [*High Temp. (USSR)* **10**, 867 (1972)].
- ⁶⁷A. J. Cunningham and R. M. Hobson, *J. Phys. Ser. B* **4**, 1773 (1972).
- ⁶⁸M. G. Dunn and J. A. Lordi, *AIAA J.* **8**, 339 (1970).
- ⁶⁹A. J. Cunningham and R. M. Hobson, *J. Phys. Ser. B* **5**, 2328 (1972).
- ⁷⁰M. G. Dunn and J. A. Lordi, *AIAA J.* **8**, 614 (1970).
- ⁷¹R. C. Gunton, *Bull. Am. Phys. Soc.* **15**, 418 (1970).
- ⁷²R. Deloche, A. Confalon, and M. Cheret, *C. R. Ac. Sci.* **267**, 934 (1968).
- ⁷³J. Berland *et al.*, *Phys. Rev. Ser. A* **1**, 887 (1970).
- ⁷⁴A. W. Johnson and J. B. Gerardo, *ibid.* **5**, 1410 (1972); *Phys. Rev. Lett.*, **28**, 1096 (1972).
- ⁷⁵R. Deloche *et al.*, *Phys. Rev. Ser. A* **13**, 1140 (1976).
- ⁷⁶D. R. Bates, collection cited in Ref. 4, vol. 15, p. 235, 1979.
- ⁷⁷O. Mikus and P. Lukac, In: *Proc. of 4th ESCAMPIG. Essen*, 1978, Rept. C30, p. 82.
- ⁷⁸I. Ya. Fugol', Author's Abstract of Doctorate Dissertation, Physico-Technical Institute of the Ukrainian Academy of Sciences, Khar'kov, 1971.
- ⁷⁹É. I. Asinovskii and V. A. Kirillin, in: *Khimiya plazmy (Plasma Chemistry)*, B. M. Smirnov (ed.), Atomizdat, Moscow, 1978, no. 5, p. 66.
- ⁸⁰R. D. DuBois, J. B. Jeffrey, and G. H. Dunn, *Phys. Rev.* **17**, 1314 (1978).
- ⁸¹D. Auerbach *et al.*, *J. Phys. Ser. B* **10**, 3797 (1977).
- ⁸²J. M. McGowan *et al.*, *Phys. Rev. Lett.* **42**, 373 (1979).
- ⁸³M. K. Vogler and G. H. Dunn, *Phys. Rev. Ser. A* **11**, 1983 (1975).
- ⁸⁴R. A. Phaneuf and D. N. Crandall and G. H. Dunn, *ibid.* p. 528.
- ⁸⁵B. Peart and K. T. Dolder, *J. Phys. Ser. B* **7**, 236 (1974).
- ⁸⁶C. Bottcher and K. Kocken, *ibid.* p. L5.
- ⁸⁷J. W. McGowan, R. Caudano, and J. Keyser, *Phys. Rev. Lett.* **36**, 1447 (1976).
- ⁸⁸M. T. Leu, M. A. Biondi, and R. Johnsen, *Phys. Rev. Ser. A* **8**, 413 (1973).
- ⁸⁹B. Peart and K. T. Dolder, *J. Phys. Ser. B* **7**, 1948 (1974).
- ⁹⁰H. H. Michels, *Air Force Cambridge Res. Lab. Rept. N3 AFCLR-TR-75-0509*, 1975.
- ⁹¹C. M. Huang, M. A. Biondi, and R. Johnsen, *Phys. Rev. Ser. A* **14**, 984 (1976).
- ⁹²R. A. Heppner *et al.*, *Phys. Rev. Ser. A* **13**, 1000 (1976).
- ⁹³V. D. Kulagin, *Dokl. Akad. Nauk SSSR* **230**, 1326 (1976) [*Sov. Phys. Dokl.* **21**, 594 (1976)].
- ⁹⁴B. M. Smirnov, *Fizika slaboionizovannogo gaza (The Physics of Weakly Ionized Gases)*, 2nd ed., Fizmatgiz, Moscow, 1978.
- ⁹⁵C. B. Collins and W. B. Hurt, *Phys. Rev.* **177**, 257 (1969).
- ⁹⁶G. F. Sauter and R. A. Gerber, and H. J. Oskam, *Physica*, **32**, 1921 (1966).
- ⁹⁷G. K. Born, *Phys. Rev.* **169**, 155 (1968).
- ⁹⁸G. E. Veatch and H. J. Oskam, *ibid.* Ser. A **2**, 1422 (1970).
- ⁹⁹C. B. Collins and H. S. Hicks, and W. E. Wells, *ibid.* p. 797.
- ¹⁰⁰L. Frommhold and M. A. Biondi, *ibid.* **185**, 244 (1969).
- ¹⁰¹M. C. Sauer and W. A. Mulac, *J. Chem. Phys.* **55**, 1982 (1971).
- ¹⁰²I. C. Plumb, D. Smith, and N. G. Adams, *J. Phys. Ser. B* **4**, 1762 (1972).

- ¹⁰³M. B. Zheleznyak, *Teplofiz. Vys. Temp.* **11**, 422 (1973) [High Temp. (USSR) **11**, 165 (1973)].
- ¹⁰⁴J. N. Fox, T. I. McLaren and R. M. Hobson, *Phys. Fluids* **17**, 161 (1966).
- ¹⁰⁵T. I. McLaren and R. M. Hobson, *ibid.* **11**, 2162 (1968).
- ¹⁰⁶S. C. Lin, R. A. Neal, and N. I. Fyfe, *ibid.* **5**, 1633 (1962).
- ¹⁰⁷S. C. Lin and J. D. Teare, *ibid.* **6**, 355 (1963).
- ¹⁰⁸R. P. Stein *et al.*, *ibid.* **7**, 1641 (1964).
- ¹⁰⁹L. N. Wilson and E. W. Evans, *J. Chem. Phys.* **46**, 859 (1967).
- ¹¹⁰D. W. Trainor, *Chem. Phys. Lett.* **5**, 361 (1978).
- ¹¹¹J. N. Bardsley, *J. Phys. Ser. B* **1**, 349 (1968).
- ¹¹²J. Sayers, *J. Atm. and Terr. Phys. Spec. Suppl.* **6**, 212 (1956).
- ¹¹³B. M. Smirnov, *Zh. Eksp. Teor. Fiz.* **72**, 1392 (1977) [*Sov. Phys. JETP* **45**, 731 (1977)].
- ¹¹⁴B. M. Smirnov, *Usp. Fiz. Nauk* **121**, 231 (1977) [*Sov. Phys. Usp.* **20**, 119 (1977)].
- ¹¹⁵L. D. Landau and E. M. Lifshits, *Mekhanika (Mechanics)*, Fizmatgiz, Moscow, 1958.
- ¹¹⁶I. C. Plumb, D. Smith, and N. G. Adams, *J. Phys. Ser. B* **4**, 1762 (1972).
- ¹¹⁷J. B. Gerardo and M. A. Gusinov, *Phys. Rev. Ser. A* **3**, 255 (1971).
- ¹¹⁸M. Whitaker, M. A. Biondi, and R. Johnsen, *ibid.* **23**, 1481 (1981).
- ¹¹⁹G. E. Keller and R. A. Beyer, *J. Geophys. Res.* **76**, 289 (1971).
- ¹²⁰M. T. Leu, M. A. Biondi, and R. Johnsen, *Phys. Rev. Ser. A* **7**, 292 (1973).
- ¹²¹W. Lindinger, *ibid.* p. 328.
- ¹²²C. M. Huang *et al.*, *ibid.* **18**, 64 (1978).
- ¹²³R. Hackam, *Planet and Space Sci.* **13**, 667 (1965).
- ¹²⁴G. L. Ogram *et al.*, *Bull. Am. Phys. Soc.* **24**, 13 (1979).
- ¹²⁵C. Bottcher, *J. Phys. Ser. B* **11**, 3887 (1978).
- ¹²⁶T. F. O'Malley, A. J. Cunningham, and R. M. Hobson, *ibid.* **5**, 2126 (1972); **14**, 773 (1981).
- ¹²⁷E. C. Zipf, *Bull. Amer. Phys. Soc.* **24**, 129 (1979).
- ¹²⁸E. C. Zipf, *Geophys. Res. Lett.* **7**, 645 (1980).
- ¹²⁹E. C. Zipf, *J. Geophys. Res.* **85**, 4232 (1980).
- ¹³⁰D. F. Bates and E. C. Zipf, *Planet and Space Sci.* **28**, 1081 (1980).
- ¹³¹E. C. Zipf, *Bull. Am. Phys. Soc.* **15**, 418 (1970).
- ¹³²J. E. Frederick *et al.*, *J. Geophys. Res.* **81**, 3923 (1976).
- ¹³³J. P. Kopp *et al.*, *ibid.* **82**, 4715 (1977).
- ¹³⁴P. M. Mul and J. W. McGowan, *Astrophys. J. (Lett.)* **227**, L157 (1979).
- ¹³⁵G. Hernandes, *Planet. Space Sci.* **19**, 467 (1971).
- ¹³⁶P. B. Hays and W. E. Sharp, *J. Geophys. Res.* **78**, 1153 (1973).
- ¹³⁷E. C. Zipf, *Geophys. Res. Lett.* **6**, 881 (1979).
- ¹³⁸R. R. O'Neil, E. T. P. Lee, and E. R. Huppi, *J. Geophys. Res.* **84**, 823 (1979).
- ¹³⁹D. W. Ruch *et al.*, *ibid.* **80**, 2300 (1975).
- ¹⁴⁰M. R. Torr *et al.*, *ibid.* **81**, 531 (1976).
- ¹⁴¹D. Kley, G. M. Lawrence and E. J. Stone, *J. Chem. Phys.* **66**, 4157 (1977).
- ¹⁴²L. L. Gogger, L. S. Smith, and R. M. Harper, *Planet and Space Sci.* **25**, 155 (1977).
- ¹⁴³D. R. Bates *et al.*, *Proc. Roy. Soc. Ser. A* **170**, 322 (1939).
- ¹⁴⁴D. R. Bates and H. S. Massey, *ibid.* **192**, 1 (1947).
- ¹⁴⁵M. A. Biondi and S. C. Brown, *Phys. Rev.* **76**, 1697 (1949).
- ¹⁴⁶M. Oppenheimer, A. Dalgarno, and H. C. Brinton, *J. Geophys. Res.* **81**, 3762 (1976).
- ¹⁴⁷M. Oppenheimer *et al.*, *ibid.* **82**, 191 (1977).
- ¹⁴⁸M. Oppenheimer *et al.*, *ibid.* p. 5485.
- ¹⁴⁹M. Whitaker, M. A. Biondi, and R. Johnsen, *Phys. Rev. Ser. A* **24**, 743 (1981).
- ¹⁵⁰D. G. Torr *et al.*, *J. Geophys. Res.*, **82**, 1631 (1977).
- ¹⁵¹D. G. Torr, *ibid.* **84**, 1939 (1979).
- ¹⁵²D. F. Strobel *et al.*, *ibid.* **79**, 3171 (1974).
- ¹⁵³D. F. Strobel, C. B. Opal and R. R. Meier, *Planet and Space Sci.*, **28**, 1027 (1980).
- ¹⁵⁴V. Yu. Baranov and K. N. Ul'yanov, *Zh. Tekh. Fiz.* **39**, 249, 259 (1969) [*Sov. Phys. Tech. Phys.* **14**, 176, 183 (1969)].
- ¹⁵⁵P. M. Mul and J. W. McGowan, *Astrophys. J.* **237**, 749 (1980).
- ¹⁵⁶A. V. Elets'kii and A. N. Starostin, *Fiz. plazmy* **1**, 684 (1975); **2**, 838 (1976) [*Sov. J. Plasma Phys.* **1**, 377 (1975); **2**, 466 (1976)].
- ¹⁵⁷A. V. Elets'kii and A. T. Rakhimov, in: *Khimiya Plazmy (Plasma Chemistry)*, B. M. Smirnov (ed.), Atomizdat, Moscow, 1977, No. 4, p. 123.
- ¹⁵⁸Yu. P. Raizer, *Osnovy sovremennoi fiziki gazorazryadnykh protsessov (Fundamentals of Contemporary Gas-Discharge Physics)*, Nauka, Moscow, 1980, Chap. V.
- ¹⁵⁹V. L. Bychkov and A. V. Elets'kii, *Pis'ma Zh. Tekh. Fiz.* **4**, 942 (1978) [sic].
- ¹⁶⁰B. M. Smirnov, *Dokl. Akad. Nauk SSSR* **183**, 554 (1968) [*Sov. Phys. Dokl.* **13**, 1148 (1969)].
- ¹⁶¹L. Ya. Efremenkova and B. M. Smirnov, *ibid.* **203**, 779 (1972) [17, 336 (1972)].
- ¹⁶²C. W. Werner *et al.*, *Appl. Phys. Lett.*, **25**, 235 (1974).
- ¹⁶³E. V. George and C. K. Rhodes, *ibid.* **23**, 139 (1973).
- ¹⁶⁴A. V. Elets'kii, *Usp. Fiz. Nauk* **125**, 279 (1978) [*Sov. Phys. Usp.* **21**, 502 (1978)].
- ¹⁶⁵P. M. Mul *et al.*, *J. Phys. Ser. B* **14**, 1353 (1981).
- ¹⁶⁶E. Herbst, *Astrophys. J.* **222**, 508 (1978).
- ¹⁶⁷T. F. O'Malley, *J. Phys. Ser. B* **14**, 1229 (1981).

Translated by R. W. Bowers