

Three-body electron attachment to a molecule

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Mechanisms for three-body electron attachment to a molecule are examined. Methods for studying this process experimentally are described. The measurements of the characteristics of the process and their dependence on the parameters of the molecule and the energy of the electron are presented. It is shown that electron attachment to a molecule in a gas and a liquid are related. It is shown that three-body attachment is important in the low-temperature plasma of the upper atmosphere, high-pressure discharges, and gaseous dielectrics.

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1. INTRODUCTION

Electron attachment to a neutral particle accompanied by the formation of a negative ion is a process in which negative charge is transferred from a light particle to a heavy particle. This process sharply reduces the mobility of negative charges, and therefore the conductivity of a plasma also. For this reason, it significantly alters the phenomena occurring in the earth's ionosphere, gas discharges, and plasmas. The attachment of an electron to an atom is possible in the presence of a third particle or as a result of the emission of a photon, which carry away the excess energy. The cross section for photoattachment is small, and this process is important only in a highly rarefied gas. When the atom is replaced by a molecule, dissociative attachment becomes possible and three-body attachment is significantly accelerated. For a large number of molecules the electron affinity of the fragments formed is less than the dissociative energy, and the process of dissociative attachment has an energy threshold. The process of three-body attachment, whose efficiency is highest at low electron energies, is free of this limitation. In addition, as the gas pressure increases the three-body process "chokes off" dissociative attachment. Thus three-body attachment of an electron to a neutral particle is a typical process in quite dense media. It is also important for rarefied gases, if for some reason the two-particle process is forbidden. For example, it is responsible for the annihilation of thermal electrons formed by an external ionizer in air under normal conditions.

The process of three-body attachment in the presence of a third body—an electron—can be important only for strongly ionized plasma, where negative ions are unimportant owing to their efficient destruction. The process of three-body electron attachment to an atom affects analogously the properties of a plasma only under very specific

conditions. For this, on the one hand, the degree of dissociation of the molecules must be high, while on the other the destruction of negative ions must be weak. Such conditions are rarely realized in practice, and there is very little information about three-body electron attachment to an atom.¹ The most important and most completely studied process is three-body electron attachment by the scheme



(A is a molecule and B is a molecule or atom), which is the process that will be studied in this review. The range of gas temperatures for which it makes sense to take this process into account extends from cryogenic temperatures up to temperatures of several thousands of degrees, and electron temperatures of up to several electron volts.

The question of how the properties of an isolated molecule change as the density of the surrounding medium increases lies at the junction of physics, chemistry, and biology. The limiting case of a dense medium are liquids, the theory of which has by no means been completed. In the last few years successful attempts have been made to explain the experimental data on electron attachment to molecules in a liquid based on data on processes occurring in dense gaseous media. This concerns primarily nonpolar liquids, where the electron is assumed to be quasifree. Aside from general theoretical interest, the study of processes with the participation of electrons in condensed media is also of purely practical interest. Such processes are important in electric breakdown of liquid dielectrics and in working with liquid ionization chambers in experimental nuclear physics.

In this review we present the latest ideas about the process of three-body electron attachment to a molecule. There are a number of reviews on this subject,^{1–8} where attachment to the O₂ molecule is primarily discussed. Even for this well-

studied reaction, new and important results have been obtained in the last ten years: a strong isotopic effect has been discovered; it has been found that van-der-Waals molecules play an important role in attachment; a series of calculations of the rate constants for three-body attachment in nonequilibrium weakly-ionized plasma has been performed. A large amount of factual material on three-body electron attachment to other neutral particles has been accumulated. Finally, the relationship between the attachment processes in gaseous and liquid phases is becoming increasingly clearer.^{4,5,9,10}

2. MECHANISMS FOR THREE-BODY ELECTRON ATTACHMENT TO A MOLECULE

The process of three-body attachment can be characterized, by analogy to two-body collisions, by the cross section σ_a and the rate constant k_a , which are related by the expression

$$k_a = \langle \sigma_a v \rangle,$$

where the brackets indicate averaging over the electron velocities v . The rate of electron loss via three-body attachment to a molecule A in the presence of a third body B usually depends quadratically on the gas pressure, and the rate constant for three-body attachment is determined from the equation of balance from the density of negative ions $[A^-]$:

$$\frac{d[A^-]}{dt} = k_a N_e [A][B], \quad (2)$$

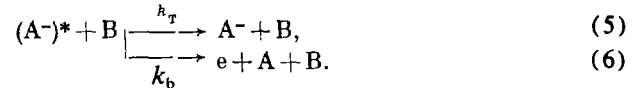
where N_e and $[A]$ are the density of electrons and molecules of type A. It has the dimensions cm^6/sec , while the cross section σ_a has the dimensions cm^5 . Unlike two-body processes the values of k_a and σ_a depend not only on the characteristics of the particle A, to which the electron is attached, but also on the properties of the particles playing the role of the third body: the type of particle, the translational temperature of the particles, and the degree of excitation.

In the case of three-body attachment to complex molecules the pressure-dependence of the rate of electron annihilation, in spite of its three-body character, is identical to the pressure dependence typical for a two-body process. It is thus more convenient to introduce the electron attachment constant based on the equation

$$\frac{d[A^-]}{dt} = \tilde{k}_a N_e [A]. \quad (3)$$

In this case the constant \tilde{k}_a and the cross section $\tilde{\sigma}_a$ have the same dimensions as for the two-body process, but their values depend, as before, on the parameters of the particle B. The intermediate case, when the dependence of the rate of formation of negative ions on the gas pressure does not reduce to the simple expressions (2) or (3), is also possible. Then the rate constant for three-body attachment, introduced by the first or second method, itself depends on the density of neutral particles.

One of the chief mechanisms of the process of three-body electron attachment to a molecule was first proposed by Bloch and Bradbury¹¹ and made more precise by Herzenberg.¹² According to this mechanism attachment proceeds in two stages:



At first the electron is attached to the molecule A and a negative ion is formed in the autoionization state $(A^-)^*$. This is followed by quenching or decay of the autoionization state in a collision with a third body B. Here k_{at} is the first constant for the formation of the unstable ion A^- , τ is the lifetime with respect to decay into the initial state; k_T and k_b are the rate constants for the formation of the stable ion A^- and break-up of the ion $(A^-)^*$ in a collision with the particle B.

An equilibrium density of $(A^-)^*$ ions is established within short times of $\sim \tau$, and the rate constant for three-body attachment equals the product of the constant k_{at} by the probability that the ion $(A^-)^*$ will be transformed into the stable ion A^- :

$$k_a = \frac{k_{at} k_T}{\tau^{-1} + (k_T + k_b)[B]}. \quad (7)$$

For gas pressures that are not too high and for sufficiently short times

$$\tau^{-1} \gg (k_T + k_b)[B], \quad (8)$$

and the formula (7) reduces to

$$k_a = k_{at} \tau k_T. \quad (9)$$

In the other limiting case three-body electron attachment outwardly appears as a two-body process with the constant

$$\tilde{k}_a = k_{at} \frac{k_T}{k_T + k_b}. \quad (10)$$

In order that the processes (4) and (5) [or (6)] be separate from one another, the characteristic time of a collision between heavy particles $\tau_{col} = a/V$ (a is the size of the heavy particles and V is their relative velocity) must be much less than τ . For gas temperature $T = 300 \text{ K}$ and small molecules $\tau_{col} \sim 2 \cdot 10^{-13} \text{ s}$. The condition $\tau \gg \tau_{col}$ implies the requirement that the width of the autoionization state must be small $\Gamma = \hbar/\tau \ll 3 \cdot 10^{-3} \text{ eV}$. Such narrow resonances in the scattering of an electron by a molecule are observed at low energies of the order of the vibrational quantum of a negative ion.^{8,13} As the energy of the autoionization state ϵ_i increases the value of Γ increases rapidly according to the law $\Gamma \sim \epsilon_i^{l+1/2}$, where l is the orbital quantum number, describing the motion of the freed electron far from the molecule.¹⁴ The states studied are usually the vibrational levels of the ion, lying above the ground state of the neutral molecule A. Figure 1 shows as an example the electronic terms of the molecule O_2 and the ion O_2^- ,⁵ whose vibrational states, starting with the fourth and higher states, are unstable.

We shall evaluate the times τ for which the condition (8) holds. Assuming that the processes (5) and (6) occur as a result of polarization capture of the ion $(A^-)^*$ by the molecule B, we have

$$k_T + k_b \sim 2\pi \left(\frac{\beta e^2}{\mu} \right)^{1/2} \sim 10^{-9} \text{ cm}^3/\text{s}, \quad (11)$$

where e is the electron charge, β is the polarizability of the particle B, and μ is the reduced mass of A^- and B. Then for a gas pressure $p \sim 10\text{--}100 \text{ torr}$, $\tau \ll 10^{-9}\text{--}10^{-10} \text{ s}$, the condi-

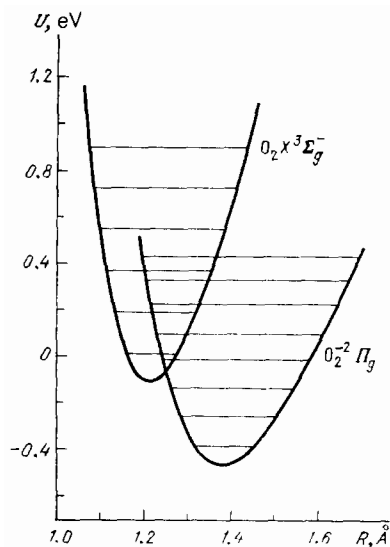


FIG. 1. Electronic terms of the O_2 molecule and the O_2^- ion.⁵

tion (8) reduces to the requirement, under which the rate of electron loss in the three-body attachment process depends quadratically on the gas pressure. Such short-lived autoionization states occur for the molecules O_2 , NO , SO_2 , and some others, for which the three-body attachment process is observed.^{2,3,8} The other limiting case of long-lived unstable negative ions is typical for complex molecules, in which the energy of the trapped electron is redistributed over internal degrees of freedom of the molecules, and this is what increases the lifetime of the ions. The three-body attachment process, outwardly manifested as a two-body process, is observed for NO_2 , SF_6 , and other complex molecules.

We shall evaluate the order of magnitude of the rate constant for three-body attachment in both cases based on the formulas (9) and (10). In thermodynamic equilibrium the product τk_{at} is determined from the law of mass action:

$$k_{at} \tau = \frac{[(A^-)^*]}{N_e [A]} = \frac{g_i}{g_e g_A} \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2} \exp\left(-\frac{\epsilon_i}{T}\right), \quad (12)$$

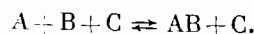
where g_e , g_A , and g_i are the statistical weights of the electron, the neutral particle A, and the ion; m is the electron mass; and T is the temperature. Setting $\epsilon_i \sim T = 300$ K we obtain $k_{at} \sim 10^{-20}$ cm³. The use of the polarization capture constant for k_T gives the estimate, based on the formula (9), $k_a \sim 10^{-29} - 10^{-30}$ cm⁶/s which is valid when the condition (8) holds. This estimate agrees well with the experimental data on the rate constant for three-body attachment to the molecules O_2 and NO , when the third body is a complex molecule.^{1-3,7,8,15} Here the efficiency of stabilization of the negative ion in the reaction (5) is high owing to the transfer of the excess energy of the ion into the vibrational degrees of freedom of the third body (V-V exchanges). If the third body is an atom or a simple molecule, then the excess energy can be transferred only into its translational degrees of freedom (V-T exchange). The rate of this transfer process is significantly lower owing to its nonresonance character. The process of three-body attachment in which the third body is a molecule of the same type as the molecule to which attachment occurs is an exception. In this case the high rate of attachment can be explained by the appearance of a new channel of the reaction (5)—resonance charge exchange.

In the case of long-lived unstable ions, when the condition (8) does not hold, the rate constant for three-body attachment $k_a \sim k_{at}$. Making the assumption that the cross section for capture of an electron by a complex molecule is of the order of the elastic scattering cross section (10^{-14} cm²), we obtain for $T = 300$ K the upper limit $\bar{k}_a \sim 10^{-7}$ cm³/s. The rate constant for three-body electron attachment to an SF_6 molecule and to other complex molecules is precisely of this order of magnitude. For simple molecules it should be expected that the rate of this process will be lower. For example, the rate of three-body attachment of an electron to the NO_2 molecule is three to four orders of magnitude lower.

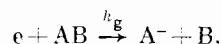
Although the process of three-body attachment is not a threshold process, for the foregoing mechanism there is an energy barrier, equal to the energy of the autoionization state of the negative ion ϵ_i . Because of this, as the temperature decreases the rate of the three-body attachment process by the Bloch-Bradbury mechanism drops off exponentially [see the formula (12)]. At cryogenic temperatures electron attachment to weakly coupled van der Waals molecules¹⁶ AB, whose concentration is determined from the law of mass action

$$[AB] = [A][B]K^{-1}(T),$$

where $K(T)$ is the rate constant of the equilibrium reaction,



may turn out to be important. If dissociative attachment of an electron to a van der Waals molecule AB is possible,



then the effective rate of electron loss and formation of negative ions is described by Eq. (2) with the rate constant

$$k_a = \frac{k_g}{K(T) + N},$$

where N is the total density of neutral particles. In the limit of low gas pressures ($N \ll K(T)$) the concentration of van der Waals molecules $[AB]$ grows linearly as the pressure increases and as a result dissociative electron attachment to a van der Waals molecule AB outwardly appears as a three-body attachment process with the rate constant $k_a = k_g/K(T)$.

At high gas pressures ($N \gg K(T)$) the quantity $[AB]$ remains virtually constant as the pressure changes and attachment acquires, as in the Bloch-Bradbury mechanism, features of the two-body process with a constant k_g .

The existence of van der Waals molecules in a gas has been proved in a number of experiments. These molecules were observed by the methods of mass spectrometry and long-wavelength IR spectroscopy in inert gases (Ar, Xe), simple molecular gases (O_2 , N_2 , H_2 , CO_2 , N_2O , etc.), and some of their mixtures.^{17,18} The binding energy of these formations is ~ 0.01 eV and their sizes are 5–10 Å. Their equilibrium concentration is determined by the equilibrium constant $K(T)$. The constant $K(T)$ can be evaluated with the help of the results of the calculation of Ref. 19, where it was determined from the force constants of the interaction between the constituent particles of the complex molecule. According to Ref. 19, $K \sim 10^{22}$ cm⁻³ at $T = 100$ –600 K and is virtually independent of the type of van der Waals mole-

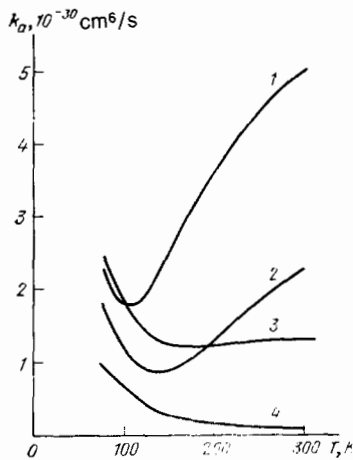


FIG. 2. The dependence of the rate constant of three-body attachment to the molecules $^{18}\text{O}_2$ (1) and $^{16}\text{O}_2$ (2-4) molecules on the gas temperature.²⁰ The third body is O_2 (1, 2), CO (3), and N_2 (4).

cule. Setting $k_g \sim \nu r_0^2$, where ν is the characteristic velocity of an electron with thermal energy, we obtain $k_a \lesssim 10^{-30} \text{ cm}^6/\text{sec}$. Thus electron attachment to van der Waals molecules could turn out to be a very efficient process, which obviously predominates at low temperatures, when the population of the autoionization states of negative ions is small. The quadratic dependence of the rate of three-body attachment on the gas pressure, according to the mechanism under study, is replaced by a linear dependence for $N > K(T)$, which corresponds to a pressure of several hundreds of atmospheres.

Figure 2 shows the dependence on the gas temperature T of the rate constant of three-body electron attachment to the O_2 molecule for a series of third bodies obtained in the experiment of Ref. 20, under conditions of thermodynamic equilibrium. The decrease in the rate of three-body attachment with increasing T indicates that van der Waals molecules, whose concentration drops in the process, play an important role. The reverse dependence in the case of the third body—the O_2 molecules—for sufficiently high values of T is characteristic for the Bloch-Bradbury mechanism, in which there is an energy barrier.

In the foregoing discussion we examined the mechanisms of three-body attachment in which the three-body process is separated into two stages with the formation of intermediate products—either unstable negative ions $(\text{A}^-)^*$ or van der Waals molecules AB . The three-body attachment process can also proceed directly without the formation of intermediate products. In this case attachment occurs as follows. The electron enters the region of strong interaction with the molecule A and undergoes there a collision with a third body B , to which it gives up part of its energy. As a result the ion A^- forms. The rate constant of this process under typical conditions, according to Ref. 7, equals $k_a \sim 10^{-33} \text{ cm}^6/\text{s}$, which is significantly lower than for the mechanisms studied above. For this reason the direct mechanism of three-body attachment can play an appreciable role only in exceptional cases. For example, it becomes important if I —the electron affinity of the molecule A —is low and therefore the region in which the electron interacts strongly with the particle A , whose size equals in order of magnitude $\hbar(mI)^{-1/2}$. Thus for the NO molecule $I \sim 0.02 \text{ eV}$ ^{2,3} and the rate constant for three-body attachment to it reaches values of $\sim 10^{-30} \text{ cm}^6/\text{s}$.⁷

The chief mechanisms for three-body attachment are now clear and the main problems in the theoretical description of this process now are to determine the properties and parameters of the intermediate particles—the van der Waals molecules and the unstable negative ions. Information about them is very fragmentary. The multichannel nature of the three-body attachment process as well as the possibility of competition between different mechanisms make it difficult to obtain experimental data from the cross sections and rate constants.

3. METHODS FOR MEASURING THE CROSS SECTION FOR THREE-BODY ATTACHMENT AND BASIC RESULTS

Significant difficulties are encountered in constructing a theory even of two-body interactions of an electron with a molecule (dissociative attachment of an electron, vibrational excitation of a molecule by electron impact, etc.). They arise both because the interaction of the incident electron with the internal electrons and the atomic nuclei must be taken into account simultaneously and because the number of intermediate and final channels is large. For this reason, this problem is substantially a many-body and multilevel problem.

The transition from a two- to a three-body process further complicates the situation. Taking into account the specific mechanism for three-body electron attachment could make it possible to reduce the three-body process to a sequence of two-body processes: resonance scattering of an electron by a molecule and vibrational relaxation of the negative ion formed by a third particle (Bloch-Bradbury mechanism) or dissociative attachment of an electron to a van der Waals molecule. But, these simplifying assumptions, even taking into account the latest progress in numerical methods, do not make it possible to investigate the process under study by nonempirical methods. For this reason, experiment plays the leading role in the study of three-body electron attachment.

The fundamental quantity for describing three-body electron attachment is the cross section, which depends on the initial and final states of the system as well as the energy of the electron and of the heavy particles. In cases of practical interest the velocity distribution of the atoms and molecules is the equilibrium distribution, and for this reason the cross section $\sigma_a(\epsilon, T)$ for the formation of stable negative ions as a function of the electron energy ϵ and gas temperature T is introduced. It takes into account the averaging over velocities and the initial states of the heavy particles as well as summation over the final states.

In most cases three-body electron attachment is a resonance process with a resonance width $< 0.1 \text{ eV}$. For this reason, highly monochromatic electron beams, whose production at energies below 1 eV is in itself a difficult technical problem, are required for studying attachment cross sections. This difficulty arises in the study of most scattering processes involving a slow electron scattered by an atom or molecule. The second obstacle, which is characteristic precisely of three-body processes, arises from the need to satisfy simultaneously two contradictory requirements. The rate constant for three-body attachment increases as the gas pressure increases, whereas it is desirable to perform the experiments at elevated pressures, so as to maintain the sensitivity of the ion detector at an adequate level. As the pressure is increased, however, the monochromaticity of the electron

beam decreases owing to scattering of electrons by atoms and molecules. For this reason, thus far, only one experiment on the attachment of an electron to a molecule, which depends quadratically on the gas pressure, has been performed with a monoenergetic electron beam. This is Ref. 21, where the process of three-body attachment to an O_2 molecule was studied as a function of the electron energy ϵ and the gas temperature T . The apparatus employed has been used many times to measure the cross section for dissociative electron attachment to a molecule. It is described in detail in Ref. 2. The electron beam was formed with the help of an iridium filament; beam monochromaticity was ensured by a system of reflecting electrodes. The beam was injected into the collision chamber, consisting of a cylindrical furnace 10 mm in diameter. The negative ions produced in the chamber were extracted with the help of an electric field, generated by two parallel iridium electrodes. The nonmonochromaticity of the electron beam constituted ~ 0.1 eV.

Figure 3 gives the values of the rate constant of the process



obtained in Ref. 21. The figure also shows the positions of the vibrational levels of the O_2^- ion, reconstructed from beam experiments on the study of the vibrational excitation of the O_2 molecule by electron impact. The dependence of the rate of the three-body attachment process on the electron energy consists of a sequence of narrow peaks at energies corresponding to the autoionization states of the O_2^- ion. This picture is a direct confirmation of the validity of the Bloch-Bradbury mechanism. As the gas temperature T increases the rate of stabilization of the autoionization states of the O_2^- ion by a third body [the process (5)] decreases, which causes the rate of electron attachment to decrease.

If the attachment process proceeds through the formation of a long-lived unstable ion [the case opposite to the case (8)], then the cross section for three-body attachment can be measured at low gas pressures also. But another difficulty arises. The frequency of stabilization of the autoionization state of the negative ion by a third body is of the same order of magnitude as the frequency of collisions between the electrons in the beam and neutral particles. So as not to destroy

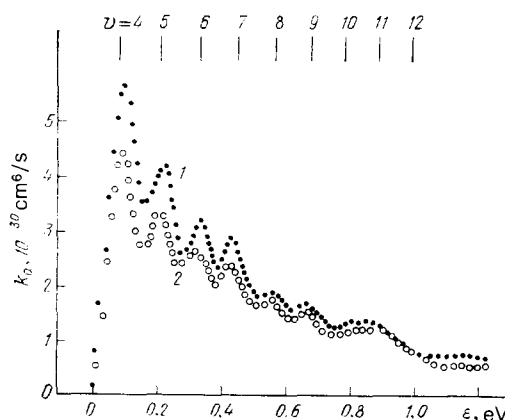


FIG. 3. The dependence of the rate constant of three-body attachment to the O_2 molecule with O_2 as the third body on the electron energy in the experiment of Ref. 21 with a monoenergetic electron beam. $T = 300$ K (1) and 500 K (2). The energies of the vibrational levels of the O_2^- ion are indicated at the top of the figure.

beam monochromaticity the experiments are performed with low gas pressures, when there is not enough time for the unstable negative ions to be stabilized. As a result, the two-body cross section for the formation of unstable negative ions and not the total cross section $\bar{\sigma}_a$ for electron attachment with the formation of a stable ion is measured. These quantities are identical only when the probability of stabilization of unstable ions by a third body is close to unity. In the opposite case the quantity measured in an experiment with an electron beam is the upper limit for $\bar{\sigma}_a$.

A process of this type that has been studied in greatest detail is attachment to the molecule SF_6 . Repeated attempts have been made to measure, by the electron-beam method, the cross section of this process with the formation of SF_6^- ion. In most cases, however, the inadequate beam monochromaticity made it impossible to determine the cross section.²²⁻²⁴ The experiment of Ref. 25, where this cross section was measured with the help of an electron beam with an energy spread of 0.1 eV, is an exception. The cross section reaches a maximum near zero and drops rapidly as the electron energy increases. The experimental apparatus of Ref. 25 was previously employed to study dissociative electron attachment to a molecule. It is described in detail in Ref. 2. The distinguishing feature of this apparatus is the identification of the negative ions formed by the method of mass spectrometry. For the SF_6 molecule this is necessary because of the large number of channels in which electron attachment to it occurs.

A fundamentally new method for producing monoenergetic electrons was employed in Refs. 26 and 27 in the study of electron attachment to the SF_6 molecule. In these works the mixture $SF_6 \cdot Xe$, in which low-energy free electrons were generated by photoionization of Xe atoms near the threshold was studied. This method permitted reducing the electron energy spread by more than an order of magnitude (to 0.004 eV) and to obtain reliable data on the attachment cross section. The type of the negative ions formed was determined with the help of a mass spectrometer.

Because of the difficulty of measuring the attachment cross section directly, methods were developed for reconstructing its value from the experimental data on the rate constant of this process. The reconstruction of the cross section based on its integral characteristics is a typical improperly posed problem and the accuracy of this procedure is not high. The largest error can be expected for the relative dependence of the cross section on the electron energy, especially if the dependence is sharp.

In Refs. 28 and 29 the cross section for electron attachment to SF_6 and a series of complex organic molecules was approximated by the formula $\bar{\sigma}_a = A/\epsilon^\gamma$ and the values of the constants A and γ were determined from the analysis of data on the rate constants for attachment, obtained in experiments with an electron bunch. The theoretical justification for this dependence of $\bar{\sigma}_a(\epsilon)$ in the case of complex molecules is discussed in Ref. 3.

A more universal approach to the reconstruction of the attachment cross section from data on the rate process is developed in Ref. 30. According to Ref. 30 (see also Refs. 4 and 8) in the experiment with the electron bunch the rate constant for attachment was measured in the widest possible range of values of the reduced electric field E/N (E is the intensity of the electric field and N is the neutral particle

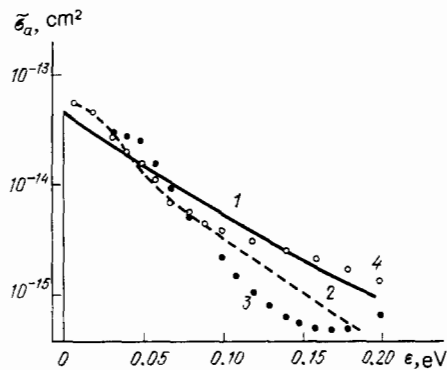


FIG. 4. Cross section for electron attachment to the SF₆ molecule: 1) Ref. 26; 2) Ref. 25; 3) Ref. 31; 4) Ref. 32.

density), on which the average electron energy depends. The study was performed with a mixture of a buffer gas with a small quantity of the gas to whose molecules the electrons become attached. The buffer gas consisted of gases (most often N₂ and Ar) for which the electron energy distribution as a function of the parameter E/N is well known from the numerical solution of Boltzmann's equation. For this reason this method can be used to study only three-particle processes, where the third body is an atom or molecule of the buffer gas. The small fraction of molecules to which attachment occurs in the mixture made it possible to neglect their effect on the electron energy distribution. The experimental data were analyzed as follows. The starting approximation for the attachment cross section, according to which the attachment rate constant was determined in a wide range of values of the parameter E/N by integration with a known electron energy distribution function, was given. After the results of the calculation of the rate constant were compared with the experimental data corrections were made in the attachment cross section, and the procedure was repeated. Iteration continued until the computational results agreed with experiment. The efficiency of this approach was checked for the process of dissociative electron attachment to a molecule, whose cross section was measured in many experiments with electron beams.

The results^{31,32} for the reconstruction of the cross section $\bar{\sigma}_a(\epsilon)$ by this method for the SF₆ molecule are presented in Fig. 4. Different data on the electron energy distribution in N₂ were employed in Refs. 31 and 32. The accuracy of the method employed can be judged from the discrepancy

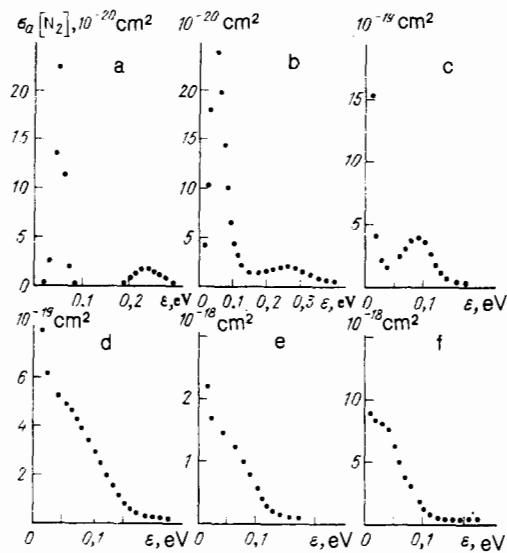


FIG. 5. Cross section for electron attachment to the O₂ molecule with N₂ as the third body³⁴ as a function of the gas pressure. p (torr) = 300 (a), 500 (b), 1000 (c), 1500 (d), 3000 (e), and 7000 (f).

between their results. This discrepancy increases appreciably for electron energies > 0.1 eV. Figure 4 also shows the results of direct experiments^{25,26} on the measurement of the attachment cross section. In the low-energy limit all approaches give close results. The experiment of Ref. 26 is most accurate; improvement of the procedure employed in this method enabled Chutjian and Alajajian³³ to obtain data indicating that the s wave plays the dominant role in attachment at low electron energies.

Figures 5 and 6 show the cross sections for electron attachment to the molecules O₂ (Ref. 34) and SO₂ (Ref. 35), obtained by the method of Ref. 30 for different pressures of molecular oxygen, employed as the buffer gas. For $p < 1000$ torr the cross section for attachment to the O₂ molecule has a resonance character, which confirms the validity of the Bloch-Bradbury mechanism for this process. The difference between the positions of the peaks in the cross section on the energy axis, equal to 0.2 eV, is close to the magnitude of the vibrational quantum of the O₂⁻ ion,^{2,3} through whose autoionization states attachment proceeds. According to Fig. 5 the first autoionization state of the ion makes the main contribution to the process of three-body attachment of an electron to the O₂ molecule in the presence of a third

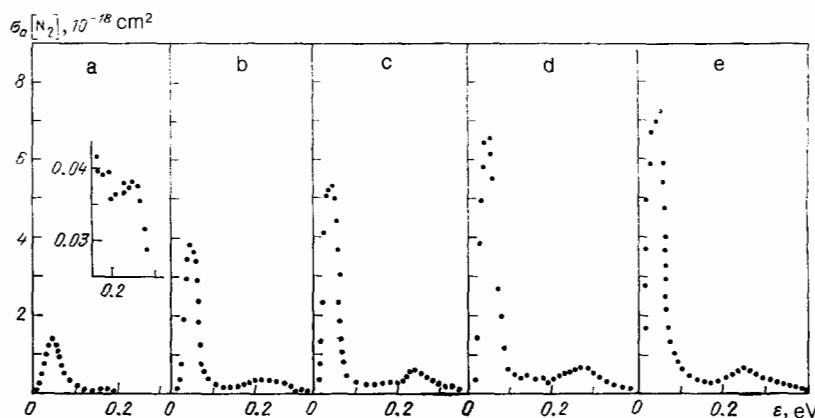


FIG. 6. Cross section for three-body electron attachment to the SO₂ molecule with N₂ as the third body³⁵ as a function of the gas pressure. p (torr) = 1000 (a), 3500 (b), 6000 (c), 9000 (d), and 12 500 (e).

body (N_2 molecule). As the gas pressure is raised the resonance structure shifts toward lower energies and gradually vanishes. This behavior of the cross section is interpreted in Refs. 4, 5, and 34 as the breakdown of the potential energy curve of the O_2^- ion in an environment of N_2 molecules.

The cross section for electron attachment to the SO_2 molecule, presented in Fig. 6, also has a resonance structure. But, unlike the case of the O_2 molecule, at the present time it is difficult to ascribe the peaks observed here at 0.06 eV and 0.26 eV to some definite autoionization states of SO_2^- . The cross sections for electron attachment for a large number of complex, primarily organic, molecules were obtained by an analogous method. These results are presented and discussed in Ref. 8.

In conclusion it should be emphasized that the direct methods traditionally employed for measuring the cross sections of two-body processes are usually not applicable in the case of three-body attachment and other three-particle reactions. Almost all the information available here was obtained by indirect methods.

4. RATE CONSTANT FOR THREE-BODY ELECTRON ATTACHMENT AND ITS TEMPERATURE DEPENDENCE

In a low-temperature plasma the average electron energy is usually much higher than the energy at which the cross section for three-body attachment changes. Here the characteristic of this process is the rate constant of three-body attachment averaged over the electron energy distribution.

For the Bloch-Bradbury mechanism it can be determined by taking into account many autoionization states, employing the Breit-Wigner theory of resonance scattering.^{7,12} The cross section for the capture of an electron with energy ε by a molecule A accompanied by the formation of the negative ion A^- in the j th autoionization state equals³⁶

$$\sigma^j(\varepsilon) = \pi\lambda^2 \frac{g_i^j}{g_e g_A} \frac{\Gamma_0^j \Gamma^j}{(\varepsilon - \varepsilon_i^j)^2 + (\Gamma_j/2)^2}, \quad (13)$$

where g_i^j , g_A , and g_e are the statistical weights of the ion A^- , the molecule A, and the electron, respectively, λ is the de Broglie wavelength of the incident electron; Γ^j and Γ_0^j are the total and partial (relative to decay into the initial state) width of the j th state of the A^- ion with energy ε_i^j . The formula (13) holds if

$$\Gamma^j \ll \varepsilon_i^j, \quad \Gamma^j \ll \Delta\varepsilon;$$

$\Delta\varepsilon$ is the energy splitting of the neighboring autoionization states.

For not very high gas pressures [when the condition (8) holds] the expression for the rate constant for three-body attachment, according to the formula (9), has the form

$$\begin{aligned} k_a &= \left(\frac{2}{m}\right)^{1/2} \sum_j \tau_j k_T^j \int_0^\infty \sigma^j(\varepsilon) f(\varepsilon) d\varepsilon \\ &= \frac{\sqrt{2} \pi^2 \hbar^3}{m^{3/2}} \sum_j f(\varepsilon_j) \frac{g_i^j}{g_e g_A} k_T^j \frac{\Gamma_0^j}{\Gamma^j}. \end{aligned} \quad (14)$$

where τ_j and k_T^j are the lifetime and rate constant for quenching of the j th state of the ion by a third body, m is the electron mass, and $f(\varepsilon)$ is the electron energy distribution function. If it is Maxwellian with temperature T_e , while at-

tachment proceeds through one autoionization state, the formula (14) simplifies:

$$k_a = \left(\frac{2\pi\hbar^2}{mT_e}\right)^{3/2} \frac{g_i^j}{g_e g_A} k_T \exp\left(-\frac{\varepsilon_j}{T_e}\right). \quad (15)$$

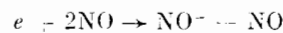
The expressions (14) and (15) can also be derived by a different method, based on analysis of the statistical equilibrium between the densities of unstable negative ions, molecules, and electrons.^{3,37} Thus, for $T_e \ll \varepsilon_j$, as T_e increases k_a increases exponentially and passes through a maximum, while for $T_e \gg \varepsilon_j$ it decreases in a power-law fashion. The value of k_T also depends on the temperature of the heavy particles in a nearly power-law fashion.

The theoretical study of mechanisms of three-body electron attachment to a molecule, differing from those studied above, is just beginning. In Refs. 38 and 39 attachment to the van der Waals molecule $O_2 \cdot N_2$ was studied and it was shown that the high efficiency of this process is explained by the reduction of the symmetry of the system accompanying attachment of the N_2 molecule to O_2 . In Ref. 40 the rate constant for three-body attachment of an electron to the molecule NO via the direct mechanism with no intermediate stages was calculated on the basis of the impulse approximation.⁴¹

Experimental methods for studying the rate constant of three-body attachment are described in detail in Refs. 2, 8, and 42. They can be divided into two large groups depending on whether or not equilibrium is established between the electron and neutral-particle temperatures. Experiments of the first group are usually based on the measurement (for example, by microwave methods) of the time dependence of the electron density in the decaying plasma generated by a beam of relativistic electrons, x-ray beams, or photoionization with an addition of an easily ionized impurity. In the early works, performed in the 1950s, the plasma was created with a pulsed gas discharge. This, however, gave rate constants for three-body attachment that were too low, owing to the destruction of the negative ions by excited particles formed in the discharge. Experiments in the second group include studies of the attenuation of electron bunches traveling through a drift tube. Here the electrons are heated by an external electric field, their energy distribution becomes nonequilibrium, and the average electron energy varies from the thermal energy up to several electron volts at room temperature of neutral particles. Experiments with a non-self-sustained gas discharge, which have been performed in the last few years, are close to this group.

Table I gives the results of these experiments for $T_e = T = 300$ K, and the methods employed, as well as the range of pressures to which the measurements refer, are also indicated.

For the process



with $T_e = T = 300$ K there is a significant spread between the data reported in different publications. According to Ref. 1, in most experiments the rate constant was determined incorrectly, since the process of collisional destruction of the NO^- ion was neglected in the analysis. Its high efficiency is explained by the low electron affinity of the NO molecule, comparable to T_e .^{2,3} The correct value of the constant is obtained by analyzing the experimental data taking

TABLE I. Rate constant k_a of the process $e + A + B \rightarrow A^- + B$ measured by different authors at $T = T_e = 300$ K.

B	$k_a, 10^{-30} \text{ cm}^6/\text{s}$	$p, \text{ torr}$	Method of measurement	References	
A = O ₂					
O ₂	2,4±0,1	30-300	a	43	
	2,2±0,2	100-400	a	44	
	2,6±0,1	250-600	c	45	
	2,8	7-55	c	46	
	2,0±0,2	10-500	c	47	
	3	3-30	b	48	
	2,12±0,14	1-10	a, d	49	
	2,2±0,1	2-100	d	50	
	1,7	10-100	a	51	
	2,1±0,2	1-150	e	52	
	2,2	5-25	a	53	
	He	0,033±0,003	160-425	c	15
		0,028	7-55	a	46
Ne	0,076	1-150	a	52	
	0,023±0,003	90-300	a	15	
Ar	0,05±0,01	100-300	a	15	
Kr	0,05±0,01	60-200	a	15	
Xe	0,085±0,005	35-170	a	15	
N ₂	0,085±0,003	30-300	a	43	
	0,5	15-150	b	48	
	0,26	10-100	d	51	
	0,11	1-150	a	52	
	0,11	5-20	e	53	
H ₂	0,48±0,03	100-300	a	44	
D ₂	0,140±0,005	140-400	c	44	
H ₂ O	14±5	250-600	c	54	
	14±2	10-760	f	55	
CO ₂	13,8	5-20	c	56	
	3,18±0,15	400-1900	c	57	
	3,1	10-760	a, d	55	
	3,0±0,2	10-200	c	50	
	3,2	5-20	e	56	
H ₂ S	3,5	5-20	a	53	
	3,2±0,3	100-760	c	58	
NH ₃	9	5-20	c	56	
CH ₄	6,8	5-20	a	56	
C ₂ H ₄	0,34±0,01	65-280	a	15	
	3	~ 100	c	16	
C ₂ H ₆	3,4±0,4	200-800	c	54	
	2,3±1,0	250-600	c	45	
	2,5	5-20	c	56	
	2,0±0,3	20-850	a	58	
	1,7±0,1	50-200	a	15	
C ₃ H ₈	3,3±0,2	50-240	a	15	
C ₆ H ₆	8,5	5-20	c	56	
n-C ₇ H ₁₀	~ 5	~ 100	a	15	
n-C ₅ H ₁₂	7,9±0,4	30-180	a	15	
neo-C ₅ H ₁₂	8,0±0,7	25-130	a	15	
n-C ₆ H ₁₄	7±1	100-600	a	58	
	8,1±0,4	30-240	a	15	
CH ₃ OH	11±2	20-70	a	15	
C ₂ H ₅ OH	8,8	5-20	c	56	
	18	10-50	a	15	
CH ₃ COCH ₃	27	5-20	c	56	
A = NO					
NO	0,068±0,034	0,05-0,7	g	59	
	0,13±0,01	0,1-5	a	60	
	0,22±0,02	0,01-16	a	61	
	0,22	0,4-4	a	62	
	0,4	4-16	a	63	
H ₂ O	0,8±0,2	60-150	c	64	
	6	5-20	c	56	
CO ₂	1,7	5-20	c	56	
NH ₃	2,5	5-20	c	56	
C ₂ H ₄	0,7	5-20	c	56	
C ₆ H ₆	4,6	5-20	c	56	
CH ₃ OH	6,5	5-20	c	56	

TABLE I. (continued)

B	$k_a, 10^{-30} \text{ cm}^6/\text{s}$	$p, \text{ torr}$	Method of measurement	References
A = N ₂ O				
N ₂ O	0,006±0,001	30-200	c	65
	0,0056±0,0002	10-200	a	66
N ₂	0,0046	10-300	a	67
	0,0047±0,0001	5-120	a	68
C ₂ H ₆	0,003±0,0005	400-900	c	69
	0,0006	30-400	a	67
C ₃ H ₈	0,001	30-250	a	67
n-C ₄ H ₁₀	0,0029	5-160	a	67
iso-C ₄ H ₁₀	0,0048	15-120	a	67
1-C ₄ H ₈	0,019±0,002	20-140	a	67
cis-2-C ₄ H ₈	0,023±0,003	30-160	a	67
trans-2-C ₄ H ₈	0,014±0,001	40-170	a	67
iso-C ₄ H ₈	0,14±0,02	15-120	a	67
n-C ₅ H ₁₂	0,013±0,001	10-100	a	67
neo-C ₅ H ₁₂	0,155±0,005	10-100	a	67
He	1500±200	1-60	a	70
Ne	1000±500	1-60	a	70
Ar	1700±500	1-60	a	70
Kr	1100±200	1-60	a	70
Xe	1100±100	1-60	a	70
H ₂	1200±200	1-60	a	70
D ₂	1200±200	1-60	a	70
N ₂	1700±200	1-60	a	70
CO ₂	1900±200	1-60	a	70
n-C ₄ H ₁₀	1900±200	1-60	a	70
A = SO ₂				
CO ₂	~ 6	3-160	c	71
C ₂ H ₄	55±4	8-30	c	71
C ₃ H ₆	12±1	4-180	c	71
CH ₃ OH	70±5	8-16	c	71
A = C ₆ H ₆				
N ₂	0,001	2000-6000	c	72

Measurement methods: a) plasma decay in a microwave resonator; b) plasma decay in a microwave waveguide; c) pulsed experiment with an electron bunch; d) quasistationary experiment with a microwave resonator; e) optical measurements under conditions of plasma decay; f) proportional counter; g) mass-spectrometric measurements under conditions of plasma decay.

into account the destruction and conversion of the NO⁻ ion.^{1,7,64}

Experimental data on the rate constant of three-body attachment to the molecules NO₂ and SO₂ in the case when the condition (8) does not hold and attachment is manifested as a two-body process were obtained in Refs. 59 and 70-74. A significant spread is observed in the experimental results for the NO₂ molecule. The question of its origin remains open. The data on three-body electron attachment to complex molecules are collected in Refs. 2, 3, and 8.

Figure 7-11 show the dependence of the rate constant for three-body attachment to the molecules O₂, NO, SO₂,

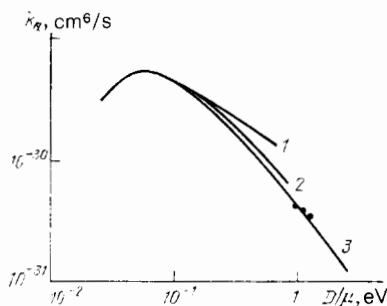


FIG. 7. Rate constant of three-body attachment to the O₂ molecule with O₂ as the third body. Experiment: 1) Ref. 46, 2) Ref. 75, dots—Ref. 76; 3) calculation (Ref. 83).

C₆H₆, and CS₂ on the characteristic electron energy D/μ , where D is the coefficient of transverse diffusion of electrons and μ is their mobility. These data were obtained in experiments in which the electrons were heated by an external electric field, while the neutral particles remained cold. If the electron energy distribution is the equilibrium distribution, then $D/\mu = T_e$ (Einstein's ratio). For the conditions of the experiments under study this does not happen owing to the low degree of ionization and the absence of Coulomb collisions. For this reason the electron energy distribution and

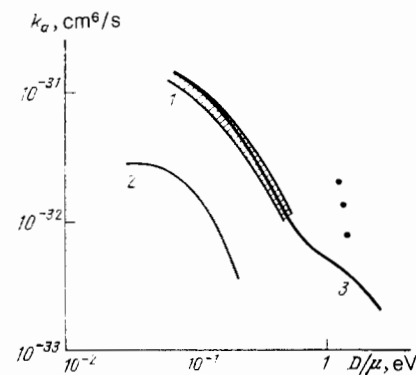


FIG. 8. Rate constant of three-body attachment to the O₂ molecule. N₂ as the third body: 1) experiment^{34,45,46}; dots—Ref. 76; 3) calculation⁸⁴; He as the third body; 2) experiment (Ref. 46).

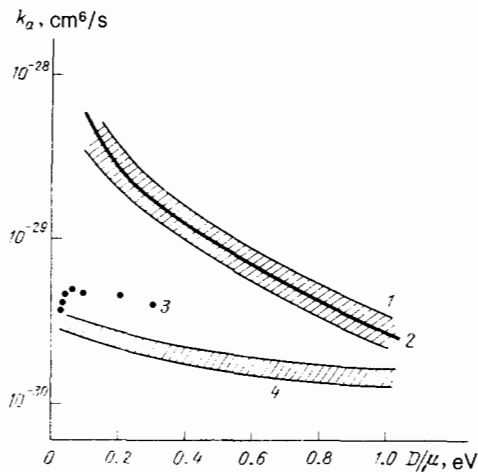


FIG. 9. Rate constant of three-body attachment to the O₂ molecule. H₂O as the third body: 1) experiment,⁷⁷ 2) calculation^{83,84}; CO₂ as the third body; 3) experiment⁷⁸ and 4) experiment.⁷⁷

therefore the rate of three-body attachment with a fixed value of D/μ depends on the type of gas in which the measurements are performed. The assumption that the function $k_a(D/\mu)$ is single-valued is an approximation, which works well, for example, for the gas mixtures employed in the active media of CO₂ lasers,⁸⁰ but poorly for the N₂:Ar mixture.⁸¹

It follows from Figs. 7–11 that the energy of the autoionization states is $\epsilon_i \sim 10^{-1} - 10^{-2}$ eV and is all the lower the more complicated is the molecule to which the electron becomes attached. The latter fact is explained by the decrease in the vibrational quantum of the negative ion, where the autoionization states are its vibrational levels. A rapidly growing dependence $k_a(D/\mu)$ for three-body attachment to the molecule N₂O, which gives the estimate $\epsilon_i \approx 1$ eV, was obtained in the experiment of Ref. 69. But the results of Ref. 69 can be explained by dissociative attachment to the molecule N₂O followed by ion-molecular reactions,⁸² including electron detachment from the negative ion and conversion of the ion.

Many autoionization states of a negative ion, whose parameters are poorly known, usually participate in the three-

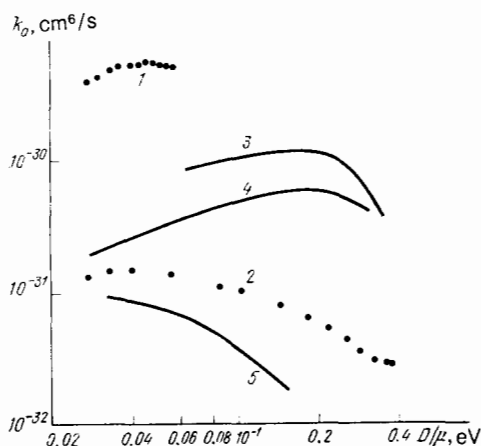


FIG. 10. Experimental data on the rate constant of three-body attachment to the SO₂, NO, and C₆H₆ molecules. 1— $e + \text{SO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{SO}_2^- + \text{C}_2\text{H}_4$ ³⁵; 2— $e + \text{SO}_2 + \text{N}_2 \rightarrow \text{SO}_2^- + \text{N}_2$ ³⁵; $e + 2\text{NO} \rightarrow \text{NO}^- + \text{NO}$; 3—⁶⁴; 4—⁵⁶; 5— $e + \text{C}_6\text{H}_6 + \text{N}_2 \rightarrow \text{C}_6\text{H}_6^- + \text{N}_2$.⁷²

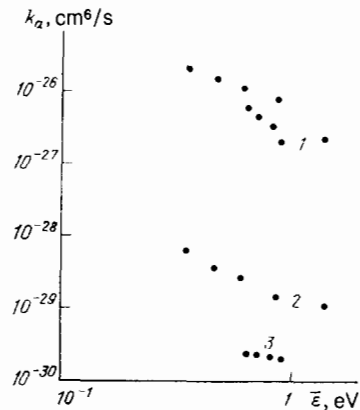


FIG. 11. Rate constant of three-body attachment to the CS₂ molecule as a function of the average electron energy, measured in the experiment of Ref. 79. The third body is CS₂ (1), CH₄ (2), and N₂ (3).

body attachment process. The O₂⁻ ion, for which they were determined with adequate accuracy,^{2,3,7} is an exception, partly because of its simplicity and practical significance and partly because of the fact that vibrational excitation of the O₂ molecule by electron impact also occurs through these ionization states. Detailed information on the O₂⁻ ion has made it possible to develop, based on the formula (14), a semiempirical approach to the calculation of the rate constant of three-body attachment to the O₂ molecule in a wide range of plasma parameters.^{7,83,84} The results of the calculation within the framework of this approach, taking into account the nonuniformity of the electron energy distribution, are presented in Figs. 7–9. It was assumed that the N₂ and H₂O molecules, unlike O₂, effectively quench only the first autoionization state of the O₂⁻ ion. (Analogous calculations for O₂ as the third body under similar assumptions were performed in Refs. 85 and 86.) The computed curves agree well with the experimental data, with the exception of Ref. 76, whose points for the first body (N₂ molecules) lie appreciably above the computed curve. A subsequent experiment,⁸⁷ performed by an analogous method, however, confirmed the correctness of the calculation.

Figure 12 shows the dependence of the rate constant for three-body attachment to the O₂ molecule on the temperature T of the gas for nonequilibrium conditions, obtained in the experiments of Refs. 46 and 47. Changing T merely changes the magnitude of the rate constant, the character of

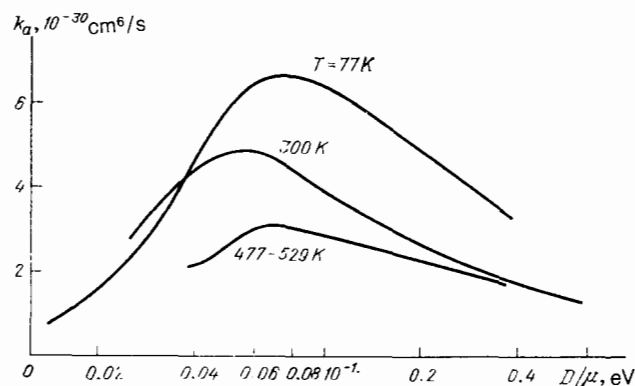


FIG. 12. The dependence of the rate constant of three-body attachment to the O₂ molecule in pure oxygen on the gas temperature.^{46,47}

the curves remains unchanged. Here only the rate of quenching of the autoionization states k_T^j depends on T [the formula (14)]. The agreement between the computational results of Ref. 88, based on the semiempirical approach of Refs. 7 and 83, for high T and the experimental data of Ref. 47 confirms this. For higher values of T , as well as in strongly nonequilibrium systems (for example, in a gas discharge), the vibrational excitation of molecules becomes significant, which should affect the three-body attachment process. This effect was studied theoretically in Ref. 89 for the example of three-body attachment to the O_2 molecule. The formula (14) for the rate constant of three-body attachment to a molecule in the ν th vibrational state is replaced by

$$k_a(\nu) = -\frac{\sqrt{2} \pi^2 \hbar^3}{m^{3/2}} \sum_j f(e^j - \nu \hbar \omega) \frac{g_i^j}{g_e g_A} k_T^j \frac{\Gamma_v^j}{\Gamma^j},$$

where $\hbar \omega$ is the vibrational quantum of the molecule, and Γ_v^j is the partial width of the j th autoionization state of the negative ion relative to decomposition into an electron and an excited molecule. The summation is performed over all autoionization levels of the ions, lying above the ν th vibrational state of the initial molecule. Here the fact that the fate of the unstable negative ion does not depend on the state of the molecule from which it was formed is employed. Figure 13 shows the results of the calculation of Ref. 89. The efficiency of attachment drops as the number of the vibrational level ν of the O_2 molecule to which three-body attachment occurs increases. Only high autoionization states of the O_2^- ion, whose rate of stabilization by a third body and hence the rate constant for three-body attachment are low, can be populated from states with higher values of ν .

The dependences of the rate constants of three-body attachment on the type of third body and the gas temperature, presented above, are characteristic precisely of three-body processes and, obviously, do not occur in the case of two-body processes. For this reason, the study of reactions

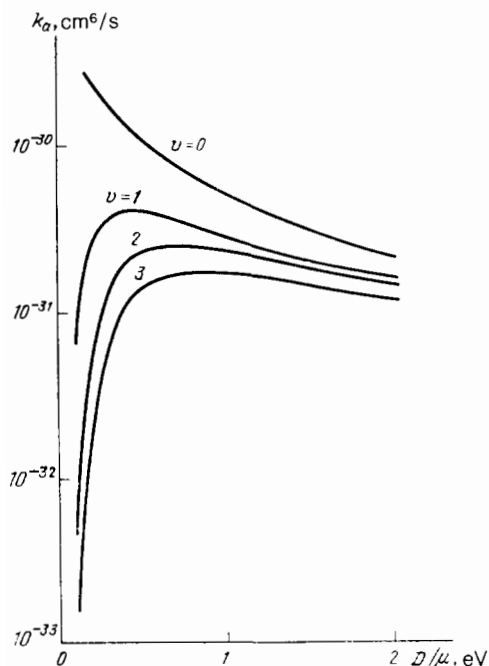


FIG. 13. Rate constant of three-body attachment to the O_2 molecule in the ν th vibrational state with O_2 as the third body.⁸⁹

with the participation of three bodies gives qualitatively new information in the physics of atomic collisions. Another feature of three-body processes is their unusual behavior at high gas pressures. This question is discussed below.

5. ATTACHMENT AT HIGH GAS PRESSURES

The interpretation of the data on electron attachment to a molecule at quite high gas pressures (≈ 100 torr) is one of the most complicated questions, in spite of the abundance of experimental information in this field.

According to the Bloch-Bradbury mechanism, increasing the gas pressure leads to "saturation" of three-body attachment; this follows from (7). It consists of the fact that for $[B] \approx (k_T + k_b^{-1})\tau^{-1}$ the constant k_a decreases as the gas pressure increases and in the limit of high pressures $k_a \sim [B]^{-1}$. (An analogous effect is also observed for attachment with the participation of van der Waals molecules, but at pressures several orders of magnitude higher than studied here.) To study the "saturation" of attachment it is convenient to rewrite the formula (7) in the form

$$\frac{1}{k_a [B]} = \frac{k_T + k_b}{k_T} \frac{1}{k_{at}} + \frac{1}{k_{at} \tau k_T} \frac{1}{[B]}. \quad (16)$$

In the absence of this effect the quantity $(k_a [B])^{-1}$ is proportional to $[B]^{-1}$. "Saturation" leads to the fact that the straight line describing the dependence of $(k_a [B])^{-1}$ on $[B]^{-1}$ passes above the origin of coordinates. The study of this effect makes it possible to calculate the constants characterizing the kinetics of unstable negative ions. Thus if $k_b \ll k_T$, then the intersection of the straight line under study and the ordinate axis determines the value of k_{at} . The evaluation of k_T , for which the rate constant for polarization capture is usually chosen, from the slope of the straight line permits calculating the lifetime τ of the unstable ion.

The experimental dependences of $(k_a [B])^{-1}$ on $[B]^{-1}$ for three-body attachment of thermal electrons to the O_2^{15} , N_2O^{67} and NO_2^{70} molecules with different molecules for the third body are presented in Figs. 14–16. These dependences, measured for gas pressures of up to several hundreds of torr,

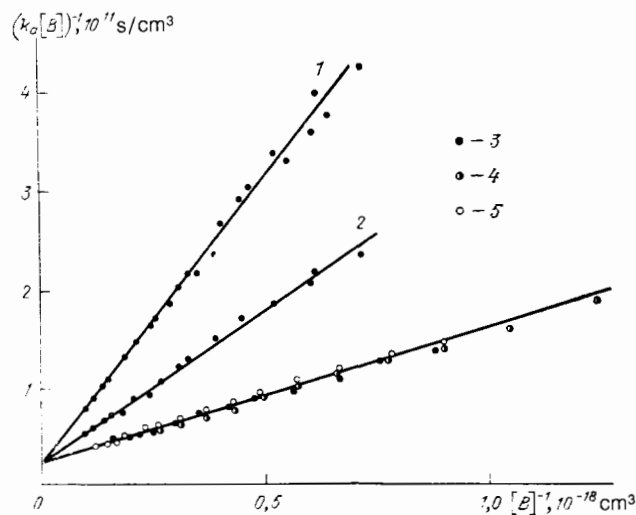


FIG. 14. $(k_a [B])^{-1}$ as a function of $[B]^{-1}$ for three-body attachment to the O_2 molecule.¹⁵ The third body is C_2H_6 (1), C_3H_8 (2), $n-C_5H_{12}$ (3), $n-C_6H_{14}$ (4), and $neo-C_5H_{12}$ (5).

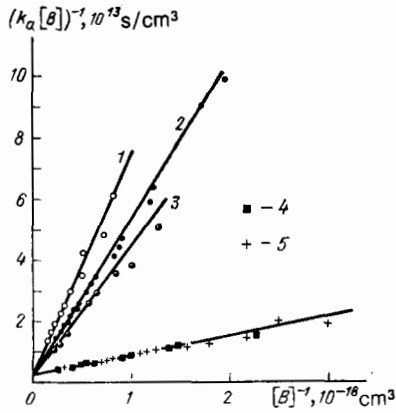


FIG. 15. $(k_a [B])^{-1}$ as a function of $[B]^{-1}$ for three-body attachment to the N_2O molecule.⁶⁷ The third body is 1—trans- C_4H_8 , 2— C_4H_8 , 3—cis- C_4H_8 , 4—iso- C_4H_8 , 5—neo- C_5H_{12} .

are described well by the formula (16). The straight lines on Figs. 14 and 15, corresponding to different third bodies, cross the ordinate axis at the same point. Since the quantity k_{at} , unlike k_T and k_b , does not depend on the type of third body, the latter indicates that $k_T \gg k_b$. The values of k_{at} , determined from Figs. 14–16 for the O_2 , N_2O and NO_2 molecules, equal $(4.8 \pm 0.6) \cdot 10^{-11} \text{ cm}^3/\text{s}$,¹⁵ $(5.8 \pm 0.6) \cdot 10^{-13} \text{ cm}^3/\text{s}$ ⁶⁷ and $1.1 \cdot 10^{-10} \text{ cm}^3/\text{s}$ (Ref. 70), respectively. Estimates of the lifetime τ , obtained from the analysis of the attachment “saturation” effect, give $(1.0 \pm 0.3) \cdot 10^{-10} \text{ s}$ for O_2 ,¹⁵ $1.8 \cdot 10^{-10} \text{ s}$ for N_2O ,⁶⁷ and 10^{-8} s for NO_2 .⁷⁰ Attachment of thermal electrons to the O_2 molecule proceeds only through the first autoionization state of the O_2^- ion, to which the quantity τ reconstructed in Ref. 15 corresponds. It agrees well with the value $\tau = 0.88 \cdot 10^{-10} \text{ s}$, obtained in Ref. 90 from an analysis of the data from electron-beam experiments, where the cross section of the vibrational excitation of the O_2 molecule by electron impact was measured. This process proceeds through the same autoionization states of the O_2^- ion as does the three-body attachment process. Similar values for τ also follow from theoretical estimates: $3 \cdot 10^{-10} \text{ s}$ (Ref. 12) and $0.74 \cdot 10^{-10} \text{ s}$ (Ref. 91). The results of the experiments of Refs. 34, 92, and 93 with an electron bunch, where the attachment “saturation” phenomenon was also observed, are an exception; their analysis gives the value $\tau \approx 10^{-12} \text{ s}$ for the O_2^- ion. But the experiments of Refs. 34, 92, and 93 were performed at pressures several orders of magnitude higher than in Ref. 15. It is possible that in this case the three-body attachment mechanism changes

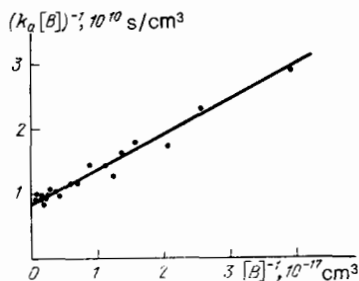
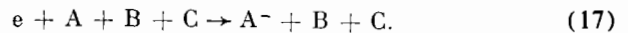


FIG. 16. $(k_a [B])^{-1}$ as a function of $[B]^{-1}$ for three-body attachment to the NO_2 molecule with $n\text{-}C_4H_{10}$ as the third body.⁷⁰

or the parameters of the O_2^- ion change substantially under the action of the environment.

In the foregoing discussion of the “saturation” effect it was assumed that only one autoionization state of the A^- ion makes the main contribution to attachment. Precisely this situation is realized for attachment of thermal electrons to the O_2 molecule. For more complex molecules or for higher electron energies attachment can proceed through many autoionization states of the A^- ion with different values of k_{at} , τ , and k_T . Then the formula (16) is no longer applicable and the foregoing discussions are suitable only for qualitative estimates. In this case, the quantitative study of the attachment “saturation” effect is possible only if detailed information about the autoionization states of the A^- ion is available. Such information exists for the O_2^- ion, which enabled the calculation⁹⁴ of the “saturation” effect for the process $e + 2O_2 \rightarrow O_2^- + O_2$ in an external electric field. The conditions typical for experiments with an electron bunch, in which the electrons are heated by an electric field and have a nonequilibrium energy distribution, were studied. The results of the calculation of Ref. 94 agree well with the experimental data of Ref. 75.

As the gas pressure increases the attachment processes with the participation of four particles become increasingly more important:



An additional attachment channel, whose contribution increases as the gas pressure increases, appears. This effect was observed in many experiments, and in many cases it was possible to obtain quantitative data on the rate of the process (17). They are presented in Refs. 7, 67, and 95 for $T_e = T = 300 \text{ K}$. The possible mechanisms of the process (17) are discussed in Ref. 96 for the example of attachment to the O_2 molecule. These could be processes with the participation of van der Waals molecules, unstable complexes of the type $(A^-) \cdot B$ or $(A^- B)^*$, etc. The existence of unstable complexes leads to effects analogous to “saturation” in the case of three-body attachment, resulting in a complex dependence of the rate of attachment on the gas pressure. The study of processes of this type is only just beginning and at the present time their characteristics are not known reliably.

When the gas pressure is further increased together with the reactions (17), processes of higher order also become important. To describe electron attachment to molecules in this case a statistical approach was proposed in Ref. 97; the interpretation of a series of experimental data on attachment to the O_2 molecule was given on the basis of this approach.

In the foregoing discussion we examined the mechanism-related dependence of the rate of attachment on the gas pressure. The rate constant for attachment also depends on the electron energy distribution function $f(\epsilon)$, which can also change as the pressure increases. Thus the function $f(\epsilon)$ for a weakly ionized plasma in an external electric field is a nonequilibrium function.⁴² The electrons acquire energy from the external field and give it up in collisions with neutral particles. The rate ν_1 is introduced to characterize the rate of relaxation of the electron energy. It usually depends linearly on the gas pressure, and the function $f(\epsilon)$ is determined by the reduced electric field E/N . In the presence of

three-body attachment the situation changes. As the gas pressure increases the ratio of the rate of attachment ν_a to ν_i increases and for $\nu_a \sim \nu_i$ the function $f(\varepsilon)$ itself depends on the rate of attachment. Then the constant k_a is determined not only by the parameter E/N , but also by N . This effect was studied theoretically in the case of attachment to the O_2 molecule for pure oxygen^{85,86} and air.⁸⁶ The computational results of Refs. 85 and 86 show that it leads to qualitatively the same dependences as the attachment "saturation" effect, but quantitatively it is appreciably smaller.

Another effect associated with the nonequilibrium nature of the function $f(\varepsilon)$ owing to electron attachment was discovered in Refs. 98 and 53. Under the conditions of these experiments, in pure oxygen at comparatively low pressures (10 torr) the rate constant for three-body attachment of thermal electrons decreased as the gas pressure increased. This effect, called "attachment cooling," is explained in Refs. 98 and 53 as follows. According to the Bloch-Bradbury mechanism only free electrons from a narrow energy region near resonance, associated with the first autoionization state of O_2^- , at energies $\varepsilon_i \sim 0.09$ eV participate in the attachment. If the rate of attachment ν_a is not small compared with the rate of relaxation of the electron energy ν_i in this region, then the loss of electrons as a result of attachment reduces the number of electrons with energy ε_i , and therefore leads to a decrease of the rate of attachment. The function $f(\varepsilon)$ for energies $\varepsilon \sim \varepsilon_i$ is not Maxwellian. Since the gas temperature $T < \varepsilon_i$, the high-energy part of $f(\varepsilon)$ is depleted, which corresponds to "cooling" of the electron gas. The rates ν_a and ν_i depend differently on the gas density N : $\nu_a \sim N^2$ and $\nu_i \sim N$, and, as the gas pressure increases, the "attachment cooling" effect must intensify.

The rate ν_i for molecular oxygen with $\varepsilon \sim \varepsilon_i$ is determined by the rotational excitation of O_2 molecules in collisions with electrons, whose probability is low. Small additions of other molecular gases (N_2 , CO_2 , H_2O) increase ν_i and therefore decrease the effect. This is confirmed by the experimental results of Refs. 98 and 53. The "attachment cooling" effect for molecular oxygen was studied theoretically in Refs. 99 and 100. In Ref. 99 good agreement with experimental data was obtained with the help of a numerical solution of Boltzmann's equation.^{98,53} In addition, new information was extracted: the absolute values of the cross sections for rotational excitation of the O_2 molecule by electron impact, which occurs through the formation of the unstable O_2^- ion. The results of Ref. 100, which work was performed by the Monte Carlo method, give a weaker effect compared to that observed in the experiments of Refs. 98 and 53. In Ref. 100 this result was obtained owing to the assumption that ν_i is infinite outside the resonance region.

It should be noted that owing to electron-electron collisions, which establish an equilibrium energy distribution, the "attachment cooling" effect vanishes as the degree of ionization increases. Estimates show that for molecular oxygen this occurs for degrees of ionization exceeding 10^{-8} – 10^{-7} .

The possible reasons enumerated above for the change in the rate of attachment as the gas pressure increases can operate in specific situations simultaneously, which complicates the analysis of the experimental data. If, however, such a superposition does not occur, then the study of attachment in dense gases yields new valuable information about the

mechanism of three-body attachment and its intermediate products.

6. ELECTRON ATTACHMENT TO A MOLECULE IN A LIQUID

The limiting case of electron attachment to a molecule at high gas pressures is attachment in a liquid. To some degree it is analogous to the process of three-body attachment in a gas, where the surrounding dense medium plays the role of the third body.

A significant amount of experimental data has now been accumulated on electron attachment to a molecule in a liquid and the first steps of the theoretical analysis of this question,^{9,10,101} which is based on the analogy between processes in a liquid and in a gas, have been taken. In the gas phase, however, the electron is free, while in the liquid phase it is not free. The concept of a quasifree electron is employed for nonpolar liquids, where, according to the experimental data, the electron mobility is high ($> 10^{-2}$ cm²/V·s). In addition, it is assumed that in liquefied inert gases an electron is always in a quasifree state, whereas in most other nonpolar liquids studied the electron is in a quasifree state for part of the time and in a bound state for the rest of the time.^{9,10} For polar liquids, a typical example of which is water, the equilibrium state of an electron is bound. Here the electron is in a potential well, created by the polarization interaction of the electron and the dipolar molecules of the medium.¹⁰¹ In what follows we shall study nonpolar liquids, in which the properties of the electron are closest to those in a gas. The characteristics of attachment in dense media and the effectiveness of the approach based on the ideas from the theory of gas phase processes, for describing electron attachment in a liquid are demonstrated for the example of such liquids.

In the condensed phase, because of the low electron mobility, the rate of attachment is lower than that in a gas. For this reason, the effective rate constant for attachment in a liquid, as in any chemical reaction, equals¹⁰

$$k^{-1} = k_d^{-1} + \tilde{k}_a^{-1}, \quad (18)$$

where k_d characterizes the rate with which the electron and molecule, participating in the process, diffuse toward one another and \tilde{k}_a is the rate constant for close particles. It is usually assumed that $k_d = 4\pi RD$, where R is the "collision radius," equal to the sum of the effective radii of the electron and molecule participating in the process. Analogously, the coefficient D is the sum of the coefficients of diffusion of an electron in a liquid D_e and the coefficient of diffusion of the molecule D_M . Because $D_e \gg D_M$ $k_d = 4\pi RD_e$. The electron mobility μ is related with D_e by Einstein's relation: $D_e/\mu = T$. For a liquid where the electron mobility and therefore the coefficient D_e are small $D_e < 10^{-2}$ cm²/s, the expression (18) reduces to

$$k = k_d = 4\pi RD_e.$$

In this case the rate of electron attachment to molecules in different liquids should be proportional to D_e or μ in these media. Such dependences have been observed in experiments, where electron attachment to SF_6 and pyrene molecules in a series of nonpolar liquids was studied.^{9,10} The values of k and D_e varied over a range of several orders of

magnitude. When the values of D_e and μ are large, diffusion may be neglected and $k = \tilde{k}_a$.

In the theoretical analysis of the mechanism of electron attachment in a liquid it is assumed that, as in the gas phase, it proceeds through an intermediate stage—an unstable negative ion.^{9,10} The rate of the process depends on the mutual arrangement of the electronic terms of the molecule and the negative ion of the molecule. Because of the interaction with the environment the energy of a quasifree electron in a liquid changes by an amount V_0 , which is determined by the balance of short-range repulsive forces and long-range attractive polarization forces. It can be both positive and negative. In recent years a number of methods have been developed and measurements of this quantity have been performed in many liquid media.¹⁰ For nonpolar liquids the values of V_0 vary from -0.6 to 0.2 eV. Analogously, because of the polarization of the molecules of the surrounding medium, the energy of the negative ion changes by an amount P_0 , which for nonpolar liquids lies in the range -1.5 ± 0.8 eV. As a result the relative arrangement of the terms of the molecule and of the negative ion, placed in a liquid, is shifted by an amount $V_0 - P_0$, equal to 0.3 – 2.5 eV for the liquids studied.

In the case of nondissociative electron capture the liquid has the effect of causing the process to proceed through higher vibrational states of the negative ion, which become its lower unstable levels. In addition, the surrounding dense medium, playing the role of the third body, stabilizes the negative ion. If the characteristics of the vibrational levels of the negative ion do not differ much from one another, then electron attachment to the molecule in a liquid is to a larger degree analogous to the corresponding process in a gas. In the case of electron attachment to a complex molecule, when the rate of this process in a gas depends linearly on the pressure, the rate constants in the liquid and in the gas should be close.

Figure 17 shows the results of measurements¹⁰² of the dependence of the rate constant for electron attachment to the SF_6 , N_2O , and O_2 molecules in liquified argon at $T = 87$ K on the intensity of the applied electric field, which, as in a gas, leads to heating of the electrons. In Ref. 102 this constant was also calculated for SF_6 taking into account the nonequilibrium nature of the electron energy distribution in a liquid as well as the attachment cross section, obtained from experiments in a gas. The computational results agree well with the experimental data for a liquid both in absolute magnitude and with regard to the dependence on the electric field. In addition, the measured rates of attachment of thermal electrons ($E \rightarrow 0$) to SF_6 molecules in a gas and in liquid argon are close to one another.

In the case when the rate of electron attachment to molecules in a gas depends quadratically on the pressure and the Bloch-Bradbury mechanism is applicable, the process in a liquid proceeds in the same manner as in the limit of high gas pressures. Then the attachment rate constant in a liquid equals k_{at} —the rate constant for capture of an electron by a molecule in the gas with the formation of an unstable negative ion. It is assumed here that the autoionization states of the ion are always stabilized in collisions with atoms and molecules of the liquid. The dependence of the rate of electron attachment to a molecule on the intensity of the applied electric field in a gas is determined by the function $k_{\text{at}}(E)$. For this reason, an analogous dependence should also be

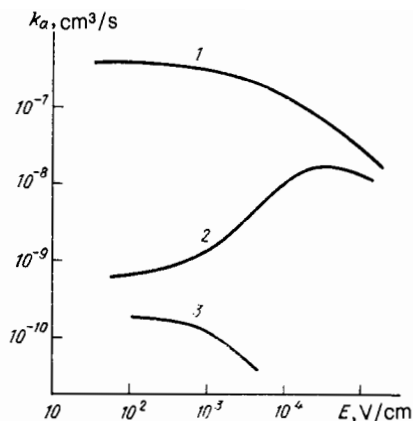


FIG. 17. Electric field dependence of the rate constant of electron attachment to the SF_6 , N_2O , and O_2 molecules in liquid argon at $T = 87$ K.¹⁰² 1) SF_6 , 2) N_2O , and 3) O_2 .

observed in a liquid. The experimental data of Ref. 102 on the rate of attachment to O_2 molecules in liquid argon, presented in Fig. 17, confirm this fact well. The absolute value of this constant for weak electric fields also agrees with the experimental result of Ref. 93 for ethylene under high pressures, which scaled to the conditions of the experiment of Ref. 102 gives the value $k_{\text{at}} \sim 1.2 \cdot 10^{-10}$ cm^3/s .¹⁰ It should be noted that in a study of attachment at lower gas pressures in Ref. 15 values of k_{at} that are 50 times lower than in Ref. 93 were obtained. To explain this discrepancy further experiments at high pressures are required.

Dissociative electron attachment to a molecule



which in a gas depends only on the molecule AB and the electron energy, acquires in a liquid features of the three-body process, since it is also determined by the environment. In a gas dissociative attachment proceeds as follows.^{2,3,8,103} When an electron collides with a molecule the system is transferred to the repulsive term of the unstable negative ion. If on separation the unstable state cannot decay into an electron and a molecule, then a stable negative ion A^- forms. The cross section for dissociative attachment σ_{da} has a resonance dependence on the electron energy and equals the product of the cross section for electron capture by the molecule σ_{cap} by the probability P that there will not be enough time for the negative ion to decay as the nuclei fly apart:

$$\sigma_{\text{da}} = \sigma_{\text{cap}} P.$$

The quantity P is given by the expression

$$P = \exp \left(- \int_{\tilde{R}}^{R_c} \frac{\Gamma dR}{v_R} \right), \quad (19)$$

here R is the internuclear distance corresponding to the capture of an electron by the molecule AB, R_c is the point of intersection of the terms of the molecule and ion, v_R is the radial component of the relative velocity of the nuclei, and Γ is the total width of the autoionization state of the negative ion.

The dependence of the cross section for dissociative attachment on the electron energy and the dependence of the rate constant on the average energy or the applied electric field in a liquid, according to the foregoing assumptions, re-

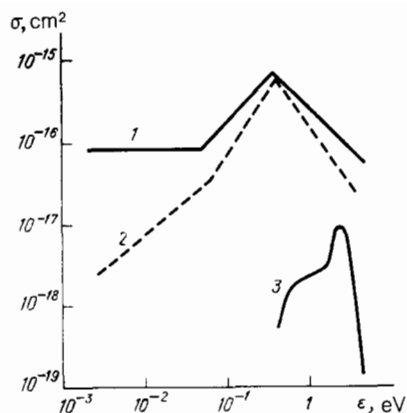


FIG. 18. The cross section for dissociative electron attachment to the N_2O molecule in liquid Ar (1),¹⁰² in liquid Xe (2),¹⁰² and in the gas phase (3).²

main qualitatively the same as in a gas. But the maximum of the cross section, in this case, shifts by an amount $(V_0 - P_0)$. Indeed, the experimental data¹⁰² on electron attachment to N_2O molecules in liquid Ar, presented in Fig. 17, are similar to the analogous curves for the gas phase.^{2,3} In Ref. 102 the cross section for attachment to N_2O in liquid Ar and Xe was also reconstructed based on the numerical determination of the electron energy distribution in a liquid. It is presented in Fig. 18, where, for comparison, the cross section of the same process in the gas phase is also shown.² Here the shift of the energy of the maximum by ~ 2 eV in a liquid, equal to $(V_0 - P_0)$, can be seen especially clearly. Unlike V_0 the value of P_0 is not measured directly in the experiments. It is evaluated with the help of approximate formulas.¹⁰ The value of P_0 can be determined from the shift in the maximum of the cross section or the rate constant as a function of the electron energy. This approach was employed in Ref. 104 in the analysis of attachment to the N_2O molecule, where for the O^- ion in liquid argon the value $P_0 = 1.8$ eV was obtained.

In going over from a gas to a liquid not only does the energy of the maximum of the cross section for attachment to the N_2O molecule shift, but, in addition, the value of this maximum increases by two orders of magnitude. The reason for this increase can be understood from the following arguments. A decrease in the energy of the autoionization state ϵ_i leads to an increase in the lifetime of the state and a decrease in the width of the resonance Γ according to the law $\Gamma \sim \epsilon_i^{l+1/2}$,^{2,14} where l is the orbital quantum number of the electron participating in the capture with the formation of the autoionization state of the negative ion, far from the molecule. The physical reason for this dependence is that when the unstable ion decays it is more difficult for the electron with a lower energy to overcome the potential barrier, which is determined primarily by the centrifugal forces and therefore increases as l increases. In the case of attachment to the N_2O molecule, $l = 1$.¹⁰⁵ Then a decrease in ϵ_i from 2.2 eV in a gas to 0.3 eV in liquid Ar should cause Γ to decrease by a factor of 20. The cross section σ_{cap} for electron capture by N_2O remains virtually unchanged. The quantity P turns out to be more sensitive to a change in Γ . For attachment to the N_2O molecule in a gas $P \sim 10^{-2}$.¹⁰⁵ Decreasing Γ and therefore the exponent in the exponential in (19) by a factor of 20 gives $P \approx 1$. As a result the maximum of the cross section for

attachment in liquid Ar must be two orders of magnitude larger than in a gas, which is confirmed in Fig. 18.

The foregoing discussion referred primarily to liquid Ar. Analogous data have also been obtained for liquid Xe.¹⁰² In nonpolar molecular liquids the description becomes more complicated, because of the possibility of localized electron states. Even here, however, the approach based on the ideas of the theory of gas-phase reactions makes it possible to explain many characteristics: the dependence of the rate of attachment to the molecule on the type of molecule, the value of V_0 , the temperature of the liquid, etc.^{9,10}

7. ISOTOPIC EFFECT IN THREE-BODY ELECTRON ATTACHMENT

The study of the isotopic effect in electron-molecular collisional processes opens up new possibilities for understanding their mechanism, since when one isotope is replaced by another the vibrational quantum and a number of other characteristics of molecules change while the electron interaction remains unchanged. Thus in the experiment of Ref. 44 this effect was employed to study the stabilization of autoionization states of the O_2^- ions with collisions with H_2 and D_2 molecules. According to Ref. 44 the process of stabilization occurs as a result of vibrational-translational relaxation.¹⁰⁶

Isotopic substitution in the O_2 molecule, in spite of the small relative change in the mass of the particles, also strongly affects the rate of the process of three-body attachment of thermal electrons,^{20,107,108} proceeding through the unstable O_2^- ion. When heavy isotopes are included in the molecule the vibrational quantum of the O_2^- ion decreases, which shifts the energy of its autoionization states. As a result the energy threshold of the three-body attachment process decreases and the rate of the process increases. For thermal electron energies only the first autoionization state of the O_2^- , which is its fourth vibrational level, is important. Estimates show that the energy of this state decreases by an amount $\Delta\epsilon = 0.025-0.03$ eV when the $^{16}O_2^-$ is replaced with $^{18}O_2^-$. The rate of three-body attachment to a molecule with heavy isotopes increases by a factor of $\exp(\Delta\epsilon/T)$ and for $T = 300$ K it must increase by a factor of 2.5-3. As the temperature increases the isotopic effect decreases.

Table II gives experimental data on the isotopic effect in three-body attachment of thermal electrons ($T_e = T = 300$ K) to the O_2 molecule with different atoms and molecules as the third body. For processes with a high rate constant ($10^{-29}-10^{-30}$ cm⁶/s) the experimental results agree well with the theoretical calculation, confirming the Bloch-Bradbury mechanism. If the rate of the process is low, then the isotopic effect is also insignificant. In Refs. 20, 107, and 108 this is interpreted to mean that the process of attachment to van der Waals molecules, for which this isotopic effect is small, predominates. This mechanism becomes dominant if attachment through an unstable negative ion is inefficient.

Figure 2 shows the experimental results²⁰ of a study of the isotopic effect in three-body attachment to the O_2 molecule in pure oxygen as the temperature decreases. The experiments were performed under conditions such that $T_e = T$. The decrease in the isotopic effect at low temperatures also indicates that the mechanism of three-body attachment changes: from the Bloch-Bradbury mechanism to the mechanism with the participation of van der Waals mol-

TABLE II. Rate constant of three-body electron attachment to the $^{18}\text{O}_2$ and $^{16}\text{O}_2$ molecules in the presence of a third body M at $T = 300$ K.

M	k_a^{18} , 10^{-30} cm 6 /s	k_a^{16} , 10^{-30} cm 6 /s	k_a^{18}/k_a^{16}	References
He	$0,028 \pm 0,004$	$0,033 \pm 0,003$	$0,85 \pm 0,2$	108
Ne	$0,024 \pm 0,005$	$0,023 \pm 0,003$	$1,0 \pm 0,4$	108
Ar	$0,01 \pm 0,01$	$0,01 \pm 0,01$	~ 1	108
Kr	$0,03 \pm 0,02$	$0,05$	$0,6 \pm 0,4$	108
Xe	$0,01 \pm 0,01$	$0,085 \pm 0,005$	$\sim 0,1$	108
H $_2$	$0,94 \pm 0,05$	$0,48 \pm 0,03$	$2,0 \pm 0,2$	107
D $_2$	$0,35 \pm 0,02$	$0,140 \pm 0,005$	$2,5 \pm 0,2$	107
N $_2$	$0,11 \pm 0,01$	$0,085 \pm 0,005$	$1,3 \pm 0,2$	107
O $_2$	$5,1 \pm 0,2$	$2,2 \pm 0,2$	$2,3 \pm 0,3$	20, 107
CO $_2$	$6,4 \pm 0,3$	$3,2 \pm 0,2$	$2,0 \pm 0,2$	107
CH $_4$	$0,43 \pm 0,03$	$0,34 \pm 0,01$	$1,3 \pm 0,2$	108
C $_2$ H $_6$	$2,8 \pm 0,3$	$1,3 \pm 0,2$	$2,2 \pm 0,6$	108
C $_3$ H $_8$	$5,8 \pm 0,4$	$3,0 \pm 0,5$	$1,9 \pm 0,6$	108
n-C $_4$ H $_{10}$	$9,1 \pm 0,1$	$4,2 \pm 0,2$	$2,2 \pm 0,1$	20
neo-C $_5$ H $_{12}$	12 ± 2	7 ± 1	$1,7 \pm 0,6$	108

ecules. This result also follows from an analysis of the shape of the curves in Fig. 2.

In Ref. 109 the isotopic effect for three-body attachment of an electron to the O $_2$ molecule was studied, based on the semiempirical approach, as a function of the electron temperature T_e and the gas pressure p with a constant gas temperature $T = 300$ K. As T_e increases the isotopic effect becomes weaker and for $T_e \gg \Delta\epsilon$ it vanishes. At high pressures an additional effect appears owing to "saturation" of attachment, which is manifested if the condition (8) no longer holds. A decrease in the energy of the autoionization state in the O $_2^-$ ion with heavy isotopes increases its lifetime τ , and therefore leads to more rapid appearance of "saturation" of attachment as the gas pressure increases and the value of k_a decreases. Because of this, at high gas pressures the total isotopic effect becomes weaker and even its sign changes.

Thus the significant isotopic effect in three-body attachment via the Bloch-Bradbury mechanism and its absence in other cases make it possible to determine quite simply the mechanism of attachment.

8. THREE-BODY ELECTRON ATTACHMENT IN A WEAKLY IONIZED GAS

The three-body attachment process, as the most rapid channel for electron loss, plays an important role in weakly ionized plasma. Here we have, first of all, a natural formation—the earth's ionosphere. The negative ions are important in the lower part of the ionosphere—the so-called D region, which lies at altitudes of 60–90 km. At higher altitudes, on the one hand, the rate of formation of negative ions decreases because the density of neutral particles decreases, while on the other hand an efficient channel for loss of negative ions in exothermal reactions with O atoms, whose relative number increases with altitude, appears.

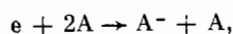
The main channel for formation of negative ions and loss of electrons in the D region is the reaction^{110–112}



The O $_2^-$ ions then enter into a complicated chain of processes, which lead either to freeing of electrons or to formation of more stable negative ions—NO $_3^-$ and HCO $_3^-$. The importance of the three-body attachment process for aeron-

omy served as an impetus to the study of this process in laboratory plasma. Analogously three-body attachment also affects artificial plasma formations in the earth's atmosphere,^{113,114} reducing the free electron density and hence altering the properties of this plasma.

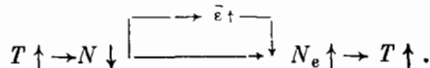
Another example of a situation where three-body attachment significantly affects the characteristics of the plasma is a gas discharge. The loss of electrons as a result of three-body attachment decreases the discharge current and therefore the energy input. In addition to quantitative changes, this process sometimes introduces qualitative changes in phenomena occurring in a gas discharge. Thus three-body attachment could be responsible for the "synergistic" effect accompanying electric breakdown of gaseous dielectrics, consisting of the fact that the threshold for the breakdown of a binary gas mixture is higher than the corresponding thresholds for pure gases.¹¹⁵ Electron attachment to molecules decreases the conductivity of the gas and impedes the development of breakdown. In a gas of molecules A electron loss is determined by the three-body attachment process



whose efficiency increases significantly when the third body A is replaced by the molecule B, whereas in a mixture of A and B molecules the total rate of attachment increases, which increases the breakdown threshold. With a transition to the pure gas consisting of molecules B the main channel whose efficiency increases significantly when the third body A is replaced by the molecule B, whereas in a mixture of A and B molecules the total rate of attachment increases, which increases the breakdown threshold. With a transition to the pure gas consisting of molecules B the main channel for electron loss—three-body attachment to the molecules A—vanishes, and the development of breakdown once again is facilitated. This effect is observed, for example, in the mixtures C $_3$ F $_8$ –SF $_6$, OCS–SF $_6$, 1-C $_3$ F $_6$ –c-C $_4$ F $_8$.¹¹⁵ These questions are important for optimizing the electric insulation properties of gaseous dielectrics for electrical apparatus operating on high current.

The process of three-body electron attachment affects not only the stationary characteristics of a gas discharge, but its stability also. It accelerates the development of the over-

heating instability of a non-self-sustained gas discharge, employed for pumping electric-ionization lasers. This instability destroys the uniformity of the discharge and causes it to contract.¹¹⁶⁻¹¹⁹ The mechanism of the overheating instability of a non-self-sustained gas discharge, where the electrons are formed under the action of an external ionizer and are removed as a result of three-body attachment, can be understood from the following arguments. Assume that in a uniform discharge plasma a local increase in the gas temperature T , owing to a small fluctuation, in a direction perpendicular to the electric current has occurred. Since the pressure in the medium is equalized rapidly (with the velocity of sound), the increase in temperature causes thermal expansion and reduces the density of the molecules N . As a result, the rate of energy transfer from electrons to molecules decreases, which increases the reduced electric field E/N and the average electron energy $\bar{\epsilon}$. Both the reduction of N and the growth of $\bar{\epsilon}$ decrease the rate of three-body attachment, and therefore increase the electron density N_e . The latter further increases the Joule heating and T . The process of heating of the gas, initiated in a random manner, will continue. As a result, the discharge contracts—the current flows along a narrow channel. The chain described can be represented as follows:



The growth increment of the overheating instability in a $\text{CO}_2\text{:N}_2\text{:He}$ mixture with plasma parameters characteristic for electric-ionization CO_2 lasers—a typical source of coherent infrared radiation with high energy parameters—was calculated in Ref. 118. Other channels for electron loss, together with three-body attachment, were also studied: dissociative attachment and recombination. According to Ref. 118 the overheating instability develops most rapidly in the case of three-body attachment; in addition, the rate of growth of the perturbations is proportional to the power injected into the discharge. Molecules to which three-body electron attachment occurs can appear instantaneously in the active medium of the laser in the form of an impurity or can form as a result of plasma-chemical reactions. The development of the overheating instability limits a number of characteristics of electric-ionization lasers.

9. CONCLUSIONS

Three-body electron attachment to molecules is one of the basic processes in the kinetics of charged particles for sufficiently dense low-temperature plasma with electronegative components. The initial interest in this process was motivated by studies of the earth's ionosphere. The important role of three-body attachment in the creation of artificial plasma formations in the atmosphere, ignition and maintenance of different forms of gas discharge, and therefore in practical applications of the physics of gas-discharge plasma was understood later. In the last ten years significant progress has been made in understanding the mechanism of three-body attachment and a large amount of factual information on its characteristics has been accumulated. In particular, the important role of van der Waals molecules has been clarified and a significant isotopic effect, making it possible to determine reliably the mechanism of three-body attachment, has been discovered.

The study of processes with the participation of three and more particles makes it possible to follow the change in the properties of an isolated molecule as the density of the surrounding medium increases. Here the first successful steps in explaining the characteristics of electron attachment to a molecule in the liquid phase based on three-body attachment in a gas have been made. Because of the undeveloped state of the theories and the diversity of competing effects in dense media, much remains to be done in this interesting and complex field.

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