

Dissociative attachment of an electron to a molecule

A. V. Eletskiĭ and B. M. Smirnov

Lenin Komsomol State University, Novosibirsk
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A review is given of the present state of research into the dissociative attachment of an electron to a molecule, which is one of the principal mechanisms for negative-ion formation in electronegative-gas plasmas. A semiclassical model is used to analyze the basic characteristics of the process and their dependence on molecular parameters and the energy of the electron. The more important experimental methods of obtaining information on the characteristics of the process are discussed, and data obtained in recent years are surveyed. Situations in which the dissociative attachment process has a significant effect on the properties of particular systems containing low-temperature plasmas are analyzed. These systems include gas lasers, optogalvanic devices, high-pressure discharges, and gaseous dielectrics.

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1. INTRODUCTION

The dissociative attachment of an electron to a molecule is a two-body collision process of the form



where A, B are the components of the molecule. The distinctive feature of this process is the formation of an intermediate autodetaching state of the negative ion of the molecule, AB^- , which subsequently decays into fragments. The cross section for the process therefore usually exhibits a resonant dependence on the energy of the electron. This explains why the influence of this process on the properties of weakly-ionized plasma manifests itself only in a particular range of plasma-parameter values, and is practically absent outside the region of dissociative attachment.

The study of the dissociative attachment of electrons to molecules has an extensive history. The process has been examined in detail in monographs and reviews on negative ions and atomic collisions.¹⁻⁹ Our overall understanding of the physics of the process was developed in the 1970's, as were the various techniques now available for its investigation. Subsequent advances in research into this subject were largely concerned with the acquisition of new data and the creation of more detailed theoretical models. The develop-

ment of new methods based on modern experimental techniques has played a particularly important role along this path. It has provided us with fundamentally new opportunities for investigating this phenomenon, with the result that very much more information has become available on the various aspects of the process, and the range of objects that have been investigated in detail has become much greater. One of the aims of this review is to illustrate the present state of research into dissociative attachment by specific examples.

The dissociative attachment of an electron to a molecule manifests itself in different phenomena in low-temperature plasmas. The process lies at the basis of a number of experimental methods used in atomic physics to obtain atomic data. Dissociative attachment in low-temperature plasmas leads to the formation of negative ions which, in turn, sharply reduces the mobility of negative charges and, hence, the conductivity of plasmas. Moreover, this opens up new possibilities for the production or neutralization of charged particles in plasmas. Dissociative attachment can give rise to changes in the conditions under which discharges are maintained in the electronegative gases and, in some cases, to the development of particular instabilities that lead to a sharp change in the state of the discharge or to the appearance of spatial structures in the plasma. Considerable

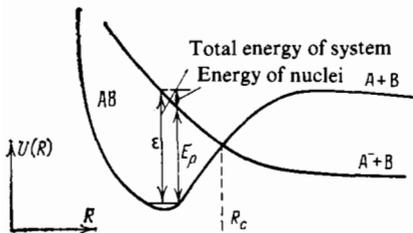


FIG. 1. Typical mutual disposition of the potential energy curves of the molecule and the molecular negative ion participating in dissociative attachment.

advances have been made in recent years in the understanding of such phenomena. This is due, on the one hand, to the development of detailed studies of the relevant elementary processes and, on the other, to the development of applications to the physics of low-temperature plasmas. One of the aims of this review is to reflect these advances by analyzing phenomena in which the properties and characteristics of the dissociative attachment of an electron to a molecule play a dominant role.

2. THE MECHANISM OF DISSOCIATIVE ATTACHMENT

We shall develop the basic ideas of the physics of dissociative attachment in terms of the quasiclassical approximation³ in which the nuclei are regarded as classical particles. This pictorial approach will enable us to examine the basic properties of the process. It is important to note, however, that the quantum-mechanical approach, developed in Refs. 10–14, is more productive in specific calculations.

The nature of the process of dissociative attachment can be understood by considering Fig. 1, which shows the electronic energy terms in the initial and final states in the most common situation. The electron undergoes resonant capture by the molecule, which takes the system to the repulsive autodetaching term of the negative ion. The subsequent motion of the nuclei in opposite directions leads, in the final analysis, to the formation of a stable negative ion, provided the autodetaching state does not succeed in decaying during this motion of the nuclei. The dissociative attachment cross section σ_{att} can thus be regarded as the product of the capture cross section σ_{cap} of the molecule and the probability P that the negative ion will survive while the nuclei fly apart:

$$\sigma_{\text{att}} = \sigma_{\text{cap}} P. \quad (2)$$

The capture cross section is given by the Breit-Wigner formula¹⁵

$$\sigma_{\text{cap}} = \frac{\pi}{2\varepsilon} \frac{\Gamma^2}{(\varepsilon - E_p)^2 + (\Gamma^2/4)}, \quad (3)$$

where ε is the electron energy, E_p is the excitation energy of the autodetaching level, and Γ is the total width of this level. Here and henceforth, we are using the atomic system of units, in which $\hbar = m = e^2 = 1$. Naturally, $E_p, \varepsilon \gg \Gamma$. When the motion of the nuclei can be described by the classical approximation, the parameters E_p, Γ of the autodetaching state depend on the separation R between the nuclei (or the

configuration of the nuclei in the case of a polyatomic molecule) as a parameter. We note that (3) leads to the following convenient relationship:

$$\int_0^\infty \sigma_{\text{cap}} \varepsilon d\varepsilon = \pi^2 \Gamma. \quad (4)$$

The probability P that the autodetaching state will not decay as the nuclei fly apart is a solution of the differential equation

$$\frac{dP}{dt} = -\Gamma_a P,$$

which is essentially a definition of Γ_a , i.e., the component of the width of the autodetaching state that is responsible for its decay with the formation of a molecule in the initial electronic state. For a simple molecule, the width Γ_a is equal to the total width of the autoionizing level. By solving this equation, we obtain the probability that the nuclei will fly apart without the decay of the autoionizing state:

$$P = \exp \left(- \int_R^{R_c} \frac{\Gamma dR}{v_R} \right),$$

where R is the separation between the nuclei at which the electron was captured, R_c is the term-crossing point (see Fig. 1), and v_R is the radial component of the relative velocity of the nuclei, i.e., $dt = dR/v_R$. Using this result together with (2) and (3), we obtain the following expression for the cross section for dissociative attachment of an electron to a molecule:¹⁾

$$\sigma_{\text{att}} = \frac{\pi}{2\varepsilon} \int_0^{R_c} \frac{\Gamma^2 |\Psi(R)|^2 dR}{(\varepsilon - E_p)^2 + (\Gamma^2/4)} \exp \left(- \int_R^{R_c} \frac{\Gamma dR}{v_R} \right), \quad (5)$$

where $\Psi(R)$ is the wave function for the relative position of the nuclei, i.e., $|\Psi(R)|^2 dR$ is the probability that the nuclei are separated by a distance between R and $R + dR$. It is clear that this result applies to a diatomic molecule, or to a polyatomic molecule with a well-defined bond. In the latter case, the parameter R is a characteristic of this bond.

The following convenient integral relation follows from (4) and (5):

$$\int_0^\infty \sigma_{\text{att}} \varepsilon d\varepsilon = \pi^2 \left\langle \Gamma(R) \exp \left(- \int_R^{R_c} \frac{\Gamma dR}{v_R} \right) \right\rangle \quad (6)$$

where the angle brackets denote averaging over the distribution of nuclear separations in the molecule.

Let us examine this result in greater detail. We shall consider (5) in the case where the width Γ of the autodetaching level is small enough for it to be much smaller than the change in the resonance energy E_p when the separation between the nuclei changes by an amount of the order the amplitude of the vibrations of the nuclei in the molecule. The integral (5) is then found to converge near the nuclear separation R_ε corresponding to precise resonance, i.e., $E_p(R_\varepsilon) = \varepsilon$. By evaluating this integral in this particular approximation, we obtain

$$\sigma_{\text{att}} = \frac{\pi^2 \Gamma(R_\varepsilon)}{\varepsilon} \frac{|\Psi(R_\varepsilon)|^2}{(dE_p/dR)|_{R_\varepsilon}} \exp \left(- \int_{R_\varepsilon}^{R_c} \frac{\Gamma dR}{v_R} \right), \quad (7)$$

$$\varepsilon = E_p(R_\varepsilon).$$

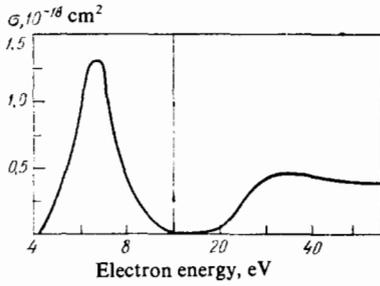


FIG. 2. Energy dependence of the cross section for the dissociative attachment of an electron to the oxygen molecule.¹

This formula²⁾ gives the resonance dependence of the attachment cross section on the incident electron energy, which is determined by the factor $|\Psi(R_\varepsilon)|^2$. Resonance occurs near the energy ε_0 for which the resonance separation R_ε between the terms is equal to the equilibrium separation R_0 between the nuclei in the molecule: $\varepsilon_0 = E_p(R_0)$. Near resonance, we have

$$R_\varepsilon - R_0 = (\varepsilon - \varepsilon_0) \left(\frac{dE_p}{dR} \Big|_{R_0} \right)^{-1}. \quad (8)$$

We can now use this result to rewrite (7) in the case where the initial vibrational state of the molecule is the ground state and $\Psi(R)$ is the wave function of the harmonic oscillator, given by¹⁵

$$|\Psi(R)|^2 = \frac{1}{\sqrt{\pi\Delta R}} \exp \left[-\frac{(R-R_0)^2}{\Delta R^2} \right], \quad (9)$$

where the amplitude of the nuclear oscillations is $\Delta R^2 = 1/\mu\omega$, μ is the reduced mass of the nuclei, and ω is the separation between the vibrational levels of the harmonic oscillator. From (7) and (8), we have

$$\begin{aligned} \sigma_{\text{att}}(\varepsilon) &\approx \sigma_{\text{att}}(\varepsilon_0) \frac{|\Psi(R)|^2}{|\Psi(R_0)|^2} \\ &= \sigma_{\text{att}}(\varepsilon_0) \exp \left[-\frac{(\varepsilon - \varepsilon_0)^2}{\Delta\varepsilon^2} \right], \end{aligned} \quad (10)$$

$$\Delta\varepsilon = \Delta R \frac{dE_p}{dR} \Big|_{R_0}.$$

As can be seen, the cross section for the dissociative attachment of an electron to a molecule exhibits a resonant behavior. Let us estimate the width of the resonance, assuming that dE_p/dR is of the order of the atomic value. Since the vibrational amplitude of the nuclei is $\Delta R \sim \mu^{-1/4}$, the width of the resonance is $\Delta\varepsilon \sim \mu^{-1/4}$, i.e., it is small in comparison with characteristic atomic quantities. Hence, usually, the electron-energy dependence of the cross section for the dissociative attachment of an electron to a diatomic molecule, or to a molecule with a well-defined bond, takes the form of a set of individual resonances, each of which corresponds to the formation of a particular autodetaching state of the negative ion of the molecule. For example, Fig. 2 shows the dissociative attachment cross section of the oxygen molecule in the energy range where this process occurs through the formation of the autoionizing state $O_2^- (^2\Pi_g)$.

We must now determine the maximum dissociative at-

tachment cross section. Substituting the expression for the nuclear wave function (9) at $R = R_0$ into (7), we obtain

$$\sigma_{\text{att}}(\varepsilon_0) = \frac{\pi^{3/2}\Gamma(R_0)}{\varepsilon_0\Delta\varepsilon} \exp \left(-\int_{R_0}^{R_0} \frac{\Gamma dR}{v_H} \right). \quad (11)$$

Let us now vary this expression with respect to the parameter Γ . For simplicity, we shall suppose that the width Γ of the autodetaching level does not depend on the separation between the nuclei. It is then readily seen that the maximum value of the cross section (11) occurs for the value of Γ for which the argument of the exponential is equal to -1 . Assuming that the excitation energy of the autoionizing level is a linear function of the separation between the nuclei, i.e., $E_p(R) = E'_R(R_s - R)$, we find from (11) that the maximum cross section is given by

$$\sigma_{\text{max}} = \frac{\pi^{3/2}}{2^{1/2}\varepsilon_0} \frac{1}{|E'_R(R_c - R_0)|} \omega^{1/2}, \quad (12)$$

where ω is the vibrational frequency of the nuclei. The formal dependence of the cross section on the reduced mass μ of the nuclei is $\sigma_{\text{max}} \sim \mu^{-1/4}$, i.e., it is less than the atomic value. Hence, it may be expected that the attachment cross section is lower at resonance than the corresponding gas-kinetic cross sections. This is confirmed by most of the special cases examined below for diatomic molecules.

As already noted, Eqs. (2)–(11) were obtained under a number of simplifying model assumptions about the width of the autodetaching term and its position relative to the ground-state term of the molecule. It will be clear from the ensuing discussion that these assumptions are often invalid. Moreover, the classical description of the motion of the nuclei is not always valid either. Hence, the above formulas can hardly be valid for the rigorous determination of the cross sections for the dissociative attachment of an electron to a particular molecule. Moreover, even when the above assumptions are valid, their practical application gives rise to problems because of inadequate knowledge of the mutual disposition of the states participating in the process and of the dependence of the width of the autodetaching level on nuclear separation. Nevertheless, (2)–(11) have a clear physical interpretation and are very convenient in the analysis of experimental data on dissociative attachment. They offer us an opportunity of visualizing the physical picture of the process, and enable us to estimate some of the parameters of the autodetaching state from experimental data, and to establish a qualitative picture of the dependence of the cross section on electron energy, the vibrational state of the molecule, its isotopic composition, and so on.

As an example of a system for which the parameters of (2) can be reliably determined, let us consider the dissociative attachment of an electron to the hydrogen molecule. In this case, the probability that the autodetaching state will survive while the fragments fly apart is low. Hence, $P \ll 1$ in (2), and the dissociative attachment cross section of the hydrogen molecule is very dependent on its isotopic composition.

Actually, measurements performed by Schulz^{17,18} show that the maximum dissociative attachment cross section of

the H_2 molecule is $1.6 \times 10^{-21} \text{ cm}^2$, and the corresponding figures for HD and D_2 are $2.1 \times 10^{-22} \text{ cm}^2$ and $8 \times 10^{-24} \text{ cm}^2$, respectively.

We must now consider these results in the light of (7), which gives the dissociative attachment cross section. Taking successively the three possible cross-section ratios for the different isotopic compositions of the molecule, we find, after some statistical analysis, that the probability that the autodetaching state of H_2^- will survive as the fragments fly apart is $(1.8 \pm 0.5) \times 10^{-6}$, and the maximum electron-capture cross section of the hydrogen molecules is close to 10^{-15} cm^2 . The corresponding width of the autodetaching state turns out to be $\Gamma \approx 2 \text{ eV}$, which is comparable with the energy of the electron at maximum cross section (about 4 eV). For this relationship between the parameters the concept of the autodetaching state (i.e., of the existence of a quasis-discrete level) is no longer valid. Nevertheless, the statistical analysis of the data on the isotopic effect, based on these ideas, shows that the theory is fully acceptable.

Thus, without pausing to consider the range of validity of our results, or other features of the behavior of the electronic term in the cross section, let us now formulate the basic conclusions that can be drawn from the above discussion and can be used as a basis for the analysis of experimental data. The cross section for the dissociative attachment of an electron to a molecule, regarded as a function of the incident electron energy, consists of individual resonances corresponding to particular autodetaching states. At the same time, the attachment cross section in a particular resonance is small in comparison with the characteristic atomic cross sections.

3. STRUCTURE OF THE CROSS SECTION FOR DISSOCIATIVE ATTACHMENT

Experiment is the main source of information about the dissociative attachment process. Traditional experimental methods, reviewed in detail in monographs on negative ions (especially that due to Massey¹) can be used for this purpose. We shall therefore give only a brief presentation of experimental methods, and will reproduce some of the experimental data that are useful in the analysis of phenomena occurring in low-temperature plasmas.

Three experimental approaches, yielding different types of data, are used to investigate dissociative attachment. One gives the cross section for dissociative attachment of the electron to a molecule as a function of the electron energy. A typical result of this kind of experiment is shown in Fig. 2. Another source of data involves measurements of the differential attachment cross sections, i.e., the angular distributions of emitted ions. These measurements can be used to elucidate the symmetry of the autodetaching state of the ion (which breaks up into the reaction products), or the contribution of individual autodetaching states to the total cross section at given electron energy. This facilitates the reconstruction of the physical picture of the process in the language of the electronic terms of autodetaching states, and hence yields their widths and positions as functions of the separation between the fragments. The third approach to the investigation of the dissociative attachment of an electron to

a molecule involves measurement of the ion energy distribution for given incident-electron energy. Analyses of such measurements yield information on the energetics of the process and can be used to determine the binding energy of the electron in the resulting ion, and the energy states of the fragments.

Finally, we must also mention the extensive measurements (see, for example, the review by Gallagher *et al.*²⁰) of the rate constants for the attachment of an electron to a molecule as a function of electron temperature, mean electron energy, and electric field at a given pressure of a gas mixture. Such data are "applied" in character and can be used in calculations of the parameters of systems with the same or similar electron-energy distribution function. Such data do not in themselves enable us to determine the parameters of the elementary process. Nor can they be used to analyze phenomena in which the distribution function has one or more singularities.

Theory plays an important role in the analysis of the dissociative attachment process. *Ab initio* calculations provide us with the possibility of determining the positions of autodetaching states and their widths, which can then be used to determine the dissociative attachment cross sections. Comparison of such calculations with experimental data helps us to understand the possibilities of the theory which, experience shows, is capable of describing simple systems. The more productive approach is to adopt the semiempirical method, in which one essentially analyzes experimental data in terms of theoretical models. It is usual to specify the shape of the potential curve for the autodetaching state of the negative ion, and the dependence of the width of this level on fragment separation. The parameters of the autodetaching state are then used to calculate a more detailed structure of the process.

The semiempirical approach is valuable in the sense that it enables us to use different types of experimental data on a given process and other processes similar to it. In particular, the symmetry of autodetaching states determining a particular process can be reconstructed from measurements of the differential attachment cross section. Next, the electron-energy dependence of the dissociative attachment cross section enables us to determine the parameters of the autodetaching state for the fragment-separation range responsible for the process. The possibilities and precision of this operation are substantially extended when additional experimental data can be introduced into the calculation. For example, when the dissociative attachment cross section is very dependent on the isotopic composition of the molecule, measurements of this dependence provide significant information about the width and disposition of the autodetaching state of the molecular negative ion. A typical example of this kind is the attachment of an electron to the hydrogen molecule, examined above. Experiments that investigate the dependence of the dissociative attachment cross section on the temperature of the molecules involved in the process provide additional information on the dependence of the dissociative attachment cross section on the vibrational state of the molecule. This information helps us to extend the range of fragment separations in which the parameters of the autodetach-

ing state can be reliably deduced.

The dissociative attachment of an electron to a molecule is accompanied by the excitation of its vibrational levels. In this process, an electron is initially captured by the molecule, the autodetaching state of the negative ion breaks up, and the molecule is formed in the vibrationally excited state. Since the cross section for the excitation of the vibrational levels of a molecule by electron impact can be expressed in terms of the parameters of the autodetaching state of the molecular negative ion, the known dependence of the cross section for this process on the electron energy, with the molecule undergoing transitions to different vibrationally-excited states, can be used to improve the values of the parameters of the autodetaching state.

The opposite process, namely, the associative decay of a negative ion on collision, provides further information. Here, the collision between a negative ion and another fragment results in the formation of a molecule and an electron. If the probability of formation of the molecule in the lower vibrationally excited states is relatively high, the cross section for this process and its dependence on the collision energy provide us with data on the parameters of the autodetaching state for fragment separations for which the dissociative attachment of the electron to the molecule occurs.

Let us consider the dissociative attachment of an electron to the HCl molecule as an example in which the above program is realized most completely. We shall consider low collision energies for which only one channel for this process is available:



To obtain the parameters of the autodetaching state of the negative ion, we must first use the parameters of the cross section for the process (13), reported in the literature.¹⁷⁻²⁷ According to these studies, process (13) has a threshold at the electron energy of 0.65 ± 0.04 eV and a maximum cross section at 0.78 ± 0.08 eV³¹. The observed threshold is close to the natural energy threshold, i.e., the difference between the dissociation energy of the HCl molecule (4.31 eV) and the affinity energy of the chlorine atom (3.62 eV), which is equal to 0.69 eV. The presence of the resonance near the threshold indicates that the potential curve of the autodetaching state passes above the bottom of the molecular well with a small slope, or the fragments may even attract in this region.

Studies of the isotopic effect in this process provide further information. According to the measurements reported by Azria *et al.*,²⁴ the maximum cross section for the attachment of an electron to the HCl molecule is 8.9×10^{-18} cm², whereas the corresponding figure for the DCl molecule is 1.8×10^{-18} cm². Analysis of these data in terms of (6) shows that the survival probability of the autodetaching state as the fragments fly apart is $P = 0.018$.

Measurements of the dissociative attachment cross section as a function of electron energy at different temperatures of the molecules are particularly valuable. For example, the measurements of Allan and Wong²⁸ at temperatures in the range 300–1200 K show that there is a rapid rise in the

maximum cross section for the attachment of an electron to a molecule with increasing vibrational excitation. These results are listed in Table I.

At first sight, the data in Table I seem to be in conflict with the above survival probability $P = 0.018$. Actually, it was assumed in our analysis of the data on the isotopic effect that the maximum dissociative attachment cross section was proportional to the survival probability and, from this, we found that the survival probability of the autodetaching state of HCl⁻ was $P \approx 0.02$. If we adopt the same standpoint in the analysis of the data of Table I, we find that $P \leq 0.001$. This contradiction can evidently be removed by using (11) for the maximum cross section for the process. The capture of the electron by different vibrational states of the molecule occurs mostly for different separations between the nuclei, i.e., it can be characterized by different values of the parameters $\Gamma(R_0), (dE_p/dR)(R_0)$. The maximum dissociative attachment cross sections of molecules in different vibrational states will therefore differ not only due to the different survival probabilities of the autodetaching state of the molecular negative ion.

The angular distribution of the Cl⁻ ions in (13) shows that the autodetaching state of the negative ion is a Σ state (see, for example, Refs. 25–27). This is not unexpected because this is the only state of the quasimolecule that can be formed when Cl⁻ (¹S) and H(²S) approach one another, i.e., the lower autodetaching state can only have this particular symmetry.

Additional data on the parameters of the autodetaching state of the negative ion are obtained by investigating the vibrational excitation of the HCl molecule by electron impact.^{25,29} The cross section for the excitation of the first vibrational levels is characterized by a sharp maximum near the threshold, at which the excitation cross section is of the order of 10^{-5} cm², and a second broad maximum at about 2.5 eV. The simplest explanation of the situation proposed in Ref. 30 is that there are two autodetaching states of the negative ion with a low excitation energy.

Some information on the parameters of the autodetaching state of the negative ion is provided by studies of the associative decay $\text{H}^- + \text{Cl} \rightarrow \text{HCl} + e$. The measured rate constant³¹ for this process at 29 K is 9.6×10^{-10} cm³/s. The rate of the corresponding vibrational transitions has been used³² to show that the relative probability of formation of the HCl molecule in the state with vibrational quantum numbers $v = 2$ and $v = 1$ is 5:3. Let us take $\pi R_c^2 = 7.6 \text{ \AA}^2$ as the cross section for the associative decay of the negative ion, where $R_c = 1.6 \text{ \AA}$ is the crossing point of the HCl and HCl⁻

TABLE I.

Molecule		HCl	DCl
Ratio of attachment cross sections	$\frac{\sigma(v=1)}{\sigma(v=0)}$	38	32
	$\frac{\sigma(v=2)}{\sigma(v=0)}$	880	580

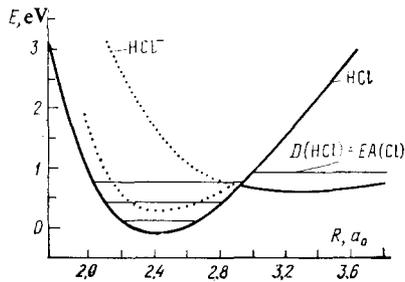


FIG. 3. Calculated autodetaching terms of the molecular ion HCl^- (dashed curve—Ref. 35, dotted curve—Ref. 30).

potential curves, which lies at about 0.69 eV above the vibrational ground state on the HCl potential curve. Assuming that this cross section is independent of the collision velocity, we find that the rate constant for the process at room temperature is $1.9 \times 10^{-10} \text{ cm}^3/\text{s}$. If we suppose that the process is due to polarization capture, we find that the rate constant for the process given by the Langevin formula is $1.9 \times 10^{-9} \text{ cm}^3/\text{s}$. Since the actual value of the rate constant lies between these two values, we may conclude that the potential curve of the molecular negative ion corresponds to attraction in the region of large fragment separations, and that the well depth is comparable with the thermal energy.⁴⁾

The above information on the dissociative attachment of an electron to the HCl molecule at low collision energies, and on processes of a similar character, can be used to deduce the parameters of the autodetaching state. These data can be augmented with other information that is of scientific interest but does not help us very much in relation to the parameters of the autodetaching state. This includes discontinuities in the dissociative attachment cross section, which occur on the cross section tail when the electron energy is equal to the energy of excitation of the corresponding vibrational level of the molecule,²⁶ narrow resonances in the cross section for the elastic scattering of an electron by a molecule at energies close to the energy of excitation of the corresponding vibrational levels,³³ and so on.

Theoretical determinations of the parameters of the lower autodetaching state of the HCl^- ion, with allowance for the corresponding experimental data, have been reported in a large number of published papers (cf., for example, Refs. 30, 34–39). Despite this intensive theoretical effort, and the variety of experimental information on which it is based, there is still no general consensus even about the qualitative shape of the potential curve of the lower autodetaching state of HCl^- . Figure 3 shows two types of autodetaching term of HCl^- . The repulsive curve near the bottom of the HCl well of the form shown here was used in Ref. 35, and the electronic term of HCl, which is similar in this region and is shown schematically in Fig. 3, was used in Ref. 30. Each of these curves is based on a particular range of the previously quoted experimental facts, and can be made to agree with them to a particular precision, partly dictated by the experimental uncertainty. As an example, Fig. 4 shows the cross sections for the dissociative attachment of an electron to the HCl and DCl molecules, as functions of the inci-

dent-electron energy at relatively high temperatures at which vibrationally excited molecules provide a significant contribution to the observed picture. The dashed curve is theoretical³⁵ and is based on the upper autodetaching state curve in Fig. 3, with the corresponding level width. It is clear that, for this process, as in any other resonance process, the theory yields a curve whose resonance structure is broadened in the experiment.

The above example of the dissociative attachment of an electron to the HCl molecule is of interest for a whole number of reasons. HCl is a typical simple molecule containing an electronegative atom, so that it can be used to illustrate the general features of the process. Next, different aspects of the process and of other similar processes have been investigated in detail in the case of HCl. In principle, this extensive information can be used to deduce the complete physical picture of the process. Finally, the process is of some applied interest, as well. It is used in the XeCl excimer laser as the source of chlorine atoms.^{41,40} It ensures a high pulse repetition frequency in this laser.

The above example also reveals the difficulties of our problem. Despite the extensive experimental information that is now available, there is still no unanimity as to the behavior of the autodetaching term through which the process proceeds. Further effort will be necessary to exploit the existing extensive experimental data and to remove current contradictions.

Let us now consider the cross section for the dissociative attachment of an electron to halogen molecules, which constitute another range of objects that has been examined in

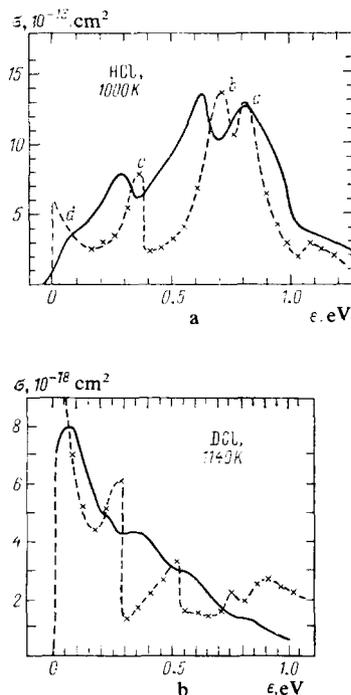


FIG. 4. Energy dependence of the cross section for the dissociative attachment of an electron to the HCl (a) and DCl (b) molecule, measured (points) and calculated³⁵ using the repulsive term shown in Fig. 3 (solid curve).

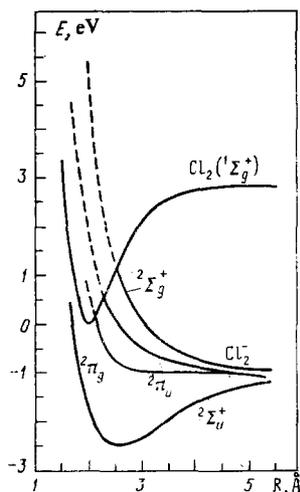


FIG. 5. Mutual disposition of the lowest electron terms of the molecular ions Cl_2^- and the ground-state term of Cl_2 .

some detail. These molecules participate effectively in our process and, at the same time, are readily accessible and simple, which is convenient in the analysis of the results. Moreover, the dissociative attachment of electrons to halogen molecules is important from the applied point of view. Extensive information is therefore available on this subject. In particular, the dependence of the dissociative attachment cross section on the incident-electron energy has been investigated for fluorine,^{43,46} chlorine,^{42,43,46-49} bromine,^{46,47,50} and iodine^{46,47,51,52} molecules.

Let us consider the physical picture of the process. The negative ion of the halogen molecule, X_2^- , consisting of the halogen negative ion $\text{X}^{-1} ({}^1\text{S})$ and the halogen atom in a low-lying electronic state $\text{X}({}^2\text{P}_1)$, has four electronic states. In the region of strong coupling, in which the fine splitting of the atomic levels is small in comparison with the electrostatic term-splitting energy, these states can be arranged in the order of increasing ion energy, as follows: ${}^2\Sigma_u^+$, ${}^2\Pi_g$, ${}^2\Pi_u$ and ${}^2\Sigma_g^+$. These states can be obtained by taking the closed-shell quasimolecule $\text{X}^{-1} ({}^1\text{S}) + \text{X}^{-1} ({}^1\text{S})$ with the structure $(\sigma_g)^2(\Pi_u)^4(\Pi_g)^4(\sigma_u)^2$, and then producing a hole by removing one electron from the electron shell. The states of the unfilled electron shell produced in this way appear in the following order as the energy spent in producing the hole increases: ${}^2\sigma_u$, ${}^2\Pi_g$, ${}^2\Pi_u$, ${}^2\sigma_g$, which indicates the symmetry of the X_2^- residue. We note, in this connection, that the bottom state of the molecular ion $\text{X}_2^- ({}^2\Sigma_u^+)$ is a stable bound state.

Whether or not particular electronic states will participate in the dissociative attachment process will depend on whether the potential curves of these states cross the ground-state potential curve of the halogen molecule $\text{X}_2 ({}^1\Sigma_g^+)$. When this crossing does occur, the states participate in the dissociative attachment process as intermediate autodetaching states. As an example, Fig. 5 shows the terms for the bottom electronic states of Cl_2^- together with the ground-state term of the chlorine molecule. As can be seen, the three Cl_2^- terms do cross the chlorine term, so that each of them

should produce its own resonance in the dissociative attachment cross section. This is confirmed by Fig. 6, which shows the energy dependence of the cross section for the dissociative attachment of an electron to the chlorine molecule at low electron energies.⁴⁹ In approximate treatments, it may be considered that this cross section consists of three individual resonances.

Table II shows the parameters of the individual resonances in the cross section for the dissociative attachment of an electron to a halogen molecule. Each resonance is compared with the corresponding autodetaching state of the molecular negative ion of the halogen. These resonances are very sharp when the crossing occurs near the bottom of the well. A typical example of this situation is the dissociative attachment of an electron to the F_2 molecule, whose energy dependence is shown in Fig. 7. As can be seen, there is a clear peak at zero electron energy, and an unresolved structure at higher energies.

The cross section for the dissociative attachment of an electron to a simple molecule is thus found to have a resonance structure, and the resonances are due to the autodetaching intermediate state of the negative ion. The parameters of these states can be determined by studying different aspects of the process or by analyzing other similar processes. Extensive studies of this type have been carried out for the HCl and other halogen molecules because of their simplicity and accessibility, as well as their applied interest. This is why these systems were chosen above as the most suitable examples for discussion.

4. RATE CONSTANT FOR THE ATTACHMENT OF AN ELECTRON TO A MOLECULE

When the dissipative attachment of an electron to a molecule occurs in a low-temperature plasma, the process can be characterized by a rate constant averaged over the electron energy distribution. If the electron velocity distribution is Maxwellian, and the width of the autodetaching level is much smaller than the thermal energy, the attachment rate constant is given by the following expression, obtained with the aid of (5):

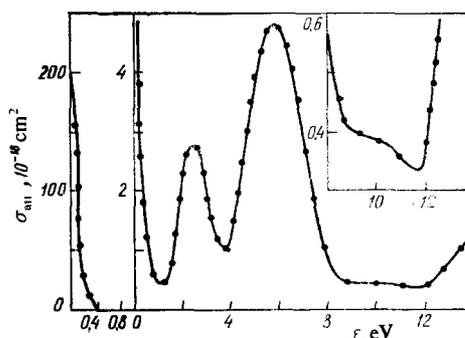


FIG. 6. Energy dependence of the cross section for the dissociative attachment of an electron to the Cl_2 molecule.⁴⁹

TABLE II. Position and width of the resonances (in eV) in the cross section for the dissociative attachment of an electron to a halogen molecule.

autodetaching state of the ion	F ₂		Cl ₂		Br ₂		I ₂	
	center	width	center	width	center	width	center	width
² Σ _u ⁺	0.09	small	—	—	—	—	—	—
² Π _g	4	—	0.03	small	0.07	small	0.05	small
² Π _u	7	—	2.5	1.3	1.4	1.2	0.9	1.2
² Σ _g ⁻	10	—	5.5	2.0	3.7	1.6	2.5	1.7

$$k_{att} = \int_0^{\infty} \frac{2}{\pi^{1/2} T_e^{3/2}} \exp\left(-\frac{\epsilon}{T_e}\right) \epsilon^{1/2} d\epsilon (2\epsilon)^{1/2} \sigma_{att}$$

$$= \left(\frac{2\pi}{T_e}\right)^{3/2} \left\langle \Gamma(R) \exp\left(-\frac{E_D}{T_e} - \int_R^{R_c} \frac{\Gamma dR}{v_R}\right) \right\rangle, \quad (14)$$

where T_e is the electron temperature and, as in (6), the average is evaluated with allowance for the distribution of nuclear separations.

It follows from (14) that the dependence of the rate constant on electron temperature does not have a resonance structure. There are, in fact, two types of dependence. If the dissociative attachment cross section has a well-defined resonance at zero energy, the attachment rate constant falls monotonically with increasing electron temperature. If the dissociative attachment of the electron to the molecule has a threshold, the rate constant increases rapidly at low temperatures with increasing temperature, and then has a broad maximum. When there are several resonances, one is usually much stronger than the others and dominates the situation. Under other conditions in low-temperature plasmas, the attachment rate constant has a similar dependence on the mean electron energy or the electric field.

As an example, Fig. 8 shows the mean-energy dependence of the rate constant for the attachment of an electron to the F₂ molecule. Table III lists the rate constants for the attachment of an electron to halogen molecules at electron temperatures $T = 300$ – 350 K and mean electron energy of 1

eV.

5. ATTACHMENT OF AN ELECTRON TO A COMPLEX MOLECULE

The particular feature of the attachment of an electron to a complex molecule is that the resulting autodetaching state of the negative ion is long-lived. The lifetime of such states is 10^{-6} – 10^{-5} s (see, for example, Ref. 68). This means that, even at low pressures of the buffer gas (≤ 1 Torr) in which the process takes place, a quenching collision with the gas particles will occur during the lifetime of the autodetaching state of the ion, and this type of electron attachment to the molecule is seen as a two-body process in the ternary collision.

When the affinity energy of an electron to an atom in a polyatomic molecule exceeds the separation energy of the atom, the dissociative attachment of the electron to the polyatomic molecule may have a two-body character even at very low electron energies. Figure 9 shows the maximum cross section for the dissociative attachment of a slow electron (≤ 0.1 eV) to different polyatomic molecules as a function of the gas temperature.⁶⁹ Table IV shows the dissociative attachment coefficient for electrons on a number of polyatomic molecules, measured at different gas temperatures.⁷⁰ It follows from these data that the temperature dependence of the rate constant for the dissociative attachment of an electron to a complex molecule can be described by the

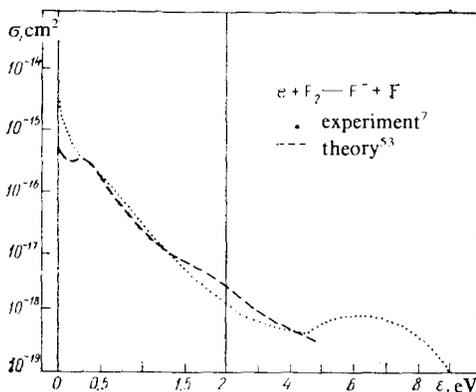


FIG. 7. Energy dependence of the dissociative attachment cross section for an electron to the F₂ molecule.²⁰

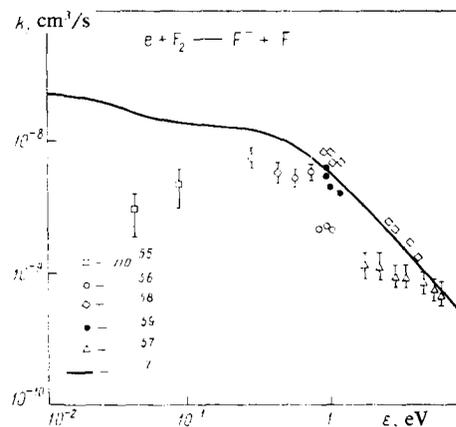


FIG. 8. Rate constant for the dissociative attachment of an electron to the F₂ molecule.²⁰

TABLE III. Rate constant for the attachment of electrons to halogen molecules.

Molecule	$k, \text{cm}^3/\text{s}$	
	$T = 300 - 350 \text{ K}$	$\bar{\epsilon} = 1 \text{ eV}$
F_2	$(3.1 \pm 1.2) \cdot 10^{-9} \text{ }^{55}$ $7 \cdot 10^{-9} \text{ }^{55}$	$(2.3 \pm 0.3) \cdot 10^{-9} \text{ }^{56}$ $7 \cdot 10^{-9} \text{ }^{56}$
Cl_2	$2.9 \cdot 10^{-10} \text{ }^{48,49}$ $(3.7 \pm 1.7) \cdot 10^{-10} \text{ }^{55}$ $3.1 \cdot 10^{-10} \text{ }^{61}$ $2.04 \cdot 10^{-10} \text{ }^{62}$ $3.3 \cdot 10^{-10} \text{ }^{63}$	$(0.34 \pm 0.1) \cdot 10^{-9} (\bar{\epsilon}_e = 0.78 \text{ eV}) \text{ }^{54}$
Br_2	$(1.0 \pm 0.9) \cdot 10^{-11} \text{ }^{55}$ $0.8 \cdot 10^{-12} \text{ }^{64}$	$1.0 \cdot 10^{-10} \text{ }^{65}$
I_2	$4.2 \cdot 10^{-9} \text{ }^{66}$ $1.8 \cdot 10^{-10} \text{ }^{67}$	

Arrhenius law

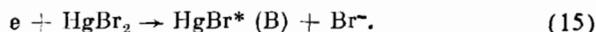
$$k = k_0 \exp \left(-\frac{E_0}{T} \right),$$

where the activation energy E_0 is 0.04, 0.08, 0.05, 0.3, and 0.025 eV for the molecules $c = \text{C}_7\text{F}_{14}$, CF_3Br , CH_2Br_2 , CH_3Br , and CH_3I , respectively. As far as the dependence of this rate constant on the composition of freon is concerned, which can be determined from the data in this table, we may conclude that the rate constant does not exhibit an unambiguous monotonic tendency as the hydrogen atoms are replaced with an increasing number of halogen atoms.

6. DISSOCIATIVE ATTACHMENT IN GAS LASERS

Dissociative attachment plays a significant role in the low-temperature plasma of molecular gases. It often determines the parameters and properties of the plasma and thus influences the output characteristics of practical devices exploiting the properties of such plasmas. Let us consider a few examples of this.

The active medium of many molecular-gas lasers contains electronegative components which can participate in dissociative attachment. Processes of this type can not only have a significant effect on the ionic composition of the active medium in the gas laser, but may also play an appreciable role, and sometimes a dominant role, in the production of population inversion. Dissociative attachment is thus the basis for the excitation of the excimer laser using the $\text{B} \rightarrow \text{X}$ transition in the HgBr molecule. The active medium of the laser contains HgBr_2 molecules which disintegrate along the following channel when a pulsed electric discharge is initiated, or a beam of fast electrons is introduced:⁹¹



The energy dependence of this process⁷ (see also the earlier paper⁹³) is shown in Fig. 10. The rate constant for the process (15), calculated from these data as a function of the mean electron energy,⁹⁴ is shown in Fig. 11.

Dissociative attachment plays an important role in chemical lasers pumped by an electron beam or an electric discharge. Here, the process is responsible for the production of free radicals, which are necessary for the initiation of the chemical reaction that produces the population inver-

sion. Thus, the most popular chemical laser exploits the vibrational transitions in HF molecules produced in vibrationally excited states as a result of the reaction



The chain reaction (16), (17) between fluorine and hydrogen is usually initiated by passing an electron beam or electric discharge through the $\text{H}_2 + \text{F}_2$ mixture. The fluorine atoms necessary for initiating the chain reaction are then formed as a result of the dissociative attachment



whose cross section is shown in Fig. 7 as a function of energy. Measurements and calculations of the rate constant for this process are shown in Fig. 8.

Because of the importance of the process of dissociative attachment of an electron to the F_2 molecule as the mechanism responsible for the appearance of free radicals of flu-

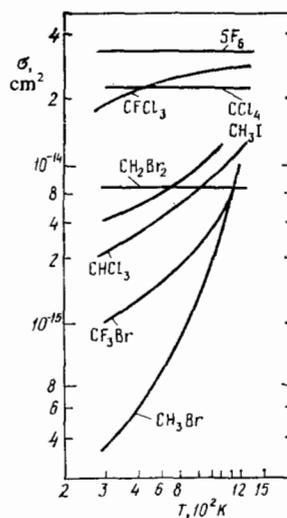


FIG. 9. Maximum cross section for the dissociative attachment of a slow electron (0.1 eV) to polyatomic molecules as a function of gas temperature. These data are averages over a large number of experimental points.

TABLE IV. Dissociative attachment coefficients (in units of $10^{-7} \text{ cm}^3/\text{s}$) for an electron on a polyatomic molecule, measured at different gas temperatures.

T, K	205	300	452	585
c-C ₂ F ₁₄	0.45 ⁷⁰	0.68 ± 0.1 ^{70, 78, 80, 85-88}	1.3 ⁷⁰	1.6 ⁷⁰
CF ₃ Br	0.53 ⁷⁰	0.15 ± 0.01 ^{70, 78}	0.49 ⁷⁰	0.77 ⁷⁰
CH ₂ Br ₂	0.81 ⁷⁰	0.62 ± 0.3 ^{70, 75}	1.6 ⁷⁰	2.2 ⁷⁰
CH ₃ Br		(5.4 ± 0.4) · 10 ⁻⁵ ^{70, 78, 80}	0.0023 ⁷⁰	0.025 ⁷⁰
CH ₃ I	0.85 ⁷⁰	1.2 ⁷⁰ ; 0.25 ⁷⁵ ; 0.22 ¹	1.8 ⁷⁰	1.1 ⁷⁰
CH ₃ Cl		5.4 · 10 ⁻⁴ ¹		
CH ₂ Cl ₂		1.4 · 10 ⁻⁴ ^{1, 71, 72, 78, 77}		
CHCl ₃		0.27 ± 0.06 ^{1, 71-73, 76}		
CCl ₄		0.37 ± 0.06 ^{1, 71, 73, 74, 78-81}		
CCl ₃ F		0.1 ¹		
CCl ₂ F ₂		0.012 ¹		
CClF ₃		10 ⁻⁶ ¹		
CF ₄		10 ⁻⁹ ¹		
CHF ₃		0.01 ^{1, 74, 77, 82, 83}		
CHFCl ₂		(2.4 ± 0.6) · 10 ⁻⁶ ^{1, 74, 76, 82}		
CHF ₂ Cl		(2.4 ± 0.6) · 10 ⁻⁶ ^{1, 74, 82, 83}		
CHCl ₃		0.27 ± 0.06 ¹		

orine in low-temperature gas-discharge plasmas, it is interesting to estimate the amount of energy necessary for the dissociation of the F₂ molecule by this mechanism. This can be done by using the measured reduced coefficient $\eta/[F_2]$ as a function of the reduced electric field E/N for the helium/fluorine mixture¹⁰⁰ at a fluorine concentration of about 1%, where η is the number of dissociative attachments per electron per 1 cm, E is the electric field, $[F_2]$ is the fluorine density, and N is the total density of the gas (Fig. 12).

It follows from the resulting values of η that the number of attachment events per electron per unit time is ηw_{dr} , where w_{dr} is the drift velocity of the electron in the gas in the external field. On the other hand, the amount of energy acquired by the electron per unit time is

$$\frac{de}{dt} = eEw_{dr}. \quad (19)$$

Hence, we find that the mean energy per dissociative attachment is

$$\epsilon_{d.a.} = \frac{eE}{\eta} = \frac{eE}{[He]} \left(\frac{\eta}{[F_2]} \frac{[F_2]}{[He]} \right)^{-1}. \quad (20)$$

Table V lists the energies expended per dissociative attachment of an electron to the fluorine molecule, calculated from (20).

When the negative fluorine ion is lost within the gas as a result of collisions with electrons in accordance with the process



the energy ϵ_{da} is related to the energy spent in forming the fluorine atom (ϵ_F) as follows: $\epsilon_{da} = 2\epsilon_F$. The process (21) can be effective in a gas discharge when the electron density, gas pressure, and the dimensions of the system are suitably chosen. Between its creation and final loss to the wall, each electron then undergoes many transformations as a result of processes (18) and (21) (recombinations within the gas can be neglected), and the energy lost by ionization is unimportant. Analysis of the dissociation of molecular fluorine in the gas discharge shows⁹⁰ that the energy necessary to produce a fluorine atom lies in the range 3–60 eV, depending on the buffer gas, type of discharge, and discharge parameters. Comparison of these quantities with the data of Table V shows that dissociative attachment can be responsible for the dissociation of fluorine in the gas discharge.

We note that, apart from F₂ molecules, other compounds are used as the fluorine-containing molecules in chemical lasers (for example, SF, NF₃, WF₆, and so on). Dissociative attachment may contribute significantly to the dissociation of these compounds under electron bombardment. The energy dependence of the cross sections for the dissociative attachment of an electron to the NF₃ molecule is shown in Fig. 13 for different dissociation products.

A further example of a significant influence of dissociative attachment on the excitation and output parameters of a laser concerns lasers using excimer molecules,^{101,102} i.e., molecules that bond chemically only in excited states. The

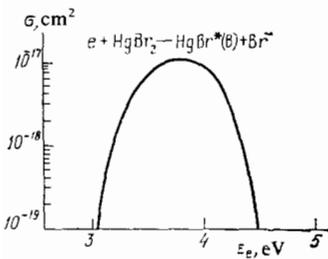


FIG. 10. Energy dependence of the cross section for the dissociative attachment of an electron to the HgBr₂ molecule with the formation of the HgBr* excimer molecule.⁷

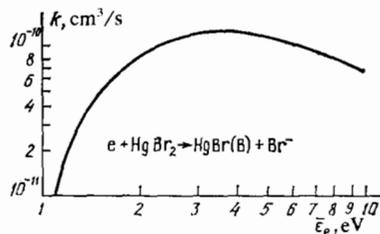


FIG. 11. Rate constant for the process (15) as a function of the mean electron energy.⁹⁴

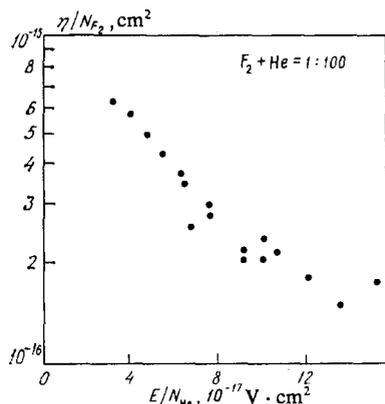


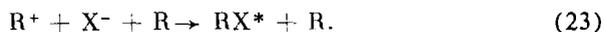
FIG. 12. Reduced dissociative attachment coefficient for an electron on F_2 as a function of the ratio E/N_{He} (Ref. 100).

active medium in the excimer laser is usually a mixture of one or more inert gases and a small proportion of a halide-containing compound. When an electron beam or pulsed electric discharge is allowed to pass through this mixture, the result is a complex sequence of processes^{101,102} that results in the formation of the metastable atoms of the inert gas, R^* . The subsequent reaction



(XY is the halide-containing molecule and X is the halogen atom) leads to the formation of the excimer molecules RX^* (for example, XeF^* , $XeCl^*$, KrF , ArF , and so on), the radiative decay of which produces the laser radiation.

Dissociative attachment plays a twofold role in excimer lasers. First, in addition to (22), the process provides a significant contribution to the production of excimer molecules.¹⁰² The halogen negative ions X^- , produced as a result of dissociative attachment, can recombine with the positive ions of the inert gas when a third particle is present, forming the excimer molecule:



We note, however, that, in contrast to (22), this process has not been adequately investigated experimentally and, although there is no doubt about the presence of an effective ion-ion recombination channel in the active medium of an excimer laser, the final state of the recombination product has not been identified experimentally. Evidently, the process (23) provides a small contribution to the formation of the excimer molecules under optimum excimer-laser parameters.

When the ion-ion recombination (23) is unimportant

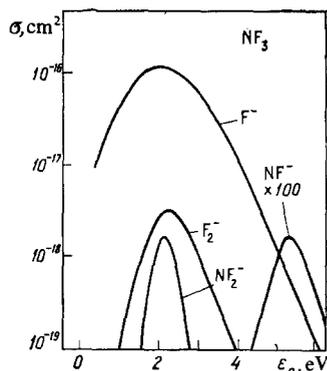


FIG. 13. Energy dependence of the cross section for the dissociative attachment of an electron to the NF_3 molecule for different ions formed as a result of the dissociative attachment process.⁷

for the formation of excimer molecules, dissociative attachment plays a negative role in the excitation of excimer lasers. In point of fact, dissociative attachment then produces a reduction in the number of halide-containing molecules capable of participating in reaction (22) which is the source of the excimer molecules, so that there is a reduction in the total energy of laser radiation which can be produced per unit volume of the active medium of given composition. In practice, the deleterious effect of dissociative attachment on the output characteristics of the excimer laser is obviated by suitably choosing the composition of the active medium. The necessary condition for this is that slow electrons produced by passing a fast-electron beam through the active medium should participate in the dissociative recombination reaction



more effectively than in the dissociative attachment reaction (1), where R_2^+ is the molecular ion of the inert gas, which is usually the dominant positive ion in the active medium of the excimer laser. Process (24) is usually the main source of excited atoms R^* of the inert gas that are necessary for the subsequent formation of excimer molecules.

The condition formulated above can be written in the form

$$[X_2] \ll N_e \frac{\alpha_p}{k_{att}}, \quad (25)$$

where α_p is the coefficient of dissociative recombination of the electron and the molecular ion (14). Substituting $\alpha_p \sim 10^{-7} \text{ cm}^3/\text{s}$, $k_{att} \sim 3 \times 10^{-9} \text{ cm}^3/\text{s}$, we find that the above condition restricts the density of the halide-containing gas to values of the order of $30N_e$.

TABLE V. Mean energy per dissociative attachment to the fluorine molecule.

$10^{-17} \text{ B} \cdot \text{cm}^2$	3	4	6	8	10	12	14
e d.a. eV	4.6	7.3	15.8	30	45	63	87

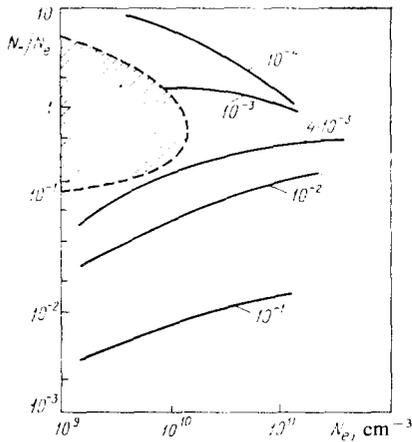
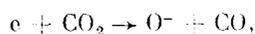


FIG. 14. Region of attachment instability of a homogeneous positive discharge column in the mixture $\text{CO}_2:\text{N}_2:\text{He} = 1:7:12$ at a total pressure of 720 mm Hg and a small amount of carbon monoxide¹⁰⁵ (the relative concentration is shown against the curves). The region of attachment instability is shown shaded.

7. ATTACHMENT INSTABILITY

Dissociative attachment is responsible for a type of instability of a low-temperature gas-discharge plasma, referred to as attachment instability.^{103,107} This instability produces the stratification of the volume filled with the gas-discharge plasma into domains lying at right angles to the direction of the electric field. Attachment instability occurs in high-pressure gas-discharge plasmas in which electrons are lost mainly by dissociative attachment. The significant point here is that the dependence of the attachment rate constant on electron temperature is stronger than the corresponding dependence of the rate of production of charged particles. A typical example of this situation is the discharge at atmospheric pressure, used for the excitation of the CO_2 laser. Free electrons are produced in this case by an additional ionizing source (ultraviolet radiation or electron beam), and an appreciable contribution to their neutralization is provided by the dissociative attachment process



whose rate constant is a rapidly-varying function of electron temperature.

The development of attachment instability can be understood in terms of the following considerations. Suppose that a local increase in electron density has occurred in the initially homogeneous plasma of a nonself-sustaining discharge as a result of a small fluctuation. We shall assume that the electron density inhomogeneity is longitudinal in character, in which case the continuity equation for the current density shows^{104,105} that the increase in electron density should be accompanied by a reduction in the electric field E and, correspondingly, in the mean electron energy $\bar{\epsilon}_e$. Since this discharge exploits an ionization source whose efficiency is independent of the processes occurring in the discharge, a reduction in the mean electron energy will affect only the attachment efficiency, which should also fall. All this upsets

the balance between the production and loss of charged particles, and the process of increasing charged-particle concentration, which began randomly, will continue further.

Figure 14 shows the calculated¹⁰⁵ plasma parameters of a self-sustaining discharge for which attachment instability sets in. The calculations were performed for the mixture used in high-pressure carbon dioxide lasers. The principal source of free electrons in this case is the detachment of electrons from negative ions by collisions with atoms, and the main source of uncertainty in the calculations is the lack of information about the parameters of the detachment process.

8. VIBRATIONAL ATTACHMENT INSTABILITY

A further form of instability due to the characteristic properties of the dissociative attachment process can develop when the dissociative attachment coefficient is a rapidly-varying function of the vibrational excitation of the molecules participating in the process. This occurs, for example, in the case of the attachment of an electron to an HCl molecule (see Section 3). Vibrational attachment instability occurs as follows. Suppose that the initial degree of vibrational excitation in the original discharge mixture is low, and dissociative attachment has no effect on the electron-number balance. Ionization of the gas particles occurs when the gas discharge is turned on, and there is also intensive excitation of the vibrational states of the molecules. The rise in vibrational temperature is accompanied by a rapid rise in the rate of attachment of electrons to the molecules, and this affects the electron-number balance in the gas and may lead to a reduction in the total number of electrons. The net effect of all this is a reduction in the rate of excitation of vibrational states of the molecules and, as a result of the vibrational relaxation of the molecules, the molecular gas is again found to be in a state with a low degree of vibrational excitation. This reduces the rate of attachment and, correspondingly, reinstates the initial rate of increase in electron density. The development of the vibrational attachment instability should thus be accompanied by periodic oscillations in electron density and, correspondingly, in the current density in the discharge containing electronegative impurities. The onset and development of vibrational attachment instability can be analyzed qualitatively by considering a simple model incorporating all the leading processes that give rise to this instability. We shall consider a high-pressure discharge in which diffusion does not contribute to the charged-particle balance. The plasma is then spatially homogeneous, and the evolution of electron density in the plasma is described by a set of balance equations for the electron density N_e and the mean number of vibrational quanta ϵ_v per molecule, namely,

$$\frac{dN_e}{dt} = N_e k_i N_a - N_e \nu_{\text{att}}(\epsilon_v), \quad (26)$$

$$\frac{d\epsilon_v}{dt} = N_e k_{eV} - \frac{\epsilon_v}{\tau_{VT}}; \quad (27)$$

where k_i is the rate constant for the ionization of neutral particles by electron impact, $\nu_{\text{att}}(\epsilon_v)$ is the frequency of dissociative attachment, k_{eV} is the rate constant for the vi-

brational excitation of the molecules by electron impact,⁵⁾ and τ_{VT} is the characteristic time for VT-relaxation of the molecules in collisions with gas particles. The above form of the balance equation for vibrational energy refers to the case where the molecular gas is under essentially non-equilibrium conditions, so that the vibrational energy of the molecule is greater on average than the equilibrium value corresponding to the gas temperature.

The stationary (quasistationary) solution of (26) and (27) is

$$v_1 = v_{att}, \quad (28)$$

$$\varepsilon_{V0} = N_{e0} k_{eV} \tau_{VT}. \quad (29)$$

The function $v_{att}(\varepsilon_V)$ and the dependence of k_i on the parameter E/N (ratio of electric field to gas-particle density) ensures that (28) is the relationship between the electron density N_e and the ratio E/N , i.e., the current-voltage characteristic of the discharge. Let us analyze the conditions for the appearance of the vibrational attachment instability, using a device that is common in the solution of such problems. We shall seek the nonstationary solution of (26) and (27) in the form

$$N_e = N_{e0} + \tilde{N}_e(t), \quad (30)$$

$$\varepsilon_V = \varepsilon_{V0} + \tilde{\varepsilon}_V(t), \quad (31)$$

where the time-dependent terms $\tilde{N}_e(t)$, $\tilde{\varepsilon}_V(t)$ are assumed to be small in comparison with the stationary values N_{e0} , ε_{V0} , respectively. At the same time, the function $v_{att}(\varepsilon_V)$ can be written in the form

$$v_{att}(\varepsilon_V) = v_{att}(\varepsilon_{V0}) + \frac{dv_{att}}{d\varepsilon_V} \tilde{\varepsilon}_V(t), \quad (32)$$

which is also time-dependent.

Substituting (30)–(32) in (26) and (27), performing some minor rearrangement, and taking into account the fact that the time-dependent terms $\tilde{N}_e(t)$ and $\tilde{\varepsilon}_V(t)$ are small, we obtain the following equation for $\tilde{N}_e(t)$ (and an analogous equation for $\tilde{\varepsilon}_V(t)$):

$$\frac{d^2 \tilde{N}_e}{dt^2} + \frac{1}{\tau_{VT}} \frac{d \tilde{N}_e}{dt} + N_{e0} \frac{dv_{att}}{d\varepsilon_V} k_{eV} \tilde{N}_e = 0. \quad (33)$$

We have thus obtained the equation for free vibrations, which has an oscillatory solution when

$$\frac{1}{\tau_{VT}^2} < 4 \frac{dv_{att}}{d\varepsilon_V} k_{eV} N_{e0}. \quad (34)$$

This solution has the form

$$\tilde{N}_e(t) = A e^{-t/2\tau_{VT}} \sin \frac{[4(dv_{att}/d\varepsilon_V) k_{eV} N_{e0} - \tau_{VT}^{-2}]^{1/2} t - \varphi}{2}, \quad (35)$$

where A and φ are constants of integration whose values have no effect on the result of the analysis in our case.

It follows from the above solution that oscillations in electron density and in the degree of vibrational excitation of the molecules, which are due to the dependence of the rate constant for dissociative attachment on ε_V , can be observed

when the characteristic time constant of the exponential in (35) is much greater than the characteristic period of the oscillations. This condition imposes a more stringent restriction on the electron density as compared with (34), namely,

$$N_{e0} \gg \frac{1}{4\tau_{VT}^2 (dv_{att}/d\varepsilon_V) k_{eV}}. \quad (34')$$

It is important to note that the simple model of the discharge examined above makes no allowances for the loss of electrons due to diffusion to the wall, or for recombinations within the gas. The former may be important at low gas pressures and the latter at pressures of the order of the atmospheric pressure or higher. When these effects are taken into account, and this can be done by the method used above, the resulting conditions for the development of instability are, of course, different from those obtained above. Thus, the condition for "true" oscillations, obtained with allowance for volume charged-particle recombinations, can be written in the form

$$4 \left(k_{eV} N_{e0} \frac{dv_{att}}{d\varepsilon_V} + \frac{\alpha_p N_{e0}}{\tau_{VT}} \right) \gg \left(\alpha_p N_{e0} + \frac{1}{\tau_{VT}} \right)^2, \quad (36)$$

where α_p is the recombination coefficient. As can be seen, this condition provides both the upper and lower bounds for the electron density.

The conditions for the appearance of vibrational attachment instability are very close to the conditions necessary for the operation of the XeCl excimer laser.^{92,94} The active medium of this laser usually consists of the Ne:Xe:HCl mixture in the ratio of approximately 1000:100:1 at approximately atmospheric pressure. The electric field E corresponds to $E/N \sim 10^{-16} \text{ V} \cdot \text{cm}^2$. The rate constant for the ionization of neon atoms by electron impact is then $k_i \sim 10^{-12} \text{ cm}^3/\text{s}$, and the rate constant for dissociative attachment to the vibrationally unexcited HCl molecules is $k_{att}(\varepsilon_V \ll 1) \simeq 5 \times 10^{-11} \text{ cm}^3/\text{s}$, while for vibrationally excited molecules $k_{att}(\varepsilon_V \ll 1) \simeq 10^{-9} \text{ cm}^3/\text{s}$. The rate constant for the vibrational excitation of a molecule by electron impact is $k_{eV} \sim 10^{-8} \text{ cm}^3/\text{s}$. The characteristic time for VT-relaxation of the HCl molecules in collisions with one another is $\tau_{VT} \sim 10^{-3} \text{ s}$ under these conditions. If we use (34'), we find that, under the conditions prevailing in the XeCl-laser active medium, the electron-density oscillations should be observed for $N_e \gg 10^6 - 10^7 \text{ cm}^{-3}$. It follows from (35) that the period of the oscillations is then inversely proportional to the square root of the electron density. When the electron density is $N_e \sim 10^{14} \text{ cm}^{-3}$ (typical for this type of laser), the period of the oscillations is about 10^{-7} s , i.e., lower by about an order of magnitude than the characteristic length of the laser pump pulse. The electron-density oscillations that we have predicted here should be observable in the discharge used to pump the XeCl laser. Our analysis of the discharge-current oscillograms recorded for this discharge⁹² shows that such oscillations are indeed present and have a characteristic period of about $10^{-8} - 10^{-7} \text{ s}$.

9. OPTOGALVANIC PHENOMENA

The dissociative attachment process plays an appreciable role in a number of optogalvanic phenomena in which the

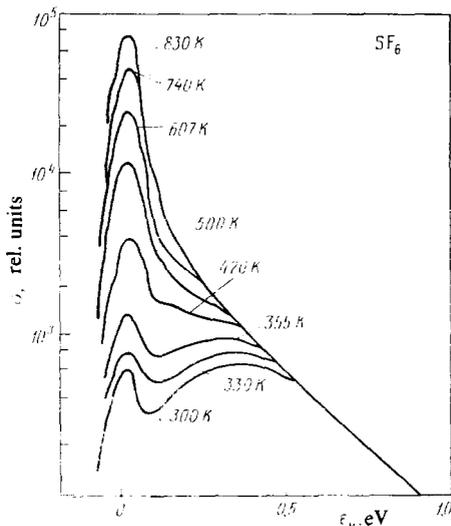


FIG. 15. Energy dependence of the cross section for the dissociative attachment of an electron to the SF_6 molecule with the formation of the negative ion SF_5^- , measured at different gas temperatures.¹¹⁴ The temperatures are indicated against the curves.

electric characteristics of the low-temperature plasma are modified by exposing it to radiation of a particular wavelength. Optogalvanic phenomena are used in the detection of low-density impurities, in the detection of radiation of a particular wavelength, in molecular spectroscopy, and in studies of fundamental processes in plasmas (Ref. 108–113). As an example illustrating the role of dissociative attachment in optogalvanic phenomena, let us consider one of the effects that has been examined in detail in Refs. 113–114. The phenomenon is based on the dependence of the dissociative attachment of an electron to the SF_6 molecule on its vibrational state.

In particular, although the resultant rate constant for the attachment of electrons to this molecule does not depend on its vibrational state, the ratio of the partial contributions of attachment processes producing negative ions of different types is appreciably dependent on the vibrational state of the molecule. This is indicated, in particular, by the measurements, shown in Fig. 15, of the energy dependence of the cross section for the process



at different gas temperatures.¹¹⁴ The cross section for the process increases appreciably with increasing gas temperature, and this indicates that the normal and vibrationally excited molecules have different cross sections.

The experiment on the optogalvanic effect in SF_6 was performed as follows.¹¹⁴ An electron beam of a given energy was passed through a chamber filled with SF_6 at 10^{-6} – 10^{-4} mm Hg. The resulting negative ions were analyzed by a mass spectrometer. The optogalvanic effect, which occurred when the chamber was exposed to CO_2 laser radiation ($\lambda \sim 10.6 \mu\text{m}$) consisted of a change in the ion current in the mass spectrometer when the laser was turned on. This was due to the dependence of the rate constant for the process

(37) on the vibrational state of the molecule.

We note that this dependence can be used for isotope separation.^{112,114} In this particular application, the laser excites the vibrational state of the molecules of given isotopic composition, and this is followed by the preferential dissociative attachment of the electron to the vibrationally excited molecules. Negative ions with enriched isotopic composition, produced in this way, are removed by an electric field or chemically.

10. GASEOUS DIELECTRICS

Dissociative attachment determines the properties of the gaseous dielectrics used in electrical power engineering to prevent undesirable breakdown phenomena and the onset of arc discharges. The properties of such dielectrics, containing electronegative components, are governed by the attachment of electrons to the molecules. This gives rise to a rapid reduction in gas conductivity, which impedes the onset of breakdown. Whether a particular electronegative gaseous dielectric can be used in this way is determined by the ratio of the rate constants for ionization and the attachment of an electron to a molecule of the given material as a function of the reduced electric field E/N (N is the density of the molecules). For values of E/N for which the attachment rate constant exceeds the ionization rate constant, an electron avalanche will not develop and the gas will remain a dielectric even when there are additional channels for the appearance of free electrons in the gas.

The above properties of the attachment rate constant are characteristic for the process of dissociative attachment, the cross section for which at lower electron energies is usually considerable, whereas the ionization cross section in this region is nearly zero. As an example, Fig. 16 shows the difference between the ionization and attachment rate constants for electrons on SF_6 as a function of the ratio²⁰ E/N . When $E/N \lesssim 3.6 \times 10^{-15} \text{ V} \cdot \text{cm}^2$, the difference is negative, which corresponds to a reduced electron density in such fields. The energy dependence of the cross section for dissociative attachment will thus govern the breakdown voltage,

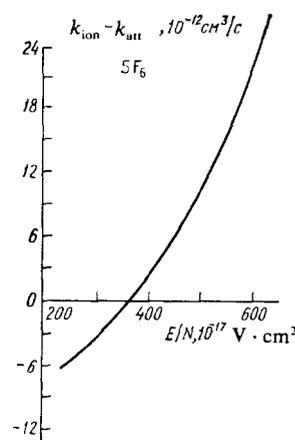


FIG. 16. Difference between the rate constants for ionization and dissociative attachment for an electron on the SF_6 molecule, plotted as a function of the reduced electric field.¹¹⁶

which is one of the basic parameters characterizing the quality of the gaseous dielectric.

Since the electrical insulating properties of gaseous dielectrics depend on the efficient attachment of slow electrons, these properties can be improved by reducing the mean energy of electrons at constant E/N . This is achieved by adding to the electronegative gas a molecular impurity with high probability of energy exchange with electrons whose energies exceed 0.5–1 eV. The most readily available gas of this type is molecular nitrogen, which is widely used as a slowing down medium for electrons when added to the gaseous dielectric. The breakdown voltage of a gas mixture consisting of 90% N_2 and 10% SF_6 at atmospheric pressure is thus practically the same as the breakdown voltage of pure SF_6 at the same pressure.¹¹⁶

Further advances in the improvement of the electrical insulating parameters of gaseous dielectrics will involve the use of three-component gas mixtures containing an electro-neutral gas capable of efficient thermalization of electrons and two types of electronegative gas. These gases must be chosen so as to ensure the efficient attachment of electrons with a broad energy distribution. An example of a successful utilization of three-component gaseous dielectrics can be found in Ref. 116, where the mixture $c-C_4F_8$ (1%), SF_6 (59%), and CO (40%) was used at atmospheric pressure to produce a twofold increase in the breakdown voltage under stationary conditions and a 30% increase in this parameter when a 40- μs voltage pulse was applied. The $c-C_4F_8$ molecules in this three-component mixture served to bind the electrons with energies between 0.4 and 1.2 eV, and the SF_6 molecules were used to trap the slower electrons. Finally, the CO_2 molecules were used to "moderate" the electrons down to energies of the order of or less than 1 eV.

11. CONCLUSION

The dissociative attachment of an electron to a molecule is one of the basic processes governing the kinetics of charged particles in low-temperature plasmas containing electronegative components. Research performed in the last few years has not only extended our understanding of the different aspects of this process and of the different mechanisms responsible for it, but has also enabled us to establish its role in the complex kinetics of low-temperature plasmas. In particular, dissociative attachment is one of the efficient mechanisms for the production of free radicals in plasmachemical and laser systems. The process also lies at the basis of certain optogalvanic phenomena, and its properties determine the conditions and nature of instabilities developing in high-pressure discharges. There is no doubt that further advances in the physics of low-temperature plasmas and its applications will extend the range of phenomena governed by the process of dissociative attachment.

¹¹ It is interesting that an analogous expression describes the cross section for the dissociative recombination of an electron with a molecular ion,^{4,16} since the two processes have similar physical mechanisms.

²¹ The criterion for the validity of this formula follows from its form: the characteristic dimension for which there is an appreciable change in the

wave function of the vibrational state $\Delta R (\Delta R \sim (\mu\omega)^{-1/2})$ is much greater than the characteristic dimensions Δr corresponding to the upper state ($\Delta r \sim ((dE_p/dR)\mu)^{-1/3}$), and also the width of the region ($\Gamma/dE_p/dR$) in which transition takes place. We note that the resulting expressions remain qualitatively the same even when these conditions are violated.

³³ These numbers were obtained as a result of a statistical analysis of different measurements.

⁴⁴ It has been shown³⁴ that the lower state of $HCl^- (I_0^2 \Sigma^+)$ is described by a well of depth 0.3 eV for nuclear separation of 2.1 Å, i.e., in the region where this state is stable. A somewhat deeper well (0.37 eV) is used in Ref. 35 with a lower equilibrium distance (1.9 Å).

⁵³ The coefficient k_{ev} is the mean number of vibrational quanta excited by one electron per second per molecule.

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