Excimer molecules

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The properties of excimer molecules and the processes in which they participate are analyzed. The parameters of the potential curves of excimer molecules and the characteristics of the radiative transitions involved in their decay are presented. The formation of excimer molecules in chemical reactions and three-body collisions as well as collision quenching of excimer molecules are examined. The information presented mainly concerns excimer molecules consisting of two inert gas atoms or an inert gas atom and a halogen atom.

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1. INTRODUCTION

Excimer molecules are excited molecules that form a stable chemical bond only in an excited state. This class of molecules includes any diatomic molecule, one atom of which contains a closed electron shell. In the ground state of this molecule, the interatomic exchange interaction due to the overlap of the electron shells is repulsive. For this reason, there is no chemical bond in the ground state. However, a chemical bond can arise when a closed-shell atom is excited. The class of excimer molecules is thus very large.

Excimer molecules have been studied along two directions. One of them involves the kinetics of ultraviolet emission accompanying the passage of an electron beam through an inert gas. In this case, an appreciable fraction of the energy of the electron beam is transformed into excitation of excimer molecules, i.e., excited diatomic inert-gas molecules. The other direction involves the construction and investigation of excimer lasers. It is clear that the output characteristics of excimer lasers depend on the parameters of the excimer molecules used. For this reason, the development of excimer lasers involved obtaining information on excimer molecules. There are a number of reviews on excimer lasers (see, for example, Refs. 1 and 2). In this paper, we shall concentrate on the excimer molecules themselves. However, applied investigations have led to the fact that most information on excimer molecules concerns molecules consisting of two inert gas atoms or one inert gas atom and a halogen atom. Such molecules will thus be the primary object of our analysis. The purpose of the review is to investigate the parameters of these molecules, as well as the processes leading to their creation or annihilation.

2. STRUCTURE AND BOND PARAMETERS OF EXCIMER MOLECULES

We shall examine the nature of the bond and its parameters in excimer molecules that have been studied. Our purpose is to clarify the laws governing the formation of excimer molecules and to compare the bond characteristics to the parameters of less complicated systems. We shall first examine excimer molecules consisting of two identical inert gas atoms. The exchange interaction of two inert gas atoms in the ground state, owing to overlap of the electronic shells of the interacting atoms, is repulsive. For two identical inert gas atoms, one of which is in an excited state, the exchange interaction is attractive. It corresponds to the exchange excitation of two interacting atoms. Thus a molecule consisting of excited and unexcited identical inert gas atoms is chemically stable in one of the states. In this case the interacting particles form a covalent bond.

If an inert gas atom is represented as an atomic core and a single valence electron, then the exchange interac-:tion leading to a bond in the excimer molecule can be described by two types of exchange integrals:

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 \begin{array}{l} \langle \psi_a\left(1\right) \varphi_b\left(2\right) | V | \psi_a\left(2\right) \varphi_b\left(1\right) \rangle, \\ \langle \psi_a\left(1\right) \varphi_b\left(2\right) | V | \varphi_a\left(1\right) \psi_b\left(2\right) \rangle. \end{array}
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Here the indices a and b indicate the atomic core on which the corresponding electron is found and the wave functions ψ and φ correspond to the ground and excited states of the valence electron, respectively; the number of the electron is indicated in the argument of the wave function and V is the electron interaction operator.

It is evident that the first overlap integral corresponds to an exchange interaction in which the elec-

TABLE I. Parameters of molecular inert gas ions.³⁻⁵

Molecular ion	Dissociation energy D _e , eV	Equilibrium internuclear distance r _m , A
He‡ Ne‡ Ar; Kr‡ Xe‡	2.47 1.16 1.23 1.15 1.03	$1.08 \\ 1.75 \\ 2.48 \\ 2.79 \\ 3.27$

trons exchange atomic cores and, in addition, the excited electron carries over its excitation. In the second case, the excitation is transferred due to the longrange interaction, primarily the dipole-dipole interaction. However, for inert gases, the oscillator strength of a transition, even into a resonant excited state, is relatively small (~ 0.1). For this reason, the exchange interaction in an excimer molecule is determined by the first type of integral. If it is assumed that the orbit of the excited electron is quite large, then the first exchange integral of the inert-gas excimer molecule will go over into the exchange integral of an inert-gas molecular ion. The parameters of the inert-gas excimer molecule can thus be compared to the parameters of an inert-gas molecular ion. Table I presents bond parameters for an inert-gas molecular ion. It should be expected that the dissociation energies for inert-gas excimer molecules will be somewhat lower, while the equilibrium distances between nuclei will be somewhat greater than the corresponding characteristics of the inert-gas molecular ions.

Let us examine the structure of the lower excited states of inert gas excimer molecules. These states correspond to interaction of an atom in the ground state and an atom in an excited state with electron-shell np^5 , (n+1)s. There are four bound states of this type corresponding to different spin states of the atomic core and the excited electron, as well as different states of the orbital angular momentum of the atomic core. We shall first investigate the states of the excimer molecule being studied for Hund's case A,^{8,9} when the spinorbital interaction is small compared to the electrostatic interaction. Then the states of the excimer molecule will be described by the following quantum numbers: 1) total spin of the molecule; 2) projection of the orbital angular momentum on the axis connecting the nuclei; 3) parity of the state with respect to reflection of electrons relative to the plane of symmetry, which is perpendicular to the axis connecting the nuclei and bisects it (for the even g-state the wave function of the electrons does not change sign under such an operation, while for the odd u-state, it changes sign); 4) parity of the state with respect to reflection of electrons relative to a plane connecting the nuclei (for the even state (+)the wave function of the electrons does not change sign under such an operation, while for the odd state (-), the wave function changes sign). In addition, as is customary, we will characterize the states of the molecule with increasing excitation by the letters X, A, B, C,... for states with zero spin and by the letters a, b, c,... for states with spin one.

However for argon and heavier inert gases the as-

TABLE II. Parameters of homonuclear inertgas excimer molecules.

Molecule, state	r _m . Å	D _e . eV	Reference
$\operatorname{He}_{2}(a^{3}\Sigma_{0}^{+})$	1.05	2.0	10, 11
$\operatorname{He}_2(\operatorname{A}^1\Sigma_g^+)$	1.06 ± 0.02	2.47 ± 0.08	12-18
$Ne_2 (a^3 \Sigma_0^{+})$	1.79	0.47	19,20 -
$\operatorname{Ar}_{2}(1_{u}, 0_{u}^{\dagger})$	2.38 ± 0.05	0.72 ± 0.06	21-23, 55
$Ar_{2}(0_{11}^{+})$	2.37 ± 0.05	0.69±0.05	22-24,55
$Xe_2(1_u, 0_u^-)$	3.03	0.79	25
Xe ₂ (0 ⁺ ₀)	3.02	0.77	25

sumptions for Hund's case A are not satisfied. For this reason, the spin of the molecule and the projection of the electronic orbital angular momentum on the axis of the molecule are no longer quantum numbers. Instead, the quantum number is the projection of the total angular momentum on the axis connecting the nuclei. In this connection, the designation used for Hund's case A for the lower states of the molecule must be changed as follows in going over to Hund's case C, in which the spin orbital interaction is not assumed to be small:

$$X^{i}\Sigma_{g}^{*} \rightarrow \theta_{g}^{*}, \quad a^{3}\Sigma_{u}^{*} \rightarrow 1_{u}, \quad \theta_{u}^{*}, \quad A^{i}\Sigma_{u}^{*} \rightarrow \theta_{u}^{*}, \quad b^{3}\Sigma_{u}^{*} \rightarrow 1_{g}, \quad \theta_{g}^{*}, \tag{1}$$

Table II presents the parameters of the lower bound states of an inert-gas molecule using the notation of Hund's case A for light atoms and Hund's case C for heavy atoms. Figure 1 shows the electronic terms of the excimer molecule Ar_2^{*} ,⁵⁵ consisting of an excited argon atom Ar (${}^{3}p{}^{5}4s$) and an argon atom in the ground state. These terms are calculated including the spinorbital interaction. It is evident that even with the large abundance of states of the quasimolecule, for a given electron shell of the atoms, only three states— 1_{u} , 0_{u}^{-} , and 0_{u}^{*} —form a chemical bond.

The dissociation energy of the excimer molecule He_2^* greatly exceeds the dissociation energy of other excimer molecules (see Table II). This is related to the large number of inner valence electrons in the other inert gas atoms. These inner valence electrons create the repulsive part of the interaction potential of the inert gas ion and its atom. The repulsive interaction in the case of the molecular ion He_2^* thus occurs at appreciably



FIG. 1. Electronic terms of the lower states of the excited argon molecule.

TABLE III. Position and height of hump in the interaction potential of inert gas atoms in the lower electronic states.

Molecule, state	Internuclear distance at the top of hump, A	Height of hump, JO ⁻³ eV	References
$\operatorname{He}_2(a^n\Sigma_0^7)$	3.1	60 ± 5	16, 26-32
$He_2(A^1\Sigma_u^+)$	2.8	50 ± 5	15, 18, 33-35
$Ne_2(a^3\Sigma_0^7)$	2.6	110	19
$\operatorname{Ne}_2(\mathbf{A}^1\Sigma_0^*)$	2.5	200	19

shorter internuclear distances than for other inert-gas molecular ions. Correspondingly, the depth of the interaction potential well in the case of He_2^* appreciably exceeds this depth for molecular ions of other inert gases.

The lowest excited states of diatomic molecules of helium and neon at large internuclear distances can be represented as a molecular ion and a valence electron: $A_2^*(^2\Sigma_p^*) + e(^2\sigma_u)$. The orbital of the valence electron σ_u leads to repulsion. For this reason, at large internuclear distances the interatomic exchange interaction is repulsive and becomes attractive at average internuclear distances. The potential curve of the state being examined thus has a repulsive hump. The same is also true of the next excited state $A^{1}\Sigma_{u}^{*}$. Table III presents the parameters of the hump for the interaction of two helium and neon atoms.¹⁾ For heavier inert gas atoms the spin-orbit interaction mixes states with different projection of the orbital angular momentum on the internuclear axis, as a result of which the hump disappears. It should be noted that the presence of a hump in the interaction potential with the participation of an excited helium atom and a neon atom is manifested in a number of processes involving these atoms, in particular, in the transfer of excitation from an excited helium atom to an unexcited atom (see, for example, Refs. 36 and 37), processes involving the formation of a metastable molecule in three-body collisions (see Sec. 5), etc.

Let us examine the interaction of an excited inert gas atom and a halogen atom. A chemical bond forms in this case as well. However the nature of this bond is different. The ionization potential of inert gas atoms in the lower excited states (Table IV) is close to the electron affinity of halogen atoms (Table V). Accordingly, excimer molecules consisting of excited inert gas atoms and halogen atoms form an ionic bond, so that the excited electron of the inert gas atom is partially transferred to the halogen atom.

Figure 2 shows the electronic terms of the excimer molecule XeF, reconstructed from the spectroscopic data on the radiation from the XeF radical in a xenon matrix.^{39,40} It is evident that attraction in the excimer molecule is determined by the intersection of the corre-

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TABLE IV. Ionization potentials of excited inert gas atoms and alkali metal atoms.³⁸

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Atom, state	He (23S)	He (21S)	Ne (3P2)	Ne (3P1)	Ne (³ P ₀)	Ne (1PI)	Ar (3Pg)	Ar (3P1)
Ionization poten- tial, eV	4.77	3.97	4.94	4.89	4.85	4.72	4.46	4.14
Atom, state	Ar (3P1)	Ar (1P1)	Kr (3P2)	Kr (3P1)	Kr (³ P ₀)	Kr (1P1)	Xe (3P2)	Xe (3P1)
Ionization poten- tial, eV	4.04	3.93	4.08	3.97	3.44	3.36	3.81	3.69
Atom, state	Xe (3P0)	Ne (1P1)	Li (22S)	Na (32S)	K (42S)	Rb (528)	Cs (62S)
Ionization poten- tial, eV	2.68	∷.56	5.39	5.14	4.34	4.18	3.	89

*The quantum numbers of the lower excited states for neon, argon, krypton, and xenon atoms with the electron shell np,⁵ (n + 1)s are given in the LS coupling scheme. In the Racah notation, the state s_5 is equivalent to the state ${}^{3}P_{2}$ in LS coupling; the state s_4 is equivalent to ${}^{3}P_{1}$; and, the states s_3 and s_2 coincide, respectively, with the states ${}^{3}P_{0}$ and ${}^{1}P_{1}$ in the LS coupling scheme. The states s_5 , s_4 , s_3 , and s_2 in Racah notation correspond, respectively, to the states $[\frac{3}{2}]_{2}^{0}$, $[\frac{3}{2}]_{1}^{0}$, $[\frac{3}{2}]_{0}^{0}$, and $[\frac{1}{2}]_{0}^{0}$ in the j-j coupling scheme.

sponding term with the term attributable to the interaction of Xe⁺ and F⁻ ions. The quasimolecule consisting of Xe (${}^{2}P_{3/2}$, ${}^{2}P_{1/2}$) and the negative ion F⁻ (${}^{1}S$) has three electronic terms. The only conserved quantum number in this case is the projection of the total angular momentum on the internuclear axis. This quantity can equal 3/2 or 1/2 for interaction of Xe⁺ (${}^{2}P_{3/2}$) and F(${}^{1}S$) and 1/2 for interaction of Xe⁺ (${}^{2}P_{3/2}$) and F(${}^{1}S$). The corresponding terms of the excited molecule, in order of increasing excitation, are designated as $B_{1/2}$, $C_{3/2}$, and $D_{1/2}$. It is in these states that a strong chemical bond is formed in the excimer molecule.

The lower electronic terms corresponding to interaction of atoms in the ground state $Xe(^{1}S) + F(^{2}P)$ are designated as $X^2 \Sigma_{1/2}$, $A^2 \Pi_{3/2}$ (in order of increasing excitation). The projection of the orbital angular momentum on the internuclear axis and the projection of the total angular momentum of the atom on this axis are indicated as indices in the corresponding term. In the case being examined, the electrons remain practically on their own atoms, so that the spin-orbit interaction, which is determined by the region of electron coordinates within the halogen atom, can be viewed as independent of the electrostatic interaction corresponding to the overlap of the electron shells of the atoms. For this reason, for internuclear distances that are not too small, we can use the projection of the orbital angular momentum of the electron as the quantum number.

The configuration of the electronic terms indicated for the interaction of an inert gas atom and a halogen atom occurs for different inert gas and halogen ele-

 TABLE V. Detachment energy of electron in negative halogen ions.³⁸

Negative ion	F- (1S)	C1- (18)	{Br ⁻ (1S)	J- (1S)
Binding energy of electron, eV	3.40	3.62	3.36	3.08

¹⁾In the case of helium, the most reliable method for determining these parameters involves analyzing the differential cross section for scattering of a metastable atom by an atom in the ground state. The data for neon in Table III were obtained based on calculations of the potential curves of the excited molecule.



FIG. 2. Shape of the potential curves of the XeF radical. The lower electronic terms X, A correspond to the ground state of the interacting atoms and the upper terms B, C, and D are formed with the participation of ionic states.

ments. In the case of the interactions in the XeF molecule, there is a small coupling in the lower state due to ion-ion interaction (the depth of the well for the ground state of XeF $(X^2\Sigma_{1/2})$ is approximately 0.146 eV^{40,41}). In the remaining cases, the chemical bond accompanying the interaction of inert gas atoms and the halogen atom is absent. For this reason, the dissociation energies of the corresponding molecules do not exceed thermal energies, while at the equilibrium internuclear distance, for the excimer molecule there is a repulsive interaction between the inert gas and the halogen atoms in the ground state. Figure 3 illustrates the lower terms of the excimer molecule consisting of an excited inert gas atom and a halogen atom, as well as the terms corresponding to the ground state of these atoms.⁴²

Table VI presents the parameters of the interaction potential of the excimer molecules under discussion. They were obtained from an analysis of the spectra of excimer molecules. Usually, B and C are states of the excimer molecule consisting of an inert gas atom and a halogen atom, separated by a small energy. Table VII presents the difference in the energies between the bottoms of the wells in the potential curves for C and B, the states of the excimer molecules examined.

The structure of the excited inert gas atom is analogous to that of an alkali metal atom. Indeed, the excited electron for the lower excited states of the inert gas atom is located in an s-state, as is the valence electron of an alkali metal atom. The ionization potentials of the excited inert gas atoms being examined are



FIG. 3. The lower terms of a molecule consisting of an inert gas atom and a halogen atom, and the intense rediative transitions between them.

TABLE VI. Parameters of interaction potential for molecules consisting of an inert gas atom and a halogen atom.

Molecule, state	r_m , Å	D _e . eV	References
NeF (B _{1/2})	2.00	6.41	43
NeF (C _{3/2})	1.99	6.35	43
ArBr (B _{1/2})	2.81	4,74	4.4
KrF (B _{1/2})	2.51	5.30	45-;7
KrF (C _{3/2})	2.44	5.24	45, 46
$KrF(D_{1/2})$	2.47	5.26	45, 16
XeF ($\Sigma_{1/2}$)	2.29	0.146	10, 41
XeF (B _{1/2})	2.63	5.30	41, 47-50
XeF (C _{3/2})	2.56	5.03	11, 18, 19
XeF (D _{1/2})	2,51	5.46	41, 48, 49
XeCl $(X\Sigma_{1/2})$	3.2	0.032	21
XeCI (B1/2)	3.22	4.23	47, 49, 50
XeCl (C _{3/2})	3,14	4.14	19
XeCl (D _{1/2})	3.18	4.17	49
XeBr (B _{1/2})	3.38	4.30	17, 19, 50
XeBr (C _{3/2})	3.31	3.95	-18
XeBr (D _{1/2})	3.34	3.98	49
Xel (B _{1/2})	3.62	4,08	17, 49
Xel (C _{3/2})	3.57	3.71	49
$X_{eI} (D_{1/2})$	3.59	3.75	19
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 $*D_{\rm s}$ is the depth of the interaction potential well, which for the excimer molecule corresponds to dissociation of a molecule into positive and negative ions; $r_{\rm m}$ is the internuclear distance corresponding to it.

of the same order as the ionization potentials of the alkali metal atoms (see Table IV). In this connection, the excimer molecules being examined must be analogous to molecules of alkali metal halides. This is confirmed by the data in Table VIII from Ref. 47.

As follows from an analysis of Table VIII, replacing the excited inert gas atom by an alkali metal atom with the same excited electron state does not greatly change the parameters of the molecule. Therefore, the alkali metal atom is a good model for an excited inert gas atom.

In the excimer molecules examined, a covalent bond (for Ar_2^* type molecules) or an ionic bond (for ArF^* type molecules) is formed. Complex molecules, such as, for example, Ar_2F^* and Kr_2F^* , can be formed from inert gas atoms and halogen atoms. In such molecules, both an ionic bond (between the fluorine atom and the excited inert gas atom) and a covalent chemical bond (between the inert gas atoms, one of which is in the excited and the other in the ground state) can form at the same time. With the formation of the bond the excited electron to a large extent goes over into the field of the halogen atom, so that the compound being examined is of the type $Ar_2^*-F^-$. The dissociation energy of an ex-

TABLE VII. Energy difference $\Delta T = T_{eC} - T_{eB}$ between minima of potential curves of excimer molecules for C_{3/2} and B_{1/2} states.²⁰⁶⁻²⁰⁸

Molecule	KrF	KrCl	XeF	XeC1	XeBr	XeI
ΔT , cm ⁻¹	200	375	6 00	130	80	200

TABLE VIII. Parameters of excimer molecules consisting of excited inert gas atoms and halogen atoms in the $B_{1/2}$ state and parameters of molecules containing halogen atoms and alkali atoms.⁴⁷

Molecule	Equilibrium in- ternuclear dis- tance r _m , Å	Dissociation energy of the molecule D_e , eV^*)	Energy of vi- brational quan- tum hw, cm ⁻¹
KrF *	2.27	5.54	310
⁸³ RbF	2.27	5.80	373
XeF *	2.49	5 30	309
CsF	2.35	5,66	353
Xe ³⁵ Cl *	2.94	4 53	195
CsCl	2.91	4.87	214
XeBr *	2.96	4.30	120
Cs ⁷⁹ Br	3.07	4.71	150
Nel *	3 31	4.08	112
Csl	3 35	4.39	119

*The dissociation energy corresponds to separation of the molecule into positive and negative ions.

cimer molecule of the type Ar₂F* is lower than the dissociation energy of the corresponding molecular ion (in this case Ar;). For this reason, triatomic excimer molecules are less stable than diatomic molecules whose dissociation energy is several times higher than that of the triatomic molecules. Of the triatomic excimer molecules, the least stable are molecules containing two different inert gas atoms. The dissociation energy of the corresponding molecular ion, including an ion and an inert gas atom of a different type, is much lower than the dissociation energy of a homonuclear diatomic molecular ion. In the latter case, a covalent chemical bond forms, while in the molecular ion with different nuclei such exchange is complicated by the different ionization potentials. As a numerical confirmation of this result, we present the dissociation energies of several molecular ions (see Table I): 0.14 eV for ArXe⁺ (Ref. 53); 0.37 eV for KrXe⁺ (Ref. 53); 0.59 eV for ArKr* (Ref. 53); 0.055 eV for NeKr* (Ref. 209); 0.04 eV for NeXe⁺ (Ref. 209); and, 1.15 eV for Kr₂^{*}.

Thus the dissociation energy of triatomic excimer molecules with different inert gas atoms is of the order of 0.1 eV and it is difficult for such molecules to form in an excited gas. For such molecules optimum bonding conditions occur when the geometric dimensions of the inert gas atom and of the halogen atom are similar. Only such triatomic excimer molecules with different inert gas atoms have been observed (see Table XI below).

3. RADIATIVE PARAMETERS OF EXCIMER MOLECULES

An important parameter of excimer molecules is their radiative lifetime. Lasing in excimer lasers arises due to radiative decay of excimer molecules. For this reason, information on the radiative lifetimes of excimer molecules can be obtained by analysing the characteristics of an excimer laser or the spectroscopic data for such a system. Table IX presents the lifetimes of excimer molecules relative to their radiative decay. Radiative decay of an excimer molecule creates a band of transitions, corresponding to different vibrational-roTABLE IX. Radiative lifetimes of excimer homonuclear inert-gas molecules. The values averaged over results of the references indicated are presented, and the error shown corresponds to this averaging.

Excited molecule*)	Radiative life- time, 10 ⁻⁹ s	References
$Ne_2(a^3\Sigma_u^+)$	8000±3000	56-58
$Ne_2 (A^1 \Sigma_{11}^+)$	2.8	56
$\operatorname{Ar}_{2}(1_{u}, 0_{u}^{-})$	3600±600	58-62
$Ar_2(0^+_{\mu})$	5.0 ± 0.6	61-64
$Kr_2(1_u, 0_u^-)$	300±40	58, 59, 65-70
$Kr_2(0^+_{\mu})$	6 ± 2	63, 69, 70
$Xe_2(1_{u}, 0_{u}^{-})$	110 ± 20	25, 61, 62, 66, 71, 77
Xe ₂ (0 ⁺ ₁)	6 ± 1	25, 61, 62, 66, 71, 77

*The designations of these states correspond to Hund's case A for light atoms and Hund's case C for heavy atoms. The transformation between these notations follows Eq. (1).

tational states of the initial and final states of the transition. In Table IX, the wavelength corresponds to the most intense transitions.

The lifetime of inert gas excimer molecules is obtained from the quenching time of the UV radiation intensity in some band of the spectrum. The inert gas is excited by an external source of short duration, as a rule, an electron beam.²⁾ The UV radiation in the given region of the spectrum corresponds to decay of one or several states of the excited molecule. For this reason, a measurement of the decay time of separate states at different pressures permits reconstructing, taking into account the kinetics of the decay of excited states, both the radiative lifetime of separate excited states of the molecule and the rate constants of two- and three-body collision processes forming the molecules and transitions between their states. Since the radiative lifetimes of the first excited states of inert-gas molecules differ considerably (see Table IX), this method can lead to an appreciable error, if the decay of separate states is not clearly separated. In constructing Table VIII, we rejected results that differed greatly from the average values. This is possible because of the large statistical sample.

For excimer molecules consisting of inert gas and halogen atoms, the method described for measuring the radiative lifetimes is reliable, since the radiative decay of each of the states is identified according to wavelength. The width of the emission band resulting from the electron transition being studied for the excimer molecule containing an excited inert gas atom and a halogen atom is usually less than the distance to the next band. For this reason, separate transitions are clearly distinguished.

Table X presents the lifetimes of excimer molecules

²⁾Transformation of the energy of the electron beam into the energy of excitation of excimer molecules, whose radiative decay creates UV radiation, occurs with an appreciable efficiency. Thus the efficiency of transformation of energy of an electron beam into energy of electronic excitation of excimer molecules is $15\pm7\%$ in argon,⁶³ $4\pm1.6\%$ in krypton,⁶⁹ $10\pm4\%$ in xenon,⁶³ and $17\pm4\%$ in a mixture of Ne, Xe, and HCl.⁷⁸

TABLE X. Radiative lifetimes of excimer molecules consisting of inert gas atoms and halogen atoms.

Excimer molecule	Transition wavelength, μm	Radiative lifetime 10 ⁻⁹ s	References
NeF (B. m)	0,108	2.5	43, 56
$\operatorname{ArF}(\mathbf{B}_{1/2})$	0.193	4	16
KrF (B, 12)	0.248	8+1	16, 87, 79~82
XeF (B, 12)	0.352	16+2	40, 49, 81, 83, 91, 210
XeF (C2/2)	0.450	100+5	40, 91-81, 214
XeF (D, (2)	0.260	11+1	10, 19, 96
$\operatorname{ArCl}(\mathbf{B}_{1/2})$	0.175	9	96
KrCl (B, , ,)	0.222	19	96
XeCl (B,)	0,308	11+1	19, 78, 97, 214
$XeCl(C_{3/2})$	0.330	120 + 10	19, 78, 211
XeCl (D,)	0.236	9.6	19
XeBr (B1/2)	0.282	15+3	19, 98
XeBr (C3/2)	0,302	120	49
XeBr (D1/2)	0.221	9	19
Xel (B1/2)	0.254	14±2	\$P. 89, 100
Xel (C _{3/2})	0.292	110	49
Xel (D _{1/2})	0.203	9	19
$Ar_2F(^2B_2)$	0.284	180 ± 20	80, 101, 102, 212
Kr2F (2B2)	0.420	170±20	80, 142, 193
Xe ₂ Cl (² B ₂)	0,490	150 ± 30	54, 101, 105
Xe ₂ Br (² B ₂)	0.440	245 ∓30	218

consisting of inert-gas and halogen atoms. The radiative lifetimes of the corresponding electronic state depend on the vibrational excitation. The equilibrium internuclear distance increases with excitation of the molecule, while the interaction of the electronic states in the transition decreases, i.e., the radiative lifetime increases. As an illustration of this fact, Fig. 4 presents the dependence of the radiative lifetime of the vibrational excitation for the excimer molecule $XeCl(B_{1/2})$. These data were computed in Ref. 211 using the spectroscopic parameters of the given molecule reconstructed from the experiment. It is evident that the radiative lifetime of the excimer molecule increases with increasing vibrational excitation.

Table X includes the radiative characteristics of some triatomic excimer molecules. These molecules have a relatively small binding energy (see Sec. 2) and for this reason are formed less efficiently in an excited



FIG. 4. Radiative lifetime of the $B_{1/2}$ state of the excimer molecule XeCl as a function of the vibrational excitation of the molecule.²¹¹

TABLE XI. Emission band of triatomic excimer molecules.

Excimer molecule	Центр полосы о тчения, мкм	Half width of band, µm	References
Ne F	0.121	0.008	89
	0 145		215
Ar.F	0 295	0.05	149, 146, 107, 148, 215, 216
AraCl	0.246	~~	106
Kr.F	0.400	0.06	106, 108
Kr.Cl	0.325	0.033	106
11.301	0.335	0.07	109
Kr.Br	0.312	0.115	108
Xe.H	0.630	0.100	216
Xe Cl	0.490	0.08	110, 218
	0.502	0.03	103
Xe.Br	0.420	0.08	109, 215
	0.440	0.03	218
XeJ	0.375		215
NeKrCl	0.247	0.025	109
ArKrF	0.305	0.065	3 11
ArKrCl	0.270	0.046	
KrXeF	0.480	0. tt0	10-
KrXeCl	0.370	0.080	111
KrXeBr	0.330	0.045	111
KrXel	0.290	_	111

gas than diatomic excimer molecules. However, they give a wide emission band with radiative decay. This could be interesting from the point of view of creating a tunable laser in the ultraviolet region of the spectrum because each such laser, in principle, can be smoothly tuned within the emission band of the excimer molecule. Table XI presents the wavelengths of the center of the emission band of triatomic excimer molecules and the bandwidth of their emission.

The structure of the mercury atom is close to the structure of an inert gas atom. It has a closed electron shell in the ground state, while in the lower excited states its electron shell is 6s6p, so that these states are described by the same quantum numbers as an excited inert gas atom. For this reason, the lower states of the diatomic excimer molecule of mercury are the same as for the inert gas excimer molecules in the lower states. The radiative lifetimes of these states are presented in Table XII. The information presented was obtained by studying the radiative characteristics of mercury vapors. As far as the excimer molecule consisting of an excited mercury atom and a halogen atom is concerned, its state with an ionic bond has the structure $Hg^{+}(6s)-R$ (R is a halogen atom). In contrast to excimer molecules consisting of an excited inert gas atom and a halogen atom, in this case, we have only one strongly bound state. This increases the efficiency of transformation of the energy of an external source exciting the mixture into radiation energy at the given transition and is of interest from the point of view of excimer lasers.

We studied only excimer molecules consisting of excited inert gas atoms or an inert gas atom and a halo-

TABLE XII.	Radiative	lifetimes	of excimer	mole-
cules contain	ing excited	l mercury	atoms.	

Excited	Photon wave-	Radiative life-	References
molecule	length, Å	time, 10 ⁻⁹ s	
$\begin{array}{c} Hg_{2} (A1_{u}) \\ Hg_{2} (BO_{u}^{+}) \\ HgCl (B_{1/2}) \\ HgBr (B_{1/2}) \\ Hg1 (B_{1/2}) \\ Hg1 (B_{1/2}) \\ Hg3 \end{array}$	0.335 0.225 0.56 0.5 0.44 0.485	$ \begin{array}{r} 1.2 \cdot 10^{3} \\ 2.4 \\ 27 \pm 3 \\ 24 \pm 1 \\ 27 \\ 1.7 \cdot 10^{3} \end{array} $	112 113 114, 115 116, 117 117 118

gen atom. Clearly, the class of excimer molecules is much larger and our choice is due only to the present state of research in this area. Among the other excimer molecules, for which information is available, we note the molecule consisting of a metastable oxygen atom $O(^{1}S)$ and an inert gas atom. Such molecules are of interest for lasers operating near the ¹S-¹D transition of the oxygen atom ($\lambda = 5577$ Å). Lasing in a mixture with krypton and xenon was achieved in Refs. 119-121. It was assumed that since metastable oxygen atoms have long lifetimes, a high density of such states can be created in a gas by photolysis. This would lead to maximum laser radiation energies that could be extracted in a pulse per unit volume and would thereby permit creating efficient lasers for thermonuclear research. However, due to quenching of metastable oxygen atoms in collisions with gas molecules, these plans have not been realized.

Excimer molecules of the type $AQ(^{1}S)$ demonstrate the fact that the interaction removes the forbiddenness of the radiative transition. Indeed, the radiative lifetime of the metastable oxygen atom $Q(^{1}S)$ is 0.8 s,¹²² the radiative lifetime of the excimer molecule $ArQ(^{1}S)$ is $3.8 \cdot 10^{-6}$ s,¹²³ while the radiative lifetime of the molecule $XeQ(^{1}S)$ is $(2 \pm 1) \cdot 10^{-7}$ s.¹²⁴⁻¹²⁷

4. FORMATION OF EXCIMER MOLECULES IN CHEMICAL REACTIONS

Excimer molecules are formed in an excited gas from initially excited atoms by two methods. In the first method, the excited atom enters into a chemical reaction and in the other method the excimer molecule is formed in three-body collisions of the excited atom with gas atoms. The first channel occurs in a mixture of inert gas and halogen atoms and the second occurs in a pure inert gas.

Let us examine the chemical reaction of an excited atom with a halogen-containing molecule. This reaction is analogous to the reaction of an alkali metal atom with a halogen-containing molecule. The reaction occurs via the "harpoon" mechanism,^{128,129} according to which the positive alkali metal ion and the negative halogen-containing molecular ion form first. Then, as a result of the Coulomb interaction of the ions, the ions approach one another, which leads to restructuring of the molecules. This mechanism yields large cross sections and rate constants, which can exceed the corresponding gas kinetic values.



FIG. 5. Behavior of electronic terms in the chemical reaction of an excited inert gas atom A^* and a halogen-containing molecule RX.

derstood from Fig. 5, which shows the electronic terms of the initial state of the system, corresponding to the excited atom and a halogen-containing molecule, as well as the ionic state of the system. As the particles approach one another, the system makes a transition into the ionic term, corresponding to a positive inert gas atom and a negative ion of the halogen-containing molecule. Then, due to the Coulomb interaction, the particles approach still closer and at some distance the system can make a transition into an electronic term corresponding to the excimer molecule and a fragment of the halogen containing molecule. The last transition leads to restructuring of the molecule and for this reason it occurs at interparticle distances comparable to the particle dimensions. A characteristic of this process is the fact that the transition to the ionic term occurs at large distances between particles, when the interaction in the initial channel is relatively small. The excited atom "transfers" its electron to the halogencontaining molecule, thereby creating a Coulomb interaction between the particles, which causes them to approach one another. For this reason, this chemical reaction mechanism is called a harpoon mechanism.

The nature of the process being examined can be un-

The values of the rate constants for formation of an excimer molecule in the reaction of an excited inert gas atom and a halogen-containing molecule RX (R is the radical, X is the halogen atom) are presented in Table XIII. The rate constant of this process appreciably exceeds the gas-kinetic value. The processes examined are equivalent to chemical reactions involving collisions of alkali metal atoms and halogen containing molecules. For this reason, in studying these processes, we shall use the extensive experience (see, for example, Refs. 134-136) that has been accumulated in studying reactions between alkali metal atoms and halogen-containing molecules.

Let us examine the theory of this process and clarify the optimum conditions for it to occur. An important parameter of the theory is the distance between the nuclei R_c at which the electronic terms of the system $A^* - Rx$ and $A^* - Rx^-$ intersect. Assuming that this distance greatly exceeds the dimensions of the colliding particles, so that in the first channel the particles practically do not interact at such a distance between the nuclei, while in the second channel the interaction is a purely Coulomb one, we find in atomic units:

$$R_{\rm c} = (J - EA)^{-1},\tag{2}$$

where J is the ionization potential of atom A* and EA is

TABLE XIII. Rate constant of the process $A({}^{3}P_{2}) + RX \rightarrow AX^{*}$ at thermal energies.¹³¹⁻¹³³

А	RX	AX	Rate constant of the process, 10^{-10} cm ³ /s	A	RX	AX	Rate constant of the process, 10 ⁻¹⁰ cm ³ /s
Ar Kr	$\begin{array}{c} F_2 \\ NF_3 \\ Cl_2 \\ F_2 \\ NF_3 \\ OF_2 \\ Cl_2 \end{array}$	ArF ArF ArCl KrF KrF KrF KrCl	$ \begin{array}{c c} 9.0 \\ 1.0 \\ 7.1 \\ 6.2 \\ 1.0 \\ 5.3 \\ 7.3 \\ \end{array} $	Xe	F ₂ NF ₃ OF ₂ Cl ₂ Br ₂	XeF XeF XeF XeCl XeBr	7.50.95.77.2 $5-20$

the vertical electron affinity of the RX molecule, i.e., the binding energy of the electron in the negative RX⁻ ion with the same nuclear configuration that occurs in the ground state of the RX molecule. Due to the exchange interaction the electronic terms examined are split (see Fig. 5). If the splitting is relatively large, while the collision velocity is quite low, then during the collision the system remains in the lower term. In this case, due to the Coulomb attractive force, the colliding particles will approach to distances of the order of their dimensions, at which a chemical reaction can occur.

The probability for the system to remain in the bottom term after passing the pseudocrossing point for the electronic terms R_c equals, according to the Landau-Zener equations,¹³⁷

$$p = 1 - \exp((-S)), \quad S = \frac{2\pi |V_{12}|^2}{v_{\rm RM}};$$
 (3)

here V_{12} is the difference between the energies of the electronic terms at the pseudocrossing point, v_R is the radial component of the relative velocity of the colliding particles, and ΔF is the difference between the slopes of the terms being examined at the point of their pseudocrossing. Taking into account the absence of interaction in one of the states and the Coulomb interaction in the other, we have (in atomic units)

$$\Delta F = \frac{1}{R_{\perp}^2}.$$
 (4)

It is evident that the unknown parameter of the theory, which is determined by the interaction between the states of the transition, is the magnitude of the pseudocrossing V_{12} . We shall use for this parameter the semiempirical expression¹³⁸

$$V_{12} = \frac{\sqrt{\alpha\beta}}{2} \gamma R_c \exp\left(-0.86\gamma R_c\right), \tag{5}$$

where $\gamma = (\alpha + \beta)/2$ and the ionization potential of the excited atom is $J = \alpha^2/2$ (in atomic units), while the electron affinity of the halogen-containing molecule $EA = \beta^2/2$.

The parameters of a number of processes involving diatomic halogen molecules are presented in Table XIV. The experimental values of the rate constants of these processes are given in Table XIII. The parameters of the processes being examined were calculated from Eqs. (2), (3), and (5). In so doing, we used for *EA* the electron affinity of the molecule, which is greater than the vertical electron affinity (for the same distance between the halogen nuclei) entering into Eq. (2). This overestimates the crossover distance R_c and, therefore, leads to underestimation of the index S. (Atomic units are used in Table XIV.)

TABLE XIV.

							Optimum	a captur	e parameters
Colliding particles	a	β	^R e	V12	S	10 ⁻¹⁰ cm ³ /s	EA _{opt} . cV	Rc	^k max, 10-10 cm ³ /s
$ \begin{array}{c} Ar ({}^{3}P_{2}) + F_{2} \\ Ar ({}^{9}P_{2}) + CI_{2} \\ Kr ({}^{3}P_{2}) + F_{2} \\ Kr ({}^{3}P_{2}) + CI_{2} \\ Xe ({}^{3}P_{2}) + F_{2} \\ Xe ({}^{3}P_{2}) + CI_{2} \\ Xe ({}^{3}P_{2}) + CI_{2} \\ Xe ({}^{3}P_{2}) + H_{2} \\ Ar ({}^{3$	$\begin{array}{c} 0.572 \\ 0.572 \\ 0.548 \\ 0.548 \\ 0.529 \\ 0.529 \\ 0.529 \\ 0.529 \end{array}$	$\begin{array}{c} 0.466\\ 0.423\\ 0.466\\ 0.423\\ 0.466\\ 0.423\\ 0.437\\ \end{array}$	18.1 13.5 24.3 16.6 32.0 19.9 22.5	$ \begin{vmatrix} 7.5 & (-4) \\ 5.1 & (-3) \\ 7.8 & (-5) \\ 6.1 & (-4) \\ 4.4 & (-6) \\ 6.5 & (-4) \\ 2.3 & (-4) \end{vmatrix} $	4.4 130 0.10 3.5 6 (4) 6.2 1.2	16 8.0 2.4 9.5 0.025 13 9.5	$2.93 \\ 2.95 \\ 2.65 \\ 2.67 \\ 2.44 \\ 2.46 \\ 2.47$	17.9 18.1 19.0 19.2 19.8 20.1 20.4	16 14 15 13 15 13 13 11

Based on this model, we shall determine the rate constant for collisions k_0 for which the system ends up in the lower electronic term. This quantity, according to (3), equals

$$k_0 = v \cdot \pi R_c^2 (1 - e^{-S}),$$
 (6)

where $\overline{v} = \sqrt{8T/\pi\mu}$ is the average relative collision velocity (*T* is the temperature, μ is the reduced mass of the colliding particles). Taking this into account, the rate constant of the chemical reaction is

 \boldsymbol{k}

$$=k_{0}\zeta, \tag{7}$$

where ζ is the probability of the chemical reaction on close approach. It is evident that k_0 is the upper limit for the reaction rate constant. Values of k_0 calculated using Eq. (6) for T = 300 K are presented in Table XIV. Comparison of these values with the experimental values in Table XIII indicates a disagreement for collision processes involving Kr*, Xe* + F2. This disagreement is related to the replacement of the vertical electron affinity of the fluorine molecule by the electron affinity. This led to overestimation of the crossover distance $R_{\rm c}$. For the value of $R_{\rm c}$ obtained, the exchange interaction is so small that the colliding particles have a small probability to make the transition to the ion-ion electronic term. In the final analysis this leads to an underestimation of the rate constant for capturing particles into the ion-ion term.

In this connection, the following question arises: what is the maximum value of the capture rate constant k_{max} , if the vertical electron affinity of the molecule *EA* can be a variable parameter? Based on Eqs. (3)-(5), including the fact that in the optimum region of parameters $\gamma R_c \gg 1$, we obtain an equation for the values of the parameter R_c and $S(R_c)$, for which the quantity (6) has a maximum:

$$\frac{e^{s}-1}{s} = 0.86\gamma R_{c}.$$
 (8)

Values of EA_{opt} , which provide the maximum value of the rate constant k_{max} for capture of particles into the ion-ion term, determined according to (6), are presented in Table XIV.

The data in Table XIII concern the simplest halogencontaining molecules and an inert gas atom in the ${}^{3}P_{2}$ state. According to the chemical reaction mechanism being examined, the value of the rate constant of the process must be of the same order for different excited states of the inert gas atom with an identical electron shell. Indeed, in units of 10^{-10} cm³/s, for the process Ar*+ F₂ \rightarrow ArF*+ F, the rate constant equals⁸⁰ 9.4, 8.9, and 12.9 for the states ${}^{3}P_{2}$, ${}^{3}P_{1}$, and ${}^{1}P_{1}$, respectively; for the process Ar₂(1_u) + P₂ the rate constant equals 5.2, 107 ; and, for the process Kr*+ F₂ \rightarrow KrF*+ F it equals⁸⁰ 7.2, 6.8, and 7.6 for the excited atomic states ${}^{3}P_{2}$, ${}^{3}P_{1}$, and ${}^{1}P_{1}$, respectively.

In the case of the chemical reactions examined excimer molecules are formed in vibrationally excited states. As a demonstration of this fact, the fraction of the energy f_v , which on the average goes into vibrational excitation of the excimer molecule XeCl*, formed as a result of the chemical reaction TABLE XV. Fraction of vibrational energy f_v for electronic states of XeCl(B_{1/2}) and XeCl(C_{3/2}) of the excimer molecule formed as a result of reaction (9).^{139, 140}

Molecule R	CI	C12	ClF	SCl2	S ₂ Cl ₂	COC12	PC13	500.1 <u>2</u>	CC11	SO2CI2
Final state:	$\begin{array}{c} B_1 \\ C_3 \end{array}$	0.77 0.73	0.71	0.69	0.73	6,20 0,30	0.47 0.64	0.71 1.74	0.67 0.67	0.71 0.74

$$Xe({}^{3}P_{2}) \rightarrow HCI \rightarrow XeCI \ast - R$$
,

is presented in Table XV.

A

5. FORMATION OF EXCIMER MOLECULES IN THREE-BODY COLLISIONS

One of the chaunels for formation of excimer molecules involves three-body collisions of excited atoms and follows the scheme

$$A^* + B + C \rightarrow AB^* + C. \tag{10}$$

The third particle C plays a fundamental role in this process: it takes up the excess energy resulting from the collision with interacting particles A and B. If the energy transferred to particle C exceeds the kinetic energy of relative motion of particles A and B, then after such a three-body collision particles A and B remain bound. The three-body process being examined is the only process of forming excimer molecules from an excited atom if the two-body process is forbidden. At high gas densities the three-body process may compete with the two-body process, even when the latter process is allowed.

The experimental method for determining the rate constant of the process (10) is based on studying the kinetics of excited molecules with pulsed excitation of the gas. The gas is excited by an electron beam of short duration or by a pulse of synchrotron radiation. Excited atoms, which emit at a definite wavelength, are formed in the gas. The rate constants of the two- and threebody processes, responsible for taking the excited atoms out of the states being examined, are determined from the decay time of the intensity of these lines and its dependence on the gas pressure. The rate of formation of the corresponding excited inert gas molecules and their radiative lifetimes are determined at the same time from the time dependence of the radiation intensity in molecular bands at different gas pressures (see Sec. 3). Since the radiation bands for neighboring states of excimer molecules of the inert gas overlap, this method requires careful analysis. Otherwise, it can lead to considerable errors.

Together with the method described above for determining the rate constants of the process (10) experimentally, in the case of helium, neon, and argon another similar method is used (see, for example, Refs. 141-143), which is based on studying the decaying plasma after termination of the discharge. We shall describe it for the example of the formation of metastable helium molecules in helium, which has been studied in detail experimentally. This process proceeds according to the scheme He $(2 \ {}^{3}S)$ $+ 2He \rightarrow He_{2} (2 \ {}^{3}\Sigma_{u}^{+}) + He$.

(9)

(11)

The corresponding measurements are made in the decaying helium plasma. The density of metastable atoms as a function of time is reconstructed from the absorption of radiation passing through the plasma at wavelength 3889 Å, which corresponds to the transition $2^{3}S \rightarrow 2^{3}P$. If the gas pressure is sufficiently high and metastable atoms are destroyed as a result of their transformation into metastable molecules, then this dependence permits reconstructing the rate constant for formation of metastable molecules. Another direct method for measuring the rate constant for three-body formation of metastable helium molecules is to make the reconstruction from the absorption of radiation at a wavelength near 4650 Å, which corresponds to the transition between the helium molecular states ${}^{3}\Sigma_{\mu}^{*} + {}^{3}\pi_{\nu}$. Based on these measurements, the time dependence of the density of metastable molecules is established, which permits reconstructing the rate constant of the three-body formation of metastable helium molecules.

The rate constant of the three-body process (10) corresponds to the balance equation

$$\frac{\mathbf{I}\left[\mathbf{AB^*}\right]}{dt} = \mathscr{K}\left[\mathbf{A^*}\right]\left[\mathbf{B}\right]\left[\mathbf{C}\right],\tag{12}$$

where [X] is the density of particles of type X. Measurements of the rate constants for formation of metastable molecules in three-body collisions are presented in Tables XVI-XIX. These quantities relate to thermal energies of the colliding particles.

The rate constant of the process (10) can be estimated on the basis of Thompson's theory.¹⁴⁴ Although this theory was initially developed for the recombination of positive and negative ions in three-body collisions, it can be easily extended to an arbitrary process of formation of a bound state of particles, if this process oc-

TABLE XVI. Rate constants for formation of a metastable inert gas molecule in three-body collisions in its own gas with participation of a metastable atoms.

Excited atom A*)	Rate constant, 10 ⁻³³ cm ⁶ /s	References
He (2 ³ S)	0.23±0.04 *) 2.4·10 ⁻³ , <i>T</i> == 77 K	142, 144, -153 141
	1.4.10 ⁻³ , $T = 77$ K 0.43, $T = 366$ K	117
Ne (31'2)	0.5 0.04-0.05 T = 77 K	142
Ne (³ P ₀)	0.07, T = 77 K	142
$Ar(P_2)$	11±4	154, 18, 60, 141, 143, 154, 163
Ar (³ P ₀) Kr (³ P ₂) **)	10 ± 2 36 ± 8	154, 164, 185 58, 64, 65, 68, 161,
	69. $T = 196$ K	165, 166 68
Kr (³ P ₀) Xo (³ P ₂) **)	54 55+20	167
NC(12) /	30120	167-176
Hg (³ P ₀)	40 ± 13 $250\pm 40, T = 470$ K,	62, 175, 177, 178 179, 160
-	160. $T = 670 \text{ K}$	181

*The rate constant corresponds to room temperature. When the temperature of the gas differs greatly from room temperature, this is so indicated. The average is formed using the results in the references indicated.

**The large statistical sample permitted rejection of those results in the papers indicated that differed greatly from the average value. TABLE XVII. Rate constant for formation of a metastable molecule in a three-body collision of a metastable atom in a foreign gas.

Process	Rate constant,*) 10 ⁻³³ cm ⁶ /s	Refer- ences
$\begin{array}{l} Xe \left({}^{3}P_{2}\right) \rightarrow Xe + He \rightarrow Xe_{2}^{*} \rightarrow He \\ Xe \left({}^{2}P_{2}\right) \rightarrow Xe + Ne \rightarrow Xe_{2}^{*} + Ne \\ Xe \left({}^{2}P_{2}\right) + Xe \rightarrow Ar \rightarrow Xe_{2}^{*} + Ar \\ Kr \left({}^{3}P_{2}\right) + 2Ar \rightarrow KAr^{*} + Ar \\ Xe \left({}^{2}P_{2}\right) + 2Ar \rightarrow XeAr^{*} + Ar \\ Hg \left({}^{3}P_{0}\right) + Hg + N_{2} \rightarrow Hg_{2}^{*} \rightarrow N_{2} \\ Hg_{2} \left({}^{*}O_{2}^{*}\right) \rightarrow Hg + N_{2} \rightarrow Hg_{3}^{*} + N_{2} \end{array}$	$ \begin{array}{c} 14 \\ 12 \\ 26\pm5. \\ 1.0 \\ 0.7 \\ 1000, T = 430 \text{ K} \\ 200 \end{array} $	170 182 73, 170, 178 161 73 183 184

curs as a result of elastic collisions of three particles. In this case, it is assumed that the motion of the colliding particles both in the initial and final channels is described by classical laws. The last assertion is justified in the case examined because initially the bound state of the particles A^*-B formed is highly excited vibrationally and for it the quasiclassical description is valid.

The convenience of Thompson's theory lies in the fact that it permits separating the three-body collision process into two-body interaction and collision processes. As a result, this theory describes the physical nature of the processes. At the same time, since the operation of separating the three-body process into two-body processes is itself not exact, it does not make any sense to require that Thompson's theory should describe the process quantitatively. The theory can only give the order of magnitude of the rate constants of the three-body process and predict its dependence on the parameters of the problem.

Thompson's theory takes into account the fact that the process (10) occurs in the range of distances separating particles A and B in which the interaction potential between them is of the order of or greater than the thermal energy T, because it is only in this case that the third particle can carry away the excess energy above the kinetic energy of particles A and B. Following Thompson, we shall introduce the critical radius according to the relation

$$U(b) \sim T. \tag{13}$$

From the arguments presented above, it follows that the rate constant of the process examined is

 $\mathscr{K} \sim b^3 k,$ (14)

where k is the rate constant for collisions of particle C with particle A or B, as a result of which energy of the

TABLE XVIII. Rate constant for formation of an excited molecule in a three-body collision with participation of a resonantly excited atom or molecule.

Process	Rate constant, 10 ⁻³³ cm ⁶ /s	References
$ \begin{split} & Ne \left({}^{1}P_{1} \right) + 2Ne \rightarrow Ne_{2}^{*} + Ne \\ & Ar \left({}^{3}P_{1} \right) + 2Ar \rightarrow Ar_{3}^{*} + Ar \\ & Ar \left({}^{1}P_{1} \right) + 2Ar \rightarrow Ar_{3}^{*} + Ar \\ & Kr \left({}^{3}P_{1} \right) + 2Kr \rightarrow Kr_{3}^{*} + Kr \\ & Kr \left({}^{3}P_{1} \right) + 2Kr \rightarrow Kr_{3}^{*} + Kr \\ & Kr \left({}^{3}P_{1} \right) + 2Xe \rightarrow Xe_{3}^{*} + Xe \\ & Hg \left({}^{3}P_{1} \right) + 2Hg \rightarrow Hg_{3}^{*} + Hg \\ & Cs \left({}^{6}P_{1} \right) + Cs + Xe \rightarrow Cs_{2}^{*} + Xe \end{split} $	5.8 12 \pm 4 14 \pm 6 30 \pm 10 1.6 \pm 0.2 70 \pm 20 160 4200, $T = 620$ K	56 60, 61, 151, 167, 159, 160, 163, 186 60, 167, 180, 160, 185, 166 60, 165, 167, 186 60, 185 168, 172, 173, 175, 175, 181 189

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TABLE XIX. Rate constant for formation of a complex excimer molecule in three-body collisions.

Process	Rate constant,*) 10 ⁻³¹ cm ⁶ /s	References
$\begin{array}{l} \operatorname{ArF}\left(B_{1/2}\right)\sim 2\mathbf{Ar}\rightarrow\operatorname{Ar}_{*}F^{*}\rightarrow\operatorname{Ar}\\ \operatorname{KrF}\left(B_{1/2}\right)\sim 2\mathbf{Ar}\rightarrow\operatorname{Ar}_{K}F^{*}\rightarrow\operatorname{Ar}\\ \operatorname{KrF}\left(B_{1/2}\right)\sim \mathbf{Kr}+\mathbf{Ar}\rightarrow\operatorname{Kr}_{F}F^{*}\rightarrow\mathbf{Ar}\\ \operatorname{KrF}\left(B_{1/2}\right)\sim \mathbf{Kr}+\mathbf{Ar}\rightarrow\operatorname{Kr}_{F}F^{*}\rightarrow\mathbf{Kr}\\ \operatorname{NeF}\left(B_{1/2}\right)+2\mathbf{Kr}\rightarrow\mathbf{Kr}_{F}F^{*}+\mathbf{Kr}\\ \operatorname{NeF}\left(B_{1/2}\right)+2\mathbf{Kr}\rightarrow\mathbf{Kr}_{F}F^{*}\rightarrow\mathbf{Kr}\\ \operatorname{NeF}\left(B_{1/2}\right)+2\mathbf{Kr}\rightarrow\mathbf{Kr}\\ \operatorname{NeF}\left(B_{1/2}\right)+2\mathbf{Kr}\rightarrow\mathbf{Kr}\right)$	$\begin{array}{c} 4.9 \pm 0.7 \\ 0.9 \pm 0.2 \\ 6 \pm 1 \\ 6 \pm 1 \\ 7.8 \\ 2.6 \\ 240 \end{array}$	<pre><0,107,100 82,101-134 101,133,151,106 50,83,163,102,101-106 107,106 107,106 107,106</pre>

*It is assumed that quenching in a three-body collision corresponds to the formation of a complex excimer molecule.

order of T is transferred to particle C. Assuming that the masses of particle C and one of the particles A or B is of the same order, we find

 $k \sim v\sigma$,

where \overline{v} is the characteristic velocity of the collision and σ is the cross section for a "strong" collision with scattering by an angle of the order of unity. In such collisions, the particles exchange energy of order T. From here, based on (14), we obtain²⁰¹

$$\kappa \sim \bar{v\sigma} b^3$$
. (15)

This relation is valid for relatively low density of particles of the third kind, when particles A and B traverse a distance of the order of the size of the critical region b without colliding with particles of the third kind

$$[C] \sigma b \ll 1. \tag{16}$$

According to this relation the mean free path of particles A and B in a gas consisting of particles C is much less than the size of the critical region. In the opposite case, the equation of balance for the density of excited molecules (12) contains on the right side a different dependence on the density of the gas particles.

Let us determine the dependence of the rate constants of the three-body process on the parameters of the problem. The cross section for elastic collisions of particles corresponding to scattering at a large angle, entering into Eq. (15), can be estimated on the basis of the relation (see, for example, Ref. 202)

$$\sigma \sim R_0^2, \text{ where } U(R_0) \sim T; \tag{17}$$

Here U is the interaction potential for particles A* and C. If particles B and C are of the same kind, then, as follows from relations (15) and (17), $\sigma \sim b^2$. From here, according to Eq. (15) we have³⁾

$$\mathscr{K} \sim \overline{v}b^5.$$
 (18)

$$\mathcal{K} \sim \sqrt{\frac{T}{M}} b^{5}$$

³⁾This equation can be obtained from dimensional considerations. In the classical case, the rate constant of the process $A^* + 2A \rightarrow A_2^* + A$ is expressed in terms of the following parameters: thermal energy of the particles *T*; particle mass *M*; parameter *b* characterizing the particle interaction $[U(b) \sim T]$. From these parameters it is possible to form only a single combination with the dimensions cm⁶/s, which has the form

Let us estimate the order of magnitude of the rate constant of the three-body process. The characteristic value of the thermal velocity is $\overline{v} \sim 10^4 - 10^5$ cm/s and the characteristic value of b is $\approx 3-6$ Å. This gives \mathscr{K} ~10⁻³⁴-10⁻³¹ cm⁶/s. In addition, with some exceptions, which we shall examine later, the temperature dependence of the rate constant of the three-body process must be weak. Indeed, if the process is determined by the interaction in the region where the attractive potential is approximated by $U(R) = CR^{-n}$ as a function of the distance between the nuclei R, then according to Eqs. (17) and (18) $\mathcal{H} T^{1/2-5/n}$. A reasonable value of n is n = 4-6. From here, we find that when the interaction potential varies monotonically with distance, the rate constant of the three-body process increases slowly with decreasing temperature. When the curve of the interaction potential of the particles contains a hump, this result is not valid.

For metastable helium and neon molecules, the potential curves of the lower states have a hump, so that for three-body formation of these molecules, the estimates presented above are not applicable. In the case of three-body formation of other molecules, the process proceeds according to the scheme described above and the rate constant falls into the range indicated previously $(10^{-31}-10^{-34} \text{ cm}^6/\text{s})$ and depends smoothly on the gas temperature. Thus, according to measurements,¹⁶³ the rate constant of the three-body process

 $A ({}^{3}P_{2}) + 2A \rightarrow N_{2}^{\bullet} + A,$

where A = Ar, Kr, Xe, is, in the temperature range 200-400 K, approximated by the dependence $\mathcal{H} \sim T^{-s}$. The index s equals 0.60 ± 0.06 for argon, 0.66 ± 0.10 for krypton, and 0.60 ± 0.06 for xenon. This corresponds to the index in the interaction potential $[u(r) \sim R^{-n}] n = 4-5$, in agreement with the estimates indicated above.

The presence of a hump in the potential curve for metastable helium and neon molecules (see Table III) can lead to a sharp drop in the rate constant of the three-body process forming a metastable molecule with decreasing temperature. Thus, according to measurements made by Ludlum et al.,¹⁴⁷ the rate constant for three-body formation of the metastable helium molecule $He_2(a^3\Sigma_u^*)$ in helium is approximated well by the dependence $\mathcal{H} = \mathcal{H}_0 \exp(-Ea/T)$ and the best values of the parameters in this equation are as follows: $E_a = 0.067 \text{ eV}$ and $\mathscr{H}_0 = 3.5 \cdot 10^{-33} \text{ cm}^6/\text{s}$. It is evident that the activation energy for this process practically coincides with the height of the hump on the potential curve (see Table III). From here we can conclude that at low temperatures only fast particles, whose kinetic energy lies above the hump in the potential curve so that these particles freely approach to distances of the order of their dimensions, participate in the process.

We should note here that such a sharp decrease in the rate constant for three-body formation of molecules cannot be explained by only a potential barrier in the interaction potential of helium atoms in metastable and ground states. In this case, the small probability for capture of a metastable atom is completely compensated by the long lifetime of the autoionization state of the metastable molecule. Such a change in the rate constant of the three-body recombination of atoms is related to quantum effects. Due to the presence of a potential barrier, the distance between the vibrational autoionization states of a metastable molecule, even with small collision momenta of atoms in the ground and metastable states, is quite large and, apparently, greatly exceeds the characteristic thermal energy.⁴⁾ This sharply restricts the number of autoionization states of the molecule into which capture is possible on recombination.

In addition to the reason examined above, the decrease in the rate constant for three-body formation of metastable helium molecules with decreasing temperature is related to the sharp drop in the rate constant for quenching of the autoionization state of the molecule in a collision with a helium atom. Since the energy of the transition in such a collision is quite high, the probability of the transition according to the adiabatic laws decreases with decreasing collision velocity.

A similar situation also occurs for neon, where the interaction potential of the excited and unexcited atom has a relatively high hump (see Table III). For this reason, the rate constant for the three-body formation of a metastable neon molecule also drops with decreasing gas temperature (see Table XVI), although not as sharply as in the case of helium. The last circumstance is related to the large density of the autoionization states and their higher collisional quenching efficiency. For this reason, in the case of neon, the three-body process leading to the formation of a metastable molecule involves subbarrier capture of a metastable neon atom by an atom and subsequent quenching of the autoionization state formed in this case. In addition, subbarrier capture of an atom leads to smaller values of the rate constant for the process than Eq. (15) (see Table XVI).

When a resonantly excited atom participates in a three-body process, we can expect higher values for the rate constant of the three-body process because the interaction of a resonantly excited atom with an atom of the same kind is more efficient than for atoms in the ground state. Rate constants for three-body processes leading to formation of an excited molecule with the participation of a resonantly excited atom are presented in Table XVIII. It is evident that for argon, for which a large number of measurements are available, comparison of data in Tables XVIII and XIX shows that the rate constant of the three-body process for a resonantly excited atom is somewhat higher than that for a metastable atom. However, the difference in these data lies within the limits of the error in the results.

We have limited our analysis to the Thompson mechanism for the three-body process, in which the formation of excited molecules involves the interaction of particles in a three-body collision. For complex particles, the formation of an excited molecule can proceed along a different channel: via the formation of an inter-

⁴⁾According to simple estimates, the distance between neighboring vibrational autoionization levels of the molecule $He_2(^3\Sigma_u^+)$ in order of magnitude equals 0.1 eV; the distance between neighboring rotational autoionization levels equals B_j , where j is the angular momentum of the nuclei, and the magnitude of B is thousandths of an electron volt.

mediate, long-lived complex. Then the rate constant for three-body formation of the excited molecule will be determined by the lifetime of the intermediate complex and its magnitude can greatly exceed the characteristic values of rate constants for the Thompson mechanism. Rate constants for three-body formation of cluster excimer molecules are presented in Table XIX. Apparently, some of these processes are accompanied by the formation of an intermediate long-lived complex.

6. COLLISION QUENCHING OF EXCIMER MOLECULES

An important process in excimer lasers is the quenching of excimer molecules by atoms and molecules in

TABLE XX. Rate constant for quenching of excimer molecules.

Excimer molecule	Quench- ing par- ticle	Quenching rate constant, cm ^a /s [*])
AFF (Br/s)	Ar	9 (12)100
(-1.2)	Kr	1.6 (-9)100
		4.5 (
$KrF(B_{1/2})$	Ar	$8(-12)^{\frac{6}{2}}; <1(-12)^{\frac{19}{3}}; 1.8(-12)^{\frac{19}{3}}; 3.6(-12)^{\frac{19}{2}}$
	Xe	$>1(-9)^{35}$
	F2	$5.7(-10)^{07}$; $8.8(-10)^{80}$; $4.8(-10)^{82}$; $7.4(-10)^{196}$; $6(-10)^{203}$
	KrF ₂	3.7 (10)86
XeF (B _{1/2})	He	$2.0(-12)^{87}$; 4.1(-13) ¹⁹⁹
	Ne Ar	$ < 3 (-13)^{87}; 7.7 (-13)^{88} 4.9 (-12)^{79}; 8 (-13)^{108}; 2.4 (-12)^{203}$
	Xe	$6.0(-11)^{67}$; $3.3(-11)^{159}$;
	N ₂	$4.3(-11)^{203}$ 7.0(-12) ²⁰³
	F ₂	$8.8(-10)^{80}$; $1.2(-10)^{87}$; 3.8(-10)^{199}; 5.1(-10)^{293}
1	CO2	$2.5(-10)^{203}$
	NF ₃	$(3.3(-12)^{57}; 2.6(-10)^{100}; 3.3(-12)^{57}; 2.8(-11)^{55};$
XeF (Carta)	н	$2.3(-11)^{203}$
	Ne	3.0 (-13)93
1	Ar Xe	$9.0(-14)^{93}$ $1.0(-12)^{93}$
XeF (C _{8/2})	N ₂	4.0 (13)93
	XeF ₂	$3(-10)^{85}$; 1.7 (-10) ⁹³
XeCl (B _{1/a})	NF3 Ne	$1.6(-11)^{93}$ 1.0(-12)78
	Xe	3.2 (11)78
XeBr (B _{1/2})	Br,	8 (10) ⁹⁸
XeI $(B_{1/2})$	Xe	$9(-12)^{129}$ 5(-10)158
	CH3I	$3.6(-10)^{100}$
HgCl ($B_{1/2}$)	He Ne	$4.1(-14)^{115}$ $3.3(-14)^{115}$
	Ar	$5.0(-14)^{115}$
	Xe	$3.1(-13)^{115}$
	N ₂ CL	$\begin{bmatrix} 6.1 (-14)^{115} \\ 1.7 (-10)^{115} \end{bmatrix}$
HaBr (B)	CC1	$1.6(-10)^{115}$
$HgB1(0_{1/2})$	Ne	$< 3.4 (-14)^{203}$; $3.4 (-14)^{203}$ $< 3.4 (-14)^{205}$
1	Ar Xe	$7.2(-14)^{203}$ 3(-13) ¹¹⁵ ; 5.8(-13) ²⁰⁴ ; 3.8(-14) ²⁰⁵
1	N,	$2.3(-13)^{201}$; $3.4(-14)^{205}$
	H8r	$1.3(-10)^{115}$
HgBr (B _{1/2})	CF ₈ Br	$8.7(-11)^{113}$ 1 8(-10)^{113}
HgI $(\dot{B}_{1/2})$	He	$< 2.9 (-14)^{206}$
	Ar	$(<2.9(-14)^{205})$ 1.1(-13) ²⁰⁵
	Xe No	$2.2(-13)^{205}$
	Ia	<1.1 (-8)205
Hgl (C./.) **)	CF ₃ l He	$2.9 (-10)^{205}$ 3.8 (-12)^{205}
	Ne	5.1 (-12) \$05
	Xe	4.1(-11)205
Ar.F (2B.)	He No	$2.4(-11)^{205}$ 5(15) ^{\$12}
	Ar	$2.2(-14)^{$12}$ 2.1(-14) ^{\$12}
	NF ₈	5.6 (-10)212
Kr ₂ F (² B ₂)	F,	5 (
1	· •	

^{*}The following notation is used in the table: 9(-12) means $9 \cdot 10^{-12}$.

**The radiative lifetime is assumed equal to 110 ns.⁴⁹

gases. These processes can proceed along different channels and in the final analysis lead to decay of the excited state of the molecule studied. Rate constants for quenching of a number of excimer molecules by some atoms and molecules are presented in Table XX.

It is evident that the values of the rate constants for quenching of excimer molecules at thermal velocities in collisions with atoms are not more than four orders of magnitude lower than the gas kinetic values of the rate constants. We note that quenching of metastable states of atoms and molecules proceeds more efficiently. This is due to the convergence of the electronic term of the excimer molecule and the electronic term of the ground state of the particles during the interaction with the incident particle. We shall demonstrate this for the specific example of the collision $KrF(B_{1/2}) + Ar$. When these particles approach, a weak bond is formed, which corresponds to the ionic term of the system ArKr*+ F⁻. In the lower term, corresponding to the interaction Kr + F + Ar, the approach of the argon atom leads to sharp repulsion. The electronic terms of the initial and final states thereby converge, which facilitates the transition.

Quenching of excited states can proceed along different channels, which include chemical reaction, transfer of excitation to a collision partner, etc. This problem has not been adequately studied. In the simplest cases the channel can be established from general considerations. In particular, quenching of ArF^* in collisions with krypton or xenon atoms leads to the formation of the excimer molecule KrF^* or XeF, respectively.

7. CONCLUSIONS

Based on the information presented above, we can get an idea of how contemporary atomic physics is developing. This review is devoted to excimer molecules, a seemingly exotic physical object, which is characterized by a short lifetime and which cannot be created by a direct method. However, the participation of an excited gas in the kinetics makes excimer molecules important not only from the point of view of relaxation of the excited gas, but also because it permits using excimer molecules for practical purposes, in this case, for a new class of gaseous lasers. There are many physical objects in addition to excimer molecules (highly excited atom, van der Waals molecules, autoionization states of atoms and ions, multiply charged ions) that have been known for a long time, but the attitude toward which has greatly changed in the last decade. The investigation of such objects largely determines the development of contemporary atomic physics.

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