UV emission from excited inert-gas molecules

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Continuous vacuum ultraviolet (VUV) spectra of diatomic inert-gas molecules are ideal objects of investigation when solving many fundamental and applied problems. Problems in plasma physics, molecular spectroscopy, development of sources of VUV radiation, and formation of inverted media in gas lasers (including those in the VUV range) are some of the principal ones. This review covering the last two decades discusses experimental and theoretical methods of studying the VUV spectra of dimers of inert gases. The principal parameters of dimers, and the rate constants for various processes involving them, are given. The most interesting practical applications of the spectroscopic properties of these molecules are examined.

INTRODUCTION

Inert or noble gases, so named because of their ability not to enter into chemical bonds, have been considered, from the very beginning of atomic spectroscopy, to ideal objects for checking the atomic theory experimentally. Even in the first experiments with low-temperature helium plasma, however, well-resolved molecular structures were clearly observed simultaneously with the classical atomic spectra. These structures were later identified as emission from diatomic molecules.[1] While investigating, in the 1930s, VUV emission from helium,[2] Hopfield discovered sections of the continuous spectrum which were unequivocally of molecular origin. Somewhat later similar continuous VUV spectra were obtained experimentally for other inert gases. The great need for such radiation together with the lack of alternative sources of continuous VUV radiation stimulated rapid development of experimental methods for obtaining continuous VUV emission from inert gases[3] as well as the development of theoretical models of the structure of emitting molecules and the mechanisms of formation of such molecules.[4] The first steps toward the experimental mastery of the new field were taken without a complete theoretical picture of the structure of the molecules and their properties. This made it necessary to employ an empirical approach in order to produce VUV sources of continuous radiation. These steps were successful only because of efforts made by such outstanding investigators as Tanaka[5] and Wilkinson and Hopfield.[3,2]

The most complete ideas about the electron-shell structure of a diatomic molecule of an inert gas, which explain the origin and main properties of VUV continua, were formulated by the beginning of the 1970's, to a large extent due to Mulliken's work. The basic features have remained unchanged since then.

These ideas were not exhaustively complete, but they did make it possible to choose optical conditions in practical applications of continuous spectra. The development of a new class of lasers, called "excimer" lasers, and the experimental demonstration of the possibility of building a VUV laser based on the xenon excimer resulted in a significant surge in the number of publications on diatomic molecules of inert gases.[6]

The term excimer (from excited dimer) appeared in the scientific literature in 1960.[7] An excimer is a homonuclear diatomic compound, whose excited states form a stable bond and the lower, ground state is unbound or weakly bound, easily dissociating. Diatomic molecules of inert gases are typical representatives of excimers. Their unexcited state is a virtually purely repulsive term and the spectroscopic resonance transitions of diatomic molecules, because of this feature of the structure of electronic shells, give continuous sections, covering the wavelength range from 58 to 200 nm, in the spectrum. This property of the emission spectra of inert gases is widely employed in practical applications, since it gives virtually the only possibility of obtaining by simple means continuous spectra in the vacuum-ultraviolet (VUV) region.

Since the discovery of continuous emission, the VUV spectra of noble gases together with the hydrogen continua have remained the basic laboratory sources of continuous short-wavelength radiation.

The solution of many fundamental and applied problems is based on the use of continuous vacuum radiation: in ecological investigations, in the solution of different technological problems in microelectronics, and in the solution of the special problem (important for practical applications) of increasing the light-emission efficiency of luminescent materials for the development of colored indicator panels, on which the flat colored television screen is based.[8] Interest in continuous emission increased sharply with the demonstration of the possibility of building VUV lasers based on heavy inert gases.[9]

The problem of studying relaxation processes in low-temperature inert-gas plasma is another important reason for the increased interest in VUV spectroscopy of inert-gas dimers. Numerous previous investigations of plasma have shown convincingly that the molecular component plays a decisive role in deionization and different relaxation processes and it determines, to a significant extent, the properties of the plasma. For example, dissociative recombination with participation of diatomic molecular ions can play an important role at the first stage of relaxation of a decaying inert-gas plasma.

The spectroscopic methods of investigating this process

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yield information about the channels via which the excited atomic states, which are formed by a recombination reaction, are populated. The mechanisms of deactivation of the excited atoms at the second stage of the relaxation processes and the role these mechanism in the formation of diatomic molecules, the dissociation of molecules after emission of sections of the continuous VUV spectrum, and other elementary processes in which inert-gas excimers participate in one way or another are also of definite interest.

Experimental investigations have shown, however, that with the exception of helium there are no visible-range and near-IR molecular spectra in the emission from inert-gas plasma. Direct information about inert-gas molecules and their participation in different elementary processes can be obtained only by studying the VUV region. Such investigations can shed the most light on the overall picture of degradation of the energy stored in a low-temperature plasma. Information about the physical processes responsible for the excitation and deexcitation of the atomic and molecular states in low-temperature plasma is necessary in order to develop efficient sources of VUV radiation and the production and optimization of population-inverted media in gas lasers (including VUV lasers).[11] Such information makes it possible to assess the course of various plasma-chemical reactions and to explain the essence of phenomena ocurring in natural and laboratory plasma objects. Investigations of the molecular spectra of inert gases are also invaluable because inert-gas excimers are the simplest molecular structures and their spectra are easy to identify, and for this reason they are a reliable object for checking different physical theories and computational methods.

The last monographs containing a review of the physics of VUV emission from inert-gas dimers were published more than 20 years ago.[13,14] For this reason, the present review focuses on works published later. The modern experimental methods of investigation of the VUV spectra of inert-gas dimers and the results of these investigations are discussed and the basic parameters of dimers, the rate constants of different processes in which dimers participate, and the most interesting practical applications of spectroscopic properties of these molecules are presented.

The methods employed for the investigation of low-temperature plasma which are considered in the present review have made it possible to determine a large number of constants of elementary processes in which excimer molecules participate and which determine the properties of excimer molecules. The list of basic reactions and their rate constants and the basic parameters of excimer molecules are presented below in Tables I–VI.

1. INVESTIGATIONS OF MOLECULAR SPECTRA

The most reliable, detailed, and complete experimental investigation of the VUV spectra of inert gases were performed by Tanaka *et al.*[5,15–19] Mulliken's investigations mark the beginning of the most systematic, modern explanations of the basic spectroscopic properties and the theory of the structure of excimer molecules of inert gases. Mulliken studied, on the example of the diatomic xenon molecule, the basic spectroscopic features of inert-gas dimers and he gave a qualitative explanation of the physical properties of the molecules. Mulliken's results served as the starting point for virtually all subsequent investigations of the physics of VUV spectra of inert-gas dimers. We shall briefly consider the basic principles of this theory.

Diatomic molecules of heavy inert gases are an example of the standard excimer molecule. The ground state ($^1\Sigma_g^+$) is a repulsive term with a shallow minimum at large internuclear distances. The minima are deeper for xenon and decrease from xenon to krypton and argon, neon and helium. The minimum is equal to $\sim 200\ \text{cm}^{-1}$ for xenon and several cm^{-1} for helium. At room temperature a molecule is not formed in the ground state $^1\Sigma_g^+$ because the binding energy is small. In the case of helium, such a molecule cannot form under any conditions because of the small depth of the well, but the excited and ionic states of inert-gas dimers do have a stable bond. The depth of the potential well of these states increases from xenon to helium: It is equal to tenths of an eV for xenon and up to ~ 2.5 eV for helium. The equilibrium distance for the excited and ionic states is maintained in the gas, and the absolute value increases with increasing atomic number of the element.

The appearance of the VUV continua of inert-gas dimers is explained by the spectroscopic transitions between the closest excited states of molecules dissociating to the atomic terms $^3P_2$ and $^3P_1$. Figure 1, taken from Mulliken's paper, shows the terms of the xenon dimer. The basic spectroscopic properties of these dimers can be qualitatively understood from these terms. The emitting states, which form the VUV continuum in this case, are the states $^1\Sigma_u^+, ^3\Sigma_u^+, ^1\Pi_u^+, ^3\Pi_u^+$.

The two excited states $^1\Sigma_u^+$ and $^3\Sigma_u^+$ make the main contribution to the formation of the VUV continua. In the scientific literature the continuous VUV spectra are conventionally separated into regions, called the "first" continuum and the "second" continuum. The first continuum refers to sections of the continuous spectrum which directly adjoin the long-wavelength side of the resonance lines and which arise in spectroscopic transitions from the highest vibrational levels. The second continua are most pronounced at high pressures. They are located at significantly larger distances than the first continua on the long-wavelength side of the resonance lines and they consist of virtually symmetric, structureless bands with a width of about 10 nm and are engendered by spectroscopic transitions from the deepest vibrational levels into the weakly bound ground state $^1\Sigma_g^+$

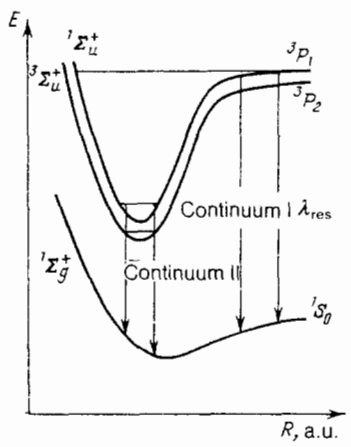


FIG. 1. Scheme of deepest states of inert-gas dimers.

(see Fig. 1). The second continua were of greatest practical interest from the very beginning of these investigations. These are the sections of the spectrum that were considered to be most promising for achieving maximum intensity of continuous VUV radiation and for obtaining super radiation from excited dimers of heavy inert gases.

We shall examine below the basic theoretical prerequisites employed in modern investigations for calculating the VUV spectra of inert-gas dimers.

2. THEORETICAL PREDICTION OF VUV CONTINUA OF INERT-GAS DIMERS

2.1. Basic relations

The theoretical prediction of molecular continua consists of calculating the expression

$$I_v(\lambda) = \frac{1}{\lambda^6}\left|\int_0^\infty \psi_v(R)\mu(R)\varphi_\varepsilon(R)dR\right|^2 \qquad (1)$$

and summing I_v over the discrete vibrational levels v of the electronic state ψ, taking into account the population of the vibrational levels. The expression (1) determines, to within a constant, the wavelength dependence of the energy density of the radiation from an excimer molecule. Here λ is the wavelength for the transition $\nu \to \varepsilon$, $\psi_v(R)$ is the vibrational wave function of the upper bound electronic state ψ, $\varphi_\varepsilon(R)$ is the vibrational wave function of the lower repulsive electronic state φ, and $\mu(R)$ is the dipole moment of the electronic transition $\psi \to \varphi$.

The most systematic method for obtaining the vibrational wave functions is to integrate the vibrational wave equation.

$$d^2\psi/dR^2 + (E - U(R))\psi = 0. \qquad (2)$$

The form of Eq. (2) corresponds to the system of units where length and energy are dimensionless. Here $U(R)$ is the internuclear potential and E is the energy eigenvalue, which takes on a negative value for discrete levels v.

It is obvious that the accuracy of the wave functions ψ obtained by integrating Eq. (2) is determined by the accuracy of the internuclear potential $U(R)$ as well as the numerical integration procedure. We note that from the purely computational viewpoint, the approximation employed for $U(R)$ when integrating Eq. (2) is not very important. The form in which the result is presented—a formula, table, or plot—is much more important. In the following sections we examine briefly the internuclear potentials given in the literature for inert-gas dimers, and we also discuss the numerical procedure for integrating Eq. (2).

2.2. Potential curves

Before reviewing briefly the internuclear potentials, we note the following. We are interested in continua arising as a result of transitions between electronic states which dissociate to the excited atomic levels $^1P_1$ and $^3P_1$ of the $np^5(n+1)s$ configurations and to the ground state $^1S_0$ of the configuration np^6. Being strictly spin-forbidden in LS-coupling, triplet states should not contribute to this transition, and for this reason they are not very important for estimating continua.

When spin-orbital interaction is taken into account, the contributions of the excited electronic states to the molecular continuum are determined by the weight of the singlet states.[11] These weight coefficients appear in the calculation of the dipole moment $\mu(R)$. If, however, there is some basis for believing that the continuum is determined by a transition from some one electronic state, then it is not as important to know $\mu(R)$ and in many cases the expression (1), neglecting the dependence of the dipole moment on the internuclear distance, gives a good estimate of the shape of the continuum. In other words, the integral (1) reduces to an overlap integral of the functions $\psi_v(R)$ and $\varphi_\varepsilon(R)$. This approximation is all the better the greater are the grounds for considering that the continuum is determined by a transition from the lower vibrational states—the domain of $\psi_v(R)$ with $v \simeq 0$ is small enough that within it $\mu(R)$ can be assumed to be constant to a good degree of accuracy. This approach is often necessary, since there is virtually no information about the transition dipole moments of inert-gas dimers. For the transitions of interest to us $^1\Sigma_u^+ \to {}^1\Sigma_g^+$ (or, taking into account spin-orbital interaction, $O_u^+ \to O_g^+$) we have data only for Xe_2 (Ref. 21) and Kr_2 (Ref. 22).

As far as the potentials are concerned, the choice is richer. The internuclear potentials obtained in Ref. 23 for the ground state $^1\Sigma_g^+$ for Ar_2, Kr_2, and Xe_2 and in Refs. 24–26 for Ar_2, Kr_2, and Xe_2, respectively, are very convenient for numerical applications. These results were obtained with the help of the experimental data on the scattering of molecular beams and are presented in the form of simple analytical formulas. In Refs. 24–26 it is noted that both macroscopic quantities (virial coefficients, viscosity, thermal conductivity) and microscopic quantities (differential scattering cross section) are reproduced well with the help of the potentials found in these publications. We call attention to the important fact that the forms of the shallow potential well in these potentials are the same in Refs. 24–26 and in Ref. 23. This agreement has the consequence that in both Refs. 26 and 23 virtually the same splitting is obtained for the vibrational levels in this well for Xe_2. A similar variant of the potentials of the $^1\Sigma_g^+$ state of helium and neon dimers can be found in Ref. 27. A purely theoretical $^1\Sigma_g^+$ potential for the helium dimer is given in Ref. 28 in a tabular form which is also quite suitable for integration of the vibrational equation.

The extensive data on the potentials of the excited states of inert-gas excimers which dissociate into the atomic states $np^6 + np^5(n+1)s$ are also quite extensive. A significant part of these results was obtained semiempirically. Thus in Refs. 21 and 22, where the molecular states Xe_2^* and Kr_2^*, respectively, were considered, the calculation is performed in the LS-coupling approximation, and the contribution of spin-orbital interaction is taken into account semiempirically. Spin-orbit interaction is also taken into account semiempirically in Ref. 29, where the excimers Ne_2^*,Ar_2^*,Kr_2^*,Xe_2^*. were investigated. The potential curves of the states AR_2^* and Kr_2^* were calculated theoretically in Ref. 30, and the curves for He_2^* were calculated theoretically in Ref. 28. We note that the potential curves obtained for excimers are presented, as a rule, in the form of fine-scale plots,[21,22,29,30] tables with a large step in R,[21] or complicated formulas.[29] For this reason, these data are quite difficult to use in applications. From this viewpoint the potentials presented in the form of the Morse potential are more convenient. The pa-

rameters of this potential for states of the excimers Kr_2^* and Xe_2^* can be found in Ref. 31.

2.3. Integration of the vibrational equation

In order to calculate the function $\psi_v(R)$ of discrete vibrational levels v it is not sufficient to integrate the differential equation (2): It is necessary to solve the eigenvalue problem for the energy of the level. For this there is a well-known approach,[32] in which Eq. (2) is integrated numerically from both ends—from the origin of coordinates, i.e., from $R = 0$, and from $R = R_{max}$, where R_{max} is some internuclear distance at which $\psi_v(R)$ is taken to be vanishingly small. The value of the energy E of the level v is then determined primarily by the number of nodes of the function $\psi_v(R)$, i.e., the vibrational quantum number v, and the final refinement of E is performed when the two branches of the function are joined. The joining procedure is determined by the conditions that the function and its first derivative be continuous and it does not always go smoothly.

There have appeared recently numerical procedures which make it possible to solve the eigenvalue problem by intergrating from one end—from the origin.[33,34] In this procedure E is determined, as before, by the number of nodes, and the final refinement is performed by checking the behavior of the function $\psi_v(R)$ at the end of the integration interval. Thus the joining procedure is no longer necessary.

The numerical procedure is simpler for the wave function of the continuous spectrum $\varphi_\varepsilon(R)$, since the solution of the eignevalue problem is replaced by integration of Eq. (2) with a fixed positive value $E = \varepsilon$. The amplitude of the function $\varphi_\varepsilon(R)$ in the limit $R \to \infty$ is normalized to the quantity $1/\sqrt{\pi}\varepsilon^{1/4}$. The technical difficulty lies in the fact that for this the amplitude must stablize. This has been found to be much more difficult to achieve the smaller is the value of ε, since the period of the oscillations of the function $\varphi_\varepsilon(R)$ increases as $2\pi/\varepsilon^{1/2}$ and a large integration interval is required in order to achieve a stable amplitude, and this is fraught with accumulation of errors.

2.4. Results

In spite of the comparative simplicity and obviousness of the above-described procedure for evaluating the expression (1), there are few results in the literature. For heavy inert gases we know of only one publication—Ref. 34—where systematic calculations of $I_v(\lambda)$ are performed, neglecting the dependence of the transition dipole moment on the internuclear distance. In Ref. 34 the transition $^1\Sigma_u^+ \to {}^1\Sigma_g^+$ ($v = 0$–9) in the spectra of krypton and xenon dimers is studied. The results are presented in tabular form with a quite small step in λ.

3. EXPERIMENTAL METHODS OF INVESTIGATION OF MOLECULAR SPECTRA

The structure, mechanisms of formation, and physical properties of molecular terms have been investigated in many experimental studies, employing the most diverse methods. We shall examine systematically the main investigations in which such experiments were performed.

3.1. Photoexcitation and photoionization of inert gases

Vacuum cells, filled with the desired gas up to a definite pressure, were employed in experiments of this type. In the first experiments the gas was excited by the atomic line radiation of the element under study. This method made it possible to study the evolution of the excitation along the radiative channels of molecules which are in only the deepest excited molecular states. The characteristic first results of the studies in this series were reported by Freeman *et al.*,[35] who investigated the excitation of xenon dimers with the help of a xenon resonance lamp. They studied the spectral composition of the VUV radiation emerging from the cell after aborption of the $\lambda = 146.9$ nm xenon resonace. The intensity as a function of the gas pressure in the cell is presented in Fig. 2. By interpreting the experimental curve Freeman *et al.* were able to prove, in a well-founded manner, that the radiating Xe_2^* molecules were produced primarily in three-body collisions of excited Xe*-atoms with netural atoms according to the scheme

$$Xe^* + 2Xe(0_g^+) \to Xe_2^* + Xe. \qquad (3)$$

The experiments made it possible to find the rate constant of this process for xenon: $\gamma = (1.5 \pm 0.7) \cdot 10^{-32}$ cm^6/s^{-1}. The main direction of the experimental investigations in the first studies in this series was determined primarily by two problems: the study of the characteristic features of the VUV spectra and reconstruction of the potential curves of the excited states of the dimers on the basis of the excited states of the dimers on the basis of these results. This approach yielded information only about the deepest excited states, since the spectroscopic transitions from higher excited levels were not observed experimentally.

A method developed in the last few years has become an effective method for studying the structure of the terms of excited inert-gas molecules. It is based on the study of the kinetics of VUV emission from inert gases which are excited as a result of selective photoabsorption (including also multiphoton absorption).

Figure 3 shows a schematic of this experiment.[36] Pulsed radiation was focused on a gas cell containing the inert gas of interest. The VUV emission from the molecules formed in the cell was separated with the help of a monochromator and recorded with a photomultiplier. The use of a pulsed source whose excitation pulse had a steep trailing edge made it possible to study the kinetics of the luminescence process as a

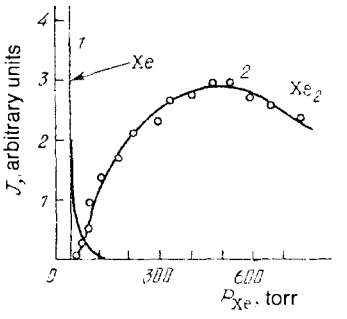
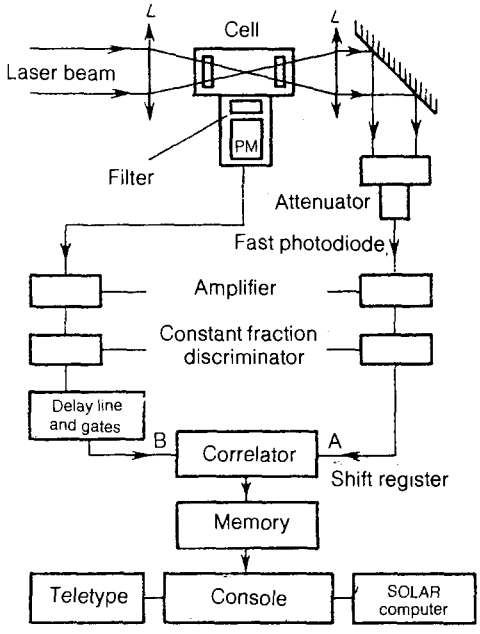


FIG. 2. Fluorescence intensity as a function of the gas pressure. *1*—fluorescence of xenon atoms, *2*—fluorescence of xenon dimers.



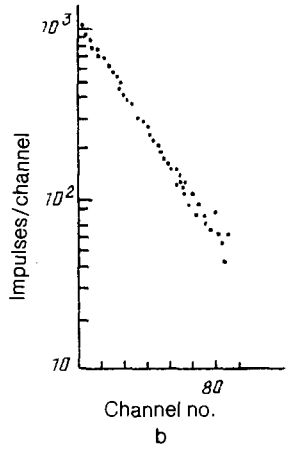
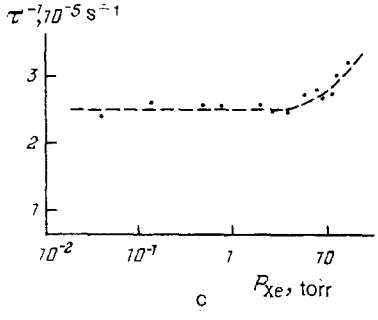


FIG. 3. Laser method of investigation of xenon luminescence. a) The experimental setup.[36] b) Investigation of the xenon luminescence kinetics (Ref. 36): decay of the intensity of the resonance line ($^3P_1$ level); the working pressure $P = 0.5$ torr. c) Decay rate of the $^3P_1$ state as a function of the xenon pressure.



function of the gas pressure in the cell, the composition of the gas filling the cell, and the characteristics of the excitation radiation.

In experiments of this type the atomic gas is excited and the kinetics of the atomic line emission and molecular band emission are studied as a function of the gas pressure. The rate of decay of the luminescence was approximated by a parabolic function of the pressure P:

$$\frac{1}{\tau} = \alpha + \beta P + \gamma P^2;$$

where τ is the experimentally measured decay constant of the excited state and α, β, and γ are the rate constants for spontaneous decay and decay in two- and three-body collisions, respectively, of the excited states under study. Figure 3b gives some results which were obtained in this series of investigations, performed in Ref. 36. This approach to the investigation of the production of inert-gas molecules by the atomic-collision mechanism made it possible to determine, directly from the experiments, the reaction rate constants. The first experiments with this method of investigation were initiated by Dixon,[37] and the main results from the study of the production of excited molecules of inert gases are reviewed by A. V. Eletskiĭ and B. M. Smirnov [Table I (Ref. 12)]. This method of investigation made it possible to study, besides the excitation of atomic states with subsequent formation of radiating molecular states, the photoexcitation of diatomic molecules directly from the weakly bound molecular ground state $^1\Sigma_g^+$ and to analyze the energy relaxation along the excited levels of the excimer molecule. The kinetic scheme of the processes in which the lower $^3P_1$ and $^3P_2$ atomic levels and the $1_u^\wedge, O_u^+$ molecular levels of xenon participate is presented in Fig. 4a.[38] This work is a continuation of the investigations performed in Ref. 39 (Fig. 4b). In it a laser which could be tuned in the region 428–454 nm was used to populate by the method of multiphoton excitation the high-lying levels of the xenon atom (5f,8p,4f,6p',7p). At the second stage of the experiment the relaxation of energy through the system of atomic and molecular levels was studied.

Such experiments can yield information about the mechanism of formation of radiating molecular states and the decay of such states in radiative and collisional processes. In subsequent publications the same authors investigated argon by a similar method.[40] An improved experimental technique was employed to investigate krypton.[41] The first step in the excitation of krypton was conducted with

TABLE I. Rate constants of formation of inert-gas molecules in the reaction (3)

Excited atom		Rate constant, 10^{-33} cm$^6\cdot$s^{-1} (Ref. 12)	T, K
He	$^3S_1$	0,23 ± 0,04	300
	$^1S_0$	$(2,0 \pm 0,5)\cdot 10^{-3}$	77
Ne	$^3P_2$	0,5	300
	$^3P_0$	0,04 ± 0,05	77
	$^3P_0$	0,07	77
Ar	$^3P_2$	11 ± 4	300
	$^3P_0$	10 ± 2	300
Kr	$^3P_2$	36 ± 8	300
	$^3P_0$	69	196
Xe	$^3P_2$	55 ± 20	300
	$^3P_0$	40 ± 13	300

VUV laser radiation, which populated the $^3P_1$ and $^1P_1$ states of the krypton atom in a single-photon process. Single- and two-photon methods of excitation were employed at subsequent steps of excitation; these methods made it possible to populate selectively virtually any excited states of the krypton atom and molecule, as well as their main ionic states. The energy-level diagram of krypton and the main processes employed in Ref. 41 are presented in Fig. 4c.

The use of synchrotron radiation as a source for exciting the molecular spectra of inert gases has opened up unique possibilities.[42–45] In this case the synchrotron radiation was employed as a source for excitation or photoionization. Synchrotron radiation is convenient because it makes it possible to obtain tunable monochromatic radiation and thus to act selectively on separate excited states of an atom, ion, or molecule and to investigate the mechanisms of elementary processes in which they participate. The drawback of this method is that it is impossible to populate levels that do not combine with the ground state. Reference 45 is an example of the use of synchroton radiation in experiments of this type. Synchrotron radiation was directed onto the input slit of the first monochromator, which gave a half-width of $\Delta\lambda = 0.1$ nm for the output radiation. The beam monochromatized in this manner was employed for photoexcitation of the gas under study in the cell. The radiation was focused with the help of an ellipsoidal mirror. The luminescence spectrum was recorded in a direction perpendicular to the excitation radiation. The half-width of the instrumental function of the second monochromator employed in Ref. 45 was equal to about 1 nm, which was adequate for investigating the continuous VUV spectra of heavy inert gases. In Ref. 45 attention was focused primarily on the dynamics of the filling of the deepest excited states of argon, krypton, and xenon. Deformations of the VUV continua and their lifetimes with a change in pressure in the gas cell were investigated. Some results of the investigations performed in Ref. 45 are presented in Fig. 5.

3.2. Excitation in supersonic jets

Experiments based on excitation of gas in supersonic jets were a fundamental improvement in the experimental method of investigation of inert-gas molecules.

This method has been elaborated the most in the last few years. The crux of the method is as follows. The gas under study was passed through a supersonic nozzle. As a result of adiabatic expansion, the gas cooled rapidly and it became supersonic. Physical conditions under which molecules are formed and relax through the vibrational levels, are realized in the supersonic flow. The method has a number of advantages over the one based on the use of gas cells. For example, here it is possible to study the spectra of atoms, molecules, and more complicated structures, whose temperatures are low. The characteristic feature of the method is that is in principle possible to observe the spectra of "supercooled" molecules, i.e., molecules whose temperatures are much lower than their condensation temperature. This possibility makes it possible to investigate subtle effects, which cannot be observed in gas cells because the thermal motion obliterates the fine-scale spectroscopic structures. These possiblities are demonstrated, in particular, in Refs. 46 and 47. A source of spectra which are free of Doppler broadening is studied in Ref. 47. The gas was excited with the help of an electric discharge in a supersonic jet in a hollow cathode. It was shown experimentally that the rotational temperature of the helium molecules and the temperature of the gas, measured from the Doppler broadening, are equal to approximately 15 K. The Doppler contour was investigated with the help of a high-resolution instrument ($r = 0.9\cdot 10^6$). Figure 6 demonstrates the basic results obtained in Ref. 47. Modern experimental setups, employed in experiments with supersonic jets,[46] for investigating the properties of dimers consist, as a rule, of three basic parts: a laser source, which generates VUV radiation; a supersonic nozzle, which produces dimers of the inert gas; and, a detecting system. Frequency-tunable lasers, pumped with a UV XeCl excimer laser, are, as a rule, employed as the laser source.

The VUV radiation is generated in a special cell by mixing the frequencies of the radiations of the tunable lasers. Fine regulation of the radiation frequencies of the tunable lasers makes it possible to act on separate components of the vibronic structure of an inert-gas molecule. In such experiments the highest spectral resolution is required for xenon dimers. Figures 7a and b show a block diagram of the experimental setup and the basic experimental results obtained by Lipson *et al.*[46]

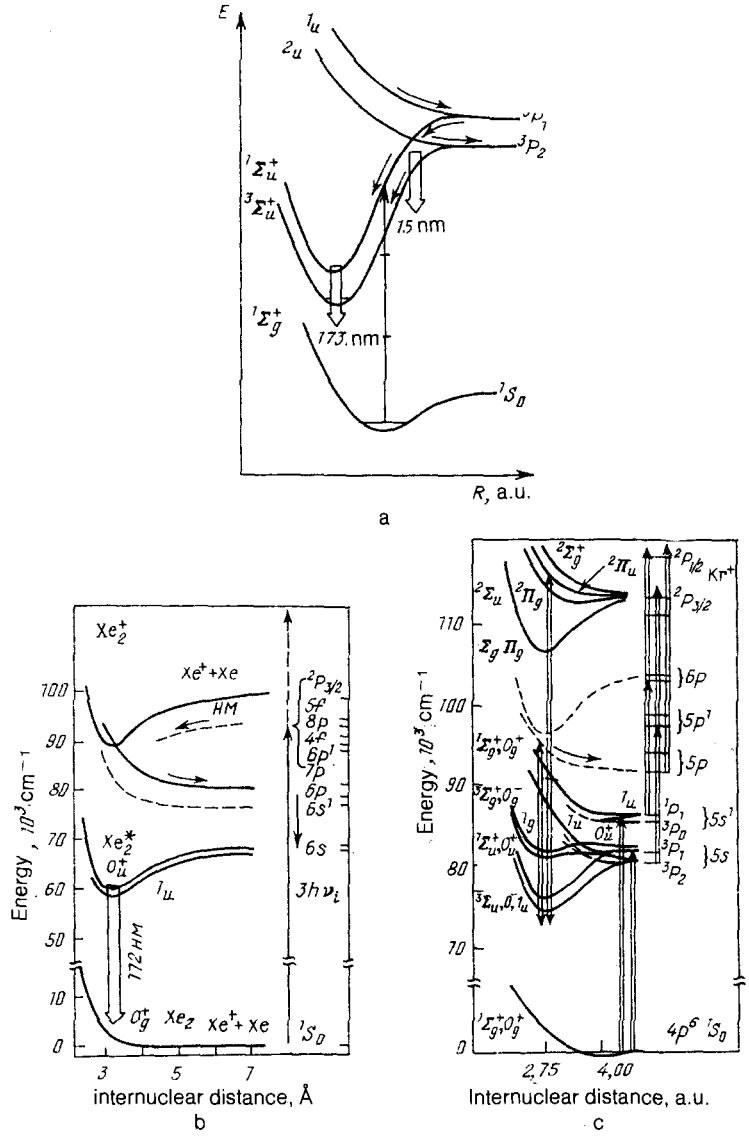


FIG. 4. a) Decay processes investigated in xenon by the three-photon excitation method[38] with excitation of the 1_u-state. b) Simplified system of xenon terms, illustrating the decay process accompanying photoexcitation of xenon.[39] c) Simplified term system of krypton and the basic channels of excitation and deexcitation of the krypton atom and molecule.[40]

Such experiments make it possible to study the basic behavioral regularities of the radiating molecules and to determine their fundamental properties, such as the vibrational and rotational constants, the anharmonicity constant, the dissociation energy of the molecules, and so on. This method has the deficiency that the luminescence only for the deepest excited states of an excimer molecule ($A^{1,3}\Sigma_u^+$) can be observed.

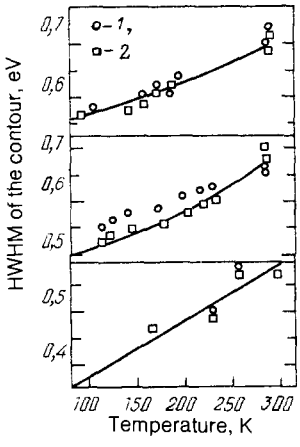


FIG. 5. Temperature dependence of the contour width for the slow component (*1*) and fast component (*2*).

Indeed, observations of the emission from a low-temperature neon, argon, krypton, and xenon plasma in the UV, visible, and IR regions show that only atomic lines are found in the spectrum. The most convincing explanation of this phenomenon is based on the fact that the probability of dissociation processes is higher than that of radiative decay of the excited molecules which are formed. For this reason, it is difficult to observe directly the spectra of diatomic molecules with the participation of highly excited states. Experiments based on the use of multiphoton ionization are of greatest interest for obtaining information about such states.[48,49] In experiments of this type the following reaction chain was traced:

$$A_2(X^1\Sigma_g^+) \xrightarrow{2h\nu} A_2^*(v') \xrightarrow{h\nu} A_2^+. \qquad (4)$$

The high sensitivity of the photoionization method as well as the fine tuning of the wavelength of the excitation and ionization radiations made it possible to obtain detailed infor-

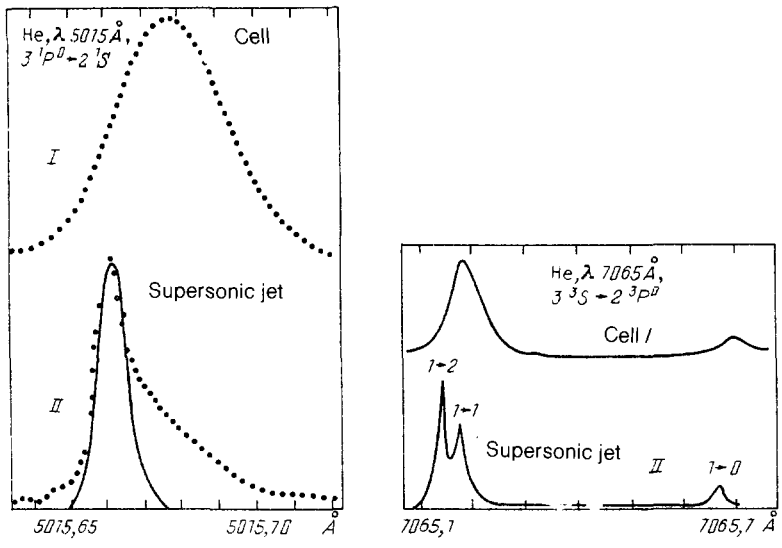


FIG. 6. Emission spectrum of a helium discharge[47] in a standard discharge (I) and in supersonic jet (II).

mation about the structure of the molecular terms.

Figure 8 shows a fragment of the photoionization spectrum of a xenon dimer.[48] The spectrum was obtained by excitation of $X^1\Sigma_g^+$ excimer molecules formed in a supersonic gas flow. The molecular parameters, found with the help of experiments using stepped photoionization (4), are presented in Table II.

The method developed in Refs. 48–50 made it possible, in principle, to solve the problem of determining experimentally the parameters of stable highly excited molecular states and to obtain detailed information about the experimentally most complicated molecule Xe_2^{**}.[49]

Experiments with supersonic jets and selective laser photoexcitation of molecules into definite vibronic states made it possible to determine important molecular constants, such as the radiative lifetimes of the molecules. The most systematic and detailed investigations of the radiative characteristics of molecules of heavy inert gases were per-

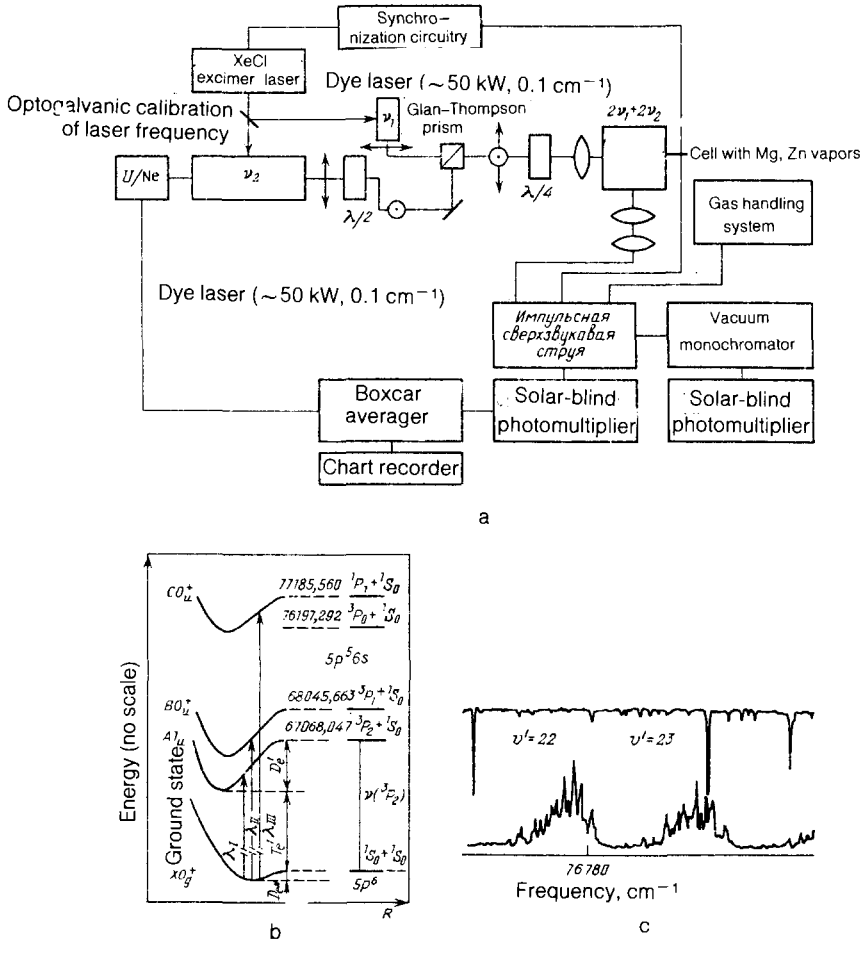


FIG. 7. a) Block diagram of the setup for investigating the VUV spectra of inert-gas dimers.[46] b) Investigation of the structure of xenon dimer: region of action of laser radiation on a xenon molecule.[46] c) Fragment of luminescence spectrum of a xenon molecule with photoexcitation by $\lambda = 130$ nm radiation.

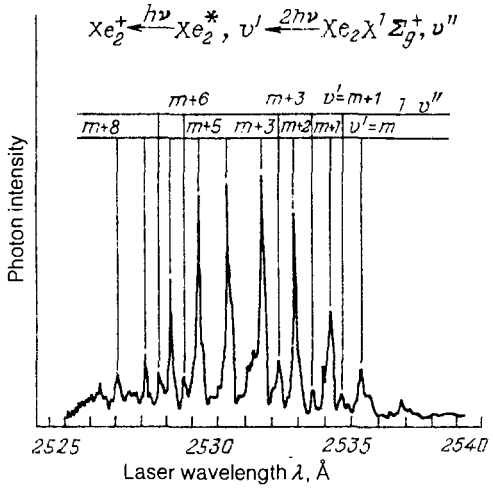


FIG. 8. Photoionization spectrum of xenon.[48] A molecular state dissociating to the atomic level $Xe^*5d[1/2]_0^1$ is investigated.

formed in Ref. 53. The experimental technique employed made it possible to investigate separate vibrational states of the radiating molecules, and in the case of argon separate rotational levels also. In Ref. 53 the radiative decay of argon, krypton, and xenon excimer molecules selectively excited in a sueprsonic flow was studied. This was achieved by using laser radiation having a half-width of ≈ 0.3 cm^{-1} for excitation. The excited inert-gas dimers were formed in a pulsed supersonic nozzle.[54] Detailed investigations of the radiative decay of the excited states made it possible in Ref. 54 not only to find the dependence of the radiative lifetimes on the vibrational quantum number of the excited radiating states of argon, krypton, and xenon dimers, but also to obtain, for a number of vibrational states, the dependence of the dipole matrix element of the spectroscopic transition on the internuclear distance. The experimental data were compared with theoretical calculations, and the agreement was found to be satisfactory. These results are of interest not only for studying possible applications of VUV radiation from inert-gas excimers, but also for understanding the general laws governing the formation of diatomic molecules and explaining the radiative properties of such molecules. In Fig. 9 the basic results obtained by Madey and Stoicheff[53] are presented and the obtained values are compared with theoretical calculations of the dipole matrix element as a function of the internuclear distance, which were obtained in Ref. 53 on the basis of an analysis of the results obtained in Refs. 55 and 56. At the same time, the most reliable data on the position of the classical left- and right-hand turning points of the vibrational motion of the molecules were found in Ref. 53. These results are extremely important for identifying the emission spectra of molecules in the UV and visible regions of the spectrum. The problem of identifying the spectra corresponding to spectroscopic transitions in the region of the classical left-hand turning points of the vibrational motion of the molecules remains unresolved.[4,56,58]

The study of the structure of the electronic terms of molecules is an important problem, without solving which it is very difficult to understand and use effectively their spectroscopic properties.[58,65] This problem is especially serious in the study of unbound or weakly bound states. The emission and absorption spectra whose spectroscopic transitions include such levels lead to the appearance of sections of the spectrum whose identification presents well-known difficulties. The experimental possibilities of investigation of unbound and weakly bound levels of xenon were first examined in Ref. 58. A novel experimental technique, presented schematically in Fig. 10a, was employed for these purposes. Xenon dimers occupying the weakly bound ground state $^1\Sigma_g^+$, were produced in a supersonic nozzle as the gas cooled adiabatically as it flowed out of the nozzle into vacuum. As a result of two-photon excitation, the molecule as transferred into one of the "g" states, which dissociate into one of three limits of the atom 6P[5/2], 6P[3/2], and 6P[1/2]. An additiona, third laser pulse ionized the excited molecule formed. The ionic photocurrent was recorded as the result of

TABLE II. Molecular bands dissociating to the limit $Xe(^1S_0) + Xe^*(SD[1/2]_1^0)$.[48]

v''	v'	Laser wavelength, nm	Two photon energy (first excitation step), cm^{-1}	$\Delta\sigma_{v+1/2}$	$\Delta\sigma^*_{v+1/2}$
0	0	2512,26	79609,7	19,8	34,3
	1	2511,17	79644,0	18,8	34,7
	2	2510,08	79678,7	18,8	34,0
	3	2509,01	79712,7	19,7	31,6
	4	2508,02	79744,3	18,3	
1	0	2512,88	79589,9	15,9	35,3
	1	2511,77	79625,2		34,7
	2	2510,67	79659,9		33,1
	3	2509,63	79693,0		33,0
	4	2508,59	79726,0	18,8	29,2
	5	2507,67	79755,2	15,6	
2	0	2513,38	79574,0		
	4	2509,18	79707,2		32,4
	5	2508,16	79739,6		28,8
	6	2507,26	79768,4	16,5	
3	6	2507,78	79751,9		

v	0	1	2	3	4	5
$\Delta\sigma_{v+1/2}$	34,8	34,7	33,6	32,3	30,8	28,8

$D_0 = 562.6$ cm^{-1} molecule dissociating to the limit $Xe^1S_0 + Xe^*5d[1/2]_1^0$.

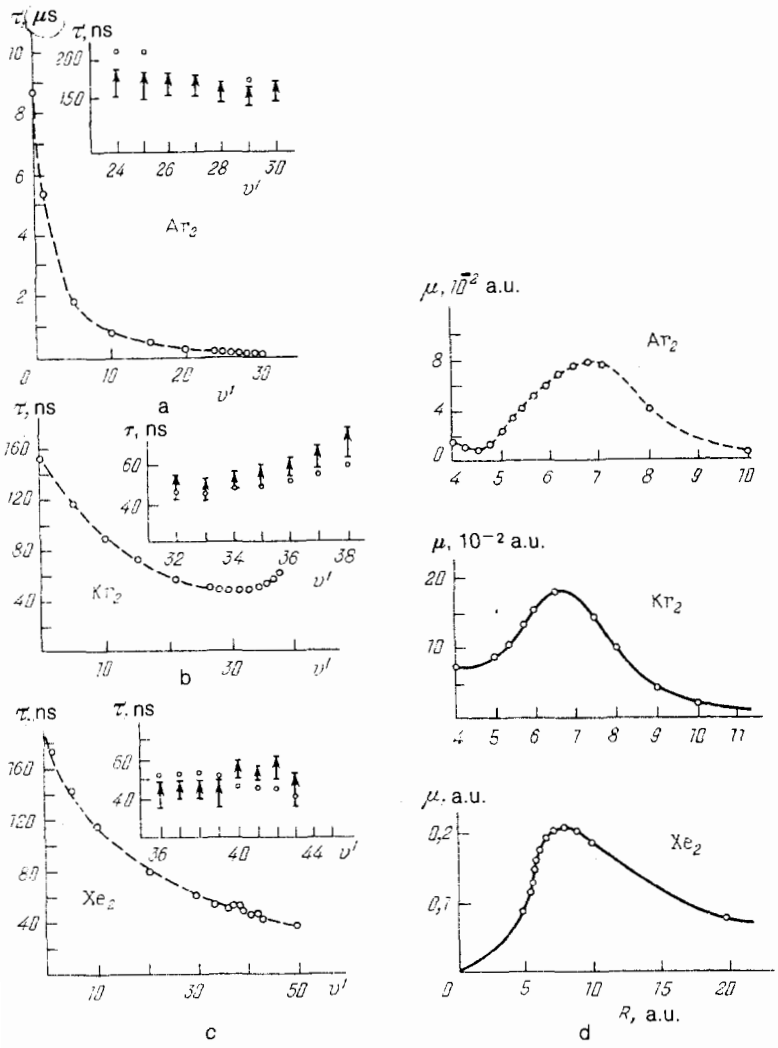


FIG. 9. Computed lifetimes of different vibrational states of argon, krypton, and xenon molecules (a–c) and dipole matrix element of spectroscopic transition as a function of the internuclear distance in argon, krypton, and xenon molecules (d).

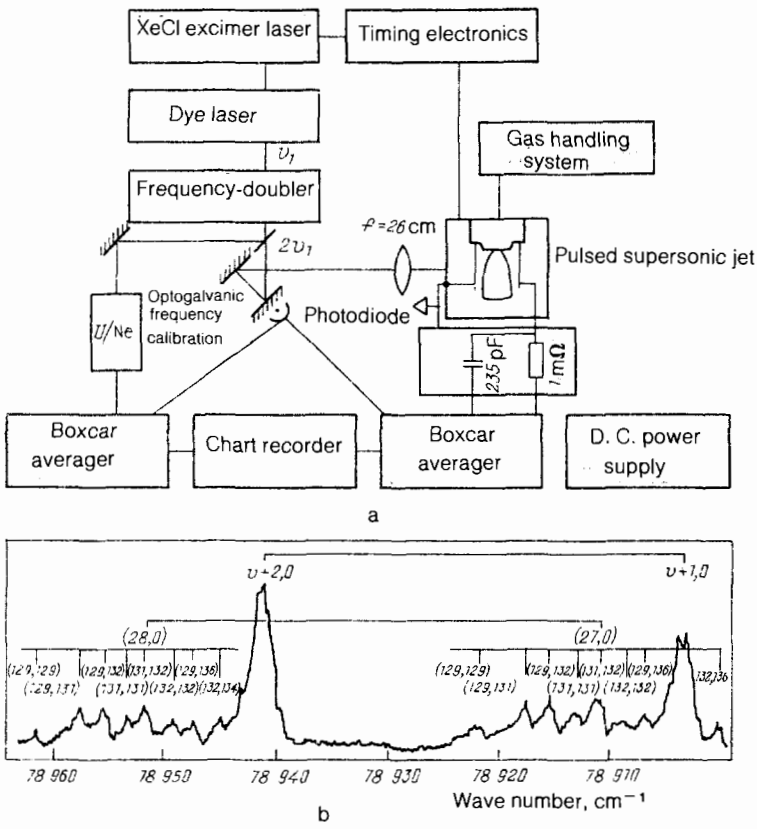


FIG. 10. a) Block diagram of setup for investigating molecules by the three-photon ionization method.[50] b) Spectrum of Xe_2^*-molecule in the region of the transitions $1_g \leftarrow 0_g^+$ and $2g \leftarrow 0_g$ (the interpretation of the isotopic structure of the transition is presented[58]).

the experiment. This experimental apparatus combined the high sensitivity of the photoionization method and the high energy resolution of the laser method of analysis. The latter property enabled Lipson *et al.*[58] to observe the isotopically resolved rotational structure of the xenon molecule (Fig. 10b) and to determine with a high degree of accuracy parameters such as the dissociation energy of the levels investigated, the rotational constant, and the anharmonicity constant.

The use of supersonic jets for producing weakly bound molecules in the ground state, followed by photoexcitation of the molecules into the upper electronic levels, is one of the powerful modern methods for studying the structure of excimer molecules. Another interesting application of supersonic flows is for studying more complicated weakly bound structures—clusters. The VUV emission spectra of such complexes are similar to the emission from excimer molecules, and we need to discuss them briefly in this review. The VUV fluorescence spectra of such complexes have been investigated in a large number of studies.[64–67] It has been established reliably that the character of the spectrum of a cluster depends, to a significant degree, on the number of atoms in the cluster. If the number of atoms in a cluster is large, the VUV emission spectra of the clusters have characteristic peaks, which make it possible to identify the type of cluster by the number of atoms in it. Figure 11 shows a fragment of the fluorescence spectrum of krypton clusters, containing different numbers of atoms.[66] The results of Ref. 66 show that as the number of atoms in a cluster increases from 10 to 2700 a characteristic structure appears near the short-wavelength wing of the resonance line. Thus the analysis of the optical fluorescence spectra of clusters in the VUV region makes it possible to judge the number of atoms in a cluster. Results, similar to those presented in Fig. 11, for other inert gases are contained in Refs. 64–67.

The results of investigations of cluster ions are summarized in the review by A. V. Eletskiĭ and B. M. Smironov.[68] The latest publications concerning this problem are devoted to the mass-spectrometric method for detecting clusters of heavy inert gases in a supersonic flow.[69,70] Direct experimental results confirm the fact that a low-temperature plasma contains supersonic jets of clusters consisting of several to thousands of atoms. Figure 12 shows a fragment of the mass spectra, taken from Ref. 70, of argon, krypton, and xenon clusters. Data on the structure of clusters, the laws of the filling of cluster layers, and the dependence of the dissociation energy and the ionization potential of a cluster on the number of atoms contained in the cluster are presented in Refs. 67–71.

When the number of atoms in a cluster is small the VUV spectrum of the cluster is virtually identical to the spectrum of diatomic molecules. For this reason, great care must be used in analyzing the spectroscopic properties of diatomic molecules in supersonic flows.

3.3. Excitation by a fast-electron beam, decaying plasma

Besides the above-examined methods for producing and investigating VUV spectra of inert-gas dimers, there are several new directions for solving this problem which are not as widely known. We shall briefly examine them.

A quite extensive series of investigations was conducted

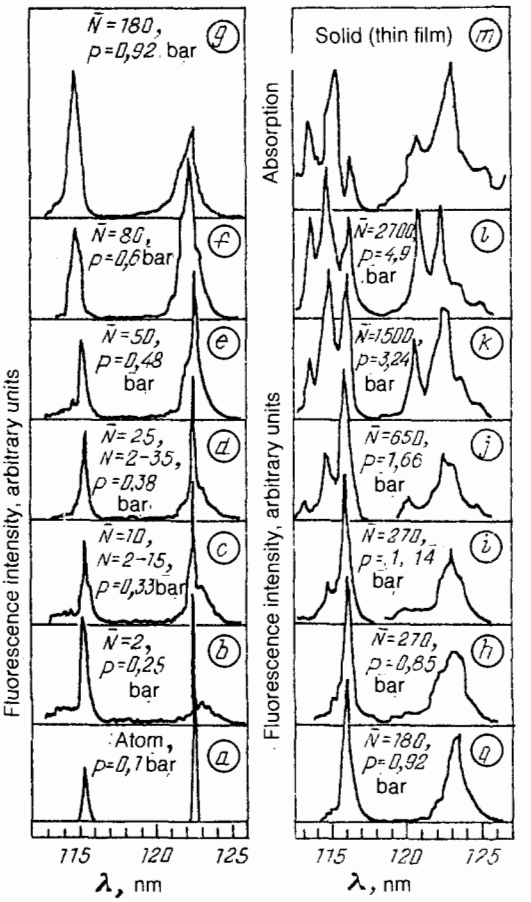


FIG. 11. Fluorescence spectra of krypton clusters with different numbers of atoms.[66]

by a method in which a beam of fast electrons was used to excite the inert gas.[72–76] The large number of different elementary processes occurring in such experiments makes it much more difficult to analyze the results. A list of reactions and their rate constants, used in the experiments of Ref. 75 with electronic excitation of xenon, is given in Table III. In

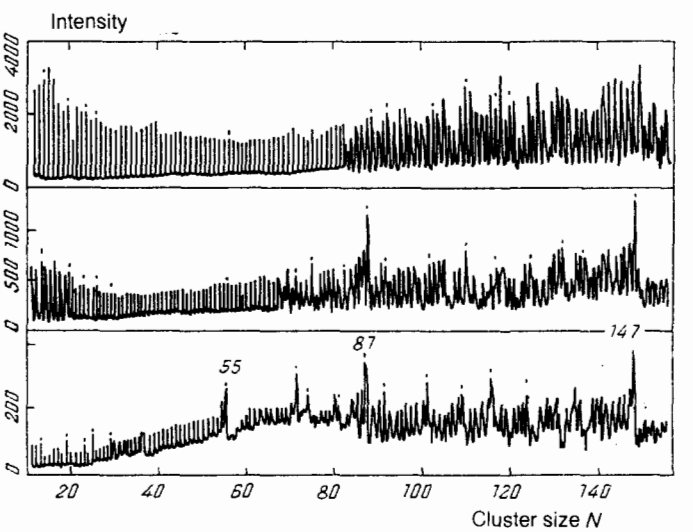


FIG. 12. Fragments of mass spectra of argon, krypton, and xenon clusters with up to 150 atoms. Clusters containing this number of atoms have filled three icosahedral shells.[70]

TABLE III. Reactions taken into account in the kinetic model of excitation of xenon[75] and krypton.[83]

Reaction	Rate constant, reaction cross section
Xe:	
1. $Xe^+ + 2Xe \to Xe_2^+ + Xe$	$2\cdot10^{-31}(300/T_g)^{1/2}$
2. $Xe_2^+ + 2Xe \to Xe_3^+ + Xe$	$6\cdot10^{-32}(300/T_g)^{1/2}$
3. $Xe_2^+ + e \to Xe + Xe$	$2{,}3\cdot10^{-7}T_e^{-0{,}7}$
4. $Xe_3^+ + e \to Xe + 2Xe$	$1\cdot10^{-5}T_e^{-0{,}5}$
5. $Xe^{**} + 2Xe \to Xe_2^{**} + Xe$	$5\cdot10^{-31}(300/T_g)^{1/2}$
6. $Xe_2^{**} \to Xe^{**} + Xe$	$1\cdot10^{8}$
7. $Xe_2^{**} + Xe \to Xe^{*} + 2Xe$	$1\cdot10^{-11}(T_g/300)^{1/2}$
8. $Xe^{*} + 2Xe \to Xe_2^{*(3)} + Xe$	$4{,}4\cdot10^{-32}(300/T_g)^{1/2}$
9. $Xe^{*} + 2Xe \to Xe_2^{*(1)} + Xe$	$2\cdot10^{-32}(300/T_g)^{1/2}$
10a. $e + Xe_2^{*(3)} \to e + Xe_2^{*(1)}$	$1{,}8\cdot10^{-8}$ (T_e = 1 eV)
10b. $e + Xe_2^{*(1)} \to e + Xe_2^{*(3)}$	$4{,}9\cdot10^{-8}$ (T_e = 1 eV)
11a. $Xe_2^{*(3)} + Xe \to Xe_2^{*(1)} + Xe$	$4{,}6\cdot10^{-15}(T_g/300)^{1/2}$
11b. $Xe_2^{*(1)} + Xe \to Xe_2^{*(3)} + Xe$	$1{,}2\cdot10^{-13}(T_g/300)^{1/2}$
12. $Xe_2^{*(1)} \to 2Xe + h\nu$	$2{,}1\cdot10^{8}$
13. $Xe_2^{*(3)} \to 2Xe + h\nu$	$1\cdot10^{7}$
14. $Xe_2^{*(1)} + h\nu \to Xe_2^+ + e$	$2\cdot10^{-18}$ cm^3
15. $Xe_2^{*(3)} + h\nu \to Xe_2^+ + e$	$2\cdot10^{-18}$ cm^2
16. $2Xe_2^{*} \to Xe_2^+ + 2Xe + e$	$8\cdot10^{-11}$
17. $2Xe^{*} \to Xe^+ + Xe + e$	$8\cdot10^{-11}$
18. $Xe_2^{*} + e \to Xe_2^+ + 2e$	$5\cdot10^{-9}$
19. $Xe^{*} + e \to Xe^+ + 2e$	$2{,}7\cdot10^{-9}$
20. $Xe_2^{*} + e \to 2Xe + e$	$4\cdot10^{-9}$
21. $Xe^{*} + e \to Xe + e$	$3\cdot10^{-9}$
22. $Xe_2^{*} + e \to Xe^{*} + Xe + e$	$2\cdot10^{-7}$
23. $Xe_2^{*} + e \to Xe_2^{**} + e$	$3\cdot10^{-7}$
24a. $Xe_2^{**} + e \to Xe_2^{*(3)} + e$	$6\cdot10^{-7}$
24b. $Xe_2^{**} + e \to Xe_2^{*(1)} + e$	$2\cdot10^{-7}$
25. $Xe^{**} \to Xe^{*} + h\nu$	$< 1\cdot10^{6}$
26. $Xe^{**} + e \to Xe^+ + 2e$	$2\cdot10^{-8}$
27. $Xe^{*} + e \to Xe^{**} + e$	$3\cdot10^{-7}$
28. $Xe^{**} + e \to Xe^{*} + e$	$8\cdot10^{-7}$
29. $Xe^{**} + h\nu \to Xe^+ + e$	$1\cdot10^{-18}$ cm^2
30. $2Xe^{**} \to Xe^+ + Xe + e$	$1\cdot10^{-10}$
31. $2Xe_2^{**} \to Xe_2^+ + 2Xe + e$	$1\cdot10^{-10}$
32. $Xe_2^+ + e \to Xe^+ + Xe + e$	$1\cdot10^{-7}$
33. $Xe_2^{**} + e \to Xe_2^+ + 2e$	$6\cdot10^{-8}$
34. $Xe_2^{**} + h\nu \to Xe_2^+ + e$	$1\cdot10^{-18}$ cm^2
Kr:	
1. $Kr^+ + 2Kr \to Kr_2^+ + Kr$	$2{,}4\cdot10^{-31}(300/T_g)^{1/2}$
2. $Kr_2^+ + 2Kr \to Kr_3^+ + Kr$	$3{,}2\cdot10^{-32}(300/T_g)^{1/2}$
3. $Kr_2^+ + e \to Kr + Kr$	$1{,}9\cdot10^{-7}T_e^{-0{,}55}$
4. $Kr_3^+ + e \to Kr + 2Kr$	$4{,}9\cdot10^{-5}T_e^{-0{,}5}$
5. $Kr^{**} + 2Kr \to Kr_2^{**} + Kr$	$1\cdot10^{-31}(300/T_g)^{1/2}$
6. $Kr_2^{**} \to Kr^{*} + Kr$	$3\cdot10^{8}$
7. $Kr_2^{**} + Kr \to Kr^{*} + 2Kr$	$1\cdot10^{-11}(300/T_g)^{1/2}$
8. $Kr^{*} + 2Kr \to Kr_2^{*(3)} + Kr$	$2{,}3\cdot10^{-32}(300/T_g)^{1/2}$
9. $Kr^{*} + 2Kr \to Kr_2^{*(1)} + Kr$	$4\cdot10^{-33}(300/T_g)^{1/2}$
10a. $e + Kr_2^{*(3)} \to e + Kr_2^{*(1)}$	$1{,}78\cdot10^{-8}$
10b. $e + Kr_2^{*(1)} \to e + Kr_2^{*(3)}$	$4{,}60\cdot10^{-8}$
11a. $Kr_2^{*(3)} + Kr \to Kr_2^{*(1)} + Kr$	$2\cdot10^{-15}(T_g/300)^{1/2}$
11b. $Kr_2^{*(1)} + Kr \to Kr_2^{*(3)} + Kr$	$5\cdot10^{-14}(T_g/300)^{1/2}$
12. $Kr_2^{*(1)} \to Kr + Kr + h\nu$	$3\cdot10^{8}$
13. $Kr_2^{*(3)} \to Kr + Kr + h\nu$	$3\cdot10^{6}$
14. $Kr_2^{*(1)} + h\nu \to Kr_2^+ + e$	$1{,}3\cdot10^{-18}$ cm^2
15. $Kr_2^{*(3)} + h\nu \to Kr_2^+ + e$	$1{,}3\cdot10^{-18}$ cm^2
16. $2Kr_2^{*} \to Kr_2^+ + 2Kr + e$	$3\cdot10^{-11}$
17. $2Kr^{*} \to Kr^+ + Kr + e$	$1\cdot10^{-10}$
18. $Kr_2^{*} + e \to Kr_2^+ + 2e$	$3{,}6\cdot10^{-9}$
19. $Kr^{*} + e \to Kr^+ + 2e$	$1{,}9\cdot10^{-9}$
20. $Kr_2^{*} + e \to 2Kr + e$	$1{,}5\cdot10^{-9}$
21. $Kr^{*} + e \to Kr + e$	$9\cdot10^{-10}$

Table III. (continued)

Reaction	Rate constant, reaction cross section
22. $Kr_2^* + e \rightarrow Kr^* + Kr + e$	$1{,}9 \cdot 10^{-9}$
23. $Kr_2^* + e \rightarrow Kr_2^{**} + e$	$2{,}9 \cdot 10^{-7}$
24a. $Kr_2^{**} + e \rightarrow Kr_2^{*(3)} + e$	$5{,}9 \cdot 10^{-7}$
24b. $Kr_2^{**} + e \rightarrow Kr_2^{*(1)} + e$	$2 \cdot 10^{-7}$
25. $Kr^{**} \rightarrow Kr^* + h\nu$	$1 \cdot 10^{6}$
26. $Kr^{**} + e \rightarrow Kr^+ + 2e$	$1{,}9 \cdot 10^{-8}$
27. $Kr^* + e \rightarrow Kr^{**} + e$	$2{,}9 \cdot 10^{-7}$
28. $Kr^{**} + e \rightarrow Kr^* + e$	$7{,}9 \cdot 10^{-7}$
29. $Kr^{**} + h\nu \rightarrow Kr^+ + e$	$8 \cdot 10^{-19}$
30. $2Kr^{**} \rightarrow Kr^+ + Kr + e$	$5 \cdot 10^{-10}$
31. $2Kr_2^{**} \rightarrow Kr_2^+ + 2Kr + e$	$5 \cdot 10^{-10}$
32. $Kr_2^+ + e \rightarrow Kr^+ + Kr + e$	$1 \cdot 10^{-7}$
33. $Kr_2^{**} + e \rightarrow Kr_2^+ + 2e$	$5{,}9 \cdot 10^{-8}$

order to construct a consistent picture of the kinetic processes occurring in the volume with this method of excitation of the inert gas it is necessary to have a large amount of preliminary information about the properties of the plasma which is formed. In order to determine the parameters of the plasma formed as a results of the interaction of the electron beam with the neutral gas, a system of coupled differential equations, which takes into account all elementary processes, is solved. The solution of such equations presents certain difficulties, because of both the large number of processes and the lack of information about the accuracies and temperature dependences of the rate constants. An approach to investigating the properties of xenon plasma on the basis of this method was demonstrated in Ref. 75. Figure 13 shows the time dependence of the rate of pumping of xenon excimer molecules and the fluorescence rate. Both calculations and experimental results are presented. The computed dependences are in satisfactory agreement with experiment.

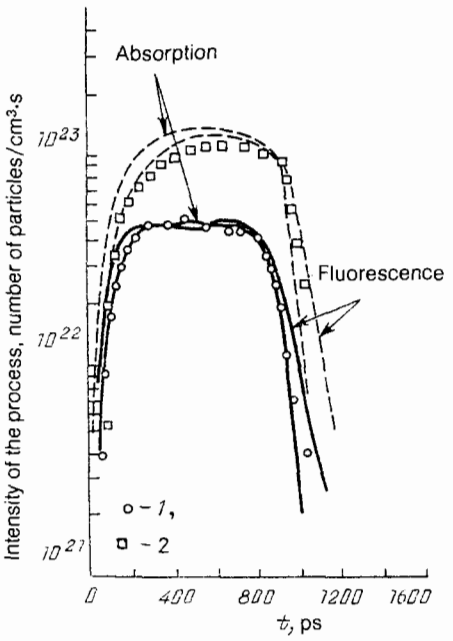


FIG. 13. Change in rate of excitation and fluoresence of xenon excited by an electron beam ($P = 3$ atm). Theory of Ref. 75 (*1*, *2*) and experiment (*1*, *2*) (indices 1 and 2): $j_1 = 5$ A/cm^2, $j_2 = 18$ A/cm^2, $P_1 = 1.4 \cdot 10^5$ W/cm^3, $P_2 = 4.0 \cdot 10^5$ W/cm.[3]

The large number of processes presented in Table III indicates how difficult it is to analyze the mechanism of the processes occurring in a low-temperature xenon plasma. However this quite detailed list of reactions is incomplete, and under certain experimental conditions it may happen that the most significant reactions are those which have been neglected. For example, Table III, which was taken from Refs. 75 and 76, does not contain chemionization reactions in which excited atoms participate. N. B. Kolokolov and his coworkers investigated processes of this type. They indicate that the rates of these inert-gas processes are high. Table IV gives the results of investigations of chemionization processes in inert gases.[77]

Experiments performed in many of the first investigations of decaying plasma have played an important role in understanding the spectroscopic properties of inert-gas dimers and the formation of VUV continua of dimers.[78,79] In these experiments a low-temperature plasma was produced, as a rule, by a pulsed electric discharge. After current ceased to flow through the discharge gap, relaxation processes, resulting in filling of the excited states and formation of molecular ions and excited molecules in three-body collisions, developed in the discharge. The study of the entire range of elementary processes occurring in a decaying plasma made it possible to investigate a large number of processes which directly affect the formation of molecular structures responsible for the emission of VUV continua. There is a large number of new original papers and reviews on this subject,[10,38,78] to which we refer the reader. A deficiency of these publications is that they do not contain any information about VUV emission, without which no analysis of this problem can be acceptable.

3.4. Method of radioluminescence excitation

This method of excitation of the VUV continua of inert gases is discussed in detail in the monograph by G. A. Mikhal'chenko.[80] Radioluminescence excitation of inert-gas dimers is employed in VUV sources of low intensity but good temporal stability. Radiators operating according to this principle consist of gas cylinders which are sealed, degassed, and filled with a purified inert gas and which have windows that transmit VUV radiation. The energy released by the

TABLE IV. Basic characteristics of ionization reactions with participation of excited inert-gas atoms at $T_g = 300$ K (Ref. 77).

Reaction	Rate constant, 10^9 cm^3/s	Yield of molecular ions, %
$He^{*(3)} + He^{*(3)} \rightarrow \begin{cases} He_2^+ + e, \\ He^+ + He + e \end{cases}$	0,9± 0,1	7± 4
$He^{*(3)} + He^{*(1)} \rightarrow \begin{cases} He_2^+ + e, \\ He^+ + He + e \end{cases}$	4,0± 0,5	16± 6
$He^{*(1)} + He^{*(1)} \rightarrow \begin{cases} He_2^+ + e, \\ He^+ + He + e \end{cases}$	4,1± 0,9	—
$Ne^{*(3)} + Ne^{*(3)} \rightarrow \begin{cases} Ne_2^+ + e, \\ Ne^+ + Ne + e \end{cases}$	0,38± 0,04	7
$Ne^{*(3)} + Ne^{*(1)} \rightarrow \begin{cases} Ne_2^+ + e, \\ Ne^+ + Ne + e \end{cases}$	1,3± 0,4	—
$Ar^{*(3)} + Ar^{*(3)} \rightarrow \begin{cases} Ar_2^+ + e, \\ Ar^+ + Ar + e \end{cases}$	1,2± 0,2	5
$Kr^{*(3)} + Kr^{*(3)} \rightarrow \begin{cases} Kr_2^+ + e, \\ Kr^+ + Kr + e \end{cases}$	1,1± 0,2	13 ± 6
$Xe^{*(3)} + Xe^{*(3)} \rightarrow \begin{cases} Xe_2^+ + e, \\ Xe^+ + Xe + e \end{cases}$	1,5± 0,2	12± 4

spontaneous decay of special radioactive substances introduced into the gas volume is transformed, after excitation and ionization of the gas, into energy stored in the excited molecular states which emit VUV continua. Due to the high stability of the energy released by the radioactive decay, the virtually unlimited service life and the autonomy of the power supply, compactness and simplicity of construction, such sources could find application in different autonomous setups, as well as for calibration of VUV radiators. Sources in which the VUV spectra of inert gases are excited in a manner similar to radioluminescence sources are examined in the monograph by Gudzenko and Yakovlenko.[81] In Ref. 81, in particular, the results of investigations of the use of nuclear-pumped active media are summarized. The mechanisms of formation of the emitting states of excimer molecules are qualitatively similar to those realized in radioluminescence sources. The difference lies only in the large amount of nuclear energy supplied to the inert gas and the large volume of the excited gas.

3.5. Investigations of continuous emission in a barrier discharge

A new direction of investigations of VUV continua of inert gases is elaborated in Refs. 82 and 85. Here a special form of a pulsed electric (electrodeless *rf*) discharge with gas pressure of a little less than one atmosphere in the discharge gap is studied. Conditions under which there is virtually no heating of the gas by the electric discharge are maintained in the volume. As a result of the high rate of the three-body process, the excited atoms produced in the pulsed discharge form a system of emitting molecular states. This mechanism of excitation makes it possible to convert with high efficiency the energy of an electric field into VUV emission. The VUV radiation flux consists mainly of the continuous molecular emission, since, as a result of reabsorption, the atomic resonance transitions competing with it are strongly degraded with increasing pressure. This method of excitation has the deficiency that the absolute density of the VUV radiation of the source is low.

4. CHARACTERISTICS OF THE SPECTRA

The basic spectroscopic properties of dimers agree satisfactorily with current ideas about their term structure and the mechanisms of production and loss of the molecules. Nonetheless, a number of features of the spectra have not been unequivocally explained in the literature. It is fundamentally important to study these features and to clarify their physical nature, since inert-gas dimers are an example of the simplest molecular structures in nature and it is very important to understand their molecular properties in order to develop ideas about the physics of molecules. We now analyze the characteristic of molecular spectra of homonuclear inert-gas dimers.

4.1. Helium and neon

The VUV spectra of helium dimers were discovered by Hopfield in the 1930s.[2] In spite of the fact that these spectra have been studied more completely than the spectra of dimers of heavy inert gases, there are a number of features which do not fit into the overall picture of the structure of inert-gas molecules and which must be excited under different experimental conditions. The main difference between the terms of dimers of heavy inert gases from helium terms lies in the fact that there are virtually no purely repulsive states among the potential curves of the excited states of helium. Another feature of these terms is that they contain local maxima—"humps"—at the large internuclear distances of these states. These two features explain, in particular, the specific nature of the excitation of the VUV continua in helium. As is well known,[74,84] the three-body-collision mechanism, which follows the scheme (3), is considered to be the main channel for the formation of excited emitting molecules of heavy inert gases at high pressures.

In the case of helium this method of formation is impeded due to the presence of "humps" in the potential curves. These humps are most likely to be "overcome" in the process of formation of excited molecules if the energies of the colliding atoms, which are capable of forming an excited molecule, are high. However, because the dissociation energy of such a

molecule is low, the molecule is more likely to exist at low gas temperatures. For this reason, radiating helium molecules are produced primarily by creating physical conditions in a low-temperature plasma under which these molecules are formed by recombination of diatomic molecular ions, bypassing the channel of dissociation of excited molecules formed in the recombination reaction. In helium the recombination mechanism in a low-temperature plasma is still disputable,[10,79,85] but the basic conditions for obtaining intense continuous VUV emission from helium have nonetheless been experimentally substantiated and formulated by Tanaka *et al.*[16–19] It has been established reliably that the best results are achieved with the use of pulsed sources of excitation of helium and that continuous VUV emission is delayed with respect to the excitation pulse; the optimal helium pressure in such sources is equal to several tens of torr. These facts fit satisfactorily into a scheme in which excited states of the helium molecule are formed primarily by a recombination process with the participation of the molecular ion, followed by relaxation of the excitation through the molecular states.

An interesting variant method for producing the helium continuum is proposed in Ref. 86. Here the VUV emission was formed by the flowing afterglow of a helium plasma; the discharge parameters and the conditions under which the plasma flows out of the nozzle were chosen so that the main parameters of the plasma of the flowing afterglow would be close to the parameters of the helium plasma in the works of Tanaka *et al.*[16–19] Figure 14 shows the experimental results and emission spectra of a jet of helium plasma. The authors attribute the low intensity of the molecular emission to emission from only the highly excited vibrational states, responsible for the formation of the VUV continuum of helium.

An interesting feature of the VUV spectra of the helium excimer molecule was discovered by Tanaka and Yoshino.[18] Using a high-resolution VUV spectrometer, they observed the vibronic-rotational emission and absorption spectra of He_2 molecules between the states $A^{1,3}\Sigma_u^+$ and $X^1\Sigma_g^+$. They established that the spectroscopic transitions between the same states, observed in emission, give transition frequencies which are different from the frequencies in the absorption spectra. This difference increases as the gas temperature decreases. In the paper it is concluded that spectroscopic transitions in which the Frank–Condon principle breaks down are observed in absorption. Figure 15 shows a fragment of the potential curves of the helium dimer and the spectroscopic transitions illustrating the difference in the emission and absorption spectra. The inclined arrows indicate transitions corresponding to absorption of quanta from the dispersing unbound state into a bound upper state. Since the greatest differences in the emission and absorption spectra are obtained with cooling, this feature of the VUV spectra of helium can be explained by "spreading" of the internuclear distance in the helium molecule in accordance with Heisenberg's uncertainty relation. The effect, observed by Tanaka *et al.*,[17] can be considered as an efficient method for reconstructing the lower repulsive state, since the difference in the energies between separate rotational components in emission and absorption carriers direct information about the ground state of the molecule.

The spectrum of neon excimer molecules in the VUV

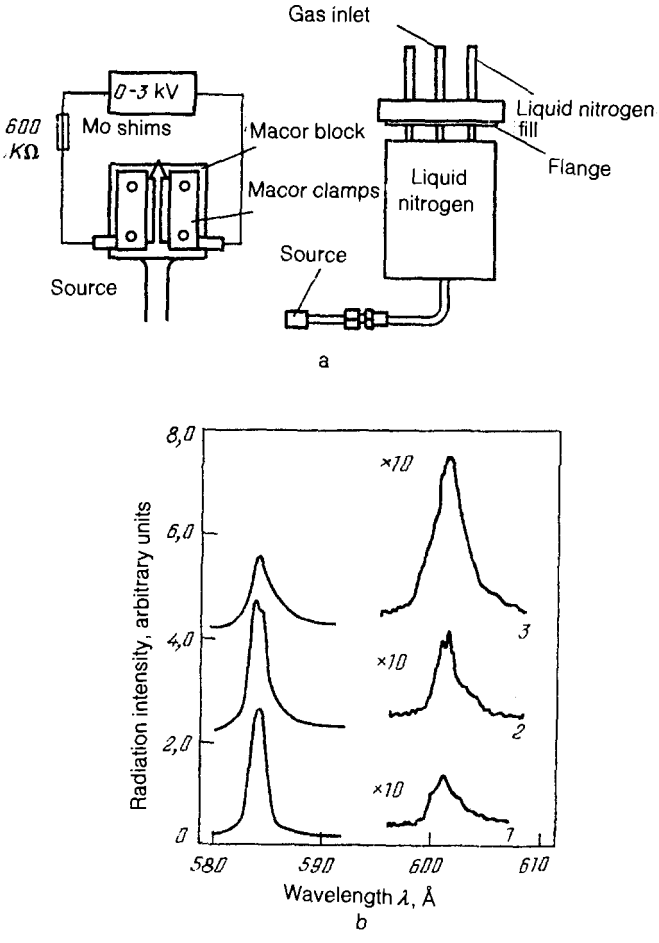


FIG. 14. a) Schematic of the nozzle source for dimer formation. b) VUV spectra obtained in radial configuration. *1*—$P_0 = 60$ kPa, nozzle at room temperature; *2*—$P_0 = 60$ kPa, nozzle at liquid nitrogen temperature; *3*—$P_0 = 70$ kPa, nozzle at liquid nitrogen temperature.

region has not been investigated as fully as the spectra of other inert gases.[15] This is probably because the VUV continuum of neon is not extensively used in practice, because it lies in the region of the spectrum overlapped by the helium continuum and many scientific and applied problems have been solved using the more universal helium source. The form of the VUV spectrum of the neon dimer is similar to the spectra of other inert gases. It has the characteristic feature that excitation in different types of discharges results in some deformation of the spectrum. Figure 16 shows the VUV spectrum of neon at high pressure in a condensed and uncondensed discharges.

4.2. Argon, krypton, and xenon

The spectroscopic properties of heavy inert gases have been studied in detail. Their VUV spectra were investigated in Refs. 72–74 and 87–95 with excitation in high-current arcs,[87] a low-density electron beam,[88,89] a proton beam,[90–95] α particles,[94–95] and in gas-jet sources.[72–74] The conditions under which gases are excited strongly affected the form of the VUV emission spectra. The general ideas about the structure and properties of the electronic terms of excimers satisfactorily described the regularities observed in the emission from the molecules, but a number of their characteristic

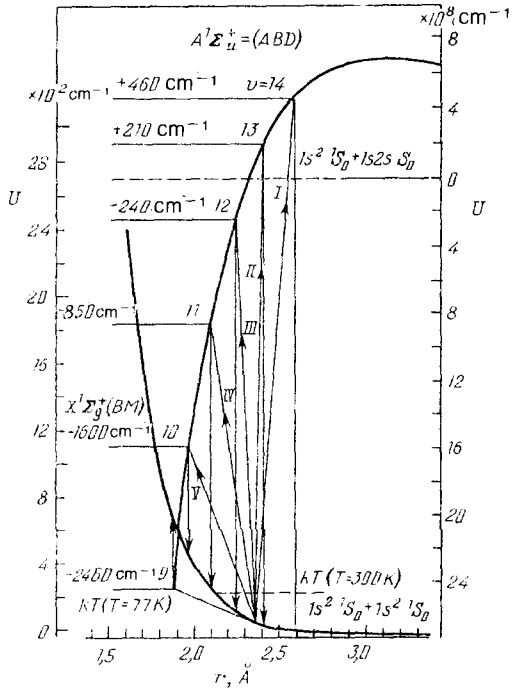


FIG. 15. $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ potential curves for internuclear distances 1.5–3.0 Å for helium.[17]

features have still not been completely explained. This pertains primarily to the weak continuous spectra, lying on the long-wavelength side of the emission from the zeroth vibrational level of the deepest electronically excited states $^{1,3}\Sigma_u^+$ into the lower weakly bound state $^1\Sigma_g^+$. This problem is discussed in a large number of papers, starting with the first investigations and up to now.[4,57,60] One of the most natural conjectures concerning the nature of the appearance of the continua under discussion is the hypothesis that they are associated with the spectroscopic transitions at the minimum internuclear distances, when the molecule is located near the classical left-hand turning points of the vibrational motion. This justification of the observed continua continua was given in Refs. 4, 57, 61, and 96. The difficulties in the interpretation of the continua are explained by the fact they are virtually structureless, they are weak, and they lie in the region where sections of the continuous spectra of different origin are concentrated (for example, recombination spectra). For this reason, it is, in principle, impossible to give a general explanation for all cases of the appearance of continuous emission. In most cases when continua are observed, additional experiments are required in order to identify them reliably. Reference 97 (Fig. 17) is, in this sense, instructive. In Ref. 97 the spectra of heavy inert gases, excited by a powerful electron beam with gas pressures of $\sim 10^5$ Pa, were investigated. It was shown experimentally that the nature of the structureless continua is explained by spectroscopic transitions between the electronic terms of the diatomic molecular ion. Proofs of the validity of this hypothesis seem to be very convincing, just as the justifications presented in Refs. 4 and 96, where the continua arise by a mechanism that is different, but associated with the spectroscopic transitions in the molecule, which correspond to transitions in the region of the classical left-hand turning points of the vibrational motion of the molecule. An unequivocal answer to the question of the emission spectra dimers of heavy inert gases, which correspond to the classical left-hand turning points of the vibrational motion, has not yet been obtained.

Interesting experimental work was performed in Ref. 98 in order to solve this problem. The experimental method employed in Ref. 98 made it possible to "prepare" weakly bound homonuclear dimers of heavy inert gases in the ground state $^1\Sigma_g^+$. The molecules formed were excited with narrow-band ($\Delta\lambda \sim 0.25$ nm) VUV synchrotron radiation. The wavelength of the exciting radiation was chosen so that photoabsorption would fill the highest vibrational states. Observations of the VUV spectra of argon, krypton, and xenon, performed under such excitation conditions, made it possible to observe weak oscillating structures in the bound-free transitions. The spectra were measured by the method of kinetic spectroscopy with a time resolution of ≈ 1 nsec. This made it possible to eliminate the effect of relaxation processes on the redistribution of populations over different vibrational states. In Ref. 98 the observed oscillations were identified as spectroscopic transitions ($^{1,3}\Sigma_u^+ - {}^1\Sigma_g^+$), corresponding to the left-hand turning points of the vibrational motion of the molecule (Fig. 18). The region of the spectrum filled with oscillating structures differs significantly from the spectrum computed theoretically and observed experimentally in different works. In the experiments of Ref. 99 "solar-blind" photomultipliers were employed. For this reason the sections of the spectrum with wavelengths from 200 nm and higher could not be observed. The possible effect of π states on the form of the spectrum investigated was not discussed. It is known that these states have a shallower min-

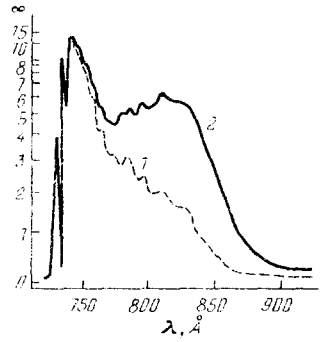


FIG. 16. Densitometer trace of VUV spectrum of neon dimer at high pressure.[15] *1*—uncondensed discharge, *2*—condensed discharge.

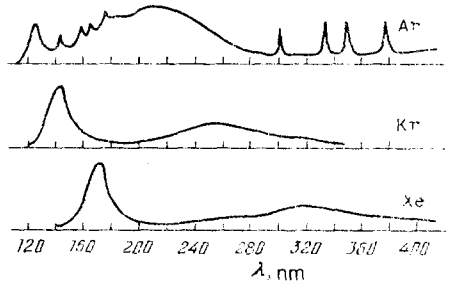


FIG. 17. Argon, krypton, and xenon emission spectra.[97] $P = 1.5 \cdot 10^5$ Pa.

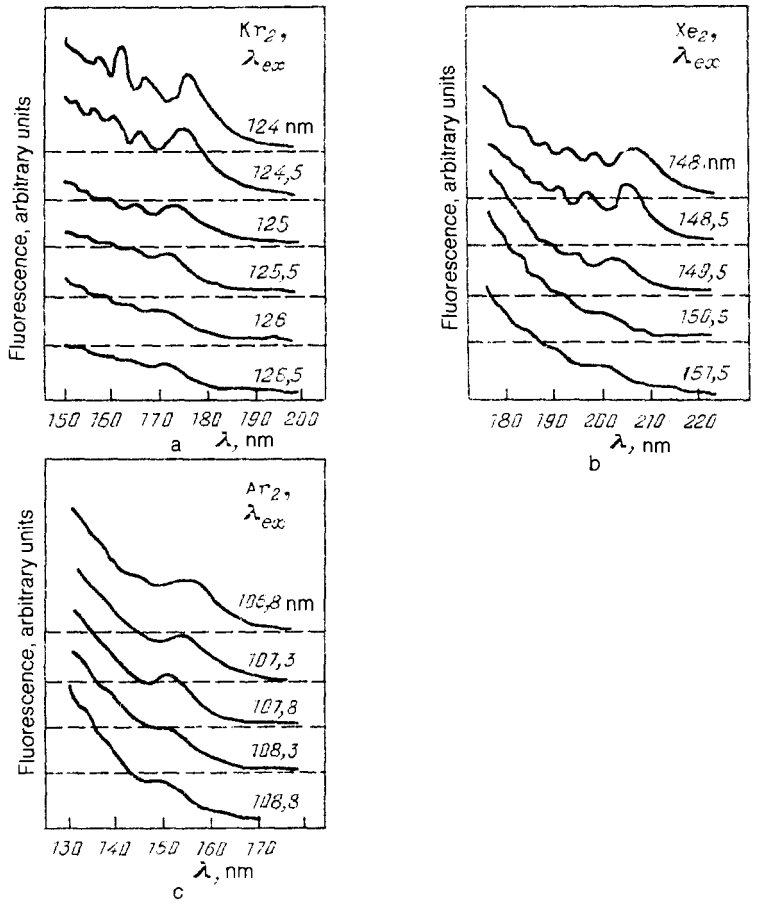


FIG. 18. Oscillating structures observed in Ref. 98 with pulsed excitation of high vibrational states.

imum that Σ states, and the repulsive part of these terms lies at large internuclear distances.

Detailed analysis of the form of the oscillations presented in the work cited raises doubts whether oscillations were identified reliably. The foregoing considerations cast doubt on the results of Ref. 98 concerning the nature of the appearance of the observed spectra.

The discrepancy between the absorption and emission spectra, which was noted in the present review for the helium dimer, is also characteristic for heavy inert gases. The emission and absorption spectra of argon, krypton, and xenon were investigated experimentally in Refs. 100–109. Spectral apparatus with record high resolution was employed. It was established that there are differences in the rotational structure of the emission and absorption spectra of argon.[100–103] The difference in the frequencies in this case is much smaller than the difference in the helium spectrum. The reasons for the discrepancies between the spectra were not discussed by the authors of these papers.

5. LASERS OPERATING ON DIMERS OF HEAVY INERT GASES

Investigations of the spectroscopic properties of dimers of inert gases have not been completed. In the present review we touched only upon individual problems which must be resolved. The wide range of investigations of inert-gas dimers, performed in the last few years, has made it possible, however, to make significant progress in understanding their physical properties and thus to construct a basis for using these properties in the solution of specific practical problems. The problem of building a VUV laser is, in our opinion, the most interesting problem.

The fundamental possibility of building a VUV laser was successfully demonstrated in 1970 by N. G. Basov *et al.*[6] They were the first to obtain lasing on a xenon dimer at the wavelength $\lambda = 173$ nm. An important stage in the study of the spectroscopic properties of inert-gas dimers and the possibility of using inert-gas dimers for producing population-inverted media lasing in the VUV region of the spectrum was the investigation by Mies.[109] Mies focused his attention on the mechanism of formation of the VUV spectrum of xenon dimers. Using the method of reflection, he constructed the theoretical contours of the emission spectra of xenon dimers, corresponding to spectroscopic transitions from the deepest vibrational levels of the excited states into the repulsive part of the lower term. He also obtained the temperature dependence of the deformation and shift of the VUV continuum contour (Fig. 19) which agree qualitatively with the experiments of Ref. 110 (Fig. 20). It was especially important to study the structure and features of the emission band of the molecule in connection with the search for optimal conditions for producing active media in the VUV region. Investigating the spectroscopic properties of the VUV emission of xenon dimers, Mies determined the criterion for a population inversion and the gain of a xenon-dimer laser. According to the data obtained in this work, a population inversion will be achieved in xenon when the concentration of emitting molecules is equal to $10^{18}\exp(-E/kT)$, where E is the en-

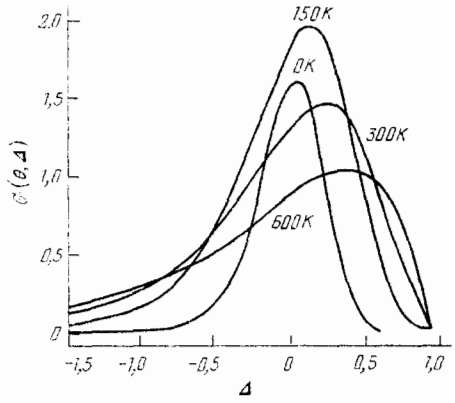


FIG. 19. Emission spectra of Xe_2-molecule calculated for different gas temperatures.[109]

ergy of the final state of the transition. The gain $\varkappa$ is equal to[11]

$$\varkappa = \frac{\lambda^2 A_{21}}{8\pi\Delta\nu} N_v;$$

where λ is the wavelength of the laser transition, $\Delta\nu$ is the width of the gain line, and A_{21} is the transition probability.

For the case of xenon the gain is $\varkappa \sim 6.5 \cdot 10^{-18} N_v$, where N_v is the concentration of molecules in the excited state. The high concentration of emitting molecules, which is necessary for achieving acceptable gains of the active medium imposes strict requirements on the physical conditions, under which lasing of VUV radiation can be achieved. Experiments directed toward obtaining lasing were performed at high gas pressures (several atmospheres) and the gas was excited with a pulsed high-density electron beam. Lasing was demonstrated in Refs. 111–112; the working gas consisted of molecules of argon, krypton, and xenon. A qualitatively different level of realization of an active medium on dimers of heavy inert gases was demonstrated in a recent paper by Canadian physicists.[9] The laser medium consisted of an argon plasma, produced in a pulsed supersonic nozzle, excited by a powerful pulsed discharge. Lasing was achieved at $\lambda = 123$ nm with a gain > 3 cm^{-1}. The pulsed electric discharge, with current strength ~ 1 kA, gave populations of excited molecules of $\sim 10^{16}$ cm^{-3}. The duration of the discharge was equal to 0.2 μs. A diagram of the experimental apparatus and the basic results obtained in Ref. 9 are presented in Fig. 21. In contrast to proceding investigations,

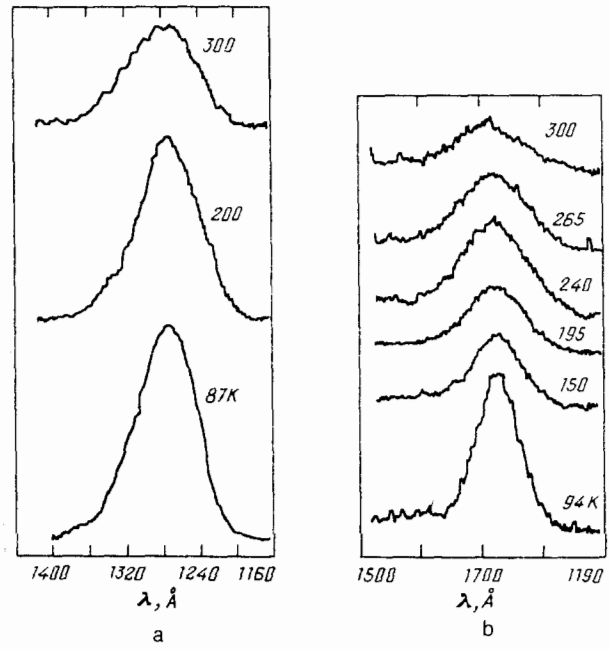


FIG. 20. Second continuum of argon (a) and xenon (b) with different gas cell temperatures.[110]

here it was possible to avoid, by using the physical properties of supersonic jets, high pressures in the active medium which are necessary for more efficient formation of radiating dimers and flow of relaxation processes. This interesting publication is in the form of a quite brief scientific report, and many experimental details as well as the physical conditions realized in this experiment are still unclear, but the high final values of the parameters of the laser and the comparative simplicity of the implementation indicate a deep understanding of the physics of inert-gas dimers. This understanding was made possible by the wide range of dimer investigations performed in the last few years.

CONCLUSIONS

The VUV spectra of inert-gas dimers have been under intense investigation for the last few decades. In the last few years these investigations have concentrated primarily on attempts to create efficient sources of VUV radiation. Ex-

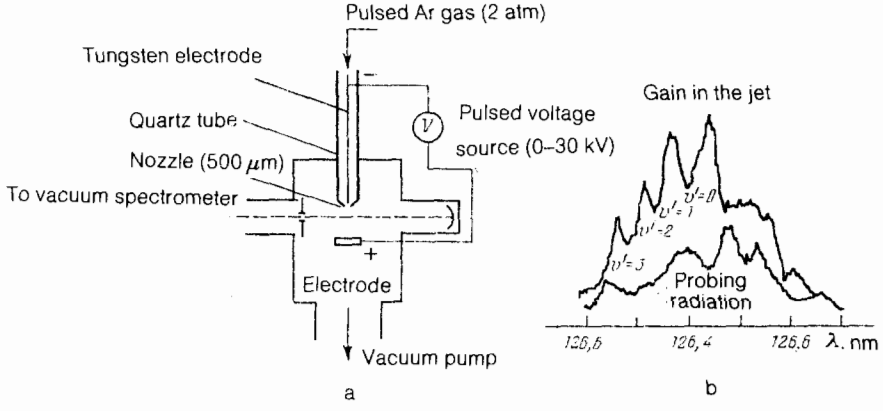


FIG. 21. a) Schematic of experimental setup. b) Spectra of VUV-source, probing an argon jet with and without a discharge.

periments on producing VUV laser radiation, begun by N. G. Basov *et al.*,[6] have led in the last few years to the realization of an efficient and experimentally comparatively simple laser operating on dimers of heavy inert gases.[9] VUV laser radiation has not yet been obtained on the basis of the helium and neon continua, but the very rich information which has been obtained about the structure and properties of the dimers of these gases has made it possible to develop efficient sources of a continuous spectrum in the region where compact alternative laboratory sources of continuous radiation are not available, and the need for such sources has been increasing during the last few years.

Besides its great applied value, the study of inert-gas dimers has made it possible to gain a deeper understanding of the nature of molecular bonds, to show that many physical and spectroscopic properties of dimers fundamentally affect the properties of low-temperature plasma of inert gases, and to understand the basic laws of specific mechanisms of volume deionization of plasma, such as dissociative recombination.[10,11] Investigations of inert-gas dimers have a direct bearing on the problem of the formation and the physical properties of weakly bound polyatomic molecular formations—clusters. Thus a bridge is being constructed between solid-state physics and atomic and molecular physics.

Thus inert gases, which for a long time were considered to be a classical object of atomic spectroscopy, have provided a new stimulus for investigations in molecular physics, the physics of clusters, and solid-state physics.

The range of physical investigations of dimers, performed in the last few years, is extremely wide, and the increasing interest in this subject allows one to hope that in the near future the study of VUV spectra of dimers will bear new fruits both in the solution of applied problems and in deeper understanding of the physical properties of atoms and molecules.

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