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Optical spectra of binary rare-gas mixtures

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Contents

Abstract. The results of experimental and theoretical investigations of the properties of heteronuclear rare-gas dimers are presented. Spectra in the vacuum ultraviolet region received primary emphasis. It is shown that the bulk of the excitation energy stored by the low-temperature plasma of binary mixtures is released by the heteronuclear dimers in a narrow spectral band near atomic resonance lines.

1. Introduction

Optical spectra of rare gases are among the simplest and most well-studied spectra. The study of the structure and properties of their electron shells has played an important part in the formation and development of atomic and molecular theories [1], has been helpful in the solution of the basic structural problems of the microworld [2] and the cosmos [3], and has come to underlie numerous applications. The aspiration to interpret the optical spectrum of helium led the outstanding Soviet physicist V A Fock to introduce a self-consistent field into the theory of the atom, which became an important milestone in the development of contemporary quantum theory, while employing the spectroscopic properties of rare gases has made it possible to realize an entire class of very important practical applications.

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The notion of rare-gas spectra has been considerably extended in recent years due to experimental and theoretical investigations of their binary mixtures. The present review primarily focuses on a consideration of the papers concerned with this subject.

The investigations of the spectra of rare-gas mixtures were largely stimulated by the development of the branch of spectroscopy related to the development of incoherent and coherent radiation sources in the vacuum ultraviolet (VUV) region. Beginning with the first steps of VUV spectroscopy progress, wide acceptance was gained by laboratory sources of monochromatic VUV radiation, the so-called resonance lamps harnessing the radiation of resonance-excited rare-gas atoms. While offering a number of advantages, these radiation sources have fundamental drawbacks. In particular, attempts to increase the power of monochromatic radiation by raising the working gas pressure result in the effect of resonance radiation 'trapping', in a reduction of the effective radiative transition probability, and the consequential decrease in monochromatic radiation intensity. As the pressure grows, an increasingly large fraction of resonance-excited atoms transforms, primarily through three-body conversion, to excited diatomic rare-gas molecules (dimers). The efficiency of this transformation is high, increasing proportionally to the pressure squared of the working gas. Therefore, the energy of resonance-excited rare-gas atoms converts to the energy of excited dimers. As is well known, rare-gas dimers belong to the class of molecules termed excimers — their ground, unexcited state is unbound. Spectroscopic transitions from an upper bound electronic term to the lower repulsive term are responsible for the emission of broad molecular continua that are practically structureless spectra. It turned out that 'typically atomic' rare gases in excited states behave like the molecular ones, radiating intense continuous spectra. Beginning with the 1930s, continuous VUV radiation sources based on the

short-wave radiation of rare-gas excimer molecules have received wide acceptance. The nature of these spectra, their properties, and the applications reliant on these properties were the subject of considerable literature [4 – 11].

Interest in the spectra of rare-gas mixtures has quickened in recent years. The attraction of this intriguing subject arises from the fact that heteronuclear dimers produced in the low-temperature plasma of gas mixtures convert the energy stored by homonuclear dimers into narrow-band VUV radiation with high efficiency. In this case, the bulk of the energy is accumulated by homonuclear dimers and is next transformed to the narrow-band radiation of heteronuclear dimers. The investigation of this chain of processes is of considerable scientific interest which goes beyond the scope of the present review. It involves the necessity of studying the term structure of heteronuclear molecules, investigating the mechanism of their production and excitation, and optimizing the output radiation parameters.

Apart from the purely scientific appeal of this subject, the attention focused on the spectra of mixtures is explained by the fact that rare gases in the majority of practical applications are, as a rule, employed in mixtures with other gases. Sasaki et al. [12], for instance, set themselves the task of developing the most efficient coherent and incoherent VUV radiation sources by taking advantage of the physical properties of plasmas created in rare-gas mixtures. Employing the radiative properties of low-temperature plasmas produced in rare-gas mixtures makes it possible to broaden the spectral region of ultraviolet emission continua [13]. The development of a plane television screen through the use of the VUV emission of rare-gas mixtures in so-called display panels is considered in Refs [14 – 16]. Rare-gas mixtures are also employed in high-power industrial ozonizers and high-voltage switches [15].

The above list of applications does not nearly exhaust the examples of practical uses of the physical properties of rare-gas mixtures, but even the above enumeration demonstrates the diversity and originality of the problems being solved. In each case under consideration, advantage is taken of various physical properties of rare-gas mixtures. Despite the wide employment of low-temperature mixed gas plasmas in practical applications, the majority of scientific publications concern the description of the physical properties of pure rare-gas plasmas. Therefore, the description of the properties of low-temperature plasmas in simple mixtures is the problem that should be solved first of all. The time has come to systematize the data on the structure and properties of heteronuclear rare-gas dimers, which are indispensable when pursuing basic research as well as numerous practical applications.

The present review discusses only the works performed during the last decades, which are devoted to the investigation of the term structure and spectra of binary rare-gas mixtures. Much consideration is given to VUV spectra, the study of which has been addressed by many researchers in the hope of developing efficient short-wave radiation sources, including lasers.

2. Emission spectra of heteronuclear ions

Experiments encompassing the studies of the spectra of excited rare gases and their mixtures are among the most traditional ones. Various techniques were used for the excitation of the active volume filled with rare-gas mixtures of varying percentage. In early investigations, the most interesting and unexpected results were obtained in the study of mixtures where the gas concentrations were close in magnitude and the total gas pressure ranged from several torrs to several hundred torrs. In this case, the best results were achieved for the most part with the use of 'hard' excitation techniques.

Among the first systematic and purposeful original papers dedicated to the study of unusual emission spectra of the mixtures, mention should be made of Ref. [17] which considered the spectra of binary helium – neon mixtures in the 360 – 700-nm wavelength range. The high-purity gases (the level of uncontrollable impurities was, according to the authors' estimate, within 10^{-5}%) were excited in the cathode region of a glow discharge at a pressure of 10 Torr and a current of 10 mA. Along with the well-known and much-studied atomic lines of helium and neon, band spectra of molecular helium [18], and the lines of sputtered molybdenum (the cathode material), the recorded emission spectrum of the mixture contained two rather broad unknown bands. They occupied the wavelength ranges from 427.0 to 423.5 nm and from 414.4 to 396.4 nm, with emission peaks located near 423.7 and 410.1 nm. A distinctive feature of these bands consisted in the fact that their origin was impossible to attribute to either pure helium or pure neon. In the view of the authors of Ref. [17], the unknown bands could belong only to a molecule involving the atoms of helium and neon, most likely to the heteronuclear diatomic HeNe molecule. Unfortunately, the authors failed to specify the electronic terms that gave rise to the spectroscopic transitions corresponding to the observed bands. Using an idem experimental technique, the same authors were soon able to record two unknown bands in the 50%Ar + 50%Xe mixture [19]. The spectral bands possessed a sharp long-wavelength limit and peaks near 508.1 and 496 nm. As in the previous case, a conclusion was drawn that the unknown bands belong to the heteronuclear ArXe molecule, the electronic terms of the observed spectroscopic transition remaining unspecified, once again. A portion of the densitogram of the spectrum taken in Ref. [19] is depicted in Fig. 1. The emission spectrum is a typical molecular band, but the nature of its origin is, in the authors' opinion, unknown. Neither the atomic argon terms nor the xenon terms could be the term asymptotes that formed the spectrum.

Von Friedl [20] recorded 'mysterious' emission bands of several gas mixtures, including the spectra belonging to the binary mixtures of krypton and xenon, which were obtained for the first time. The gas mixtures were excited by a fast electron beam (50 keV). A new intense band with a sharp long-wavelength limit located near 495 nm was observed in the krypton – xenon mixture. The earlier observed spectra of an argon – xenon mixture were also given in that paper. Two new bands with emission peaks at 550 nm and 510 nm were recorded either. Using the same technique of gas mixture excitation, von Kugler [21] analyzed the visible spectra radiated by different binary gas mixtures, including the Ar-Xe, Ar-Kr, and Kr-Xe mixtures. The inferences of Refs [17 – 20] about the presence of new emission bands in the Ar-Xe and Kr-Xe mixtures were amply borne out by the results obtained. In addition, bands belonging to the Ar-Kr mixture were likewise discovered here. Figure 2 shows the spectra obtained in Ref. [21]. The care taken in the performance of the experiments allowed the authors of Refs [17 – 21] to state with assurance that all new emission

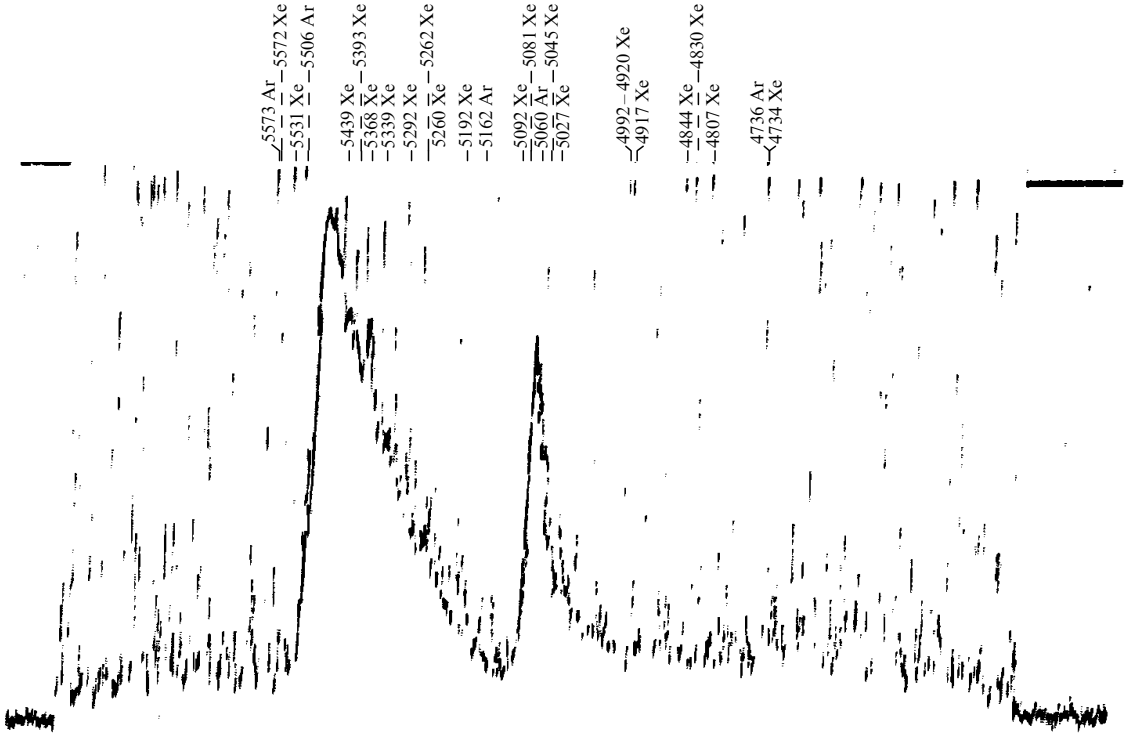

Figure 1. Portion of the densitogram for the spectrum of the binary mixture of argon (50%) and xenon (50%), obtained in Ref. [19]. In the view of the authors, two clearly visible molecular bands could not be attributed to either the presence of an uncontrollable impurity or the molecular transitions of pure xenon or argon.

bands belonged to diatomic heteronuclear molecules. It was shown that they could not be ascribed to any other molecules present in the volume under investigation as uncontrollable impurities. Nevertheless, in Ref. [21], as in the previous case, the electronic terms explaining the origin of the observed new emission bands were not yet specified.

A qualitatively new step in the study of the visible spectra of heteronuclear molecules was made by Tanaka et al. [22], who explained the nature of the origin of the spectra of binary mixtures. The authors of Ref. [22] studied the emission spectra of discharges of various types: pulsed and continuous arc discharges, the positive column and cathode region of a d.c. discharge, a hollow cathode discharge, as well as microwave and high-voltage Tesla discharges. The new unidentified bands were found to emerge primarily for a high electron temperature in the volume under investigation, specifically in the pulsed arc discharge, in the cathode region of a glow discharge, and in the hollow cathode discharge. Isolated bands were observed in the microwave discharge and in the Tesla discharge. No new bands were detected in the continuous arc discharge and in the positive column of a d.c. glow discharge, where the electron temperature is lower than in other cases investigated.

As early as 1959, it was hypothesized [19] that the observed bands must be related to ions rather than to neutral particles. The observations made in Ref. [22] confirmed this assumption. Having performed systematic measurements of the band positions and structure, and having compared them with the structure of ion terms, the authors of Ref. [22] arrived at the following conclusion about the origin of the new molecular bands. The spectra under discussion can be attributed to the electronic transitions between ionized heteronuclear molecules, namely those involving charge transfer from one atom of the molecular ion to another according to the scheme

$$A^+B \Leftrightarrow AB^+ ,$$

where A, B and A^+, B^+ are the rare-gas atoms and ions, respectively, and AB^+ is the molecular ion comprising the atom A and the ion B^+.

By way of example, Fig. 3 shows some electronic terms of excited helium and neon atoms, as well as the terms of unexcited singly charged ions. Also shown here is the schematic of the origin of the bands corresponding to the transition

$$He^+Ne \Leftrightarrow HeNe^+ .$$

The wavelengths calculated from the energy difference between the He^+ ion state and two Ne^+ ion states are equal to 410.15 and 423.73 nm. The experimentally examined positions of the emission peaks in the corresponding bands are 409.8 and 423.6 nm, which agree with the calculated values to within a fraction of a percent. A similar agreement was obtained by the authors of Ref. [22] for other atomic pairs, as well. The experimental wavelengths of emission band peaks for all rare-gas pairs investigated are collected in the table given in Ref. [22].

Figure 4 is a schematic representation of the main electronic terms and the spectroscopic transitions between them, which explain the origin of the new spectra observed in Refs [17–22]. From the experimental results given in Ref. [22] one can see that the unusual bands in different spectral regions emerge in marvelous agreement with the results of calculations based on the determination of the energy difference between the ionic states of the mixture atoms. The results of these calculations coincide with the observed

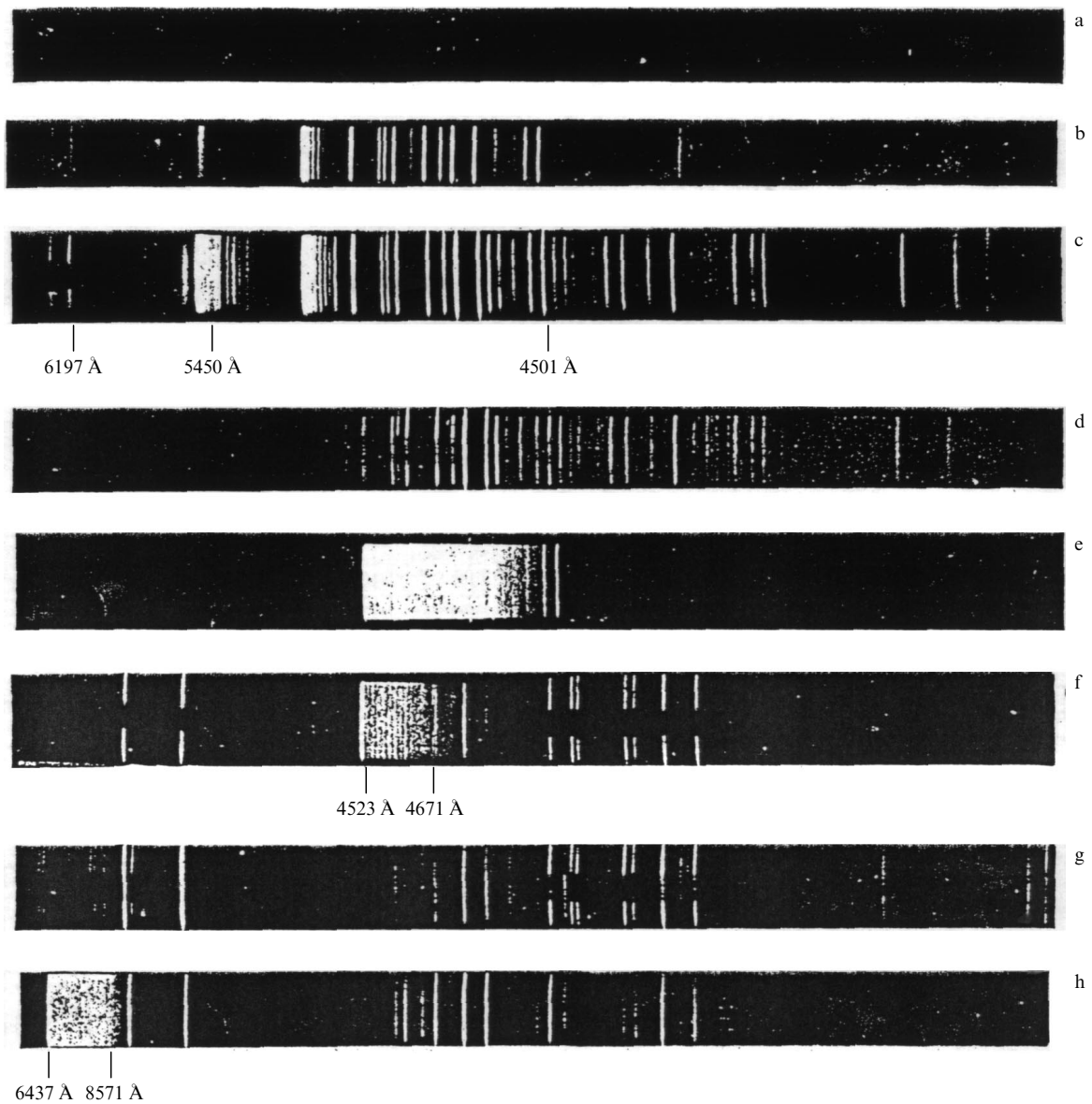

Figure 2. Spectra of argon, krypton, xenon, and their binary mixtures obtained in Ref. [21]: (a) Ar (100 Torr); (b) Ar (180 Torr) + Xe (20 Torr); (c) Ar (20 Torr) + Xe (180 Torr); (d) Xe (200 Torr); (e) Kr (80 Torr) + Xe (70 Torr) (the band was overexposed); (f) Kr (80 Torr) + Xe (70 Torr); (g) Kr (200 Torr); (h) Ar (100 Torr) + Kr (200 Torr). The molecular bands depicted in Figs (b, c, e, f, h) belong, in the view of the authors of the paper, to heteronuclear dimers. The terms between which there occur molecular transitions were not specified in the above paper.

spectral regions of the occurrence of these bands to within several percent. Apart from that, our attention is drawn to the fact that the energy differences of the ionic states coincide with the energy differences of the emission bands. The above coincidences cannot be regarded as accidental: they bear out the idea of the authors of Ref. [22] that the nature of the emission bands is related to the $A^+B \Leftrightarrow AB^+$ type transitions.

Therefore, Tanaka et al. [22] provided a well-reasoned interpretation of the nature of the origin of the molecular bands which had remained inexplicable for a long time. The mysterious bands emitted by binary rare-gas mixtures were shown to arise from the spectroscopic transitions between different states of heteronuclear molecular ions. Subsequent papers [23 – 25] confirmed these conclusions; they also adhered to this viewpoint and evolved the thesis about the origin and properties of the molecular bands described. So far, the findings of these works have not been directly embodied in practical applications, but the implications they have for understanding the nature of emission in mixed rare gases, as well as the structure and properties of heteronuclear molecules, are difficult to overestimate.

3. Vacuum ultraviolet emission continua of heteronuclear dimers

Of all the emission spectra of heteronuclear dimers, the broadband VUV spectra have long been known and comparatively well studied [26 – 32]. These spectra are radiated near the atomic resonance line of the heavier atom in the mixture, on its long-wavelength side. The continua of heteronuclear molecules are several nanometers in width. The nature of the origin of these spectra was explained in Refs [26 – 32]. The spectra were shown to arise from the spectroscopic transitions from the bound excited state of heteronuclear molecules to the repulsive part of the ground state term, much as it takes place in homonuclear dimers (see,

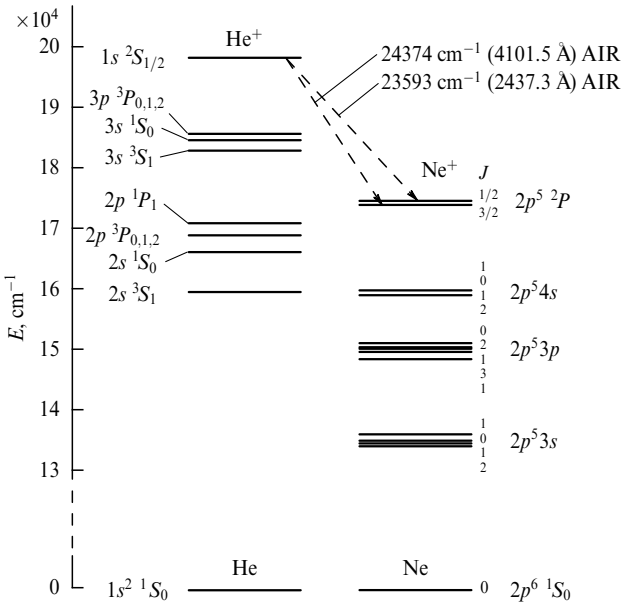

Figure 3. Energy levels of helium and neon atoms (the highest excited states of helium and neon are omitted). The authors of Ref. [22] pointed out for the first time that the molecular bands observed in the helium–neon mixture under investigation can be attributed to $AB^+ - BA^+$ type transitions between ionized heteronuclear molecules. On the assumption that the dissociation energies of the He^+Ne and $HeNe^+$ molecular ions are equal, the presumptive wavelengths of the transitions between the ground states of the heteronuclear ions He^+Ne and $HeNe^+$ were calculated from the energy difference of the unexcited atomic ions He^+ and Ne^+. The calculated wavelengths coincide with the experimentally examined wavelengths to within a fraction of a percent. E is the energy, and J is the level quantum number. Shown at the right top of the diagram are the air wavelengths.

for instance, Ref. [5]). Figure 5 displays the emission spectrum of a barrier discharge in a krypton–xenon mixture, which was borrowed from Ref. [33]. The pulsed barrier discharge was excited in the gas mixture which filled a sealed-off tube of rectangular section with a magnesium fluoride window. The discharge operated between the tube walls, with the metal electrodes being tightly pressed against the outer side of the tube. The electric power was supplied from a high-voltage sinusoidal wave generator at a frequency of 20 kHz. Not enlarging on the properties of this kind of discharge, which is one of the most efficient ways of exciting excimer molecules, we note the following. For a total mixed gas pressure of 400 hPa and a xenon concentration of 0.2%, the continuum of the heteronuclear $KrXe^*$ molecule prevails (with an intensity peak near 156 nm). Increasing the impurity concentration from 0.4 to 1% results in a rise of the continuum intensity and in a simultaneous redistribution of the emission energy in favor of the continuum with an intensity peak in the 172–175 nm range. The spectrum with an intensity peak in this range belongs to the homonuclear dimer of xenon. It is pertinent to note that the emergence of broadband heteronuclear molecular spectra is characteristic of all techniques of mixture excitation for concentrations of the heavier rare-gas impurity above 0.1% and a total binary mixture density of more than several dozen torrs.

The processes responsible for the emergence of the broadband VUV heteronuclear molecular spectra have been discussed in considerable detail in many papers (see, for instance, Refs [28–34]). The excitation mechanism of these spectra in low-temperature plasmas of gas mixtures is qualitatively clear. It involves a chain of elementary processes leading to the excitation of parent gas atoms at the first stage. Owing to three-body conversion processes, homonuclear dimers radiating broad, well-known continua arise at later stages. Then, the excited atoms and molecules of the parent gas partly lose the excitation energy in collisions with impurity atoms. At the final stage of spectrum transformation, the excited impurity atoms transform to a heteronuclear molecule. This sequence of reactions is schematically represented as follows:

$$A^* + A + A = A_2^* + A\,, \tag{1}$$

$$A_2^* + B = B^* + A + A\,, \tag{2}$$

$$B^* + A + A = B^*A + A\,. \tag{3}$$

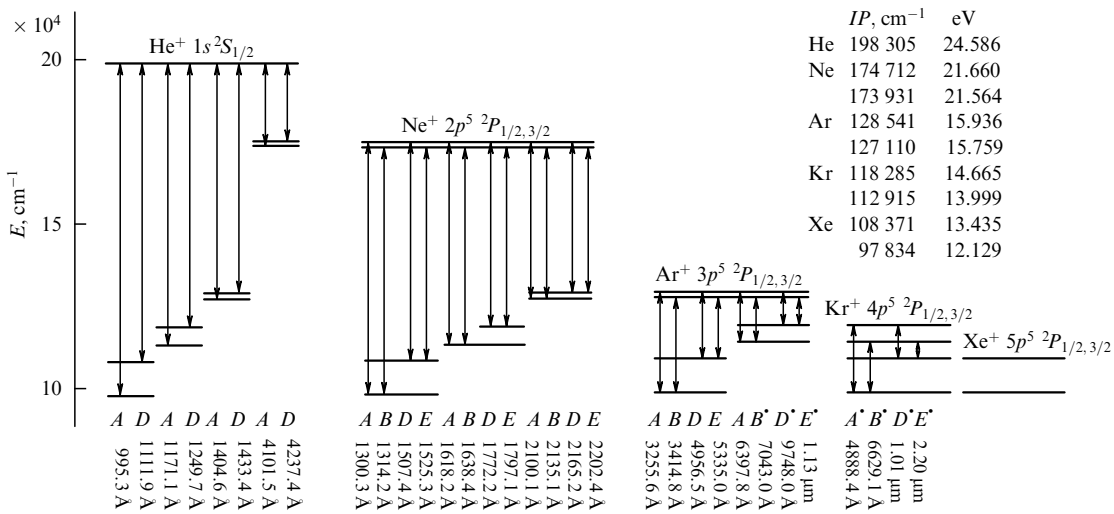

Figure 4. Diagram and table of rare-gas atomic ionization potentials IP and the wavelengths corresponding to ionization potential differences between pairs of atoms. Indicated in the diagram are the wavelengths of all possible pair combinations of rare-gas ions. A, B, D, E — molecular band types introduced by the authors of Ref. [22] (superscript black dots mark the bands predicted by the authors and not discovered experimentally). (Data were taken from Ref. [22]).

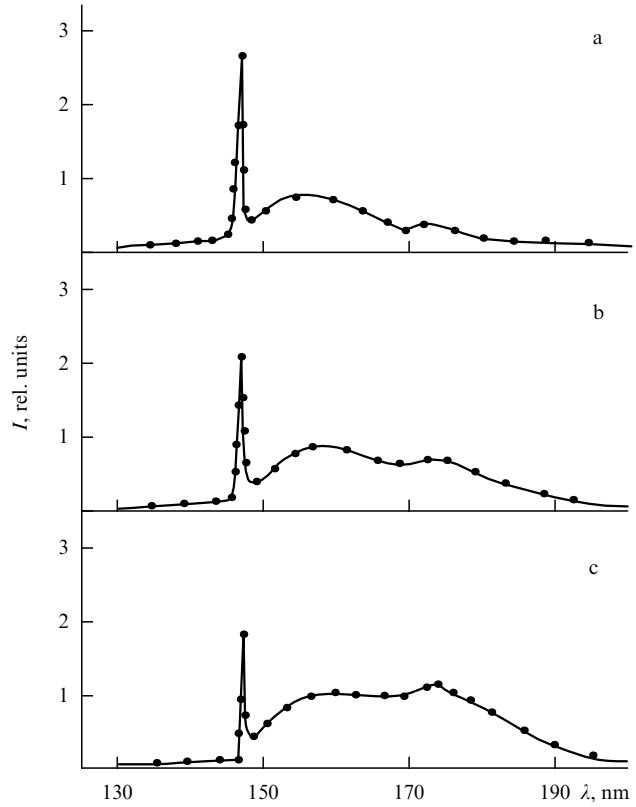

Figure 5. VUV spectrum of the krypton – xenon mixture excited in a barrier discharge [34]. The total mixture pressure is 400 hPa, the concentration of xenon impurity is 0.2% (a), 0.5% (b), and 1% (c). The broadband spectrum of the mixture consists of two overlapping continua: that with an intensity peak at 150 – 160 nm, belonging to the heteronuclear KrXe* molecule, and the continuum with an intensity peak at 170 – 175 nm, belonging to the homonuclear Xe_2^* molecule. Raising the impurity density from 0.2 to 1% has the effect that the excitation energy stored by excited krypton 'flows', via the excited state of the heteronuclear KrXe* molecule, to the continuum radiation of the homonuclear Xe_2^* dimer.

Here, A^*, A, and A_2^* are the excited atoms, unexcited atoms, and homonuclear dimers of the parent gas, respectively, while B^*, B, and B^*A are the excited atoms, unexcited atoms of the impurity (the heavier atom), and the heteronuclear dimers, respectively. It is likely that the heteronuclear molecules can also be produced in the reaction

$$A_2^* + B = B^*A + A\,.$$

Apart from the 'obvious' sequence of reactions (1 – 3) responsible for the production of the radiating heteronuclear B^*A molecules, several papers discuss more complex chains of processes that have an effect on the formation of excited heteronuclear molecules. For instance, more than 30 elementary processes were considered by Kawanaka et al. [32] in the kinetic analysis of the processes leading to the emission of broad heteronuclear molecular spectra in an Ar-Kr mixture. The scheme of kinetic processes [34] that account for the dynamics of excitation and deexcitation of the VUV barrier-discharge spectrum in a krypton – xenon mixture numbers more than 100 elementary processes. In this case, the system of transient kinetic balance equations for the determination of plasma component densities is of the form

$$\frac{\mathrm{d}N}{\mathrm{d}t} = F_i^+ - F_i^-\,, \qquad (4)$$

where i is the number of plasma components, while F_i^+ and F_i^- are the total plasma-component population and depopulation fluxes. Invoking a large number of reactions in the solution of kinetic equations that describe the dynamics of the processes occurring in a mixed gas plasma makes it possible to obtain a better agreement between calculations and experiment. However, the seemingly efficient use of as many elementary processes as possible may prove to be unjustified. The reason lies with the uncertainty in the rate constants of the elementary processes employed in the calculation. The approach outlined above is efficient only when all the rate constants of the elementary processes included in the model are known with the requisite accuracy. Otherwise, the solution may yield distorted information on plasma component concentrations, and the difficulties associated with the work with large systems of differential equations prove to be unjustified.

Therefore, the origin of broadband continua is qualitatively clear and is satisfactorily substantiated by theoretical evaluations.

4. Narrow-band vacuum ultraviolet emission spectra of binary rare-gas mixtures

Going from the well-studied intense broadband VUV spectra of heteronuclear molecules to the discussion of intense narrow-band VUV spectra investigated in recent years, we should first of all note the following. Modern notions of the nature of intense narrow-band VUV emission spectra arising in an excited gas mixture near the resonance lines of rare gas atoms were formed during the last decades. A start on the systematic investigations was made by the authors of Refs [35 – 37], who studied the VUV spectra of binary rare-gas mixtures in the 1970s. Along with the well-known broadband spectra of heteronuclear molecules, mentioned in Section 3, they discovered intriguing features in the VUV emission spectra of the mixed gases. These features were recorded when a minor addition (less than 0.1%) of a heavier gas was used as the admixture. The above-cited works made a large contribution to the understanding of the nature of the observed spectra and marked the beginning of large-scale investigations of this interesting effect by many scientific groups. The VUV spectrum radiated by the gas mixture was shown, practically irrespective of the excitation technique (the investigations employed excitation by electric discharges, electron and heavy-particles beams), to be radically different from the spectrum of a pure gas, even though the small concentration of the heavier-gas admixture introduced into the volume. The well-known continuous VUV spectrum emitted by homonuclear molecules, which was typical of pure rare gases, showed a sharp decrease in intensity. Near the resonance line of the impurity atom there simultaneously emerged a strong narrow-band radiation which was long mistaken for the radiation of resonance line wings.

Figure 6 illustrates one of the results of Ref. [35] — a portion of the VUV emission spectrum excited in krypton containing a small addition of xenon. The admixture of xenon (0.25 Torr) in krypton, which was equal to about 0.04%, nevertheless resulted in a significant change in the emission spectrum. In lieu of a broad, virtually structureless continuum of the homonuclear krypton molecule, extending from 120 to 180 nm and having an intensity peak at about 150 nm [29], they observed a significant emission peak localized in the vicinity of the 146.96 nm resonance line of xenon. The

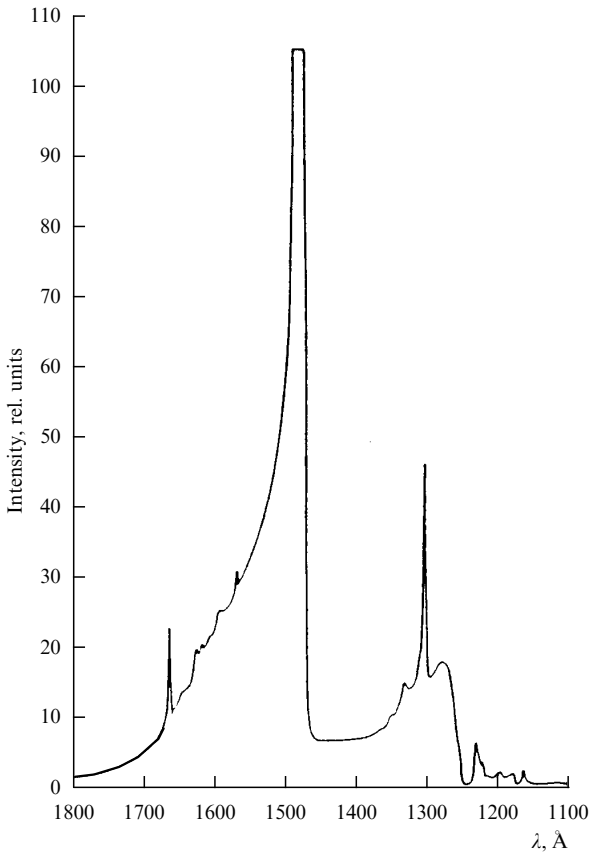

Figure 6. Spectrum of a krypton – xenon mixture [35]. The total pressure of the mixed gas is 600 Torr, and the xenon impurity concentration is 0.04%. The drawing demonstrates radical changes in the krypton spectrum upon addition of a small admixture of xenon. Instead of a continuous structureless continuum, the spectrum is dominated by a narrow-band emission, which the authors mistook for the radiation of resonance xenon lines.

intensity of the spectrum near 147 nm proved to be so high relative to other parts of the VUV spectrum that the authors of the above-cited paper had to employ a saturated operating mode of the recording system near 147 nm in order to demonstrate the variation of the broadband spectrum of the homonuclear krypton dimer in a wide wavelength range.

The emission spectra of other rare gases with an admixture of xenon yield similar results [32]. Specifically, the continuum of the parent gases of a mixture are hardly present, while the intensity peak near 147 nm is prevalent. Detailed investigations into the VUV emission spectra of other rare-gas mixtures [32 – 38] provided support for the exposed rule. The continua of the homonuclear molecules of the parent gas with small additions of heavier gases decay, while the narrow-band spectra localized in proximity to the resonance lines of the impurity atoms rise in intensity. The authors of Refs [35 – 37] hypothesized that the excitation energy in the mixtures investigated is transferred from the atoms and molecules of the parent gas to the impurity atoms of the heavier gas. In this case, the radiation energy of the mixture transforms from the broadband homonuclear molecular radiation of the major gas to the narrow-band radiation localized in the wings of the resonance line of the impurity atom. The effective cross section for the excitation energy transfer, derived by analyzing experimental data, was found to be equal to $10^{-14} - 10^{-13}$ cm^2 (i.e., 2 – 3 orders of magnitude greater than the conventional gas-kinetic cross section).

The recognition that the observed phenomenon has important implications for science and applied areas drew to its study the attention of numerous researchers. The aim of the works that soon followed [38 – 41] was a detailed study of the mechanism of excitation energy transfer from the atoms and molecules of the parent gas to impurity atoms. Unlike the pioneering works [35 – 37], not only did they analyze the form of the mixed gas spectra in this case, but they also conducted kinetic investigations which made it possible to calculate the energy transfer probability by analyzing the dynamics of the concentration variations for different plasma components. By and large, these works lent support to the main conclusions about the high efficiency of deactivation of the parent gas on addition of low-concentration impurities of a heavier rare gas.

Of all the numerous data obtained, the high efficiency of transformation of the energy accumulated by homonuclear molecules into a narrow-band radiation proves to be the most attractive fact. This gives grounds to employ it in the development of high-efficiency VUV radiation sources, including lasers. In recent years, the solution of the last-named problem has become the subject of investigation for many scientific groups.

5. Vacuum ultraviolet absorption spectra of binary rare-gas mixtures

Practically simultaneously with the study of narrow-band emission spectra (with a lag of about five years), recording was made of absorption VUV spectra of binary mixtures with then unrivaled spectral resolution. The absorption spectra were investigated by Y Tanaka's and M Castex's groups [42 – 48]. The numerous and careful experiments described in these publications embrace all possible rare-gas pair combinations. As a result of the investigations conducted, narrow bands located near the resonance lines were discovered in the VUV absorption spectra along with other features. The high quality of the available spectra (use was made of classical VUV diffraction grating spectrometers with a spectral resolution at a level of ~ 0.01 Å), a comparison of the resultant absorption spectra of binary mixtures with the absorption spectra of pure gases, and a careful analysis of experimental evidence allowed the authors to soundly reach the following important conclusion. All narrow-band structures in the neighborhood of the resonance lines belong to heteronuclear dimers — diatomic molecules consisting of different rare-gas atoms. By way of example, Fig. 7 displays the VUV absorption spectra of xenon – helium and neon – argon binary mixtures [44]. Only the spectra lying near the first resonance line of xenon ($\lambda = 129.559$ nm) are given here; the xenon pressure in a 20-cm long absorption cell was 0.1 Torr, and the pressures of the other gases were 6, 162, and 486 Torr. The use of high-resolution instruments in combination with measurements of the spectra for different lengths and temperatures of the absorbing media enabled the discovery and tabulation of the fine structure of the narrow absorption bands that show up in the spectra of the mixtures of rare gases in the vicinity of their resonance lines.

The observed narrow-band absorption spectra of the binary gas mixtures were not attributed for long to any specific spectroscopic transitions in heteronuclear molecules due to the absence of reliable data on the excited states of

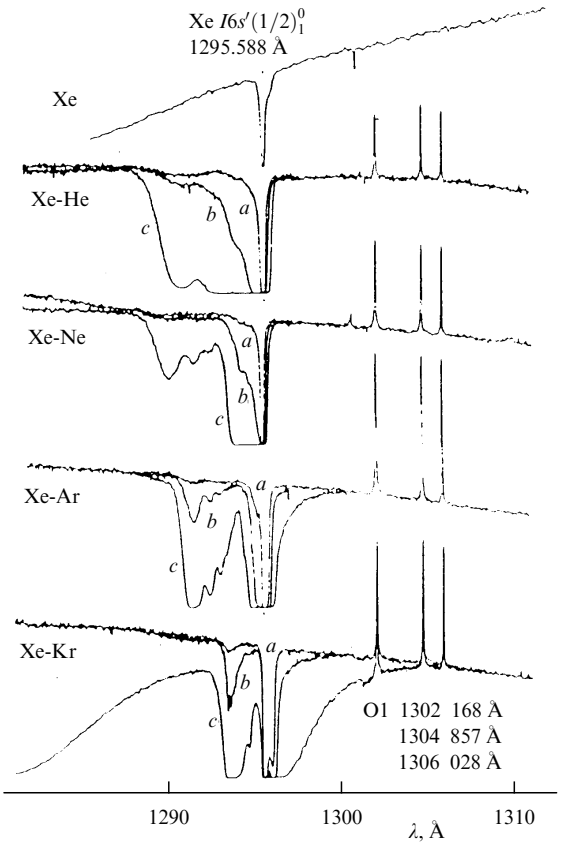

Figure 7. Absorption spectra of xenon mixtures with helium, neon, argon, and krypton [44]. The structures observed near the 1295.588-Å [Xe I $6s'(1/2)_1^0$] resonance line of xenon arise from the absorption by heteronuclear molecules residing the weakly bound ground state. The xenon pressure in the mixtures was 0.1 Torr, and the pressures of helium, neon, argon, and krypton were 2, 162, and 486 Torr (curves *a*, *b*, and *c*, respectively). Also seen in the spectrum is the well-known oxygen triplet O I 1302.168 Å, 1304.857 Å, 1306.028 Å.

these molecules. In Refs [45–48], attempts were made to construct the potential curves responsible for the observed narrow-band spectra. As is well known, the molecular band profile depends on the potential curves of the upper and lower states. The existence of narrow bands in the absorption spectra of binary mixtures signifies that the corresponding spectroscopic transitions have to be made between two bound states possessing a low dissociation energy. The localization of the spectra near the resonance line and their small width allow another conclusion. Specifically, these spectral features may be attributed to the fact that the asymptotes of the molecular states at long internuclear distances should be resonance atomic states. By the time of publication of Refs [46–48], papers containing reliable data on the potential curves of the excited and ground states of rare-gas homonuclear dimers had already come out, for instance, Refs [49, 50]. As regards the potential curves of heteronuclear rare-gas dimers, which make it possible to explain the observed narrow-band VUV absorption spectra, the information on these curves was practically unavailable at the time of publication of Ref. [48]. Only one paper [51], which had come out not long before, gave the potential curves of the ground states of heteronuclear dimers. A distinctive feature of these curves is that they exhibit, along with the repulsive portion for short internuclear distances, a shallow well at long internuclear distances. The depth of this potential well amounts to 150 cm^{-1} for the KrXe dimer, and does not exceed 100 cm^{-1} for the dimers in which one of the atoms is helium or neon. In this case, the ground state of the KrXe molecule furnishes a room for about ten vibrational levels, while the well in the helium – neon interaction potential is so shallow that it is void of vibrational levels. Unfortunately, the information about the potential curves of excited states of heteronuclear dimers, which could be taken advantage of to interpret the experimental absorption spectra, was lacking at that time.

Based on an analysis of experimentally obtained absorption spectra, Castex [48] proposed, for the upper excited state participating in the formation of the narrow-band spectrum, a potential curve of a form which could, in principle, account for the spectra observed. According to the estimate given in Ref. [48], for the $ArXe^*$ and $KrXe^*$ molecules this state should possess respective dissociation energies of about 70 and 120 cm^{-1}, and the same equilibrium internuclear distance as the unexcited state. This estimate called for verification by independent experimental or theoretical calculations.

The experiments with the VUV absorption spectra of binary rare-gas mixtures were of considerable importance in the understanding of the nature of heteronuclear molecules. More recently, they played one of crucially important parts in elucidating the nature of narrow-band emission structures.

6. Potential curves for the excited states of heteronuclear diatomic molecules

Absorption experiments with binary rare-gas mixtures allowed the conclusion that among the potential curves of excited heteronuclear dimers there are bound to exist weakly bound states with large equilibrium internuclear distances. However, precise computation of pair interaction potentials of rare gases (especially of the heavy ones) is a labor-consuming procedure owing to the complexity of the electron shell structure for the interacting atoms. This calculation was limited by the available computer power. This is the reason why the solution to the problem involved was possible, until some time ago, only on the basis of using approximate computing methods. The results of calculating the interaction potentials by approximate methods, obtained in early works, allowed the explanation of the origin of broadband VUV spectra, but they failed to elucidate the mechanism underlying the emergence of the narrow-band structure in the VUV spectra of binary rare-gas mixtures. The answer to this question was obtained with the use of the effective operator technique proposed in by Nikitin et al. [52–54] and adapted for rare gases in Refs [55–65]. The treatment included the states of heavy rare gases (termed quasi-molecular in Refs [55–65]) $X[np^5(n+1)^{1,3}P_j] - Y(^1S_0)$, where $X, Y = \mathrm{Ar, Kr, Xe}$. Two atomic states which are the asymptotes of molecular terms with an increase in the interatomic distance to infinity appear to be most interesting. The case in point is, in the first place, the resonance atomic $^3P_1$ state which serves as a basis for the resonance molecular state $\Omega = 0^+(^3P_1)$ (0_u^+ for homonuclear molecules with $X = Y$), and the metastable atomic $^3P_2$ state which forms the metastable molecular state $1(^3P_2)$ (1_u for homonuclear molecules with $X = Y$). For the bound states 0_u^+ and 1_u of the homonuclear molecules Ar_2^*, Kr_2^*, and Xe_2^*, the dissociation energies were found to be approximately equal to ~ 5000 cm^{-1}. For heteronuclear molecules in the states 0^+

and 1 they are significantly lower and are equal to about ~ 300 cm^{-1} for the ($Xe^* - Ar$) pair, and to ~ 1100 cm^{-1} for the ($Xe^* - Kr$) pair.

Figure 8 displays the portions of potential interaction curves for the atoms Kr (4^1S_0) and Xe (6^3P_1, 6^3P_2), as well as for Kr (4^1S_0) and Xe (5^1S_0). In the construction of the curves, use was made of parameters borrowed from Refs [49 – 51, 64]. Compared to the findings of earlier papers, a distinctive feature of the results given in Fig. 8 is the existence of a shallow well in the molecular state 1. The minimum of this state is practically coincident in location with the minimum of the ground state of the KrXe (4^1S_0 and 5^1S_0) molecule. In the view of the authors of Ref. [63], these curves may be considered to be similar for all pair combinations $X\left[np^{3,4,5}(n+1)\,^3P_1\right] - Y(^1S_0)$ and $X\left[np^{3,4,5}(n+1)\,^3P_2\right] - Y(^1S_0)$ of heavy rare gases, with the only difference that the dissociation energy is lower for lighter molecules.

The spectroscopic transitions of heteronuclear molecules between the excited states $0^+(^3P_1)$, $1(^3P_2)$ and the ground state 0^+ give rise to the broad continua already mentioned in Section 3. The broad structureless spectra result from transitions from the upper bound state to the repulsive part of the lower state. Two overlapping continua are typically observed in experiment — the homonuclear and heteronuclear dimer continua. Both continua lie from the long-wave side of the wing of the resonance line for the heavier gas in a mixture. For the heteronuclear Xe^*Kr molecule, for instance, the continuous spectrum lies from the long-wave side of the wing of the 146.96-nm xenon resonance line and exhibits a gently sloping emission peak at about 153 – 156 nm [31, 32], while the emission continuum of the homonuclear xenon dimer peaks at approximately 172 – 174 nm [4, 5] (see Fig. 5).

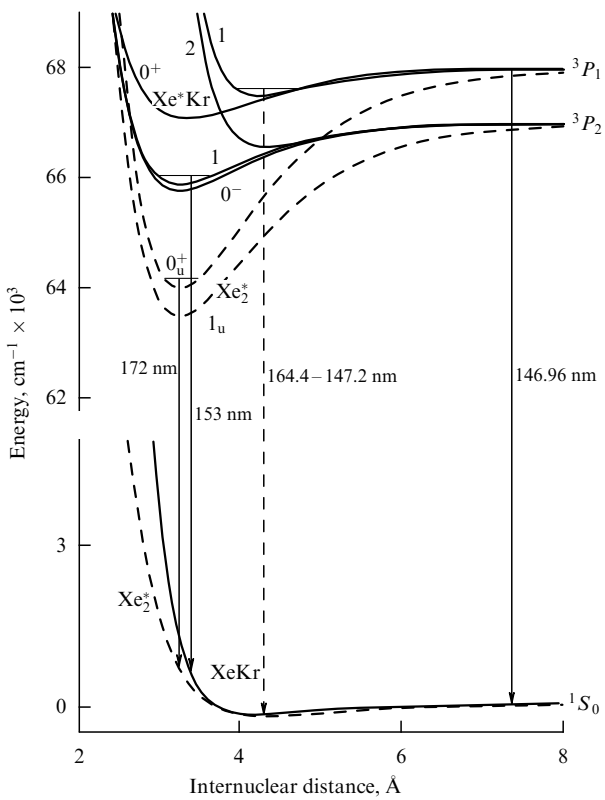

Figure 8. Portion of the potential krypton – xenon interaction curves constructed with the aid of parameters borrowed from Refs [49 – 51, 64]. The dashed lines show the electronic terms of the homonuclear dimer Xe_2^*; $0, 0^+, 0^-, 0_u^+, 1, 1_u$, and 2 are the excited molecular states; $^3P_1$, $^3P_2$, and $^1S_0$ are the excited states of xenon atoms. The spectroscopic transitions between weakly bound states, the excited state 1 and the ground state 0^+, account for the narrow-band structure near the resonance line 146.961 nm of atomic xenon.

As noted above, the specific feature of the potentials depicted in Fig. 8 is that the molecular states $1(^3P_1)$ and $2(^3P_2)$ possess a very shallow well with a long equilibrium distance in comparison with the states $0^+(^3P_1)$ and $1(^3P_2)$. The spectroscopic transitions from the states $1(^3P_1)$ and $2(^3P_2)$ to the ground level 0^+ should give rise to a significantly narrower spectrum than the spectrum corresponding to the transition from the $0^+(^3P_1)$ state to the $1(^3P_2)$ state. In this case, the minima of the $1(^3P_1)$ and $2(^3P_2)$ states are projected onto precisely the binding part of the weakly bound ground state 0^+, which leads to the narrowness of the spectrum lying near the resonance line.

Correctly identifying the observed narrow VUV emission spectra of heteronuclear molecules requires a rather precise knowledge of the potentials pertaining to the initial and final states of the transitions that produce the spectrum. Known most safely are the potentials of the ground states of heteronuclear dimers [50, 51]. The data available in the literature on the excited states are less reliable. For the first time, the information on approximate parameters of weakly bound excited states (see Section 5) was given by Castex [48]. This result was obtained by analyzing proper absorption experiments. In Ref. [66], some data were derived from the analysis of VUV emission spectra. The theoretical calculations that demonstrated the existence of weakly bound excited states with relatively large equilibrium distances (approximately equal to the equilibrium distances of the ground states) were first performed in a large series of computational works [55 – 65]. Until recently, the derivation of reliable data on the potential curves was hampered by the limited precision of theoretical calculations. This is due to the fact that typical dissociation energies of these states are equal to 50 – 150 cm^{-1} (~ 150 cm^{-1} for the Xe^*Kr molecule), while the absolute term energies amount to 10^5 cm^{-1} ($\sim 70{,}000$ cm^{-1} for the Xe^*Kr molecule). To put it another way, the uncertainty of excited-state potential computations should not exceed 0.1% of the term energy being calculated. In recent years, remarkable progress in the accuracy of direct calculations of weakly bound states was made in Refs [67 – 69]. An unquestionable virtue of these papers is the derivation of weakly bound molecular states by way of purely theoretical calculations, as opposed to previous papers.

Therefore, the theoretically evaluated excited-state potentials of rare-gas heteronuclear dimers have confirmed that weakly bound states responsible for the emergence of narrow-band VUV spectra near atomic resonance lines can, in principle, exist.

7. Experimental investigation of the term structure of excited heteronuclear molecules

Simultaneously with the development of theoretical computational techniques, considerable progress has been made in recent years towards the experimental investigation of the electronic terms of excited heteronuclear dimers. The knowledge of the potentials pertaining to excited molecular dimers provides the basis for the construction of simple physical

models which describe these bound states [70 – 73] and is also necessary for an understanding of the physics of processes occurring in plasmas of rare-gas mixtures and, in particular, in excimer laser plasmas. That is why the experimental determination of the interaction potentials of rare-gas heteronuclear dimers (like rare-gas homonuclear dimers) in excited electronic states is of special interest.

Various modifications of laser spectroscopic techniques [74 – 82] have underlain the development of original methods of term structure investigation of rare-gas atoms and molecules. Among the most efficient are photoionization spectroscopy, multiphoton laser spectroscopy, and laser-induced fluorescence techniques. It is precisely the technique of laser-induced fluorescence that recently made it possible to obtain valuable data on the potential curves of excited heteronuclear dimers. This technique relies on an analysis of the spectra emerging in the excitation of heteronuclear molecules in a gas-dynamic jet of the gas mixture, which is cooled due to its adiabatic expansion in transit through a supersonic nozzle. The heart of the technique and the principal findings of the investigation, outlined in Refs [75 – 78], are as follows. A pulsed molecular beam of a rare-gas mixture was excited by a tunable VUV radiation source. The pulsed gas-dynamic stream of a gas mixture was cooled down to cryogenic temperatures due to adiabatic gas expansion in the supersonic flow, resulting in the efficient production of weakly bound heteronuclear molecules in the ground state, at the lowest vibrational levels. The source of tunable short-wavelength radiation, which excited the heteronuclear molecules from the ground state, depended for its operation on the four-wave mixing of the radiation from tunable lasers. The frequency uncertainty in the scanning exciting radiation was less than 0.3 – 0.5 cm^{-1}, which enabled the term structure to be investigated with a resolution exceeding the capabilities of classical VUV spectrometers.

The high spectral resolution furnished by the laser-induced fluorescence technique is nevertheless insufficient for the observation of rotational components in the spectra of heavy molecules (for the XeKr molecule, the rotational constant is $B = 0.018$ cm^{-1}), but the technique in use makes it possible to safely record the electronic – vibrational spectra of molecules. Not only did the accuracy of scanning ensure the resolution of the vibrational structures for weakly bound molecules, but it also furnished the possibility of distinguishing the contributions from the strongest isotopic components. The latter circumstance is of particular importance, because the experiments were conducted with natural isotopic mixtures of pure rare gases.

The method under discussion was employed to investigate the XeKr molecule in Ref. [77]. A mixture of helium, krypton, and xenon in the ratio of 95 : 5 : 0.1 was supplied to a high-pressure chamber (5 – 6 atm). The flow of gas through a nozzle with a critical cross-section 0.2 mm in diameter ensured its cooling. The heteronuclear XeKr molecule produced in the mixed gas outflow through the supersonic nozzle resided in the zero vibrational state owing to the low gas temperature. The potential well depth of the XeKr molecular ground state is known from the spectroscopic experiments carried out in Ref. [75]: it is equal to 150.5 (2) cm^{-1}.

Under exposure to the scanning exciting VUV laser radiation, the molecule under investigation exhibited luminescence at the excitation frequencies coinciding with its energy level structure. Figure 9 shows the VUV laser-induced

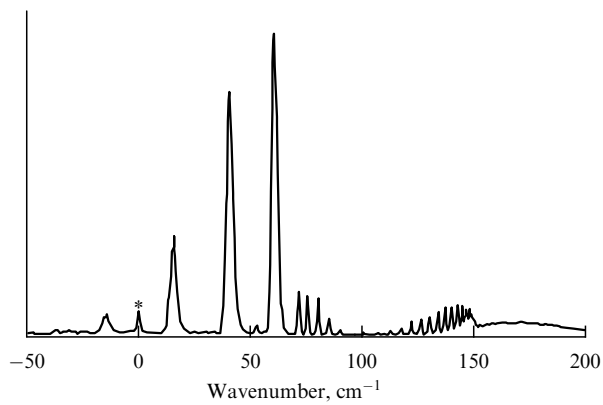

Figure 9. Experimentally examined induced-fluorescence VUV spectrum [76]. The wavenumber scale is given relative to the position of the atomic resonance transition $6s[3/2]_1^0 - {}^1S_0$ (68045 cm^{-1}) in Xe; the position of the atomic resonance transition is marked with an asterisk. The observation of two band types testifies, in the opinion of the authors of Ref. [76], to the existence of two different kinds of interaction potentials for the upper excited state in the heteronuclear KrXe* molecule.

fluorescence spectrum of the heteronuclear XeKr molecule, obtained experimentally [76]. The energy scale is given in cm^{-1}, the Xe ($6s[3/2]_1^0 - {}^1S_0$) resonance transition energy equal to 68045.663 cm^{-1} is adopted as the zero point. The spectrum consists of two band systems lying in the range from −50 to 200 cm^{-1}, which correspond to the excitation of the heteronuclear molecule from the zero vibrational level of its ground state 0^+ to the vibrational levels of the excited states 0^+ and 1. The band system lying between −50 and 100 cm^{-1} is identified by the authors with the spectroscopic transitions from the excited states 0^+, while the spectrum lying above 100 cm^{-1} corresponds, in their view, to the transitions from the excited state 1. The molecular continuum lying in the frequency range above 150 cm^{-1} and the resonance atomic radiation are depressed owing to reabsorption of the tunable VUV radiation that excites the luminescence.

An analysis of the spectrum depicted in Fig. 9 allowed the authors to draw a conclusion about the nature of the luminescence spectrum and construct the conjectural potential curves for the excited states of the heteronuclear XeKr* molecule. Figure 10 demonstrates the relevant interaction potentials (solid curves) for the $\Omega = 0^+$ and $\Omega = 1$ states of the Xe ($6s[3/2]_1^0$) Kr molecule, which were derived from best fit considerations for the observed laser-induced fluorescence spectra. The potential of the $\Omega = 0^+$ state has a double minimum, while the potential of the $\Omega = 1$ state has only one shallow well at long internuclear distances. Also given here are the potentials (the parameter Ω is not defined) constructed by Castex [48] (two dashed curves for different parameters C_6 used in the work). It should be emphasized that neither the purely theoretical calculations [55 – 65] nor the computations performed in Refs [67 – 69] yield potentials with two minima, similar to those obtained in Ref. [78]. It is also pertinent to note that the spectroscopic investigation reported in Ref. [48] was characterized, as compared to the technique employed in Ref. [78], by a somewhat lower spectral resolution, which did not enable an equally detailed study of the structure of electronic – vibrational spectra of rare-gas heteronuclear molecules as in [78]. We nevertheless believe that the result achieved by Castex [48] is more realistic than that of Tsuchizawa et al. [78]. The reason for the possible error may lie in the incorrect interpretation of the data

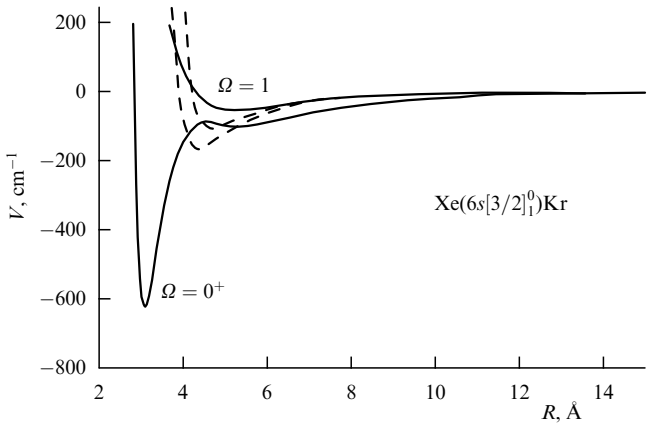

Figure 10. Interaction potentials obtained by analyzing induced-fluorescence emission spectra [76]. The solid curves show the potentials constructed on the basis of analysis of the experimental results obtained by the laser-induced fluorescence technique in Ref. [76]. The dashed curves correspond to the potentials proposed on the basis of the analysis of the absorption spectra taken from krypton – xenon mixture in Ref. [44].

obtained by the laser-induced fluorescence technique. In particular, the assumption of the authors of Ref. [78] that helium, which comprises 95% of the mixture under study, is a buffer gas having no effect on the molecular composition of the mixture being excited can be disputed. As will be seen from Section 8, the emission spectra of a mixture of heavy rare gases with lighter gases (including helium) give narrow bands which can be interpreted as the emission of heteronuclear molecules.

The laser-induced VUV fluorescence technique, which was further elaborated in Refs [79 – 82] and was employed to investigate the homonuclear dimers of rare gases, enable a study of their binary mixtures. It was determined that there exist, along with the well-known bound excited states $\Omega = 0^+$ responsible for the continuum emission of heteronuclear molecules, weakly bound excited states $\Omega = 1$ caused by dispersion forces. The equilibrium internuclear distances of such electronic terms are significantly longer than the equilibrium distances of the states $\Omega = 0^+$. For the first time, an investigation was made of the vibrational structure of these states, and their isotopic components were observed. Along with isolated investigations of the term structure, performed by the classical VUV absorption spectroscopy [44 – 48] and emission spectroscopy techniques [83], the laser-induced VUV fluorescence technique [79 – 82] brought out clearly the existence of weakly bound molecular states. Despite the debatable character of some conclusions of the above-cited works, this technique has become a new powerful tool for the experimental investigation of excited weakly bound states of heteronuclear dimers.

8. Experimental investigation of the structure of vacuum ultraviolet emission spectra of rare-gas mixtures

The effect of transformation of broadband VUV homonuclear dimer spectra on addition of small admixtures of a heavier rare gas to the radiating plasma, as noted in Section 4, was discovered and investigated in detail in Refs [35 – 41]. In these publications, particular attention was given to the derivation, by way of processing experimental data, of the rate constant for the excitation transfer from an excited molecular gas to the impurity atoms of the heavier rare gas. In the analysis of energy transfer in these papers it was assumed that the strong narrow-band VUV radiation localized near the resonance lines of impurity atoms belongs to these atoms and is the ordinary atomic resonance emission. Only Wieme and Lenaerts [83] hypothesized that the observed strong narrow-band VUV radiation arose not from atomic transitions, but from the spectroscopic transitions in a heteronuclear molecule. However, the stated idea was not elaborated further, probably because of the absence of computational works making available the requisite potential curves by the time of publication of Ref. [83].

In Refs [84 – 91], an investigation was conducted into the structure of intense narrow-band VUV radiation generated in the glow and barrier discharges in a binary krypton – xenon mixture near the 146.96-nm xenon resonance line. The observed narrow-band emission was shown to be a mixture of two kinds of radiation: atomic and molecular. The atomic radiation belongs to the resonance xenon transition, and the molecular radiation to the heteronuclear $XeKr^*$ molecule, with the energy radiated in the molecular band being stronger than the atomic emission over a broad range of experimental conditions. Figure 11 shows the emission spectrum (curve *1*) of the krypton – xenon mixture, obtained in a d.c. capillary discharge [85], and the absorption spectra (curves *a*, *b*, *c*) from Ref. [44]. The identity of emission and absorption spectra supports the conclusion that their origins are analogous in nature, which was reached in Refs [84 – 92]. At the same time, Freeman et al. [44] brought out clearly that the observed narrow-band spectra cannot belong to any of the individual gases in the mixture and that they emerge only in the gas mixture and belong to heteronuclear molecules.

In Refs [89 – 92], a study was made of the VUV spectra of the Xe-X and Kr-Y type mixtures in the 115 – 200 nm range, where X = He, Ne, Ar, Kr, and Y = He, Ne, Ar. Observed in this case were 14 strong narrow emission bands localized near the four resonance lines of atomic krypton and xenon. The results of calculations [55 – 65] and absorption experiments [42 – 48], together with the emission spectra with a spectral resolution ensuring partial observation of the band structure examined experimentally in Refs [84 – 93], gave grounds to

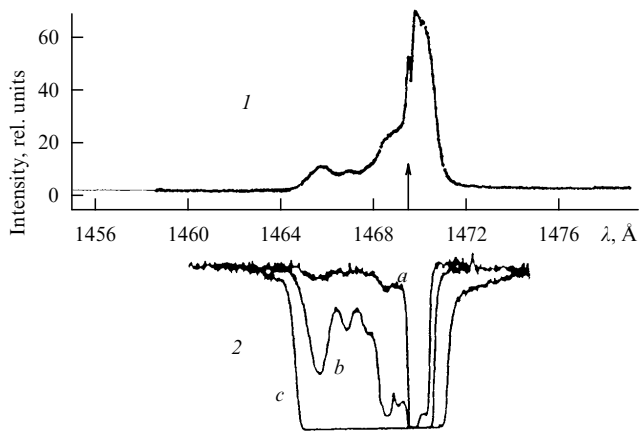

Figure 11. Emission spectrum and absorption spectra of a krypton – xenon mixture [44, 85]. The position of the main features for the absorption spectrum is reproduced in the emission spectrum. For the absorption spectrum, the xenon pressure is 0.1 Torr, the krypton pressure is 2, 162, and 486 Torr (curves *a*, *b*, and *c*, respectively).

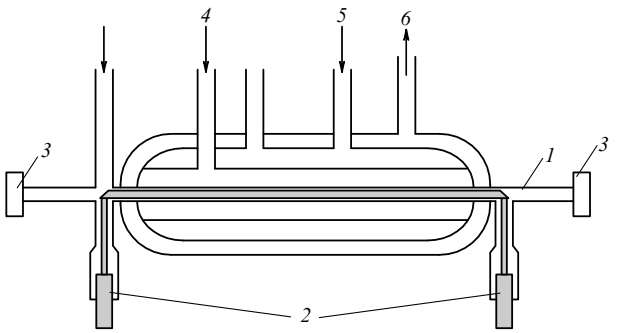

Figure 12. Schematic drawing of the experimental discharge tube employed to obtain the VUV emission spectra from a d.c. discharge: *1* — discharge capillary with a 1.5-mm bore; *2* — tungsten field-emission cathodes; *3* — windows of magnesium fluoride transparent in the VUV spectral region; *4* — heat conducting gas volume which prevents heavy rare gases from rapid freezing upon pouring liquid nitrogen; *5* — volume for pouring liquid nitrogen, and *6* — evacuated volume which prevents liquid nitrogen from a rapid boil-off.

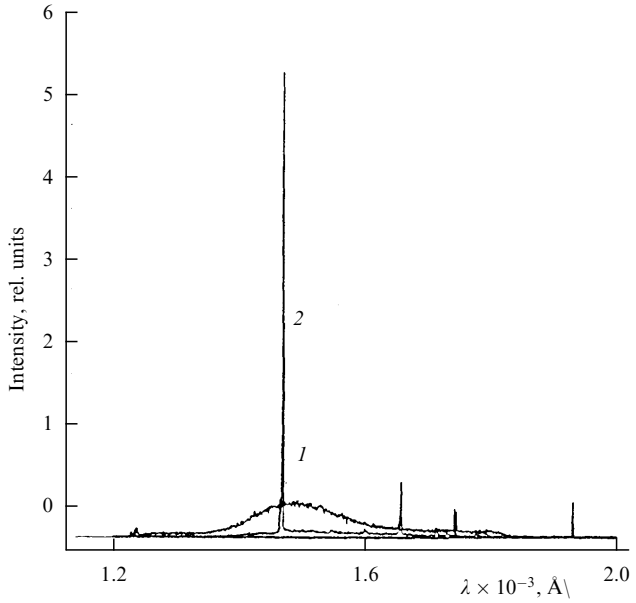

Figure 13. Panoramic VUV emission spectrum of pure krypton (curve *1*) and the spectrum from the mixture of krypton with 0.1% xenon (curve *2*) excited in a glow capillary discharge [89]. The excitation energy stored by homonuclear krypton molecules is transformed to the narrow-band radiation of the heteronuclear KrXe* dimers.

identify the observed narrow-band VUV emission spectra. The similarity of emission and absorption spectra (see Fig. 11), which was observed for all pair combinations of gas mixtures examined, is essentially the main argument in favor of the viewpoint that the narrow VUV emission bands belong to heteronuclear dimers. Another matter of principle is the understanding of the most probable physical processes bringing about the excitation of narrow-band heteronuclear dimer radiation, which are responsible for the transfer of the bulk of the stored excitation energy to these bands. Clarifying this matter requires comparing the physical conditions for the excitation of narrow-band VUV radiation in different gas mixtures. In this connection, we will enlarge on the results of Refs [84–93] devoted to the experimental investigation into the VUV spectra of a d.c. capillary glow discharge and a barrier discharge, with the electrode gaps being filled with gas mixtures. Figure 12 outlines the design of the discharge tube employed in the d.c. discharge experiments. The radiation was extracted through MgF_2 windows mounted perpendicular to the axis of the discharge tube at a distance of about 5–7 mm from the discharge capillary. The capillary discharge

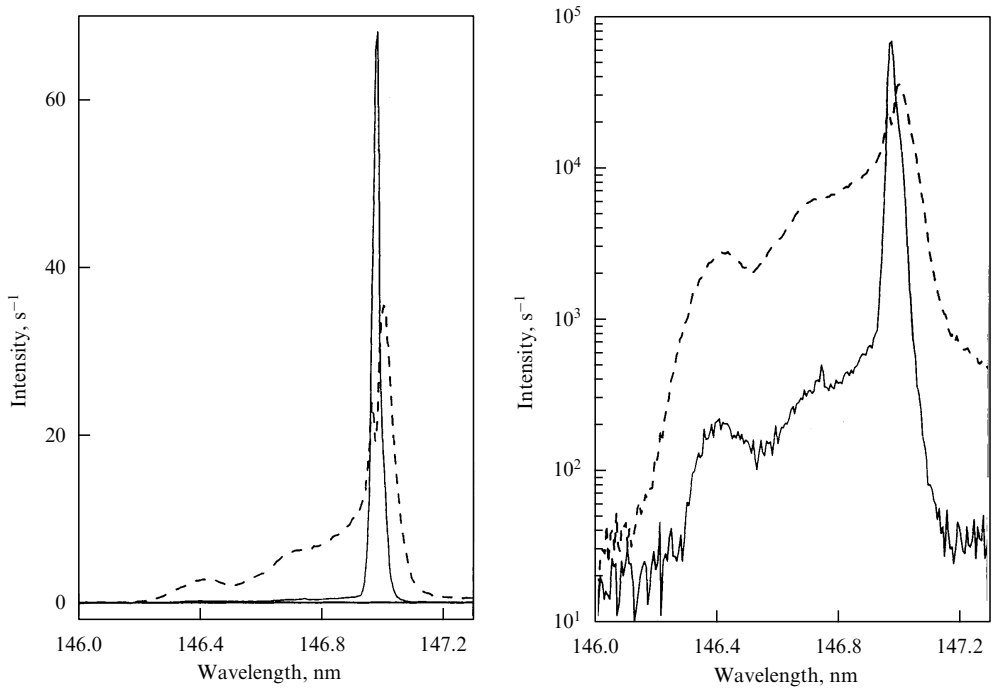

Figure 14. VUV emission spectrum of the gas discharge in an argon – xenon mixture. The dashed line shows the spectrum for an argon pressure of 100 hPa and a xenon pressure of 1 hPa, and the solid line depicts the spectrum for an argon pressure of 50 hPa and a xenon pressure of 0.05 hPa. The spectra are drawn on linear and semilog scales.

tubes with a 1.5-mm bore were made of quartz. The spectrum was recorded in the 115–200-nm wavelength range on a 1-meter normal-incidence vacuum spectrometer with a plate scale of 0.83 nm mm^{-1}. The spectral resolution amounted to 0.015 nm. Apart from the molecular continua of rare gases and their mixtures, the spectrum exhibited the atomic resonance lines of krypton ($\lambda = 116.5$, 123.6 nm) and xenon ($\lambda = 129.5$, 146.96 nm). The lines of hydrogen ($\lambda = 121.6$ nm) and carbon ($\lambda = 156.1$, 165.7 nm) impurities were also identified in the spectrum.

The dominant bulk of the subject matter of Refs [33, 84–93] consists in the demonstration of the emission bands from binary rare-gas mixtures with krypton or xenon and in the elucidation of the origin of the narrow-band spectra and their properties. The concentration of krypton or xenon in the mixture ranged over 0.1–0.5%. The spectra were obtained for a total gas mixture pressure of 50–120 hPa and a discharge current of 20 mA.

The experimental conditions listed above were not selected by accident. It is at this total pressure of gas mixtures and in this concentration range of heavier rare-gas impurity that the narrow-band structures were observed. In this case, the great bulk of radiation in the VUV region involved belonged to the bands under investigation. By way of example, Figs 13 and 14 show the panoramic emission spectra of a capillary discharge in Kr-Xe and Ar-Xe mixtures in the VUV region. One can see from Figs 13 that the narrow-band spectrum of the heteronuclear KrXe molecule prevails in the 120–200 nm range, while the emission spectrum of the ArXe* molecule (see Fig. 14) is essentially the high-intensity monochromatic VUV radiation with a halfwidth of about 0.3 Å. The ArXe* emission spectrum in Fig. 14 is plotted on linear and semilogarithmic scales, thereby enabling an estimate of the monochromaticity of the heteronuclear molecular emission.

As noted above, the nature of the origin of the narrow-band spectrum near the 146.691-nm resonance ($^3P_1 - {}^1S_0$) line of atomic xenon in a Kr-Xe mixture was discussed in detail in Refs [84–87]. The KrXe molecular emission, which concentrates the excitation energy in a narrow band (see Fig. 13) resembling the absorption spectrum of a krypton–xenon mixture, was found to arise from the spectroscopic transition between the excited (1) and ground (0^+) states of the heteronuclear KrXe molecule. A numerical simulation of the observed structure, which was based on the knowledge of the corresponding dimer energy levels, was performed by Morozov et al. [86] to support the idea that the observed emission spectrum can be satisfactorily explained by the transitions between the excited (1) and ground (0^+) states of the heteronuclear KrXe dimer.

Referring to Fig. 15, the emission spectra of xenon mixtures with helium, neon, and argon (spectra *1*, *2*, and *3*, respectively) near the same 146.961-nm resonance line as in the case of the Kr-Xe mixture have a narrow emission band; in this case, the band exhibits a fully individual structure inherent to every gas mixture. As shown by investigations, at different mixture pressures and concentrations of xenon additions there occurs a redistribution of radiation intensity in the emission bands of all gas mixtures. As this takes place, the positions of inflections and local peaks in the spectra, which are distinct for each mixture, remain unchanged (which was also observed for the KrXe molecule [84, 85]). As in the case of a krypton–xenon mixture, the similarity of emission and absorption spectra is also observed in this situation. The

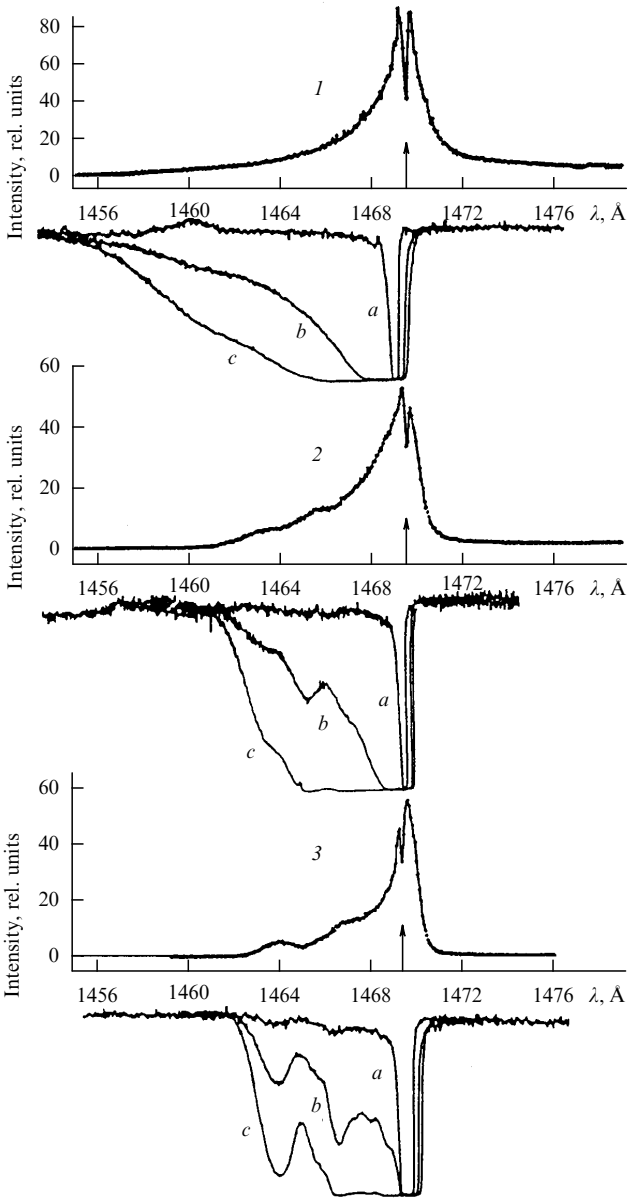

Figure 15. VUV emission and absorption spectra of xenon mixtures with helium (curve *1* — 60 hPa, 0.2% xenon), neon (curve *2* — 100 hPa, 0.2% xenon), and argon (curve *3* — 70 hPa, 0.1% xenon). Here, *a*, *b*, and *c* mark the absorption spectra of gas mixtures at xenon pressures of 2, 162, and 486 Torr, respectively. The arrow indicates the location of the xenon 146.961-nm atomic resonance line [44, 89].

spectrum of the helium–xenon mixture exhibits a special feature in its long-wave part. The red wing in the emission spectrum terminates less abruptly than in the absorption spectrum. In this case, it can be traced up to 147.65 nm, while the absorption spectrum terminates at 146.97 nm. This special feature of the emission spectrum can be attributed to transitions from the 'ordinary' (not loose) $0^+(^3P_1)$ state to the ground state 0^+.

The emission bands near the xenon second resonance line 129.559 nm ($^1P_1 - {}^1S_0$), like the spectra discussed above, are similar to the absorption spectra for xenon mixtures with helium and neon (Fig. 16), as well as argon and krypton (Fig. 17). A more extensive long-wave wing (beyond 130 nm) is characteristic of the emission spectrum for the xenon mixture with helium. In the absorption spectrum it termi-

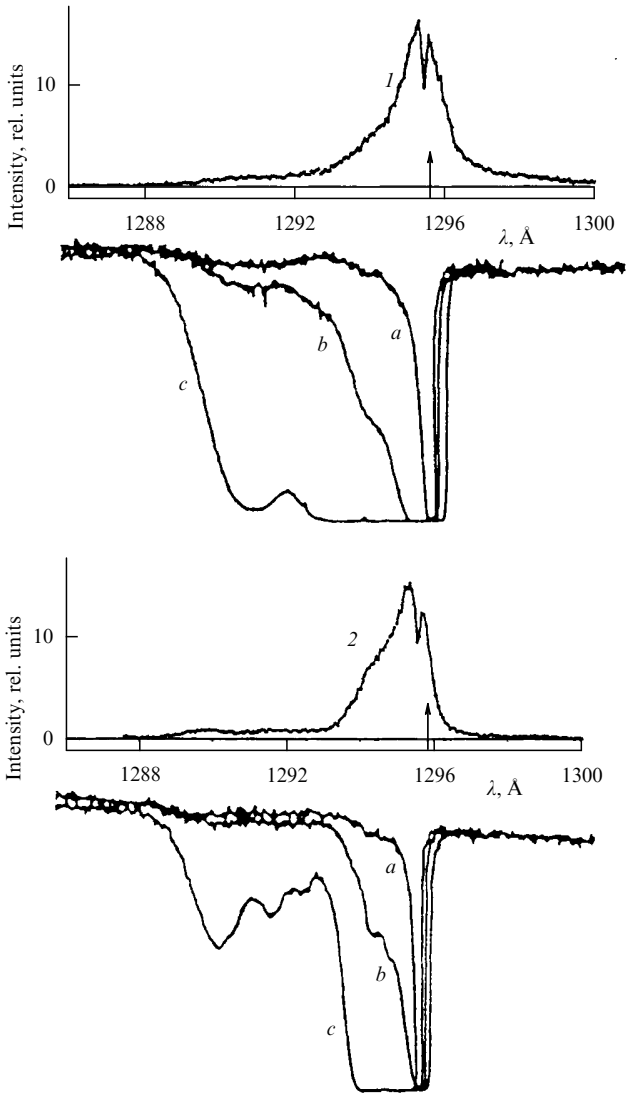

Figure 16. VUV emission and absorption spectra of xenon mixtures with helium (curve *1* – 40 hPa, 0.2% xenon) and neon (curve *2* – 80 hPa, 0.5% xenon). Here, *a*, *b*, and *c* mark the absorption spectra of gas mixtures at xenon pressures of 2, 162, and 486 Torr, respectively. The arrow indicates the location of the xenon 129.587-nm atomic resonance line [44, 89].

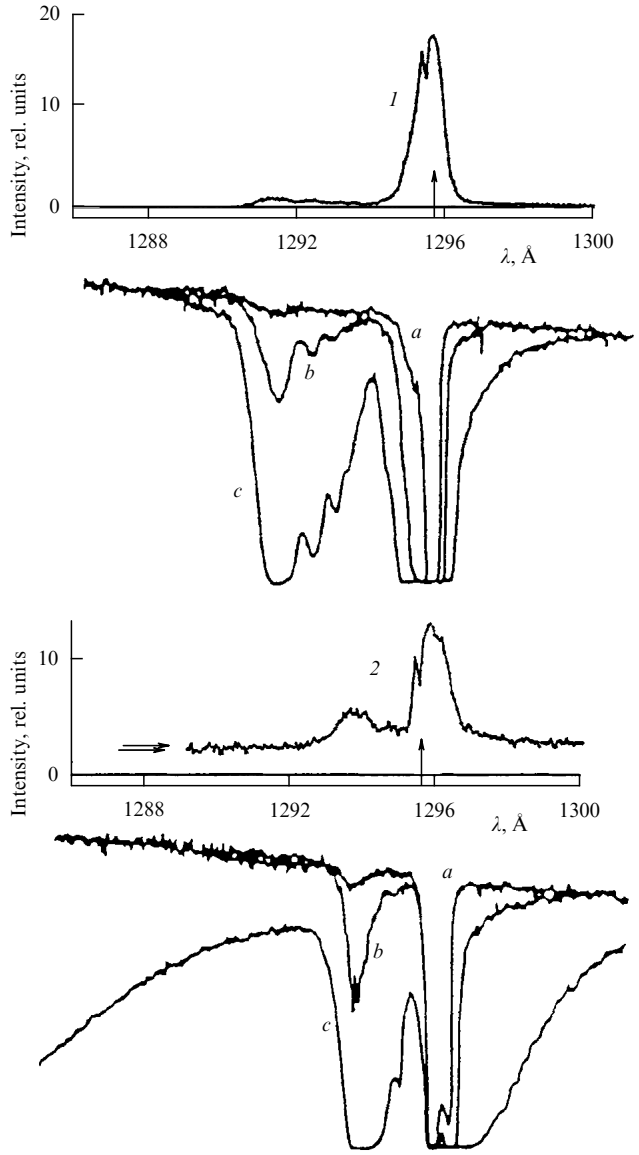

Figure 17. VUV emission and absorption spectra of xenon mixtures with argon (curve *1* – 90 hPa, 0.4% xenon) and krypton (curve *2* – 60 hPa, 0.2% xenon). Here, *a*, *b*, and *c* mark the absorption spectra of gas mixtures at xenon pressures of 2, 162, and 486 Torr, respectively. The arrow indicates the location of the xenon 129.587-nm atomic resonance line [44, 89].

nates abruptly at 129.6 nm (see Fig. 15). This feature is explained in the same way as for the spectrum of the same molecule in the vicinity of the first resonance line.

Exact data on the potential curves of excited heteronuclear dimers produced on excited xenon atoms in the $^1P_1$ state are not available from the existing literature, making it impossible to perform simulations of the spectra and draw a definite conclusion about the unambiguous identification of the spectra under investigation. Nevertheless, judging by the similarity of the emission and absorption spectra, it is believed that the observed spectral bands also belong to the radiation of heteronuclear dimers.

Figures 18 and 19 depict the emission spectra of the discharges in krypton mixtures with helium, neon, and argon. The emission bands localized near the krypton 123.584-nm ($^3P_1 - {}^1S_0$) and 116.487-nm ($^3P_1 - {}^1S_0$) resonance lines exhibit, as for mixtures with xenon, structures distinct for each gas mixture. The structure shows up most clearly in krypton mixtures with neon and argon, and it is hardly present in the krypton mixture with helium. In the last-mentioned case, the long-wave wing is not as extensive as for the xenon – helium mixture.

In the consideration of the nature of the emission spectra plotted in Figs 18 and 19, a conclusion was reached in Ref. [87] that this radiation may also arise from spectroscopic transitions in heteronuclear dimers.

Therefore, the VUV emission spectra excited in a d.c. capillary discharge comprise, under certain conditions, a set of strong, practically monochromatic spectra covering the near-VUV region.

9. Modeling of the narrow-band vacuum ultraviolet spectra of heteronuclear molecules

The most reliable way of checking the validity of calculated potential curves is to compare the experimentally obtained spectra with the spectra simulated by employing these curves

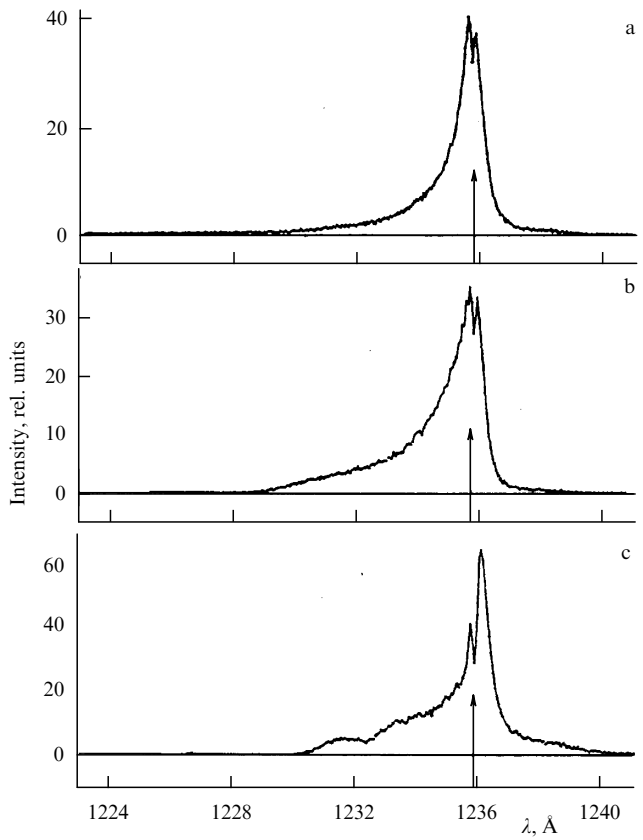

Figure 18. Emission spectra of the rare-gas mixtures: (a) He-Kr (for a helium pressure of 50 hPa and a krypton pressure of 0.1 hPa); (b) Ne-Kr (for a neon pressure of 120 hPa and a krypton pressure of 0.5 hPa), and (c) Ar-Kr (for an argon pressure of 70 hPa and a krypton pressure of 0.3 hPa). The arrow indicates the location of the krypton 123.584-nm resonance line [89].

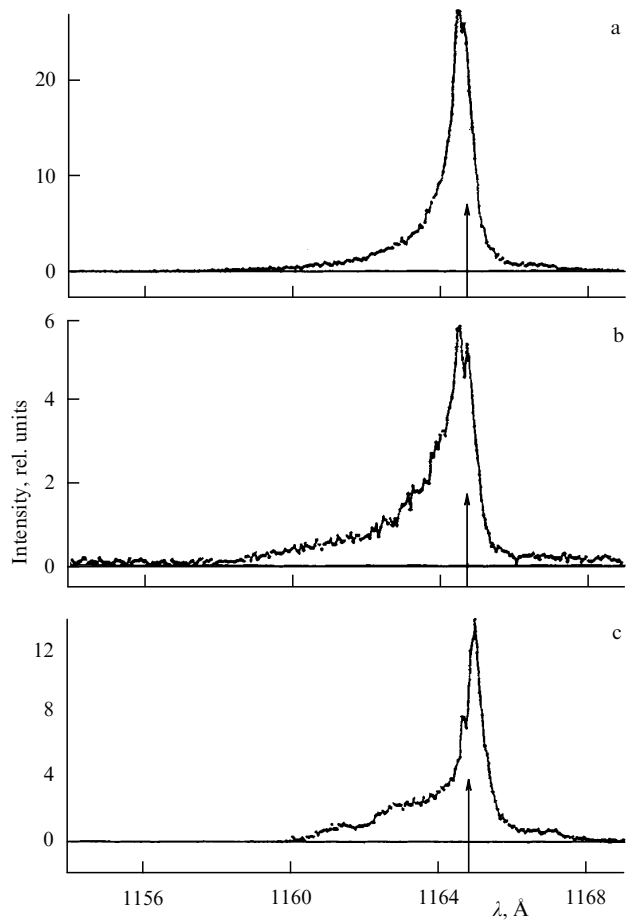

Figure 19. Emission spectra of the rare-gas mixtures: (a) He-Kr (for a helium pressure of 50 hPa and a krypton pressure of 0.1 hPa); (b) Ne-Kr (for a neon pressure of 120 hPa and a krypton pressure of 0.5 hPa), and (c) Ar-Kr (for an argon pressure of 70 hPa and a krypton pressure of 0.3 hPa). The arrow indicates the location of the krypton 116.487-nm resonance line [89].

as the base. Of all the narrow-band VUV spectra investigated, the band of the heteronuclear KrXe* molecule, located near the xenon 146.691-nm resonance line, proved to be best suited to the computations. This is due to the fact that this absorption band was thoroughly investigated in Refs [42–48], and the potential curves corresponding to the transition in precisely the heteronuclear KrXe* dimer were given in Ref. [95]. The theoretical calculation of the absorption spectra of the KrXe dimer was performed by Morozov et al. [86]. The result of the simulation was compared with the experimental absorption band obtained in Refs [42–48].

For the ground molecular state, advantage was taken of the potential described by the Morse function [51]

$$V(r) = D\{1 - \exp[-\alpha(r - R_m)]\}^2 - D, \quad (5)$$

where

$$\alpha = \frac{\ln 2}{R_m - R_0},$$

$D = 159$ cm^{-1}, $R_m = 4.18$ Å, $R_0 = 3.73$ Å, D is the ground-state dimer dissociation energy, R_m is the equilibrium internuclear distance, and R_0 is the distance at which the potential turns to zero. The same parameters were also employed for the multiparameter potential in Ref. [96]. However, comparing the results of calculations made with the use of the last-mentioned potential and of those made with the use of potential (5) showed the appropriateness of the simpler Morse potential. When the calculations were done using the simple potential, reliable results were obtained in the simulation of all portions of the absorption spectrum taken from heteronuclear KrXe molecules. In this case, the following parameters were employed for the molecular $1(^3P_1)$ excited state:

$$D = 170 \text{ cm}^{-1}, \quad R_m = 4.4 \text{ Å}, \quad R_0 = 3.7–4.0 \text{ Å}.$$

Simulating the absorption spectrum with the use of potential (5) for the above parameter values made it possible to provide a satisfactory explanation for all the most significant features of the spectrum. However, the narrow-band structure localized near the atomic resonance line on its short-wavelength side, which was observed in the absorption spectra, could not be explained without complicating the form of the molecular potential in the upper excited state $1(^3P_1)$. To gain the closest agreement between the results of simulations and the experimentally obtained spectra, the Morse potential employed for short internuclear distances was supplemented with a more complex potential for long internuclear distances, which consisted of a third-degree polynomial and a new Morse potential with the parameters

$$D = -25 \text{ cm}^{-1}, \quad R_m = 6.5 \text{ Å}, \quad R_0 = 6.0 \text{ Å}.$$

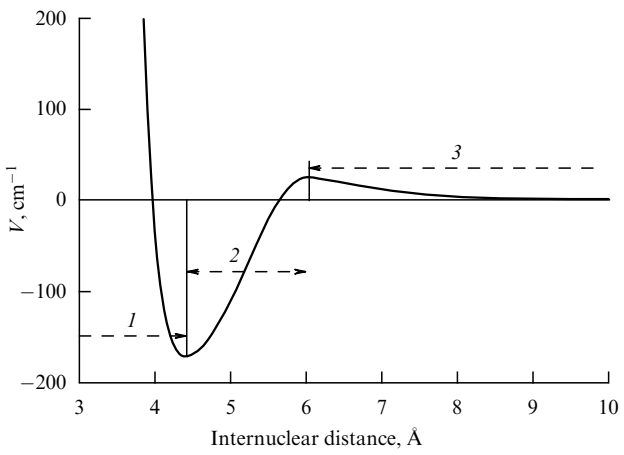

Figure 20. Interaction potential employed in Ref. [86] in the simulation of the absorption spectrum of a krypton – xenon mixture. The potential is made up of three different functions, the bounds of each of them are denoted by *1*, *2*, and *3*.

Therefore, simulation of the absorption spectrum of a heteronuclear molecule necessitates employing a potential which has a 'hump' at long internuclear distances. Figure 20 shows the form of the potential employed in Ref. [86]. The existence of small humps on the interaction potentials of molecular excited states in rare gases at long internuclear distances had been firmly determined in many previous works (see, for instance, Ref. [97]), and the emergence of this special feature in the potential curve of a heteronuclear molecule comes as no surprise. Simulating the narrow-band absorption spectrum of the heteronuclear KrXe molecule near the atomic xenon 146.961-nm resonance line showed that the potential curves calculated in Ref. [95] can be used to advantage in the theoretical simulation of the molecular spectra.

10. Mechanism of heteronuclear dimer excitation

Recognizing the significance of studying the nature of the strong narrow-band VUV radiation that emerges in low-temperature plasmas of rare-gas mixtures, we should emphasize that the problem related to understanding the mechanism of its excitation remains no less important. Only when both of these problems are understood, can the best use of this interesting phenomenon be made.

Discussing the physical nature of narrow-band VUV radiation, the authors of Refs [88, 89] take into consideration two possible mechanisms of its origin. The first is associated with the radiation of so-called free pairs [48], and the second one with the radiation of weakly bound molecules. A specific property of the first mechanism is the absence of structure in the emission spectrum. The second mechanism is, unlike the first one, formed of conventional spectroscopic molecular transitions. In the latter case, the spectrum should exhibit features that reflect the specific character of molecular term structure. The spectrum should possess vibrational and rotational structures. Not drawing a sharp distinction between these mechanisms, we note that the majority of emission bands under discussion exhibit features which characterize them as molecular transitions.

Gerasimov et al. [88, 89] discuss an intriguing feature common to all the emission spectra described. Namely, an investigation is made of the causes responsible for the production of radiating heteronuclear molecules and the reasons underlying the transfer of the bulk of excitation energy with the accumulation of this energy on specific molecular states. Of all possible emission bands of heteronuclear molecules, under the experimental conditions investigated it was possible to observe only the narrow-band radiation localized near the atomic resonance lines of the heavy gas present in the form of a small addition. For instance, the krypton – xenon mixture radiation is effected under physical conditions where the spectrum is dominated by a narrow emission band in the 147 nm range. In a number of cases, the well-known continuum of the KrXe molecule with the emission peak at a wavelength of 154 – 156 nm (see Fig. 5) was missing or had a lower spectrum-integrated intensity in comparison with the narrow band in the 147 nm range.

In considering the KrXe dimer excitation mechanism in Ref. [33], of all the diversity of reactions responsible for the excitation of the heteronuclear molecule, preference is given to the multistage mechanism of energy transfer from the parent gas in inelastic collisions. Briefly, in the initial stage this mechanism involves excitation and ionization of parent gas atoms. Then, excited atoms and atomic ions transform to excited molecules and molecular ions as a result of three-body conversion. At later stages, there occurs energy transfer from the excited molecules and atoms of the parent gas to xenon impurity atoms in particle collisions, to atoms which serve as a basis for the production of excited heteronuclear Xe^*Kr dimers. In Ref. [33], the most probable mechanism of Xe^*Kr dimer production is associated with the three-body conversion of excited xenon, involving krypton atoms. This scheme of processes cannot be applied to all gas mixtures investigated in this work. For instance, when studying the spectra of discharges in helium – xenon and krypton – xenon mixtures, different sets of processes should be taken into account due to a significant difference in the ionization and excitation energies of these gases. However, despite the radical distinction in the excitation mechanisms, intense emission bands in the vicinity of xenon resonance lines in Kr-Xe and He-Xe mixtures (as in other mixtures, though) emerge at like mixture pressures and heavy-gas concentrations. It is improbable that mixtures composed of different gases and excited due to various processes will produce similar intense spectra localized near the resonance line under similar excitation conditions. It is believed that there is a mechanism for the excitation of narrow-band radiation, which operates with equal efficiency in different gas mixtures.

In the consideration of the excitation of narrow-band VUV spectra in Refs [84 – 91], attention was drawn to the fact that their intensity increases with heavy-gas concentration at low magnitudes of the latter to subsequently stabilize with a downward trend when the concentration is above 1% and the total mixture pressure is greater than 200 hPa. The stabilization of intensity growth of the band emission may be attributed to the increase in resonance radiation absorption from the ground states of atoms and heteronuclear molecules. The following reasons can explain why the spectrum under study rises sharply in a relatively narrow pressure range of 10 – 100 hPa and for impurity concentrations below 0.5%.

The above range of physical conditions is characterized by the following property. Under these pressures, in all low-temperature rare-gas plasmas the molecular component is prevalent [11], i.e., the bulk of excitation energy is accumulated by homonuclear dimers. It would appear natural to

relate the effect of high brightness of the narrow emission bands to the emergence of parent-gas dimers in the discharge plasmas.

Several processes involving parent-gas dimers are considered in the analysis of the origin of narrow-band radiation in Ref. [93]. Among them we note the substitution reactions [94]

$$A_2^* + B \rightarrow AB^* + A\,, \tag{6}$$

$$A_2^+ + B \rightarrow AB^+ + A\,. \tag{7}$$

The substitution reactions (6) and (7) fall into the category of little-investigated elementary processes [94], and there is no way of drawing the final conclusion about the part they play in the interpretation of the experiments described. However, if it is assumed that the effective cross section for the reactions (6) and (7) is close in magnitude to the ordinary gas-kinetic cross section, these reactions provide a good qualitative description of the properties of the phenomenon under investigation.

In the consideration of possible mechanisms for the production of excited heteronuclear dimers, it may appear that there is a good reason to include the effect of the reaction of the type

$$A^* + B + A \rightarrow AB^* + A\,. \tag{8}$$

A numerical estimate of the probability of process (8) shows that its significance is far less than the probability of the substitution reactions (6) and (7) [provided the assumptions as to the magnitude of the effective cross section for reactions (6) and (7) are valid].

Considering the problem of excitation of the spectra of heteronuclear molecules we note that their production can be basically attributed to A^*B-AB^* type transitions. As already noted in Section 2, such reactions were observed in Refs [17, 19–22], but being proceeded between ion levels A^+B-AB^+. These transitions were shown to be accompanied by the radiation of relatively weak yet unambiguously identifiable bands. Similar bands should also be observable for the A^*B-AB^* transitions. A verification of this possibility performed in Ref. [92] showed that weak emission bands corresponding to the A^+B-AB^+ transitions were observed only for high concentrations (over 10%) of the heavier-gas impurity. Under the conditions whereby the strong narrow VUV radiation bands are prevalent, the spectra typical for the A^*B-AB^* or A^+B-AB^+ type transitions escaped detection. Therefore, among the most probable processes we point to the substitution reactions (6) and (7) when considering the possible causes for collisional excitation of the narrow-band spectra under investigation.

Reverting to the interpretation of the abnormally high intensity of the VUV radiation from molecular energy levels with a low dissociation energy and large equilibrium distances we note the following. For any molecular transition, the radiation intensity I is defined by the expression [11]

$$I = \lambda^{-6}\left[\int \psi(R)\,\mu(R)\,\varphi(R)\,\mathrm{d}R\right]^2. \tag{9}$$

Here, λ, $\psi(R)$, $\varphi(R)$, and $\mu(R)$ are the transition wavelength, the vibrational wave functions of the upper and lower states, and the transition dipole moment for the electron transition, respectively. Therefore, the intensity of a radiative transition at a given wavelength is defined by the magnitude of the overlap integral which depends, in particular, on the product of the upper- and lower-state wave functions oscillating around an internuclear distance.

Estimating the contribution from the states 1 and 0^+ to the VUV radiation of a heteronuclear molecule, we emphasize that the wave-function overlap integrals of the ground state and the excited state 1 may exceed in magnitude the wave-function overlap integrals of the ground state and the excited state 0^+. The reason for the possible superiority lies with the proximity of the parameters of the potential curves for the ground state and the state 1. This has the effect that the oscillation phases of the wave functions are practically coincident. The transition dipole moments $\mu(R)$ for the states 1 and 0^+ are, according to Refs [67–69], close in magnitude and remain practically invariable throughout the internuclear distances under consideration. The above circumstances supposedly determine the magnitudes of the overlap integrals. The proximity of the energies of the upper vibrational levels in the excited states 1 and 0^+ (see Fig. 8) ensures the collisional energy 'transfer' to the vibrational levels of the molecular state 1.

The above considerations given to account for the salient features of the excitation of weakly bound states in heteronuclear dimers cannot be regarded as exhaustive. It should be reminded that the dissociation energy of the most stable molecule among the excited molecules under study amounts to 150–160 cm^{-1} on evidence derived by different researchers. The high level populations (confirmed by selective radiation of the gas mixtures) of such weakly bound molecules, existing even at room temperature of the mixed gas being excited, call for a serious substantiation. That is why, recognizing the possible effect of reactions (6) and (7) and taking into granting the above reasoning, we nevertheless arrive at the conclusion that the problem of the high intensity of the emission bands remains to be solved.

It is appropriate to recall here the radiation mechanism of free pairs, whereby narrow-band structures are radiated not by heteronuclear molecules but by resonance-excited impurity atoms in their collisions with unexcited atoms of the parent gas. This mechanism of radiation necessitates substantiation on two most fundamental accounts. First, it needs to be understood why the emission bands of the gas mixtures exhibit well pronounced structures (particularly, the emission bands of heavy rare-gas mixtures). Second, it remains to explain the low value of free-pair radiative probability, which results from numerical estimation for moderate gas mixture pressures employed in the experiments described in Section 2.

It seems plausible that the nature of emission of narrow-band structures is not quite similar for light- and heavy-gas mixtures. Further investigations into the low-temperature plasma physics of rare-gas mixtures should provide the ultimate answer to this and other questions.

11. Prospects for the investigation of the spectra of heteronuclear rare-gas molecules

The experimental and theoretical investigations of the spectra of heteronuclear rare-gas dimers are still at their early stages, which does not permit us to answer many questions concerning their physical properties. Nevertheless, the investigations conducted have significantly extended our notions of the properties of low-temperature plasmas of pure rare gases and their mixtures. Apart from the general scientific

significance, the spectroscopy of rare-gas mixtures makes it possible to view the prospects of harnessing the newly explored properties for the solution of applied problems. For instance, the capacity of VUV heteronuclear molecular spectra to transform the broadband emission of homonuclear molecules and concentrate it in a narrow band localized near the resonance line of the heavier-gas impurity atom can be employed in the development of VUV radiation sources with a high spectral density, including, with a good chance of success, coherent radiation sources.

In Refs [96–99], a study was made of the fundamental possibility of forming an active medium amplifying the radiation in the VUV spectral region. Experiments with discharge tubes of different lengths showed that the narrow-band radiation of the heteronuclear KrXe* molecule, which lies near the xenon 146.961-nm resonance line, experiences amplification when the krypton – xenon gas mixture is excited in a barrier discharge and in a cryogenically cooled capillary discharge. In capillary and barrier discharges, the amplification effect shows itself on the structures of the heteronuclear KrXe* molecule. For a capillary discharge operating at a lower gas mixture pressure than the working pressure of the barrier discharge, the radiation being amplified concentrates in the most intense, long-wavelength 'shoulder' of the emission band of the molecule, approximately at a wavelength of 147 nm. The amplified radiation bandwidth is approximately equal to 0.06 nm. In the case of a barrier discharge, the radiation being amplified is somewhat more distant from the atomic xenon resonance transition and emerges both on its long- and short-wave wing sides [98]. The larger shift of radiation being amplified from the center of the atomic resonance transition, observed in the barrier discharge, is supposedly due to the higher pressure of the working medium and the higher excited-dimer level populations in the barrier discharge than in a d.c. discharge.

Figure 21 shows the results of experiments carried out in Ref. [97]. Three pairs of the emission spectra of a d.c. capillary discharge are given. For every pair, the lower spectrum constitutes the emission of an uncooled capillary discharge, and the upper spectrum corresponds to a cooled capillary discharge which exhibits the property of amplification. Since a direct comparison of experimental VUV spectra emitted by capillary discharges of different length is hampered by the uncertainty of capillary adjustment relative to a spectrometer and by the changes in window transmission [101, 103], the work took advantage of a simple methodical trick. The trick, in essence, lies in the fact that the values of spectral intensity for the cooled and uncooled discharges in tubes of different lengths are obtained under similar conditions for the passage of recorded radiation through the window and under invariable tube arrangement relative to the spectrometer. At the same time, the spectral intensities for the uncooled capillary discharges of different lengths are normalized to the same value. This way of estimating the intensities for cooled capillary discharges of different lengths results in underrated values of the gain coefficient but prevents it from being overestimated. An analysis of the experimental data reveals a nonlinear enhancement of the spectrum of time-continuous radiation from capillary discharges of different lengths, the gain coefficient being estimated at 0.1 cm^{-1}. Attempts to realize so high a gain coefficient using the active medium of a capillary discharge encounter a serious obstacle: the gas density nonuniformity in the capillary radius, with the consequential strong radiation refraction which hinders the

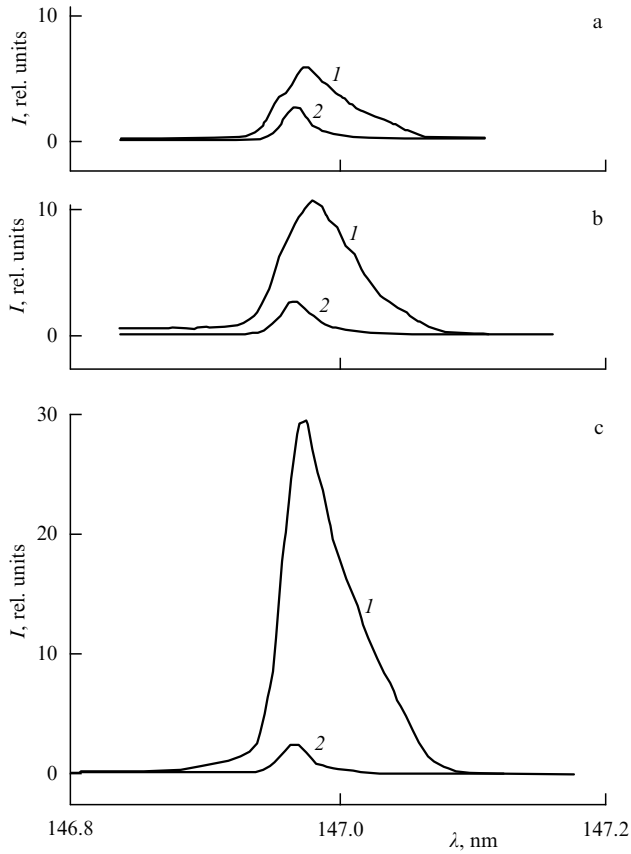

Figure 21. Emission spectrum of a heteronuclear molecule excited in cooled (curve *1*) and uncooled (curve *2*) capillary discharges of different lengths: 10 cm (a); 20 cm (b), and 40 cm (c) [97].

use of cooled capillary discharges in a laser cavity. Nevertheless, experiments with barrier and cooled capillary discharges have demonstrated the feasibility, in principle, of developing a VUV laser which operates at wavelengths coinciding with the radiative transitions of the heteronuclear KrXe* molecule. The practical implementation of the VUV laser operating at the KrXe* molecular transitions calls for developmental engineering work.

Another serious difficulty encountered when operating with cooled capillary discharges longer than 40 – 50 cm is a rapidly decreasing transmission of magnesium fluoride windows [102, 103] under exposure of their surfaces to high-intensity VUV radiation. The problem of rapidly decreasing window transmittance in long cooled capillaries remains to be solved. However, the very fact of its existence is an indirect indication of a significant growth of VUV radiation intensity, lending credence to the idea of a cooled capillary discharge as a time-continuous source of stimulated radiation.

Checking for the gain on the narrow-band radiative transitions of other heteronuclear molecules in low-temperature plasmas of gas mixtures has not been verified. It is not inconceivable that these transitions also exhibit amplification.

The experimental capabilities of Refs [85 – 92] were limited to the $\lambda > 115$-nm wavelength range. This prevented the study of narrow-band emission structures located in the shorter-wave spectral region (six new bands near the four resonance lines of argon and neon atoms escaped investigation). It cannot be doubted that these bands do exist.

Employing low-temperature plasmas that contain rare-gas heteronuclear molecules as the active medium gives promise that VUV laser radiation will span a broad wavelength range, beginning with the neon resonance line (73.5 nm) and ending with the xenon resonance line (147 nm). For a method of low-temperature plasma excitation it is expedient to employ the techniques whereby the gas temperature remains low either due to its efficient cooling or due to the use of pulsed excitation methods not resulting in gas heating. Among the most promising techniques of low-temperature gas-discharge plasma production, mention should first of all be made of a barrier type discharge [104–112], creeping discharges [113], discharges cooled by way of adiabatic gas expansion [114–117], and cryogenically cooled discharges [118–121].

12. Conclusions

The spectroscopic rare-gas research at the formation stage of contemporary atomic physics favored the origin and practical realization of many elegant physical ideas in the theory of atomic structure, astrophysics, and other realms of physics and its diverse applications. Recent work shows that not nearly all physical properties of low-temperature plasmas of rare-gas mixtures are known and by no means all possibilities for their practical use have been exhausted. This branch of physics continues to surprise and please the imagination of researchers by the uncommonness of individual features of the processes, which had earlier been believed to be thoroughly studied, and which are of significance both in understanding the physics of the phenomena and in solving specific applied problems.

The narrow-band VUV spectra investigated in recent years, which arise from the spectroscopic transitions between the weakly bound states of heteronuclear molecules, once again demonstrate the 'inexhaustibility' of notions of such a well-studied subject as rare gases. Despite the well-established fact that the high-intensity narrow-band VUV spectra of gas mixtures arise from transitions in heteronuclear molecules, the question nevertheless remains open: why, of all the possible ways of radiation loss for the excitation energy, is the channel involving such 'unusual' weakly bound states the one mainly realized? The following experimental facts remain to be understood: why is the heteronuclear dimer radiation, which prevails in the VUV region, not attended by radiation in other spectral regions; why is it not possible to observe the transitions between their states, for instance, in the visible and near-infrared spectral regions? Explanations for these intriguing properties of low-temperature plasmas of rare-gas mixtures are supposedly a short distance in the future.

A deeper insight into the processes involving excited atoms and ions in low-temperature plasmas of rare-gas mixtures will make possible new efficient VUV radiation sources.

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