Photochemical lasers on electronic molecular transitions

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Abstract. **The main stages of the development of the photochemical method for exciting near-IR, visible, and UV gas lasers are briefly reviewed on the basis of studies performed at the Department of Quantum Radiophysics at the P.N. Lebedev Physics Institute and jointly with other institutes within the framework of a program for creating high-power explosion-pumped lasers under the supervision of academician N.G. Basov.**

Keywords*: photochemical laser, pumping source, open discharge, photodissociation wave, photochemical processes.*

1. Introduction

Studies on the development of the photochemical method for exciting active laser media on electronic transitions were initiated at the P.N. Lebedev Physics Institute (LPI) in 1965 by a report by P.A. Bazhulin, N.G. Basov, O.N. Krokhin, A.N. Oraevsky, and I.I. Sobel'man [1]. They formulated, for the first time, the basic principles of designing high-power photodissociation lasers on metastable atoms pumped by such unconventional sources as a high-temperature discharge and a strong shock wave. A detailed project of a high-power explosion-pumped photodissociation laser was presented in [2]. The new concept was based on the initiation of a photodissociation of molecules to obtain an inverse population of atomic states [3] and on the results of papers [4, 5], in which, for the first time, this pumping technique was implemented and lasing was obtained on the $^2P_{1/2} - {}^2P_{3/2}$ transition between the fine structure levels of iodine atoms ($\lambda = 1.315$ μm).

The physical basis and design features of an iodine laser, whose systematic investigations were pioneered by the studies performed at the LPI on the initiative of N.G. Basov, were analysed in detail in a number of reviews and monographs (e.g., [6 – 8]). An extensive development of the iodine photodissociation laser stimulated extensive and detailed studies of the potentialities of the photodissociation pumping method and the search for new active media for high-power optically excited lasers. The main goal of these studies

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was to achieve a shorter wavelength than that of an iodine laser in order to increase the efficiency of the interaction of laser radiation with matter. It should be noted that similar studies on the search for new active media for photodissociation lasers were also performed at some laboratories in other countries. However, in these cases, flashlamps, lasers, and spontaneous emission of excimers of noble gases excited by an electron beam served as pumping sources, whose energy characteristics were much lower than those of high-temperature discharges and strong shock waves proposed in [1]. On the whole, laser effects were observed for 24 elements of the periodic table and 18 molecular transitions in the range of 11.35 μm – 223 nm upon optical excitation, including photodissociation and other pumping mechanisms discussed in this review.

A high-temperature discharge and a strong shock wave were used for the first time to excite a photodissociation laser on atomic iodine [6, 7, 9]. These experiments demonstrated such advantages of the photochemical excitation method as the possibility of increasing the laser energy proportionally to the active-medium volume and pumping energy, as well as the technical simplicity and low cost of generating high-energy laser radiation. Due to their versatility and high radiation energy in the UV and VUV spectral regions, where the most intense absorption bands for most of molecules are located, these pumping sources appreciably extended the experimental potentialities of the photochemical method and made it possible to obtain unique results. In addition, their application has led to the development of not only the photodissociation technique but also methods for direct optical excitation of molecular gases and their excitation in secondary photochemical reactions. The possibility of easily controlling rather complex photochemical processes by directing their development in the required channel through changes in the composition and pressure of the working mixture or the excitation wavelength has been shown experimentally. Despite fairly long chains of chemical transformations, it was possible to achieve a high selectivity in obtaining laser-active states characterised by quantum yields of their formation close to 100 %.

For the present, the iodine photodissociation laser is the only laser on an atomic transition excited by the radiation of an open discharge and a strong shock wave. Subsequently, for the reasons that are discussed below, the photochemical method was developed by using molecular transitions as active media of lasers with the pump sources considered. Table 1 lists the molecules for which lasing was obtained upon pumping by the radiation of an open discharge and a strong shock wave, the lasing and pump wavelengths λ_g and

λ_p, respectively, and references of priority. Not all of the realised lasing mechanisms have received a due development so far. However, almost all of them are fundamentally important and indicate that certain trends in the search for new active media are promising.

Table 1.

Molecule	λ_g/nm	λ_p/nm	References
CN	1150	180	[10]
S_2	1100	220	[11]
XeO	538	140	[12]
Xe_2Cl	520	137	[13]
HgCl	558	190	[14]
HgBr	504	200	[15]
HgI	443	225	[16]
IF	491	130	[17]
XeF $(C-A)$	485	160	[18]
Kr_2F	450	160	[19]
XeF $(B-X)$	351	160	[20]
I_2	342	190	[21, 22]
KrCl	223	137	[23]

Consider the key aspects of the development of the photochemical excitation method at the LPI. Part of the results has been obtained in a cooperation with the All-Russian Research Institute of Experimental Physics (an S_2 laser), 'Astrofizika' Research and Production Association (a XeF laser pumped by the radiation of a shock wave and a surface discharge), the State Institute of Applied Chemistry (a XeF laser pumped by the radiation of a shock wave and a CN laser), the N.E. Bauman Moscow State Technical University (a mercury halide laser pumped by the radiation of a surface discharge), and the St. Petersburg State University (spectral and kinetics investigations). A more detailed description of the systems considered below is presented in [24] and in the original works cited in this review.

2. Pump sources

The main results were obtained upon pumping by an open emitting discharge representing a pulsed extended discharge, which was initiated directly in the laser working mixture and occupied a small part of the laser cell volume. The discharge plasma radiation excites the working gas mixture located in the discharge-free part of the volume. The most widespread discharge-initiation methods are an electric explosion of thin metal wires and discharges over dielectric surfaces. Upon a wire explosion, a regularly shaped cylindrical plasma column forms and expands at a radial velocity of ~ 1 km s^{-1}. The absence of a shell separating the discharge plasma from the active medium makes it possible to utilise the radiation in any spectral range, including the VUV. For brightness temperatures of $30-35$ kK typical of such a discharge and usually reached at a discharge-supplying energy of > 1 kJ stored in a capacitor-bank, the emission intensity of the plasma column within the actual absorption bands of the working substance achieves 1 MW cm^{-2}. The high specific excitation power density, which usually amounts to 10^2-10^3 kW cm^{-3},

leads to the formation of up to 10^{18} cm^{-3} free atoms and radicals within a time of $\sim 10^{-5}$ s.

The priority in the study and application of exploding wires as a pump source belongs to works carried out at the LPI. The attention in their study was chiefly drawn to the investigation of the energy balance in the discharge and its emission and gas-dynamic characteristics [7, 25, 26]. It was found that the formation of UV and VUV radiation upon an electric explosion of wires has specific features associated with the selection of the wire material and thickness [24, 27–30]. The wires $10-50$ μm thick made of such refractory materials as molybdenum and tungsten turned out to be optimal. Upon their electric explosion, the emissive and gas-dynamic properties of a 50-kV discharge weakly depend on its length (at least, between 10 and 100 cm) and on the working-mixture composition and pressure. This allows one to vary the experimental conditions within a wide range without changes in the electric circuit. The latter was a decisive circumstance in choosing exploding wires as a pump source in the search and studies of new active media for photochemical lasers.

At the same time, in order to design practically useful lasers with higher performance characteristics, some other methods for the formation of extended optical pump sources have been developed. All of them are based on discharges over a dielectric surface, allowing one to obtain a repetitively pulsed pumping mode, and differ only in the devices for the spatial discharge stabilisation. Sectioned [31], linearly stabilised [32, 33], and multichannel surface discharges [34] refer to this type of discharge. At equal specific energy inputs ensuring a high optical discharge-plasma density, a surface discharge has emission characteristics close to those of an exploding wire. At low energy inputs, when the discharge plasma is optically transparent, its radiation spectrum depends to a large degree on the substrate material, thus making it possible to control the spectrum and output power of radiation within a required spectral range.

A pump source on the basis of an open discharge formed along the surface of a ferrite rod was proposed in [35, 36]. Its operating principle is based on the ohmic heating of the material of a conducting filament preliminarily burned out on the rod surface. The discharge formation and the wire explosion mechanisms are close to each other, but the former ensures a multiple operating mode. This pump source was used to excite I_2 and XeF lasers [35, 37–39].

In practice, the most important characteristic of an electric-discharge optical pump source is the efficiency of conversion of the electric power supplied to the discharge into its emission within the actual absorption band of the working medium. As a rule, this efficiency is 5 %–10 % and depends mainly on the absorption spectrum width. For example, the measured efficiency of the pump source of a XeF photodissociation laser excited in the VUV region ($\lambda_p = 160$ nm and $\Delta\lambda = 20$ nm) was 8.5% [40]. Almost the same value was obtained for the pump efficiency of an iodine photodissociation laser in the UV region ($\lambda_p = 270$ nm and $\Delta\lambda = 40$ nm) [7].

A strong shock wave excited by a detonation of an explosive in the initial working mixture occupies a special place among the optical pump sources of photochemical lasers [2, 9, 41]. When Kr, Xe, or their mixtures at a pressure of 1 atm are used as buffer gases, a shock wave propagating at a velocity of $5-8$ km s^{-1} emits as a black-body with the brightness temperature of $25-30$ kK.

3. Optical-excitation mechanisms

An inverse population may be produced upon photo-chemical excitation due to primary or secondary photo-processes. Photodissociation of molecules upon their transition to states with a continuous spectrum and their optical excitation to bound states are classified as primary processes. The states of dissociation products and states of the initial molecule are inversely populated in the first and second cases, respectively.

Reactions of the products of primary photoprocesses between each other or with a reagent added beforehand to the working mixture belong to secondary processes. In some cases, secondary processes produce more favourable conditions for lasing or shifting the radiation wavelength to another spectral region. In this case, it is generally unnecessary to produce an inversion in primary photoprocesses.

Among molecular transitions on which lasing was initiated by photochemical pumping, ion–covalent transitions are the most numerous ones (except for CN, S_2, and XeO molecules). This is explained by several reasons.

The first reason is that the excited ionic states are easily produced in charge-transfer reactions, which have the largest cross sections among the processes involving neutral reagents. Note that this class of reactions is very wide and affords ample opportunities for selecting particular mechanisms for exciting ionic states of molecules. The most well-known reactions of this type are harpoon reactions. Among them, there are reactions between excited atoms of rare gases and halogen-containing molecules, underlying excitation kinetics of excimer lasers. They are characterised by a charge transfer from excited rare-gas atoms to halogen-containing molecules, such as F_2, Cl_2, etc. with a large electron affinity. The charge transfer occurs in the region of avoided crossing of covalent and ion terms of the complex that forms upon the approach of reagents (Fig. 1). Since, due to a long-range Coulomb interaction, this region usually lies at large internuclear distances (~ 10 Å), such reactions are characterised by large cross sections of a few hundreds of Å^2. The internuclear distance r_0, at which a charge transfer takes place, can be estimated from an obvious relation (Fig. 1) $r_0 \simeq (I - U_e - E^*)^{-1}$ au, where I is the ionisation potential of one of the reagents; U_e is the energy of the vertical electron affinity of the other reagent; and E^* is the excitation energy of one of the reagents. On the other hand, it was found ([24, 42] and references therein) that the cr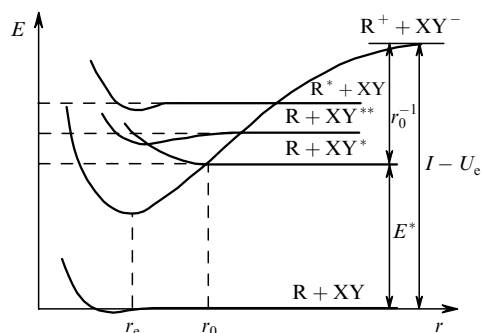oss section for the reactions of halogen-containing mole-cules with rare-gas atoms is virtually independent of which of the reagents is excited (Fig. 1). This circumstance opened a new trend in the search for active media for photochemical lasers and, in particular, allowed the use of broadband molecular absorption for obtaining excimer states, which were previously excited only by an electron beam and a fast discharge. Estimates of the spectral threshold of the initiation of such reactions of krypton and xenon with optically excited molecules containing halogen atoms or CN have shown [42] that, as a rule, they proceed upon excitation at $\lambda > 130$ nm, which can be achieved upon pumping by an open discharge and a strong shock wave.

The second reason is that, in ionic states of molecules, the equilibrium internuclear distance is usually much larger than in a covalent state. This leads to a situation where, upon a direct optical excitation of molecules into ionic states, transitions from lower vibrational levels of the ground covalent state to high-lying vibrational levels of the upper state take place. At these levels, the repulsive branch of the potential curve becomes very steep. In this case, according to the Franck–Condon principle, a large number of vibrational bands is observed in the absorption spectrum, thereby determining a wide pumping spectrum. Moreover, for the same reason, this facilitates the attainment of an inversion on ion–covalent transitions, since they occur to high vibrational levels of the lower covalent state. In this case, the total population inversion of the electronic states involved in lasing is unnecessary, and a rapid depopulation of lower laser levels is ensured due to a vibrational relaxation. The latter circumstance is especially important for the case of optical pumping of allowed laser transitions by the radiation of thermal sources (flashlamps, an open discharge, and a strong shock wave), because they are characterised by pump pulses of micro- or millisecond duration.

A proposal of using an absorption induced by colliding particles ($A + B + h\nu$) for exciting active media, which was put forward in [43], should be also noted. In particular, it is pointed out [43] that lasing can be obtained in dimers of rare gases formed during the photoassociation of rare-gas atoms into a bound excited state (see [44–46] for details of the formation of absorption spectra during photoassociation). A practical interest in this pumping technique is determined primarily by the fact that it makes it possible to reduce the Stokes shift almost to a minimum (10 %–20 %) and to obtain VUV laser radiation. Subsequently, this proposal was developed in several experimental studies [47–52], helping to formulate the conditions for achieving lasing on Xe$_2$ at 172 nm [51]. Moreover, the obtained results show that, in a broad excitation region ($\sim 115 - \sim 150$ nm) with a small transparency window of $135 - 145$ nm, the yield of the $1_u/0_u^-$ states of Xe$_2$ approaches 100 %, allowing us to expect a highly efficient optical excitation of lasing not only on Xe$_2$ but also on other excimers forming in reactions of excited xenon with halogen-containing molecules or H$_2$ [49, 51].

Figure 1. Potential curves explaining the formation of excited products in charge-transfer reactions.

4. Spatial effects

A high radiation power of such pump sources as an open discharge and a strong shock wave leads to a number of features of its interaction with an absorbing medium, which manifest themselves, in particular, in the formation of bleaching and emission waves. A bleaching wave can be observed by emission of products excited at the wave front

at a sufficiently large transverse size of the cell $d \gg (\sigma N_0)^{-1}$, where σ and N_0 are the absorption cross section and the initial concentration of the absorbing substance, respectively. Fig. 2 demonstrates this effect for a XeF_2 photodissociation wave (PDW) in an explosion-pumped XeF laser.
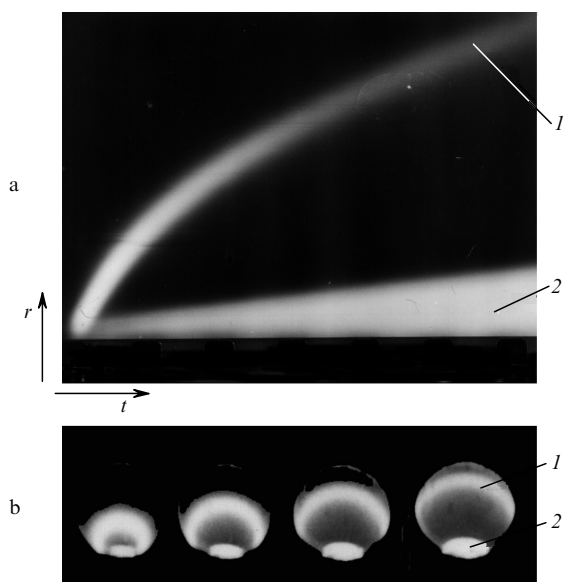

Figure 2. Streak photographs of (*1*) the emission wave and (*2*) shock-wave radiation in a XeF laser with an exit aperture of 48 cm: (a) a slit scan and (b) a frame-by-frame scan, frames with an exposure of 0.5 μs follow every 2 μs.

The problem of bleaching a substance and forming a PDW was considered for the first time in 1965 in the report [1] during the discussion on large-aperture high-energy photodissociation lasers, in which this phenomenon was expected to be observed. Its essence can easily be understood from the following considerations. The lifetime of absorbing molecules in a pump field is $\tau_d = (\sigma I_0)^{-1}$, where I_0 (photon cm^{-2} s^{-1}) is the photon flux within the substance absorption band. If the pumping occurs during the time $T > \tau_d$, then all the substance in front of the pump source dissociates and the pumping radiation penetrates into deeper substance layers and produces a similar effect. The velocity D of the bleaching wave can be estimated taking the ratio between the optical layer thickness $l = (\sigma N_0)^{-1}$ and the lifetime of this layer: $D = l/\tau_d = I_0/N_0$.

In the simplest case, when the pump source is flat, the radiation is monochromatic, and the photodissociation products do not absorb at the pump wavelength, a dissociation wave, characterised by a stationary particle-concentration profile at the wave front, propagates in the medium. This case was analysed in detail in [53] for a flow of an absorbing medium incoming to the pump source at a velocity v, which is naturally equivalent to the case of a source moving in a medium at rest. On the basis of the equations of radiation transfer and conservation of the number of particles in a two-level absorbing medium, an analytic expression for the profile of a bleaching wave was obtained. It has a simple form for $D \gg v$:

$$N/N_0 = \{1 + \exp[\sigma N_0(Dt - x)]\}^{-1},$$

where N is the concentration of absorbing particles and x is the coordinate along the propagation direction of the bleaching wave.

If the lifetime of the excited particles forming at the wave front is small compared to the characteristic time of the pumping rate change, which is equal to the lifetime $(\sigma I_0)^{-1}$ of the absorbing molecules, then a stationary excited-particle concentration profile is established, and the FWHM of the distribution function is $\sim 3.5 \times (\sigma N_0)^{-1}$ [24, 54]. An excited-particle emission wave propagating at the velocity of the bleaching wave is observed in experiments.

The regime with $D \gg v$ is usually called a free-running bleaching wave mode. For the first time, it was observed in a photodissociation XeF laser. The characteristic PDW-formation time in this laser, which also coincides with $\tau_d < 10^{-6}$ s, is small compared to the pumping duration of $10^{-5} - 10^{-4}$ s. Therefore, at an initial XeF_2 concentration meeting the PDW observation condition $(\sigma N_0)^{-1} \ll d$, the photodissociation wave front has enough time to be completely formed. In this case, the PDW velocity reaches 10 and > 100 km s^{-1} upon pumping by radiation from an open-discharge and a strong shock wave, respectively.

In an iodine photodissociation laser, the absorption cross section of the working substance (CF_3I, C_3F_7I, etc.) is two orders of magnitude smaller ($\sigma \sim 10^{-19}$ cm^2), and the characteristic lifetime $(\sigma I_0)^{-1}$ of the absorbing molecules near the pump source proves to be comparable with the pump duration. As a result, the free-running bleaching wave does not have enough time to be formed, and the case of $D < v$ is realised. In this case, the substance layer absorbing the pump radiation is kept close to the source, and we deal with a standing (in a coordinate system fixed to the pumping source) bleaching wave. The number of particles that dissociated at the boundary with the pump source is independent of the initial concentration N_0 of the absorbing substance and amounts to $N_0\tau/\tau_d = I_0/v$ [9], where $\tau = l/v$ is the lifetime of the optical layer determined by the substance inflow to the pump source during its motion.

The model considered in [53] and based on collimated monochromatic radiation is an ideal one. Such a model obviously differs from actual experimental conditions, in which a pump source with a Lambert-type radiation pattern and an absorbing substance with a complex spectral distribution of the absorption cross section are commonly used. Despite this fact, this model turns out to be useful at a level of approximate estimates and yields a qualitatively correct pattern of spatial effects. In a general case, an exact solution of a radiation transfer equation with a variable number of absorbing particles can be obtained only using numerical methods. These questions were considered in a number of papers ([54] and references therein).

The photodissociation-based bleaching mechanism considered above is not a sole one. For example, an induced transparency in mixtures of Cl_2 with noble gases arises during reactions between the latter and optically excited chlorine molecules. In iodine vapours, this transparency results from the collisional dissociation of the lower laser A' state, in which molecules find themselves as a result of a radiative decay of the optically excited upper state. In both cases, emission waves are observed due to the radiation of products of excitation at the bleaching wave front, as it

happens during photodissociation. However, in these particular cases, there is a specific feature associated with the fact that the final products of the laser cycle are chlorine or iodine atoms, which, at sufficiently high buffer-gas pressures, can recombine into the initial molecules at rates comparable to their production rate. This leads to an experimentally observed decrease in the velocity of the photochemically driven decomposition wave which transforms to a standing wave, as the buffer-gas pressure increases [55].

The observation of the bleaching-wave propagation dynamics by the emission of excitation products from the wave front is presently used as a method of spectrally selective dynamic actinometry of high-power radiation sources [40, 56, 57].

The pumping radiation absorption, which is nonuniform over the active-medium volume, gives rise to optical inhomogeneities caused by a heat release during photochemical reactions and by a change in the chemical composition of the mixture in the pumped region. This effect is illustrated by Fig. 3, which shows a time-resolved interferogram obtained upon illuminating the active medium of a Kr_2F laser by ruby laser radiation. The active medium is placed in one of the arms of a Michelson interferometer with a tilted mirror. A shift of fringes observed in Fig. 3 corresponds to a decrease in the refractive index in the bleaching wave by 5×10^{-7} due to a change in the chemical composition of the substance [58]. Estimates of the gas-dynamic perturbations resulting from a nonuniform heat release in the active medium yield an opposite sign and a ~ 10 times smaller value of the refractive-index change [58]. In similar measurements for the active medium of a XeF laser, the change in the refractive index at the bleaching-wave front has an appreciably smaller magnitude: $\Delta n = -10^{-7}$ [59].
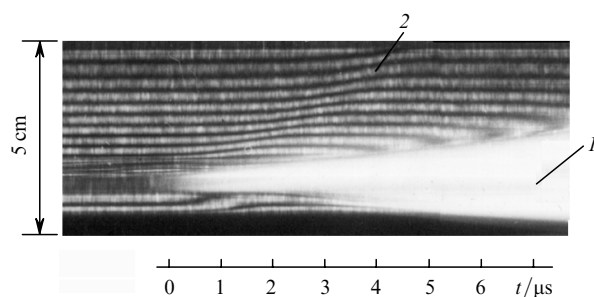

Figure 3. Time-resolved interferogram of the bleaching wave in KrF_2: (*1*) discharge emission and (*2*) bending of fringes in the bleaching wave.

Nonuniformities of the refractive index in the active medium result in an increased divergence of laser radiation, which, for a plane-parallel resonator, can be estimated using formula [60] $\theta = 2(2\Delta n)^{1/2}$. For a XeF laser, this relation gives $\theta = 10^{-3}$ rad, which is close to the experimentally observed values.

5. Lasers based on secondary photochemical reactions

5.1 Reactions of atoms of the VI group

Photochemical lasers on S_2 and XeO molecular transitions are the most striking examples of the fruitful use of secondary photochemical processes for improving the lasing conditions. The development of these lasers is historically linked to a proposal to use atoms of the IV group (the principal subgroup) as active media of photodissociation lasers. This idea was proposed in 1965 within the framework of a high-power photodissociation laser [1] as an alternative to an iodine system, and the following circumstances making these atoms promising were emphasised. First, the transitions between the $^1S_0$ and $^1D_2$ metastable states and transitions from them to the ^3P_j ground state made it possible to reduce the Stokes shift of laser radiation compared to the radiation shift of an iodine photodissociation laser. Second, the physicochemical activity of atoms of the oxygen group in the D state is much higher than in the S state, which significantly facilitates the attainment of an inversion on the $^1S_0 - {}^1D_2$ transition. However, as it was revealed later, despite a large difference between the quenching rates for these states, the rates of quenching the upper state by parent molecules and products of their photolysis are rather high. This substantially complicated the practical implementation of lasing on the proposed forbidden transitions upon pumping by radiation of flashlamps, an open discharge, and a strong shock wave, because the low probability of the transition (the radiative lifetimes of, for example, the $^1S_0$ state of sulphur and oxygen atoms are ~ 0.6 and ~ 0.8 s, respectively) requires to store rather high concentrations of atoms in the excited state. However, as was shown in OCS photodissociation experiments [11], the high chemical activity of these states can be used for attaining an inversion in secondary photochemical reactions. Paper [11] reports on lasing obtained on the forbidden $S_2(b\,^1\Sigma_g^+ - X\,^3\Sigma_g^-)$ molecular transition, whose upper state forms as a result of a fast reaction of $S(^1D_2)$ atoms produced during the OCS photodissociation in the spectral range of $190-255$ nm with OCS as parent molecules. The results of detailed studies of an S_2 laser are presented in [61].

Despite its moderate output parameters (the specific energy output is 5×10^{-4} J cm^{-3} [61]), an S_2 laser is exceptionally interesting, since it is the first laser that can be called a chemical laser on an electron transition. However, this classification is valid only from the viewpoint of chemical kinetics rather than from the energy point of view, since the laser energy is taken mainly from an external source. This laser was the first to demonstrate the fruitfulness of the idea of using secondary photochemical reactions for exciting active media and thus initiated a systematic search for new excitation mechanisms in secondary processes. Beginning with this moment, the active laser volume was actually regarded as a chemical reactor that can be used to search for secondary photoprocesses resulting in inverse populations of electronic states of the reaction products [6]. An equally important fact is that, for the first time, induced emission was obtained on a molecular transition upon optical pumping. The matter is that, unlike atomic transitions, molecules in an excited state are distributed over a large number of internal degrees of freedom. With all factors being equal, this reduces the gain of the active medium by one – two orders of magnitude. Therefore, the observation of a laser effect on sulphur molecules stimulated an extensive search for new active media based on molecular transitions. Finally, the formation of the $S_2(b\,^1\Sigma_g^+)$ state was experimentally discovered in the reaction between $S(^1D_2)$ and OCS in an S_2 laser, and the $S_2(^1\Sigma_g^+ - {}^3\Sigma_g^-)$ transition was also observed for the first time.

The fruitfulness of this approach was subsequently confirmed in a XeO laser, in which the forbidden $O({}^1S_0 - {}^1D_2)$ transition was stimulated by collisions with Xe. The physical essence of this phenomenon is as follows. When the O and Xe atoms approach each other, the point symmetry of the oxygen atomic potential is violated by a perturbing action of the xenon atomic potential, and a cylindrical symmetry with respect to the internuclear axis appears. In this case, the selection rules become molecular and become dependent on the symmetry of the wave function relative to the plane, in which the internuclear axis lies, and on the changes in the spin and angular-momentum components along the symmetry axis. A similar phenomenon was also observed in collisions with other rare-gas atoms, Ar and Kr, and for other atoms (S and Se) from the oxygen group [62]. However, the interaction of oxygen atoms in the ${}^1S_0$ state with xenon is characterised by a much stronger coupling (~ 690 cm^{-1} [62]), which allows us to definitively assert that a weakly bound molecular state forms upon collisions of these atoms with a participation of a third particle. The molecular selection rules result in the appearance of a transition from the $2^1\Sigma^+$ state of the complex to the lower $1^1\Sigma^+$ molecular state correlating to the ${}^1D_2$ state of oxygen atom. This transition is allowed in the dipole approximation. Note that the lower laser state is a short-lived one: since its potential curve crosses the repulsive potential of the ground state, it decays virtually within a single molecular vibration.

The effect of collisional stimulation of the ${}^1S_0 - {}^1D_2$ transition significantly reduces (approximately by two orders of magnitude [24]) the requirements for the threshold pump power, at which lasing can be obtained. In 1975, this has finally led to the attainment [12] of a laser effect on the $O({}^1S_0 - {}^1D_2)$ transition stimulated by collisions with Xe. $O({}^1S_0)$ atoms were formed during the photodissociation of N_2O exposed to the radiation of an open discharge at wavelengths < 150 nm. The results of detailed studies of this laser are presented in [29]. The analysis of the data obtained allowed one to make an important conclusion testifying to a high efficiency of the XeO-laser pumping mechanism: $\sim 60\%$ of singlet oxygen atoms forming during pumping emit induced radiation through the XeO ($^1S_0$) bound state despite an almost gas-kinetic quenching rate of excited oxygen.

From the viewpoint of the development of the photochemical method, the significance of the works on the creation of a XeO laser consisted primarily in the fact that it became possible to appreciably reduce the lasing wavelength and to advance to the visible region. The output energy of the XeO laser (2.2 J) obtained later was significantly higher than the output gas-laser energies in the visible region achieved by that time, including electron-beam-pumped lasers on rare gas oxides [62]. In addition, an example of the XeO laser demonstrated the high radiation characteristics of an open discharge in the VUV region and showed promise of using this radiation for pumping photochemical lasers. This was subsequently confirmed by direct photoelectric measurements [30]. The extension to the VUV spectral region of pumping and the use of secondary photochemical processes had a decisive effect on the development of the photochemical pumping technique and resulted in the implementation of several new mechanisms of lasing at short wavelengths considered below. Note that the XeO laser was the first photochemically pumped excimer laser.

In connection with the possibility of obtaining laser action on atoms of the VI group discussed above, it should be noted that the subsequent advent of pump sources based on electron-beam-excited excimer radiation, whose power exceeded the power of conventional flashlamps, made it possible to achieve a laser effect on the $S({}^1S_0 - {}^1D_2)$ transition during the OCS photolysis [63] and on the $Se({}^1S_0 - {}^1D_2, {}^1S_0 - {}^3P_1)$ transitions during the OCSe photolysis [64, 65]. Unlike open-type sources, the sources of excimer radiation are isolated from the active medium, and allow one to independently optimise its composition and to obtain the Doppler width of the amplification line, thus increasing the laser gain.

5.2 Mixtures of KrF$_2$ with rare gases and nitrogen

Lasers based on the photodissociation of KrF$_2$ vapours, as well as the active media on mixtures of Cl$_2$ with noble gases considered below, are striking examples showing how optical excitation allows one to control easily the kinetics of active media by varying the working-mixture composition and pump spectrum. This guides chemical reactions into one or other channel with the luminescence quantum yield being kept at a high level. Fig. 4 presents a scheme of the processes upon optical excitation of KrF$_2$ mixtures with Xe, Kr, and N$_2$. When KrF$_2$ vapours absorb radiation in a region of a wide continuum with a maximum at 164 nm, they dissociate with the formation of excimers KrF(B) (the quantum yield is $41\% \pm 11\%$ [66]), emitting at 248 nm upon the $B - X$ transition to the ground state. The utilisation of KrF(B) in secondary processes is different, depending on the composition and pressure of the working mixture. For example, at low-concentration Xe admixtures, XeF(B) forms with a yield close to 100 % [66, 67]. Being mixed with Kr at a Kr pressure of ~ 1 atm, KrF(B) forms the Kr$_2$F* excimer in three-body processes [68], and the KrF(B) luminescence completely vanishes. An unexpected effect was observed, when Kr was replaced by N$_2$: the emission of Kr$_2$F* at 420 nm not only failed to vanish but
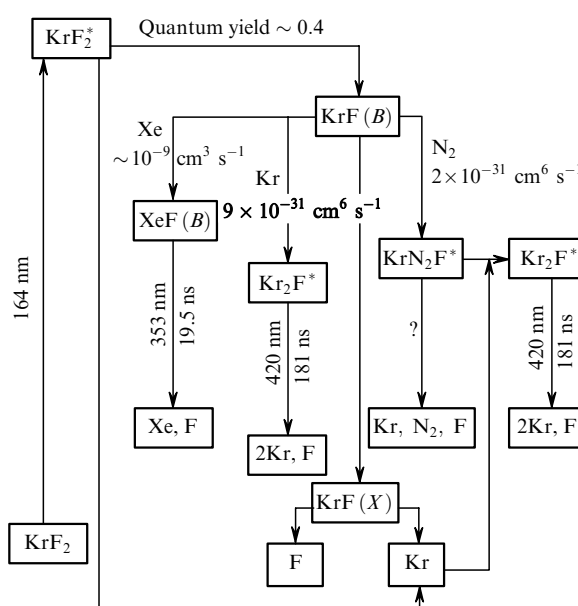

Figure 4. Scheme of the photoprocesses in mixtures of KrF$_2$ with noble gases and N$_2$.

became even stronger. As was found in [68], in this case, Kr_2F^* forms due to exchange reactions of Kr atoms, which are produced during photochemical decomposition of Kr_2F exposed to the open-discharge radiation, with mixed KrN_2F^* four-atomic excimers. These results indicate to the existence of the KrN_2F^* excimer, which was not observed previously. Note that, despite a complex Kr_2F^* formation mechanism, which, in mixtures with nitrogen, involves three stages of chemical transformations (at one of the stages, products of photochemical processes react between each other), the Kr_2F^* production efficiency is rather high: $\sim 70\,\%$ of $KrF(B)$ molecules transform into the Kr_2F^* excimers [68]. The discovery of the new excimer shows that the class of laser-active excimers can be expanded by including excimers with a more complicated structure. Indeed, the $COKrF^*$ excimer emitting in the range of $280-380$ nm upon optical excitation of a Kr_2-He$-$CO mixture was detected later in [69].

Lasing of XeF at 350 nm in a $KrF_2 : Xe : N_2 : Ar = 4 : 6 : 160 : 1500$ Torr mixture [67] and of Kr_2F at 450 nm in $KrF_2 : N_2 = 1 : 1500$ Torr and $KrF_2 : CF_4 : Kr = 1 : 300 : 1200$ Torr mixtures [19] was observed upon pumping by the radiation of an open discharge.

5.3 Mixtures of Cl_2 with rare gases

Another example that demonstrates an efficient control of photochemical reactions is the optical excitation of a mixture of molecular chlorine with rare gases (Fig. 5). When the mixture is excited at 137 nm in the presence of Ar, a singlet$-$triplet relaxation of Cl_2 to the $^3\Pi_{2g}$ state takes place followed by emission at 258 nm upon the transition to the $^3\Pi_{2u}$ state with a quantum yield of luminescence of 55 % per one absorbed pumping quantum [70]. In the presence of Kr or Xe, excited chlorine forms $KrCl(B)$ or $XeCl(B)$ excimers emitting upon the $B-X$ transition at 222 and 308 nm with the luminescence quantum yields of 70 % and 80 %, respectively [70]. In a mixture with Xe, as the Xe pressure increases to ~ 1 atm, almost all of $XeCl^*$ molecules are bound into Xe_2Cl^* emitting at ~ 490 nm with a luminescence quantum yield of $\sim 75\,\%$ [71]. Fig. 5
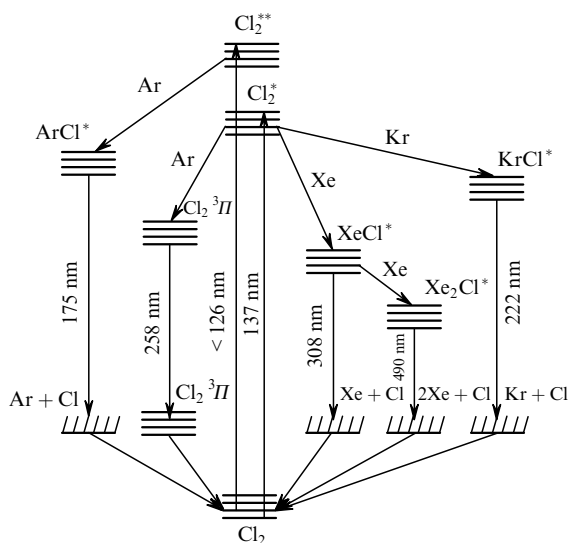

Figure 5. Scheme of the photoprocesses in mixtures of Cl_2 with rare gases.

also shows the $ArCl^*$ formation process upon excitation of chlorine at a shorter wavelength [72]. The reaction rate constants of excited chlorine molecules measured in [70] are as high as the rate constants for harpoon reactions of excited rare-gas atoms with halogens [62].

According to estimates [70], upon pumping by the 137-nm radiation of an open discharge, lasing is attainable in almost all of the products of reactions in mixtures of chlorine with rare gases: Cl_2^* ($\lambda = 258$ nm), $XeCl^*$ (308 nm), Xe_2Cl^* (490 nm), and $KrCl^*$ (222 nm). No estimates were performed for $ArCl^*$ because of a lack of the necessary data. More recently, these conclusions were confirmed for Xe_2Cl^* [13] and $KrCl^*$ [23]. No attempts to attain lasing on other products were undertaken.

Studies of mixtures of Cl_2 and KrF_2 with rare gases and N_2 have demonstrated a variety of laser-active states that can be obtained in primary and secondary photoprocesses, large cross sections for the reactions involving excited molecules, and a yield of the excited states close to 100 %.

5.4 Kinetics of the IF-laser active medium

The kinetics of the IF-laser active medium is interesting, because the $IF(D'\,^3\Pi_{2g})$ upper laser state in a CF_3I-NF_3-Ar mixture is excited simultaneously in the primary and secondary photochemical processes [17]. During the CF_3I photodissociation, products simultaneously are formed in the $IF(D'\,^3\Pi_{2g})$ and $I(^4P_{1/2,3/2})$ states; the latter state also leads to the excitation of $IF(D'\,^3\Pi_{2g})$ in a reaction with NF_3. In this case, the competing process of $I(^4P)$ radiative decay, whose rate ($\sim 10^8$ s^{-1}) exceeds the reaction rate with NF_3 by two orders of magnitude, is suppressed due to radiation trapping.

An output energy of 0.1 J achieved in [73] was more than an order of magnitude higher than the known values obtained upon pumping by a fast discharge and an electron beam. However, the potentialities of the photochemical excitation of an IF laser are not yet studied. An essentially important consequence of the results of its investigation is that they confirmed the diversity of secondary processes, which are capable of producing a population inversion upon photochemical pumping, and showed a highly efficient mechanism of depopulating the lower levels of the $IF(D'-A')$ laser transition. This mechanism ensures a quasi-continuous lasing mode and makes this transition attractive for obtaining induced emission upon optical pumping.

6. Lasers based on primary photoprocesses

6.1 Photodissociation lasers

Lasing upon photodissociation was obtained on mercury halides HgX (X = Cl, Br, I), XeF, and CN. The most advanced devices are lasers on mercury halides and XeF.

The operation of mercury halide lasers is based on the photodissociation of HgX_2 vapours excited at wavelengths of < 230 nm with the formation of excited HgX radicals in the $B\,^2\Sigma^+_{1/2}$ ionic state emitting on the allowed transition to the $X\,^2\Sigma^+_{1/2}$ ground covalent state. Mercury halides are attractive as laser active media due to the recombination of photolysis products into the initial substance, which makes it basically possible to obtain a repetitively pulsed or even a continuous lasing regime for closed-cycle or sealed-off lasers.

The output energy of these lasers was $0.5-3$ J at pulse durations of $3-8$ μs and an instantaneous electric efficiency (at the peak of the laser pulse) of 1 %. An important fact is that the specific energy output achieved in a photodissociation HgBr laser was ~ 15 times higher than the known values of the specific energy output for other pumping techniques ([74] and references therein).

During studies of HgX lasers, the basic technologies to designing photochemical lasers have been significantly developed. In this connection, it should be mentioned that a considerable experience in constructing high-temperature laser cells (the operating laser temperature was $\sim 250\,°C$) and new optical pump sources based on a surface discharge has been gained. Moreover, for the first time, a repetitively pulsed lasing mode was realised in these lasers pumped by the radiation of an open discharge [14, 16] and multicolour laser oscillation in a multicomponent active medium was obtained [75].

Induced emission in a XeF laser is observed on two ion–covalent transitions: $B-X$ ($\lambda_g = 353$ nm) and $C-A$ ($\lambda_g = 480$ nm). Of two X and A lower laser states, the first one is weakly bound (the binding energy is ~ 1200 cm^{-1} [62]), and A is a repulsive state. The repulsive character of the A state, on the one hand, ensures its virtually instantaneous depopulation during lasing at any working-mixture pressures and, on the other hand, determines a wide emission continuum observed upon the $C-A$ transition ($\Delta\lambda = 60$ nm). The B state is formed during the XeF$_2$ photolysis at wavelengths of < 220 nm [24, 59]. The C state, which is ~ 600 cm^{-1} lower than the B state, is populated upon a collisional relaxation of the B state in the presence of a buffer gas.

Lasing in an optically pumped XeF medium was obtained for the first time in 1977 on the $B-X$ transition with an exploding wire as a pump source [20]. Almost simultaneously and independently, a laser action on XeF $(B-X)$ was observed upon pumping by the Xe$_2$ excimer radiation excited by a relativistic electron beam [76]. More recently, lasing was also observed on the XeF$(C-A)$ transition upon excitation by both the radiation of an open discharge [18] and spontaneous radiation of Xe$_2$ [77].

Studies of a XeF laser pumped by the radiation of an open discharge have led to a number of significant achievements, which allow us to regard it as one of the most promising and practically useful photochemical lasers. The energies obtained in the UV and visible spectral regions are ~ 170 and ~ 120 J [31], respectively, and model experiments have shown the possibility of achieving an electric efficiency of the XeF laser of 1 % at specific energy outputs of up to 18 and 9.5 J L^{-1} in the UV and visible regions, respectively [59].

The most detailed results of experimental investigations of a photodissociation XeF laser pumped by the radiation of an open discharge are presented in [59]. An important inference drawn from them is that the advantages of optical excitation of lasing in the visible region over an electron excitation (a fast discharge or an electron beam) were pronounced to the highest degree in a XeF$(C-A)$ laser. In contrast to electron pumping, which is based on plasmochemical reactions involving ionised and highly excited atoms and molecules, in the case of photochemical pumping, an inversion is produced in reactions involving neutrals excited to low-lying states. This difference results in two practically important consequences. First, during optical pumping, an induced absorption determined by ionised and highly excited states is negligibly small. Upon electron

pumping, these states are sources of losses preventing the obtainment of efficient lasing in the visible region. Second, unlike the case of electron pumping, the competition of the $B-X$ transition is rather weak in a XeF $(C-A)$ laser, since the populations of the B and C states are determined by the buffer-gas temperature, which is close to room temperature, while, during electron pumping, the main role in the energy exchange between these states is played by electrons at a temperature of ~ 1 eV characteristic of this pumping.

Experiments on obtaining lasing in explosion-pumped XeF are of special interest. In essence, the objective of these experiments is to answer two fundamental questions: (1) can a strong shock wave serve as a high-power VUV source for laser pumping and (2) can a laser operating in the free-running bleaching wave mode be scaled in proportion to the volume of the active medium and pump energy, as was earlier shown for an iodine photodissociation laser operating in the standing PDW mode.

As to the first problem, the technique of laser pumping by the shock-wave radiation was initially developed for exciting an iodine photodissociation laser using near UV (270 nm). The radiative properties of a shock wave in the VUV region have not been studied earlier. This is evidently caused by technical problems related to the extraction and transmission of VUV radiation. The PDW propagation dynamics in laser experiments was studied by observing the luminescence at the XeF$(C-A)$ transition from the PDW front (see Fig. 2). As a result, it was established that the brightness temperature of a shock wave in krypton within the spectral range of $130-170$ nm averaged over the pumping duration is ~ 20 kK [56]. At the initial part of the bleaching-wave path, its velocity was as high as 130 km s^{-1}, which exceeds the velocity of the wave observed under pumping by the open-discharge radiation by more than an order of magnitude [59]. An energy of coherent radiation of 1 kJ in a 24-μs pulse was obtained in a laser on the XeF$(B-X)$ transition with an aperture of 48 cm and an active-medium volume of 200 L [56]. The obtained results clearly show that a strong shock wave is a promising VUV pump source.

The second problem is associated with the fact the XeF-laser active medium, which is formed in the PDW front moving away from the pump source, has a cross-sectional size much smaller than the laser aperture. In this case, due to refraction, the radiation field is expelled from the PDW in the direction of its propagation. Taking into account that the feedback in the optical resonator in the transverse direction is provided by the diffraction at the aperture edges, we may expect an increase in the lasing threshold and a decrease in the output laser energy with an increase in the laser aperture due losses through the exit semitransparent mirror [78]. This effect was actually observed in the first experiments with explosion pumping, and only sectioning of resonator mirrors 48 cm in diameter made it possible to raise the output energy of a XeF$(B-X)$ laser by an order of magnitude and to reach an energy of 1 kJ [56], so that the specific energy yield (5 J L^{-1}) was no less than in a laser with a much smaller aperture (10 cm) pumped by the surface-discharge radiation [31]. The problem of scaling the active medium excited in the free-running PDW mode was studied in detail later [79]. It was shown that the lasing threshold depends not only on the ratio between the cross size of the active zone and the resonator aperture but also on the matching of their shapes.

6.2 I_2 laser with direct optical pumping

The principle of obtaining a population inversion due to a direct optical excitation of a molecular transition, which was proposed in [80, 81], was implemented for the first time in a molecular iodine laser generating in the UV region at 342 nm. The laser operation is based on a four-level scheme [55], according to which a source of 183-nm radiation excites iodine vapour to the $D\,^1\Sigma_u^+$ ionic state, from which molecules undergo the collision transition to the $D'\,^3\Pi_{2g}$ state lying ~ 500 cm^{-1} lower. The laser transition is the allowed transition from the D' state to the weakly bound $A'\,^3\Pi_{2u}$ state that dissociates into iodine atoms, which close the laser cycle by recombining to the $X\,^1\Sigma_g^+$ ground molecular state. At present, the record output energy of a laser pumped by the radiation of an exploding wire is 27 J (the specific energy output is 18 J L^{-1}) [82].

The I_2 active medium is a unique system also because it successfully combines several features important for practice: the laser excitation spectrum lies within the quartz transmission region, the medium is self-recovered after a pump pulse, and its excitation threshold is low (100–200 W cm^{-3} [82]). These properties allowed the creation of a sealed-off flashlamp-pumped laser, which was demonstrated in [83]. The laser excited by a quartz flashlamp operated in a repetitively pulsed mode at a frequency of 0.5 Hz and an energy of 50 mJ per pulse with a duration of 3–5 µs.

The aforementioned positive features of the active medium along with its high thermal stability [82] allow us to regard it as one of the most promising laser media. Subsequently, optical pumping of I_2 attracted the attention of experimental groups at the Rutherford Laboratory (pumping by ArF laser radiation [84]), the Los Alamos Laboratory (exploding wires [85]), and Japan (discharge over a ferrite [35]).

7. Conclusions

The results of studies of the photochemical method for exciting active media allow us to consider the wideband optical pumping of gases as a fruitful and versatile technique for attaining lasing in the spectral range from the IR to UV regions. There are proposals to photochemically excite other active media [42, 86]. From the technical point of view, photochemical pumping has such advantages as a simple design and low cost of the devices for obtaining a high output energy, as well as the possibility of increasing it in proportion to the active volume and pump energy. The developed method of the optical excitation of active media using open-type pump sources (a high-temperature discharge and a strong shock wave) has no foreign analogues and has allowed us to achieve laser parameters that significantly exceed those obtained with other optical pumping techniques.

An important result of these investigations is also the fact that the photochemical pumping method turned out to be an efficient means of exciting stimulated emission on molecular transitions. Among them, a special place belongs to active media with wide amplification bands, $XeF\,(C-A)$, Xe_2Cl, and Kr_2F, which are of practical interest for amplifying femtosecond optical pulses. The amplification bandwidth for these media is 60–100 nm which corresponds to a duration of transform-limited pulses $\tau_{\lim} \sim \lambda^2/(c\Delta\lambda) \sim 10$ fs. At the same time, the gas nature of these media

determining their low optical nonlinearity allows the direct amplification of femtosecond pulses without using the chirp-pulse amplification technique, which is based on the application of complicated and expensive systems for stretching and compressing the amplified pulses. The latter factor becomes especially important at a high output power approaching the petawatt level (10^{15} W). Moreover, due to comparatively small amplification cross sections σ_{st} (10^{-17}, 2.8×10^{-18}, and 2.3×10^{-18} cm^2 for $XeF(C-A)$, Xe_2Cl, and Kr_2F, respectively), the saturation energy density at the laser transition $\varepsilon_{sat} = hc/(\lambda\sigma_{st})$, which determines the output energy per unit area of the amplifier aperture, is sufficiently high (0.04, 0.15, and 0.2 J cm^{-2} for the aforementioned active media, respectively), which allows one to construct compact systems generating femtosecond pulses of multi-terawatt power. Finally, let us consider one of the most characteristic parameters of these systems. This is the maximum attainable intensity of focused radiation per unit area of the output aperture, $I_f = \varepsilon_{sat}/(\tau_{\lim}\lambda^2)$, where λ^2 characterises the physical limit of the focusing region for diffraction-limited radiation. For the active media considered, this parameter is 1.5×10^{21}, 8×10^{21}, and 1.8×10^{22} W cm^{-2}, respectively. For comparison, a solid-state Ti:Sa system, which is the most widespread in the range of pulse durations of 10–100 fs, has $I_f = 1.3 \times 10^{22}$ W cm^{-2}. It should be taken into account that scaling can much easier be applied to gaseous media. Note also that the combined use of such media as Xe_2Cl and Kr_2F allows one to achieve an almost twofold broadening of the amplification bandwidth and create favourable conditions for amplifying extremely short optical pulses. In order to reach an output power at a petawatt level and higher, along with an emitting discharge, the use of a strong shock wave as a pump source for an amplifier of femtosecond pulses can be of interest. This wave is characterised by a steep front of rising radiation ($< 10^{-7}$ s) upon the emergence of detonation from an explosive, which is important for obtaining an aperture-uniform gain in the working mixture optically dense for the pumping radiation [34].

Studies on the development of a XeF amplifier excited by the radiation of a multichannel surface discharge are currently underway. They are aimed at the elucidation of the prospects for creating multiterawatt–petawatt-power laser systems [34, 87–89]. The first positive results on the amplification of femtosecond optical pulses in such an amplifier are reported in [87–89].

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