High-power excimer lasers and new sources of coherent radiation in the vacuum ultraviolet

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CONTENTS

1. INTRODUCTION

The invention of excimer lasers is undoubtedly one of the most striking achievements in laser physics and technology of the last decade. The tremendous interest in these lasers stems first of all from the fact that with them it is possible to obtain a high-power pulse of radiation over a wide range of wavelengths, from 126 nm (Ar_2 laser)[1] to 1100 nm (emission from excimers of the LiHe type).[2]

The idea of using the bound-free transitions of excimers as the active medium for lasers was put forth for the first time in 1960.[3] However, operating laser systems appeared only at the beginning of the 1970's.[4,5] The rather high excitation rate necessary to obtain optical amplification of excimers was achieved with the use of new capabilities in the technique of powerful pulsed sources of excitation. At the present time some tens of different types of excimer lasers have been made operational, with both electron beam[6] and optical[7] pumping, as well as pumping with electrical[8] and rf discharges.[9] The average power of these systems reaches hundreds of watts,[10] the maximum energy in a pulse is as much as several hundred Joules,[11] and the efficiency exceeds several per cent. Of particular interest is the possibility of continuous tuning of the frequency of excimer lasers. The transitions from the excited state of the excimer into the ground state (which is as a rule repulsive) provide a rather wide band of amplification, of the order of 100–200 cm^{-1}. The last may also be used for the generation of short pulses having a duration of the order of hundreds of femtoseconds.

At the present time excimer lasers are widely used in photochemistry, laser purification of materials, isotope separation, lidar investigations, as well as programs in laser fusion.[12–18] An extremely attractive application of excimer lasers is their use in obtaining coherent radiation in the vacuum ultraviolet and soft x ray region.

Sources of tunable coherent ultraviolet radiation are opening up wide possibilities associated with their use in various areas of science and technology. They make it possible to improve substantially the methods of spectroscopy of highly excited states of atoms and molecules. With their use the continuous absorption spectra and photoionization of various materials can be studied. The wavelength region 100–200 nm is of the greatest interest for these purposes, since the ionization potentials of atoms and molecules lie in the range 6–13 eV. The solution of a large number of practical problems such as plasma diagnostics for thermonuclear fusion, manufacture of microelectronic components, the preparation of devices with size-dependent operating characteristics (field effect transistors, charge-coupled devices), etc., all these depend on the development of these sources.

During the last decade considerable progress has been made in the generation of coherent radiation in the vacuum ultraviolet and soft x ray regions with the use of nonlinear optics of gaseous media.[19] The appeal of this approach is that it is based on the use of well developed lasers that operate in the visible and the ultraviolet regions, and it does not require resonators for the short wavelength radiation, the spectral width of which is determined by the corresponding characteristics of the pumping lasers. Tuning the frequency of the pumping radiation makes it possible to tune the generated radiation over rather wide limits.

At the present time all efforts in obtaining coherent radiation in the vacuum ultraviolet and soft x ray region by means of excimer lasers can be provisionally divided into three main directions:

1. Generation of high harmonics and nonlinear optical frequency mixing in atomic and molecular gases.

2. Multiphoton resonance pumping of atoms and molecules with the subsequent stimulated emission in the vacuum ultraviolet region.

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3. Development of lasers based on anti-Stokes Raman scattering.

At the present time a whole series of remarkable results have been obtained in the generation of harmonics in gaseous media and multiphoton pumping of atoms and molecules. These results have been primarily due to progress in obtaining high-power ultrashort pulses of ultraviolet radiation from excimer lasers. This article is a brief review of the advances that have been made in these areas.

In 1982-1984 a number of schemes were devised and implemented for lasers based on anti-Stokes Raman scattering at a wavelength shorter than 200 nm, where excimer lasers have been used as sources of pumping radiation and for producing the concentrations of metastable atoms of the active medium necessary for optical amplification.

2. GENERATION OF POWERFUL ULTRASHORT PULSES OF ULTRAVIOLET RADIATION WITH EXCIMER LASERS

In the above-mentioned processes a decisive role is played by the intensity of the initial laser radiation, since the conversion coefficient depends strongly on this parameter in a nonlinear way. The most highly developed excimer lasers at the present time are electric-discharge lasers based on the inert gas halides.[20,21] However, in spite of their high radiated energy, which approaches 14 J, and the high peak power, which reaches hundreds of megawatts for the XeCl laser having a lasing wavelength of 308 nm,[22] their effective use in nonlinear optics is limited by the large divergence of their emission (of the order of tens of mrad) and the spectral width of their free generation ($\approx$10–50 cm^{-1}).

There exist a large variety of ways of improving and controlling the quality of the emission of excimer lasers. For narrowing the lasing line it is usual to place dispersive elements (Fabry-Perot etalon or a diffraction grating) within the resonator,[23,24] while control of the mode structure is accomplished with the use of spatial filters or unstable resonators.[25] One of the methods of obtaining radiation with diffraction limited dispersion is reversal of the wavefront in liquids.[26] An alternate possibility for obtaining high quality emission is injection of radiation of given parameters into the active medium of an excimer laser, with the subsequent amplification of the radiation.[27] Because of the wide spectral band ($\sim$100 cm^{-1}) and the high amplification coefficient (linear coefficient $\alpha \sim 0.1$ cm^{-1} for KrF and XeCl lasers), the most promising scheme for obtaining the maximum laser power is the amplification of picosecond pulses of harmonics of dye lasers tuned to a frequency lying in the amplification band of the excimer media. Over the past several years there have been many attempts to shorten the pulse length of the excimer laser itself. The methods of active[28,29] and passive mode locking[30] have been used, as well as short pulse slicing[31] and pulse shortening outside the resonator in a saturable absorber based on various dyes.[32] However, it has not yet proved possible to obtain a pulse width less than 300 psec.[33] With the use of dye lasers it is possible to obtain subpicosecond pulses and attain the theoretical limit for the duration of effectively amplifiable pulses (for XeCl $\tau_{\text{lim}} = 150$ fsec).

The first efforts to amplify picosecond pulses of the second harmonic of a dye laser by means of an excimer laser were the experiments of M. Maeda and coworkers, where 4 psec pulses were amplified in a XeCl amplifier to a power level of 710 MW.[34]

At the present time a number of different schemes have been implemented for amplifying picosecond pulses in excimer lasers, making it possible to obtain ultraviolet radiation at the gigawatt power level.

P. Corkum and R. Taylor used as a master oscillator a dye laser with synchronous pumping from a continuous sequence of picosecond pulses of an Ar^+ laser with passive mode locking.[35] The duration of a single pulse was 2 psec and its energy was 0.5 nJ. Then this radiation was amplified in a four-stage dye amplifier chain pumped with an XeCl laser to an energy of 0.5 mJ per pulse. To suppress the spontaneous emission background of the amplifier chain stages, spatial filters and saturable dye filters were used. After frequency doubling in a KDP crystal, the picosecond radiation was sent into the input of a wide-aperture ($5\times4.5\times50$ cm^3) XeCl gain module, where it was finally amplified to an energy of 8 mJ in a single pass. In the double-pass amplification scheme under nonoptimized conditions the peak radiation power was 20 GW. The main advantages of this scheme are the high stability of master oscillator radiation and, consequently, of the amplified pulses, as well as the simplicity of synchronous pumping, leading to the synchronization of the two electric discharge lasers.

C. K. Rhodes and his coworkers have used as a master oscillator a dye laser tuned to a wavelength of 580 nm with synchronous pumping from the second harmonic of a YAG:Nd^{3+} laser with active mode locking[36] (Fig. 1). The

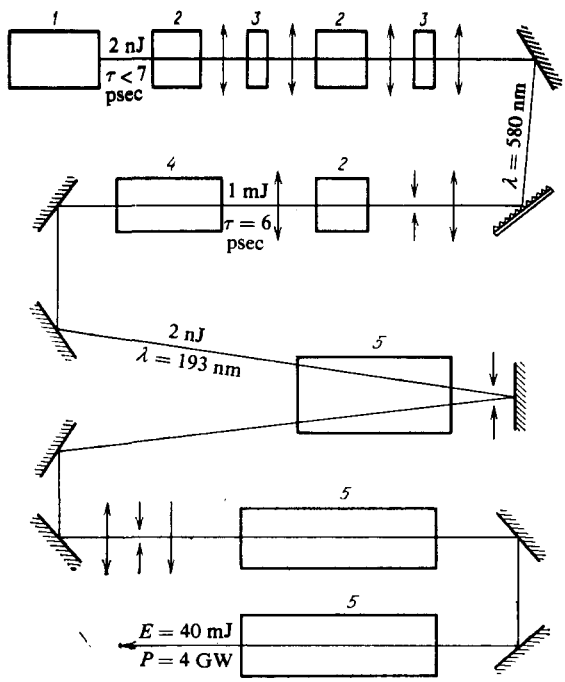

FIG. 1. Laser system for generating high-power ($P = 4$ GW) picosecond ($\tau_p = 10$ psec) radiation at the wavelength of 193 nm. 1) Picosecond dye laser; 2) Dye amplifier; 3) saturable absorber; 4) cell with Sr vapor; 5) ArF amplifier.

duration of a single pulse was 6 psec and its energy was 2 nJ. After amplification in a three-stage dye amplifier chain pumped with an XeF laser, the radiation, with an energy of 1 mJ per pulse was focused onto a heatable cell containing strontium vapor, where the frequency was tripled. The radiation pulses, of energy 2 nJ at a wavelength 193 nm, was preliminarily amplified in a double-pass ArF amplifier and in two single-pass ArF amplifiers. As a result, radiation was obtained at the output with an energy 30 ± 10 mJ in a 10 psec pulse with a divergence and a spectral width close to the theoretical limit.

This apparatus did not have such a high output emission stability as the system of P. Corkum and R. Taylor. In addition, because of the large number of stages of amplification, and in spite of the multiple spatial filters, the level of amplified spontaneous emission was about 200 mJ. However, the short wavelength ($\lambda = 193$ nm), the high power ($P = 4$ GW), and the nearly diffraction-limited divergence of the radiation open up great possibilities for the use of this apparatus.

S. Szatmari and F. Schäfer have proposed and realized a fundamentally different scheme for obtaining picosecond pulses of ultraviolet radiation and subsequently amplifying them with a commercial laser (Lambda Physik EMG 150); this scheme being a "generator-amplifier"-type system.[37] The radiation of an excimer generator ($\lambda = 308$ nm, $\tau_p = 15$ nsec, $E = 100$ mJ) was used for pumping a whole series of cells containing various dyes (Fig. 2), the first of which was a PTP dye laser with a quenched resonator[38] providing a pulse of duration < 300 psec for pumping with a 15 nsec pulse. The spectral width of the radiation obtained, which was a few nanometers in the range of 340 nm, was too great for pumping a laser with distributed feedback (DF laser).[39] To narrow the lasing line a diffraction grating was used in combination with a lens and a diaphragm. Then, after amplification in two stages of dye lasers, this radiation was used to pump a DF laser with a holographic grating based on RhB dye. The DF laser radiation that was generated had the following parameters: $\lambda = 616$ nm, $\tau_p = 10$ psec, and $E = 100$ nJ. After amplification in a four-stage dye amplifier chain and frequency doubling in a KDP crystal, the pulse, with an energy of $10\,\mu$J, was fed into the input of an XeCl amplifier, where it was amplified in two passes to an energy of 10 mJ. The spontaneous emission background was less than 5% of the energy of the picosecond pulse. The duration of the amplified ultraviolet pulse, as measured by two-photon ionization of the $N(C_2H_5)_3$ molecule and by a streak camera, was no greater than 5 psec. Thus, this system made it possible to obtain 2 GW ultraviolet radiation with a small divergence.

In this apparatus experiments were also carried out with the aim of obtaining powerful ($P = 4$ GW) picosecond ($\tau_p < 10$ psec) pulses at 248 nm by replacing the XeCl laser mixture with KrF laser mixture in the excimer amplifier and with a corresponding change of dye in the DF laser and amplifiers that form the initial radiation.

The undoubted advantage of the system described here is that there is no need to synchronize separate lasers because the generator and the excimer laser amplifier are triggered by a single switching thyratron and all the processes occurring in the dye lasers are rigidly coupled in time.

A scheme for amplifying picosecond pulses of a dye laser with synchronous pumping with the second harmonic of a concentrated phosphate glass laser with passive mode locking (Fig. 3) has been proposed and put into operation in the laboratory of S. A. Akhmanov.[41] The duration of a single pulse, at a wavelength of 616 nm, was 5 psec, and its energy

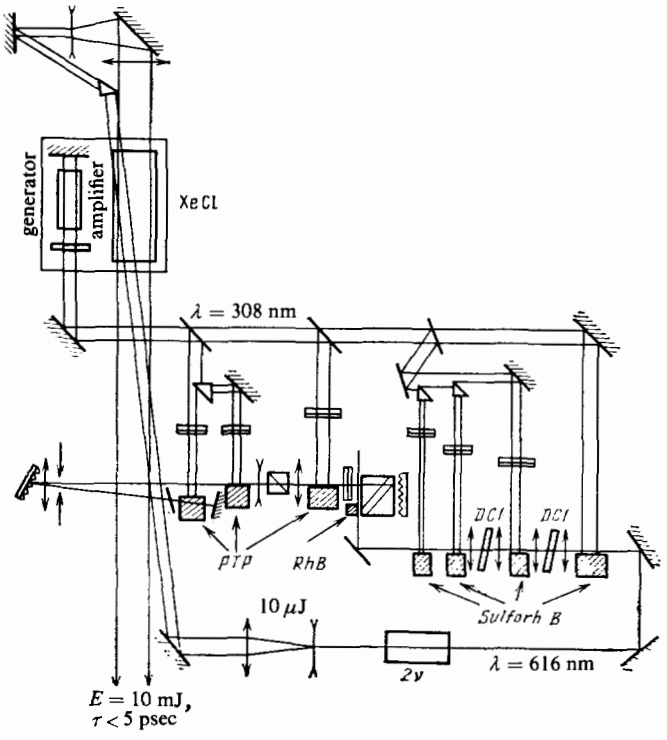

FIG. 2. Diagram of experimental arrangement of S. Szatmari and F. Schafer.

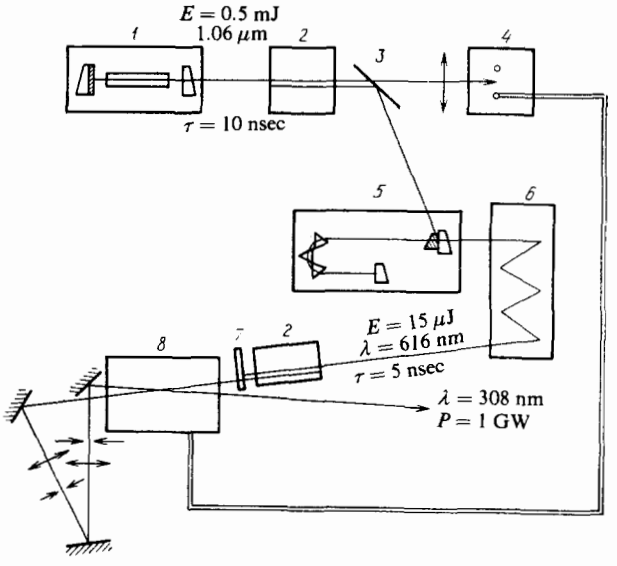

FIG. 3. Diagram of experimental arrangement of S. A. Akhmanov and coworkers. 1) Solid state picosecond generator; 2) Second harmonic crystal; 3) Dichroic mirror; 4) Optical spark gap; 5) dye laser; 6) Optical delay line; 7) filter; 8) XeCl amplifier.

was 20 μJ. After frequency doubling in an ADP crystal, the radiation was fed into a double-pass XeCl amplifier. The maximum power of the radiation output was 1 GW. The use of a spatial filter and apertured diaphragms after the first pass of the radiation through the amplifier made it possible to reduce the level of the amplified spontaneous emission to 1 mJ. Thus, the power contrast of the useful picosecond signal was $5 \cdot 10^4$.

The main advantage of this arrangement is that the powerful picosecond pulses of ultraviolet radiation ($\lambda = 308$ nm, $P = 1$ GW) are synchronized with powerful picosecond pulses of the visible ($\lambda = 532$ nm, $P = 10$ MW; $\lambda = 616$ nm, $P = 3$ MW) and infrared ($\lambda = 1.06\,\mu$m, $P = 50$ MW) ranges. It is also relatively simple because of the small number of components compared to those systems described above. However, synchronization of the train of picosecond pulses with the firing of the excimer laser presents certain difficulties. In passive mode-locked operation the instant at which the pulse train appears has an instability of several microseconds.[42] Therefore firing of the excimer amplifier is done from an optical spark gap, which in turn is fired by the first pulse of the train. This scheme imposes stringent requirements on the delay and the stability of the firing of the XeCl amplifier.[43] With the use of a wide-aperture excimer module as the second stage of amplification it appears possible to obtain radiation with a power up to 10 GW with spectral and spatial characteristics which are governed by the radiation of the dye laser.

At the present time there seem to be no fundamental limitations to scaling up excimer laser systems to where one can obtain pulses of ultraviolet radiation less than 1 psec duration and of ~ 10 J energy. With sharp focusing, this permits an energy density of 10^{21} W/cm^2 to be obtained, as well as an electric field of $\sim 6 \cdot 10^{11}$ V/cm, which corresponds approximately to the field acting on the 1s electron of argon.[44]

3. GENERATION OF HIGH HARMONICS AND NONLINEAR FREQUENCY MIXING IN ATOMIC AND MOLECULAR GASES

During the first decade of development of quantum electronics gaseous media occupied a very modest place in experimental investigations of frequency conversion of radiation. The development of nonlinear optics was in the first place associated with the study of the quadratic nonlinearity of noncentrosymmetric crystals, which comprise the majority of present-day quantum electronics devices.[45] Because of their symmetry properties, gases are characterized by only higher order nonlinearities (third, fifth, seventh, etc.). The use of these nonlinearities in gases was considered unpromising in view of the fact that the particle density in them is five to six orders of magnitude lower than in condensed media. However, investigations into the physics of gas lasers showed that nonlinear effects in gases under resonance conditions may play an important role.[46] In the monograph of N. Bloembergen[47] it was shown that in the region of resonance gases have a better nonlinearity to absorption coefficient ratio than condensed media by virtue of the high Q of atomic and molecular resonances. Besides, the use of crystals for conversion of radiation to the short wavelength region is limited by their opaqueness in the vacuum ultraviolet region of the spectrum. Gaseous media, having a spread-out spectrum and narrow spectral lines, are free of these deficiencies.[48]

The expression for the nth order nonlinear susceptibility, which is responsible for the generation of waves with the combination frequencies $\omega = \omega_1 + \omega_2 + \cdots + \omega_n$, can be written in the form[49]

$$\chi^{(n)}(\omega) = \frac{N}{\hbar^n} \frac{\mu_{01}\mu_{12} \cdots \mu_{(n-1)n}\mu_{n0}}{(\omega_1 - \omega_{01})(\omega_1 + \omega_2 - \omega_{02}) \cdots (\omega - \omega_{0n})},$$

where μ_{ij} are the dipole moment matrix elements connecting levels i and j (0 means the ground state; only it is occupied), ω_{oi} are the resonance frequencies, and N is the particle density. Typical values for the nonlinear hyperpolarizabilities $\gamma^{(3)}$ and $\gamma^{(5)}$ of gases and metal vapors (the nonlinear susceptibilities per atom) lie in the ranges 10^{-34}–10^{-36} and 10^{-43}–10^{-46} cgse units, respectively.[50] For $N = 10^{16}$–10^{17} cm^{-3} the nonresonance susceptibilities of gases $\chi^{(n)} = N\gamma^{(n)}$ have approximately the same orders of magnitude as the nonresonance susceptibilities of crystals. Nevertheless, the efficiency of frequency conversion of radiation in gases can be considerably greater. This is because of two circumstances. First, gases and metal vapors have a much higher threshold for optical breakdown, which, for the densities ordinarily used, is determined wholly by multiphoton ionization of the atoms, and this makes it possible to increase the intensity of the incident radiation by several orders of magnitude. The use of noble gases and positive ions having high ionization potentials for frequency conversion at high frequencies and high intensities is preferred to the use of metal vapors, which have lower ionization potentials. Second, by diluting the nonlinear medium with a buffer gas having a suitable index of refraction it is possible to satisfy the condition of phase synchronization $k_n = nk_1$. Thus, it is possible to make a rather extended optically transparent nonlinear medium, in which the phase velocities of the interacting waves will coincide.[51]

The great progress that has been made in the development of excimer lasers and in their use for amplifying picosecond pulses to a power level of several gigawatts has made it possible to realize effectively processes of nonlinear interaction of powerful radiation with atomic and molecular gases, leading to the generation of coherent radiation at wavelengths shorter than 1000 Å. Progress in this direction has been made along the lines of high harmonic generation and nonlinear frequency mixing of the radiation of excimer lasers and dye lasers as a result of process of the form

$$h\nu\ (\lambda < 100\text{ nm}) = (2n+1)\,h\nu_{\text{excim}}, \qquad n = 1, 2, 3,$$
$$h\nu\ (\lambda < 100\text{ nm}) = 2nh\nu_{\text{excim}} - h\nu_{\text{dye}}, \qquad n = 1,2,$$
$$750\text{ nm} \geqslant \lambda_{\text{dye}} \geqslant 217\text{ nm}.$$

With the use of nanosecond pulses from excimer lasers third[52] and fifth[53] harmonics of an XeCl laser were obtained, as well as the third harmonic of an ArF laser[54] and the third harmonic of a KrF laser.[55] Experiments in generating sum frequencies of excimer lasers and dye lasers have been carried out with KrF and ArF[56] lasers. Figure 4 shows the spec-

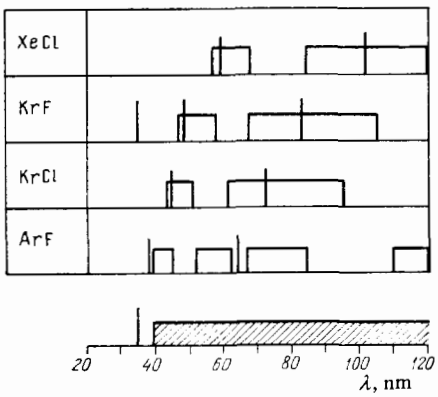

FIG. 4. Coherent radiation shorter than 100 nm wavelength obtained with the use of excimer lasers by high harmonic generation (vertical lines) and four- and six-wave mixing of excimer and dye laser radiation (rectangles).

tral range that is covered continuously by coherent radiation obtained as a result of four- and six-wave mixing of radiation of the corresponding excimer and dye lasers.[44]

Because there are no optical materials that are transparent at wavelengths shorter than 100 nm, all these experiments were carried out using systems with differential pumping of the gases[55] (Fig. 5), where the nonlinear medium (H_2, CO, Ar, Kr, etc.), in which the conversion occurs, and which as a rule is absorbing at the lasing wavelength, is surrounded by a buffer gas (i.e., Ne), which has no appreciable absorption in this range.

With the use of the third harmonic of a KrF laser ($\lambda = 83$ nm), obtained with a similar system, where Xe was used for the nonlinear medium, detailed spectroscopic information was obtained on the predissociation levels of the H_2, HD, and D_2 molecules.[57] In generating in H_2 radiation with the combined frequencies of two quanta of the ArF laser and one quantum ($\lambda = 436$ nm) of a dye laser, tunable radiation was obtained in the 79 nm range and was successfully used for observing the wide (≈ 160 cm^{-1}) autoionization structure in Ar and narrow (≈ 2 cm^{-1}) autoionization states in D_2.[56]

With the appearance of sources of high-power picosecond pulses of ultraviolet radiation a unique record was established in obtaining short-wavelength radiation with the use of excimer lasers. The group of J. Bokor has carried out an experiment in the generation of the third ($\lambda = 82.8$ nm),

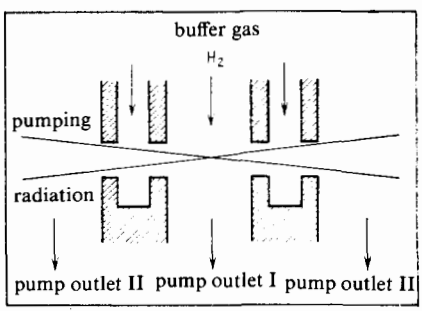

FIG. 5. Diagram of differential pumping of gases for generation of vacuum ultraviolet radiation.

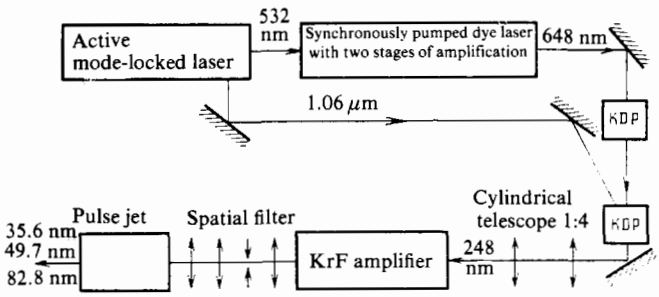

FIG. 6. Block diagram of the experimental arrangement for generating the seventh harmonic of the KrF laser radiation.

fifth ($\lambda = 49.7$ nm), and seventh ($\lambda = 35.6$ nm) harmonics of the radiation of a KrF laser in a supersonic jet of helium.[58] A block diagram of the experimental arrangement is shown in Fig. 6. The radiation from a dye laser tuned to 648 nm was frequency doubled in a KDP crystal and then combined with the fundamental of the pumping laser ($\lambda = 1.06$ μm) in a second KDP crystal. The resulting radiation at a wavelength 248 nm was amplified to an energy of 20 mW in a separate 15 psec pulse. Then it was focused with a 10 cm focal length lens onto a 10 μm diameter spot, so that an intensity of 10^{15} W/cm^2 could be attained in the region of interaction with the gaseous flow.

Using the recent advances in pulsed jet technology it is possible to produce a high-density (to 10^{19} cm^{-3}) supersonic gas flow[59] of a rigidly specified configuration, surrounded by a high vacuum ($\sim 10^{-4}$ Torr), and for an orthogonal geometry of interaction of the radiation with the gas jet, it is possible to minimize the Doppler broadening of the absorption lines in the gas, which is important for resonance processes.

The maximum coefficient of conversion of the radiation into the seventh harmonic was $3 \cdot 10^{-11}$ (10^5 photons per pulse at 35.5 nm) for a helium concentration of $2 \cdot 10^{17}$ in the flow. For concentrations below 10^{16} cm^{-3} only the third and fifth harmonics were observed. In the work on seventh harmonic generation ($\lambda = 38$ nm) of radiation with $\lambda = 266$ nm (the fourth harmonic of a YAG:Nd^{3+} laser)[60] for comparable incident radiation intensities the conversion coefficient was 10^{-8} for a helium density of $4.5 \cdot 10^{18}$ cm^{-3}. Thus, increasing the atom density in the interaction region as long as absorption at the lasing wavelength plays no role, and decreasing the pulse duration of the first harmonic thereby increasing its intensity (for the KrF laser the theoretical limit is ~ 0.2 psec) to a level at which optical breakdown of the medium occurs, one can substantially increase the efficiency of conversion of radiation into high harmonics.

The next advance into the short wavelength region of the spectrum is obviously generation of the ninth harmonic of the KrF laser and the seventh harmonic of the ArF laser, both lying in the region of 27.6 nm. With the development of subpicosecond excimer laser systems there appears to be a real possibility of generating coherent radiation in the 10 nm region.

Until 1979 the only sources of coherent radiation of wavelength shorter than 1000 Å were synchrotrons. The first laser source with $\lambda = 83$ nm (the third harmonic of the

KrF laser) and a power of 40 mW had an average spectral brightness (power density per unit solid angle and frequency interval) that was two orders of magnitude greater than that of the best synchrotrons. Pico-second laser sources have a spectral brightness greater by five orders of magnitude than synchrotron radiation.[44] However, synchrotron radiation spans continuously a substantially greater range of wavelengths, including wavelengths below 100 Å, and moreover, one synchrotron can be used by several groups of investigators at the same time. Therefore, as they are further developed, laser and synchrotron sources will complement one another, giving the experimenter a unique instrument for the understanding of nature.

4. MULTIPHOTON PUMPING OF ATOMS AND MOLECULES WITH SUBSEQUENT STIMULATED EMISSION IN THE VACUUM ULTRAVIOLET REGION

By optical pumping we understand a wide class of processes that lead to the creation of highly nonequilibrium populations of atomic or molecular systems as a result of a combination of resonance or quasiresonance optical excitation and various relaxation processes. These phenomena were well studied before the laser appeared. The use of nonmonochromatic (lamp) sources of pumping for solid state and liquid lasers has become widespread in the past twenty years. With the development of laser pumping sources, the radiation of which can be efficiently absorbed in gases, and which have narrow spectral lines, new possibilities have been opened up for obtaining coherent radiation in various regions of the spectrum. For example, molecular lasers operating in the far infrared (the FIR laser) with optical pumping from CO_2, HF, and N_2O lasers have been intensively developed, and they make it possible to obtain radiation in the range from 30 μm to 2 mm both with cw operation at milliwatts of power, and in the pulsed mode at a power level greater than several MW.[61]

In developing lasers with optical pumping it is necessary to take into account two conditions that must be satisfied: the pumping source must be powerful enough, and its wavelength must coincide with an absorption line of the active medium or be close to it. There are a large number of different schemes for creating a population inversion using optical pumping. These are the simplest three-level laser schemes and schemes that incorporate cascase and multiphoton excitation processes.

Electronic transitions in atomic and molecular gases, having large oscillator strengths, are extremely advantageous for use in lasers with optical pumping. However, the fact that the majority of the electronic absorption bands lie in the ultraviolet and the vacuum ultraviolet has severely limited the experimenter because of the lack of appropriate pumping sources. With the appearance of high-power tunable excimer lasers the idea of generating stimulated emission in the vacuum ultraviolet by multiphoton pumping processes has been realized. One of the first efforts in this direction has been a series of experiments on two-photon excitation of molecular hydrogen by ArF laser radiation and the observation of stimulated emission over a broad range from 117 to 158 nm.[62]

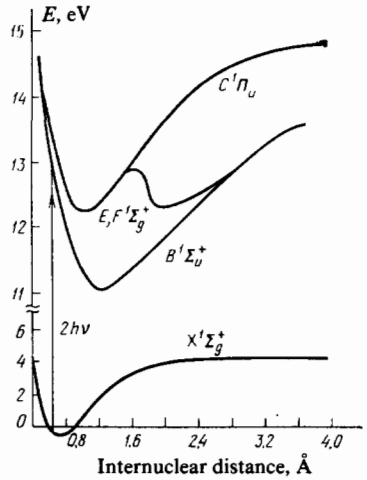

FIG. 7. Simplified energy level diagram of the electronic terms of the H_2 molecule.

Molecular hydrogen was chosen because there exists a great deal of spectroscopic information about its excited electronic states, and in particular, the two-photon resonance transition $X^1\Sigma_g^+ \rightarrow E,F^1\Sigma_g^+$ at 193 nm is well known,[63] so that it can be considered the most suitable candidate for experiments on conversion of radiation to the vacuum ultraviolet region. Figure 7 shows a simplified diagram of the electronic terms of the H_2 molecule. For two-photon excitation of the state $E,F^1\Sigma_g^+$ the transitions in the Q-branch ($X(J) \rightarrow E,F(J)$) are the strongest.[64] By tuning the radiation from the ArF source[36] it was possible to tune exactly to the Q(1), Q(2), and Q(3) lines of the $X^1\Sigma_g^+ \rightarrow E,F^1\Sigma_g^+$ transition. The pump power was $\approx$2 GW at a pulse length of 10 psec. The width of the laser line was 5 cm^{-1} and the divergence of the radiation was 10 μrad. The pumping radiation was focused by a 1.6 m focal length lens onto the center of a two-meter cell filled with hydrogen at a pressure of 20 to 500 Torr. The exit window of the cell was attached directly on the entrance slit of the vacuum monochromator.

The stimulated emission spectrum of the excited hydrogen consisted of 25 separate intense lines between 142.9 and 158.5 nm (the $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition), between 117.6 and 117.8 nm (the $C^1\Pi_u \rightarrow B^1\Sigma_u^+$ transition), and between 754 and 922 nm (the $E,F^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$ transition). The $C^1\Pi_u$ state was populated, in the opinion of the authors, as a result of excitation by collisions of excited H_2 molecules with electrons formed by photoionization of the state $E,F^1\Sigma_g^+$. At H_2 pressures above 500 Torr efficient conversion of the pumping radiation into the first Stokes component occurred, and two main channels of photoexcitation of the vibrational-rotational sublevels of the state $E,F^1\Sigma_g^+$:1 were distinguished: 1) two-photon excitation at the 193 nm (51 656 cm^{-1}) wavelength and 2) excitation by a photon of the fundamental frequency (51 656 cm^{-1}) in combination with a photon at the first Stokes frequency (47 501 cm^{-1}). The optical Stark effect also played an important role in the excitation process, shifting the resonance levels of the molecule by up to $\approx$45 cm^{-1}.

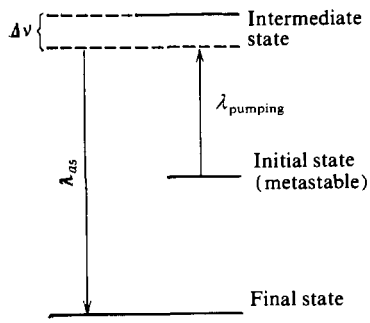

FIG. 8. Diagram of radiation conversion in an anti-Stokes laser.

The maximum energy in a pulse of radiation at the strongest line ($B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ (1→7)P(4) with $\lambda = 149.96$ nm) was approximately 100 μJ, which corresponds to a conversion efficiency of 0.5%. The pulse length was estimated to be around 10 psec. Thus, the maximum power of the vacuum ultraviolet radiation was 10 MW. Using the large set of transitions in the HD and H_2 molecules, one can substantially expand the set of frequencies that can be generated by this method.

These same authors have achieved multiphoton excitation of Kr atoms at pressures from 5 to 1000 Torr using radiation from an ArF laser source ($\lambda = 193$ nm, $P = 1$ GW, $\tau_p = 10$ nsec) and they obtained powerful stimulated emission at 91.6, 93.1, 97.5, 98.5, and 100.3 nm.[65]

The following scheme has been proposed for excitation and subsequent emission:

$$4\gamma\ (193\text{ nm}) + \text{Kr}\ (4s^24p^6) \rightarrow \text{Kr}\ (4s4p^64d)$$

$$\gamma'\ (93\text{ nm}) + \text{Kr}\ (4s4p^64d) \rightarrow 2\gamma'\ (93\text{ nm}) + \text{Kr}\ (4s^24p^5nl).$$

The radiation at 93 nm has been tuned experimentally over 600 cm^{-1} even though the width of the upper level ($4s4p^64d$) was not greater than 100 cm^{-1}. This result was explained by the existence of a large number of close-lying levels and the rapid redistribution of energy among the excited states by collisions. The maximum conversion coefficient for the strongest line was 10^{-4}.

This system is the first operating source of coherent vacuum ultraviolet radiation having the shortest wavelength and based on transitions between inner electron shells on an atom. One of the important results of this work was the experimental confirmation of the selectivity of multiphoton excitation of autoionized states in Kr.

The results of the two works presented above, which were obtained by C. K. Rhodes and coworkers, are a clear illustration of the promising possibilities of using powerful picosecond excimer systems for multiphoton pumping of various atoms and molecules.

5. LASERS BASED ON ANTI-STOKES RAMAN SCATTERING

Anti-Stokes sources of coherent radiation (anti-Stokes Raman laser)[66–68] are based on stimulated Raman scattering of photons of a pumping laser by excited atoms or molecules in long-lived (~ 0.5 μsec) metastable states. A diagram illustrating the conversion of the pumping radiation into radiation at the anti-Stokes frequency, is shown in Fig. 8. The expression derived in the quasiresonance approximation for a three-level system, for the cross section for amplification of stimulated emission at the anti-Stokes frequency has the form[70]

$$\sigma_{as} = \frac{e^4 f_1 f_2 \nu_{as}}{32\pi^3 \varepsilon_0^2 m^2 \hbar c^2 \nu_i \nu_f\ (\Delta\nu)^2 \gamma}, \qquad (5.1)$$

where f_1 and f_2 are the oscillator strengths for the dipole transitions between the initial and intermediate and intermediate and final states, respectively, ν_i and ν_{int} are, respectively, the initial and intermediate state frequencies, ν_{as} is the anti-Stokes frequency, $\Delta\nu$ is the frequency difference, and γ is the width of the anti-Stokes line. The gain of the anti-Stokes signal in a single pass through the amplifying medium is $\exp(\Delta N \sigma_{as} I L)$ where ΔN is the density of atoms in the metastable state, I is the pumping intensity, and L is the length of the amplifying medium. For the typical values $\sigma_{as} = 3 \cdot 10^{-22}$ cm^4/W, $\Delta N = 3 \cdot 10^{16}$ cm^{-3}, $L = 30$ cm, and $I = 10^6$ W/cm^2, the gain in a single pass would be e^{270} (without allowing for saturation).

The metastable states can be obtained in various ways: in electric and rf discharges,[73] with the ionization of atoms in the ground state, by the soft x rays of the laser plasma,[74] by the flash photolysis of a salt such as NaI or KBr[75] and of various organic compounds,[76] or by the selective photodissociation of a salt of the type TlI, TlCl, or InI by an excimer laser.[69] Table I shows data on the production of coherent radiation in the ultraviolet and vacuum ultraviolet regions using stimultaed anti-Stokes scattering by various atoms.[70–72,77] The quantum efficiency of conversion in these systems reaches 50%. The characteristic density of atoms in metastable states is 10^{16}–10^{18} cm^{-3}. It can be seen from Table I that the shortest wavelength ($\lambda = 149$ nm) is that of the

TABLE I. Spectroscopic characteristics of actual anti-stokes lasers in the ultraviolet and vacuum ultraviolet regions of the spectrum.

Element	Initial state	Final state (в $см^{-1}$)	Laser pumping (λ, nm)	$\Delta\nu$, cm^{-1}	Intermediate state (energy in cm^{-1})	λ_{as}, nm	σ_{as}, cm^4/W
Tl	$6p^2P^0_{3/2}$	$6p^2\ P^0_{1/2}$ (7793)	XeF (353)	11	$6d^2\ D_{3/2}$ (36117)	277	$1{,}3 \cdot 10^{-21}$
Br	$4p^52P^0_{1/2}$	$4p^52\ P^0_{3/2}$ (3625)	F_2 (157)	8	$5s^2\ P_{3/2}$ (67176)	149	$8{,}6 \cdot 10^{-23}$
I	$5p^52P^0_{1/2}$	$5p^52\ P^0_{3/2}$ (7603)	2nd anti-Stokes from KrF laser in H_2 (206)	77	$6s^2\ P_{3/2}$ (56093)	178	$7{,}4 \cdot 10^{-24}$

radiation obtained by the pumping of Br atoms in the state Br* ($4p^2{}^2P^0_{1/2}$) by the radiation of an F_2 laser ($\lambda = 157$ nm).[71]

In this experiment the Br* atoms were formed as a result of selective dissociation of NaBr vapor by radiation of wavelength $\lambda = 250$ nm (the sum of the frequencies of the second harmonic of a dye laser and the fundamental of a YAG:Nd^{3+} laser). NaBr was chosen because it does not absorb the sodium radiation at 157 and 149 nm. The density of NaBr molecules at 860°C was $2 \cdot 10^{16}$ cm^{-3}. For 2.5 mJ energy in the incident radiation from the F_2 laser, the energy per pulse at 149 nm was ≈ 0.1 mJ at a 5 nsec pulse width (as for the F_2 laser). The shapes of the anti-Stokes pulse and the pumping pulse were similar. From the expression for the cross section for the gain of the anti-Stokes signal (5.1) the density of Br* atoms formed as a result of the dissociation of NaBr was determined to be $2 \cdot 10^{15}$ cm^{-3}. If a powerful KrF laser were used as the source of the dissociating radiation the Br* concentration could be made considerably higher, which would bring about an increase in the conversion efficiency.

The vibrationally excited CO molecule is a good choice for use as the active medium for an anti-Stokes laser in the vacuum ultraviolet primarily because of the simple means of exciting it (a multistep chemical reaction involving N_2, NO, and CS_2, and initiated by an rf discharge), the large Stokes shift ($\sim$3–4 eV), and the very large cross section for the radiative transition from the intermediate state (electronically excited) $A^1\Pi(v = 1\text{–}7)$ to the final (ground) state $X^1\Sigma^+(v = 0 - 5)\sigma \sim 10^{-14}$ cm^2. The idea of using the CO molecule for a Raman scattering laser was put forward for the first time by G. Hancock and H. Zacharias.[78] In their first experiments in pumping a mixture of Ar, O_2, and CS_2, at low pressure by an rf discharge, relatively small densities $\sim 10^{12}$ cm^{-3} of CO in high vibrational states ($v = 10\text{–}15$) were obtained.

In the work of J. White and coworkers[79] a density of CO* $\approx 2 \cdot 10^{14}$ was obtained, making it possible to produce efficient conversion of the radiation from an ArF laser and a tunable dye laser ($\lambda = 219\text{–}250$ nm) to the region 134–174 nm. By pumping with an ArF laser the molecule $COX^1\Sigma^+(v = 10 - 15)$ intense emission lines at 152, 157, 167, and 173 nm, corresponding to transitions from the state $A^1\Pi(v = 1)$ to the state $X^1\Sigma^+(v = 2 - 5)$ were observed. With the use of the second harmonic of a dye laser as the pumping radiation, strong absorption of the radiation at 222 nm was observed, and following that, powerful stimulated emission at 134, 138, 143, 152, 162, and 174 nm was observed, corresponding to the transitions $A^1\Pi(v = 7) \rightarrow X^1\Sigma^+(v = 2 - 7)$. In this way it was shown that the most suitable source of pumping for the CO anti-Stokes laser in this wavelength region is the KrCl laser ($\lambda = 222$ nm). Further improvement in the parameters of this laser will, in the opinion of the authors, make it possible to obtain an energy of $\sim 10^{-3}$ J in the radiation at these wavelengths.

A promising class of lasers from the point of view of creating new sources of coherent radiation in the range 100–200 nm has been proposed by J. White[80]; this is the class of anti-Stokes lasers based on the group VI elements such as O, S, Se. The means of exciting the metastable states of these atoms by the selective dissociation of the corresponding molecules with vacuum ultraviolet radiation are well known.[81–82]

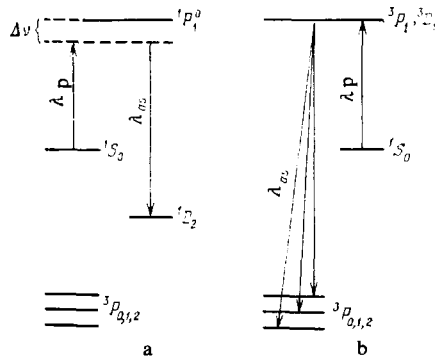

FIG. 9. Energy level diagram of the group VI elements, illustrating the two types of anti-Stokes lasers. a) Nonresonance frequency conversion utilizing the transitions between the singlet states; b) resonance frequency conversion utilizing the intercombination transitions.

The group VI elements have a common electronic structure, as depicted in Fig. 9: the ground electronic state is $3P_{0,1,2}$ and the excited states are $^1D_2$ and $^1S_0$. Murray and Rhodes first suggested the use of the transition $^1S_0 \rightarrow {}^1D_2$ (the so-called auroral transition) and $^1S_0 \rightarrow {}^3P_{0,1,2}$ the transauroral transition) as laser transitions. The main impediment to this idea is the necessity of producing a large density of $^1S_0$ states just as in the case of using these transitions in anti-Stokes lasers.

Two types of anti-Stokes lasers based on the group VI elements are possible. In the first type (Fig. 9a) the conversion of radiation occurs wholly between singlet states of the atom. The dipole matrix elements of the $^1S_0 \rightarrow {}^1P_1$ and $^1P_1 \rightarrow {}^1D_2$ transitions are large and, consequently, the anti-Stokes radiation will be tuned over a broad range. In the second type of laser (Fig. 9b) the conversion proceeds through the intercombination transition to the triplet state ($^3P_1$,$^3D_1$) with the subsequent emission via the transition to the ground state. Since the intercombination transitions are usually weak, it is clear that the frequency of the pumping laser radiation must lie close to resonance between these states. The second type of anti-Stokes laser will have a considerably narrower tuning range than the first type.

The experimentally measured lifetimes of the metastable states of $S(^1S_0)$ and $Se(^1S_0)$ being of the order of 1 μsec,[84–86] and the high density of these atoms obtained in these studies allows these systems to be regarded as highly promising media for anti-Stokes sources of vacuum ultraviolet radiation.

Table II shows data for the possible sources of radiation based on the singlet transitions in the O, S, and Se atoms (anti-Stokes lasers of the first type). Of particular interest is the laser based on atomic oxygen and having a wavelength of 99.9 nm. To produce the necessary density of $O(^1S_0)$, besides an Ar_2 laser,[83] the third harmonic ($\lambda = 122$ nm)[87] of a dye laser at a power level of several kilowatts can be used.

TABLE II. Spectroscopic characteristics of possible anti-stokes lasers based on transitions between singlet states of the group VI elements (Lasers of the first type).

Element	Initial state (energy in cm^{-1})	Final state (energy in cm^{-1})	Intermediate state (energy in cm^{-1})	λ (nm) of pumping laser	λ_{as}, nm	σ_{as}, cm^4/W
O	$2p^{41}S_0$ (33 792)	$2p^{41}D_2$ (15 867)	$3p^33s^1P_1^0$ (115 918)	121,7	99,9	$1{,}2\cdot10^{-22}$
S	$3p^{41}S_0$ (22 181)	$3p^{41}D_2$ (9 239)	$3p^34s^1P_1^0$ (78 290)	178,2	144,8	$1{,}1\cdot10^{-21}$
Se	$4p^{41}S_0$ (22 446)	$4p^{41}D_2$ (9 576)	$4p^35s^1P_1^0$ (72 568)	199,5	158,7	$3{,}7\cdot10^{-22}$

In Table III data are given for anti-Stokes lasers based on intercombination transitions in S and Se atoms (the second type of laser). Even though the intercombination transitions are as a rule weak with oscillator strengths of 10^{-3}–10^{-4}, they saturate at rather modest pumping intensities, and, consequently, under conditions of resonance pumping high conversion efficiencies and radiated power can be obtained in the vacuum ultraviolet with these systems.

6. CONCLUSIONS

The sources of tunable vacuum ultraviolet radiation and soft x rays that have been developed to the present time span continuously the wavelength range down to 39 nm. They have the highest spectral brightness as compared to all other sources of radiation in this range (synchrotrons, arc lamps). The power levels that have been obtained are sufficient for not only linear spectroscopy, but they also allow multiphoton excitation of atoms and molecules to be achieved.

With the appearance of high-power sources of ultrashort pulses of ultraviolet radiation based on excimer lasers, a wide field of activity that has been inaccessible before has opened up for the experimenter. Even the first efforts in using the picosecond ArF laser to study collective processes in atoms have produced unique results in multiphoton collisionless multiple ionization of atoms with Z from 2 to 92. In these experiments at an incident radiation intensity of $\sim 10^{15}$ W/cm^2 at 193 nm wavelength tenfold-charged uranium ions U^{+10} were obtained, the formation of these ions requiring the absorption of 99 quanta of ArF laser radiation by the uranium atom (Fig. 10). In addition, new regularities in the interaction of atoms having $Z > 10$ with an intense radiation field were revealed.[65]

Picosecond laser sources of radiation with $\lambda < 100$ nm make it possible to carry out investigations of surface phenomena with high temporal and spatial resolution (for instance, diagnostics of the recrystallization process during laser annealing of semiconductors).[88] It has been predicted that the use of pulses of duration ~ 10 psec and a power of the order of 100 kW will make it possible to observe the formation of single atomic layers.

Further development and improvement of excimer laser systems and methods of nonlinear conversion of optical radiation to the short wavelength region of the spectrum will in the near future permit the creation of powerful tunable sources of coherent radiation which span continuously the wavelength range from the visible to the x-ray region. The prospects and possibilities that are promised by the appearance of these sources are powerful stimuli for the solution of the problems that may stand in the way.

TABLE III. Spectroscopic characteristics of possible anti-stokes lasers based on intercombination transitions of the group VI elements (Lasers of the second type).

Element	Initial state (energy in cm^{-1})	Final state (energy in cm^{-1})	Intermediate state (energy in cm^{-1})	λ (nm) of pumping laser	λ_{as}, nm	σ_{as}, cm^4/W
S	$3p^{41}S_0$ (22 181)	$3p^{43}P_2$	$3p^34s^3P_1^0$ (77 151)	181,9	129,6	$4{,}9\cdot10^{-14}$
		$^3P_1$			130,3	$3{,}7\cdot10^{-14}$
		$^3P_0$			130,5	$1{,}7\cdot10^{-13}$
			$3p^34s^{33}D_1^0$ (67 817)	219,1	147,5	$1{,}7\cdot10^{-15}$
					148,3	$3{,}3\cdot10^{-14}$
					148,7	$1{,}2\cdot10^{-13}$
Se	$4p^{41}S_0$ (22 446)	$4p^{43}P_2$	$4p^35s^3P_1^0$ (71 199)	205,1	140,4	$1{,}5\cdot10^{-14}$
		$^3P_1$			144,5	$1{,}8\cdot10^{-14}$
		$^3P_0$			145,6	$1{,}1\cdot10^{-13}$
			$4p^35s^3D_1^0$ (61 681)	254,9	162,1	$2{,}0\cdot10^{-15}$
					167,5	$3{,}7\cdot10^{-14}$
					169,1	$9{,}0\cdot10^{-14}$

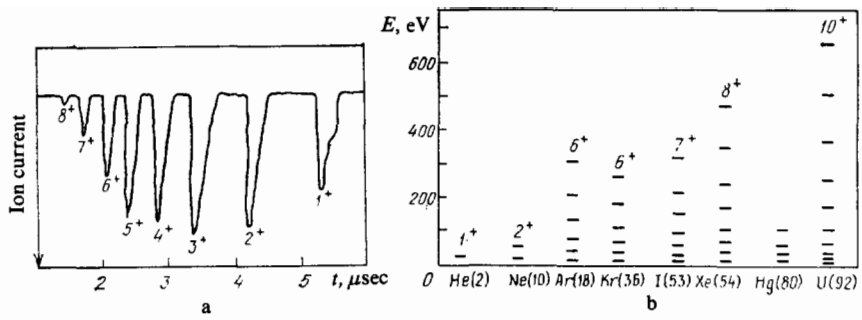

FIG. 10. Multiple ionization of atoms by radiation with $\lambda = 193$ nm and power density $\sim 10^{15}$ W/cm^2. a) Ion current in time of flight mass spectrometer as a function of time for Xe atoms; b) Energies of the states of the ions as a function of atomic number Z.

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