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Viricidal and bactericidal exciplex barrier-discharge lamps

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Abstract. **A brief review is presented of investigations performed in 2002–2020 on ultraviolet inactivation of bacteria, vital cells, and viruses by using excilamps. The excilamp models that have been developed at the Institute of High-Current Electronics, SB RAS are briefly described. Scientific data acquired by now show that excilamps on KrCl*, KrBr*, and XeBr* molecules are an alternative to low-pressure mercury lamps with respect to optical parameters. These sources of optical radiation exhibit a bactericidal effect, and emission of KrCl and KrBr excilamps demonstrates viricidal action. The latter is actual due to expansion of coronavirus disease.**

Keywords: *action spectrum, ultraviolet, exciplex molecule, excilamp.*

The idea to use excimer radiation discovered in 1913 for obtaining laser emission [1] was suggested just at the beginning of the quantum electronics era. In 1960, it was suggested by F.D. Houtermans [2] and ten years later it was experimentally realised by N.G. Basov et al. [3]. In 1973, it was reliably established that, in addition to excimers, heteronuclear excited molecules or exciplexes can be formed, and for the first time, generation on exciplex molecules XeO^* (λ = 540 nm), KrF^* (λ = 248 nm), $XeBr^*$ (λ = 282 nm), $XeCl^*$ (λ = 308 nm), ArF^* (λ = 193 nm), $KrCl^*$ (λ = 222 nm) was obtained [4, 5].

Evolution of physics and technique of lasing on excimers and exciplexes stimulated the creation of spontaneous emission sources. For example, in 1974, luminescence of exciplexes ArO^* and $ArCl^*$ was detected in a dc discharge [6]. Afterwards, spontaneous emission of excimer and exciplex molecules in VUF and UV spectral ranges was detected under various kinds of excitation [7–11].

In 1994, the general term excilamps was suggested for designating the scope of spontaneous radiation sources on transitions of excimer and exciplex molecules [12]. Presently, the most popular are excilamps excited by a barrier discharge [13–18]. They possess a high operational life (of at least several thousand hours), quickly switch on and reach the operation mode. Such sources are widely used in scientific research and are already implemented in such fields as photomedicine and microelectronics [11, 14, 19].

One promising field of excilamp application is inactivation of microorganisms (breaking their vital activity down to death). The present paper briefly reviews optical parameters of excilamps employed in solving this problem. In addition, a brief summary is given of the most important experimental data on bactericidal and virilicidal action of UV (the range of 200 < λ < 290 nm) excilamp radiation on microorganisms.

The study is actual due to the necessity of controlling the spread of new lethal respiratory infections such as severe acute respiratory syndrome (SARS, 2003), Middle East respiratory syndrome (MERS, 2012), and COVID-19 (2019–2020), provoked by novel coronaviruses (SARS-CoV, MERS-CoV, and SARS-CoV2).

Nowadays, low-pressure mercury lamps (LPML) are the sources of UV radiation, which are most frequently used for inactivating microorganisms [20]. About 70% of the total radiation power of such lamps are in the UV range of 250–370 nm, from which approximately 60% are emitted into the resonance mercury line 253.7 nm and provide the maximal bactericidal action. LPML-based devices have simple power supplies and are easy in service, which favours their wide employment. The maximum of LPML emission line at λ = 253.7 nm [Fig. 1, curve (*1*)] is close to the long-wavelength (first) maximum of the DNA absorption spectrum [curve (*2*)] and is not far from the first maximum of the action spectrum for inactivation [curve (*3*)]. A serious drawback of these lamps is mercury included in the construction. If the lamp envelope is broken, mercury contaminates environment, which is inadmissible in medical and biological applications. Now, amalgam lamps are widely used; however, utilisation of the latter is also problematic. Since 2011, EU countries gradually reduce the employment of lamps containing mercury.

For a long time it was assumed there is no alternative to LPML. Nevertheless, our papers in 2002–2013 demonstrated the possibility of substituting LPML for excilamps. Various excilamp models were developed for investigations, some examples are shown in Fig. 2.

Devices of the BD_P (barrier-discharge, portable) series are portable units comprising a coaxial barrier-discharge excilamp placed in a case with a reflector and air cooler (Fig. 2a). Such radiation sources have comparatively small dimensions 240 × 80 × 80 mm, an output window of size 60 × 90 mm, and a weight of 0.7–0.8 kg. In some years, in

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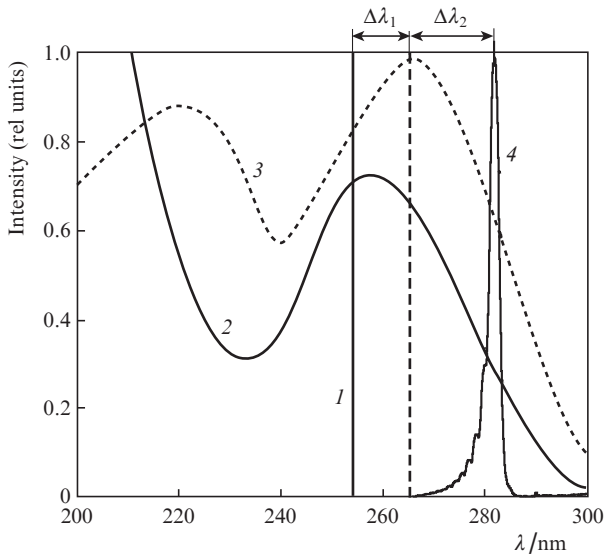
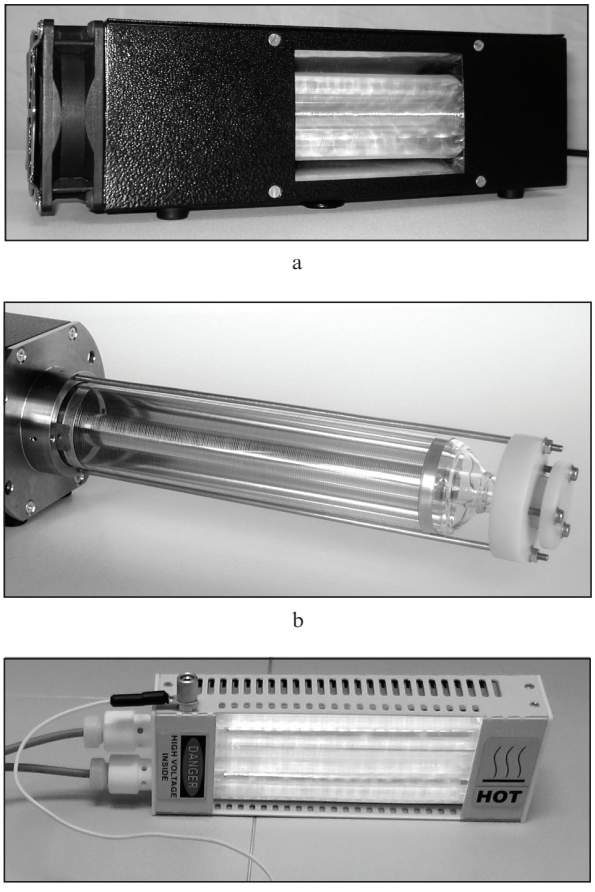


Some spectral characteristics of biological objects and radiation sources:
(*1*) mercury atomic line in LPML at $\lambda = 253.7$ nm; (*2*) DNA absorption spectrum [21]; (*3*) action spectrum for inactivation of UV radiation on bacterium *Escherichia coli* [21]; (*4*) B → X band emission spectrum of XeBr barrier-discharge excilamp.



a

b

c

Figure 1. Appearance of a series of excilamps produced at the Institute of High Current Electronics, SB RAS: (a) BD_P, (b) BD_E, and (c) 2BD_E.

our microbiological investigations we used excilamps of this series on molecules $XeBr^*$ (λ = nm), $KrCl^*$ (λ = 222 nm), $KrBr^*$ ($\lambda = 206$ nm), and Cl_2^* ($\lambda = 257.8$ nm), which provided the radiant exitance on a window surface of up to 30, 20, 10, and 2 mW cm^{-2}, respectively. By increasing the model size and rate of air pump through the case and by covering the irradiator, Sosnin et al. [22] designed a high-power UV recirculator for air disinfection.

In addition, air irradiation in rooms (free of people) is more efficient if devices of the BD_E (barrier-discharge, external) series are used, in which an excilamp is placed outside the case (Figs 2b and 2c). For better antibacterial action they may additionally comprise a unit for pumping air on a surface of the excilamp [23].

Our studies have shown that emission of XeBr, KrBr, and KrCl excilamps exhibit the most pronounced antibacterial action. In Fig. 1, curve *4* presents an emission spectrum of excilamp on $XeBr^*$ molecules. In this case, at least 95% of the radiant flux in the UV range are concentrated in the B → X band of the working molecule with the maximum at $\lambda = 282$ nm and HWFM width $\Delta\lambda_{0.5} \sim 1.8$ nm. In 2006, we noticed that the maximal intensity of this emission band is separated from the maximum of the inactivation action spectrum by approximately the same value as the LPML, that is, $\Delta\lambda_1 \approx \Delta\lambda_2$ (see Fig. 1). In addition, the excilamp spectrum has a short-wavelength tail in the range of 260–282 nm, which covers half the first absorption peak of DNA and of the action spectrum [24]. Issuing from these facts, we assumed that both the emission sources (a XeBr excilamp and LPML) have equal inactivation action. The following verification on a test-culture *Escherichia coli* (ATCC 25922) proved this hypothesis: both the sources provided a comparable bactericidal effect at equal energy expositions.

Following comparison of inactivation action of LPML and a XeBr excilamp [25] we performed with test strains of bacteria *E. coli* (501), *Klebsiella pneumonia* (ATCC 2482), *S. aureus* (209P) and clinical isolators *Proteus vulgaris*, *Pseudomonas aeruginosa* and *Candida albicans*. It was shown that emission of a XeBe excilamp has a more pronounced bactericidal effect on gram-negative microorganisms (*E. coli*, *K. pneumonia*, *P. aeruginosa*) than emission of LPML. Cultures *S. aureus* and *C. albicans* demonstrated similar sensitivities to emission of both radiation sources. The different sensitivity of tested cultures might be related to different structures of the cell walls of gram-positive and gram-negative microorganisms. The thickness of a cell wall for gram-positive bacteria (*S. aureus*) may be 40–80 nm, for gram-negative bacteria it may be about 7–8 nm [26, 27]. In addition, UV resistance of *S. aureaus* may be increased due to the carotenoid pigment synthesised by this microorganism. *C. albicans* is a yeast-like fungus pertaining to eukaryotes, its DNA is protected not only by cytoplasmic membrane and cell wall, but also by nuclear membrane. A low sensitivity of *K. pneumoniae* to XeBr-excilamp emission is possibly related to a capsule that absorbs part of emission, reducing in this way the number of RNA damages. Note that different strains of the same species may differ in the sensitivity to UV radiation as well.

One more UV radiation source is a barrier-discharge excilamp on a $Kr-Br_2$ mixture conventionally called a KrBr excilamp [16]. It emits in the two strong bands: the B → X band of $KrBr^*$ exciplex ($\lambda = 207$ nm) and D′ → A′

band of excited dimer Br_2^* (λ = 291 nm) (Fig. 3). By varying the composition ratio for Kr and Br_2 gases in the mixture and the total pressure one can obtain the emission spectrum mostly close to the DNA absorption spectrum [Fig. 1, curve (*2*)]. In 2004, the bactericidal action of such an excilamp on test-cultures *Escherichia coli*, *Staphylococcus aureus* and *Penicillium expansum* was studied and compared to the bactericidal action of a XeBr excilamp [28]. Results confirmed the more efficient bactericidal action of a KrBr-excilamp emission.

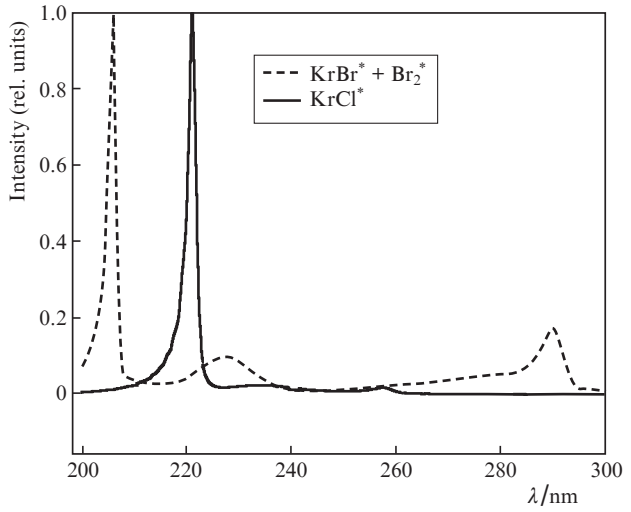


Figure 2. Emission spectra of KrBr and KrCl barrier-discharge excilamps.

In [29], the response of the culture of Chinese Hamster Ovary vital cells (CHO-K1) to UV emission of a XeBr excilamp was studied and the obtained data were compared with the results of XeBr excilamp action on bacteria. CHO-K1 cells are fibroblasts, that is, cells of the basal type involved in many processes occurring in organism, in particular, wound repair. We assume that obtaining such data may initiate new methods in medicine.

Experiments showed that the inactivation action of UV radiation on a living cell substantially differs from such action on bacteria. In contrast to bacteria, DNA of a living cell in the case of direct UV action is destructed slightly. The destructions occur in the result of mediated transformation chain: 1) photon + substrate → radicals; 2) radicals + cell components (including DNA) → oxidation and inactivation of cell components. Inactivation is additionally hindered because the cell produces antioxidants and can control the rate of their formation in its internal environment. Thus, it was shown that fibroblasts exhibit a higher resistivity against UV radiation as compared to bacteria. From the practical point of view, it means that UV radiation may become a method for selective wound bacterial sterilisation without inactivating vital cells in a body. For this purpose, one should use the irradiation dose, which is sufficient for inactivating bacteria (and viruses) and insufficient for fibroblast inactivation.

A separate search was aimed at determination of the viricidal action of excilamp UV radiation. In 2011, viricidal effects of the UV radiation of LPML and XeBr excilamp were compared on an example of the bacteriophage MS2 (strain VKPM PH-1505) breeding on *E. coli* culture K 12 F+ (strain VKPM B-3254) [30]. It was shown that UV radiation of both sources efficiently inactivates bacteriophage MS2; however, the sensitivity to the action of the XeBr excilamp was higher. From the optical point of view, this can be explained by the fact that the emission spectrum of the excilamp [Fig. 1, curve (*4*)] covers the wavelengths corresponding to active absorption of albumens [27], in particular, amino acids with a rigid structure (tryptophan, tyrosine, phenylalanine) and nucleic acids. Therefore, we assume that the effect obtained is explained by a destruction of albumens, which form the phage envelope and protect the genome, and by destruction of bacteriophage DNA.

Safe testing radiation sources on bacteriophages rather than on original viral organisms is a widespread practice [31]. Accurate characteristics of UV radiation action spectra for five bacteriophages in the range of 210–290 nm with a step of 10 nm and error of 1 nm have been obtained at the National Institute of Standards and Technology (NIST) by using a tunable laser of the NT242 Ekspla series [32]. Here, the action spectrum for inactivation was determined as a function of S(λ), which describes the reaction of organism to identical UV radiation doses at various wavelengths. The value of S for LPML (λ = 253.7 nm) was taken equal to unity [33]. The obtained spectra are presented in Fig. 4. It was stressed that action spectra for inactivation all all bacteriophages are specific in a noticeable increase of the sensitivity to UV radiation at wavelengths shorter than 240 nm.

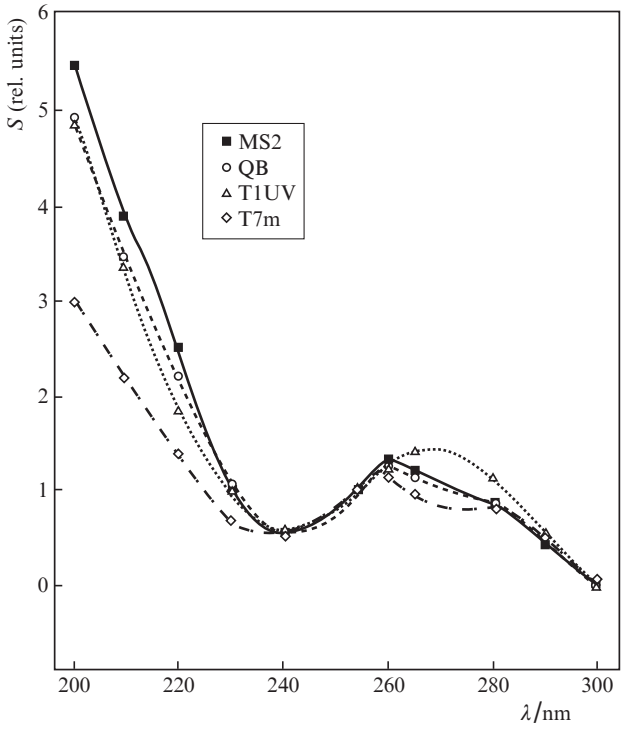


Figure 3. Action spectra for inactivation of bacteriophages MS2, QB, T1UV, and T7m (reconstructed from the data of [32]). Points for λ = 200 and 300 nm are extrapolated.

There may be several reasons for increased phage sensitivity to the radiation in the range $200 < \lambda < 240$ nm as compared to the radiation at $\lambda = 253.7$ nm. One assumption is that the short-wavelength UV radiation destructs not only a nucleic acid of a virus (DNA or RNA), but also albumins, which form a capsid (virus envelope). These albumins not only protect a nucleic acid of the virus, but also provide virus adsorption (attachment) to a host cell. Amino acids, which form these albumins, absorb an energy at $\lambda < 230$ nm more efficiently that DNA [34]. Hence, the hypothesis is reasonable that the destruction of phage albumins by UV radiation may affect their attachment to host cells, that is, influence the loss of infection capability.

From this consideration, it follows that better inactivation of viruses (as compared to LPML) will be provided by sources of UV radiation in the wavelength range $200 < \lambda < 240$ nm. Such sources are excilamps on KrBr* and KrCl* molecules, whose emission spectra are presented in Fig. 3. Both spectra have intense $B \rightarrow X$ bands with the maxima at $\lambda = 207$ and 222 nm and FWHMs of 2.18 and 2.04 nm, respectively.

As was mentioned, such sources can be used for selective cure wound, because living cells of the human body are less sensitive to UV radiation as compared to those of viruses and bacteria. This fact was verified in 2015 at the Centre for Radiological Research (New York, USA) by using our KrCl and KrBr excilamps (model BD_P, see Fig. 2a). It was asserted that comparatively low doses of UV short-wavelength radiation ($207 < \lambda < 222$ nm) efficiently inactivated bacteria and viruses, however, without destructing mammalia dermis. In addition, it was shown that UV excilamps (the BD_P model) at doses of 2 mJ cm^{-2} inactivate more than 95 % of H1N1 virus in the form of aerosol. The conclusion was made that this excilamp is a promising, safe, and cheap instrument for controlling droplet passing infections [35].

In 2020, at the time of COVID-19 epidemic, the same authors have shown that radiation of a KrCl excilamp (model BD_P) is efficient against two types of coronaviruses [36]. The authors concluded that a continuous action of a KrCl excilamp in public places at the limits established presently (3 mJ cm^2 h^{-1}) would result in 99.9% virus inactivation for ~25 minutes in the case of beta-coronavirus HCoV-OC43. Since all human coronaviruses have the same genome length, one may expect that the efficiency of inactivation by KrCl-excilamp radiation will be comparable to that for other coronaviruses, for example, SARS-CoV2.

Thus, the methods for obtaining luminescence of excimer and exciplex molecules, which initially were widely employed in laser physics, gave rise to a new series of spontaneous emission sources and presently make a basis for developing photon sources for inactivating microorganisms. Such radiation sources may become an alternative to classical low-pressure mercury lamps. By now, the bactericidal effect of KrCl, KrBr, and XeBr excilamps has been confirmed. In addition, data available confirm promising capabilities of KrCl and KrBr excilamps with a viricidal effect stronger than that of low-pressure mercury lamps. All discussed above is a scientific base for formulating new scientific and design and development studies.

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