INTRODUCTION

Modern excilamps are based on the formation of rare gas \( \text{Rg}^* \) or halogen excimers \( \text{X}_2^* \) or of rare gas halide exciplexes \( \text{RgX}^* \), and the efficient fluorescence of these molecules in different types of discharges. These so-called “electrodeless” lamps, in which the electrodes are without contact to the irradiating plasma, may be driven either by dielectric barrier discharge (DBD) (Kogelschatz 2004) or by capacitive discharge (CD) (Lomaev et al. 2005; Sosnin et al. 2005a; Sosnin 2004). If the pressure of the gas in a bulb exceeds 20-30 kPa they emit narrow-band radiation (Figure 1) in the ultraviolet (UV) or vacuum-UV (VUV) range of the electromagnetic spectrum depending on the type of filling gas or gas mixture (see Table 1). In the literature, these sources of incoherent VUV/UV radiation are commonly referred to as “excimer lamps”, “exciplex lamps” or in short as “excilamps”. However, the reader should notice that they are not laser sources!

Excilamps are most attractive for applications in photo-science, mainly because they exhibit a very long lifetime (in the range of several thousand hours) (Sosnin et al. 2002; Zhang and Boyd 2000). Further, the use of CD and DBD gives an extraordinary freedom with respect to the geometric design of excilamps (Figure 2), which allows, for the first time in photoscience, adjustment of the lamp’s geometry to the optimum conditions of a desired photo-

Table 1: Matrix of excimers \( \text{X}_2^* , \text{Rg}_2^* \) and exciplexes \( \text{RgX}^* \) obtained from halogens and rare gases and their emission maxima.
Commercially available excilamps are in boldface (c.f., Kogelschatz, 2004).

<table>
<thead>
<tr>
<th>Rare Gas (Rg)</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>74 nm</td>
<td>84 nm</td>
<td>126 nm</td>
<td>146 nm</td>
<td>172 nm</td>
</tr>
<tr>
<td>Ne</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ar</td>
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<td>Kr</td>
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</tr>
<tr>
<td>Xe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>157 nm</td>
<td>108 nm</td>
<td>193 nm</td>
<td>248 nm</td>
<td>354 nm</td>
</tr>
<tr>
<td>Cl</td>
<td>259 nm</td>
<td></td>
<td>175 nm</td>
<td>222 nm</td>
<td>308 nm</td>
</tr>
<tr>
<td>Br</td>
<td>289 nm</td>
<td></td>
<td>165 nm</td>
<td>207 nm</td>
<td>282 nm</td>
</tr>
<tr>
<td>I</td>
<td>342 nm</td>
<td></td>
<td></td>
<td>190 nm</td>
<td>253 nm</td>
</tr>
</tbody>
</table>

ABSTRACT

This paper reviews recent experimental results concerning the use of modern excilamps (excimer lamps) in photoscience and photochemical technology. The special characteristics of these sources of incoherent vacuum-UV (VUV) and UV radiation are presented and application trends of excilamps are specified.

Keywords: excimer lamps, excilamps, 172 nm irradiation, VUV-oxidation, photo-mineralization, UV-disinfection, AOP, AOT, excilamp flow-through photoreactor, gas-phase photo-oxidation.
process, and not vice versa, as is common in photochemical technology using mercury based lamp systems regarding their rigid geometry. Due to the special characteristics of excilamps (c.f., Figure 3) many potential applications in photochemistry, photobiology, photomedicine and photochemical technology have been studied on laboratory and pilot scales, and some of them have already reached commercial dimensions (c.f., Oppenländer 2003a).

The intrinsic efficiency of rare gas excimer fluorescence emission was calculated to be in the range of 45% to 80%

\[
\begin{align*}
Xe_2^+ & : \lambda_{\text{em}} = 172 \text{ nm} \\
KrCl^+ & : \lambda_{\text{em}} = 222 \text{ nm} \\
XeCl^+ & : \lambda_{\text{em}} = 308 \text{ nm}
\end{align*}
\]

but commercial XeCl*, KrCl*, XeBr*, KrBr* lamps reach only radiant efficiencies of 5-18% (Lomaev et al. 2003). However, the Xe2* excilamp was optimized to emit VUV radiation at a wavelength of 172 nm with a half-width of about 14 nm and with a radiant efficiency of 40% at 20 W or 100 W of electrical input power (http://www.xeradex.de/). Today, it is possible to easily obtain an average radiant power of up to 100–150 W, especially in case of KrCl* and XeCl* DBD-driven excilamps. Powerful XeCl* excilamps with an electrical power input of 15-25 kW are used in UV-curing technology for operating sheet and web offset printing processes at very high speeds (Mehnert 1999).

The positive radiation geometry of the inward radiating DBD-driven excilamp is exceptionally useful for the irradiation of aqueous or gaseous media. The typical dimensions and electrode configurations of an excilamp flow-through photoreactor are demonstrated in Figure 4. This concept uses the excilamp itself as a continuous tubular photoreactor, which leads to a space-saving photoreactor design.

APPLICATION

Although the development and improvement of modern excilamps is mainly triggered by the lighting industries (e.g. LINEX™ and PLANON™ lamp systems from OSRAM) their applications in photochemical technologies are outstanding. Some of them are listed below with reference to the cited literature:

- Cleaning of surfaces by VUV irradiation
- VUV/UV induced modification of polymer surfaces
- UV induced grafting on synthetic polymers
- Reduction of the contact angle of water on surfaces
- UV curing of printing inks, varnishes, coatings and adhesives
- VUV/UV assisted low-temperature oxidation of Si, SiGe and Ge
- VUV/UV induced material deposition (metallic, semiconducting and dielectric films)
- Room temperature deposition of metal patterns on heat sensitive substrates
- Excilamps in analytical instrumentation
- instrument for the detection of HDO and H2O
- measurement of particle-bound polycyclic aromatic hydrocarbons (PAHs) in the gas phase
- time-of-flight mass spectrometry (TOFMS) with VUV excilamps as potent alternatives to Laser sources for the initiation of single-photon ionization processes
- photochemical release of iodide ions (I-) by double irradiation of “organo”-iodine in urine with XeBr* and KrCl* excilamps followed by quantitative determination of I- by cathode stripping voltammetry
• organic carbon, nitrogen and phosphorus detection in solutions
• wavelength-selective photochemical destruction of metal-organic complexes
• photochemical titration
• Photochemical synthesis of fine chemicals
• Chemical evolution on the primitive Earth: formation of aspartic acid by 172-nm-irradiation of aqueous solutions of urea and maleic acid
• Medical applications: e.g., VUV modification of PTFE vascular grafts
• Photomedical applications: phototherapy of skin diseases, e.g., treatment of psoriasis

These recent examples selected from the current literature again demonstrate the enormous application potential of excilamps, especially in analytical processes.

WATER PURIFICATION USING EXCILAMP FLOW-THROUGH PHOTOREACTORS

Photochemical detoxification and purification of water decontaminated with organic substrates and with bacteria aim at the oxidation or mineralization of the dissolved organic material being accompanied by the efficient disinfection of the water. Advanced oxidation processes (AOPs) for the treatment of water and air (Oppenländer 2003b) are mainly based on the efficient production of hydroxyl radicals (•OH) and on their kinetically controlled reaction with substrate molecules leading to substrate oxidation and finally to the mineralization of organic material. The production of short-lived and highly reactive •OH radicals can be achieved by different techniques, including photochemical methods. Hence, the VUV photolysis of water (Gonzalez et al. 2004) represents a powerful method of •OH radical production without addition of any chemical additives (e.g. hydrogen peroxide or ozone). It depends on the photochemically induced homolysis of water molecules according to:

\[ \text{H}_2\text{O} + h\nu_{\text{VUV}} \rightarrow \text{H}_2\text{O}^* \rightarrow \text{H}^* + \cdot \text{OH} \]

The photochemical production of •OH radicals can be accomplished by irradiation of liquid water using VUV lamps, for example Xe excilamps at a wavelength of 172 nm with a moderate quantum yield $\Phi(\cdot \text{OH})$ of 0.42. Due to the extreme radial heterogeneity of the VUV-initiated photochemical reactions in water, the inwardradiating DBD-driven excilamp is a non-ideal plug flow reactor system characterized by zones of fast photoreactions, consecutive thermal radical reactions and diffusion processes.

Recently, Oppenländer et al. (2005) introduced a simple and convenient set-up that defeats the local oxygen deficit of the irradiated volume during VUV photolysis of water in the presence of dissolved organic compounds within a xenon excilamp flow-through photoreactor by injection of O$_2$ (or air) via an integrated axially mounted ceramic oxygenator. Thus, the rate of mineralization of several organic substrates dissolved in water was enhanced significantly by oxygen or air injection directly into the VUV irradiated zone. Therefore, small or large excilamp systems with incorporated tube aerators of different sizes and material are possible. This simple method opens up new dimensions in the technical development of VUV-induced oxidative degradation, mineralization, and disinfection processes.

VUV-INITIATED GAS-PHASE PHOTOOXIDATION AND PHOTODIMERIZATION

Traditional techniques for the removal of volatile organic compounds (VOCs) or of awkward odors from polluted air streams include absorption, condensation and incineration or biological treatment. During the past decade ultraviolet-initiated oxidation methods, such as photocatalytic oxidation (PCO) using titanium dioxide (TiO$_2$) as photocatalyst and photochemical oxidation, have been extensively studied related to their ability to remove or destroy various VOCs and odors in polluted air streams (c.f., Oppenländer 2003b).

The VUV irradiation of gases is not as restricted as that of the aqueous phase with respect to the heterogeneity of the primary photoprocess, the magnitude of diffusion constants, and the quantum yields of the underlying photoreactions. The irradiation of air or oxygen with 172 nm radiation leads immediately to the production of ozone, and the photolysis of water vapor at a wavelength of 165 nm yields H$_2$, O$_2$ and H$_2$O$_2$. Therefore, VUV-induced oxidation and mineralization of VOCs using excilamp photoreactor systems seem to have great potential for the remediation of polluted air streams.
Excilamps also allow the photochemical syntheses of hydrocarbon components. This action of incoherent VUV- and UV-radiation using Xe₂⁺ and KrCl⁺ excilamps (radiant power of 2 and 40 W, respectively) was demonstrated by Sosnin and Erofeev (2004). Their study has shown that VUV/UV-irradiation of natural gas from a gaseous condensate field increases higher molecular weight gas components (C₆-C₈ isomers) in the mixture according to equations 2 and 3. Simultaneously, the concentration of water vapor decreased noticeably. This process is very interesting for application in gas industry (Medvedev et al. 2004).

\[
\begin{align*}
[2] & \quad C_nH_{2n+2} + \cdot OH \rightarrow C_nH_{2n+1} + H_2O \\
[3] & \quad C_nH_{2n+1} + C_mH_{2m+1} \rightarrow C_{(n+m)}H_{2(n+m+1)}
\end{align*}
\]

Consequently, at the High Current Electronics Institute SB RAS (Tomsk, Russia) novel photochemical reactors were developed incorporating Xe₂⁺ DBD-driven excilamps (Figure 5). The irradiation area of these reactors ranges from 700 up to 2500 cm². They are applied to irradiate natural gas mixtures at pressures of up to 40 atm. In the summer of 2005, this type of reactor was successfully tested at the gaseous condensate field of Tomsk region (Russia).

**DISINFECTION OF WATER AND AIR**

Obviously, there exist two different processes of disinfection: the inactivation of microorganisms by UV irradiation or their total VUV-induced photomineralization. The disinfective efficacy of incoherent VUV- and UV-radiation using Xe₂⁺ and KrCl⁺ excilamp flow-through photo reactors (electric input power Pid of 150 W) was demonstrated by Oppenländer and Baum (1996). Thus, the colony-forming units (CFUs) of psychrophilic and mesophilic bacteria of four liters of greywater could be reduced by reduction factors R₀ of 2.81 (172 nm) and 2.95 (222 nm) after 20 min of irradiation. Using the Xe₂⁺ excilamp the reduction of CFUs was accompanied by a defoaming effect of the ten side containing greywater. In addition, photomineralization of the organic load of the water by 172 nm irradiation led to a significant TOC and COD diminution.

Further, the KrCl⁺ excilamp’s inactivation effect was confirmed on other microbiological objects (vegetative bacteria and the yeast Candida, B. subtilis spores and cells, heterotrophic bacteria). It was shown recently that the KrBr⁺ excilamp is also suitable for this aim (Sosnin et al. 2005b). The spectrum of this excilamp is assembled from radiation of the KrBr⁺ exciplex (207 nm) and the Br₂⁺ excimer (289 nm). The disinfection ability of this excilamp was verified using E. coli, St. aureus, and Penicillium expansum microorganisms.

**CONCLUSION AND OUTLOOK**

The excilamp technology offers a multitude of potential applications in photoscience and especially in advanced oxidation technologies (AOTs) for the treatment of water and air. For example, the xenon excimer lamp with its emission maximum at a wavelength of 172 nm makes it possible to irradiate liquid and gaseous media at high photon energy \(Q_\lambda\) of 7.21 eV and with high radiant power.

Finally, we allocate the following tendencies in the development of excilamps and accompanying technologies:

- improvement of excilamp equipment that is already on the market (for example psoriasis treatment by 308-nm-irradiation with XeCl⁺ lamps (c.f., Köllner et al. 2005)
- development of multiwave excilamps that emit radiation from several exciplex and/or excimer molecules
- excilamp miniaturization (e.g. manufacturing of so-called micro discharge devices (MDD))
- inclusion of excilamps in multicomponent analytical systems and substitution of mercury-containing lamps in existing apparatus
- studies of “fast” photoprocesses by applying flash-excilamps with high pulse radiant power up to several hundreds of kW cm⁻² and variable radiation pulse duration of several nanoseconds
- photochemistry of gas mixtures at elevated pressures
- design of powerful and efficient excilamp purification and disinfection modules for water and air treatment, which could be far more convenient than using mercury low- or medium-pressure lamps

The application of reactor systems that use for example cylindrical excilamps as flow-through photo reactor systems opens up new and space-saving applications for water and air remediation and disinfection. Many other CD- or DBD-driven excilamp geometries may be adjusted to the requirements of the desired photoprocess. Thus, an optimal freedom in lamp design is possible using the excilamp technology. Consequently, excilamps could become a high-volume market in photoscience and environmental technology. Thus, to answer the title question we have demonstrated with this short article that modern excilamps exhibit a grand future!

**ACKNOWLEDGMENTS**

The authors thank Dr. Ulrich Kogelschatz (retired from ABB, Baden, Switzerland) and Prof. Victor Tarasenko (High Current Electronics Institute SB RAS, Tomsk, Russia) for stimulating discussions about the development of excilamps. Edward Sosnin thanks the German Academic Exchange Service (DAAD) and the Russian Education Ministry for financial support (Mikhail Lomonosov Program).
REFERENCES


