

Scattering and Chlorine Absorption in Discharge-Pumped XeCl Excimer Lasers

H.-J. Weigmann, P. Taubert, R. König, and H.-J. Pätzold

Central Institute of Optics and Spectroscopy, Rudower Chaussee 6, O-1199 Berlin, Fed. Rep. Germany

Received 17 September 1990/Accepted 10 December 1990

Abstract. Scattering microparticles were found to determine the characteristic behavior of the laser energy of discharge pumped XeCl excimer lasers with aluminium electrodes. All experimental results indicate that sputtered aluminium reacts with chlorine, a constituent of the laser gas, and forms aluminium chloride particles. Chlorine was observed to be formed by a reaction of oxygen, contained as an impurity, with the halogen donor hydrogen chloride under discharge conditions.

PACS: 42.55 G, 82.40 Z

At the beginning of XeCl excimer laser development, aluminium electrodes were used. They influenced gas lifetime and the temporal change of energy output in a characteristic manner. With the technological progress of the last years these problems have been solved by the use of nickel plated electrodes and gas-purification systems.

Discussions in the literature interpret the energy minimum during the first 10^2 – 10^5 impulses of excimer lasers at this low level of technological development in various ways [1–9]. In particular, the distinction between absorption and/or scattering is still ambiguous.

In this paper, spectroscopic investigations are presented to give new insights into reasons for the observed changes in laser energy.

Experimental Results

The experiments were performed with a home-made UV preionized discharge pumped XeCl laser without a gas circulation system as described in [10] (repetition rate: 1 Hz; laser pulse energy: 70 mJ; pulse width (FWHM): 7.5 ns; gas volume: 1.5 l; standard gas mixture: 2.5 Torr HCl, 10 Torr xenon, helium to 3 atm.). The electrodes were made of aluminium, the gasket rings from silicon rubber and the chamber of PMMA.

Classical UV and IR absorption measurements ranging from 200 nm to 400 nm and from 2900 cm^{-1} to 3000 cm^{-1} , respectively, were used to determine changes in chlorine and hydrogen chloride content inside the laser vessel during laser operation. For detectable concen-

trations, the removed laser gas was condensed before measuring within a liquid nitrogen cooled trap, mounted at the absorption cell.

Transmission measurements carried out longitudinally in the laser cell used pulsed dye laser radiation, synchronized to the investigated XeCl laser pulses with a constant delay of 0.5 s. In order to distinguish between absorption by chlorine and scattering by microparticles, two wavelengths were selected. At 450 nm the chlorine absorption can be neglected, and thus changes in transmission result from scattering particles only. On the other hand, the 342 nm radiation can be influenced additionally by chlorine absorption if the concentration is large enough (cross section: $2.3 \times 10^{-19}\text{ cm}^2$; this is 30% larger than for the XeCl laser wavelength).

Scattered radiation was detected perpendicular to the optical axis of the XeCl laser by using very intense dye laser radiation of 576 nm and the same trigger regime as before.

The Initial Phase of Laser Action

Using standard gas mixtures, the measured laser energy goes through a minimum at the very beginning (Fig. 1). Later on, a continuous decrease can be observed (Fig. 5, curve A). During the initial phase, the optical density of the laser gas at 342 nm shows nearly the same behavior with coinciding minima (Fig. 1). This implies that the behavior of the laser energy is determined mainly by optical losses.

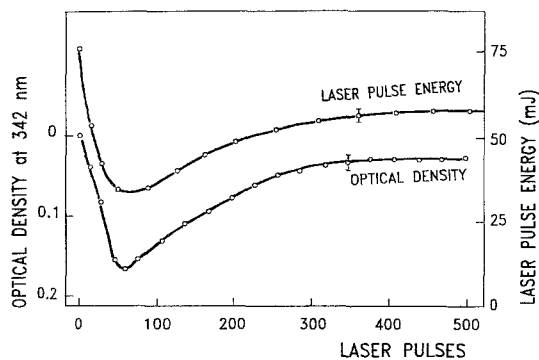


Fig. 1. Dependence of laser energy and optical density at 342 nm on pulse number during the initial phase of laser action (standard conditions)

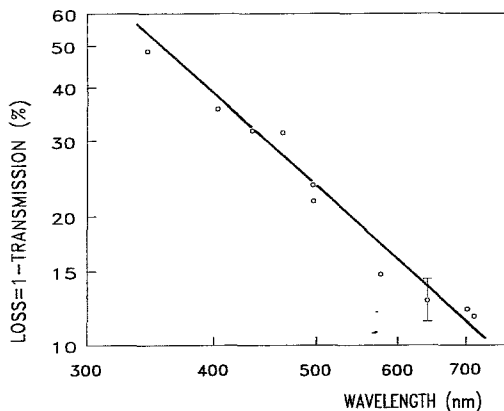


Fig. 2. Wavelength dependence of the transmission loss L ($L = 1$ minus transmission at the minimum) in the range from 340 nm to 710 nm (double logarithmic scale)

In order to differentiate between absorption and scattering as possible reasons for these losses, we measured the spectral dependence of the transmission around the energy minimum, tuning the dye laser from 340 nm to 710 nm. The result is given in Fig. 2, where the depth of the transmission minimum is plotted against the probe

wavelength. The straight line observed is characteristic for Mie scattering [11] corresponding to

$$L \sim \lambda^{-k} \tag{1}$$

(with $k = 2.2 \pm 0.3$), demonstrating the predominant influence of scattering under standard conditions. On the other hand, we must exclude any influence of chlorine absorption disturbing the measured curve.

Further results characterizing the situation in the initial phase are summarized in Fig. 3. The existence of microparticles is once more confirmed by the direct detection of perpendicular scattered light. A close correlation of reduced laser energy and scattered light intensity is observed. The small shift between the maximum of scattered light and the minimum of laser energy may be due to the much greater wavelength of the probe beam (576 nm) in comparison to the 308 nm XeCl laser radiation. We suppose the scattering particle formation to be connected with an initial rise of the mean particle size thus influencing radiation of longer wavelengths at later times (corresponding to decreasing coefficient k) more strongly.

Furthermore, we observed formation of molecular chlorine during the initial phase (Fig. 3). From the optical density, measured UV-spectroscopically, a maximum chlorine content of $(1.1 \pm 0.3) \times 10^{15} \text{ cm}^{-3}$ results. This yields an absorption coefficient inside the laser cavity at 308 nm of about $0.02\% \text{ cm}^{-1}$. Comparing this value to the typical small-signal gain of several $\% \text{ cm}^{-1}$ for such lasers [12, 13] allows one to conclude, in agreement with McKee et al. [2], that the chlorine concentration is too low to observably disturb the gain from direct absorption.

To gain information about the chlorine formation channel, we added small amounts of different gases to the standard mixture. We found the surprising result that, if 3 Torr oxygen are added at the beginning, the maximum chlorine content becomes tenfold higher, with an absorption at 308 nm, again too low to influence the gain directly. Moreover, Cl_2 concentrations larger than in

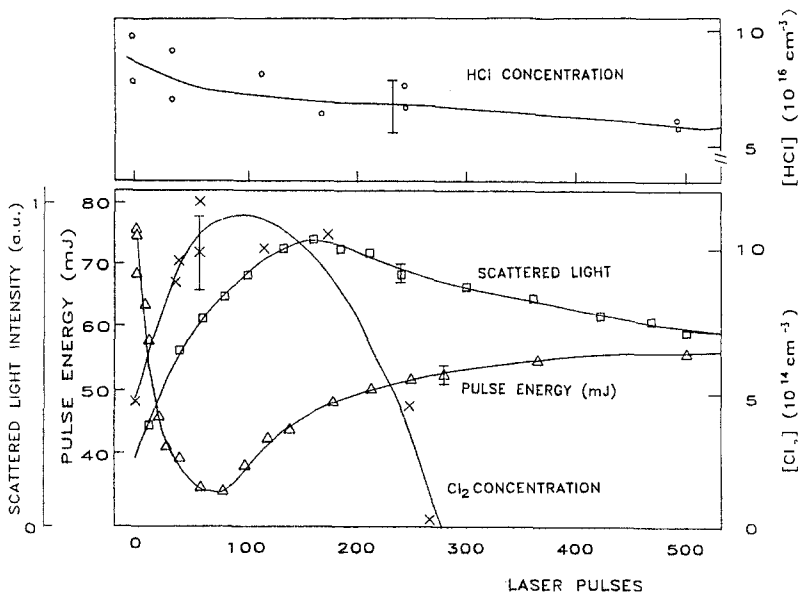


Fig. 3. The initial phase of laser action (standard conditions): Δ laser pulse energy, \square perpendicular scattered light intensity ($\lambda = 576 \text{ nm}$, arbitrary units), \circ hydrogen chloride concentration, \times chlorine concentration

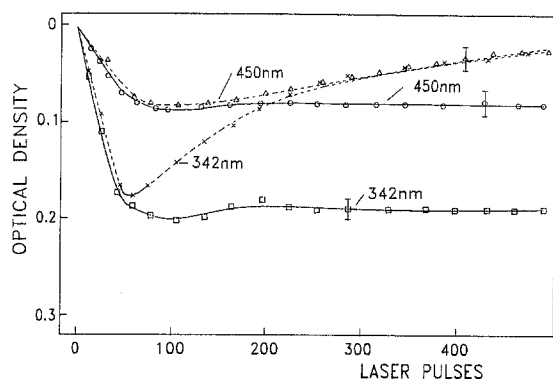
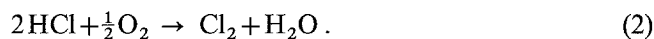


Fig. 4. Optical density measured longitudinally through the laser axis at 342 nm and 450 nm in standard gas mixture (dotted lines) and in a mixture with 3 Torr oxygen added (solid lines), as a function of pulse number

the standard case could be detected over several thousand pulses. Both observations can be understood only if an additional reaction is taken into account:



Allmand and Franklin [14] found that this reaction is initiated photochemically with radiation of 254–365 nm. We have not found any evidence that this reaction has been considered in connection with chemical processes in XeCl lasers.

In Fig. 4, the optical density of the laser chamber is given at 342 nm and 450 nm for the standard mixture (dotted line) and for the standard mixture with 3 Torr oxygen added (solid line). In the case of added oxygen, both curves coincide with those of the standard case until the minimum is reached; later on they remain at this low level for several hundreds of pulses. The course of the 450 nm curve then reflects a constant presence of scattering particles while the optical density at 342 nm is larger in agreement with (1) but does not reflect chlorine absorption. This is confirmed by identical values of optical density observed at 342 nm after about 60 pulses in the two investigated systems, not affected by the different chlorine concentrations measured (10^{15} cm^{-3} and 10^{16} cm^{-3} respectively).

These results imply that scattering particle formation is connected with chlorine occurrence. We suppose that the aluminium sputtered from the electrodes during each discharge reacts favorably with the chlorine present during the initial phase or as a result of oxygen addition, thus forming scattering particles of aluminium chloride:



Going back to Fig. 3, it is now possible to understand the appearance and disappearance of chlorine during the initial phase. We must assume a contamination of the standard gas mixture with traces of oxygen, probably diffusing from the atmosphere through the silicon rubber used for gasket rings. This material is known to have a high gas permeability. After consumption of the available oxygen by reaction (2), the production of chlorine and consequently the appearance of Al_2Cl_6 terminates. This involves a decrease in the number of scattering micro-

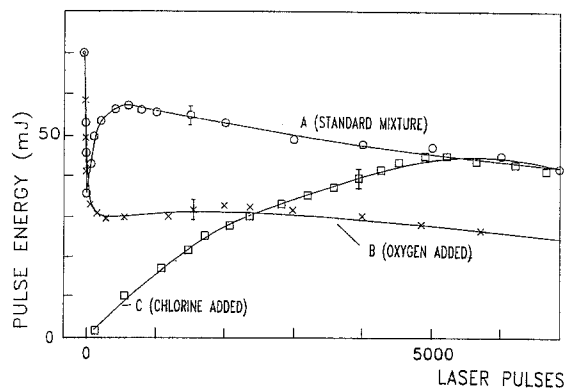


Fig. 5. Influence on XeCl laser energy of different gases added to the standard mixture. (A) standard mixture: 2.5 Torr HCl, 10 Torr Xe, He at 3 atm., (B) standard mixture, 3 Torr oxygen added, (C) standard mixture, 2 Torr chlorine added

particles as a result of conglomeration and sedimentation, thus explaining the increase of laser pulse energy. In agreement with the postulated reaction (2), we found a significant decrease of the HCl content until the Cl_2 maximum is reached (upper curve in Fig. 3).

Long Term Behavior of Laser Energy

The postulated model is confirmed by the long term behavior of laser energy observed after the addition of chlorine or oxygen (Fig. 5).

In the initial phase, the laser energy (curve B) has the same temporal behavior as the longitudinal transmission in Fig. 4, with oxygen as an additive. Later on we observe the same slope of curve B as in the standard case (curve A) but at a lower level of energy. This behavior is in agreement with reaction (2). After some thousand pulses, the oxygen disappeared due to chlorine formation as verified by the UV spectroscopic determination of Cl_2 concentration. During this process a considerable amount of hydrogen chloride is consumed, leading to decreased laser energy in the last part of curve B.

A quite different behavior of laser energy is observed after the addition of 2 Torr chlorine. The pure chlorine absorption prevents laser action during the first pulses. After that, the output energy increases slowly. At about 5000 pulses, the system emits the same energy as under standard conditions (curve C in Fig. 5). Consequently, there must exist a very effective reaction decreasing the chlorine concentration without influencing the hydrogen chloride content. This is the same reaction between chlorine and sputtered aluminium already described (3).

Furthermore, the occurrence of this reaction is confirmed by the following facts:

(i) Aluminium chloride is found as a white powder inside the laser chamber in agreement with [5].

(ii) Goldhar et al. [15] observed the aluminium resonance line at 308.215 nm in absorption against the XeCl 0-2 band in old laser gas, attributing it to a dissociation of Al_2Cl_6 in the discharge.

(iii) The minimum in the output energy disappeared if the aluminium electrodes were exchanged for nickel and the silicon rubber was replaced by viton rings.

Independent of the materials used, the results demonstrate that oxygen is a very dangerous impurity in XeCl lasers, consuming hydrogen chloride and producing water.

Summary

The occurrence of scattering particles in the discharge region of the investigated XeCl laser is the reason for the observed behavior of laser energy. Chlorine absorption influences laser energy directly if chlorine is added to the laser gas in higher concentrations (e.g., 2 Torr).

Indirect conclusions imply that the observed micro-particles consist of aluminium chloride, produced in a reaction between sputtered material of the electrodes and chlorine.

A discharge-initiated reaction of oxygen with hydrogen chloride yielding chlorine was demonstrated by spectroscopic measurements. This is a prerequisite for understanding the observed changes in output energy of special XeCl lasers.

Acknowledgement. We would like to thank Mrs. R. Lendt for her valuable technical assistance in many of our experiments.

References

1. R.C. Sze: IEEE J. QE-15, 1338-1347 (1979)
2. T.J. McKee, D.J. James, W.S. Nip, R.W. Weeks, C. Willis: Appl. Phys. Lett. **36**, 943-945 (1980)
3. L. Burlamacchi, P. Burlamacchi, R. Salimbeni: Appl. Phys. Lett. **34**, 33-35 (1979)
4. V.I. Donin, Ju.I. Khapov: Sov. J. Quantum Electron. **16**, 1034-1088 (1986)
5. M.C. Gower, A.J. Kearsley, C.E. Webb: IEEE J. QE-16, 231-235 (1980)
6. R. Tennant: Laser Focus **17**, 65-68 (1981)
7. W. Hans, P. Scott: Laser Focus **19**, 86 (1983)
8. P.N. Mace: Opt. Eng. **20**, 935-940 (1981)
9. G. Rilov, V. Sargsyan, M. Sharkhatunyan, T. Karapetyan: Abstracts III. National Conference "Lasers and their Applications", Plovdiv, Bulgaria (Oct. 1988)
10. J. Lademann, R. König, Yu. Kudryavtsev, H. Albrecht, G. Fritsch, R. Grunwald, G. Winkelmann: Exp. Techn. Phys. **32**, 235-246 (1984)
11. G. Mie: Ann. Phys. **25**, 377 (1908)
12. S. Watanabe, A.J. Alcock, K.E. Leopold, R.S. Taylor: Appl. Phys. Lett. **38**, 3-6 (1981)
13. A.B. Treshchalov, V.E. Peet, V.T. Mihkelsoo: IEEE J. QE-22, 51-57 (1986)
14. A.J. Allmand, R.G. Franklin: J. Chem. Soc. **1930**, 2073-2092
15. J. Goldhar, W.R. Rapoport, J.R. Murray: IEEE J. QE-16, 235-241 (1980)