Kinetics of charge transfer processes in photochemical lasers

L.D. Mikheev

Lebedev Physics Institute, Leninsky prospekt 53, 117294 Moscow, USSR

Abstract

The review presents the results of the investigations of the kinetics of charge transfer photoprocesses underlying the so-called photochemical lasers at electronic transitions in molecules. These lasers are now being developed at Quantum Radiophysics Division of Lebedev Physics Institute of the USSR Academy of Sciences. The main goal of these investigations is to demonstrate that application of photochemical processes, based on broadband optical excitation of molecules and subsequent secondary physical and chemical processes, to laser physics presents a universal and fruitful method of practical lasers pumping. In a number of cases such lasers have similar or even higher parameters as compared to e-beam and fast-discharge excimer lasers.

PUMPING SOURCE

The advances in photochemical excitation of gas lasers were mainly conditioned by the application of such high intensity pumping sources as open emitting discharges and shock waves which can produce up to 10^{18} of excited atoms or molecules in cubic centimeter [1-3]. Below are some details on open discharge technique based on exploding wire initiation. Sliding sparks are also used to initiate open discharge, and this gives a possibility of operating in repetitive regime. The open discharge has no shell and is immersed in the studied gas. Figure 1 shows the experiment with the exploding wire initiation. The cell is filled with the mixture of the studied gases at a typical pressure of the buffer gas 1 to 3 atm. Typically the open discharge is initiated by a 0.5-1 m long tungsten wire stretched along the cell axis. When the wire is exploded the intensively
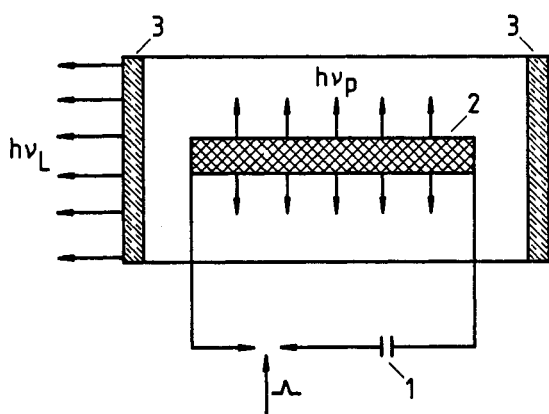
Fig. 1. Scheme of experiments
with the open discharge.

emitting plasma column is formed. It is ideally cylindrical and fills part of the cell volume. The unturbed gas adjacent to the open discharge is affected by the plasma radiation. As the discharge has no shell it becomes possible to use radiation in any spectral region including the VUV one.

The used radiation within the actual spectral band has the power up to 1 MW/cm^2 at brightness temperatures of 30-35 kK. The excitation power density is usually about hundreds kW/cm^3. Radiation of the open discharge can produce up to 10^{18} electronically excited particles or free atoms and radicals in 1 cm^3 within 10 μs. Such high concentrations of active particles open wide possibilities to produce powerful stimulated emission from both primary and secondary photochemical products when the active medium is placed between two parallel resonator mirrors. Moreover, this gives a possibility to study the interaction of primary or secondary products between themselves.

KINETICS OF ACTIVE MEDIA

Among molecular electronic transitions in which lasing has been achieved with optical, e-beam and fast discharge pumping the charge transfer ones between ionic and covalent states are numerous, and play an important role in the development of these lasers. Their application to inversion production has led to the appearance of a large number of lasers based on halides of rare gases (excimer lasers), on halides of metals of the second group of the periodic system, as well as on halogens and interhalogens as active

media. Among the gas lasers of visible and UV spectral bands, these systems have gained rapidly leading positions because of their energy characteristics. This is due to two reasons.

The first one related to bound-bound transitions is that in ionic states the equilibrium internuclear distance is, as a rule, far longer than that in the covalent one. As a result, laser transitions proceed from a minimum of the upper ionic state term to high-lying vibrational levels of the covalent state. This circumstance facilitates depletion of the lower laser levels due to vibrational relaxation, and is particularly important in the case of allowed laser transitions excited optically by thermal sources (flash lamps, open discharges or shock waves) since their typical durations of pumping pulses lie within the micro- and millisecond ranges.

Moreover, under direct optical excitation of molecules into ionic states charge transfer transitions take place from lowest vibrational levels of ground state to high lying vibrational levels of the upper state, where the repulsive branch of the potential-energy curve becomes very steep. According to the Franck-Condon principle, the absorption spectrum should display a great number of vibrational bands, which determines a wide pumping spectrum. The width of excitation spectrum is the one of the most significant characteristics of an active medium because it determines spectral matching of the active medium absorption with the pumping source radiation and, consequently, efficiency of photochemical lasers.

The second circumstance underlying the success in the development of lasers at charge transfer transitions is extremely high cross-sections of excited ionic states production in reactions between halogen containing molecules and rare gas atoms, when one of the reagents is in an electronically excited state. The best known class of these reactions present harpooning reactions between excited rare gas atoms and halogen containing molecules.

These reactions underlie the well known excimer lasers [4]. In their lowest excited configuration, $np^5(n+1)s$, the noble gas atoms display properties similar to those of the corresponding alkali metal atoms. One such similarity is their tendency to react with halogen-containing molecules to produce electronically excited diatomic noble gas-halide molecules in strongly bound ionic states. This is due to the fact that the energy of ionization for excited rare gas atoms is close to the ionization potential of the corresponding normal alkali metal atoms. Behind the harpooning reactions is crossing in diabatic sense between the covalent and ionic terms of an intermediate complex that forms on reactant encounter (see Fig. 2). If the coupling between ion pair and covalent terms in the diabatic crossing point is high enough, an electron of the rare gas atom jumps over the reagent having great affinity for an electron and the intermediate complex dissociates to produce new products. Due to long range character of Coulomb interaction the cross-section of these reactions reaches several hundred $Å^2$.
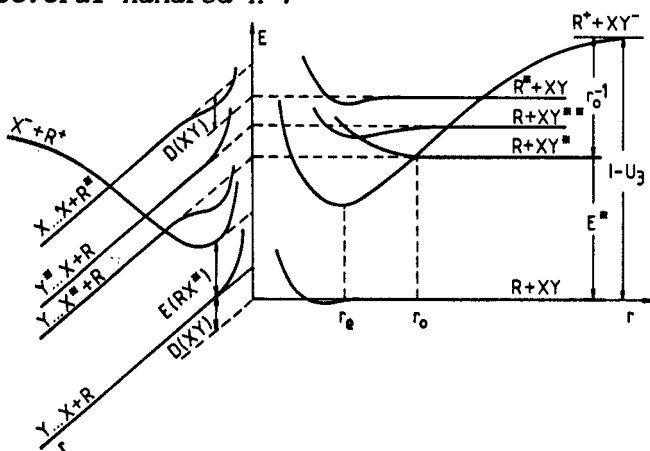

Fig. 2. Energy diagram describing the excited products formation via harpooning and charge transfer displacement reactions.

Rare gas atoms are easily excited by electron impact but it is not the case for photon excitation. To produce active laser media it was suggested [5] to use charge transfer reactions between normal rare gas atoms and excited molecules which can effectively be excited by radiation from thermal sources due to their broad-band absorption.

As seen from Fig. 2 the internuclear distance r_o, where the ion term crosses the neutral reagent term, does not depend on the fact which of the initial reagents is excited to the given energy level. And under sufficiently effective coupling between the terms one can expect that the reactions of the excited molecules with normal rare gas atoms may result in the same products and with similar cross-sections as the reactions of excited atoms.

Actually, the first measurements of the cross-section performed in [6] for process

$$Br_2^* + Xe \Rightarrow XeBr^* + Br$$
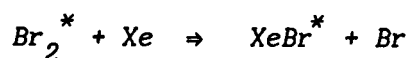
showed that its value may reach ~100 $\mathring{A}^2$. Later on some other reactions of excited halogen and interhalogen molecules with rare gas atoms were investigated, and in all the cases the reaction cross-sections were measured to be higher than those for hard-sphere collisions.

Table 1 shows the expected spectral thresholds for onset of some charge transfer reactions of excited halogen-containing molecules with rare gas atoms and the expected cross-sections of the reactions which correspond to these excitation thresholds. It is easily seen that the thresholds for formation of excited products lie in the spectral regions accessible to the excitation by the open discharge and a shock wave. The experimental values of spectral thresholds (in parenthesis) for reactions I_2 with Xe and Cl_2 with Ar were obtained correspondingly in [7]and [8]. As was pointed in [8], the fact that the observed spectral thresholds for these reactions coincide with the expected one, which equals to the sum of excimer energy and of dissociation energy of the molecular reactant, indicates that there is no barrier to the reactions of excited halogens with rare gas atoms. In the most cases the threshold cross-sections for expected reactions considerably exceed the gas-kinetic ones. The cross-sections should increase with the excitation energy.

Table 1.

Reaction product	XeF			XeCl			XeBr		
Molecular reagent	NF_2	ClF	F_2O	Cl_2	ICl	ClF	Br_2	IBr	HBr
λ^*_{thr}, nm	202	218	258	187	206	193	200	204	152
σ^{**}_{thr}, $Å^2$	250	–	–	65	55	–	65	110	170

Reaction product	XeI			KrF		
Molecular reagent	I_2	ICl	IBr	NF_2	ClF	F_2O
λ^*_{thr}, nm	193 (195)	177	185	157	167	190
σ^{**}_{thr}, $Å^2$	65	110	170	65	–	–

Reaction product	KrCl			KrBr			ArCl
Molecular reagent	Cl_2	ICl	ClF	CBr_4	Br_2	IBr	Cl_2
λ^*_{thr}, nm	146	158	151	150	154	166	129 (128.5)
σ^{**}_{thr}, $Å^2$	65	55	–	50	55	45	15

$^*\ \lambda_{thr} = hc[E(RX^*) + D(XY)]^{-1}$;

$^{**}\sigma_{thr} = \pi r_o^2$, where $r_o = e^2[IP(R) - EA(XY) - hc/\lambda_{thr}]^{-1}$,

$IP(R)$ - ionization potential of rare gas atoms;

$EA(XY)$ - energy of molecule affinity for electron.

It was proposed by Zimmerer and coworkers [8] to call the reactions between excited chlorine and noble-gas atoms as "displacement reactions", reasoning from the fact that R^+ ion replaces the excited ion Cl^{+**}, to which the Cl_2 excited state correlates. Although the charge transfer from the neutral atom R to Cl ion takes place in this case like in the harpooning reactions.

One of the most important parameters of these reactions which determines the efficiency of photochemical lasers is the yield of the excited products. To get an answer to the question what yield values can one expect in this kind of reactions, the absolute quantum yields fluorescence for mixtures of Cl_2 molecules with different rare gases were measured [9,10].

Cl$_2$**

Ar

Cl$_2$*

ArCl*   Kr   KrCl*

Ar

Cl$_2^3$ Xe

XeCl*

Xe

Xe$_2$Cl*

175 nm   126 nm 137 nm   222 nm

258 nm   308 nm 490 nm

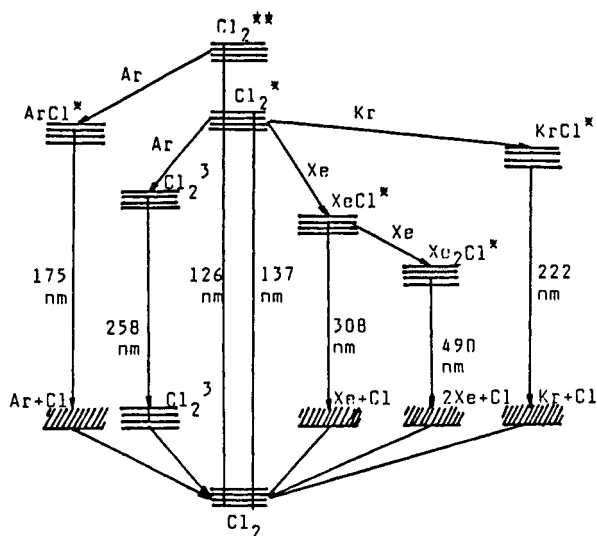Ar+Cl   Cl$_2^3$ Xe+Cl   2Xe+Cl Kr+Cl

Cl$_2$

Fig. 3.
Kinetic scheme of photochemical
processes in the mixture of Cl$_2$
with rare gases.

Figure 3 shows the variety and quantum yields of formation of excited products that can be produced in charge transfer processes under direct optical excitation of Cl$_2$ molecules. Formation of certain excited states depends on the composition and pressure of the buffer gas. But there is an additional possibility to control the secondary reactions by excitation wavelength.

Under excitation of a mixture containing xenon of 0.1 atm pressure at a wavelength of 137 nm, XeCl is effectively produced. The fluorescence quantum yield reaches 0.77. When xenon pressure is raised up to 1 atm all XeCl is bound into Xe$_2$Cl, the fluorescence quantum yield being 0.7. KrCl is formed in the mixtures containing Kr as the buffer gas and the quantum yield is 0.7, too.

When argon is used as a buffer gas the processes depend on the excitation wavelength. When excitation takes place at λ = 137 nm, a singlet-triplet relaxation of molecular Cl$_2$ is observed into the state emitting at λ = 258 nm. Under shorter wavelength excitation ArCl formation has been observed [8]. The measured rate constants of the investigated reactions correspond to cross-sections exceeding considerably the gas-kinetic ones and indicate the charge transfer origin of these reactions [9]. The idea of utilizing charge transfer displacement reactions to achieve laser action was first materialized in KrCl* [11] and Xe$_2$Cl* [12].

The obtained results - near to unity yield of excimers and high cross sections of their production - are of principle, since they demonstrate that charge transfer displacement reactions may play an important role in laser physics and herald a new trend in search of active media for visible and UV lasers.

There is a variety of other charge transfer photoprocesses which can produce electronically excited states. Some of them are given in Fig. 4, which illustrates the processes that take place under optical excitation of
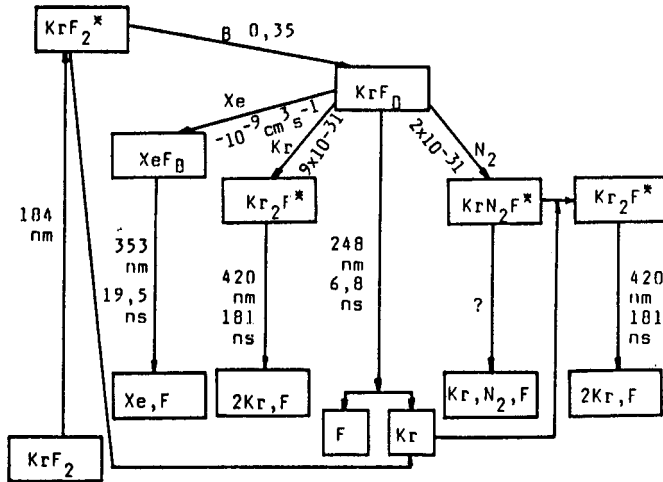

Fig.4. Kinetic scheme of photochemical processes in the mixtures of KrF_2 with "inert" gases.

the mixtures of KrF_2 with Xe, Kr and N_2. Short-wavelength absorption of KrF_2 results in the formation of excimers KrF in B-state. Utilization of KrF(B) in the secondary processes is different and depends on the composition and pressure of the mixture components. In more detail the results are presented in [13]. It is important to point out the fact that under irradiation of KrF_2 and N_2 mixtures new KrN_2F excimers are formed which have not been observed earlier. The existence of the excimer is confirmed by the presence of stable N_2Kr^+ ion observed experimentally elsewhere [14], which may form ionic bond to the negative F^- ion.

The discovery of a new excimer indicates the fact that the class of laser-active excimers can be extended by including excimers of a more complex structure. Actually, later on in [15], COKrF* excimer was discovered emitting in

the region of 280 to 380 nm with a maximum at 330 nm under optical excitation of KrF_2 + He + CO mixture.

SUMMARY

Practical significance of photochemical charge transfer processes is illustrated in Table 2. The table summarizes the molecules, lasing wavelengths and output energy in Joules which have been obtained with photochemical excitation. Some of the circumstances should be noted. The first: photochemical pumping has almost equal capability to produce laser action in different spectral regions. By now photochemical lasers are studied to a different extent. The most highly developed lasers in scientific and technical aspects are XeF at (C-A) and (B-X) transitions, as well as mercury halide and I_2-lasers.

Table 2.

Active molecule	Xe_2Cl	HgCl	HgBr	HgI	IF
Lasing λ, nm	520	558	554	443	491
Output energy, J	-	2.1	3	1	0.1
References	[12]	[16]	[17]	[16]	[18,19]
Active molecule	XeF_{C-A}	Kr_2F	XeF_{B-X}	I_2	KrCl
Lasing λ, nm	485	450	351	342	223
Output energy, J	150	-	1000	27	-
References	[20,21]	[22]	[20,21,23]	[24]	[11]

It is also important to note the record-breaking value of the energy (150 J) in the visible region. Up to now it has been impossible to reach hundreds of Joules of the energy of the coherent radiation in this region with other methods of exciting gases. In some cases photochemical pumping allows one to obtain significantly higher specific output energy, e.g. by one order of magnitude for mercury bromide as compared with electron impact pumping.

The above mentioned circumstances, along with the possibility to enhance the emitted radiation in proportion to the active volume, as well as simplicity and low cost of photochemical lasers show that photochemical pumping may be of great practical importance.

REFERENCES

1. *B.L.Borovich, V.S.Zuev, V.A.Katulin, L.D.Mikheev, F.A.Nikolaev, O.Yu.Nosach and V.B.Rozanov: High-current radiating discharges and optically pumped gas lasers (Radio Engineering Series) (in Russian), VINITI, Moscow, (1978).*

2. *V.S.Zuev: "Photodissociation laser with shock and thermal waves pumping". Preprint #161 (in Russian), P.N.Lebedev Phys. Inst. of the USSR Academy of Sciences, Moscow, 1990.*

3. *V.S.Zuev, L.D.Mikheev: "Photodynamical lasers", in "Laser Science and Technology", v.11, Harwood Academic GmbH, 1991.*

4. *Excimer Lasers, ed. by Ch.K.Rhodes, Springer Verlag, Berlin-Heidelberg, (1984).*

5. *L.D.Mikheev: Preprint #296 (in Russian), P.N.Lebedev Phys. Inst. of the USSR Academy of Sciences, Moscow, 1983.*

6. *D.J.Ehrlich, R.M.Osgood Jr.: J. Chem. Phys., 1980, **73**, p.3038.*

7. *N.K.Bibinov, I.P.Vinogradov, L.D.Mikheev: Kvantovaya Elektron. (Moscow), **10**, 794 (1983) [Sov. J. Quantum Electron. **13**, 516 (1983)].*

8. *T.Moller, B.Jordan, G.Zimmerer, D.Haaks, J.LeCalve, M.-C.Castex: Z. Phys. D - Atoms, Molecules and Clusters, **4**, 73 (1986).*

9. *V.S.Zuev, A.V.Kanaev, L.D.Mikheev: Kvantovaya Elektron. (Moscow), **11**, 354 (1984) [Sov. J. Quantum Electron. **14**, 242 (1984)].*

10. *V.S.Zuev, A.V.Kanaev, L.D.Mikheev: Kvantovaya Elektron. (Moscow), **14**, 1397 (1987) [Sov. J. Quantum Electron. **17**, 884 (1987)].*

11. *N.G.Basov, V.S.Zuev, A.V.Kanaev, L.D.Mikheev: Kvantovaya Elektron. (Moscow), **12**, 2197 (1985) [Sov. J. Quantum Electron. **15**, 1449 (1985)].*

12. *N.G.Basov, V.S.Zuev, A.V.Kanaev, L.D.Mikheev: Kvantovaya Elektron. (Moscow), **12**, 1954 (1985) [Sov. J. Quantum Electron. **15**, 1289 (1985)].*

13. *V.S.Zuev, A.V.Kanaev, L.D.Mikheev, D.B.Stavrovskii: Kvantovaya Elektron. (Moscow), **7**, 1562 (1980), **8**, 2183 (1981) [Sov. J. Quantum Electron. **10**, 898 (1980), **11**, 1330 (1981)].*

14. *T.H.Miller, J.H.Ling, R.P.Saxon, J.T.Moseley: Phys. Rev. A, **13**, 2171 (1976).*

15. *N.K.Bibinov, I.P.Vinogradov: Opt. Spektrosk. (USSR), **57**, 729 (1984).*

16. *S.P.Bazhulin, N.G.Basov, S.N.Bugrimov, V.S.Zuev, A.S.Kamrukov, G.N.Kashnikov, N.P.Kozlov, P.A.Ovchinnikov, A.G.Opekan, V.K.Orlov, Yu.S.Protasov: Kvantovaya Elektron. (Moscow), 13, 1017 (1986) [Sov. J. Quantum Electron. 16, 663 (1986)].*

17. *S.P.Bazhulin, N.G.Basov, S.N.Bugrimov, V.S.Zuev, A.S.Kamrukov, N.P.Kozlov, A.G.Opekan, Yu.S.Protasov: ZhTF Pis. Red., 12, 1423 (1986).*

18. *N.G.Basov, V.S.Zuev, L.D.Mikheev, V.I.Yalovoi: Kvantovaya Elektron. (Moscow), 9, 1064 (1982) [Sov. J. Quantum Electron. 12, 674 (1982)].*

19. *L.D.Mikheev: Izv. Akad. Nauk. SSSR, Ser. Fiz., 51, 1377 (1987).*

20. *V.S.Zuev, L.D.Mikheev, D.B.Stavrovskii: Kvantovaya Elektron. (Moscow), 11, 1750 (1984) [Sov. J. Quantum Electron. 14, 1174 (1984)].*

21. *S.B.Mamaev: Design and study of photodissociative XeF-laser emitting in visible and UV regions under pumping by radiation from surface discharge. Ph. D. Thesis (in Russian). Astrophysics, FIAN, Moscow, 1990.*

22. *N.G.Basov, V.S.Zuev, A.V.Kanaev, L.D.Mikheev, D.B.Stavrovskii: Kvantovaya Elektron. (Moscow), 7, 2660 (1980) [Sov. J. Quantum Electron. 10, 1561 (1980)].*

23. *S.V.Anisimov, E.M.Zemskov, V.S.Zuev, V.M.Kazanskii, G.N.Kashnikov, L.D.Mikheev, R.O.Nesterov, V.V.Sokolov, D.B.Stavrovskii, V.I.Cheremiskin: "Spectrally selective dynamic actinometry of the VUV irradiation from a moving gas dynamic discontinuity". Preprint #140 (in Russian), P.N.Lebedev Phys. Inst. of the USSR Academy of Sciences, Moscow, 1989.*

24. *V.S.Zuev, L.D.Mikheev, A.P.Shirokikh: Kvantovaya Elektron. (Moscow), 9, 573 (1982) [Sov. J. Quantum Electron. 12, 342 (1982)].*