Lasing Mechanism of the Discharge-Pumped KrF Laser and Experimental Relations between Output Powers and Gas Concentrations

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Using a home-made Blumlein-type laser apparatus provided with a simple preionization device, output powers of the 248 nm KrF laser were measured for various mixture of F2/Kr/He at several total pressures ranging from 500 Torr to 2.65 atm. From the detailed investigation of the relation between the laser power and the mixing ratios of F2/Kr/He, three rules are deduced. To give theoretical basis for these rules computer simulation are carried out for a mixture experimentally found optimal at 2.65 atm. Forty-four processes were taken into account, and eleven simultaneous differential equations are solved numerically. By varying nine parameters the observed laser pulse shape and delay time are well reproduced. Independent simulations for several different mixtures at a total pressure in the range 2.45-2.87 atm reproduced the three rules. Temporal behaviours of the electron temperature, concentrations of the electron and transient species, and the laser gain are analysed, and a reasonable lasing mechanism is deduced.

1. Introduction

Since the prediction of potentially efficient laser action in rare-gas halides was given in 1975\(^1,2\), laser action in KrF has subsequently been achieved by direct electron-beam\(^3\) and fast-discharge excitation\(^4\). The former type excitation uses Ar as a carrier gas, while the latter prefers He to Ar, because the more uniform discharge is obtainable with He. Although NF\(_3\)\(^5,6,8\), N\(_2\)F\(_4\)\(^5,8\) or SF\(_6\)\(^6,8\) was found to be useful as a F donor for the KrF laser, most efficient laser actions were obtained in He/Kr/F\(_2\) mixtures at high pressures (1.33-6 atm) using a special device for UV preionization\(^7-9\). Dominant formation and quenching processes of KrF excimers in Ar/Kr/F\(_2\) mixtures were discussed in several reports\(^10-19\), and summarized by Rokni et al.\(^14\). Lacina et al.\(^15\) also published a report on a theoretical analysis of an electron-beam excited KrF laser. However, for the discharge-pumped KrF laser no report on theoretical studies accompanied by the computer simulation has been published before the very recent work by Greene and Brau\(^16\). They studied theoretically UV-preionized transverse dis-
charge KrF and ArF lasers based on the experimental data given by Sze and Loree\textsuperscript{17)}, who used a mixture of 0.2% F\textsubscript{2}/1% Ne/5% Kr in He. For only this mixture laser output energies were studied as a function of pressure, and theoretical values are compared with experimental ones.

Here, we present results of our experiments and simulations for various constituent mixtures of F\textsubscript{2}/Kr/He. The relations experimentally found between output powers and gas concentrations were reproduced by simulations using a simplified model in which forty-four processes in gas kinetics were taken into account. Absorption losses were also considered\textsuperscript{18)-22)} for several absorbers which are supposed to reduce the laser light over the whole lasing region, although discrete absorptions\textsuperscript{23), 24)} were disregarded this time.

2. Experimental Method

Experimental studies were carried out using a homemade Blumlein-type laser apparatus similar to that described previously\textsuperscript{25}); the storage capacitor was made from a copper-clad, fiberglass-epoxy-laminated circuit board 0.8 mm thick. Both wings of the Blumlein circuit have the same size (90×42 cm\textsuperscript{2}), and the capacitance was estimated to be 18.8 nF. Fig. 1 shows a cross-sectional view of the laser tube, which was designed to be durable for high pressures up to 3 atm. A cylinder tube (46 mm inner diameter) made of Lucite, and aluminium electrodes were used. Two tungsten wires, W, were provided for preionization each of which spanned two holders, P, without any supporter. The two wires were placed symmetrically above and below the anode maintaining a distance between the wire, W, and the anode, A, at approximately 8 mm, which was found to be the best distance among 3, 5, 8 and 10 mm for obtaining efficient laser action. To avoid contamination from the inside walls of the discharge tube all parts were carefully cleaned and constructed to make a discharge volume=1×1.5×90=135 cm\textsuperscript{3}. The cavity was constructed between the fixed CaF\textsubscript{2} coupler and the multilayer dielectric coated reflector (99% reflectivity); the cavity length was 103 cm. The laser output was measured at a voltage fixed at 20 kV.

A gas handling system consisted of stainless-steel cylinders and valves, copper pipes and brass pressure gauges, was constructed. Several times passivation with increasing F\textsubscript{2} density in He were necessary before introducing F\textsubscript{2} into the mixing system.

The laser output energy was measured with a Molectron joulemeter (model J3-05) through fine mesh screen attenuators and the measured output energies were compared with a Gentec joulemeter (model ED-200). The laser output pulse shape was observed by a biplaner phototube (R617, Hamamatsu TV, Inc.) and a 350 or 400 MHz oscilloscope (485 or 7834, Sony/Tektronix Corporation). The current pulse shape was detected by the voltage difference between both ends of the resistor R, shown in Fig. 1, which was made of 174 film-coated resistors (resistance: 0.3 Ω) in parallel connection to produce a total resistance of 0.00172 Ω. In order to observe the time relation between current and laser output pulse shapes both of these signals were simultaneously displayed on a 400 MHz storage...
oscilloscope and the delay time of the latter from the former was determined considering all the delaying factors such as the propagation time of light in air, the signal delay in 50Ω coaxial cables, and the response time of the detector.

3. Experimental results

3.1 Relation between output energies and gas concentrations

Varying the mixing ratio in the range of F₂:Kr=1:(1.25-16.4) and the partial pressures of F₂ and Kr in the range of (1.4-15) and (4.7-122) Torr, respectively, the laser output energies were measured at several total pressures in the range, 400 Torr-2.72 atm. The mixing ratio of F₂:Kr=1:7.14 was chosen for the following experiments, because stable and efficient laser actions were always obtained at any pressures between 500 Torr and 2.72 atm. In Fig. 2 variation of the output energy vs. partial pressures of F₂ and Kr is shown for each of the total pressures, 500 Torr, 1, 1.25, 1.85 and 2.65 atm. Fig. 2 shows the existence of an optimal gas concentration ratio for obtaining the maximum energy at a certain total pressure, as far as the mixing ratio of F₂ and Kr is fixed (rule I).

From Fig. 2 the optimal gas concentrations of He, Kr and F₂ can easily be determined for each of the total pressures, 500 Torr, 1, 1.25, 1.85 and 2.65 atm. These optimal condition are labelled a, b, c, d and e in Table I, where the third, fourth and fifth columns show partial pressures (in Torr) of He, Kr and F₂, together with errors arisen from the gas mixing system. Since in discussion on the lasing mechanism the absolute partial concentration is preferable to the partial pressure, the latter value is converted to the former using the conversion factor, 1 Torr=3.21×10¹⁶ cm⁻³ at 300K, and listed in the last three columns of Table I. Output energies corresponding to gas concentrations shown in Table I are plotted in Fig. 3, where P_H, P_K and P_F are partial pressures, and [He], [Kr] and [F₂] are concentrations of He, Kr, and F₂, respectively. Against the He concentration represented by the ab-

Table I. The Optimal gas concentrations of Kr, F₂ and He under fixed ratio of F₂:Kr=1:7.14

<table>
<thead>
<tr>
<th>Total pressure</th>
<th>Partial pressure in Torr</th>
<th>Concentration in cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>Kr</td>
</tr>
<tr>
<td>a 500 Torr</td>
<td>443±13 (89%)</td>
<td>50.0±3.1</td>
</tr>
<tr>
<td>b 1 atm</td>
<td>720±12 (94.7%)</td>
<td>35.8±3.5</td>
</tr>
<tr>
<td>c 1.25 atm</td>
<td>911±30 (96.7%)</td>
<td>33.9±4.4</td>
</tr>
<tr>
<td>d 1.85 atm</td>
<td>1376±29 (97.6%)</td>
<td>26.1±2.6</td>
</tr>
<tr>
<td>e 2.65 atm</td>
<td>1994±20 (99.0%)</td>
<td>18.0±1.8</td>
</tr>
</tbody>
</table>

*: Gas condition.

Each of gas conditions, a, b, c, d and e, was taken from the maximum point on each curve in Fig. 2, which corresponds to a fixed total pressure written in the second column.

1) Errors arisen from the mixing technique.
2) Concentrations at 300 K.
The output energy vs. [He], [Kr], and [F2] for [F2] : [Kr] = 1 : 7.14; a, b, c, d, and e gas conditions are the same as those in Table I. This figure shows that the output energy increases along with the increase of [He], although [F2] and [Kr] should be remarkably reduced (rule II).

Fig. 3. Output energy vs. [He], [Kr] and [F2] for [F2] : [Kr] = 1 : 7.14; a, b, c, d and e gas conditions are the same as those in Table I. The optimum concentrations of F2 and Kr are shown by × marks and output energies and over-all efficiencies are plotted by ○ marks using units of mJ and %, respectively. This figure shows that the output energy increases along with the increase of the He concentration although the concentrations of F2 and Kr should be remarkably reduced (rule II). Since this fact contradicts our simple deduction that the more concentration of F2 and Kr should be effective for obtaining the more powerful excimer laser, the computer simulation on the lasing mechanism was carried out.

Fixing the He pressure at 1376 Torr (4.41 × 10^19 cm⁻³) and the F2 pressure at 3.4 Torr (1.17 × 10^17 cm⁻³), variation of output energy vs. Kr partial pressure was observed, and the result is shown by ○ marks in Fig. 4, where the maximum output energy, 34 mJ, was normalized to one. The data plotted by × are the results obtained by Rothe et al., who obtained the maximum output energy of 300 mJ, which is normalized to one for comparison’s sake with our data. The results of the two different experiments show that under fixed concentrations of F2 and He the output energy increases with the increasing Kr concentration and tends to saturate (rule III).

3.2 Observation of the laser output-and the discharge current-pulse shapes

Using the same mixtures as shown in Table I, the pulse shapes of the laser output and the discharge current were observed. The measured half widths of laser pulses were averaged and shown in Fig. 5 by ○ marks and the lengths of the bars connected to ○’s represent the ranges of errors for the pulse width measurements. In Fig. 5, except for the middle data corresponding to the He pressure around 1140 Torr, all the other data were taken under the conditions represented by a, b, c, d, and e in Table I. According to this figure the pulse width does not change remarkably against the He concentration; the

Fig. 4. Variation of output energy vs. [Kr]. when [He] and [F2] are fixed. × : present work, ○ : Rothe et al. The output energy increases along with the increase of [Kr] and tends to saturate (rule III).

Fig. 5. Half widths of laser output pulses vs. gas concentrations; abscissa represent [He] and the ratio [F2] to [Kr] is fixed at 1 : 7.14. Gas conditions represented by a, b, c, d and e are shown in Table I.
half width of the output pulse increased from 20 to 24 ns when conditions changed from a to e.

The time relation between the discharge current and the laser output pulses was measured for the same gas mixtures as shown in Table I, and the results for the e mixture is shown in Fig. 6. The value of the peak current and the pulse width of the current did not change appreciably from a to e; the former was 4.8±0.7×10⁴ A and the latter 13±2.5 ns. By means of the time integration of the measured currents, the number of electrons supplied into the main discharge was estimated at 3.9±0.6×10¹⁵. From Fig. 6 output pulses were found to delay by 13±2.5 ns from the current peak, B. In the case of the N₂ laser, the laser pulse rises without so much delay that it almost completely decays before the current pulse reaches its peak, B. Therefore, the observed evidence for a fairly long time (~13 ns) delay for the KrF excimer should be explained by the lasing mechanism.

4. Lasing mechanism

4.1 Preliminary considerations

Before having performed computer simulations to lasing mechanisms all conceivable gas and electron kinetics were considered in the search for a model as reliable yet as simple as possible.

4.1.1 Possible processes to produce KrF excimers

The potential curves of the KrF excimer are shown in Fig. 7, where electronic states are labelled in conventional way, i.e. X²Σ, A²Π etc., as well as the corresponding designation in parentheses given by Dunning and Hay, who obtained these low-lying potential curves by means of the ab intio calculation. The intense laser emission at 2484 Å arises from the charge transfer transition between the lowest stable ionic and the unstable ground states, i.e. B²Σ→X²Σ. Since the dissociation limit of B²Σ, i.e. Kr⁺(⁴P³/₂)+F⁻, is higher than that of E²Σ, i.e. Kr⁺(⁴S)+F, the potential curves of B and E states should cross each other at a certain internuclear distance, at least in the zeroth approximation. Therefore, the reactions, Kr⁺(⁴P₃/₂)+F⁻ and Kr⁺(⁴S)+F, should play an important role for producing the upper state of the laser transition (B²Σ).

4.1.2 Considerations of gas kinetics, absorption losses and electron kinetics in the He/Kr/F₂ mixture

a) Gas kinetics The observed temporal relation between the output and the current pulses shows that the delay time of the KrF laser pulse amounts to 13 ns (Fig. 6). This fact suggests that the laser emission occurs in an afterglow of the discharge, which is initiated by the following processes due to direct electron impacts:

\[
\begin{align*}
  e+\text{He} &\rightarrow \text{He}^++e+e, & \text{(D1)} \\
  e+\text{He} &\rightarrow \text{He}^++e, & \text{(D2)} \\
  e+\text{Kr} &\rightarrow \text{Kr}^++e+e, & \text{(D3)} \\
  e+\text{Kr} &\rightarrow \text{Kr}^++e. & \text{(D4)}
\end{align*}
\]

This afterglow must be alike to that of pure...
Table II. Summary of considered processes and their rate coefficients for transient species which are possibly produced in discharge pumped He/Kr/F₂ mixtures.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Units</th>
<th>Ref.</th>
<th>Dest. frequency (S⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>He⁺</strong></td>
<td><strong>He⁺+2He</strong> → <strong>He⁺+He</strong></td>
<td>R 1</td>
<td>(\eta) ((6.5±0.5) \times 10^{-32})</td>
<td>b</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td><strong>He⁺+2e</strong> → <strong>He⁺+e</strong></td>
<td>R 2</td>
<td>(k_{e1}(6±2) \times 10^{-20})</td>
<td>b</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>production of **He²⁺ (2Σ))</td>
<td>R 3</td>
<td>(k_{31a3}(k_{31}=1.0))</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td><strong>He²⁺</strong></td>
<td><strong>He²⁺+e</strong> → [**He²⁺]+hν</td>
<td>R 4</td>
<td>(\alpha_{e2} \leq 5 \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td><strong>He²⁺+e+He</strong> → [**He²⁺]+He</td>
<td>R 5</td>
<td>(k_{e2}(5±1) \times 10^{-27})</td>
<td>b</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td><strong>He²⁺+2e</strong> → [**He²⁺]+e</td>
<td>R 6</td>
<td>(k_{e2}(4.0±0.5) \times 10^{-30})</td>
<td>b</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>production of **He⁰ (2Σ))</td>
<td>R 7</td>
<td>(k_{31a3}(k_{31}=0.70±0.05))</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>production of **He²⁺ (2Σ))</td>
<td>R 8</td>
<td>(k_{32a3}(0&lt;k_{32}&lt;0.2))</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td><strong>He⁰</strong></td>
<td><strong>He⁰+Kr</strong> → <strong>Kr⁺+He+e</strong></td>
<td>R 9</td>
<td>(k_{F}^{Kr}(2.2±0.5) \times 10^{-10})</td>
<td>a</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰+Kr+He</strong> → <strong>Kr⁺+2He+e</strong></td>
<td>R 10</td>
<td>(k_{F}^{Kr}(8.6±0.5) \times 10^{-30})</td>
<td>b</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰+F₂</strong> → F⁺+F⁺+He</td>
<td>R 11</td>
<td>(k_{F}^{F}(1.7±0.5) \times 10^{-10})</td>
<td>a</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰+F₂+He</strong> → F⁺+F⁺+2He</td>
<td>R 12</td>
<td>(k_{F}^{F}(8.2±0.5) \times 10^{-30})</td>
<td>b</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰+He⁻</strong> → <strong>He⁺+He⁻+e</strong></td>
<td>R 13</td>
<td>(\delta(1.9±0.4) \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰+He⁰</strong> → <strong>He⁺+He⁺+e</strong></td>
<td>R 14</td>
<td>(\beta_{11}(1.5±0.3) \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>→ <strong>He⁻+e</strong></td>
<td>(x_1=0.3±0.05)</td>
<td>a</td>
<td>27</td>
<td>(\beta_{11}(1–x_1))</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰+He⁰</strong> → <strong>He⁺+2He⁻+e</strong></td>
<td>R 16</td>
<td>(\beta_{12}(2.5±1.5) \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>→ <strong>He⁺+He⁺+e</strong></td>
<td>(0&lt;x_2&lt;0.3)</td>
<td>a</td>
<td>27</td>
<td>(\beta_{12}(1–x_2))</td>
</tr>
<tr>
<td></td>
<td><strong>He⁺+He⁺</strong></td>
<td>R 17</td>
<td>(\gamma_1(4.2±0.6) \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td><strong>He⁰⁺</strong></td>
<td><strong>He⁰⁺+Kr</strong> → <strong>Kr⁺+2He+e</strong></td>
<td>R 19</td>
<td>(K_{F}^{Kr} \times 1.5 \times 10^{-10})</td>
<td>a</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰⁺+F₂</strong> → <strong>F⁺+2He+F</strong></td>
<td>R 20</td>
<td>(K_{F}^{F} \times 1.5 \times 10^{-10})</td>
<td>b</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰⁺+F₂</strong> → 2He+e</td>
<td>R 21</td>
<td>(\tau_3(3.8±0.4) \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td><strong>He⁰⁺+He⁰⁺</strong> → <strong>He⁺+3He⁻+e</strong></td>
<td>R 22</td>
<td>(\beta_{22}(1.5±0.5) \times 10^{-10})</td>
<td>a</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>→ <strong>He⁺+2He⁺+e</strong></td>
<td>(0&lt;x_2&lt;0.3)</td>
<td>a</td>
<td>27</td>
<td>(\beta_{22}(1–x_2))</td>
</tr>
<tr>
<td><strong>Kr⁺</strong></td>
<td><strong>Kr⁺+F⁻+He</strong> → <strong>Kr⁺+He</strong></td>
<td>R 24</td>
<td>(k_1(0.25, 0.38) \times 10^{-6}) #</td>
<td>a</td>
<td>29, 30</td>
</tr>
<tr>
<td></td>
<td><strong>Kr⁺+F⁺+Kr</strong> → <strong>Kr⁺+Kr</strong></td>
<td>R 25</td>
<td>(k_2(0.20, 0.14) \times 10^{-6}) #</td>
<td>a</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td><strong>Kr⁺+Kr⁺+He</strong> → <strong>Kr⁺+He</strong></td>
<td>R 26</td>
<td>(\eta_{He} 1.9 \times 10^{-31})</td>
<td>b</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td><strong>Kr⁺+Kr⁺+Kr</strong> → <strong>Kr⁺+Kr</strong></td>
<td>R 27</td>
<td>(\kappa_{Kr} (2.74±0.12) \times 10^{-31})</td>
<td>b</td>
<td>37</td>
</tr>
<tr>
<td><strong>Kr⁺⁺</strong></td>
<td><strong>Kr⁺⁺+F⁻+He</strong> → [<strong>Kr⁺⁺F⁺</strong>]+He</td>
<td>R 28</td>
<td>(k_3(0.29, 0.43) \times 10^{-6}) #</td>
<td>a</td>
<td>29, 30</td>
</tr>
<tr>
<td></td>
<td><strong>Kr⁺⁺+F⁺+Kr</strong> → [<strong>Kr⁺⁺F⁺</strong>]+Kr</td>
<td>R 29</td>
<td>(k_4(0.11, 0.08) \times 10^{-6}) #</td>
<td>a</td>
<td>30, 31</td>
</tr>
<tr>
<td><strong>KrF⁺</strong></td>
<td><strong>KrF⁺</strong> → <strong>KrF⁺+hν</strong></td>
<td>R 30</td>
<td>(1/\tau(\tau=6.5\text{ ns}))</td>
<td>c</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td><strong>KrF⁺+F₂</strong> → products</td>
<td>R 31</td>
<td>(q_1(7.8,5.7,4.8) \times 10^{-10})</td>
<td>a</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td><strong>KrF⁺+Kr⁺+Kr⁺</strong> → products</td>
<td>R 32</td>
<td>(q_2(6.7,2.9,7.9) \times 10^{-10})</td>
<td>b</td>
<td>11, 34</td>
</tr>
<tr>
<td></td>
<td><strong>KrF⁺+Kr</strong> → products</td>
<td>R 33</td>
<td>(&lt;1.6,8.6\times 10^{-12})</td>
<td>b</td>
<td>33, 34</td>
</tr>
<tr>
<td></td>
<td><strong>KrF⁺+2He</strong> → products</td>
<td>R 34</td>
<td>(&lt;10^{-33}, 5 \times 10^{-23})</td>
<td>b</td>
<td>41, 46</td>
</tr>
<tr>
<td></td>
<td><strong>Kr⁺</strong></td>
<td><strong>Kr⁺+F₂</strong> → <strong>KrF⁺+F</strong></td>
<td>R 35</td>
<td>(k_5 0.72±0.09)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td><strong>F⁻</strong></td>
<td><strong>F⁻+F₂</strong> → <strong>F⁻+F</strong></td>
<td>R 36</td>
<td>(k_{F⁻}^F 8 \times 10^{-6}) (th.)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
helium, because the mixed gas optimal for laser operations at higher pressures has less concentrations of F2 and Kr (cf. rule II). Therefore, dominant reactions in pure helium afterglow investigated by Deloche et al.27), i.e. R1~R8, R13~R18 and R21~R23 shown in Table II, can be considered also dominant in the lasing medium, and the more energy deposited to the more concentrated helium should be efficiently transferred to the less concentrated F and Kr atoms which must be playing the most important role in lasing mechanism. Possible processes in the afterglow of the He/Kr/F2 mixture are summarized in Table II, where for each transient species, He+, He, He+, He+, Kr+, Kr+, KrF*, Kr* and F-, destruction processes are listed, while for F- the listed process is productive. Other processes neglected in our simulation are shown in Table III.

Notations and values of reaction coefficients and destruction frequencies are listed in the third and sixth columns of Table II. Deloche's notations27) are used for rate coefficients of reactions in the pure He afterglow, and ours are used for the other coefficients. The electron-ion recombination rate coefficients, α1 and α2 in Table II, were calculated using the following formulae given by Deloche et al.27).

\[
\alpha_1 = k_{e1} \left( \frac{T_e}{T_g} \right)^{-\nu_1} n_e \quad \text{(Eq. 1)}
\]

\[
\alpha_2 = (\alpha_{e2} + k_{e2}[\text{He}]) \left( \frac{T_e}{T_g} \right)^{-\nu_2} + k_{e2} n_e \left( \frac{T_e}{T_g} \right)^{-\nu_1}
\quad \text{(Eq. 2)}
\]

where \( k_{e1}, \alpha_{e2}, k_{e2} \) and \( k_{e2} \) are rate constants of R2, R4, R5 and R6, respectively, \( n_e \) and \( T_e \) are the electron concentration and temperature, and \( T_g \) is the gas temperature. The values of \( \nu_1, \nu_2, k_{e2}, k_{e2} \) and \( \nu_1 \) were determined by Deloche et al. based on experimental data for the pressure range 5~100 Torr were used in our calculation. \( k_{e1} \) is the rate coefficient of dissociative electron attachment reaction and its theoretical formula27) as a function of electron temperature was used up to 3.5 eV in our simulation. Concerning rate coefficients of reactions R11, R12, R19, R20, R24, R25, R28 and R29, observed values have not been reported. Therefore, the values for ion-ion recombination reactions R24, R25, R28 and R29 were obtained for each of the He concentrations 4.4×1019 and 6.4×1019 cm\(^{-3}\) by using Natanson's formula generalized by Flannery29)~31). As substitutes for the rate coefficients of reactions R19, R11, R12 and R20, the quenching coefficients of reactions He+Ar, He++O2, He+O2+He and He2+Na are given in Table II for reference's sake.

The observed rate coefficient of reaction N1 was found to be negligible compared to that of reaction R27). Non-resonant charge transfer reaction N2 was neglected based on the estimated destruction rates of He\(^m\) due to R1 and N2, 2.7×10\(^8\) and <5.8×10\(^6\) s\(^{-1}\), respectively. These values were obtained for the mixture, by using the rate coefficient for the reaction between Ne\(^+\) and Kr, 10\(^{-11}\) cm\(^3\)/s at 300K. Because of the measured branching ratio, N4 : R9 = 0.114 : 0.88446), reaction N4 was disregarded. Since the products of N7 reaction go back to Kr\(^+\) and Kr\(^+_2\) through reactions N8 and N9, of which cross-sections are so large as 470 and 15×10\(^{-16}\) cm\(^2\), respectively, these cyclic reactions were disregarded. All other reaction in Table III were assumed to be neglected because their rate coefficients can not be estimated.
Table IV. Photoabsorption cross section of transient species which can absorb the light near 249 nm

<table>
<thead>
<tr>
<th>Photoabsorption process</th>
<th>$\lambda_{\text{abs}}$ (Å)</th>
<th>$\lambda_{\text{max}}$ (Å)</th>
<th>$\sigma$ (cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F^+ (X^1\Sigma^+) + h\nu \rightarrow F^+ (A^3\Pi_u)$</td>
<td>A 1</td>
<td>2100–5000</td>
<td>2845</td>
<td>6.6 x 10^{-21}</td>
</tr>
<tr>
<td>$F^+ (S^3\Sigma^+) + F^+ (\Pi_{\nu, \pi}, \nu_{\pi}) \rightarrow F^+ (S^3\Pi^+)$</td>
<td>A 2</td>
<td>$\lambda \leq 3595$</td>
<td>nearly flat</td>
<td>5.1 x 10^{-18}</td>
</tr>
<tr>
<td>$Kr^+<em>2 (X^3\Sigma_u^+) + F^+ (\Pi</em>{\nu, \pi}) \rightarrow Kr^+ (X^3\Pi_u) + F^+ (S^3\Pi^+)$</td>
<td>A 3</td>
<td>2480–5000*</td>
<td>3400</td>
<td>0.31 x 10^{-10}</td>
</tr>
<tr>
<td>$He(2s^23s^2) + F^+ (\Pi_{\nu, \pi}) \rightarrow He^+ (1s^23s^2) + F^+ (S^3\Pi^+)$</td>
<td>A 4</td>
<td>$\lambda \leq 2605$</td>
<td>2605</td>
<td>4.8 x 10^{-10}</td>
</tr>
<tr>
<td>$Kr(5s^2P_{o,2}) + F^+ (\Pi_{\nu, \pi}, \nu_{\pi}) \rightarrow Kr^+ (5P_{o,2}) + F^+ (S^3\Pi^+)$</td>
<td>A 5</td>
<td>$\lambda \leq 3031$</td>
<td>3031</td>
<td>1 x 10^{-20}</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$KrF(B^2\Sigma^+) + h\nu \rightarrow KrF(B^2\Sigma^+)$</td>
<td>NA 1</td>
<td>2480–2493 (discrete)</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>$HF(X^2\Sigma, \nu=13\sim16) \rightarrow HF(B^2\Sigma)$</td>
<td>NA 2</td>
<td>whole region (discrete)</td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>

I, II: Absorptions listed in I were taken into account, whereas those in II neglected.

* theoretical values.

b) Absorption losses Some of the transient species mentioned in the foregoing section which can absorb the laser light are summarized in Table IV, where $\sigma$ is the absorption cross section, $\lambda_{\text{abs}}$ and $\lambda_{\text{max}}$ stand for the wavelength region at which absorption was or can be observed, and the wavelength of the maximum absorption, respectively. Processes NA 1 and NA 2 are discrete absorptions, while all others are supposed to be continuous. NA 1 is the self-absorption of KrF which arises from the laser upper state ($B^2\Sigma^+$)$^{23}$, and following this process dissociation to Kr*$^+ (3P) + F^+ (2P)$ can easily occur. However, it is also possible that on the way of dissociation the recombination to KrF*$^+ (B^2\Sigma_u)$ would take place because of the crossing of the two potential curves which are correlated with Kr$^+ (3P) + F^+ (2P)$ and Kr$^+(5P_{o,2}) + F^+ (S^3\Pi)$ (cf. Fig. 7). It is difficult to quantitatively express this complicated process related to the self-absorption, of which cross section has not yet been measured. NA 2 is the absorption due to HF possibly existing in F$_2$ as an impurity. Because the effect of discrete absorption should be far less than that of continuous one, this time we neglected NA 1 and NA 2.

c) Electron kinetics In Table II there are some reactions involved electron kinetics. Since photon density in the cavity is high under lasing conditions, contributions of absorption to electron production must be considered. The table for production and destruction processes of electron in the He/Kr/F$_2$ mixture are easily obtained from processes listed Tables II and IV. In addition to electron kinetic processes in pure He, reactions R2, R4~R6, R14~R18, R22 and R23, production processes of R9, R10, A2, A4 and A5, and destruction processes of R36 had to be taken into account to determine the electron temperature. However, actually in this work reactions R9, R10, R36, A2, A4, and A5 were neglected in the estimation of the electron temperature. Namely, we used the differential equations for the electron temperature, equation (12) (cf. Table V), obtained by Deloche et al.\textsuperscript{27} The first and second terms represent cooling terms by elastic electron-neutral collisions, and by elastic electron-ion collisions, respectively. The other heating terms of electrons are due to collisions between electrons and metastable atoms, R18, super-elastic collisions between electrons and molecular metastables (R21), vibrational relaxation of molecular ions

$$He^+_2 (v, K) + 2e \rightarrow He^+_2 (v-1, K) + 2e + KE,$$

and metastable-metastable ionizations (R14~R17, R22 and R23).

4.2 Modeling

The theoretical model for a discharge-pumped laser requires a coupled analysis including plasma kinetics, laser output extraction and the external driving circuit, which consists of a preionizer and an L-C inversion circuit. In our model, the effects of the external circuit is treated simply by varying initial values of $n_e$, [He$^+$], [He$^{em}$], [Kr$^+$] and [Kr$^*$] as parameters, because our model is simplified based on the following assumptions:

(a) Excitation of the laser medium takes place quite instantaneously at the moment ($t$
Table V. System of coupled differential equations

\[
\begin{align*}
\frac{d[n_e^{He^+}]}{dt} &= 0 \quad \text{when the current peaks (cf. Fig. 6). Consequently, the lasing occurs in the afterglow of the instantaneous discharge.} \\

\text{b) The laser plasma always satisfies the following conditions:} \\
1) \text{Plasma is uniformly distributed between the anode and the cathode.} \\
2) \text{The charge density equals to zero in each elementary volume of the ionized gas, that is,} \\
\frac{d[n_e^{He^+}]}{dt} &= 0 \quad \text{(Eq. 1)} \\
3) \text{Because the pressures used mostly in these studies exceed one atmospheric pressure, diffusion losses of the transient species can be neglected in the time less than 100 ns.} \\
4) \text{The gas and ion temperatures, } T_g \text{ and } T_i, \text{ are assumed to be 300K because of the high gas concentration.} \\
5) \text{Because in the gas mixture } [F_2] \text{ and } [Kr] \text{ are very small, the differential equation for the electron temperature in the pure He afterglow\textsuperscript{27}, can be used.} \\
6) \text{The gain in the laser medium is assumed to be unsaturated.} \\
7) \text{The laser output extraction assumes the following condition:} \\
1) \text{The fractional part of the total spontaneous emission, which was emitted from KrF\textsuperscript{*} excimer to be amplified, is } \frac{\Omega}{4\pi}, \text{where } \Omega \text{ is taken to be the solid angle subtended by cross section 1.0 \times 1.5 \text{ cm}^2 \text{ at the end of the gain medium on the side of coupler viewed from the opposite end of the gain medium.} \\
2) \text{The laser medium which contributes to amplification of the light has the same shape as the discharge volume, i.e. 1.0 \times 1.5 \times 90 \text{ cm}^3.} \\
\text{Based on the above assumption, gas kinetics in Table II and photoabsorption in Table IV, simultaneous differential equations, (1)\textasciitilde(12) in Table V, were obtained. The equation for photon density, } n_p(t), \text{ can be represented by the equation (2)\textsuperscript{15},} \\
\frac{dn_p(t)}{dt} &= \frac{\Omega}{4\pi} \frac{1}{\tau} [KrF^*] + \frac{L_g}{L_e} c(g(t) - g_a) n_p(t), \quad \text{(Eq. 2)} \\
\text{and this should be coupled with the equations (3)\textasciitilde(12). In this equation terms arisen from spontaneous emission, amplification of this stimulated emission and losses due to output coupling and absorption are included. }\}
\end{align*}
\]
net gain coefficient in the laser medium (i.e., gain coefficient by absorption),
\[ g(t) = \sigma_0 [\text{KrF}^*] - \sum_A \sigma(A) [A], \quad (\text{Eq. 3}) \]
where the sum is over all absorbers (A's) in the laser medium,
\[ \sum_A \sigma(A) [A] = \sigma(F_2)[F_2] + \sigma(F^-)[F^-] + \sigma(\text{He}^m)[\text{He}^m] + \sigma(\text{Kr}^+)[\text{Kr}^+] + \sigma(\text{Kr}^*)[\text{Kr}^*], \quad (\text{Eq. 4}) \]
\( g_{th} \) represents the threshold loss coefficient**
\[ g_{th} = \frac{1}{2L_g} \ln \left( \frac{1}{R} \right), \quad (\text{Eq. 5}) \]
\( L_g \) and \( L_c \) are the length of the gain medium and optical cavity, respectively. Based on our assumption instantaneous output power extracted from the cavity through the coupler can be represented by
\[ p(t) = \frac{L_c}{L_g} \cdot \frac{1}{2L_g} \ln \left( \frac{1}{R} \right) h \nu V n_{op}(t), \quad (\text{Eq. 6}) \]
where \( V \) stands for discharge volume, 135 cm³, and \( h \nu \) is photon energy at 2484 Å.

4.3 Method of simulation

First, unknown or uncertain rate coefficients were divided into three groups, i.e. destruction rate coefficient of \( \text{He}^m \) by Kr, destruction rate coefficient of \( \text{He}^m \) by \( F_2 \), and collisional frequencies for quenching of \( \text{KrF}^* \) excimers by \( F_2 \), Kr and He, and are treated as parameters using the following \( R_1 \), \( R_2 \) and \( R_3 \):
\[ R_1 = k_{f1}^t + k_{f1}^p[\text{He}], \quad R_2 = k_{f2}^t + k_{f2}^p[\text{He}], \quad R_3 = k_{f3} \]
\( (\text{Eqs. 7, 8}) \)

Table VI. Unknown factors used as parameters in the lasing mechanism simulation: Possible lowest values for each of the parameters, and its range considered in the simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Possible lowest value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial conditions</td>
<td>[He⁺][o] ( 2.9 \times 10^{16} \sim 5.0 \times 10^{16} \text{ cm}^{-3} )</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>[He⁺][o] ( 1.0 \times 10^{16} \sim 3.0 \times 10^{16} \text{ cm}^{-3} )</td>
<td>1.2 \times 10^{16} \text{ cm}^{-3}</td>
</tr>
<tr>
<td></td>
<td>[Kr⁺][o] ( 2.0 \times 10^{16} \sim 1.5 \times 10^{16} \text{ cm}^{-3} )</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>[Kr⁺][o] ( 2.0 \times 10^{16} \sim 1.5 \times 10^{16} \text{ cm}^{-3} )</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>( T_{eo} ) ( 300 \sim 40617 \text{ K} )</td>
<td>300K</td>
</tr>
<tr>
<td>Destruction factors</td>
<td>( R_{1}^{(a)} ) (He⁺ by Kr) ( 2.0 \times 10^{-10} \sim 1.0 \times 10^{-8} \text{ cm}^{-3} \text{s}^{-1} )</td>
<td>2.2 \times 10^{-10} \text{ cm}^{-3} \text{s}^{-1}</td>
</tr>
<tr>
<td></td>
<td>( R_{2}^{(b)} ) (He⁺ by ( F_2 )) ( 1.0 \times 10^{-10} \sim 6.4 \times 10^{-8} \text{ cm}^{-3} \text{s}^{-1} )</td>
<td>7.0 \times 10^{-10} \text{ cm}^{-3} \text{s}^{-1}</td>
</tr>
<tr>
<td></td>
<td>( R_{3}^{(c)} ) ( 2.0 \times 10^5 \sim 2.0 \times 10^8 \text{ s}^{-1} )</td>
<td>6.3 \times 10^5 \text{ s}^{-1}</td>
</tr>
<tr>
<td></td>
<td>( k_{f}^- (T_{eo})^{(d)} ) ( \left( \frac{1}{50} \right)^{1/2} \times k_{f}^- (T_{eo}) )</td>
<td>maximum value</td>
</tr>
<tr>
<td></td>
<td>( 8.0 \times 10^{-9} \text{ cm}^{2} \text{s} \text{ (Theo.)}^{(e)} )</td>
<td>5.0 \times 10^{-9} \text{ cm}^{2} \text{ (exp.)}^{(e)}</td>
</tr>
</tbody>
</table>

a) \( R_1 = k_f^t + k_f^p[\text{He}] \), where \( k_f^t \) and \( k_f^p \) are rate constants of \( \text{He}^m + \text{Kr} \to \text{Kr}^+ + \text{He} + e \) and \( \text{He}^m + \text{Kr} + \text{He} \to \text{Kr}^+ + 2\text{He} + e \), respectively.

b) \( R_2 = k_f^t + k_f^p[\text{He}] \), where \( k_f^t \) and \( k_f^p \) are rate constants of \( \text{He}^m + \text{F}_2 \to \text{products} \) and \( \text{He}^m + \text{F}_2 + \text{He} \to \text{products} \), respectively.

c) Estimated from coefficients for reactions of \( \text{He}^m \) with \( O_2 \).

d) \( R_3 \): Collisional frequency of \( \text{KrF}^* \) with \( F_2 \), Kr and He.

e) \( k_{f}^- (T_{eo}) \): Rate coefficient of the dissociative electron attachment reaction, \( F_2 + e \to F^- + F \). Theoretical formula\((43)\) for \( k_{f}^- \) as a function of \( T_{eo} \) was approximated by a polynomial which was certified to fit the theoretical values in the range 0.03~3.5 eV, where the simulation was carried out.

f) Since the theoretical \( k_{f}^- \) value was too large to reproduce the observed output pulse width, \( k_{f}^- \text{n} (n = 1\sim30) \) values were used in the simulation.

g) \( 8.0 \times 10^{-9} \) is the value of \( k_{f}^- \) at \( \sim 0.3 \text{ eV} \) where theoretically it reaches a maximum according to ref. 43 whereas the experimental value at \( \sim 0.3 \text{ eV} \) is \( 5.0 \times 10^{-9} \text{ cm}^{3} \text{s}^{-1} \text{e}^{-40} \).

* The electron concentration, \( n_{op} \) is assumed to be equal to \( [\text{He}^+]_0 + [\text{Kr}^+]_0 > 2.9 \times 10^{16} \text{ cm}^{-3} \).

** The absorption by \( F_2 \) outside the lasing medium was taken into account as a term contributing to the threshold loss coefficient. However, this contribution was small enough to be neglected being 6/1000 of the right hand term of (Eq. 5), i.e. 0.0123.
and

\[ R_3 = q_d[F_2] + q_d[Kr]^3 + q_d[Kr] + q_d[He]^3 + \delta, \]  

(Eq. 9)

where \( k_1^R \) and \( k_2^R \) are rate coefficients of \( \text{He}^m + \text{Kr} \rightarrow \text{Kr}^+ + \text{He}^+ + e \) and \( \text{He}^m + \text{Kr} \rightarrow \text{Kr}^+ + 2\text{He}^+ + e \), and \( k_1^F \) and \( k_2^F \) are rate coefficients of \( \text{He}^m + F_2 \rightarrow \text{products} \) and \( \text{He}^m + F_2 + \text{He} \rightarrow \text{products} \), respectively. \( \delta \) represents the quenching frequencies other than those by \( F_2 \), \( Kr \) and \( He \). \([\text{He}^+]_0, [\text{He}^m]_0, [\text{Kr}^+]_0 \) and \([\text{Kr}^*]_0 \) are summarized along with the rates \( R_1, R_2 \) and \( R_3 \) as parameters in Table VI, where the possible lowest value for each parameter is given. The lowest value of \( n_e \) at \( t = 0 \), i.e., \( n_{e0} = [\text{He}^+]_0 + [\text{Kr}^+]_0 \) was estimated to be \( 2.9 \times 10^{13} \) cm\(^{-3} \) in the following procedure; the total current fed to the discharge was estimated from the total area of the current pulse and converted to the electron number, then divided by the total discharge volume to obtain \( n_{e0} \) in unit volume.

The lowest value of \( R_3 \) is equal to the bimolecular rate coefficient of Penning ionization, namely \( R_3 = k_1^R = 2.2 \times 10^{-10} \text{cm}^3/\text{s} \). The value of \( R_2 \) was obtained for the gas condition, \( e \), using the rate coefficients for destruction reactions of \( \text{He}^m \) with \( O_2 \). The lowest limit of \( R_3 \) was estimated using only the quenching rate coefficient \( q_1 \) for the gas condition, \( e \). The rate coefficient of the dissociative electron attachment reaction \( (F_2 + e \rightarrow F^- + F) \) as a function of the electron temperature, \( k_{F^-}(T_e) \), was calculated by Hall. However, this value was too large to reproduce the observed output pulse width, therefore, \( k_{F^-} \) had to be treated as a parameter in the simulation.

The simulation was carried out by using nine parameters, \([\text{He}^+]_0, [\text{He}^m]_0, [\text{Kr}^+]_0, [\text{Kr}^*]_0, T_{e0}, R_1, R_2, R_3 \) and \( k_{F^-} \) each of which took a value among several values in the range shown in Table VI. In order to obtain a set of parameters which makes the simulated shape of the output pulse best fit to that of observed, computations were carried out for all the set of possible combinations of the nine parameters each of which can take several values.

### 4.4 Results and Discussion

#### 4.4.1 Computer simulation for the mixture at 2.65 atm

a) Pulse shape and parameters

The simulated pulse shape of the laser output is shown by a dashed curve in Fig. 6 to compare with observed one. Quite satisfactory coincidences were obtained not only for the laser pulse shape but also for the delay time of the pulse; the simulated delay time is 14 ns corresponding to the observed value, 13 ns. First, a simpler simulation was carried out disregarding \([\text{Kr}^*] \) and assuming \([\text{Kr}^*]_0 = 0 \), and obtained values of the seven parameters and characteristics of the laser output are listed in column B of Table VII, I and II, respectively. The simulated energies in Table VII, II

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulated value</th>
<th>Exp. value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{e0} )</td>
<td>2.96</td>
<td>2.6</td>
</tr>
<tr>
<td>([\text{He}^+]_0 )</td>
<td>2.56</td>
<td>2.6</td>
</tr>
<tr>
<td>([\text{He}^m]_0 )</td>
<td>6.4</td>
<td>6.0</td>
</tr>
<tr>
<td>([\text{Kr}^+]_0 )</td>
<td>0.4</td>
<td>0 (assumed)</td>
</tr>
<tr>
<td>([\text{Kr}^*]_0 )</td>
<td>0.4</td>
<td>neglected</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>( R_3 )</td>
<td>3.1</td>
<td>2.6</td>
</tr>
<tr>
<td>( k_{F^-} )</td>
<td>( k_{F^-}/6 )</td>
<td>( k_{F^-}/6 )</td>
</tr>
<tr>
<td>( T_{e0} )</td>
<td>10000</td>
<td>10000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulated value</th>
<th>Exp. value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>Peak power</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Pulse width</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>Delay time</td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

Column A: Values obtained when \( \text{Kr}^* \) was taken into account.

Column B: Values obtained when \( \text{Kr}^* \) was neglected.

I: Values of parameters were determined by the computer simulation method explained in 4.3.

II: Laser outputs were calculated using the values of the parameters.
are obtained by integrating the instantaneous output power from 0 to 50 ns, because the lasing appears to cease before 50 ns. Next, the simulation including \([\text{Kr}^+]_0\) and \([\text{Kr}^+]_0\) as parameters was performed, and values of the nine parameters as shown in column A of Table VII, I were obtained. Simulated laser characteristics shown in column A of Table VII, II are very close to those in column B, and also agreements with experimental values listed in the fifth column are quite satisfactory. Although the simulated power is about a half of observed one, this amount of discrepancy can be regarded small enough for this sort of calculation. Moreover, all the parameters have values larger than the lowest limit shown in Table VI, although the simulations were carried out in the range extending over the lowest limit as shown in the same table.

b) Influence of the rate coefficient of the electron dissociative attachment to \(\text{F}_2\), \(k_{F^-}\), on the laser power, \([\text{He}_2^+]\), \([\text{F}^-]\) and \([\text{Kr}^+]\)

Fig. 8 shows that the rate coefficient \(k_{F^-}\) for the reaction \(\text{F}_2 + e \rightarrow \text{F}^- + \text{F}\), is quite effective on the output power, pulse shape and delay time, therefore, its influence on electron temperature, electron concentration, concentrations of transient species and gain were computed. The results for \([\text{He}_2^+]\), \([\text{F}^-]\), and \([\text{Kr}^+]\) are shown in Fig. 9 (a), (b) and (c) respectively;

\[
e + \text{F}_2 \xrightarrow{k_{F^-}} \text{F}^- + \text{F}
\]

**Fig. 8.** Influence of the rate coefficient of the electron dissociative attachment to \(\text{F}_2\) on the laser output pulse; \(k_{F^-} = 1, \frac{1}{5}, \frac{1}{6}\) and \(\frac{1}{7}\) of theoretical value is assumed as a function of electron temperature in the mixture \(e\) shown in Table I.

\(k_{F^-}\) was taken to be \(1/5, 1/6, \) and \(1/7\) of the theoretical values as a function of electron temperature in the same mixture as \(e\) in Table I. When theoretical value of \(k_{F^-}\) itself is used \([\text{He}_2^+]\) and \([\text{F}^-]\) increase with time and tend to saturate, whereas \([\text{Kr}^+]\) decreases very rapidly. Consequently, the output power peaks so early as shown in Fig. 8. The rate coefficient of the electron dissociative attachment
Fig. 10. Temporal behaviours of $T_e$, $n_e$ and concentrations of transient species in the mixture $e$ in Table I.
to F₂ cannot be more or less than \( k_F / 6 \), in order to fit our observed pulse shape and delay time. Only with \( k_F / 6 \) reasonable temporal behaviours of transient species as describe in the next section were obtained.

c) Temporal behaviours of the electron temperature, concentrations of transient species and the laser gain. Computed values for electron temperature and concentrations of transient species are shown as a function of time in Fig. 10. Now, it is possible to estimate each term value of the differential equations in Table V at any time of interest. Since each term represents a reaction, the relative values of the estimated terms would suggest what reactions are dominant at a certain time or time interval. As a result of detailed investigations in this way the flow of dominant reactions were inferred as follows: Fig. 10 (a) \( T_e \): Electron temperature decays from 10000 to 3055K or 1808K after 9 or 15 ns from \( t=0 \), respectively. This decay is mostly due to an electron-neutral elastic collision process, \( e(E_1) + He(E_2) \rightarrow e(E_1-\delta) + He(E_2+\delta) \). Fig. 10 (c) \( [He^+] \): \( [He^+] \) steeply decays due to reaction R1, and He+ ions are converted to He₂⁺ ion molecules within about 10 ns. Fig. 10 (d) \( [He^+] \): Thus increased He₂⁺ ion molecule starts to decay at 9 ns due to the decay of electron temperature (3055K), and the electron density \( (n_e=1.16 \times 10^{16} \text{ cm}^{-3}) \), and also due to recombination reactions R5 and R6. The reaction R6 becomes dominant after 23 ns, when \( n_e \) and \( T_e \) take values 2.6 \times 10^{14} \text{ cm}^{-3} \) and 933K, respectively. Fig. 10 (g) \( [F^-] \): Corresponding to the decay of electron temperature the production of F⁻ ions increases by the electron dissociative attachment reaction R36; the decay of \( [F^-] \) starts at 15 ns (when \( T_e \) and \( n_e \) becomes less than 1808K and 5.74 \times 10^{14} \text{ cm}^{-3} \), respectively), because the ionic recombination reaction R24 becomes dominant. Fig. 10 (b) \( n_e \): Corresponding to destruction of He⁺ ions and production of F⁻ ions, \( n_e \) decreases; the reaction R5 is dominant before 23 ns, and the reaction R36 becomes dominant after 23 ns. At 20 ns \( n_e \) reduces to 10% of the initial value; this result agrees with the observed fact that the current damped to zero after 20 ns from the first current peak, B (cf. Fig. 6). Fig. 10 (e) \( [He^m] \): At first, \( [He^m] \) decays steeply due to reactions of He⁺ with Kr, i.e. R9 and R10; however, corresponding to the destruction of He⁺ ions the production of metastable Heᵐ increases and then the decay of [Heᵐ] becomes so slow to make a plateau. Fig. 10 (f) \( [Kr'] \): Corresponding to the rapid, and the slow decay of [Heᵐ], the rapid increase of [Kr⁺] at about 3 ns and its slow decay after 3 ns are obtained. Fig. 10 (i) \( [KrF^*] \): The production process of KrF* from Kr⁺ and F⁻ ions, R24, is always most dominant compared with other reactions. However, when the sum of the rates for destruction processes of KrF* excimer by spontaneous and stimulated emissions, and the rates of quenchings by F₂, Kr and He through R31–R34, exceeds the production rate of KrF* through R24, the KrF* concentration should start to decrease; therefore, the curve has a peak at 7 ns.

In Fig. 11, the instantaneous net gain is shown by curve I along with the temporal behaviours of the total absorption (curve II) and \( \sigma_{st} \) [KrF*] curve (III), where \( \sigma_{st} \) stands for the coefficient of the stimulated emission (cf. R30). The total absorption as a function of t was
computed based on the time variations of the concentrations of the transient absorbers listed in Table IV, and their absorbing cross-sections. The dotted curve close to the curve II represents the absorption by F\(^{-}\) only. Consequently, most of the total absorption was found to be due to F\(^{-}\). The dotted horizontal line represents threshold gain \(g_{th}\); \(g_{th} = 0.0123 \text{ cm}^{-1}\) was obtained by the formula (Eq. 5) for our cavity system, i.e. \(R = 0.11^{*}\) and \(L_g = 90 \text{ cm}\). The net gain which is equal to \(\sigma_{e} [\text{KrF}^*](\text{total absorption})\) is positive from 3 to 21 ns, and has a maximum at 7 ns. After 21 ns the curve becomes flat near zero level, and starts to decay at 24 ns. The simulated output pulse shape shown in Fig. 6 by a dotted curve has a peak at 33 ns where the net gain reaches zero; the peak of the laser output delays by 13 ns from the maximum of the net gain. The rise time of the simulated pulse delays from the current peak, B, by 14 ns, which well agrees with the observed delay 13 ns. The simpler simulation in which [Kr\^*] was disregarded showed the temporal behaviours of \(n_e, T_e, \) and transient species quite similar to those described above.

d) Summary of lasing mechanisms

A diagram schematically representing the flow of each of the excited particles considered in the present work is shown in Fig. 12, where the flows judged to be dominant by our simulation are represented by heavy arrows. Most important species for lasing are surrounded by double circles, and the arrows aimed at nothing mean the quenching losses of which rates were taken into account. For each of \(\text{He}^m, \) \(\text{Kr}^+ \) and \(\text{KrF}^*\) species the production rates through various processes are compared and percent ratios are given for each of the arrows; the same alphabetical super suffixes are given to ratios comparable each other. These ratios were determined by comparing the time integrated value of each of the contributing terms in the rate equations listed on Table V; the integral range was set from 0 to 50 ns, because the lasing appears to cease before 50 ns.

From the simulated initial values of \([\text{He}^+], \) \([\text{He}^m], \) \([\text{Kr}^+], \) and \([\text{KrF}^*]\) shown in Table VII, column A, production rates of these four species were deduced to be 78 : 19.5 : 1.2 : 1.2%, which suggest that most of the discharge energy is deposited to \(\text{He}^+ \) and \(\text{He}^m\). However, the production rates of \(\text{He}^m\) through direct electron impact, electron-ion recombin-
tions of He$_2^+$ and He$^+$, calculated to be 28:71:1\% show that the most dominant process is through He$_2^+$, which is formed by an ion conversion process from He$^+$. Thus enriched He$_m^+$ contributes to produce most (83\%) of the Kr$^+$ ions by the Penning ionization, i.e. R9 and R10, while only 15.4\% of Kr$^+$ is produced through the Penning ionization, R19, by the He$_3^+$ molecule. Thus the direct electron impact to produce Kr$^+$ from Kr is almost negligible (1.6\%).

Most destructive processes of electrons are the dissociative attachment of F$_2$ to produce F$^-$ (55\%) and the recombination of He$_2^+$ to produce He$_m$ (34\%) and He$_n^+$ (10\%), although both He$_m^+$ and He$_n^+$ realease some electrons back to the plasma when they produce Kr$^+$ by the Penning ionization. Most (96\%) of the excited KrF$^*$ is produced from Kr$^+$ and F$^-$ through reactions R24 and R25, and the production from Kr$_3^+$ and F$^-$ through R28 and R29 is almost negligible (1.6\%). The KrF$^*$ formation through R35, i.e. Kr$^+$+F$_2$→KrF$^*$+F, was found to be only 1/40 of that from Kr$^+$+F$^-$ when the rate coefficient of R35 determined by Velazco et al.12, i.e. $k_5=0.72\times10^{-9}$, was used. When the coefficient adopted by Greene et al.16, i.e. $k_5=1\times10^{-9}$ was used, the effect of Kr$^*$ on KrF$^*$ formation became ten times the former, i.e. 1/4.

The quenching rate of KrF$^*$ due to F$_2$, Kr and He amounts to 54\% and the rest (46\%) of KrF$^*$ must be able to emit photons of various energies. The absorption losses around 249 nm due to F$^-$, F$_2$, He$_m^+$, Kr$^*$ and Kr$_3^+$ was found to be 12\%, and the calculated extraction rate of our optical system was 29\%. The rest (59\%) of the photon energy was found to be emitted as spontaneous radiation. However, the effect of this radiation on the laser beam is negligible because of the small solid angle ($\Omega/4\pi=5.3\times10^{-8}$, cf. P. 9). Finally, the over-all efficiency was calculated to be 0.6\%, which agrees fairly well with the experimental value, i.e. 1\%.

4.4.2 Trials of simulations for various constituent gas concentrations

In order to confirm the observed relations between the constituent gas concentrations and the laser output, mutually independent simulations were carried out for various mixtures within the total pressure range between 2.45 and 2.87 atm. For simplicity the effect of Kr$^*$ on the KrF$^*$ formation was disregarded, because the result described in the preceding section showed that the Kr$^*$ contribution to the lasing mechanism is almost negligible at least for total pressures in the vicinity of 2.65 atm. Moreover, 1/6 of the theoretical rate coefficient of the electron dissociative attachment to F$_2$ was used for all simulations, because any other value could not reproduce the observed pulse shape, which was assumed to be the same as shown in Fig. 6 based on the observed fact that the laser output width is almost independent of gas conditions (Fig. 5). a) A trial to show sensitive dependence of output power on [F$_2$]: For fixed [He] and [Kr] at $6.4\times10^{19}$ and $5.8\times10^{17}$ cm$^{-3}$, respectively. The result plotted in Fig. 13 shows how the laser energy is sensitive to [F$_2$] in accordance with experimental fact obtained by us as well as Rothe et al.8 Detailed examination of our calculation shows that the main factor affecting the output power is the quenching of KrF$^*$ due to F$_2$ rather than the absorption loss, although the absorption due to F$^-$ slightly increases along with the increase of [F$_2$].

b) Trials to realize rules I, II and III. (Rule I) Output energy vs. [Kr] or [F$_2$] for fixed [He] at $6.4\times10^{19}$ cm$^{-3}$ and [Kr] = $5.8\times10^{17}$ cm$^{-3}$.

The result is shown in Fig. 14(a), in which for the mixture represented by the filled circle the experimental as well as the simulated data are obtained. The output energy takes a maximum value around [Kr] = $5\times10^{17}$ cm$^{-3}$, although in our experiments the maximum energy was obtained at around [Kr] = $5.8\times10^{17}$ cm$^{-3}$, which was read from the dashed curve standing for experimental data. The exist-
Fig. 14. Output energy variations (a) versus [Kr] and [F₂] simulated for [He]=6.4×10¹⁹ cm⁻³ and [F₂]:[Kr]=1:7.14 (rule I), (b) versus [He], [Kr] and [F₂] simulated for [F₂]:[Kr]=1:7.14 (rule II) and (c) versus [Kr] simulated for [He]=6.4×10¹⁹ cm⁻³ and [F₂]=8.1×10¹⁶ cm⁻³ (rule III). Each ordinate scale is normalized at the value of the filled circle, for which experimental data is available. All curves are obtained by the interpolation or extrapolation of the experimental points. ◆ represents simulated point.

ence of a mixture for which the power takes the maximum value, i.e. rule I (cf. 3.1 and Fig. 2) can be concluded from the simulated points.

(Rule II) Output energy vs. [He], for fixed [Kr]/[F₂] at 7.14. Fig. 14 (b) shows the result of the simulation, for which data were taken from Fig. 3 in the region of [He]=6×7 ×10¹⁹ cm⁻³. From the solid curve representing the experimentally obtained optimal concentration of [F₂] or [Kr] versus [He], the constituent gas concentrations were determined for which the independent simulations were carried out. Simulated output energies represented by circles show the same tendency as the dashed curve representing the experimental points. Namely, the output energy increases along with the increase of [He] in spite of the decrease of [F₂] and [Kr]. Experimentally, by using Fig. 3, i.e., rule II, we were able to predict the optimal mixture for laser performance at a certain total pressure. Detailed examination of our calculation shows that the quenching factor of KrF* decreases as the total pressure increases for the optimal mixture satisfying the relation in Fig. 3.

(Rule III) Output energy vs. [Kr], for fixed [He] and [F₂] at 6.4×10¹⁹ and 8.1×10¹⁶ cm⁻³, respectively. The simulated result is shown in Fig. 14 (c), in which the laser output gradually increases along with the increase of [Kr] and tends to saturate. Namely, the same behaviour as shown in Fig. 4 is obtained, and rule III is almost realized by our simulation.

The results of the trials 4.4.2 a) and b) can be regarded to support that the present simulation method as well as the experimentally found rules are reliable, even though under limited conditions.

5. Summary and Conclusion

In search for mixtures optimal for laser operations a home-made laser apparatus was used to observe outputs for various He/Kr/F₂ constituent gases of the total pressure ranged 500 Torr—2.65 atm, and three rules between output powers and gas mixing ratios were deduced. Pulse shapes of the laser output and the discharge current were observed, and the delay time of the laser pulse relative to the current peak was determined to be ~13 ns.

Lasing mechanisms which can reproduce the observed characteristics in laser operations are investigated by computer simulations using a quite simplified model as follows: The effect of external circuit and preionization are treated by varying initial values of the electron temperature and concentration, and concentrations of ions and excited species in the plasma, which is assumed to be pro-
duced by the instantaneous excitation due to the discharge at the moment when the current peaks (cf. Fig. 6). Consequently, all electron and gas kinetics and photoabsorptions are considered in the afterglow. Simulations were carried out for the mixture experimentally found to be optimal at 2.65 atm. Forty-four processes were taken into account, and eleven simultaneous differential equations were numerically solved. By varying nine parameters in the reasonable range the laser pulse shape and its delay time were reproduced quite satisfactorily. However, this best fitting to the observed pulse shape could not be obtained without using one sixth of the theoretical value for the rate coefficient of the electron dissociative attachment to F₂, \( k_{F^-}(T_e) \), and only with this value temporal behaviours of transient species were reasonably analysed (cf. Fig. 10). \( k_{F^-}(T_e) \) was assumed to have the same type dependence on the electron temperature as that obtained by Hall\(^{43} \), and the electron temperature varies with time as shown in Fig. 10(a). The simulated decay time of the electron density is 23 ns coincident with the observed damping time of the current, \( \sim 20 \) ns. It seems to be worthy that Greene et al.\(^{16} \) used the \( k_{F^-} \) value fixed at \( 5 \times 10^{-10} \) cm³/s, which is always smaller than our value, \( k_{F^-}(T_e)/6 \), at any electron temperature, \( T_e \), between 550 and 10000 K.

A summary of the simulated lasing mechanism is schematically shown in Fig. 12, in which some production or destruction ratios for different processes are compared and percent ratios are given. The contribution of Kr* to the KrF* production through Kr*+F₂ → KrF*+F was found to be 24% or 24% depending on the rate coefficient to be 0.72\(^{23} \) or 1\(^{116} \) x 10\(^{-9} \), respectively. Consequently, in our model the dominant reactions were judged to make an energy flow on the route, He⁺ → He^+ → He^2⁺ → Kr⁺ → KrF*, in which the Penning ionization plays an important role.

Although the model is oversimplified, the three experimental rules are reproduced by independent simulations for various gas mixtures of the total pressure ranged 2.45~2.87 atm. The observed fact that the increase of [F₂] reduces the laser energy is also reproduced by independent simulations, and the cause of this fact is attributed to the increase in quenching of KrF*.

Now, some fundamental data are required before more accurate theoretical models will be treated. First, the F₂-electron attachment rate, \( k_{F^-}(T_e) \), must be known more accurately in the absolute value as well as the electron temperature dependence, because our results indicate that it affects seriously the laser output, the pulse width, the delay time, and the gas and electron kinetics (cf. Figs. 8 and 9). Greene et al.\(^{10} \) also mentioned the importance of knowing accurate value of the F₂ electron attachment rate. Second, all photoabsorption processes have to be studied in more detail to obtain accurate cross sections and their dependence on wavelengths. Particularly, investigations on the molecular structure of the KrF excimer are necessary, because self-absorptions can play important roles in the lasing mechanism, although we neglected them this time. Thirdly, it is desirable to know the nature of quenching losses, because the result of this work shows that the losses amount to 54% which was determined as one of the parameters. Experimentally, we have to try to exclude impurities so as to make experimental conditions closer to the simple conditions theoretically tractable.

References

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