Peculiarities of KrF Excimer Vibrational Relaxation in Low-Pressure Kr/F₂ Mixtures Excited by a Short Pulse

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Abstract. The importance of excimer vibrational relaxation is manifested once again by the example of the low-pressure Kr/F₂ gain medium excited by a short pulse. The pressure is determined at which a sharp fall of the population efficiency of low KrF(B) vibrational levels should appear. Time peculiarities of the gain are investigated analytically for short-pulse excitation operation.

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Recently, both theoretical calculations [1] and measurements [2] have been performed on the amplification of 248 nm emission in excited Kr/F₂ mixtures. It was expected that the amplifier medium has to be used in the superhigh intensity mono-beam amplifier chain [3] for realizing an X-ray laser. In accordance with technological peculiarities of the system, a low pressure operation of the KrF amplifier is desirable. It is the low pressure Kr/F₂ mixtures that have been studied in [1, 2]. A net gain g has been measured down to pressure p of 50 mbar in the mixtures excited by a 60 ns electron-beam [2]. However, a drastic decrease of g has been observed when p was lowered below 100 mbar. In [1] the fall of g has been attributed to the slowing down of KrF* formation. The decrease of g was additionally attributed to a slowing of vibrational relaxation of KrF excimers formed on high vibrational levels.

In kinetics studies the KrF* internal energy was conventionally treated to be distributed over a few vibrational states [1, 2, 4]. However, population of a large number of KrF* vibrational levels should be taken into account when the pressure of the buffer gas is low. In [5] vibrational relaxation of excimers has been examined in a diffusional approximation and non-equilibrium populations of high vibrational levels have been found. The model has been especially applied to the study of the KrF laser in [6]. Results of [5, 6] can be directly applied to the investigation of the low-pressure KrF amplifier medium without the use of adjustable parameters. Such application is made in Sect. 1 of this paper. It is shown that at p < 100 mbar the bottleneck appears in the population kinetics of low vibrational levels.

There is another peculiarity that should be investigated in more detail. It is the time dependence of g. Answers should be found for the following questions: 1) How long is the delay of the gain pulse with respect to the excimer formation pulse, and 2) has gain to be reduced due to time broadening of the pulse. We detail the latter question by the following consideration. Let excimers be formed during the short time tₑ on high vibrational levels (under conditions of [3] tₑ is of the order of 10⁻⁸ s). A large number of vibrational levels are populated in the course of vibrational relaxation. Excimers will appear on the low vibrational levels during the time tᵍ. If tᵍ > tₑ the gain g' at the short-pulse excitation should be lower than the gain g₀ at the long-pulse excitation. Really, if the number of excimers formed per 1 s is the same in both cases, the relationship should be fulfilled: g' = (tₑ / tᵍ) g₀. The time characteristics of the gain, including the dependence of tᵍ on tₑ, are analytically calculated in Sect. 2 of this paper.

1 Influence of Vibrational Relaxation on Gain

In [5, 6] stationary distributions of KrF excimers over vibrational levels have been found from the Fokker-Planck equation. Let us briefly note the parameters of the equation to clear up the use of the formulae of [5, 6]. Excimer diffusion in the space of vibrational energy ε is described by the coefficient Tb(ε)/τ₀, where T is the temperature in energetic units, τ₀ is the vibrational relaxation time (τ⁻¹₀ = kₑ[Kr], [Kr] is the Kr number density), b(ε) = ε for the harmonic oscillator, and

\[ b(\varepsilon) = 2D(1 - \sqrt{1 - \varepsilon/D})1 - \varepsilon/D \]

for the Morse oscillator. D is the dissociation energy of the excited electronic state. Excimer pulling down in the energetic space is described by the coefficient nearly equal
Table 1. Rates, rate constants, and probabilities of physical-chemical processes in Kr/F2 mixture

<table>
<thead>
<tr>
<th>Process</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr* + F2 → KrF(B, ε* ≈ 1.8 eV) + F</td>
<td>$R_1$</td>
</tr>
<tr>
<td>Kr* + F* + Kr</td>
<td>$R_2$</td>
</tr>
<tr>
<td>Kr* + F* + Kr</td>
<td>$R_3$</td>
</tr>
<tr>
<td>KrF(C) → KrF(A) + hν'</td>
<td>$A_C = 1.33 \times 10^7$ s$^{-1}$</td>
</tr>
<tr>
<td>Kr* + 2 Kr → KrF + Kr</td>
<td>$k_1 = 2.0 \times 10^{-12}$ cm$^3$/s</td>
</tr>
<tr>
<td>KrF*(e') + Kr → KrF*(e' - Δν) + Kr</td>
<td>$k_{ν} = 10^{-10}$ cm$^3$/s</td>
</tr>
</tbody>
</table>

* The kinetic parameters are taken from [4] with the exception of $A_B(ε)$ and $k_ν$ (see the text).

b(ε)/τu. Formation of excimers on the levels with energy $ε_ν$ is characterized by the rate $R_ν$ (see Table 1). Finally, KrF* deactivation is described by the reverse time 1/τu. A value of 1/τu allows for rapid B- and C-states mixing and is calculated by the formula:

$$1/τ_u = 1/2 A_B(ε) + 1/2 A_C + k_0[F_2] + k_n e$$

where Einstein coefficients and quenching rate constants are presented in Table 1, [F2] and $n_e$ are the F2 and electron number densities, respectively. Here the laser flux in the active medium $ϕ$ is assumed to be zero.

In [6] the following formula has been obtained for small signal gain at 248 nm

$$g_0 = Rστ_u \sum \beta_i η_i^p$$

where $R \equiv \sum R_i$, $β_i \equiv R_i/R$, $ε' = n\hbarω$, $n = 3$ is the number of low vibrational levels which are available for the laser transition [1], and $\hbarω$ is the KrF(B) vibrational quantum. The quantum yield of stimulated emission $η$ and the internal efficiency $η_{int}$ of KrF laser have been also found,

$$η = \left( \frac{σ}{σ + σ_s} - \frac{σ}{γγ_s} \right) \sum \beta_i η_i^p$$

$$η_{int} = \left( \frac{hν}{\sum ε_i} \right) η,$$

where $σ_s \equiv (στ_u)^{-1}$, $γ$ is the ratio of the small-signal gain to the nonsaturated absorption coefficient, $hν$ is the photon energy, $ε_i ≈ 20$ eV [7] and $ε_i = 24.1$ eV [8], are the energies expended per Kr* atom and ion pair formation, respectively.

The $B \rightarrow X$ radiative transition is the main channel of KrF* relaxation at low pressure. It is important that the Einstein coefficient $A_B$ decreases when $ε$ increases. The dependence of $A_B$ on the number of KrF(B) vibrational levels $ν$ taken from [9] is presented in Fig. 1 as a solid line. This dependence was used for $ν ≤ 53$ and is not a satisfactory one when $ν > 1.8$ eV. A value of $A_B$ for high vibrational levels can be easily calculated if the semiclassical motion of nuclei is assumed [10]. The result of such calculation with the $B \rightarrow X$ transition moment and the potentials for $B$ and $X$ electronic states from [9] is presented in Fig. 1 as a dotted line. The empirical formula

$$A_B(ε) = 1.4 \times 10^8 s^{-1} - α(1 - \sqrt{1 - ε/D}) \times \exp[-α(1 - \sqrt{1 - ε/D})],$$

where $α = 6.7 \times 10^8 s^{-1}$, $α = 1.84$ is in good agreement with both [9] and $A_B$ found with the WKB approximation.

The calculations of $g_0$ have been performed for a F2 concentration of 0.5% that was kept at Kr/F2 mixtures [2]. We used the value of electron density $n_e = 2 \times 10^{14}$ cm$^{-3}$ found from Fig. 6 of [1]. A similar value of $n_e$ can also be estimated from the formula of [2, 11]: $n_e = R_2/(γa[F_2])$. Here $a$ is the electron attachment rate constant. For example, $a = 4.5 \times 10^{-9}$ cm$^3$/s at an electron temperature of 1 eV [4, 11]. We adopted the vibrational relaxation rate constant $k_ν = 10^{-10}$ cm$^3$/s of [12] that has been used for calculation of KrF laser parameters in [5, 6].

The terms $η_i^p$ in (2) respond for vibrational relaxation. Their dependences on $p$ are presented in Fig. 2. The dependences are used for calculating of small signal gain $g_0$ with (2). In accordance with Fig. 7a of [1] we estimate the values of $β_i$ as: $β_1 = 0.3$ and $β_2 = 0.7$. From Fig. 3 of [2] we found the upper estimation for the energy deposition rates $W/p = 1.06$ kW/(cm$^3$ mbar). The pumping rate $R$ could be thereupon found from the equation $R = W/(β_1ε_1 + β_2ε_2)$.

To simplify the comparison of theoretical and experimental results we multiplied $g_0$ by 0.944 and the product was equated to the net gain $g$ (see [2]). The calculated pressure dependence of $g$ is compared with the measured one in Fig. 3. It is seen that the experimental and theoretical values of $g$ agree well. Note that it is the third, after [1] and [2], explanation of the experiment made without adjustable parameters.