SIMULATION OF VIBRATIONAL RELAXATION IN THE EXCIMER LASERS

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The ways to model vibrational relaxation in the rare gas halide excimer lasers are analyzed. The phenomenological approach applied commonly to understand the molecular kinetics is compared with more strict level–to–level and Fokker–Planck models. The validity conditions of the models as well as definitions of the kinetic parameters are discussed. The quantum yield of stimulated emission, the time delay between the pumping and emission pulses, the gain recovery after fast depletion of the upper laser level are examined. Principle contradictions between the models are stressed using diagrams.
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I. INTRODUCTION

The progress in laser physics during the two past decades was associated with the construction and development of the excimer lasers, the most high power gaseous lasers of the UV spectral range [1–10]. Current studies of these lasers are caused by a number of technological applications including chip production in the world's semiconductor industry using the UV lithography. The development of the excimer lasers stimulated extensive research of the excimers, the rare gas halide (RgX) diatomic molecules. This paper is devoted to the understanding of some experimental and theoretical data achieved during the excimer laser research. Namely, the goal of the study is to compare all the known concepts of vibrational relaxation.

Kinetics of the RgX excimers is an interesting example of the multiparametric problem. Indeed, most excimers are typically formed near the dissociation limit of the $RgX(B)$ and $RgX(C)$ electronic states. Collisions of the excimers with buffer gas atoms result in the energy conversion between the $RgX(B)$ and $RgX(C)$ electronic states and vibrational–to–translational (VT) energy transfer. In a series of these multiquantum transitions the vibrational excitation flows from the highest vibrational levels to the lowest ones. This relaxation process is concomitant with radiative and collisional deexcitation of the electronically excited states. Thus, populations of hundreds of vibrational levels should be taken into account [11]. To simulate the population of any vibrational level it is necessary to define a variety of kinetic parameters. The characteristic feature of the relaxation is that rates of vibrational transitions are comparable with the rates of electronic deactivation. Therefore, the assumption about near–equilibrium vibrational distribution of the excimers appears not to be a proper approach.

In order to simulate vibrational relaxation, one has (i) to choose one of several modeling methods and (ii) to determine reliable values of the rate constant of vibrational relaxation, k_{VT}. This paper is basically concerned the first part of the problem. Namely, we describe and compare phenomenological, numerical, and analytical approaches. As to kinetic parameters k_{VT}, their numerical values, reported in various papers, differ by the orders of magnitude [18]. In part, this can be due to that those parameters have different physical senses in the above–mentioned models.

In the next section, we give an historical overview of the methods which were applied for modeling the relaxation kinetics. We show that phenomenological, numerical, and analytical models both use different definitions of the relaxation parameters, and assume distinct validity conditions for the kinetic equations. The main goal of this paper is to compare predictions of different kinetic models, as is done in Sec. III. Concluding remarks are given in Sec. IV.

II. AN HISTORICAL OVERVIEW

A. Phenomenological Models

In the literature several approaches were applied to simulate kinetics of vibrational relaxation of the excimers. The most common approach was proposed by Jacob *et al* in 1979 [19,20]. In paper [20] KrF(B) sidelight fluorescence of the 249–nm $B \to X$ transition was monitored in the active medium of the KrF laser. Comparing the signals observed in the presence and absence of stimulated emission, the ability of the laser photons was evaluated to depopulate the upper laser level. The conclusion from these experiments was that some of the KrF population was at higher vibrational levels and could not be effectively extracted by stimulated emission at the normal laser operating wavelength.

In the excimer lasers the upper laser level is typically the zeroth vibrational level of the $RgX(B)$ state. In order to determine the population of this level n_0 comparatively to its equilibrium value $n_{0\mathrm{e}}$ Jacob *et al* proposed the following rate equations:

$$\frac{dn_0}{dt} = -\frac{n_0 - n_{0\mathrm{e}}}{\tau_\mathrm{v}} - \frac{n_0}{\tau_\mathrm{u}} - \frac{\sigma\Phi}{h\nu}\,n_0. \tag{1}$$

$$\frac{dN}{dt} = -\frac{N}{\tau_\mathrm{u}} + R - \frac{\sigma\Phi}{h\nu}\,n_0. \tag{2}$$

Here $n_{0\mathrm{e}} = \theta_0\,N$, $\theta_0 \equiv \exp\big(-\frac{\epsilon_0}{T}\big)\,/\sum_v \exp\big(-\frac{\epsilon_v}{T}\big)$ is the Boltzmann factor, ϵ_v is the energy of v–th vibrational level, T is the gaseous temperature in the energetic units, $N = \sum_v n_v$ and τ_u are correspondingly the number and the lifetime of the electronically excited molecules, τ_v is called the time of vibrational relaxation, it is related to the rate constant of vibrational relaxation k_VT ($\tau_\mathrm{v}{}^{-1} = k_\mathrm{VT}\,[\mathrm{M}]$, where [M] is the density of the buffer gas M), Φ is the light flux in the active medium, σ is the cross section of stimulated emission, $h\nu$ is the photon energy, R is the pumping rate for producing the electronically excited molecules.

Equations (1) and (2), as well as their modifications, were applied in a number of papers [3,6–8,10,21–30]. The modified models took into account contribution to the stimulated emission of several vibrational levels of KrF(B) [25,6,27,29,30], collisional mixing between the $RgX(B)$ and $RgX(C)$ states [23,25,7,29,30], and interaction of the $RgX(B,C)$ excimers with plasma electrons [23,28,30]. The reliability of any model of course depends on the way of determining the parameter τ_v.

On the one hand, any parameter $\tau_\mathrm{v}(M)$ of Eq. (1) is in fact an adjustable parameter of a specific kinetic model. According to Kannari, Obara, and Fujioka [25], it cannot be thought that Eq. (1) describes the exact physical processes of the vibrational energy transfer. Otherwise stated, the parameter τ_v found in the framework of certain phenomenological model is valid only for this model.

On the other hand, the condition under which the rate $\tau_\mathrm{v}{}^{-1}$ of Eq. (1) is related with the rates of elementary energy transfer processes can be found. The application of Eq. (1) can be proved as follows.

B. Level–to–Level Models

In the most general case, n_0 can be found from the system of the rate equations of level–to–level kinetics:

$$\frac{dn_v}{dt} = -\frac{1}{\tau_0}\sum_{v'}\left(P_{v'\,v}\,n_v - P_{v\,v'}n_{v'}\right) - \frac{n_v}{\tau_\mathrm{u}} - \frac{\sigma\Phi}{h\nu}\,\delta_{v\,0}\,n_0. \tag{3}$$

Here $P_{v'\,v}$ is the probability of transition from the v–th vibrational level to level v' during one collision with a buffer–gas atom, τ_0 is the time of a free passing of the excimer in the gas, $\tau_0{}^{-1} = k_0\,[\mathrm{M}]$, k_0 is the rate constant of gas–kinetic collisions. Equation (1) obviously follows from system (3) if one sets the populations n_v to be equal

$$n_v = \exp\big(-\frac{\epsilon_v - \epsilon_0}{T}\big)\,\frac{\theta_0\,(N - n_0)}{1 - \theta_0} \qquad (v \neq 0), \tag{4}$$

and defines k_VT as

$$k_\mathrm{VT} = k_0\,(1 - \theta_0)^{-1}\sum_v P_{v\,0}. \tag{5}$$

Consequently, equation (1) will be a proper one under Boltzmann distribution (4) of the molecules on vibrational levels which do not contribute to the light amplification.

Because of the importance of vibrational relaxation several advanced kinetic models based on the rate equations of state–to–state relaxation (3) were developed.

In 1981 Dreiling and Setser examined the XeCl($B-X$) and XeCl($C-A$) emission spectra obtained from the reaction of Xe$(\,^3P_2\,\mathrm{or}\,^3P_1\,)$ with Cl_2, CCl_4, and $COCl_2$ in the presence of He, Ne, Ar, and N_2 bath gases [31]. Due to low buffer gas pressure varying in the interval of one tenth to ten torr, the XeCl(B,C) excimers predominantly populated high vibrational levels. The dynamics of the found vibrational distributions was used to determine the rate constants of vibrational relaxation and transfer between the B and C states of XeCl [31] :

$$k_R = k_0\,P^\mathrm{R}_{ij}, \;\; k_T = k_0\,P^\mathrm{T}_{ij}. \tag{6}$$

Here P^R_{ij} and P^T_{ij} are the probabilities of the transitions in one collision of the XeCl excimer with a buffer gas atom M:

$$RgX(B,j) + \mathrm{M} \xrightarrow{P^\mathrm{R}_{ij}} RgX(B,i) + \mathrm{M}, \quad RgX(C,j) + \mathrm{M} \xrightarrow{P^\mathrm{R}_{ij}} RgX(C,i) + \mathrm{M}, \tag{7}$$

$$RgX(B,j) + \mathrm{M} \xrightarrow{P^\mathrm{T}_{ij}} RgX(C,i) + \mathrm{M}, \quad RgX(C,j) + \mathrm{M} \xrightarrow{P^\mathrm{T}_{ij}} RgX(B,i) + \mathrm{M}, \tag{8}$$

It could be mentioned that the relaxation of vibrational distribution can be determined mainly by the energy conversion between the B and C states (8), but not relaxation transitions (7), if $P^\mathrm{R}_{ij} \ll P^\mathrm{T}_{ij}$.

A similar approach was used in paper of Kvaran, Shaw, and Simons [32]. In this paper the steady–state, chemiluminescence technique was used to measure the effective rate constants for vibrational transitions between blocks of vibrational levels for KrF^* in collisions with He, Ne, and Ar and $XeCl^*$ with Ar. The reported effective rate constants included contributions to relaxation due to intersystem crossing between the B and C states, in addition to direct relaxation within the B state. Authors of [33] studied XeF(B) excimer and determined the rate constants of transitions (7) and (8) between the individual vibrational levels for He, Ar, and N_2 buffers.

Further improvements of the chemiluminescence technique were achieved in several experiments fulfilled by Setser and co–workers [34,35]. Thus, in paper [34] definite low vibrational levels of XeCl(B) and XeCl(C) were populated due to a laser–assisted photoassociation from the Xe + Cl atoms, as well as photoabsorption from the XeCl(X) van der Waals molecules.

A theoretical model assembled by Morgan, Winter, and Kulander [36] described the flow of excitation through vibrational levels of the KrF excimers. This model involved numerical integration of rate equations for the populations of all the KrF(B) vibrational states. They calculated the populations of 20 low vibrational levels are and 100 groups of vibrational levels in the range between $v = 20$ and the dissociation limit of the KrF(B) state (5.3 eV above $v = 0$). The rate equations included recombination (feeding the highest levels of KrF), VT–transitions, spontaneous emission, collisional quenching, and stimulated emission from the lowest levels with $0 \le v \le 4$. The rates of vibrational energy transfer were calculated with a model of the symmetric charge exchange reaction between the thermal Kr atom and the Kr^+ ion of the ionic KrF(B)–state molecule. According to the model, a maximum of 2500 cm^{-1} per collision is to be removed for a collision of Kr atom with the KrF(B) excimer with $\epsilon_v \simeq 2$ eV. By solving the kinetic equations it was found that this rapid vibrational deexcitation is still slow enough for the excitation to be lost by a spontaneous emission and by collisional quenching. The numerical simulations demonstrated the effects of vibrational relaxation on the saturation characteristics of the KrF(B) state during the extraction of laser light. The results of the calculations were in qualitative agreement with the experimental results of [20].

The experimental investigations of the state–to–state relaxation kinetics showed that the process of vibrational relaxation is provided with multiquantum transitions and requires many collisions with the buffer gas atoms. To simulate such a process in the most general way one can apply the diffusion Fokker–Planck equation [37–39].

C. The Fokker–Planck Approach

This approach to modeling vibrational relaxation treats the relaxation process as a motion of the molecules in the energy space. The kinetic equation has the following form

$$\frac{\partial f}{\partial t} - \frac{\partial}{\partial \epsilon} B(\epsilon)\, \rho(\epsilon) \left(\frac{\partial}{\partial \epsilon} \frac{f}{\rho} + \frac{f}{T\, \rho} \right) + \frac{1}{\tau_{\mathrm{u}}} f = r(\epsilon, t). \quad (9)$$

Here $f(\epsilon, t)$ is the distribution function which is introduced so that $f(\epsilon, t)\, d\epsilon$ is a number of the molecules in the interval of vibrational energy of ϵ to $\epsilon + d\epsilon$ in time t. Normally, $f(\epsilon, t)$ describes vibrational distribution of the molecules in a claster of collisionally mixed electronic states. For instance, the B and C states of RgX are mixed by collisions with the buffer gas atoms at the pressures of $p \ge 50$ Torr [25,27,32,35]. Under this condition, the vibrational distribution within certain electronic state s is described by the function $f_s = (g_s / \sum\limits_s g_s)\, f$, where g_s is the electron degeneracy of the state s; $\rho = \sum\limits_s \rho_s$, ρ_s is the density of vibrational states in the electronic state s, $1/\rho_s(\epsilon_v) = \epsilon_{v+1} - \epsilon_v \simeq \hbar\omega$, $\hbar\omega$ is the vibrational quantum of the state s. Population n_v of any vibrational level v of the electronic state s can be expressed via $f(\epsilon, t)$ as follows: $n_v = (g_s / \sum\limits_s g_s) f(\epsilon_v, t) / \rho_s(\epsilon_v)$, here the term $g_s / \sum\limits_s g_s$ is due to the collisional mixing of the electronic states. For the $RgX(B, C)$ excimers, the latter is $(g_s / \sum\limits_s g_s) = 1/2$.

In Eq. (9), the term $-\dfrac{\partial^2}{\partial \epsilon^2} Bf$ describes the diffusion as a result of the energy transfer in random collisions. The term $\dfrac{\partial}{\partial \epsilon} Af$, where $A(\epsilon) = -\dfrac{B}{T} + \dfrac{1}{\rho} \dfrac{d}{d\epsilon} B\rho$, takes into account the directed motion of molecules from the upper vibrational levels to the lower ones. The parameter A can be regarded as the velocity of this motion. The combination $j \equiv -B\rho \left(\dfrac{\partial}{\partial \epsilon} \dfrac{f}{\rho} + \dfrac{f}{T\, \rho} \right)$ is the flow of the molecules in the energy space. The term $r(\epsilon, t)$ in (9) is a generation rate *i. e.* the number of excited molecules created per unit interval of ϵ per unit time. The reverse lifetime $1/\tau_{\mathrm{u}}$ is the sum of the probabilities for spontaneous emission and collisional quenching in 1 s. Generally, τ_{u} depends on ϵ.

The Fokker–Planck equation can be applied if $f(\epsilon)$ is a steady function of ϵ:

$$\left| \sum_{k=3}^{\infty} \frac{(-1)^k}{k!} \frac{\partial^k}{\partial \epsilon^k} \langle (\Delta\epsilon)^k \rangle f \right| \ll \left| \sum_{k=1}^{2} \frac{(-1)^k}{k!} \frac{\partial^k}{\partial \epsilon^k} \langle (\Delta\epsilon)^k \rangle f \right|, \quad (10)$$

here $\Delta\epsilon$ is the energy which transfers one molecule to a buffer gas atom in one collision, the brackets $\langle ... \rangle$ denote the averaging over all collisions.

In the case of vibrational relaxation of excimers, the steady–state distribution function at $\epsilon \gg T$ varies as [40]

$$f(\epsilon) \simeq C\, \epsilon^{\tau_{\mathrm{v}}/\tau_{\mathrm{u}} - 1}, \quad (11)$$

where C is a constant. Thus, the validity criterion (10) is satisfied for excimer relaxation. It should however be noted that the Fokker–Planck approach yields the distribution function (11) which is contrary to the above discussed criterion (4).

The important kinetic peculiarity of the rare gas halide excimers is that the vibrational transitions are multi-quantum. Therefore, the transitions from any vibrational level v to the higher ones can be neglected if $v \gg 1$. The coefficient $B(\epsilon)$ of (9) has consequently to be defined from the equation

$$B(\epsilon) = k_0\,[\mathrm{M}]\,T\,\langle\Delta\epsilon\rangle.$$

The linear approximation of the diffusion coefficient in the region of low vibrational levels is used to introduce the parameter k_{VT} [38]:

$$B(\epsilon) = k_{\mathrm{VT}}\,[\mathrm{M}]\,T\,\epsilon.$$

In particular, if the probabilities of reactions (7), (8) are known, then the value of k_{VT} can be calculated as follows

$$k_{\mathrm{VT}} = k_0\,\frac{1}{\epsilon_v}\left[\sum_{v'} P^{\mathrm{T}}_{v'v}\,(\epsilon_v - \epsilon_{v'}) + \sum_{v'} P^{\mathrm{R}}_{v'v}\,(\epsilon_v - \epsilon_{v'})\right], \tag{12}$$

where ϵ_v lies in the region of low vibrational levels.

Thus, the approaches applied to modeling vibrational relaxation of the excimers have different definitions (5), (6), and (12) of the parameter called the rate constant of vibrational relaxation. Furthermore, according to (4) and (10), the phenomenological and the Fokker–Planck models have different validity conditions which depend on populations of high lying vibrational levels. In the next section we compare the results obtained with the solution of different kinetic equations.

III. COMPARISON OF THE MODEL PREDICTIONS

The most general goal of the relaxation theory lies in calculating the distribution of the molecules over vibrational levels. Both the numerical and the Fokker–Planck models predict similar vibrational distributions formed under a steady–state pumping. The typical vibrational distribution found with the level–to–level relaxation model [36] is shown in figure 1. Let us compare the curve in figure 1 with the solution of the Fokker–Planck equation (9).

The Fokker–Plank equation (9) has an analytical solution if the following simplifying approximations are applied:

$$B(\epsilon) = \frac{T\,\epsilon}{\tau_{\mathrm{v}}}, \;\; \rho = \mathrm{const}, \;\; \tau_{\mathrm{u}} = \mathrm{const}, \;\; r = R\,\delta(\epsilon - \epsilon^*).$$

In the case, the distribution is given by the function

$$f(\epsilon) = C_0\,F\big(\kappa, 1, \frac{\epsilon}{T}\big)\,\exp\big(-\frac{\epsilon}{T}\big), \tag{13}$$

where the constant C_0 depends, in a known way, on the pumping rate R, F is the degenerate hypergeometric function of the first kind, $\kappa \equiv \tau_{\mathrm{v}}/\tau_{\mathrm{u}}$. Thus, the character of the vibrational distribution depends only on the parameter κ. For KrF excimers, the value of κ can be determined using the rate constants of the Fokker–Planck vibrational relaxation model of [41]. Calculating the parameter κ for the 0.958/0.04/0.002 $\mathrm{Ar/Kr/F_2}$ mixture at $p = 1$ bar, the mixture of [20] for which $N(\epsilon)$ of Fig. 1 was calculated in [36], one finds $\kappa = 0.2$. The dependence (13) at $\kappa = 0.2$ is presented in Fig. 1 as a short–dash line.

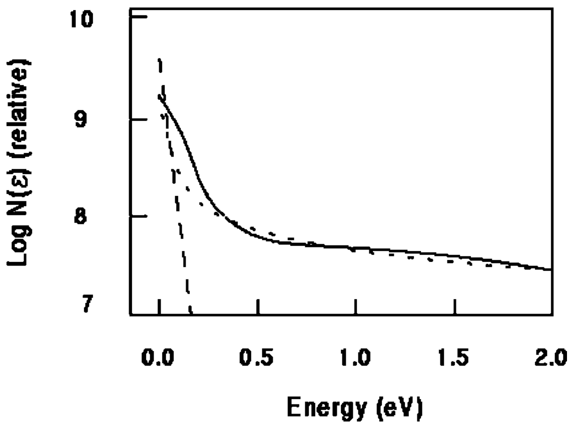


Fig. 1. The KrF vibrational populations *vs.* vibrational energy. Buffer gas (Kr) pressure is 1 bar. The long–dash line presents the equilibrium 300 K Boltzmann distribution, the solid curve was calculated in [36] with the level–to–level relaxation code, the short–dash curve corresponds to the Fokker–Planck relaxation model.

Though we use no adjustable parameters and apply the simplest analytical solution of the relaxation problem, the curves found with the Fokker–Planck and the complex level–to–level models agree surprisingly well.

The solution $f(\epsilon)$ of Eq. (9) correspondent to the steady–state pumping of high vibrational levels has two characteristic features. The function of vibrational distribution is close to the Boltzmann one in the region of low vibrational levels [47]:

$$f(\epsilon) \simeq \frac{N}{T}\,\eta^{\mathrm{v}}\,\exp\big(-\frac{\epsilon}{T_{\mathrm{v}}}\big), \tag{14}$$

where $\eta^{\mathrm{v}} = \exp\Big(-\int_T^{\epsilon^*} \frac{T\,d\epsilon}{\tau_{\mathrm{u}}(\epsilon)\,B(\epsilon)}\Big)$, ϵ^* is the energy of born molecules, T_{v} is the vibrational temperature,

$$T_{\rm v} = \frac{T}{1 - \frac{\tau_{\rm v}}{\tau_{\rm u}}}. \tag{15}$$

A tail of the distribution function exists in the region of high vibrational levels where

$$f(\epsilon) = \frac{RT}{B(\epsilon)} \exp\Big(-\int_{\epsilon}^{\epsilon^*} \frac{T\,d\epsilon}{\tau_{\rm u}(\epsilon)\,B(\epsilon)}\Big), \tag{16}$$

Thus, the populations of hundreds of high vibrational levels within a few–eV energy interval essentially deviate from the Boltzmann ones.

The latter peculiarity of vibrational distribution affects a number of kinetic phenomena which will be studied below.

It was mentioned in Sec. II of this paper that the parameter $k_{\rm VT}$ of phenomenological models is an adjustable parameter. Hence, it can be applied if nothing is known about the distribution of molecules over high vibrational levels. However, it would be useful to study whether predictions of the phenomenological model are correct if operating conditions are changed. Secondly, it is interesting to study whether one kinetic parameter correctly describes various, for example steady–state and temporal, kinetic processes. To study these issues we collected in Table 1 the solutions of the simple kinetic problems found with distinct models.

The first problem addresses the calculation of the ultimate quantum yield of the stimulated emission $\eta_{\rm st}$. This important characteristic of laser efficiency is introduced as the maximum available ratio of the number of emitted coherent photons to the number of molecules born in the active medium. This parameter corresponds to hypothetical laser operation under saturation of laser transition and absence of any photon absorption in the active medium. It is seen from Table 1 that the phenomenological and Fokker–Planck models yield the formulae for $\eta_{\rm st}$ which are different in essence.

In particular, model A does not show any dependence of $\eta_{\rm st}$ on the energy of the born molecules ϵ^*. Let us consider the operation regimes of a KrF laser. Under typical conditions, there are two mechanisms of KrF production. Most excimers are formed in the ionic recombination reaction

$$\mathrm{Kr^+ + F^- + M \longrightarrow KrF(B}, \epsilon_1^* \simeq 5.3\,\mathrm{eV}) + \mathrm{M}. \tag{17}$$

However, approximately one third of excimers are born on lower vibrational levels due to harpoon reaction

$$\mathrm{Kr^* + F_2 \longrightarrow KrF(B}, \epsilon_2^* \simeq 1.8\,\mathrm{eV}) + \mathrm{F}. \tag{18}$$

According to model A, reaction (18) gives no improvement in $\eta_{\rm st}$ in comparison with reaction (17). This would be valid if KrF excimers were to pass a vibrational energy interval of 3.5 eV without noticeable electronic deexcitation. At the same time, model C predicts that the values of $\eta_{\rm st}$ differ by a factor of $\left(\epsilon_1^*/\epsilon_2^*\right)^{\kappa} \simeq 1.4$. Thus, the dependence of $\eta_{\rm st}$ on ϵ^* should be taken into account if new type of pumping or active medium composition changes the percentage of the ionic recombination and harpoon reactions.

Thus, the prediction of the phenomenological model is unlikely to be correct under broad variation of the operating conditions.

The second analysed problem is that of the delay of pulse luminescence with respect to a pumping pulse. For simplicity, let us consider an instantaneous pumping process which produces excimers on high vibrational levels with the energy ϵ^* at the time $t = 0$. Due to vibrational transitions the lowest vibrational level will be populated at a later time with the maximum population at $t = t_{\rm d}$. The formulae for $t_{\rm d}$ obtained with different kinetic models are presented in Table 1.

Let us examine the experimental observation of the pulse luminescence of XeCl(B) in a 100 Torr Xe mixture [35]. In the experiment the XeCl(B, C) molecules were generated due to two-photon, laser–assisted reaction between Xe and $\mathrm{Cl_2}$. In this work XeCl(B, C) excimers were born on high vibrational levels with $\epsilon_v \simeq 1.2$ eV during a short (4–6 ns) time period. The spectral analysis of the XeCl($B - X$) emission from $v = 0$ to 3 vibrational levels was fulfilled to trace down the change of $T_{\rm v}$, the vibrational temperature of XeCl(B), with time. In a 100 Torr Xe mixture, the XeCl(B) excimers acquired the equilibrium vibrational distribution with $T_{\rm v} = 300$ K in 30–150 ns time interval, whereas the averaged $T_{\rm v}$ was found to be about 500 K for the full 0–150 ns time integration period.

Using the radiative lifetime and the quenching rate constants from [35] we calculate $\tau_{\rm u} = 14$ ns for the experimental mixture. In the framework of the Fokker–Planck model we can determine $\tau_{\rm v}/\tau_{\rm u} = 0.4$ from the measurement of $T_{\rm v} = 500$ K and Eq. (15). For the known $\epsilon^* = 1.2$ eV [35] we get $t_{\rm d} = 27$ ns. The observation of the pulse luminescence was fulfilled in [35] for the 0–30 and 30–150 ns time intervals. We hence conclude that the estimated time scale of the relaxation process, 27 ns, is in accord with the experimental one, 30 ns.

In the framework of the phenomenological model we can estimate $k_{\rm VT}(\mathrm{Xe}) > 5 \times 10^{-11}\ \mathrm{cm^3 s^{-1}}$ according to [23]. We then find that $\tau_{\rm v} < 5$ ns and $t_{\rm d} < 7$ ns for $\tau_{\rm u} = 14$ ns. The later value of $t_{\rm d}$ is four times shorter than the characteristic transient time 30 ns. Thus, the prediction of the phenomenological model is likely to be incorrect if one studies temporal relaxation processes.

The third analysed problem is a problem of the gain recovery in short-pulse laser amplifier. This problem relates to experimental data obtained with the pump–and–probe technique [42]. The measurements of the probe pulse amplification after the passage of saturating high intensity pulse was performed for XeCl [43,13], XeF [14], KrF [44,13,16], and ArF [45]. The recovery of the gain on a nanosecond time scale was found to be one–exponential for all these excimers.

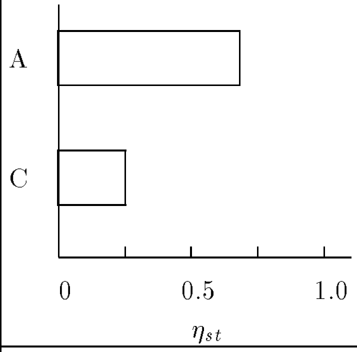
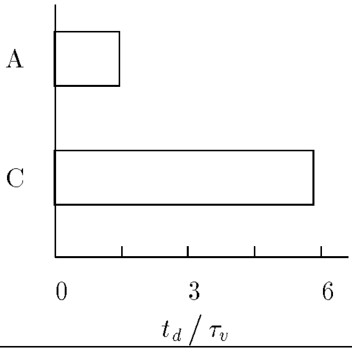
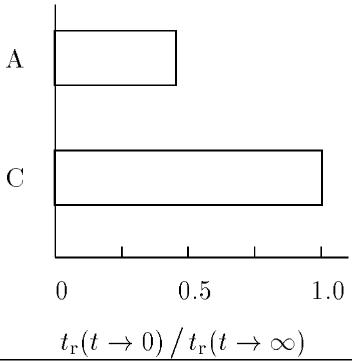
Value [a]	Model (A)	Model (C)	Bar Diagram [b]
$\eta_{\rm st}$	$\left(1+\frac{1}{\theta_0}\,\frac{\tau_{\rm v}}{\tau_{\rm u}}\right)^{-1}$	$\left(\frac{T}{\epsilon^*}\right)^{\frac{\tau_{\rm v}}{\tau_{\rm u}}}$ c)	
$t_{\rm d}$	$\tau_{\rm v}\ \ln\left(\frac{\tau_{\rm u}}{\tau_{\rm v}}+1\right)$	$\tau_{\rm v}\ \ln\left(\frac{\tau_{\rm u}}{\tau_{\rm v}}\ \frac{\epsilon^*}{T}\right)$	
$g(t)$	Eq. (20)	Eq. (19)	

Table 1. Comparison of the predictions of the phenomenological (A) and Fokker–Planck (C) relaxation models.

a) The parameter $\eta_{\rm st}$ is the ultimate quantum yield of stimulated emission, $t_{\rm d}$ is delay of the emission pulse with respect to the pumping pulse, and $g(t)$ is the law of the gain recovery, $t_{\rm r} \equiv 1\,/\,\frac{d}{dt}\ \ln\,[g_0 - g(t)]$;

b) Numerical data correspond to the characteristic values of $\tau_{\rm v} = 0.3\,\tau_{\rm u}$, $\epsilon^* = 100\,\hbar\omega$, $\epsilon_0 = \frac{1}{2}\,\hbar\omega$, and $\hbar\omega = T$;

c) More strict expression for $\eta_{\rm st}$ is $\eta^{\rm v}/G(\frac{\tau_{\rm v}}{\tau_{\rm u}}, 1; \frac{\epsilon_0}{T})$, where $\eta^{\rm v}$ is defined in the comment to Eq. (13), G is the degenerate hypergeometric functions of the second kind, ϵ_0 is an energy of the upper laser level.

This finding is in accord with the theoretical predictions of both the Fokker–Planck relaxation model [46] and the numerical code of [25]. According to the Fokker–Planck model, the law of the gain recovery is

$$g(t) = g_0 - \Delta g\ \exp\left(-\frac{t}{t_{\rm s}}\right), \qquad (19)$$

where g_0 is the stationary gain value, $g = g_0 - \Delta g$ at $t = 0$, and $t_{\rm s} = \tau_{\rm u}$. Although paper [25] applies phenomenological segregation of high and low vibrational levels, it takes into account populations of ten lowest vibrational levels of KrF(B) and KrF(C). In the framework of this relatively complete model, the dependence of $g(t)$ was found in the form of Eq. (19) with $t_{\rm s}$ independent of $\tau_{\rm v}$.

If one applies phenomenological equations (1) and (2), the following law of the gain recovery will readily be found:

$$g(t) = g_0 - \Delta g\left[\theta \exp\left(-\frac{t}{\tau_u}\right) + (1-\theta)\exp\left(-\frac{t}{\tau_v} - \frac{t}{\tau_u}\right)\right]. \tag{20}$$

The value of the parameter θ is about 0.6 if $\hbar\omega \simeq T$, which is the case for the XeCl excimers [48]. Thus, $\theta \simeq 1 - \theta$, and nanosecond gain dynamics should be two–exponential with one recovery time equaling to τ_v and the second one equal to τ_u. This conclusion is definitely in a qualitative disagreement with the wealth of experimental data.

According to Table 1, none of the analysed problems brings satisfactory agreement between the phenomenological (A) and the Fokker–Planck (C) relaxation models. Since the model C is in accord with other level–to–level relaxation models and multifarious experimental data [18], we conclude that a correct kinetic theory must define distribution of the molecules over a broad interval of vibrational levels [49].

IV. CONCLUSIONS

The modelers of the excimer lasers commonly used simple phenomenological approach for modeling vibrational relaxation of the excimers. This paper compares predictions of this approach with other kinetic theories and experimental data. The scope of the considered phenomena includes the reduction of the quantum yield of stimulated emission, the time delay between the pumping and emission pulses, the gain recovery after rapid depletion of the upper laser level. It is discovered that the phenomenological approach cannot describe the whole of these effects correctly. As to specialized calculation of the efficiency of excimer laser, the application of phenomenological model is likely to be mistaken under untypical experimental conditions.

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[49] There is an interesting consequence of the above conclusion. If one uses the phenomenological concept of vibrational relaxation, parameters of excimer electronic relaxation (quenching rate constants and radiative lifetimes) should, of course, be constant. However, if one takes into account the populations of many high vibrational levels, these constants are variables. The influence of vibrational relaxation on the parameters of electronic deexcitation of the excimers was studied elsewhere [47].

МОДЕЛЮВАННЯ КОЛИВНОЇ РЕЛАКСАЦІЇ В ЕКСИМЕРНИХ ЛАЗЕРАХ

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Проаналізовано способи моделювання коливальної релаксації галогенідів інертних газів в ексимерних лазерах. Проведено порівняння загальновідомого феноменологічного підходу з більш строгими моделями, які застосовують рівняння балансу для заселеностей енерґетичних рівнів або рівняння Фоккера–Планка. Обговорено умови застосування моделей, а також визначення кінетичних параметрів. До кола аналізованих ефектів увійшли квантовий вихід змушеного випромінювання, затримка часу між імпульсами збудження активного середовища та випромінювання світла, динаміка поновлення коефіцієнта підсилення світла після швидкого знищення оптично активних молекул. Принципові розбіжності моделей підкреслено за допомогою діяграм.