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Kinetic Modelling of Krypton Fluoride Laser Systems

Kenneth S. Jancaitis

(Ph.D. Thesis)

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LAWRENCE LIVERMORE NATIONAL LABORATORY
University of California • Livermore, California • 94550

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By

Kenneth Stephen Jancaitis

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Sumner P. Davis 12-23-82
Chair
Wm. B. Kruene 7-18-83
Date
Richard J. Saphaly 7-20-83

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Kenneth S. Jancaitis

Abstract

A kinetic model has been developed for the KrF* rare gas halide laser system, specifically for electron-beam pumped mixtures of krypton, fluorine, and either helium or argon. The excitation produced in the laser gas by the e-beam was calculated numerically using an algorithm checked by comparing the predicted ionization yields in the pure rare gases with their experimental values. The excitation of the laser media by multi-kilovolt X-rays was also modeled and shown to be similar to that produced by high energy electrons. A system of equations describing the transfer of the initial gas excitation into the laser upper level was assembled using reaction rate constants from both experiment and theory. A one-dimensional treatment of the interaction of the laser radiation with the gas was formulated which considered spontaneous and stimulated emission and absorption. The predictions of this model were in good agreement with the fluorescence signals and gain and absorption measured experimentally.

To gather input for this model, rare gas halide dimer and trimer fluorescence signals were studied using 50 ns 600 keV electron-beam excitation of binary mixtures of Ar or Kr combined with either F_2 , NF_3 , or SF_6 , and buffered mixtures containing Kr, F_2 , and either He, Ne, or Ar. A simple model was developed to analyze the data at both high and low (≤ 50 A/cm²) current densities, yielding estimates for the trimer radiative lifetimes and collisional quenching coefficients and the rate constants for the formation of the trimers.

The apparatus used to study rare gas halide fluorescence was converted into a laser cavity by placing mirrors inside the gas cell. With either helium or argon as the buffer gas the krypton and fluorine pressures yielding the maximum laser efficiency were determined for two values of the current density (160 and 430 A/cm²). The predictions of the laser kinetics model for these systems were compared to the experimental observations. Within the limits of the one-dimensional model good agreement was obtained over the range of parameters typical of laser operation.

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Chapter I

Introduction

A. Historical Perspective

The KrF* rare gas halide (RGH) laser is a member of a larger class of systems known as excimer lasers, which may be loosely defined as those lasers which operate on electronic molecular transitions having a repulsive lower state potential. Before we begin the detailed discussion of the physical principles which are relevant to excimer laser performance in general, and KrF* laser performance in particular, it will prove useful to present a brief outline of the events which have led to the current level of development and understanding of these systems. This will provide a backdrop to the understanding of both the physical problems involved and the place this thesis is meant to fill in the literature.

The history of excimer lasers may be said to have begun with the identification of the bound-free continuum radiations from the rare gas dimers and the development of lamps for their efficient production by Tanaka and Zelikoff in the 1950's.¹⁻³ The first suggestion that such transitions might be used to provide gain was made by Houtermans

in 1960,⁴ and is illustrated in Figure 1. Atoms which in their ground state interact along a repulsive potential are excited via a non-thermal mechanism to a level where their interaction is attractive, upon which they form a bound state. Provided there are no potential curve crossings from this bound complex to the ground level, it will decay primarily via radiation (if the transition is optically allowed). In this case, when the ground state curve is sufficiently repulsive (i.e. when $\Delta E \gg kT_g$, where ΔE is the energy of the decay product relative to the ground state atoms at infinite separation and T_g is the gas temperature) the radiative decay product will be rapidly dissociated and any problems with bottlenecking in the lower state eliminated.

The first efforts toward the development of an excimer laser sought to obtain gain using the $H_2(a^3\Sigma_g - b^3\Sigma_u)$ transition.⁴ The analysis of Palmer⁵ however indicated that competing processes would lead to absorption at the relevant wavelengths; later experimental work examining the 490 nm. fluorescence continuum in Hg also showed loss rather than gain.⁶ In 1971 Basov and coworkers finally constructed the first working excimer laser, obtaining gain at 171 nm. on the Xe_2^* continuum using liquid Xe pumped with an electron beam.⁷ Gas phase electron beam pumped rare gas dimer lasers were soon developed on the Ar_2^* , Kr_2^* and Xe_2^* excimer transitions, although the observed gains were much less than initially predicted from the fluorescence efficiencies measured under similar conditions.⁸⁻¹⁰

The concept of the excimer laser was extended to non-homonuclear systems in 1974 when lasing from the rare gas oxides ArO^* , KrO^* , and XeO^* between molecular levels corresponding to the oxygen $^1\text{S}_0 - ^1\text{D}_2$ auroral transition was demonstrated by Powell et. al.¹¹ An electron beam was again used to obtain energetic pumping of the laser medium. Gain was observed only after the excitation of the gas by the e-beam had ceased, while during the current pulse the medium acted as an absorber at the laser wavelength.

Bound-free emission from the rare gas halide dimers was first observed in the identification of the ArCl^* continuum by Golde and Thrush in 1974.¹² Fluorescence from other RGH dimers (XeF^* , XeCl^* , etc.) was soon reported, and the KrF^+ B-X emission observed and discussed by Brau and Ewing in 1975.¹³ Gain in RGH systems was obtained in the same year by both Searles and Hart (XeBr^*)¹⁴ and Brau and Ewing (XeF^*).¹⁵ The pumping thresholds for the RGH lasers were found to be significantly less than that for the previously demonstrated excimer lasers. The most promising of these systems was the KrF^* laser, for which medium efficiencies as high as 75% were reported.^{16,17}

Because of the volume scalability of the electron beam pumped RGH lasers, interest has been generated in their probable use as drivers for inertial confinement fusion systems.^{18,19} To this end, high power KrF^* lasers are currently under development at several laboratories.²⁰⁻²¹ Such systems have been designed to produce small-

signal gains on the order of $e^{10} - e^{15}$, with output energies of around 1 kilojoule in a pulse lasting on the order of 100 nanoseconds.

B. Physical Considerations

The development of excimer lasers as related in the previous section was hindered by the discovery of initially unexpected media absorptions and the relatively high pumping rates ($\geq 1\text{MW/cm}^3$) required to obtain gain. In this section we will discuss the physical properties of excimer lasers which result in these limitations. At the same time we will introduce terms and concepts which will be referred to in the following chapters.

We begin with a simple analysis of the excimer laser transition illustrated in Figure 1. The stimulated emission cross section as a function of frequency is given by

$$\sigma_s(\nu) = \frac{\lambda^2}{8\pi} \frac{1}{\tau_r} g(\nu) \quad (1)$$

where $\lambda=c/\nu$, τ_r is the radiative decay lifetime of the upper state, and $g(\nu)$ is the normalized lineshape factor ($\int g(\nu)d\nu=1$).²² At the laser wavelength, $g(\nu)$ is given approximately by $\Delta\nu^{-1}$, where $\Delta\nu$ is the width of the spontaneous emission spectrum. The magnitude of this

linewidth may be estimated according to the Frank Condon principle²³ as

$$h\Delta\nu = -V_L'(R_0)\Delta R_U \quad (2)$$

where $V_L'(R_0)$ is the radial derivative of the lower state potential evaluated at the equilibrium separation of the bound upper level and ΔR_U is the spatial extent of the upper state in its potential well.

We see from Eq. 2 that the width of the excimer emission continuum is directly proportional to the repulsive nature of the lower state potential, as measured by the force that the radiative decay product feels toward dissociation. Coupling this result with Eq. 1 we find that the steeply repulsive nature of the excimer lower state potential curves results in small values for the stimulated emission cross section (typically $10^{-18} - 10^{-16} \text{ cm}^2$), as compared with the values for bound-bound molecular ($10^{-17} - 10^{-14} \text{ cm}^2$) and allowed atomic transitions ($10^{-14} - 10^{-17} \text{ cm}^2$).

It is the low value of the stimulated emission cross section which mandates the high pumping powers required to obtain significant gain in excimer lasers, as can be shown via a simple analysis. In a steady-state system g_0 , the small-signal gain coefficient in the absence of medium absorptions is given by

$$g_0 = \sigma_s f N^* \quad (3)$$

where N^* is the excited state density and f is the fraction of the upper state molecules available to the laser transition (e.g. in KrF* the excited state density is believed to be divided equally between two levels [the B and C states], so for the B-X laser transition $f=.5$). The pumping power required to achieve the excited state density N^* is given by

$$P_D = \frac{N^* E'}{\tau_u \eta_B} \quad (4)$$

where τ_u is the effective lifetime of the upper state, E' is the average energy of the initial excitation produced in the laser medium by the pumping mechanism, and η_B is the branching ratio from the initial excitations to the laser upper state. Combining Eqs. 3 and 4 yields an estimate for the pumping power required to achieve a given gain:

$$P_D = (E'/\tau_u \eta_B f \sigma_s) g_0. \quad (5)$$

Inserting parameters corresponding to the KrF* system ($E' \approx 15$ eV, $\tau_u \approx 5$ ns., $\eta_B \approx 1$, $\sigma_s \approx 2.5 \times 10^{-16}$ cm²), we find that even ignoring any losses pumping on the order of .5 MW/cm³ would be necessary to reach a gain of 10% cm⁻¹. Similar calculations for the rare gas excimers and the rare gas oxides indicate that they would require on the order of 5 and 50 MW/cm³, respectively to achieve a similar value for g_0 .

The next point which must be noted is that the simple pumping

scheme implied by Figure 1 is not realized in actual excimer lasers. The energy deposited in the laser medium by the excitation mechanism generally passes through a number of intermediate states before it is transferred to the upper state of the laser transition. Taking the formation of KrF^* as an example, atomic ions (e.g. Kr^+ , F^-), excited atoms (e.g. Kr^* , Kr^{**}), dimer ions (e.g. Kr_2^+), and rare gas excimers (e.g. Kr_2^*) are just some of the precursors to the formation of the KrF^* dimer. The gas excitation is exchanged between these species through a series of two- and three-body chemical reactions, which require a gas pressure ≥ 1 atm. (which is in general provided by the addition of a lower-Z rare gas buffer) for the efficient formation of the lasing state.

We see by the arguments above that the operation of excimer lasers requires a pumping mechanism which can deliver $\geq 1 \text{ MW/cm}^3$ into a gas medium at pressures ≥ 1 atm. Historically, this was achieved with the development of high current density ($\geq 100 \text{ Amp/cm}^2$) electron beam sources, as was indicated in Section A. It is only for the RGH excimer lasers with their lower pumping thresholds that discharge pumping was subsequently found to be sufficient,^{24,25} albeit with lower medium efficiencies than demonstrated for e-beam pumped systems.

The simple picture presented in Figure 1 also fails in that it does not take into account any possible transitions leading to absorption at the laser wavelength. In reality, the chemical nature of the upper level formation introduces into the laser medium a number of states for which absorption of the laser photon via a

bound-continuum process is energetically possible (e.g. for the KrF^* system we have F^- , Kr_2^+ , Kr_2^* , etc.). Even the proposed laser upper state itself may prove to be a significant absorber, as has been suggested by Werner et. al. for the Xe_2^* excimer laser.²⁶ Finally, those excimers which are not destroyed by radiative means may produce through further chemical reactions species which also absorb at the laser wavelength.

Absorption in the laser medium has an additional influence on the performance of excimer lasers beyond the reduction of the net gain, In steady-state the gain coefficient for a driven laser in the absence of absorption is given by

$$g' = \frac{g_0}{1 + I/I_s} \quad (6)$$

where I is the local laser intensity and g_0 and I_s are defined by

$$g_0 = \sigma_s f N^* ; \quad I_s = h\nu / f \sigma_s \tau_u \quad (7)$$

where N^* and τ_u are the laser upper state density and lifetime, respectively, in the limit of vanishingly small laser intensity. When absorption is taken into account, the net gain coefficient becomes

$$g = \frac{g_0 - \gamma_0}{1 + I/I_s} - \gamma_n \quad (8)$$

where γ_0 is that portion of the total absorption coefficient stemming

from either the lasing state itself or its "descender s", defined as the saturable absorption; and γ_n is the non-saturable absorption caused by the precursors to the formation of the laser upper level.

The division of the loss into its saturable and non-saturable components has two consequences. The first is that the non-saturable loss limits the maximum intensity which can be passed through the laser to the value :

$$I_{\max} = I_s \left[\frac{g_0 - \gamma_0}{\gamma_n} - 1 \right] . \quad (9)$$

Secondly, it affects the local extraction efficiency Θ , defined as the ratio of the rate of the removal of the upper states by the laser field to their production rate

$$\Theta = \frac{1 \left\{ \frac{g_0 - \gamma_0}{1 + I/I_s} - \gamma_n \right\}}{(N^*/\tau_u) h \nu} = \frac{\frac{I}{I_s} \left\{ \frac{g_0 - \gamma_0}{1 + I/I_s} - \gamma_n \right\}}{g_0} . \quad (10)$$

Optimizing Θ as a function of the laser intensity, we find that the maximum extraction efficiency is given by

$$\Theta_{\max} = \left[\sqrt{1 - \frac{\gamma_0}{g_0}} - \sqrt{\frac{\gamma_n}{g_0}} \right]^2 . \quad (11)$$

In Figure 2 we show the dependence of $\Theta_{\max}$ on γ_{tot}/g_0 (where $\gamma_{\text{tot}} = \gamma_0 + \gamma_n$ is the total absorption coefficient) for several values of $\gamma_n/\gamma_{\text{tot}}$. The importance of determining the sources of the medium absorption to the construction of efficient high power excimer lasers

is indicated by examining the case $\gamma_{\text{tot}}/g_0 = .1$. For the situation where the losses are totally saturable we have $\theta_{\text{max}} = 90\%$; while for a scenario where the non-saturable absorption dominates, the maximum medium extraction efficiency is only 47%.

C. Outline

The purpose of this thesis, as indicated by its title, is to develop a kinetic model for the KrF* rare gas halide laser system. Specifically, we have chosen to analyze the behavior of electron beam pumped Kr - F₂ mixtures, buffered with either helium or argon. High energy ($\geq 1\text{keV}$) electron beams as opposed to gas discharges were selected as the excitation mechanism of interest both because of the scalability of e-beam pumped systems to high power and gain, and because of the simpler electron kinetics which applies in the former case. Helium and argon were picked as the buffer gases because they represent the extremes available, neon being an intermediate case displaying some of the behavior of each of the other two choices.

We begin the analysis in Chapter II with a discussion of the excitation of the laser media by high energy electrons. A technique known as the Fowler equation²⁷ is described which determines the distribution of the energy deposited by the e-beam over the various levels available to the gas atoms once a specification of the relevant energy levels is given along with the electron collisional cross sections for their formation from the ground state. Such a

specification is determined for each of the rare gases from helium through xenon, and the yields of the excited states in the pure rare gases resulting from e-beam pumping is calculated. The inverse ionization efficiencies (defined as the mean energy deposited per ion pair created) determined in this manner for the pure rare gases compare well with those measured experimentally. Finally, the excitation in two cases representative of krypton fluoride laser gas mixtures is calculated and the qualitative behavior of the variation of the excitation yields with gas mixture is discussed.

In Chapter III we digress slightly by developing a model for the calculation of the excitation of KrF* laser media by multi-kilovolt X-rays. We begin by describing how proposed second generation inertial confinement fusion systems may provide X-ray fluxes sufficient to pump high energy RGH lasers. This is followed by an analysis of the physical processes which dominate the transfer of the energy from the X-ray flux to the various gas excited levels. The chapter is concluded with a calculation of the excitation yields coming from kilovolt X-ray pumping of the representative KrF* laser mixtures described in Chapter II, along with a comparison of the results to those obtained for e-beam pumping. This comparison indicates that the excitation caused by high energy photons is very similar to that produced by high energy electrons, although the difference in the magnitudes of the X-ray and electron interaction cross sections means that the pumping in the former case generally takes place over much larger volumes.

In Chapter IV we treat the transfer of the primary excitation produced in the laser medium by the pumping mechanism into the laser upper state, and from thence into the laser output spectrum. The chemical nature of the krypton fluoride laser system requires that this transfer take place via a series of two- and three-body reactions in the laser gas. We therefore begin with an identification of the atomic and molecular species and the reaction processes relevant to the formation and destruction of the KrF^* dimer, along with an estimation of the rates at which these reactions proceed. We then continue with a discussion of the interaction between the laser radiation field and the laser gas, taking into account stimulated and spontaneous emission, along with medium absorption. All this information is combined in a one-dimensional model which integrates the laser kinetic equations taking into account the spatial, as well as temporal variations of the various quantities. Finally, the results from this model are compared with fluorescence signals and gain and absorption measurements determined from experiment.

In Chapter V we present the experimental work performed by the present author and Dr. H. T. Powell on the kinetics of the rare gas halide (RGH) dimer - trimer system. RGH dimer and trimer fluorescence signals were measured from e-beam excited mixtures of either Ar or Kr combined with either F_2 , NF_3 , or SF_6 , and also from buffered mixtures containing Kr and F_2 and either He, Ne, or Ar. A simple model is developed to analyze this data at both high and low ($\leq 50 \text{ Amp/cm}^2$) current densities. At low current densities this analysis results in

estimates for the RGH trimer radiative lifetimes, the rate coefficients for their destruction in collisions with heavy particles, and the rate constants for their formation from the corresponding RGH dimers. At higher current densities we find that electron quenching becomes the dominant factor in the trimer decay rate, although we have found no model which accurately predicts the magnitude of its effect.

The laser performance of electron beam pumped mixtures of Kr, F₂, and either He or Ar is studied in Chapter VI. The experimental setup described in Chapter V was converted into a laser cavity by the addition of U. V. laser mirrors into the gas cell. With either argon or helium as the buffer gas, the krypton and fluorine pressures yielding the maximum laser efficiency were determined for two values of the average current density (160 and 430 A/cm²). The laser kinetics model was then used to predict the output performance of the gas mixtures and laser configurations investigated experimentally. Finally, the successes and shortcomings of the present state of the model are discussed, and suggestions made for possible future improvement.

Fig. 1. Potential energy diagram illustrating the scheme of excimer laser excitation and decay.

Fig. 2. Maximum laser extraction efficiency vs loss to gain ratio plotted for several values of the relative nonsaturable loss coefficient.

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Chapter II

The Excitation of Krypton Fluoride Laser Media by High Energy Electrons

A. The Fowler Equation

The determination of the effectiveness of a high energy electron in pumping the krypton fluoride laser transition must include not only a specification of the amount of energy deposited in the gas by the electron, but also the detailed partitioning of this energy over the various levels of excitation available to the gas atoms. The first attempt at a solution to a problem of this type was made by R. H. Fowler in 1923, who sought to determine the total ionization produced by the passage of an alpha particle through a gas.¹ In recent years, Fowler's treatment has been extended to the calculation of the yield of all gas excitations produced during the stopping of high energy electrons. Other workers have developed alternate approaches to the solution of this same problem; among them Monte Carlo approximations,² the Spencer-Fano degradation spectrum technique,³ and the continuous slowing down approximation.⁴

Garvey and Green have compared several of these methods using a common set of cross sections for the excitation of H_2 .⁵ They

found that provided sufficient care was taken in the application of the various approximations all approaches yielded the same solution for the partitioning of the deposited energy. In addition, Inokuti et. al. have shown that the degradation spectrum of the Spencer-Fano equation is the universal adjoint to the solutions of the Fowler equation for the excitation yields.⁶ The method of solution is thus seen to be primarily a matter of individual preference. We have chosen the Fowler equation for reasons to be described below.

The Fowler equation approach calculates $J_k(E)$, the average yield of excitations of state k produced by the stopping of an electron of energy E . We have (Equation 1)

$$J_k(E) = p_k(E) + \sum_j p_j(E) J_k(E-E_j) + \sum_i \int_0^{(E-E_i)/2} p_i(E,T) [J_k(E-E_i-T) + J_k(T)] dT$$

In this equation the subscripts j label the excited states having excitation energies E_j and the subscripts i label the ionic states with ionization energies E_i ; the label k may refer to either an ionic or excited state. The "p's" are defined as follows: if $\sigma_j(E)$ ($\sigma_i(E)$) is the cross section for electron collisional excitation of the excited (ionic) state j (i) by an electron of energy E , and n_j (n_i) is the number density of ground state atoms or molecules which may produce state j (i) upon this collision we have

$$p_k(E) = n_k \sigma_k(E) / \left[\sum_j n_j \sigma_j + \sum_i n_i \sigma_i \right] \quad (2)$$

where the label k again may represent either an excited or ionic state. Similarly, if $\sigma_i(E,T)$ is the cross section for the production of an ionic state i along with a secondary electron of energy T upon collision of an electron of energy E with the ground state species having density n_i , then

$$p_i(E,T) = n_i \sigma_i(E,T) / \left[\sum_j n_j \sigma_j + \sum_i n_i \sigma_i \right] \quad (3)$$

The quantities $p_i(E)$ and $p_i(E,T)$ are related by

$$p_i(E) = \int_0^{(E-E_i)/2} p_i(E,T) dT \quad (4)$$

where the upper bound on the integral is a consequence of the convention that the electron of lower energy after the ionization is defined as the *secondary electron*.

Using Eq. 2 one can easily show that

$$\sum_j p_j(E) + \sum_i p_i(E) = 1 \quad (5)$$

Thus, in physical terms $p_j(E)$ is the probability that an electron of energy E will lose energy by producing the excited state j . A similar interpretation applies for both $p_i(E)$ and $p_i(E,T)$.

With this definition of the "p's" the meaning of each of the terms

on the right hand side of Eq. 1 becomes readily apparent. The first term is the number of excitations of state k that the primary electron produces directly at energy E ; The quantity $p_j(E)J_k(E-E_j)$ is the product of the probability that the electron will directly create an excited state j times the number of excitations of state k that it would subsequently produce in slowing down in the gas; the second term on the right of Eq. 1 sums these contributions to $J_k(E)$ over all excited states j . The integral over the secondary electron energy determines the contribution to $J_k(E)$ as a result of ionization collisions; the subsequent slow-down of both the primary electron and the secondaries which it produces have to be considered in this case.

The Fowler equation is solved for $J_k(E)$ upon noting that the energies at which $J_k(E)$ must be evaluated on the right hand side of Eq. 1 are all lower than the energy of interest on the left hand side. Using the initial condition that $J_k(E)$ is equal to zero for all $E < E_k$, Eq. 1 may then be iterated upward to an arbitrarily high primary electron energy.

Before proceeding with a description of the solution of the Fowler equation for the particular problem of interest, it will be useful to derive some general results which make this approach particularly attractive. It is a well known fact that for sufficiently high energy E , the ionization efficiency defined as $\Theta_i = J_i(E)/E$ approaches a constant value, equal to the inverse of W_i , the mean energy loss per ion pair created. Inokuti has shown that this behavior can be derived theoretically starting with the Fowler equation.⁷ In what follows

we extend his treatment to a description of the asymptotic behavior of the excitation efficiency $\Theta_k = J_k(E)/E$ for any state k , whether ionic or excited.

Following Inokuti's treatment we postulate that $J_k(E)$ may be well approximated (at least at high energies) as

$$J_k(E) = (E - U_k)/W_k \quad (6)$$

Inserting this approximation into Eq. 1, and using Eq. 4 results in

$$(E - U_k)/W_k = p_k(E) + \sum_j p_j(E)(E - E_j - U_k)/W_k + \sum_i p_i(E)(E - E_i - 2U_k)/W_k \quad (7)$$

Using Eq. 5, this may be manipulated to yield

$$W_k = \sum_j E_j p_j(E)/p_k(E) + \sum_i E_i p_i(E)/p_k(E) + U_k \sum_i p_i(E)/p_k(E) \quad (8)$$

Although W_k is not strictly a constant, the energy dependence of the various terms given by $p_j(E)/p_k(E)$ and $p_i(E)/p_k(E)$ becomes weak for sufficiently large electron energy E ($>1\text{keV}$). This is a result of the high energy behavior of the electron collisional cross sections.⁸ For sufficiently large energy for both ionization and optically allowed excited state transitions $\sigma_k(E)$ approaches the form

$$\sigma_k(E) \sim A_k \ln(E)/E \quad (9)$$

while for non-allowed transitions we have

$$\sigma_k(E) \sim A_k/E \quad (10)$$

asymptotically as E increases.

The evaluation of W_k still requires an estimate for U_k . Again paralleling the work of Inokuti, we note that while Eq. 6 may be an accurate approximation for $J_k(E)$ at high energies, it is obviously invalid at low energies, trivially so for $E < E_k$ where $J_k(E)$ is identically zero. Since the secondary electron spectrum for electron collisional ionization is typically peaked around $T=0$ with a width of a few times E_i ,⁹ we see that the substitution of Eq. 6 into Eq. 1 is valid at all positions except for the last term involving the excitation caused by the slow-down of the secondaries. Specifically, if the approximation of Eq. 6 is accurate only for E less than some energy Z_k the error introduced by its substitution in Eq. 1 is given by

$$D_k = \sum_i \int_0^{Z_k} p_i(E, T) [J_k(T) - (T - U_k)/W_k] dT \quad (11)$$

Setting $D_k=0$ leads to an estimate for U_k

$$U_k = \sum_i \int_0^{Z_k} p_i(E, T) [T - W_k J_k(T)] dT / \sum_i \int_0^{Z_k} p_i(E, T) dT \quad (12)$$

At sufficiently high primary electron energy, the shape of the

secondary electron energy distribution function becomes independent of E ,⁹ and U_k (as well as W_k) is then well represented by a constant.

While the argument above demonstrates that $J_k(E)$ must asymptotically approach the functional form of Eq. 6, equations 8 and 11 are in general too imprecise to be used for the evaluation of W_k and U_k . However, it does allow for a simplification of the solution to the Fowler equation in that rather than iterating Eq. 1 all the way to the energy of interest, we need only proceed to sufficiently large energy to obtain accurate estimates of W_k and U_k .

The solution of the Fowler equation strictly applies to the excitation produced in the case where the primary electron, as well as all secondaries it produces, stop in the gas. However, because the secondary electron energies are typically much smaller than that of the primary, there often exist cases where while the primary electron proceeds through the gas, the secondaries that it creates stop in it. When this is the case, we have that the excitation yields generated in the gas by a primary whose energy is degraded from E_i to E_f is given by

$$J_k(E_i, E_f) = J_k(E_i) - J_k(E_f) \quad (13)$$

Furthermore, if E_f is large enough, we may use Eq. 6, in which case $J_k(E_i, E_f) = (E_i - E_f)/W_k$.

B. Electron Collisional Excitation and Ionization Cross Sections

The first step in proceeding towards a solution of the Fowler equation for the excitation yields is the specification of the excited and ionic states which are important in the stopping of electrons in the gas mixture of interest. In addition, the electron collisional cross sections for excitation of these states are required in order to determine the excitation probabilities $p_k(E)$.

Collections of inelastic electron collisional cross section data have been compiled and utilized by numerous workers in the study of electron slow-down in some of the lighter rare gases.¹⁰⁻¹⁶ Such data sets range in complexity and accuracy, and are generally a combination of experimental measurement, empirical approximation, and theoretical extrapolation. In the selection of the cross sections for this work, we attempted to survey all of the relevant literature to come up with the most consistent and accurate approximations.

The krypton cross sections for the effective levels listed in Table I were taken from the collection gathered by Hyde and Roberts.¹⁰ The ionization cross section was taken from Rapp and Golden¹⁷ while the secondary electron energy distribution is that of Green and Sawada.⁹ For the allowed transitions the empirical cross

sections of Ganas and Green were used.¹⁸ The cross section for the forbidden 4p - 5p transition was assumed to be of the form

$$\sigma_k(E) = A_k(1-E_k/E)/E . \quad (14)$$

Hyde and Roberts determined the magnitude of A_k by requiring that the solution of the Fowler equation using their cross section data for a pure krypton gas yield the experimentally determined value for the mean energy deposited per ion pair.

For argon we chose to use the empirical cross sections of Peterson and Allen,¹¹ who considered ionization from both the argon M- and L-shells as well as the optically allowed and forbidden transitions of the 3p electron. Their ionization cross sections, secondary electron energy distributions, and composite forbidden transition cross section (identified as 3p $\rightarrow$ 4p) were used as given. For the allowed excited state transitions we have followed Hyde and Roberts in consolidating the levels of Peterson and Allen into the effective levels listed in Table II.¹⁰ In addition, we fitted the high energy end of the optically allowed cross sections to the proper functional form of Eq. 9.

For neon, the excited and ionic states considered are presented in Table III. The ionization cross sections, secondary electron energy distribution functions, and dipole allowed excitation cross sections were taken from the collection gathered by Soong.¹³ As for

krypton, we included the forbidden $2p \rightarrow 3p$ transition, for which we used the cross section assumed by Hyde and Roberts, which has the energy dependence of Eq. 14.¹⁰

Though several collections of inelastic cross section data for helium exist,¹⁴⁻¹⁶ we singled out no one source in making our selection of the relevant helium excited states and the cross sections for their production. The levels used in our treatment of the electron slowdown in helium are presented in Table IV along with the sources of the inelastic cross section data for transitions to these states. Figures 1-5 show the helium inelastic cross sections used in this work. At high energies the cross section for the forbidden singlet - triplet transition was assumed to be of the form

$$\sigma_k = A_k/E_k^{n_k} \quad (15)$$

(Ref. 28) where A_k and n_k were determined by fitting to the experimentally determined cross sections at the highest energies.

C. The Numerical Solution of the Fowler Equation

The numerical solution of the Fowler equation begins with the choice of a mesh of energy points E_n , followed by the evaluation of $p_k(E)$ and $p_i(E,T)$ on this mesh, and concludes with the estimation of the various $J_k(E)$ at each of the mesh points. Below we shall

discuss the method of solution, and give the results for a few gas mixtures of interest.

One complication which becomes immediately apparent in finding the solution to this equation is a result of the fact that it is solved in a iterative manner, proceeding to ever higher values of the electron energy. Any errors present in the solution for $J_k(E)$ at small energies propagate through the iteration procedure. An accurate solution at large values of the electron energy requires that particular attention be paid to the solution close to threshold. This in turn requires the energy mesh to be sufficiently "fine" at the lowest relevant energies.

Computationally, however, there are two reasons why we would like to make the mesh as coarse as possible. First, a coarse mesh requires fewer evaluations of $J_k(E)$ to reach a given value of the electron energy. More important is the fact that in order to calculate $J_k(E)$ the values of all the "p's" are required at all mesh points E_n such that $E_n \leq E$, along with all of the parameters required to specify the secondary electron energy distribution functions at the primary energies E_n . A mesh which is too fine places unacceptable storage requirements on the storage capacity of the computer chosen to carry out the solution, as well as making such a solution prohibitively expensive in terms of computer time.

We see in this way that the solution of the Fowler equation

requires a compromise between accuracy and expediency. The prescription which was chosen for the solution of this problem is as follows. The energy mesh was started at an energy E_1 , which was less than the excitation energy of any of the states of interest. The mesh was then extended by the relation $E_{n+1} = (1+\alpha)E_n$, which continued until the mesh size $E_{n+1} - E_n$ was greater than $\epsilon/(1+\alpha)$. From this point on, the mesh was continued by setting $E_{n+1} = E_n + \epsilon$. In practice, the choice $E_1 = 8.00$ eV, $\alpha = .015$, $\epsilon = 4.00$ eV was found to be sufficient for an accurate solution of $J_k(E)$; further decreasing any of these parameters had a negligible effect on the solution.

Once the mesh was chosen, and the various $p_k(E)$ and secondary electron energy distribution parameters were calculated on this mesh, the solution required two final components: a method for the evaluation of $J_k(E)$ at an arbitrary energy E , and a technique for the integration of $J_k(E)$ over the primary and secondary electron energy distributions resulting from ionization. For the former, a quadratic interpolation scheme was found sufficient; for the latter a four-point integration scheme was chosen.

The actual solution of the Fowler equation was calculated using two computer programs. The first, CROSS, generated the energy mesh and evaluated the cross sections σ_k and secondary electron distribution function parameters for all states k at all the grid points. The program STOPPER then used this data to calculate $J_k(E)$, given the relative densities of the various gas components, and fitted

the solutions at high energy to the form of Eq. 6. A listing of both of these programs is presented in the microfiche at the end of this thesis.

(At this point, the reader may have noticed that the above two programs allow the inclusion of a xenon component in the gas mixture, and includes cross sections for the excitation of various xenon states. The state selection and cross sections for xenon were taken from the work of Hyde and Roberts,¹⁰ and were included as a matter of completeness. In KrF* laser media, xenon is an unwanted impurity however, and no calculations involving xenon as a gas component will be presented in this thesis.)

A typical example of the behavior of the energy dependence of the numerical solution of the Fowler equation is shown in Fig. 6. At first, as the electron energy increases above the threshold for the state of interest, $\Theta_k(E)$ (defined as $J_k(E)/E$) decreases as additional channels for electron energy loss come into play. When the electron energy equals $E_k + E_i$ where E_i is the ionization energy of any of the gas atoms, $\Theta_k(E)$ rapidly increases as excitation of the state k by post ionization electrons becomes possible. Finally, as the energy continues to increase, the fluctuations in $\Theta_k(E)$ damp out as it approaches its high energy form $(1 - U_k/E)/W_k$.

The high energy solution of the Fowler equation is contained in the values of U_k and W_k . These are presented in Table V for the

pure rare gases, and in Tables VI and VII for two gas mixtures representative of krypton fluoride laser mixes. For the pure rare gases the calculated values of W_i are of good agreement with the experimentally determined values of the mean energy loss per ion pair created by a high energy electron (46 eV for He, 37 eV for Ne, 26 eV for Ar and 24 eV for Kr).²⁹ For neon and krypton this is not surprising as the magnitudes of the forbidden $p \rightarrow p$ cross sections were chosen by requiring this to be the case. Although the calculated value for argon initially appears too large, when the Auger decay of the Ar L-shell ion is taken into account along with the subsequent excitation of the gas by the Auger electron, it decreases to 27.1 eV, more in line with the experimental value.

D. Discussion

The solutions of the Fowler equation contained in Tables V through VII illustrate the fundamental difference between determining the effect of the passage through a gas of a high energy electron on the electron, and determining the effect of the high energy electron on the gas. At energies above 1 keV the primary energy loss process for the electron is ionization. Not only does the ionization cross section greatly exceed that for excitation (by a factor of 5 - 10 in the pure rare gases), but the average energy loss per ionizing collision is several times that lost in creating an excited gas atom. The values of W_k in Table V indicate however, that the number of excited states the high energy electron produces in the gas is

typically one half the yield of ions.

This difference can be understood when one realizes that the energy lost by the primary electron in creating an ion is divided roughly equally between the ion and the secondary electron created. Because the secondary electron energy distribution is peaked at low energies, a significant fraction of these secondary electrons have insufficient energy to cause additional ionization, but are energetic enough to create a gas excited state. It is these secondary electrons which demand the complicated "bookkeeping" of the Fowler equation for the correct evaluation of the character of the gas excitation.

With this point in mind, the qualitative behavior of the variation of the W_k with gas mixture shown in Tables VI and VII can be explained. Comparing Tables V and VI, we see that while the addition of a small quantity of krypton ($\approx 6.7\%$) to argon has only a slight effect on the distribution of the excitation over the argon excited and ionic states, the number of krypton excited states produced now exceeds the number of krypton ions. This is a consequence of the fact that while the lowest krypton excited levels are still the lowest levels in the gas, the krypton ionization cross section must now compete with the excitation cross sections of argon for its share of the secondary electron spectrum. This results in a reduction in the number of krypton ions formed relative to the number of krypton excited states.

Finally we note that in mixtures of the rare gases, the higher- Z component of the gas mix receives a larger proportion of the total excitation than is indicated by its concentration. This is illustrated in Table VII, which indicates that although the ratio of the krypton and helium atomic densities is less than 1%, greater than 25% of the gas excitation (defined as the sum of the ionic and excited state densities) lies in krypton excitation. This is a result of two facts. First, both the cross sections for excitation and ionization by electrons increase with increasing Z . More importantly, however, the thresholds for excitation and ionization are lower for the higher- Z states, which are therefore accessible to a greater fraction of the secondary electron spectrum.

Table I

Krypton Energy Levels Used in Electron Slowdown

5s	9.98 eV
5p	11.47 eV
4d, 6s	12.2 eV
Higher Neutral	12.85 ev
Ion	14.00 ev

TABLE II

Argon Energy Levels Used in Electron Slowdown

4s	11.76 eV
4p	13.0 eV
3d, 5s	14.1 eV
4d, 6s	14.96 eV
Higher Neutral	15.4 eV
Ion (M-shell)	15.76 eV
Ion (L-shell)	250. ev

Table III

Neon Energy Levels Used in Electron Slowdown

3s	16.70 eV
3p	18.64 eV
3d,4s,5s	20.10 eV
Higher Neutral	21.21 eV
Ion (L-shell)	21.60 eV
Ion (K-shell)	870. eV

Table IV

Helium Energy Levels Used in Electron Slowdown

Source of inelastic cross section data		
2^3S	19.82 eV	(Ref 19,20,21,22)
2^1S	20.615 eV	(Ref 19,21,23,24,25)
2^3P	20.96 eV	(Ref 19,21,22,26)
2^1P	21.22 eV	(Ref. 24,26)
Ion	24.59 eV	(Ref 9,17,27)

Table V

Asymptotic Solution of the Fowler Equation for
Electron Energy Deposition in the Rare Gases

Helium

	U_k (eV)	W_k (eV)
He 2^3S	-32.4	691.
He 2^1S	-63.3	747.
He 2^3P	-47.8	1,500.
He 2^1P	-22.3	119.
He Ion	16.1	42.6

Neon

	U_k (eV)	W_k (eV)
Ne 3s	-20.2	174.
Ne 3p	-45.4	194.
Ne 3d,4s,5s	-18.7	818.
Ne Higher Neutral	-22.4	1,730.
Ne Ion (M-shell)	1.10	36.8
Ne Ion (L-shell)	---	5,170.

Table V (continued)

Asymptotic Solution of the Fowler Equation for
Electron Energy Deposition in the Rare Gases

Argon

	U_k (eV)	W_k (eV)
Ar 4s	-53.6	165.
Ar 4p	-78.5	182.
Ar 3d,5s	-46.2	372.
Ar 4d,6s	-42.2	1,240.
Ar Higher Neutral	-40.1	330.
Ar Ion (M-shell)	-29.3	29.4
Ar Ion (L-shell)	532.	3,180.

Krypton

	U_k (eV)	W_k (eV)
Kr 5s	-8.97	111.
Kr 5p	-63.2	208.
Kr 4d,6s	-33.9	217.
Kr Higher Neutral	-56.4	206.
Kr Ion	23.0	24.7

Table VI

Asymptotic Solution of the Fowler Equation for Electron
Energy Deposition in a 15/1 Ar/Kr Gas Mixture

Argon

	U_k (eV)	W_k (eV)
Ar 4s	-52.5	246.
Ar 4p	-80.1	227.
Ar 3d,5s	-44.2	405.
Ar 4d,6s	-40.2	1,340.
Ar Higher Neutral	-38.2	357.
Ar Ion (M-shell)	-27.1	31.7
Ar Ion (L-shell)	534.	3,410.

Krypton

	U_k (eV)	W_k (eV)
Kr 5s	-46.4	247.
Kr 5p	-60.2	851.
Kr 4d,6s	-54.4	1,500.
Kr Higher Neutral	-68.2	1,820.
Kr Ion	-10.3	330.

Table VII

Asymptotic Solution of the Fowler Equation for Electron
Energy Deposition in a 116/1 He/Kr Gas Mixture

Helium

	U_k (eV)	W_k (eV)
He 2^3S	-37.1	1,800.
He 2^1S	-67.7	866.
He 2^3P	-51.2	1,760.
He 2^1P	-22.0	130.
He Ion	17.3	45.2

Krypton

	U_k (eV)	W_k (eV)
Kr 5s	-17.7	272.
Kr 5p	-23.8	529.
Kr 4d,6s	-22.2	833.
Kr Higher Neutral	-26.7	833.
Kr Ion	-4.19	272.

Fig. 1. Cross section vs electron energy for excitation of helium to the $\text{He } 2^3\text{S}$ state assumed for the solution of the Fowler equation

Fig. 2. Cross section vs electron energy for excitation of helium to the $\text{He } 2^1S$ state assumed for the solution of the Fowler equation

Fig. 3. Cross section vs electron energy for excitation of helium to the $\text{He } 2^3P$ state assumed for the solution of the Fowler equation

Fig. 4. Cross section vs electron energy for excitation of helium to the $\text{He } 2^1P$ state assumed for the solution of the Fowler equation

Fig. 5. Cross section vs electron energy for excitation of helium to the He ionic state assumed for the solution of the Fowler equation

Fig. 6. Results of a Fowler equation calculation of the specific yield of $\text{He } 2^3\text{S}$ states produced vs. electron energy by the slowing down of an electron in a pure helium gas. The solid line is the numerical solution; the dashed line is the fit to this solution at high energy described in the text.

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Chapter III

The Excitation of Krypton Fluoride

Laser Media by Kilovolt X-rays

A. Introduction

Krypton fluoride lasers constructed to date have depended on the excitation of the laser media by electrons, either in a discharge or via high energy electron beam pumping. With the advent of the inertial confinement fusion (ICF) program however, interest has grown in the possibility of pumping such lasers directly with the output of a fusion microexplosion. *Bypassing the conversion of the fusion output to electrical energy would reduce both the recirculating fraction of the plant energy required to power the laser and the capital cost of plant construction.*

Most of the direct pumping proposals so far have focussed on the excitation of the laser by neutrons, relying on the fact that the bulk of the energy from a first generation ICF plant driven by the D-T fusion reaction would reside in 14 MeV neutrons.^{1,2} The low value of the neutron reaction cross sections for most materials however necessitates the doping of the laser medium with a suitable neutron

absorber (e. g. boron or uranium) in high concentrations, which invariably degrade the laser performance.

Work done on possible second generation ICF power plants (specifically those which would burn "isotopically self sufficient" fuel pellets, requiring no tritium breeding in the reactor walls³) has indicated that a significant fraction of the fusion energy in such plants could reside in multi-kilovolt X-rays. Such schemes require the compression of the fusion fuel to a ρr product (defined as the product of the fuel density and the characteristic pellet length at the time the fusion reaction takes place) of $\geq 5 \text{ gm/cm}^2$. At these high values of ρr a significant fraction of the fusion neutron energy would redeposit in the fusion plasma. More importantly, however, such high values of ρr would require the bremsstrahlung photons generated in the pellet to undergo multiple inverse Compton scatterings with the thermal electrons, by which they would be rapidly amplified in energy to a value just below that of the electrons (typically somewhere in the 20 - 60 keV energy range). Adjustment of the bremsstrahlung yield by doping the fusion fuel with high-Z materials could lead to as much as 30% of the fusion energy leaving the plasma as multi-kilovolt X-rays.

In Figure 1 we present the time-integrated X-ray yield calculated in the computer simulation of the burn of such a high ρr pellet.⁴ The spectrum is dominated by two peaks, at X-ray energies of about 1 and 40 keV. The low energy peak is due to the thermal bremsstrahlung

emitted during the expansion and cooling of the fuel plasma; the high energy peak comes from the Compton-hardened bremsstrahlung spectrum described in the preceeding paragraph.

In what follows we will first describe the physical processes which we believe to be important in the excitation of rare gas mixtures by kilovolt X-rays. This will be followed by a description of the computational techniques used to calculate the effect of an X-ray flux on specific gas mixtures. It will be demonstrated that in many ways the pumping of krypton fluoride laser media by kilovolt X-rays is similar to their pumping by kilovolt electrons.

B. Physical Processes

The dominant interaction of X-rays in the energy range of interest (1 - 100 keV) in the higher-Z rare gases (i. e., other than helium) is by photoionization. The qualitative behavior of the interaction is displayed in Fig. 2, showing the variation of the total photon interaction cross section of krypton as a function of the X-ray energy.⁵ As the photon energy increases the ionization of more tightly bound electron shells becomes possible, leading to discontinuous jumps in the total cross section (K-edge, L-edges, etc.). Between the edges the cross section decreases inversely as the third power of the photon energy, characteristic of the photoionization process.⁶

Due to the rapid decrease in the photoionization cross section with decreasing atomic number, additional processes must be taken into account when considering the interaction of the X-ray spectrum with helium. As Fig. 3 indicates, photoionization, incoherent scattering, and coherent scattering (scattering the photon with no energy loss) all contribute to the total interaction cross section⁵

Returning to the heavier rare gases ($Z > 2$), after photoionization the energy initially present in the X-ray is shared between the ion and the ionization electron. The fraction of the energy residing in the ion is not necessarily negligible, especially for the inner shells of the heavier gases. A 30 keV X-ray will interact with krypton primarily through the creation of a K-shell ion with an energy of 14.3 keV or about 48% of the energy of the incident X-ray.

The inner shell hole resulting from a photoionization event can decay via either of two modes, fluorescence or the ejection of an Auger electron. For the lower- Z ions, and for the outer shells of the higher- Z atoms, Auger decay dominates; for the high- Z inner shell holes the fluorescence probabilities are appreciable (e. g., the probability of the decay of the krypton K-shell ion via fluorescence is $\approx 65\%$).⁷ The fluorescence photons produced in this fashion propagate through the gas forming an additional contribution to the total X-ray flux seen by the medium.

The decay of the inner shell ion, beginning with the initial fluorescence or Auger event, rapidly continues via either additional Auger emission or by shakeoff of outer shell electrons. The cascade continues downward in energy until a stable charge state configuration is reached. The final configurations resulting from the excitation of a given initial hole have been measured and calculated.

At this point the energy originally present in the incident X-ray resides in multiply charged gas ions, and in the electrons produced as a result of the initial ionization and decay of the inner shell holes. The multiply charged ions themselves decay via charge stripping reactions with the neutral gas atoms, converting in the process a fraction of their energy into gas thermal energy. We estimate that the cross section for a reaction of the form

(where X and Y represent any of the rare gases, e. g. Ne, Ar, etc.) has a value proportional to the square of the interatomic radius at which the potential curves for the initial and final states cross, i. e.:

$$\sigma \propto R^2 \propto \left\{ \frac{n-1}{E_n} \right\}^2 \quad (2)$$

where E_n is the ionization potential of the $X^{(n-1)+}$ atomic state.¹³ With this assumption the distribution of singly charged

states resulting from the decay of the multiply-charged ions may be determined. This crude model for the charge exchange process is mitigated by the fact that in most of the cases of interest $\leq 1\%$ of the initial X-ray energy finds its way into multiply charged ions, as will be demonstrated in Section C.

The final step in the excitation of the gas by the X-ray flux is the degradation of the electrons produced in the various processes described above. In this we are aided by the fact that most of the electron energy resides in high energy electrons, and that the average electron energy is typically > 1 keV. In this case the excitation of the gas by the electrons may be calculated using the high energy solutions of the Fowler equation for the gas mix of interest as described in Chapter II.

C. Numerical Solution of the X-ray Deposition Problem

The determination of the gas excitation produced by an incident X-ray flux requires first and foremost a method for calculating the spatial transport of the X-ray spectrum. This was accomplished using the TARTNP photonics code, developed at LLNL.¹⁴ Given the definition of the problem geometry (including the material composition) and an incident X-ray flux, the TARTNP program uses a Monte Carlo approach to propagate the photons, both incident and generated by fluorescence, taking into account coherent and incoherent

scattering and photoionization. The output of this program is a spatially dependent reaction spectrum, giving the number of photons of each energy which react in each problem zone.

The program XRAYDEP (presented in the microfiche at the end of this thesis) uses this reaction spectrum to calculate the spatially dependent gas excitation, according to the prescription of Section B. In addition to the X-ray interaction data, and the inner shell vacancy cascade data described above the construction of this program made use of literature values for the energies of the various multiply charged ions.^{15,16} In order to determine the excitation of the gas produced by the high energy electrons, XRAYDEP also requires the results of a STOPPER calculation (described in Chapter II) for the asymptotic solutions of the Fowler equation for the gas mix in the zone of interest. In calculating the spatially dependent gas excitation, XRAYDEP assumes that the electrons deposit all their energy locally, which is reasonable as the electron ranges at the energies of interest are much shorter than those of the X-rays.

The solution for the deposition in a realistic ICF geometry is well beyond the scope of this thesis. The more important results of such a calculation may be equally well demonstrated in the solution of a simpler problem. To this end we chose the geometry shown in Fig. 4. A monoenergetic 30 keV X-ray source was assumed incident on a 1 meter long, 1 meter diameter 50 Torr krypton, 750 Torr argon gas mixture. The X-ray flux of 7.8×10^{15} per cm^2 is typical of what

might be found at the inner wall of a second generation ICF reaction chamber.

In this geometry we specified as a "typical" region a 10 cm. long, 10 cm. diameter cylinder at the center of the gas volume; all results quoted are for this region. The disposition of the gas excitation at various points in the calculation is presented in Tables I and II. In Table I, we note that the energy present in multiply charged ions is $\approx 1\%$ of the total deposited, and that the average electron energy is 3.13 keV, justifying the approximations for the fate of these energies described in the preceding section.

The excitation of the gas produced by the X-rays may be converted into a set of W_k similar to those calculated for electron excitation by dividing the results of Table II by the total X-ray energy deposited; these values are shown in Table III. Comparing this Table to Table VI in Chapter II we see that the yields of the various states produced by X-ray and high energy electron excitation are quite similar.

There is, however, one caveat which should be made before taking such a similarity too seriously. The difference in the magnitude of the X-ray and electron interaction cross sections means that both the local magnitude and the spatial variation of the energy deposition will be different for the two modes of pumping. Pumping with X-rays generally takes place over larger volumes, and allows a larger energy flux without overdriving the laser medium.

Table I

Energy Deposition in a 50 Torr Kr, 750 Torr Ar
Gas Mixture by 30 keV X-rays

Initially...

Energy deposited by X-rays	$1.74 \times 10^{18} \text{ eV/cm}^3$
Energy loss due to fluorescence	$0.07 \times 10^{18} \text{ eV/cm}^3$
Net energy deposition	$1.67 \times 10^{18} \text{ eV/cm}^3$

After the decay of the inner shell holes...

Energy in multiply charged ions	$1.97 \times 10^{16} \text{ eV/cm}^3$
Total energy in electrons	$1.65 \times 10^{18} \text{ eV/cm}^3$
Average electron energy	3.13 keV

Table II

Excitation of a 50 Torr Kr, 750 Torr Ar
Mixture by 30 keV X-rays

Excited State and Ion Densities

Argon	(#/cm ³)
Ar 4s	7.16×10^{15}
Ar 4p	7.81×10^{16}
Ar 3d,5s	4.34×10^{15}
Ar 4d,6s	1.31×10^{15}
Ar Higher Neutral	4.92×10^{15}
Ar Ion (M-shell)	5.65×10^{16}
Krypton	(#/cm ³)
Kr 5s	7.14×10^{15}
Kr 5p	2.07×10^{15}
Kr 4d,6s	1.17×10^{15}
Kr Higher Neutral	9.74×10^{14}
Kr Ion	5.41×10^{15}

Table III

Effective Values of W_k for the Excitation of a
50 Torr Kr, 750 Torr Ar Gas Mixture with 30 keV X-rays

Argon	W_k (eV)
Ar 4s	233.
Ar 4p	213.
Ar 3d,5s	384.
Ar 4d,6s	1,274.
Ar Higher Neutral	339.
Ar Ion (M-shell)	29.5
Krypton	W_k (eV)
Kr 5s	234.
Kr 5p	804.
Kr 4d,6s	1,420.
Kr Higher Neutral	1,710
Kr Ion	308.

Fig. 1. X-ray energy spectrum calculated by the computer simulation of the burn of a high *pr* ICF fuel pellet⁵

Fig. 2. Total photon interaction cross section of krypton vs. photon energy.⁴

Fig. 3. Helium X-ray scattering cross sections vs photon energy: T - total cross section, I - incoherent cross section, P - photoionization cross section, C - coherent cross section

Fig. 4. X-ray gas excitation geometry chosen for the illustration of the solution of the energy deposition. The X-ray flux ($7.85 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$, 30 keV) is incident on a 1 meter long, 1 meter diameter cylinder containing a 50 Torr Kr, 750 Torr Ar gas mixture. The reference volume is a 10 cm. long, 10 cm. diameter cylinder in the middle of the gas; all results quoted in the text refer to the deposition in this volume.

References - Chapter III

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Chapter IV

Krypton Fluoride Laser Kinetics

A. Introduction

The two previous chapters have shown how the energy of the laser driving mechanism (either high energy electrons or multi-kilovolt X-rays) is transferred to the laser medium in the form of ions, excited gas atoms, gas thermal energy, and sub-excitation (i.e. with an average energy which is below the lowest excitation energy of the ground state gas atoms) electrons. We now determine how this initial gas excitation is channeled into the laser upper state and then into the laser output spectrum.

The chemical nature of the KrF^* excimer laser system, described in Chapter I, requires that the initial gas excitation pass into the KrF^* upper state through a series of two- and three-particle reactions. In Section B we identify the atomic and molecular species and the reaction processes relevant to a description of the formation and destruction kinetics for the KrF^* excimer. The rates at which these reactions take place are estimated, and the approximations utilized in the construction of the kinetic model are discussed.

The interaction between the radiation field and the gas components is the last step in the conversion of the energy of the driver into laser energy, and is treated in Section C. The bound-free nature of the radiative transitions typical of excimer lasers leads to a unique spectral line shape which is a function of the gas temperature. In addition to stimulated and spontaneous emission, absorption of the laser photons by the gas medium must be considered in the determination of the laser efficiency.

The numerical methods used to integrate the laser kinetic equations are presented in Section D. Not only the time dependence of the various quantities, but also the spatial variations caused by the propagation of the laser beam must be taken into account. Finally, the solution of the kinetics problem for some simple cases are computed and compared with experiment.

B. Particle Kinetics

Excited atoms, atomic ions, dimer and trimer molecular excimers and ions, and electrons all play important roles in the formation and destruction of the KrF^* upper state, each to varying degrees according to the composition of the laser medium and the strength of the excitation source. In Table I we present a list of the species which we have determined are relevant to the description of the particle kinetics in electron-beam (or X-ray) excited mixtures of helium, argon, krypton, and fluorine, along with the energies of each of these

states relative to their unexcited gas components. For argon we have assumed that the more energetic excited states (e.g. Ar 3d,5s) created in the gas by the high energy electrons (both directly and indirectly) rapidly cascade down in energy to the Ar 4p level, in line with other treatments of rare gas kinetics.^{1,2} A similar rate has been assigned to the krypton excited states above the 5p level. In both cases the energy released in the cascade is presumed to convert rapidly into gas thermal energy.

Table II is a list of the gas reactions considered in the model for the krypton fluoride laser kinetics. Comparison of the various reaction rates under typical operating conditions (e.g. a 750 torr Ar, 100 torr Kr, 5 torr F₂ gas mixture with an energy deposition of .5 MW/cm³ from a high energy e-beam) indicates that the excitation initially present in the excited gas atoms and ions is converted with $\geq 90\%$ efficiency into the KrF* upper state. The energy conversion efficiency is typically 20-30%, resulting from the disparity in the energies of the atomic states and the KrF* excimer. This high conversion efficiency does not however allow the details of the formation kinetics to be ignored. Many of the precursors to the formation of KrF* (e.g. Kr₂⁺, Ar₂⁺, etc.) have significant photabsorption cross sections at the laser wavelength (248 nm.) as will be discussed in Section C. The particular path which the excitation takes to reach the KrF* upper state thus affects the net gain coefficient of the gas medium. Similarly, the post-KrF* formation

kinetics must be followed as the products of the upper state destruction can also be strong absorbers (e.g. Kr_2F^*).

While many of the reaction rates listed in Table II have been determined experimentally, others have been estimated using various theoretical approximations. A full description of the kinetics model therefore requires in addition to the Tables a discussion of the assumptions which went into their construction. This information is presented in the following paragraphs.

The most important assumption implicit in Table II is that the electron energy distribution may be represented by a Maxwellian at some temperature T_e (which is in general different from the gas temperature T_g). While the validity of this assumption has not been proven in general, solutions of the Boltzman equation for the energy distribution function under conditions relevant to electron beam pumping of krypton fluoride laser media have shown that a Maxwellian distribution is a reasonable approximation.^{3,4} The generation of "holes" in the distribution by the inelastic processes is prevented due to the presence of the super-elastic channels.

For electron collisional excitation and ionization processes where the rate constants were not known the two-temperature model allowed their calculation as a function of the electron temperature via the integration of the corresponding cross section over the Maxwellian velocity distribution. The super-elastic rate constants were

determined using the principle of detailed balance.⁵ The electron-atom thermal equilibration rate (from elastic collisions) was calculated from the momentum transfer cross sections using the formulation of Shkarofsky et. al.⁶ For the electron-ion thermal energy exchange rate the result given by Spitzer for a partially ionized gas was used.⁷ In all cases the results were fit to a suitable expansion in terms of the electron temperature.

For exothermic bimolecular reactions of the form $A + B \rightarrow \text{Products}$, the temperature dependence of the rate constant, if not known from experiment, was estimated by assuming that the corresponding cross section was roughly constant over the relevant energy range, in which case the rate scales as T_g^{-5} .⁸ For ternary reactions of the form $A + B + C \rightarrow AB + C$ the reaction was pictured as consisting of two collisions: first of A and B to form the product in an unstable state, followed by a stabilizing collision with C.⁹ In this case the rate again scales as T_g^{-5} , and as a function of the masses m_{AB} and m_C it is proportional to $(1/m_{AB} + 1/m_C)^{-5}$. This last result was used to estimate the value of unknown ternary reaction rates in terms of known values.

For the recombination of the rare gas ions with F^- the calculation of Flannery and Yang (for $Ar^+ + F^-$ in Ar, etc.)¹⁰ was extended to other rare gas ions (e.g. Ar_2^+) and other buffer gases (e.g. $Ar^+ + F^-$ in He). The results of this calculation reduce to the Thomson theory at low pressure (<1 atm.) and that of Langevin at high pressure (>10

atm.),¹¹ and required both values for the polarizability of the buffer gases¹² and the reduced mobilities of the ions in the buffers.¹³⁻¹⁵ For ion-buffer pairs where the mobility was not known it was scaled from known values in the same buffer by assuming the reduced mobility to be proportional to the ion-buffer atom reduced mass; for gas mixtures the mobility was calculated using Blanc's law.¹²

Two assumptions have been made concerning the behavior of the collisionally formed KrF^* dimer. First, the shape of the radiative decay spectra measured by Murray and Powell¹⁶ indicate that the relaxation of the vibrational excitation to a thermal distribution at the gas temperature is rapid at pressures of interest for electron beam pumped lasers (≥ 1 atm); we assume that it takes place instantaneously. Furthermore, we assume that the KrF^* excitation is divided equally between the B and C states, so that only half of it is available to the laser transition.

Where neither the rate constant nor the cross section for a particular process was known (from either theory or experiment), the rates were approximated in various ways. For electron collisional ionization of the Ar 4p excited state, the cross section was assumed to have the semi-empirical shape suggested by Green and Barth.¹⁷ When the rate constant for a similar process was available, the unknown rate constant was assumed equal to it. In the case of the fluorine excited state reactions, all processes were assumed to take place at their gas kinetic values.

C. Interaction of the Radiation Field with the Laser Medium

(i) Spontaneous and Stimulated Emission

The calculation of the strength of the KrF* laser transition requires first of all a description of the wavefunctions of the upper and lower states it connects and the magnitude of the transition moment between them. This problem is most easily treated in the Born-Oppenheimer approximation,¹⁰⁶ in which the molecular state is expressed as a product of an electronic and a nuclear wavefunction:

$$|\Phi\rangle = |\Phi_e\rangle |\Phi_n\rangle \quad (1)$$

Ignoring terms on the order of the ratio of the electronic and nuclear masses, the Schrodinger equation for the molecular wavefunction becomes separable. The eigenvalues of the electronic Hamiltonian are then dependent on the inter-nuclear separation R , contributing to the potential for which the nuclear wavefunction must be solved.

Hay and Dunning have performed ab initio calculations for the electronic states of KrF*, obtaining both the nuclear potential curves and the transition moments for the states relevant to the 248 nm. krypton fluoride laser transition.¹⁰⁷ Figure 1 shows the potential curves for the $B(\frac{1}{2})$ and $X(\frac{1}{2})$ states involved. The eigenfunctions $|v\rangle$ for the upper state potential curve are bound, with a vibrational spacing of about .042 eV. The repulsive nature of the lower state

potential leads to a continuum of unbound states $|\epsilon\rangle$ which are normalized by requiring $\langle\epsilon'|\epsilon\rangle = \delta(\epsilon' - \epsilon)$.

The total radiative lineshape is the sum of the contributions from each of the vibrational eigenstates to the continuum of lower state energy levels. For any single vibrational state the spontaneous decay rate with the emission of a photon of frequency ν is given by

$$A_V(\nu) = \frac{64\pi^4}{3\lambda^3} \left| \langle \epsilon | t(R) | v \rangle \right|^2 \quad (2)$$

where $h\nu$ is the energy difference between the initial and final state energies, $\lambda = c/\nu$, and $t(R)$, defined as

$$t(R) = \left\langle \phi_e^u \left| \frac{\vec{d} \cdot \vec{R}}{R} \right| \phi_e^l \right\rangle \quad (3)$$

is the electronic dipole moment between the initial and final states.¹⁰⁸ The stimulated emission cross section at the frequency may be calculated from the decay rate using the relation

$$\sigma_V(\nu) = \frac{\lambda^2}{8\pi} A_V(\nu) = \frac{8\pi^3}{3\lambda} \left| \langle \epsilon | t(R) | v \rangle \right|^2 \quad (4)$$

In thermal equilibrium at the temperature T_g the relative population of each of the vibrational upper states is given by

$$n(v) = \exp(-E_v/kT_g) / \sum_v \exp(-E_v/kT_g) \quad (5)$$

where E_v is the energy of the vibrational level $|v\rangle$. The total radiative decay rate into the continuum with the emission of a photon of frequency ν is then equal to

$$A(\nu) = \sum_v \exp(-E_v/kT_g) A_v(\nu) / \sum_v \exp(-E_v/kT_g) \quad (6)$$

with a similar relation holding for the total stimulated emission cross section as a function of the frequency.

The program SPECTRA, developed by the TAMP group at LLL¹⁰⁹ was used to calculate the factors $A_v(\nu)$ for the $\text{KrF}^* \text{B-X}$ laser transition, using the potential energy curves and transition moments of Hay and Dunning as input. These were combined with the proper weighting to calculate the spontaneous emission probability $A(\nu)$ as well as the stimulated emission cross section as a function of temperature. The results of this calculation are illustrated in Figures 2 and 3. The tendency of both quantities to "blue shift" with increasing temperature is a consequence of the increasing contribution of the higher vibrational states via the Boltzman factor. Not only does the energy of the photon from a transition to a lower state of a given energy ϵ increase due to the greater energy of the vibrational state, but the higher lying states extend to larger values of the inter-nuclear separation, overlapping unbound states of lower energy which leads to even larger photon energies.

(ii) Absorption

It is not simply the magnitude of the absorption cross section which must be taken into account in determining the optical loss in the gas but rather its product with the expected concentration of the absorber in the medium at the time of laser action. The species causing significant absorption of the laser radiation are presented in Table III, along with the absorption cross sections at 248 nm. All of the absorption processes are broad band, corresponding to photodetachment, photoionization, or photodissociation.

The Ar_2^+ and Kr_2^+ absorptions have been identified as bound-free transitions, similar in nature to the $\text{KrF}^* \text{B} \rightarrow \text{X}$ stimulated emission. The program SPECTRA was used to calculate the vibrational line shapes from the potential curves and transition moments of Michels et al.,¹¹⁴ which were then combined to determine the absorption cross sections as a function of wavelength and temperature. The variation of the cross sections with frequency at 300 K is presented in Figure 4. The 248 nm. absorption, lying in the wings of both curves, rises with increasing temperature as the contribution to the total cross section from the higher lying vibrational states increases.

The cross sections for photon absorption of both the rare gas excimers (e.g. Ar_2^*) and the rare gas halide trimers (e.g. Ar_2F^*) were estimated as equal to that of the corresponding rare gas dimer ion. The excimers are Rydberg states consisting of an outer electron around a dimer ion core; the trimers are essentially ionic complexes of the

form Ar_2^+F^- . In both cases we would expect the absorption at 248 nm. to be similar to that of the dimer ion.

D. Numerical Methods

Unlike the particle concentrations, whose kinetics involve simple differential equations, the growth of the flux of laser photons ϕ is determined by a partial differential equation in both space and time:

$$\frac{1}{c} \frac{\partial}{\partial t} \phi = - \frac{\partial}{\partial x} \phi + \alpha \phi \quad (7)$$

where c is the light velocity in the laser medium, and α is the net gain coefficient at the laser wavelength. Under conditions where the integral of the gain coefficient over the laser path length exceeds unity, the laser flux varies significantly with position and may induce corresponding variations in the particle concentrations. An accurate description of the kinetics in even its simplest non-trivial cases requires a prescription for transporting the laser photons according to Eq. 7 and must allow for spatial as well as temporal variations in all relevant quantities.

The most direct approach would be to integrate Eq. 7 numerically in both space and time, where for accuracy the spatial step in the integration would be limited to values $\ll \alpha^{-1}$. For large strongly pumped systems (such as the LLNL B-amplifier, which is expected to have a small signal gain of between e^{10} and e^{15}), with lengths much

greater than α^{-1} , the number of grid points required makes such schemes computationally unfeasible. To treat such cases, an approximation to the spatial integral must be used.

The method used for the treatment of the laser transport was as follows. The laser path length was divided into N separate zones, each of length $L_z \leq \alpha^{-1}$. Either one (for a single pass amplifier configuration) or two (for the simulation of a laser resonator) spatially dependent counter propagating fluxes ϕ^+ and ϕ^- were allowed. The quantities tracked in time were the zonal averages of these fluxes

$$\phi_n^{\pm}(t) = \int_{nL_z}^{(n+1)L_z} \phi^{\pm}(x,t) dx / L_z \quad (8)$$

and the similarly defined averages of the concentrations of all the gas components. Inside each zone ϕ^+ (ϕ^-) was assumed to have a profile proportional to $\exp(\alpha_n x)$ ($\exp(\alpha_n (L_z - x))$), where α_n was the gain coefficient determined from the average particle concentrations. The time dependence of the average fluxes was determined by the equations:

$$\frac{1}{c} \frac{d}{dt} \phi_n^{\pm} = \alpha_n \phi_n^{\pm} - \phi_{out,n}^{\pm} + \phi_{in,n}^{\pm} \quad (9)$$

where

$$\phi_{out,n}^{\pm} = \frac{\alpha_n \exp(\alpha_n l_z)}{(\exp(\alpha_n l_z) - 1)} \phi_n^{\pm} \quad (10)$$

and for $2 \leq n \leq N$, $\phi_{in,n}^+ = \phi_{out,n-1}^+$. The value of $\phi_{in,1}^+$ was set by considering the boundary conditions. When modelling a laser resonator, $\phi_{in,1}^+$ was set equal to $R \cdot \phi_{out,1}^-$, where R was the mirror reflectivity; for a single pass amplifier, $\phi_{in,1}^+ = c \cdot \phi_{input}/l_z$, and $\phi_n^- = 0$. The values of $\phi_{in,n}^-$ were defined in a similar manner. The effect of the laser photons on the particle concentrations was determined by assuming that the relevant species were created or destroyed at a rate dependent on the total average photon flux $\phi_n^+ + \phi_n^-$.

Before this approximation was included in the model of the krypton fluoride laser kinetics, it was tested by applying it in some simple kinetic situations which could be solved analytically. First, we calculated the steady state output flux ϕ_f for the system of equations:

$$\frac{\partial}{\partial t} n = S - n/\tau - n\sigma\phi; \quad \frac{1}{c} \frac{\partial}{\partial t} \phi = - \frac{\partial}{\partial x} \phi + n\sigma\phi; \quad 0 \leq x \leq L \quad (11)$$

with $\phi(0,t) = \phi_i$. The analytic solution in this case is given

implicitly by

$$\ln(r_f/r_i) + (r_f - r_i) = g_0 \quad (12)$$

where $g_0 = S\sigma\tau L$ is the logarithm of the small signal gain, and the "r's" are the ratios of the relevant fluxes to the saturation flux $\phi_s = (\sigma\tau)^{-1}$. Applying the approximations described above to this case using only one value yields

$$r_f = r_i \exp(g_0/(1+r)) \quad (13)$$

where r is determined from the equation

$$\frac{g_0 \cdot r}{(1+r)} \frac{1}{(\exp(g_0/(1+r)) - 1)} = r_i \quad (14)$$

For g_0 ranging from .1 to 100, and r_i from .1 to 10 the values of r_f obtained from equations 12 and 13 were identical to the limits of computation, and are presented in Table IV.

The second test case chosen corresponded to the kinetic equations

$$\frac{\partial}{\partial t} n = -cn\phi; \quad \frac{1}{c} \frac{\partial}{\partial t} \phi = -\frac{\partial}{\partial x} \phi + n\sigma\phi; \quad 0 \leq x \leq L \quad (15)$$

with the boundary conditions $n(x,0) = n_0$, $\phi(x>0,0) = 0$, and $\phi(0,t) = \phi_i$. In this case the output flux can be found analytically as function of time; defining $\tau = ct/L$ and $r_f = \phi(L,t)/cn_0$ (similarly

for r_i) and with $g_0 = n_0 \sigma L$, we have

$$r_f(\tau) = \frac{r_0 \exp(r_0 g_0 (\tau - 1))}{\exp(r_0 g_0 (\tau - 1)) - 1 - \exp(-g_0)} \quad (16)$$

The agreement between this analytic solution and the result obtained by applying the approximate photon transport method described above (again using only one zone) is shown in Figure 5 for the case $g_0 = 1$, $r_0 = 0.1$ (assuming a 1 cm. zone length, this choice of parameters would imply an initial KrF* upper state density of $3.8 \times 10^{15} \text{ cm}^{-3}$, a stored energy density of 3 J/liter, and an incident flux of 1 MW/cm^2). Further analysis indicates that the condition for the applicability of our transport approximation is that the zone length be less than $\alpha(d\alpha/dx)^{-1}$, the scale length for variations in the gain coefficient, a much weaker constraint than that imposed when Eq. 7 is integrated directly, and one which can be readily satisfied in all the cases considered.

In addition to tracking the laser flux, we must consider the amplification of the spontaneous emission in directions other than the laser axis. Such processes may drastically reduce the laser performance in cases where the transverse gain is greater than 1, and would require at least a two-dimensional calculation for an accurate representation. In this work we have treated only those geometries with small transverse gains, in which case we have assumed that in each zone the density of the "stimulated-spontaneous" emission $\rho_s(\nu)$

grows according to the equation

$$\frac{1}{c} \frac{d}{dt} \rho_s(\nu) = S(\nu) + \alpha(\nu) \rho_s(\nu) - \rho_s(\nu)/R \quad (17)$$

where $S(\nu)$ is the local source term due to radiative decay of KrF^* , $\alpha(\nu)$ the local gain coefficient at the frequency ν , and R is the average path length that a spontaneously emitted photon emitted in the zone will travel before hitting a laser wall

With this approximation for the solution to Eq. 7, the laser kinetics reduces to a system of coupled nonlinear differential equations in time, requiring only numerical integration for the completion of the kinetic model. Such systems are generally solved using a variable time-step stiff predictor-corrector technique such as those described by Gear,¹¹⁵ however application of these methods to the laser kinetics leads to an instability (in which the photon fluxes become and grow increasingly negative due to "stimulated absorption") which can only be avoided at prohibitive computational cost. For this reason we decided to use instead of the standard methods a four-point Runge-Kutta scheme with the time step being set by requiring $\dot{y}\Delta t \leq .05y$ for $\dot{y} > 0$ (and $\dot{y}\Delta t \leq -.5y$ for $\dot{y} < 0$), where y and $\dot{y}$ are respectively the values and time derivatives of any of the quantities integrated.

Several checks were written into the integration scheme to catch any errors in inputting the form of the various reactions. The local electron density was calculated by integrating its kinetic equation, rather than by setting it equal to the net heavy particle positive

charge density. The density of fluorescence photons from the various excited states, as well as the gas and electron thermal energy densities were also followed via integration. This allowed verification of the computer input by requiring that the net charge density, net atom densities, and total energy be conserved to the round-off accuracy of the computer (typically better than 1 part in 10^{12}).

To avoid computational waste, several computer codes are written to implement the kinetics model depending on the physical characteristics of the problem under consideration. In cases where the initial gas mixture was restricted (e.g. containing only Kr and F_2) all reactions requiring the forbidden gas components were removed. For those systems where the gas temperature remained essentially constant any dependence on T_g was removed and all rate constants were set equal to their room temperature values. When the effect of the spontaneous KrF^* emission was determined to be negligible its spectrum was compressed to a delta function at the peak wavelength. Finally, for each set of conditions separate programs were written to model the behavior of single pass amplifier and laser resonators.

The code to model the single pass behavior of electron beam pumped mixtures of krypton, argon, helium and fluorine, CELLKIN, is presented in the microfiche at the end of this thesis. It assumes that the transverse gain is negligible, and that the gas temperature rise caused by the electron beam deposition is small. It may be

compiled for up to a maximum of 20 zones in the laser region, and outputs both the spatial and temporal dependence of the gas parameters and amplifier output.

CELLKIN was used to model the behavior of electron beam pumped mixtures in the MEG I gas cell at LLNL, which will be described in detail in the following chapter. For the current densities ($\leq 200 \text{ amp/cm}^2$) and gas pressures of interest here, the product of the gain coefficient and the cell length was ≤ 1 , allowing a single zone treatment of the photon transport.

The time dependence of the KrF^* and Kr_2F^* fluorescence signals from a 1500 Torr Ar, 100 Torr Kr, 5.00 Torr F_2 gas mixture pumped with a 50 nsec., 600 keV electron beam at an average current density of 33 Amp/cm^2 is presented in Figure 6. Both the results determined from experiment¹¹⁶ and those calculated by the model are shown, all normalized to their peak values. In Figure 7 we show the corresponding results for a 11,600 Torr He, 100 Torr Kr, 5.00 Torr F_2 mixture pumped with a similar e-beam current pulse. Although a direct comparison of the model and experiment could not be made because the fluorescence detection efficiencies were not known, it is relevant to note that the conversion ratios, defined as the peak experimental KrF^* signal divided by the peak model KrF^* signal, agree to within 20% for the argon- and helium-buffered mixtures. A similar result holds for the Kr_2F^* ratios.

The model and experimental results differ slightly both during and after the current pulse. The disagreement between the experimental and model dimer signals at the end of the current pulse is probably due to a failure in modelling the time-dependent destruction (presumably by electrons) of KrF^* . The longer decay time for the trimer predicted by the model than obtained in the experiment might be caused by the neglect of rare gas quenching of Kr_2F^* in the model. Both of these points will be discussed in the next chapter.

In Figure 8 we show the spectral dependence (at the end of the current pulse) of the absorption by a 1500 Torr Ar, 100 Torr Kr, 5.00 Torr F_2 gas pumped with a 50 nsec., 600 keV electron beam at an average current density of ≈ 140 Amp/cm². The experimental data is that of Powell.¹¹⁶ The energy deposition into the gas is assumed to be twice the value calculated for a single pass, in line with pressure rise measurements and numerical calculations of the electron beam transport.¹¹⁷ While the model appears to accurately estimate the gain at 248 nm., it fails to predict the currently unidentified sharp absorption feature at ≈ 220 nm. In addition the calculation underestimates the broad-band absorption centered at ≈ 320 nm., which could be the result of overestimating the effects of electron collisional quenching of the Kr_2F^* trimer, to be discussed in Chapter V.

The breakdown by absorber of the absorption spectrum predicted by the model is illustrated in Fig. 9. The continuum absorption at long

wavelengths is primarily from Kr_2F^* . At the laser wavelength, the saturable absorption due to Kr_2F^* is approximately one-third of the total. The remainder of the loss is predicted to be nonsaturable, and mainly due to KrF^* precursors (e.g. $\text{Ar } 4p$, $\text{Kr}2+$, etc.), with a small portion ($\approx 10\%$) from absorption by Ar_2F^* .

We conclude by determining the effect that this breakdown of the medium absorption would have on the performance of a KrF^* laser operating using this gas mixture and current density. At the pulse lengths of interest (>10 ns.), the gas kinetics reaches a quasi-steady state, in which case the analysis of Chapter I dealing with the consequences of medium absorption is applicable. Specifically, inserting the gain and loss coefficients obtained above into Eq. 11 of that chapter results in a prediction of less than 50% for the maximum local extraction efficiency. Due to spatial variations in the laser intensity one would expect the average extraction efficiency in the laser to be even lower. In Chapter VI we will consider this problem in detail and present the results obtained under actual laser operation.

Table I
Particle Concentrations Tracked
In Laser Kinetics Model

<u>State</u>	<u>Energy (eV)</u>	<u>State</u>	<u>Energy (eV)</u>
Ar	0.0	Kr	0.0
Ar ⁺	15.76	Kr ⁺	14.00
Ar ₂ ⁺	14.50	Kr ₂ ⁺	12.90
Ar* (Ar 4s)	11.76	Kr* (Kr 5s)	9.98
Ar** (Ar 4p)	13.00	Kr** (Kr 5p)	11.50
Ar ₂ *(³ Σ)	11.06	Kr ₂ *(³ Σ)	9.08
Ar ₂ *(¹ Σ)	11.135	Kr ₂ *(¹ Σ)	9.20
ArF*	7.24	KrF*	5.90
Ar ₂ F*	6.10	Kr ₂ F*	4.40
ArKrF*	5.20		
He	0.0	He 2 ³ S	19.82
He ⁺	24.59	He 2 ¹ S	20.615
He ₂ ⁺	22.23	He 2 ³ P	20.96
He ₃ ⁺	22.06	He 2 ¹ P	21.22
He ₂ * ⁺	17.97		
F ₂	0.0	F*(3s)	13.57
F	0.80	F*(3p)	15.30
F ⁻	-2.66	F ₂ *	11.05
electrons	-----		

Table II
Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Krypton-Krypton Reactions</u>		
$\text{Kr}^+ + \text{Kr} + \text{M} \rightarrow \text{Kr}_2^+ + \text{M}$	$R \times 2.5 \times 10^{-31} \text{A}$ (a)	(18,19)
$\text{Kr}^{**} + \text{Kr} + \text{M} \rightarrow \text{Kr}^* + \text{Kr} + \text{M}$	$R \times 5.4 \times 10^{-32} \text{A}$ (b)	(20)
$\text{Kr}^* + \text{Kr} + \text{M} \rightarrow \text{Kr}_2^* + \text{M}$	$R \times 2.6 \times 10^{-32} \text{A}$ (b)	(20)
$2\text{Kr}^* \rightarrow \text{Kr}^+ + \text{Kr} + \text{e}^-$	$1.5 \times 10^{-10} \text{A}$	(21)
$2\text{Kr}_2^* \rightarrow \text{Kr}_2^+ + 2\text{Kr} + \text{e}^-$	$1.0 \times 10^{-10} \text{A}$	(1)
$\text{Kr}^{**} + \text{Kr} + \text{M} \rightarrow \text{Kr}_2^* + \text{M}$	$R \times 2.6 \times 10^{-32} \text{A}$ (c)	(20)
$\text{Kr}^{**} + \text{Kr} \rightleftharpoons \text{Kr}^* + \text{Kr}$	$3.0 \times 10^{-11} \text{A}$ (d)	(22)
$\text{Kr}_2^*(^1\Sigma) + \text{M}$ $\rightleftharpoons \text{Kr}_2^*(^3\Sigma) + \text{M}$	$2.8 \times 10^{-13} \text{A}$ (e)	(1)
<u>Krypton-Argon Reactions</u>		
$\text{Ar}_2^+ + \text{Kr} \rightarrow \text{Kr}^+ + 2\text{Ar}$	$7.5 \times 10^{-10} \text{A}$	(23)
$\text{Ar}^* + \text{Kr} \rightarrow \text{Kr}^* + \text{Ar}$	$6.2 \times 10^{-12} \text{A}$	(24,25)
$\text{Ar}_2^* + \text{Kr} \rightarrow \text{Kr}^* + 2\text{Ar}$	$1.0 \times 10^{-10} \text{A}$	(26,27)

Note $\text{A} = (T_g/300^\circ\text{K})^{.5}$

(a) $\text{M}=\text{He}$, $R=.25$; $\text{M}=\text{Ar}$, $R=1.3$; $\text{M}=\text{Kr}$, $R=1$.

(b) $\text{M}=\text{He}$, $R=4.$; $\text{M}=\text{Ar}$, $R=1.3$; $\text{M}=\text{Kr}$, $R=1$.

(c) Rate constant equals that for the Kr^* reaction.

(d) Rate constant equals that for the similar Ar reaction.

(e) Rate constant given is for the forward reaction, that for the reverse reaction is calculated from detailed balance.

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Argon-Argon Reactions</u>		
$\text{Ar}^+ + \text{Ar} + \text{M} \rightarrow \text{Ar}_2^+ + \text{M}$	$R \times 2.5 \times 10^{-31} A$ (a)	(18,28-30)
$\text{Ar}^{++} + \text{Ar} + \text{M} \rightarrow \text{Ar}^+ + \text{Ar} + \text{M}$	$R \times 1.0 \times 10^{-31} A$ (b)	(31)
$\text{Ar}^{++} + \text{Ar} + \text{M} \rightarrow \text{Ar}_2^{++} + \text{M}$	$R \times 1.1 \times 10^{-32} A$ (b)	(32,33)
$2\text{Ar}^* \rightarrow \text{Ar}^+ + \text{Ar} + e^-$	$1.0 \times 10^{-10} A$	(21,34)
$2\text{Ar}_2^* \rightarrow \text{Ar}_2^+ + 2\text{Ar} + e^-$	$1.0 \times 10^{-10} A$	(34,35)
$\text{Ar}_2^*(^1\Sigma) + \text{M}$ $\rightleftharpoons \text{Ar}_2^*(^3\Sigma) + \text{M}$	$1.5 \times 10^{-13} A$	(1)
<u>Helium-Krypton Reactions</u>		
$\text{He}_2^+ + \text{Kr} \rightarrow \text{Kr}^+ + 2\text{He}$	$2.3 \times 10^{-11} A$	(36)
$\text{He } 2^3\text{S} + \text{Kr} \rightarrow e^-$ $+ (\text{HeKr}^+ \text{ or } \text{He} + \text{Kr}^+)$	calculated from cross section (d)	(37,38)
$\text{HeKr}^+ + \text{Kr} \rightarrow \text{Kr}^+ + \text{He} + \text{Kr}$	$1.1 \times 10^{-8} (kT_g/1\text{eV})^{-5}$	(39)

Note $A = (T_g/300^\circ\text{K})^{-5}$

(a) $M = \text{He}$, $R = .3$; $M = \text{Ar}$, $R = 1.$; $M = \text{Kr}$, $R = .8$

(b) $M = \text{He}$, $R = 2.5$; $M = \text{Ar}$, $R = 1.$; $M = \text{Kr}$, $R = .8$

(c) Rate constant given is for the forward reaction, that for the reverse reaction is calculated from detailed balance.

(d) Rate constant is the integral of the cross section over a Maxwellian. See the microfiche listing of the kinetics.

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Helium-Krypton Reactions</u> (continued)		
$\text{HeKr}^+ + \text{Kr} \rightarrow \text{Kr}_2^+ + \text{He}$	$3.6 \times 10^{-10} (\text{kT}_g / \text{eV})^{-5}$	(39)
$\text{He } 2^3\text{S} + \text{Kr} + \text{M} \rightarrow$ $\text{e}^- + \text{Kr}^+ + \text{He} + \text{M}$	$2.2 \times 10^{-30} \text{A}$ (a)	(40)
$\text{He } 2^1\text{S} + \text{Kr} \rightarrow \text{e}^-$ $+ .2\text{HeKr}^+ + .8(\text{He} + \text{Kr}^+)$	4.8×10^{-10}	(38,41)
$\text{He}_2^+ + \text{Kr} + \text{M} \rightarrow \text{Kr}^+ + 2\text{He} + \text{M}$	$2.4 \times 10^{-29} \text{A}^{-1.5}$ (a)	(40)
$\text{He}_2^+ + \text{Kr} \rightarrow \text{Kr}^+ + 2\text{He} + \text{e}^-$	$3.1 \times 10^{-10} \text{A}$ (a)	(42)
<u>Helium-Argon Reactions</u>		
$\text{He}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + 2\text{He}$	$2.3 \times 10^{-10} \text{A}$	(43)
$\text{He } 2^3\text{S} + \text{Ar} \rightarrow \text{e}^-$ $+ (\text{HeAr}^+ \text{ or } \text{He} + \text{Ar}^+)$	calculated from cross section (b)	(37,38,40)
$\text{HeAr}^+ + \text{Ar} \rightarrow \text{Ar}^+ + \text{He} + \text{Ar}$	$1.1 \times 10^{-8} (\text{kT}_g / \text{eV})^{-5}$	(39)
$\text{HeAr}^+ + \text{Ar} \rightarrow \text{Ar}_2^+ + \text{He}$	$1.1 \times 10^{-9} (\text{kT}_g / \text{eV})^{-5}$	(39)
$\text{He } 2^3\text{S} + \text{Ar} + \text{M} \rightarrow$ $\text{e}^- + \text{Ar}^+ + \text{He} + \text{M}$	$2.2 \times 10^{-30} \text{A}$	(40)
$\text{He}_2^+ + \text{Ar} \rightarrow \text{Ar}^+ + 2\text{He} + \text{e}^-$	$3.1 \times 10^{-10} \text{A}$	(42)

Note $\text{A} = (\text{T}_g / 300^\circ\text{K})^{-5}$

(a) Rate constant equals that for the similar Ar reaction.

(b) Both the rate constant and yield for this reaction are temperature dependent. See the microfiche listing.

Table II (continued)
Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Helium-Argon Reactions</u> (continued)		
$\text{He } 2^1\text{S} + \text{Ar} \rightarrow e^-$ + .18 HeAr^+ + .82($\text{He} + \text{Ar}^+$);	2.6×10^{-10}	(41)
$\text{He}_2^+ + \text{Ar} + \text{M} \rightarrow \text{Ar}^+ + 2\text{He} + \text{M}$	$2.4 \times 10^{-29} A^{-1.5}$	(40,43)
$\text{He } 2^1\text{P} + \text{Ar} \rightarrow e^- + \text{Ar}^+ + \text{He}$	$1.7 \times 10^{-10} A$	(41)
<u>Helium-Helium Reactions</u>		
$\text{He}^+ + \text{He} + \text{M} \rightarrow \text{He}_2^+ + \text{M}$	$9.0 \times 10^{-32} / A$	(36,44,45)
$2\text{He } 2^3\text{S} \rightarrow .7\text{He}_2^+$ + .3($\text{He} + \text{He}^+$) + e^-	9.0×10^{-10}	(46,47)
$\text{He } 2^3\text{S} + 2\text{He} \rightarrow \text{He}_2^* + \text{He}$	8.3×10^{-31} $\times \exp(-.15(17.5 + 1\text{ev}/kT_g))$	(46,47)
$\text{He } 2^3\text{S} + \text{He}_2^* \rightarrow e^- + .85\text{He}_2^+$ + .15($\text{He} + \text{He}^+$) + He	1.2×10^{-9}	(46)
$2\text{He}_2^* \rightarrow e^- + .85\text{He}_2^+$ + .15($\text{He} + \text{He}^+$) + 2He	1.2×10^{-9}	(47)
$\text{He } 2^1\text{P} + \text{He} \rightarrow 2\text{He}$	$9.3 \times 10^{-13} A$	(48,49)
$\text{He } 2^1\text{P} + 2\text{He} \rightarrow \text{He}_2^* + \text{He}$	$3.1 \times 10^{-31} A$	(48,49)
$\text{He } 2^1\text{S} + \text{He} \rightarrow 2\text{He}$	$6.8 \times 10^{-15} A$	(50)
$\text{He } 2^1\text{S} + 2\text{He} \rightarrow \text{He}_2^* + \text{He}$	$1.3 \times 10^{-33} A$	(50,51)

Note $A = (T_g/300^\circ\text{K})^{.5}$

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Electron elastic collisions</u>		
$e^- + M \rightarrow e^- + M$	calculated from momentum transfer cross sections	(6,52,53)
$e^- + \text{Ion} \rightarrow e^- + \text{Ion}$	Spitzer's result used for energy exchange	
<u>Electron Attachment and Recombination</u>		
$e^- + F_2 \rightarrow F^- + F$	$K(1+2(R+R^2))$ (a)	(54-57)
$e^- + Kr_2^+ \rightarrow Kr^{**} + Kr$	$3.9 \times 10^{-7} (1\text{eV}/kT_e)^{-5}$ $\times (1 - \exp(-.022\text{eV}/kT_g))$	(58-61)
$e^- + Ar_2^+ \rightarrow Ar^{**} + Ar$	$7.8 \times 10^{-7} (1\text{eV}/kT_e)^{-6.7}$ $\times (1 - \exp(-.037\text{eV}/kT_g))$	(20)
$2e^- + He_2^+ \rightarrow e^-$ $+ .7He\ 2^3S + 1.3He$	$4.0 \times 10^{-20} (T_g/T_e)^4$	(46)
$e^- + He_3 \rightarrow .7He\ 2^3S$ $+ 2.3He + e^-$	(b) $4.6 \times 10^{-6} (T_g/T_e)^{1.2}$	(38,46)

Note $A = (T_g/300^\circ K)^{-5}$

(a) $R = \exp(-.1146\text{eV}/kT_g)$ and if $kT_e \leq 1/3$, $K = 1.0 \times 10^{-8}$;

if $1/3 \leq kT_e \leq .8$, $K = 1.0 \times 10^{-9} (3.3 + 30.4(.8 - kT_e)^2)$;

if $kT_e > .8$, $K = 3.0 \times 10^{-9}$.

(b) He_3^+ is assumed in equilibrium with He_2^+ .

Table II (continued)

Reaction Kinetics

Electron Collisional Ionization

Reaction	k_R (cm^3/s or cm^6/s)	Source
$e^- + \text{Kr}_2^*(^3\Sigma) \rightarrow \text{Kr}_2^+ + 2e^-$	$7.7 \times 10^{-7} B^{-.5}$ (a)	
	$\times \exp(-B)/(.97+B)$	(62)
$e^- + \text{Kr}_2^*(^1\Sigma) \rightarrow \text{Kr}_2^+ + 2e^-$	$7.7 \times 10^{-7} B^{-.5}$ (b)	
	$\times \exp(-E)/(.97+B)$	(62)
$e^- + \text{Ar}_2^*(^3\Sigma) \rightarrow \text{Ar}_2^+ + 2e^-$	$9.0 \times 10^{-7} B^{-.5}$ (c)	
	$\times \exp(-B)/(.97+B)$	(62)
$e^- + \text{Ar}_2^*(^1\Sigma) \rightarrow \text{Ar}_2^+ + 2e^-$	$9.0 \times 10^{-7} B^{-.5}$ (d)	
	$\times \exp(-B)/(.97+B)$	(62)

Reaction	Source (e)
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$e^- + \text{Kr} \rightarrow \text{Kr}^+ + 2e^-$	(63,64)
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$e^- + \text{Kr}^* \rightarrow \text{Kr}^+ + 2e^-$	(65)
--	------

$e^- + \text{Kr}^{**} \rightarrow \text{Kr}^+ + 2e^-$	(16,66)
---	---------

$e^- + \text{Ar} \rightarrow \text{Ar}^+ + 2e^-$	(52,67)
--	---------

$e^- + \text{Ar}^* \rightarrow \text{Ar}^+ + 2e^-$	(68)
--	------

$e^- + \text{Ar}^{**} \rightarrow \text{Ar}^+ + 2e^-$	(16,66)
---	---------

$e^- + \text{He} \rightarrow \text{He}^+ + 2e^-$	(63,68)
--	---------

$e^- + \text{He } 2^3S \rightarrow \text{He}^+ + 2e^-$	(69,70)
--	---------

(a) $B = (3.82 \text{ eV}/kT_e)$ (b) $B = (3.70 \text{ eV}/kT_e)$ (c) $B = (3.44 \text{ eV}/kT_e)$ (d) $B = (3.365 \text{ eV}/kT_e)$

(d) Rate constant is the integral of the cross section over a Maxwellian. See the microfiche listing of the kinetics.

Table II (continued)

Reaction Kinetics

Electron Collisional Excitation and Superelastic Collisions

Reaction	Source
$e^- + \text{Kr} \leftrightarrow e^- + \text{Kr}^{**}$	(71)
$e^- + \text{Kr}^* \leftrightarrow e^- + \text{Kr}^{**}$	(72)
$e^- + \text{Kr} \leftrightarrow e^- + \text{Kr}^*$	(73,74)
$e^- + \text{Ar} \leftrightarrow e^- + \text{Ar}^{**}$	(75,76)
$e^- + \text{Ar}^* \leftrightarrow e^- + \text{Ar}^{**}$	(41)
$e^- + \text{Ar} \leftrightarrow e^- + \text{Ar}^*$	(77)
$e^- + \text{He} \leftrightarrow e^- + \text{He } 2^3\text{S}$	(78-82)
$e^- + \text{He} \leftrightarrow e^- + \text{He } 2^1\text{S}$	(78-80,83-85)
$e^- + \text{He} \leftrightarrow e^- + \text{He } 2^3\text{P}$	(78,80,86)
$e^- + \text{He} \leftrightarrow e^- + \text{He } 2^1\text{P}$	(78,80,83,84,86-88)
$e^- + \text{He } 2^3\text{S} \leftrightarrow e^- + \text{He } 2^1\text{S}$	(89)
$e^- + \text{He } 2^3\text{S} \leftrightarrow e^- + \text{He } 2^3\text{P}$	(89)
$e^- + \text{He } 2^3\text{S} \leftrightarrow e^- + \text{He } 2^1\text{P}$	(89)
$e^- + \text{He } 2^1\text{S} \leftrightarrow e^- + \text{He } 2^3\text{P}$	(89)
$e^- + \text{He } 2^1\text{S} \leftrightarrow e^- + \text{He } 2^1\text{P}$	(89)
$e^- + \text{He } 2^3\text{P} \leftrightarrow e^- + \text{He } 2^1\text{P}$	(89)

Note The rate constants for the forward (endothermic) reactions are calculated by integrating the cross sections over a Maxwellian. The reverse rates are calculated from detailed balance. See the microfiche listing of the kinetics.

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Electron Collisional Excitation and Superelastic Collisions (cont.)</u>		
$e^- + \text{Kr}_2^* \rightarrow e^- + 2\text{Kr}$	$5.7 \times 10^{-9} (kT_e / \text{eV})^{-5}$	(1)
$e^- + \text{Kr}_2^* (^1\Sigma) \rightleftharpoons e^- + \text{Kr}_2^* (^3\Sigma)$		(a)
$e^- + \text{Ar}_2^* (^1\Sigma) \rightleftharpoons e^- + \text{Ar}_2^* (^3\Sigma)$	$1.5 \times 10^{-7} (kT_e / \text{eV})^{-5}$	(1)
		(a)
	$7.5 \times 10^{-8} (kT_e / \text{eV})^{-5}$	(1)
<u>Fluorine Reactions</u>		
$e^- + \text{F}_2 \rightarrow \text{F}^- + \text{F}$	$K(1+2(R+R^2))$ (b)	(54-57)
$\text{He}^+ + \text{F}^- \rightarrow \text{He} + \text{F}^*(3p)$	see the microfiche listing (c)	(10,90,91)
$\text{He}_2^+ + \text{F}^- \rightarrow 2\text{He} + \text{F}^*(3p)$	see the microfiche listing (c)	(10,90,91)
$e^- + \text{F}_2^* \rightarrow \text{F}^- + \text{F}$	$K(1+2(R+R^2))$ (d)	(54-57)

Note $A = (T_g / 300^\circ\text{K})^{-5}$

(a) Rate constant given is for the forward reaction, that for the reverse reaction is calculated from detailed balance.

(b) See the fifth page of this Table.

(c) The reaction rates for atomic recombination were calculated according to the method of Flannery and Yang.

(d) Rate constant equals that for the similar F_2 reaction.

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>Fluorine Reactions</u>		
$F^*(3p) + F_2 \rightarrow F_2^* + F$	$1 \times 10^{-9} A$	(a)
$F^*(3s) + F_2 \rightarrow F_2^* + F$	$1 \times 10^{-9} A$	(a)
$He\ 2^3S + F_2 \rightarrow He + F + F^*(3p)$	$1 \times 10^{-9} A$	(a)
$He\ 2^1S + F_2 \rightarrow He + F + F^*(3p)$	$1 \times 10^{-9} A$	(a)
$He\ 2^3P + F_2 \rightarrow He + F + F^*(3p)$	$1 \times 10^{-9} A$	(a)
$He\ 2^1P + F_2 \rightarrow He + F + F^*(3p)$	$1 \times 10^{-9} A$	(a)
$He_2^* + F_2 \rightarrow 2He + F + F^*(3p)$	$1 \times 10^{-9} A$	(a)
$Kr + F^*(3p) \rightarrow Kr^+ + F + e^-$	$1 \times 10^{-10} A$	(a)
$Kr + F^*(3s) \rightarrow Kr^{**} + F$	$1 \times 10^{-10} A$	(a)
$Ar + F^*(3p) \rightarrow Ar^{**} + F$	$1 \times 10^{-10} A$	(a)
$Ar + F^*(3s) \rightarrow Ar^{**} + F$	$1 \times 10^{-10} A$	(a)
<u>KrF* Formation</u>		
$Kr^+ + F^- \rightarrow KrF^*$	see the microfiche listing (b) (10,90,91)	
$Kr_2^+ + F^- \rightarrow KrF^* + Kr$	see the microfiche listing (b) (10,90,91)	

Note $A = (T_g/300^\circ K)^{-5}$

(a) These reactions were assumed to go at their gas kinetic rates.

(b) The reaction rates for atomic recombination were calculated according to the method of Flannery and Yang.

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>KrF* Formation (continued)</u>		
$\text{Kr}^{++} + \text{F}_2 \rightarrow \text{KrF}^* + \text{F}$	$7.6 \times 10^{-10} \text{A}$	(93,94)
$\text{Kr}^{*} + \text{F}_2 \rightarrow \text{KrF}^* + \text{F}$	$7.6 \times 10^{-10} \text{A}$	(93,94)
$\text{Kr}_2^{*} + \text{F}_2 \rightarrow \text{KrF}^* + \text{Kr} + \text{F}$	$3.0 \times 10^{-10} \text{A}$	(93,95)
$\text{Kr} + \text{F}_2^{*} \rightarrow \text{KrF}^* + \text{F}$	$7.6 \times 10^{-10} \text{A}$	(a)
<u>ArF* Formation</u>		
$\text{Ar}^{+} + \text{F}^{-} \rightarrow \text{ArF}^{*}$	see the microfiche listing (b) (10,90,91)	
$\text{Ar}_2^{+} + \text{F}^{-} \rightarrow \text{ArF}^{*} + \text{Ar}$	see the microfiche listing (b) (10,90,91)	
$\text{Ar}^{++} + \text{F}_2 \rightarrow \text{ArF}^* + \text{F}$	$7.5 \times 10^{-10} \text{A}$	(94-96)
$\text{Ar}^{*} + \text{F}_2 \rightarrow \text{ArF}^* + \text{F}$	$7.5 \times 10^{-10} \text{A}$	(94-96)
$\text{Ar}_2^{*} + \text{F}_2 \rightarrow \text{ArF}^* + \text{Ar} + \text{F}$	$7.5 \times 10^{-10} \text{A}$	(94-96)
$\text{Ar} + \text{F}_2^{*} \rightarrow \text{ArF}^* + \text{F}$	$7.5 \times 10^{-10} \text{A}$	(a)
<u>ArF* Quenching</u>		
$\text{ArF}^* + \text{F}_2 \rightarrow \text{Ar} + 3\text{F}$	$2.0 \times 10^{-9} \text{A}$	(96,97)
$\text{ArF}^* + \text{Ar} \rightarrow 2\text{Ar} + \text{F}$	$1.3 \times 10^{-11} \text{A}$	(97)
$\text{ArF}^* + \text{Kr} \rightarrow \text{KrF}^* + \text{Ar}$	$1.0 \times 10^{-9} \text{A}$	(97)

Note $\text{A} = (\text{T}_g/300^\circ\text{K})^{-5}$

(a) These reactions were assumed to go at the same rates as that for the excited rare gas and F_2 .

(b) The reaction rates for atomic recombination were calculated according to the method of Flannery and Yang.

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>ArF* Quenching</u> (continued)		
$\text{ArF}^* + \text{Ar} + \text{M} \rightarrow \text{Ar}_2\text{F}^* + \text{M}$	$R \times 3.2 \times 10^{-31} \text{ A}$ (a)	(96,97)
$\text{ArF}^* + e^- \rightarrow \text{Ar} + \text{F} + e^-$	$1. \times 10^{-7}$	(98)
<u>KrF* Quenching</u>		
$\text{KrF}^* + \text{F}_2 \rightarrow \text{Kr} + 3\text{F}$	$1.0 \times 10^{-9} \text{ A}$	(99-101)
$\text{KrF}^* + \text{Kr} \rightarrow 2\text{Kr} + \text{F}$	$7.4 \times 10^{-13} \text{ A}$	(99,101)
$\text{KrF}^* + \text{He} \rightarrow \text{Kr} + \text{F} + \text{He}$	$2. \times 10^{-12} \text{ A}$	Chapter VI
$\text{KrF}^* + \text{Ar} + \text{M} \rightarrow \text{ArKrF}^* + \text{M}$	$R \times 7.6 \times 10^{-32} \text{ A}$ (b)	(101)
$\text{KrF}^* + \text{Kr} + \text{M} \rightarrow \text{Kr}_2\text{F}^* + \text{M}$	$R \times 5.8 \times 10^{-31} \text{ A}$ (c)	(99-101)
$\text{KrF}^* + e^- \rightarrow \text{Kr} + \text{F} + e^-$	$2. \times 10^{-7}$	(98)
<u>Kr₂F* Quenching</u>		
$\text{Kr}_2\text{F}^* + \text{F}_2 \rightarrow 2\text{Kr} + 3\text{F}$	$1.6 \times 10^{-10} \text{ A}$	Chapter V
$\text{Kr}_2\text{F}^* + \text{Kr} \rightarrow 3\text{Kr} + \text{F}$	$< 10^{-13} \text{ A}$	Chapter V
$\text{Kr}_2\text{F}^* + e^- \rightarrow 2\text{Kr} + \text{F} + e^-$	$8. \times 10^{-8}$	Chapter V
<u>Ar₂F* Quenching</u>		
$\text{Ar}_2\text{F}^* + \text{F}_2 \rightarrow 2\text{Ar} + 3\text{F}$	$1.8 \times 10^{-10} \text{ A}$	Chapter V
$\text{Ar}_2\text{F}^* + \text{Ar} \rightarrow 3\text{Ar} + \text{F}$	$< 10^{-14} \text{ A}$	Chapter V
$\text{Ar}_2\text{F}^* + e^- \rightarrow 2\text{Ar} + \text{F} + e^-$	$2. \times 10^{-8}$	Chapter V

Note $A = (T_g/300^\circ \text{K})^{-5}$

(a) $\text{M} = \text{He}$, $R = .4$; $\text{M} = \text{Ar}$, $R = 1.$; $\text{M} = \text{Kr}$, $R = .8$

(b) $\text{M} = \text{He}$, $R = 1.$; $\text{M} = \text{Ar}$, $R = 1.$

(c) $\text{M} = \text{He}$, $R = .4$; $\text{M} = \text{Ar}$, $R = 1.0$; $\text{M} = \text{Kr}$, $R = 1.$

Table II (continued)

Reaction Kinetics

Reaction	k_R (cm^3/s or cm^6/s)	Source
<u>ArKrF* Quenching</u>		
$\text{ArKrF}^* + \text{F}_2 \rightarrow \text{Ar} + \text{Kr} + 3\text{F}$	$1. \times 10^{-10} \text{A}$	(a)
$\text{ArKrF}^* + \text{Kr} \rightarrow \text{Kr}_2\text{F}^* + \text{Ar}$	$3. \times 10^{-10} \text{A}$	(2)
<u>Radiative Decay</u>		
Transition	Lifetime (μs)	Source
$\text{KrF}^* \rightarrow \text{Kr} + \text{F}$	6.8	(99,100,102)
$\text{ArF}^* \rightarrow \text{Ar} + \text{F}$	4.2	(102)
$\text{ArKrF}^* \rightarrow \text{Ar} + \text{Kr} + \text{F}$	20.	(25)
$\text{Kr}_2\text{F}^* \rightarrow 2\text{Kr} + \text{F}$	220.	Chapter V
$\text{Ar}_2\text{F}^* \rightarrow 2\text{Ar} + \text{F}$	200.	Chapter V
$\text{Kr}_2^*(^3\Sigma) \rightarrow 2\text{Kr}$	670.	(1)
$\text{Kr}_2^*(^1\Sigma) \rightarrow 2\text{Kr}$	5.9	(1)
$\text{Ar}_2^*(^3\Sigma) \rightarrow 2\text{Ar}$	3,100.	(103,104)
$\text{Kr}_2^*(^1\Sigma) \rightarrow 2\text{Ar}$	4.2	(103,104)
$\text{F}^*(3p) \rightarrow \text{F}^*(3s)$	24.	(105)
$\text{He } 2^1\text{P} \rightarrow \text{He}$	.55	(105)
$\text{He } 2^1\text{P} \rightarrow \text{He } 2^1\text{S}$	500.	(105)
$\text{He } 2^3\text{P} \rightarrow \text{He } 2^3\text{S}$	100.	(105)

Note $A = (T_g/300^\circ\text{K})^{.5}$

(a) Rate estimated from the corresponding rate for the other rare gas trimers

Table III
Photoabsorption Cross Sections at 248 nm.

Absorber	(10^{-18} cm^2)	Source
F^-	5.5	(110)
F_2	.013	(57,111)
F_2^*	.013 (a)	(57,111)
$\text{He } 2^3\text{S}$	4.8	(112)
$\text{Kr } 5\text{s}$	.013	(112,113)
$\text{Kr } 5\text{p}$	4.3	(113)
$\text{Ar } 4\text{s}$	.015	(112,113)
$\text{Ar } 4\text{p}$	6.0	(113)
Kr_2^+	1.8 (b)	(114)
Kr_2^*	1.8 (c)	(114)
Kr_2F^*	1.8 (c)	(114)
Ar_2^+	10. (b)	(114)
Ar_2^*	10. (c)	(114)
Ar_2F^*	10. (c)	(114)

(a) Cross section is assumed the same as for F_2

(b) Cross section is a function of the gas temperature.

Value quoted is for $T_g = 300^\circ\text{K}$.

(c) Cross section is assumed equal to that for the rare gas dimer ion transition.

Table IV
Steady State Results for a Uniformly
Pumped Laser (see Eq. 11)

	<u>Input Flux</u> <u>Saturation Flux</u>	<u>Output Flux</u> <u>Saturation Flux</u>
<u>$g_0 = .1$</u>		
	.1	.10947
	1	1.0506
	10	10.091
<u>$g_0 = 1.$</u>		
	.1	.73702
	1	1.5571
	10	10.913
<u>$g_0 = 10.$</u>		
	.1	6.0048
	1	8.8227
	10	19.340
<u>$g_0 = 100$</u>		
	.1	93.262
	1	96.431
	10	107.62

Fig. 1. Nuclear potential curves for KrF, taken from the work of Hay and Dunning.⁽¹⁰⁷⁾ The KrF laser operates on the B(1/2) - X(1/2) transition. The C(3/2) population serves primarily as a reservoir for the upper level excitation.

Fig. 2. Calculated spontaneous transition probability vs wavenumber for the KrF B - X laser transition at 300 and 450°K.

Fig. 3. Calculated stimulated emission cross section vs wavelength for the KrF B - X laser transition at 300 and 450°K.

Fig. 4. Calculated Ar_2^+ and Kr_2^+ photoabsorption cross sections vs wavelength at 300°K.

Fig. 5. Result of the second test of the photon transport method described in the text. The difference between the analytic solution for the output flux and that predicted by the model is less than the width of the plotted curve.

Fig. 6. Comparison of the calculated and experimental dimer and trimer fluorescence signals from a 1500 torr Ar, 100 torr Kr, 5 torr F_2 gas mix at 33 A/cm^2 : (d) KrF (calc), (D) KrF (exp); (t) Kr_2F (calc), (T) Kr_2F (exp). All signals are normalized to the same peak value.

Fig. 7. Comparison of the calculated and experimental dimer and trimer fluorescence signals from a 11,600 torr He, 100 torr Kr, 5 torr F_2 gas mix at 33 A/cm^2 : (d) KrF (calc), (D) KrF (exp); (t) Kr_2F (calc), (T) Kr_2F (exp). All signals are normalized to the same peak value.

Fig. 8. Spectral dependence of the absorption in a 1500 torr Ar, 100 torr Kr, 5 torr F_2 gas mixture at the end of a 140 A/cm^2 current pulse. The solid line is the result of the calculation described in the text. The error bars are the experimental results of Powell.¹¹⁶

Fig. 9. Breakdown of the calculated absorption cross section shown in Figure 8. by absorbing species.

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Chapter V

The Formation and Quenching of Ar_2F^* and Kr_2F^*

A. Introduction

The rare gas halide (RGH) trimers Ar_2F^* and Kr_2F^* are important species in krypton fluoride laser media. Their creation from the RGH dimers represents either an interception of the gas excitation en route to the laser upper state (e.g. in the formation of Ar_2F^* , rather than KrF^* , from ArF^*) or a loss mechanism from the laser state via the formation of Kr_2F^* from KrF^* . In addition, the large concentrations of RGH trimers formed in the gas may contribute significantly to its optical absorption coefficient at the laser wavelength, as demonstrated in the preceeding chapter.

The formation and quenching of the RGH trimers has been studied at Lawrence Livermore National Laboratory by this author along with Dr. H. T. Powell. A paper describing our work on the trimer kinetics of e-beam excited mixtures of either Ar or Kr combined with either F_2 , NF_3 , or SF_6 is presented in the Appendix to this chapter. Buffered gas mixtures containing Kr, F_2 and either He, Ne, or Ar have also been examined, and are discussed in Section B of this chapter.

The experimental apparatus designed by Dr. Powell to both excite the gas mixtures and observe the resultant fluorescence is described in Section II of the Appendix. A unique feature of this setup is the ease with which the gas mixture, total gas pressure, and electron beam current density could all be varied over a wide range, while the electron energy and electron beam pulse shape remained roughly constant. Variations in average current density of 2 to 500 Amp/cm², and in total pressure of 200 to 20,000 Torr were attainable.

For the purpose of determining the trimer formation and destruction kinetics, measurement of both the RGH dimer and trimer time-dependent fluorescence decays was required. The experimental results obtained by Dr. Powell for binary gas mixtures are described in Section III of the Appendix. Similar data obtained by this author for buffered gas mixtures is discussed in Section B of this chapter.

In either binary mixtures of a rare gas with a fluorine donor, or in buffered mixtures where the buffer gas does not form a bound excited state with fluorine (i.e. with either helium or neon as the buffer), both theoretical arguments¹ and experimental measurements^{2,3} indicate that the RGH trimers are formed solely by three-body reactions with the corresponding dimer molecule (e.g. Kr₂F* from KrF*). In this case, the trimer kinetics simplifies greatly in that the time dependence of the trimer formation rate is determined solely by the relevant dimer concentration. It is this simplification that allows us to develop a simple model which ignores

the complicated processes involved in the transfer of energy from the e-beam to the RGH dimer molecule, and permits us to unambiguously determine the RGH trimer formation and decay rate constants.

The analysis developed by this author to determine the RGH trimer kinetic rate coefficients from the measurements of the dimer and trimer fluorescence signals is presented in Section IV of the Appendix. The results of this analysis when applied to the binary gas mixture data are discussed in Section V. Section B of this chapter contains the results obtained for the helium- and neon-buffered gas mixtures, and in addition discusses the results obtained for argon-buffered mixtures, where the assumption that KrF^* is the only precursor to the Kr_2F^* trimer does not apply

B. Buffered Kr-F₂ Gas Mixtures

The experimental technique described in Section II of the Appendix was used to measure the KrF^* and Kr_2F^* fluorescence signals from 20/1 Kr/F₂ gas mixtures buffered with either helium, neon or argon excited at low current density ($\approx 33 \text{ Amp/cm}^2$). To simplify the comparison of the performance using different buffers, the partial pressure ratios ($\text{He:Kr:F}_2 = 1,897:20:1$; $\text{Ne:Kr:F}_2 = 422:20:1$; and $\text{Ar:Kr:F}_2 = 246:20:1$) were chosen to yield the same energy deposition per unit volume from the 600 keV e-beam pulse as a "standard" 150/1 Kr/F₂ mixture at identical F₂ partial pressures, as calculated using the stopping powers of Berger and Selzer.⁴

Both the KrF^* and Kr_2F^* fluorescences from all of the buffered mixtures were qualitatively similar to those from the Kr-F_2 binary mixtures described in Section III of the Appendix. The peak dimer and trimer signals as a function of the average energy deposition rate for each three-component gas mix, along with those from the "standard" Kr-F_2 mixture are presented in Figures 1 and 2 respectively. The energy deposition was assumed to be twice that indicated by the stopping powers of Berger and Selzer⁴ for a single pass, as suggested by detailed numerical calculations using the three-dimensional deposition code SANDYL.⁵

The magnitude of both of the fluorescence signals changes with the buffer gas used for a number of reasons. First, as the average Z of the mixture is reduced the energy of the average initial excitation produced by the e-beam increases, as indicated by the solutions of the Fowler equation discussed in Chapter II. This implies that a fewer excitations are produced in the lower- Z gas mixtures at a given energy deposition rate, which would then yield a smaller KrF^* production rate at a given yield of RGH dimers produced per initial excitation. Secondly, as the buffer gas is changed the permitted energy pathways for transfer of energy into the KrF^* excimer themselves vary. For example, with helium as the buffer the energy in the excited states of the buffer atoms may be rapidly transferred directly to the krypton atoms via Penning ionization, which is not possible when either neon or argon is used. Finally, the kinetics of the RGH dimer-trimer system itself changes, due to the increased

pressures required with the lower-Z gases, changes in the magnitudes of the kinetic rate constants, and differences in the available kinetic pathways (e.g. the formation of ArKrF^* from KrF^* , which has no analog for either helium or neon).

The low current density analysis developed in Section IV of the Appendix for binary gas mixtures was applied to the fluorescence signals from the buffered mixes to determine the changes in the $\text{KrF}^*-\text{Kr}_2\text{F}^*$ kinetics with the various buffer gases. The best fit values of the trimer decay rate τ^{-1} determined from this analysis are plotted vs the total gas pressure in Figures 3, 4, and 5 for the helium, neon, and argon mixtures, respectively. The solid lines in each of the figures are the results of a least squares fit of the decay rate to a form linear in the gas pressure; in all cases the intercepts are consistent with the 225 nsec. radiative lifetime for Kr_2F^* obtained in the analysis of the binary gas mixture data in the Appendix.

Assuming that the pressure dependence of τ^{-1} is given by

$$\tau^{-1} = \tau_{\text{rad}}^{-1} + k_{\text{Kr}} n_{\text{Kr}} + k_{\text{buf}} n_{\text{buf}} + k_{\text{F}_2} n_{\text{F}_2} \quad (1)$$

where the "n's" represent the concentrations of the various gas species, and using the values of k_{Kr} and k_{F_2} given in Table 2 of the Appendix, the linear fits shown in Figures 3-5 yielded values for the rate constants for the quenching of Kr_2F^* by the buffer

gases. In all cases the pressure dependent quenching was dominated by its fluorine contribution (>80%), allowing us to obtain only rough estimates for the values of k_{buf} . For helium we calculate $k_{\text{He}} = (2 \pm 1) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ while for neon and argon we could only place an upper bound on k_{Ne} and k_{Ar} of $10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

The low current density analysis developed in the Appendix is strictly applicable only when the sole kinetic pathway into Kr_2F^* is directly from the KrF^* dimer. One may then question its use in the analysis of the data with argon as the buffer gas, as the additional trimer formation channel

(with the reaction rate constants $k_{2\text{Ar}}$ and k_{disp} , respectively) is available in this case. However, at the krypton partial pressures of interest here (>25 torr), the value of $k_{\text{disp}} = 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ quoted in Chapter 5 indicates that the lifetime of ArKrF^* for decay via displacement is less than 4 nsec., a value considerably less than both the characteristic time required for a significant change in the KrF^* dimer concentration and the ArKrF^* radiative lifetime. We would therefore expect the ArKrF^* concentration to be in approximate equilibrium with that of the KrF^* dimer, and to decay with nearly unit efficiency into Kr_2F^* . The treatment given in Section IV of the

Appendix then remains valid, provided that we include a term in the trimer formation rate of Kr_2F^* from KrF^* proportional to the square of the argon concentration.

The values of the trimer formation rate α determined in the analysis of the fluorescence data from all of the buffered gas mixtures, as well as that from the "standard" Kr-F_2 mix, are plotted vs the total gas pressure in Figure 6. For the binary Kr-F_2 mixture, as well as for the helium and neon buffered cases, the assumption that the trimer is formed via three-body collisions would require

$$\alpha = A_{2\text{Kr}} n_{\text{Kr}}^2 + A_{\text{buf},\text{Kr}} n_{\text{buf}} n_{\text{Kr}} \quad (3)$$

with $A_{2\text{Kr}} = S_Y k_{2\text{Kr}} / S_W$, where S_Y and S_W are the trimer and dimer detector sensitivity factors derived in the Appendix, and $k_{2\text{Kr}}$ is the rate constant for the formation of Kr_2F^* in a three-body collision of KrF^* with 2 krypton atoms. $A_{\text{buf},\text{Kr}}$ and $k_{\text{buf},\text{Kr}}$ are defined similarly. Though the data deviates slightly from the expected p^2 dependence implied by this assumption (possibly for the same reasons as suggested in the interpretation of similar results in the Appendix), we have used it to obtain estimates for the relative values of the three body formation rate constants. First, a least-squares fit of Eq. 3 to the values of α for the binary Kr-F_2 mixture yielded an estimate for $A_{2\text{Kr}}$. Using this value in a fit of

Eq. 3 to the values of α with helium or neon as the buffer then resulted in an estimate for $A_{\text{buf},\text{Kr}}$, in which case we have

$$k_{\text{buf},\text{Kr}}/k_{2\text{Kr}} = A_{\text{buf},\text{Kr}}/A_{2\text{Kr}} \quad (4).$$

The values obtained in this way for the three-body formation rate constants are $k_{\text{He},\text{Kr}} = (.25 - .6)k_{2\text{Kr}}$, and $k_{\text{Ne},\text{Kr}} = (.5 - .7)k_{2\text{Kr}}$, where the range in each of these values is given by the deviation of from its expected p^2 dependence.

For the case where argon is used as the buffer, Eq. 4 for the source term α must be modified by adding a term equal to $A_{2\text{Ar}}n_{\text{Ar}}^2$ (where $A_{2\text{Ar}}$ is defined in the same manner as $A_{2\text{Kr}}$), which corresponds to the formation of Kr_2F^* through the ArKrF^* channel. In this case the analysis of the pressure dependence of α yields only the result

$$k_{\text{Ar},\text{Kr}} + k_{2\text{Ar}}(n_{\text{Ar}}/n_{\text{Kr}}) = k_{\text{Ar},\text{Kr}} + 12.3k_{2\text{Ar}} = (2.1 - 2.5)k_{2\text{Kr}} \quad (5)$$

which is consistent with the values of $k_{\text{Ar},\text{Kr}} \approx k_{2\text{Kr}}$ and $k_{2\text{Ar}} \approx .13k_{2\text{Kr}}$ quoted in Chapter IV.

C. Discussion and Conclusions

The results obtained in the analysis of the binary gas mixtures of either krypton or argon with the various fluorine donors are reviewed in the main in Section VI of the Appendix. Regarding the excitation dependent quenching of the RGH trimers at high current densities, though we are forced to conclude that it is caused by electrons, we have found no model which can accurately predict the magnitude of its effect. Such a determination appears to require in the least a method for measuring the electron density in the e-beam excited gas on a nanosecond time scale, which to date has eluded us.

In both the binary and buffered gas mixtures the formation of the RGH trimers appears to proceed through three body collisions with the dimers. Estimates for the three-body formation rate constants for the binary gas mixtures and the helium and neon buffered mixtures have been calculated. In the argon buffered Kr-F₂ gas mix, the importance of the kinetic pathway from KrF* through ArKrF* to Kr₂F* has been demonstrated, and the trimer formation rate has been shown to be consistent with the accepted rate constants.

At the lower current densities ($< 50 \text{ A/cm}^2$), the trimer decay rate is dominated by radiative decay and heavy particle quenching in all the cases considered. Values for the trimer radiative lifetimes and either estimates or upper bounds for the heavy particle quenching rate constants have been calculated. In those cases where the

quenching of the trimer by the fluorine donor was small, we have found indications of quenching of the trimer by dissociation products of the donor.

In retrospect, it is easy to suggest improvements in the experimental work described above. By studying gas mixtures with a smaller relative concentration of the fluorine donors, it might have been possible to calculate values rather than upper bounds for the rate constants for the quenching of the trimers by the rare gas atoms, though it is possible that problems would arise due to both the resultant decrease in the fluorescence signals and the probable depletion of the fluorine donor. More significant is the fact that, if the fluorescence signals for a gas mixture with a different ratio of the argon concentration to krypton and fluorine concentrations had been measured and analyzed, values of the formation rate constants of Kr_2F^* and ArKrF^* in three body collisions involving KrF^* and an argon atom could have been obtained. For the present, however, such corrections have been precluded by a study of the performance of KrF^* laser mixtures as laser mixtures, which is treated in the following chapter.

Fig. 1. Peak KrF* fluorescence signal vs average energy deposition rate for each of the gas mixtures described in the text at an average current density of 33 A/cm^2 .

Fig. 2. Peak Kr_2F fluorescence signal vs average energy deposition rate for each of the gas mixtures described in the text at an average current density of 33 A/cm^2 .

Fig. 3. Kr_2F^+ decay rate vs gas pressure for the helium buffered mixture at an average current density of 33 A/cm^2 . The solid line is the result of the linear regression analysis described in the text.

Fig. 4. Kr_2F^* decay rate vs gas pressure for the neon buffered gas mixture at an average current density of 33 A/cm^2 . The solid line is the result of the linear regression analysis described in the text.

Fig. 5. Kr_2F^* decay rate vs gas pressure for the argon buffered gas mixture at an average current density of 33 A/cm^2 . The solid line is the result of the linear regression analysis described in the text.

Fig. 6. Kr_2F^* formation rate vs gas pressure for each of the gas mixtures described in the text at an average current density of 33 A/cm^2 .

Appendix - Chapter V

Quenching of Ar_2F^* and Kr_2F^* By Radiation,
Heavy Particles, and Electrons

K. S. Jancaitis and H. T. Powell

Abstract

Rare gas halide dimers (ArF^* and KrF^*) and trimers (Ar_2F^* and Kr_2F^*) have been studied using 50 ns, 600 keV, electron-beam excitation of two component gas mixtures. Fluorescence produced by excitation of either Ar or Kr mixed with either F_2 , NF_3 , or SF_6 was studied as a function of e-beam current density ($2\text{-}500\text{ A/cm}^2$), gas pressure (200-2000 Torr), and mixture ratio. Trimer decay rates were determined by fitting the time dependence of trimer fluorescence to the solution of a single rate equation having a driving term proportional to the experimental dimer signal. Trimer lifetimes and collisional quenching coefficients have been determined at low current density ($<50\text{ A/cm}^2$) and electron quenching of the trimer has been studied at high current density.

I. Introduction

Rare gas halide (RGH) trimer molecules such as Ar_2F^* and Kr_2F^* are important species in excimer laser media.¹⁻⁶ RGH trimers are formed by three-body collisions of excited RGH dimers with rare gas atoms. This is a major loss process for the dimers and often produces for laser conditions a greater concentration of excited trimer than dimer molecules. In addition, as discussed in the following paper, Ar_2F^* and Kr_2F^* exhibit strong absorption bands in the 300 nm region which contribute to the background optical absorption in the excited medium at the 249 nm, KrF laser wavelength. Recently, RGH trimers have also been shown to be interesting laser candidates themselves with the demonstration of laser action from Kr_2F^* and Xe_2Cl^* .⁷

RGH trimer emission occurs in broad (roughly 50 nm wide), unstructured bands approximately 2 eV to the red of the main dimer transitions.¹ Emission from Ar_2F^* is observed at 290 nm from mixtures of argon with fluorine atom donors excited by an electron beam or discharge. The Ar_2F^* emission increases with Ar pressure relative to the ArF^* dimer emission at 193 nm. The Kr_2F^* emission occurs at 410 nm and behaves similarly with respect to Kr pressure in relation to the 249 nm dimer emission. This pressure dependence as well as the observed quenching of the dimers in three-body collisions with rare gases² suggest that the RGH trimers are formed collisionally from the dimers. This view is supported by

the similarity of their excited state structures--both dimers and trimers are ionically bound in their excited states (i.e., Ar^+F^- and Ar_2^+F^- are good descriptions of the excited states).⁸⁻¹⁰

Although several authors have suggested that trimers might be produced by reactions without involving a dimer precursor^{1,11,12} (e.g., $\text{Ar}_2^+ + \text{F}^- + \text{M} \rightarrow \text{Ar}_2\text{F}^* + \text{M}$ or $\text{Ar}_2^* + \text{F}_2 \rightarrow \text{Ar}_2\text{F}^* + \text{M}$), both theoretical arguments¹⁰ and experimental measurements^{2,3} suggest that such reactions are not dominant for usual conditions.

Previous studies have determined the radiative lifetimes of Ar_2F^* and Kr_2F^* and their quenching rates by some fluorine donors using the RGH fluorescence which followed short pulse excitation of gas mixtures by either proton beams,³ uv radiation,⁴ or electron beams.¹³ In this study, we have experimentally measured the radiative lifetimes of Ar_2F^* and Kr_2F^* and their quenching coefficients by F_2 and NF_3 . We have also placed an upper limit on the trimer quenching coefficients by SF_6 . We have used 50 ns e-beam excitation of simple two-component mixtures of either Ar or Kr with F_2 , NF_3 , or SF_6 . We have simultaneously monitored both the dimer and trimer fluorescence and have applied a unique analysis to determine trimer quenching rates. The observed dimer time dependence was utilized as a source term for trimer production in a simple rate equation describing the trimer. Solutions of the rate equation were compared to the experimental trimer time dependence to determine the trimer decay rate. In addition, to observe the effect of electron quenching we have studied the dimer and trimer

fluorescence over a large range of e-beam current densities, 5 to 500 A/cm². We find that electron quenching is a major factor in the trimer kinetics but produces for our conditions no obvious effect on the dimer. This difference is largely accounted for by the normally longer decay time of the trimers (≈ 50 ns) compared to the dimers (≈ 5 ns) so that additional quenching by electrons causes a much larger relative effect for the trimers.

II. Experimental Setup

We have used a 600 keV, 50 ns-duration e-beam of variable current density to excite gas mixtures producing RGH fluorescence. The e-beam was powered by a Maxwell Pocobeam accelerator¹⁴ consisting of: a 28-stage Marx generator; a 10Ω , water dielectric, pulse-forming line; a self-breakdown output switch; and a field emission diode. A schematic diagram of the e-beam diode, beam-drift region, and laser cell is shown in Fig. 1. The pulsed output voltage between the carbon cathode and the 1.3×10^{-2} cm-thick, titanium diode foil was approximately 1 MV and the diode current was approximately 50 kA. The cross section of the e-beam was roughly 1×10 cm² at the diode foil.

Confined between two metal plates separated by 2.5 cm, the beam propagated to the cell through a 15 cm long, beam-drift region. The gas pressure (air) in the beam drift region was 15 Torr. To reduce the beam current density, carbon attenuator plates (each 0.6 cm-thick and perforated with numerous holes ranging from 0.1 to 1 cm diam) were

individually placed midway in the drift region as shown schematically in Fig. 1. As judged by chlorostyrene dosimetry at the cell the beam profile was quite uniform with the attenuators in place. Self-forces apparently cause the beam to homogenize within the drift region after passing through an attenuator plate. The electron beam finally passed through a foil support structure and 7.6×10^{-3} cm-thick Inconel foil to excite gas mixtures in the cell. Inconel was used as foil material because of its resistance to fluorine attack. The support structure had a transmitting area of 2.5 cm x 10 cm with transverse ribs to support the foil. The 14 ribs individually presented a width of 0.18 cm to the beam producing a geometric transmission factor for the support structure of 75 percent.

We measured the e-beam current density impinging on the gas for the various attenuators by placing a Faraday cup in the gas cell immediately behind the cell foil. The current collector consisted of a 2.5 cm x 10 cm x 0.6 cm thick carbon plate attached top and bottom along its 10 cm dimension to thin stainless steel sheets which provided a $13.6 \text{ m}\Omega$ path to ground. To minimize inductance the stainless steel conductors were held firmly against a thin insulator separating them from the top and bottom surfaces of the cell at ground potential. The Faraday cup was calibrated using a mercury-pulsar-driven current source and its risetime was measured to be less than 10 ns.

The gas volume of the cell available for e-beam excitation was 10 cm long with a cross section of 2.5 cm by 2.5 cm. However, to insure that our detectors viewed only fluorescence from a homogeneously-excited region, we placed a stainless steel insert in the cell to reduce the excited volume as shown schematically in Fig. 1. The insert defined an excited volume having a length of 2.5 cm, a height of 1 cm, and a depth of 1.5 cm. The e-beam excitation within this region was presumed to be uniform. We determined the current density impinging on this volume by removing the insert and using the Faraday cup with an appropriate metal mask.

Fluorescence was observed endwise through 1 cm diam holes in the insert block and transversely through a 0.3 cm diam hole. The hole diameters were made as small as possible (consistent with adequate signal levels) compared to the depth of gas observed to minimize edge effects. We also chose the fluorescence volume to be small to minimize the effects of amplification and absorption on the observed fluorescence signals. This assumption was checked by comparing the shape of fluorescence signals from the 2.5 cm and 1 cm directions. At the highest current densities, a small difference was found for the two dimer signals. To eliminate effects due to gain, the dimer fluorescence was measured in the 1 cm direction for current densities greater than 200 A/cm^2 . The gain and absorption coefficients described in the following paper also suggest the medium was optically-thin (when spectrally averaged over the emission bands) for these dimensions.

For our excitation depth, gas pressures, and beam voltage (approximately 600 keV in the cell), the energy deposition in the gas is simply proportional to current density since the percentage of the beam energy deposited in the gas is very small (<1%). The energy deposition was calculated for 1 and 2 atm of Ar using the three-dimensional deposition code SANDYL.¹⁵ The calculated depositions were approximately twice the values predicted by simply using the stopping powers tabulated by Berger and Selzer.¹⁶ This difference is largely caused by electron back-scatter from the stainless steel walls. Although the SANDYL-calculated deposition was roughly confirmed by pressure-rise measurements, we still regard our energy deposition values as somewhat uncertain. Our best estimate (+25%) is that the deposited energy was 25 mJ/cm³ per atmosphere of Ar at 100 A/cm² and 45 mJ/cm³ per atmosphere of Kr at 100 A/cm².

The gas cell and its fill system, constructed of stainless steel, were thoroughly passivated with F₂ and evacuated between fills to less than 10⁻⁴ Torr. We measured subatmospheric pressures with a capacitance manometer and higher pressures with a strain gauge. Gas mixtures were composed in 1 liter mixing bottles using commercially pure F₂ and NF₃ and research grade rare gases. To insure complete mixing the bottles were left several hours before use. We typically used gas from the same mixture batch for each data set and refilled the cell with fresh gas from the mixture bottle for each shot.

Biplanar vacuum photodiodes, 2.5 cm in diameter, viewed the fluorescence from the excited volume through bandpass filters. The photodiodes were shielded by 1 cm-thick lead to prevent x-ray induced signals. An S-20-photocathode detector monitored the trimer fluorescence while a CsTe-photocathode detector monitored the dimer fluorescence. We isolated the Kr_2F^* fluorescence with a Corning 5-56 filter¹⁴ and the Ar_2F^* fluorescence with a Corning 7-54 filter.¹⁴ The detector response curves, filter transmissions, and trimer spectra are shown in the following paper (see Figs. 2 and 3). We isolated the ArF^* and KrF^* B-X emissions with interference filters having bandwidths of 20 nm and 10 nm centered at 195 and 250 nm, respectively. For absolute calibration purposes the photodiodes viewed the excited volume through pinholes as described in the following paper. However, for these studies the photodiodes were typically placed immediately behind the MgF_2 output windows located approximately 5 cm from the excited volume.

The photodiode signals were monitored by Tektronix 7904 oscilloscopes¹⁴ housed in a screen room where the traces were photographed on a single-shot basis. The cable lengths for the two photodiodes were adjusted to be equal and a terminating resistor of 50Ω was used both at the detector and oscilloscope to eliminate reflected voltage signals. The risetime of the detection system was approximately 1 ns. A saturating photodiode viewed light produced by the breakdown of the output switch and thus provided a trigger pulse. This signal was also split, differentiated, and delayed to provide a

fiducial pulse. Since the timing of the e-beam pulse incident on the cell was fixed relative to the switch breakdown, this method permitted accurate relative timing of the signals to within 2 ns.

III. Experimental Results

A. Ar-F₂ and Kr-F₂ mixtures

The most exhaustive set of experiments was performed using F₂ as the fluorine donor. The dimer and trimer fluorescence signals were observed for independent variations in the electron beam current density, the total gas pressure, and the ratio of rare gas to F₂ partial pressures. The fluorescence signals from Ar-F₂ mixtures were qualitatively similar to those from Kr-F₂ mixtures in all cases studied.

Comparisons of the e-beam current density, ArF* fluorescence, and Ar₂F* fluorescence are shown in Fig. 2 for low (33 A/cm²) and high (400 A/cm²) current density for a typical gas mixture and pressure. The negative pulse at the end of each trace is the common fiducial pulse. The current pulse was approximately rectangular and constant in shape as the current density was varied as shown in Fig. 2(a). Figure 2(b) shows that the ArF* signal followed the current pulse with about a 10 ns delay and was also roughly constant in shape. However, as shown in Fig. 2(c), the Ar₂F* time dependence varied considerably with current density.

The Ar_2F^* signal is unlike the ArF^* signal mainly because of its longer radiative lifetime. At low current density the trimer signal appears to integrate the dimer signal and then decay with a time constant which is the same during and after the e-beam current pulse. This behavior is consistent with the view that the trimer is formed from the dimer by three-body collisions and then decays by a time-independent loss process consisting of radiative decay plus collisional quenching. At high current density, the trimer appears to approach a steady state more rapidly during the current pulse than it decays after the pulse. This suggests a larger quenching rate for the trimer during the pulse, presumably by electron collisions.

The peak fluorescence amplitudes plotted versus average current density also suggest an e-beam-related quenching of the trimers. Figures 3 and 4 show the peak ArF^* and Ar_2F^* signals and peak KrF^* and Kr_2F^* signals, respectively, as a function of average current density. While the dimer signals increase almost linearly with current density, the trimer signals roll-off strongly at the highest current densities. Because the trimer's normal decay time is much longer than the dimer's, electron quenching (or any other excitation-density dependent quenching) is comparatively more important for the trimer. Indeed to predict the trimer concentration accurately it appears necessary to include this additional quenching in a description of the trimer kinetics for current densities as low as 50 A/cm^2 . Figures 3 and 4 also show that for these mixtures electron quenching does not cause a significant reduction in the dimer

intensity for e-beam current densities up to 500 A/cm^2 . The same general behavior of the KrF^* and Kr_2F^* intensities with current density was also found for a typical KrF laser mixture consisting of 1500 Torr Ar, 100 Torr Kr, and 5 Torr F_2 .

L. Ar- NF_3 and Kr- NF_3 mixtures

Using NF_3 as the fluorine donor, we varied the experimental parameters in much the same way as that described for F_2 mixtures. In both Ar- NF_3 and Kr- NF_3 mixtures, the dimer fluorescence followed the e-beam current density in a manner similar to that observed for F_2 mixtures. The dimer fluorescence intensities using NF_3 were roughly 40 percent of those using F_2 mixtures. Although the behavior of the Ar_2F^* fluorescence was similar for F_2 and NF_3 mixtures with argon, the Kr_2F^* behavior was radically different for F_2 and NF_3 mixtures with krypton.

The Kr_2F^* fluorescence signals from a typical Kr- NF_3 gas mixture are shown in Fig. 5 for high and low current densities. At low current density the trimer decayed after the current pulse with a decay constant comparable to its radiative lifetime implying that NF_3 collisional quenching of Kr_2F^* is small. At high current density the trimer decayed with a fast rate both during and after the current pulse. This suggests that the excitation-dependent quenching of Kr_2F^* is more important and that its importance is relatively longer-lived for NF_3 mixtures than for F_2 mixtures. Thus to determine the heavy particle quenching rate of Kr_2F^* by NF_3 it

was necessary to use very low current densities ($<10 \text{ A/cm}^2$). To increase the fluorescence signals at these very low excitation rates, we generally removed the metal insert in the cell since we were not concerned about excitation uniformity or optical depth in that case.

C. Ar-SF₆ and Kr-SF₆ mixtures

We found SF₆ to be a relatively inefficient fluorine donor for producing RGH fluorescence. Although SF₆ mixtures produced dimer signals similar in time dependence to either F₂ or NF₃ mixtures, the peak dimer intensities were less than 10 percent of the comparable F₂ case. The trimer signals were also smaller by a similar factor.

For both Ar-SF₆ and Kr-SF₆ mixtures the trimer fluorescence varied with current density much like the Kr-NF₃ case. That is, there was a long-lived excitation-dependent quenching. Thus to observe the heavy particle quenching rates of the trimer by SF₆ we again used very low current densities ($<10 \text{ A/cm}^2$). For these conditions both the Ar₂F* and Kr₂F* signals decayed in times comparable to their radiative lifetimes suggesting that trimer quenching by SF₆ is quite small.

IV. Analysis

The study of the trimer kinetics is considerably simpler than that for the dimer. First, the trimer decays on a relatively long time scale so that it may be easily observed after its production has

ceased to determine its decay rate. Second, the dimer emission provides the time dependence of the source of trimer production. The dimer on the other hand is produced by several ionic recombination as well as neutral reaction processes which follow e-beam excitation. To analyze the trimer kinetics we made the following assumptions:

- (i) That the dimer and trimer fluorescence signals are proportional to the corresponding species densities;
- (ii) That the trimer is formed solely from the dimer, the formation rate being proportional to the dimer density;
- (iii) That at low current densities the trimer is quenched with a time independent rate constant.

Under these assumptions at low current densities the trimer fluorescence signal ($Y(t)$) and the dimer fluorescence signal ($W(t)$) are related by a single equation

$$\dot{Y} = \alpha W - \tau^{-1} Y \quad (1)$$

the source term α is given by

$$\alpha = S_Y K / S_W \quad (2)$$

where K is the pressure dependent trimer formation rate constant, and S_W and S_Y are detector sensitivity factors defined by $W = S_W n_W$, $Y = S_Y n_Y$ where n_W and n_Y are the dimer and trimer number densities, respectively. The determination of these factors is discussed in detail in the Appendix. The decay term τ^{-1} in

Eq. (1) is the sum of radiative decay (τ_{rad}^{-1}) and two body quenching processes ($k_i n_i$).

Using the dimer fluorescence as input, we fitted the observed trimer time dependence at low current densities to the solution of Eq. (1) to determine best fit values for α and τ^{-1} . The oscillograms of the fluorescence signals were first digitized at approximately 40 points chosen to allow full definitions of the curves. Quadratic interpolation yielded the "experimental" values $Y_i \approx Y(t_i)$ and $W_i = W(t_i)$ on a 1 ns-spaced mesh of points in time.

Before solving Eq. (1) for a prediction of the trimer fluorescence to be matched to the experimental results, it is convenient to define an auxiliary variable $U(t) = Y(t)/\alpha$, so that Eq. (1) becomes

$$\dot{U} = W - \tau^{-1}U. \quad (3)$$

Using the experimental values of the dimer fluorescence as input, Eq. (3) was integrated numerically to get the values u_i , the predicted value $U(t_i)$, as a function of the parameter τ^{-1} (see Appendix). Notice that we represent experimental fluorescence intensities by capital letters and predicted values by lower case letters. The predicted value of the trimer fluorescence signal y_i is then given as a function of α and τ^{-1} as $y_i = \alpha u_i$.

The best-fit values of the parameters α and τ^{-1} were then determined by minimizing the error

$$\Delta^2 = \sum_i (y_i - \hat{y}_i)^2 \quad (4)$$

between the experimental and predicted values for the trimer fluorescence signal. Minimizing Δ^2 with respect to α gives

$$\alpha = \sum_i u_i y_i / \sum_i u_i^2 \quad (5)$$

Thus α is a scale factor which relates the reduced variable u_i to the predicted y_i which best fits the experimental data.

Using Eq. (A1) in the Appendix and Eq. (5) to find u_i and α we determined the error Δ^2 associated with a given value of τ^{-1} . The error was then minimized with respect to τ^{-1} using a modified Gauss-Newton method where the derivatives were calculated numerically using finite differencing. The error in the best-fit value of τ^{-1} was estimated as that increase (or decrease) required to increase the error sum Δ^2 to twice its minimum value. The error in the best-fit value for α was simply estimated to be that associated with the error range for τ^{-1} .

Values for the trimer radiative lifetimes and quenching coefficients were obtained from the variations of the trimer decay

rate τ^{-1} with total gas pressure and gas mix. Specifically, we assumed τ^{-1} to be of the form

$$\tau^{-1} = \tau_{\text{rad}}^{-1} + k_r n_r + k_d n_d \quad (6)$$

where the subscripts r and d imply a rare gas or a fluorine donor, respectively. Taking the decay rate data at two different mixture ratios, we used multiple linear regression on Eq. (6), weighting each point according to its error range, to determine the trimer radiative lifetime and its quenching coefficient by the rare gas and the fluorine donor.

The analysis of the trimer time dependence at high current densities was performed in a different manner because of the presence of an additional current dependent quenching term. Defining the experimental trimer and dimer fluorescence signals as in Eq. (2), we expect them to be related at high current density by

$$\dot{Y} = \alpha W - \tau^{-1} Y - \gamma(t) Y \quad (7)$$

Notice that we make no assumptions about the time dependence of the additional quenching labeled $\gamma(t)$ but we presume that the values of α and τ^{-1} determined at low current density to continue to apply. Notice that we make no assumptions about the products of trimer decay. In fact the analysis would still be correct even if the trimer

decay led to the production of dimers since we have used the experimental dimer signal as input.

The function $\gamma(t)$ was determined first by digitizing the fluorescence curves to yield the experimental points Y_i and W_i , as was done for the low current density data. Numerical differentiation of the function $Y(t)$, followed by a subtracting out of the radiative and heavy particle decay rates then yielded the current dependent quenching term $\gamma(t)$ (see the Appendix for details).

V. Results and Interpretation

A. Low Current Density

At low e-beam current density, the agreement between the experimental ($Y(t)$) and model ($y(t)$) trimer fluorescence was extremely good. Figure 6 shows the results of analyzing the low current density data of Fig. 2. An excellent match between the model and experiment was generally obtained when the current density was low enough to make any excitation-dependent quenching contribution negligible.

The best-fit values of τ^{-1} obtained from the low-current analysis are plotted in Fig. 7 for Ar-F₂ mixtures as a function of total gas pressure. Results are shown for two Ar-F₂ mixture ratios and for two e-beam current densities. Notice that for these low current densities the fitted decay rates do not vary with current density. The Ar-NF₃ and Kr-F₂ results behaved similarly. The

solid lines in Fig. 7 are the results of the multiple linear regression fit of the values of τ^{-1} to the form shown in Eq. (6). In this way we determined both the Ar_2F^* radiative lifetime and the rate coefficients for Ar_2F^* quenching by both Ar and F_2 . The results from fitting the Kr- F_2 and Ar- NF_3 data were generally similar to those shown in Figs. 6 and 7.

The best fit values of τ^{-1} for Kr_2F^* in Kr- NF_3 mixtures are shown in Fig. 8. The small quenching rate constant for Kr_2F^* by NF_3 suggested in the discussion of the experimental results is evident by the slower increase in the quenching rate with gas pressure. The fitted trimer quenching rates for SF_6 mixtures varied so slowly that there was no clear dependence on gas pressure in that case.

The trimer radiative lifetimes and quenching rate constants obtained in this manner are summarized in Tables I and II, along with the results of other workers for comparison. The radiative lifetimes are somewhat longer than both the calculated values and previous measurements. Our F_2 and NF_3 quenching rate coefficients are in the range of several previous determinations. There appears to be no previous data for trimer quenching by SF_6 .

The values of the trimer formation rate constant α determined by our fitting procedure are shown in Figs. 9 and 10 for Ar_2F^* and Kr_2F^* , respectively. Because of the large number of overlapping

data points we have found it convenient in both figures to shift some of the data either up or down a factor of 2 in pressure. For comparison, we have associated with each data group a common line having a p^2 -slope which has been similarly shifted in pressure. Representative error bars are shown for only one set of data points.

It is evident from Figs. 9 and 10 that the trimer formation rate is independent of fluorine donor, mixture ratio, and e-beam current density. The values of α obtained from SF_6 mixtures were also consistent with this conclusion. This result is expected if the trimer is formed solely from the dimer and would not be expected for trimer formation via alternative mechanisms. Although we expect a simple p^2 -dependence for a three-body formation rate, the curves for the various conditions all deviate from the p^2 -line at high pressures. Though we have no clear explanation of this effect it is consistent with a decrease in the effective radiative lifetime of the dimer at high pressure, as previously reported for KrF^* .⁴ A decrease in effective dimer lifetime might be caused by B-C state mixing as well as vibrational relaxation since the radiative lifetime differs for the B and C states and for different vibrational levels.¹⁷

Using the sensitivity factors described in the Appendix and Eq. (2), one can convert the p^2 lines in Figs. 8 and 9 to three-body formation rate coefficients k defined by $K = kn_r^2$. However, since the effective radiative lifetime of the dimer is uncertain, we leave

it as a parameter τ_d . Thus we obtain $k\tau_d$ products of $3.1 \times 10^{-39} \text{ cm}^6$ for Ar_2F^* formation from ArF^* in argon and $2.1 \times 10^{-39} \text{ cm}^6$ for Kr_2F^* formation from KrF^* in krypton. These values have roughly a ± 25 percent uncertainty resulting from the uncertainty in the sensitivity factors. The $k\tau_d$ product for argon is in the range of previous measurements.^{2,3,13} The value for krypton is somewhat smaller than previous determinations.^{2,3,18}

B. High Current Density

Figure 11 shows the results of analyzing the high current data shown in Fig. 2 using the analysis described in Sect. IV. During the current pulse, the excitation-dependent quenching rate is about three times greater than the sum of the radiative and heavy particle quenching. In addition, this additional quenching goes to zero after the current pulse as expected for quenching by a transient species.

Figures 12 and 13 show characteristic values of the current-dependent quenching rates obtained by averaging over the current pulse for Ar-F_2 and Kr-F_2 mixtures, respectively. Again, representative error bars are shown on only one set of data points in each figure. The error range shown in the average current density is the full range of the current variation over the pulse length. Each solid line is a linear fit to the data at a given gas mixture. Within the scatter of the data, the additional quenching increases linearly with current density as expected. However, it does not vary inversely with F_2 density as one would expect quenching by electrons to vary

in a simple model discussed below. Although the current-dependent quenching generally declines with added F_2 the dependence is weak.

In a simple model when the primary electron loss is dissociative attachment to F_2 , the electron density is given by the production rate of electron-ion pairs divided by the attachment rate to F_2 . The production rate of electron-ion pairs can be determined from the e-beam energy deposition rate assuming an energy cost of 26.2 eV/electron-ion-pair in argon and 24.3 eV/electron-ion-pair in krypton.¹⁹ Because the electron attachment rate coefficient by F_2 is very fast, approximately $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$,²⁰ the electron density should track the current pulse with a delay of less than 2 ns for our conditions. Presuming the electron attachment rate coefficient by F_2 to be constant, the electron density should vary inversely with F_2 density in this model.

One complication to this model is that the addition of F_2 can cause a deviation in the electron energy distribution because of the large loss rate for electrons near zero energy.²⁰ This could cause the effective attachment coefficient referenced to the total electron density to decline. In principle this might be the cause of the behavior shown in Figs. 12 and 13. However, a clear resolution of this problem is not possible without an independent measurement of the electron density for these conditions.

We can estimate the trimer quenching coefficient by electrons via the simple prescription above and the energy deposition values given in Sect. II. Using the data in Figs. 12 and 13 at 2.5 Torr of F_2 and assuming an electron attachment coefficient of $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, we estimate the electron quenching rate coefficient of Ar_2F^* is $4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and that of Kr_2F^* is $1.3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. These quenching coefficients are similar in magnitude to those previously measured for ArF^* and KrF^* ,²¹ and estimated for Ar_2F^* .⁶ Because of their ionic structure, RGH trimers may be quenched by a mechanism analogous to rare gas dimer ion recombination. However, because the trimers have no net charge, it is not surprising that these rate coefficients are significantly less than measured rare-gas, dimer-ion, recombination coefficients.²²

We have also considered the possibility that the excitation-dependent quenching of the trimers might be caused by a transient species other than electrons. The trimers themselves are the transient species of greatest concentration ($\geq 5 \times 10^{15} \text{ cm}^{-3}$) as discussed in the following paper. To account for the additional quenching in F_2 mixtures by trimer-trimer collisions would thus require a quenching coefficient of order $10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Such a value seems unreasonably large for a heavy-particle quenching rate. Attributing this quenching to any of the other short-lived species in the gas would require an even larger quenching coefficient.

When either the initial fluorine donor quenching coefficient is small (such as for the Kr-NF₃ and rare gas-SF₆ mixtures), or the excitation of the gas is sufficient to deplete the fluorine donor, fragments produced from the fluorine donor could contribute significantly to the trimer decay rate. The simultaneous presence of quenching by both electrons and fragments complicates the interpretation of the results. Consider the Kr-NF₃ data shown in Fig. 8. If we assume that one fragment was produced per initial excitation in the gas and also assume that the current-dependent quenching at late times was entirely caused by fragments, it would require a fragment quenching coefficient on the order of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Hence, it seems quite reasonable in this case to attribute the late-time quenching to fragments.

In the highly-excited rare gas-F₂ mixtures at low F₂ pressures, a similar calculation indicates that nearly all of the F₂ was dissociated. However, we still found from the analysis that the trimer quenching rate after the current pulse corresponded closely to that expected from the initial F₂ density (see Fig. 11). This suggests that the quenching rate coefficient of the RGH trimers by fluorine atoms is between .5 and 1 times the corresponding value for F₂. The dissociation of F₂ could also effect the predicted electron densities and thus the interpretation of the data in Figs. 12 and 13.

VI. Conclusions

The time dependence and pressure dependence of Ar_2F^* and Kr_2F^* fluorescence observed using e-beam excitation of Ar or Kr mixtures with either F_2 , NF_3 , or SF_6 are consistent with trimer formation by three-body collisions of rare gases with the corresponding RGH dimer. At low excitation rates (e-beam current densities less than 50 A/cm^2) the trimer decay is usually dominated by radiative decay plus heavy particle collisional quenching. We have determined trimer decay rates by fitting the time dependence of trimer fluorescence to the solution of a rate equation having a driving term proportional to the experimental dimer signal. Stern-Volmer plots of the fitted rates have yielded trimer radiative lifetimes and collisional quenching coefficients by F_2 and NF_3 . Quenching coefficients of the trimers by rare gases and SF_6 are very small.

Excitation dependent quenching of the trimers is observed for e-beam current densities greater than 50 A/cm^2 . This additional decay causes a change in the trimer amplitudes which is consistent with the observed change in trimer time dependence. For F_2 mixtures the excitation-dependent decay rate follows the current pulse suggesting that it is caused by a transient species. Based on the magnitude of this additional decay we are forced to conclude that it is caused by electrons even though the expected dependence on F_2 pressure is not found. In cases where the trimer quenching by the

fluorine donor is small, trimer deactivation by dissociation fragments also appears to be significant.

Appendix to the Appendix - Chapter V

Assuming that the dimer fluorescence signal is accurately approximated by a linear function in any time interval t_i to t_{i+1} , the solution of Eq. (3) for the predicted values u_i in terms of the W_i and τ^{-1} is given by the recursion relation

$$u_{i+1} = u_i \exp(-\Delta t/\tau) + W_i \tau \left\{ \frac{\tau}{\Delta t} \left[1 - \exp(-\Delta t/\tau) \right] - \exp(-\Delta t/\tau) \right\} + W_{i+1} \tau \left\{ 1 - \frac{\tau}{\Delta t} \left[1 - \exp(-\Delta t/\tau) \right] \right\} \quad (A1)$$

with appropriate initial conditions where $\Delta t = t_{i+1} - t_i$.

Assuming that both the dimer and fluorescence signals can be approximated by linear functions in any time interval t_i to t_{i+1} , and defining $t_i^+ = (t_{i+1} + t_i)/2$, the solution of Eq. (7) for $\gamma(t)$ is given by

$$\gamma(t_i^+) = \alpha \frac{(W_{i+1} + W_i)}{(Y_{i+1} + Y_i)} - \frac{2(Y_{i+1} - Y_i)}{\Delta t (Y_{i+1} + Y_i)} - \tau^{-1} \quad (A2)$$

where again $\Delta t = t_{i+1} - t_i$.

The detector sensitivity factors S_Y and S_W were determined by measuring the absolute emission intensities of both the dimer and trimer for a well-defined geometry. Pinholes of radii 0.36 cm were located at the cell output window and at the detector. The pinholes

were separated by 54 cm. The projection of an illuminated field at the detector through the pinholes demonstrated that the field of view through the 2.5 cm excited length was unobstructed. For this simple geometry the detector sensitivity factor S_Y for the trimer fluorescence is given by

$$S_Y = \frac{Y}{n_Y} = D R_L \frac{h\nu}{\tau_{\text{rad}}} \left\{ \frac{\pi r_1^2 r_2^2}{4d^2} L \right\} \quad (\text{A3})$$

with the following definitions:

Y = trimer detector signal in volts

n_Y = trimer density

D = detector response in A/W averaged over the emission band

R_L = load resistance

$h\nu$ = quantum energy of the trimer fluorescence photon

r_1, r_2 = pinhole radii

L = length of excited gas

d = pinhole separation.

A similar formula holds for the dimer fluorescence detector sensitivity S_W . The factor in parenthesis, an effective volume, can be derived by simple application of the brightness theorem.²³ The determination of the detector response will be discussed in detail in a future paper on optical absorption in e-beam excited rare gas and rare gas halide laser mixtures.

Table I
Ar₂F* Decay Constants

Radiative Lifetime

$$\begin{aligned}\tau_{\text{rad}} &= 205 \pm 20 \text{ ns} \quad (\text{this work}) \\ &= 185 \pm 46 \text{ ns} \quad (\text{Ref. 3}) \\ &= 219 \pm 15 \text{ ns} \quad (\text{Ref. 13}) \\ &= 132 \text{ ns} \quad (\text{Theory, Ref. 10})\end{aligned}$$

Quenching Rate Coefficients

$$\begin{aligned}k_{\text{Ar}} &< 10^{-14} \text{ cm}^3 \text{ s}^{-1} \quad (\text{this work}) \\ &< 10^{-14} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 13}) \\ \\ k_{\text{F}_2} &= (1.79 \pm .06) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{this work}) \\ &= (2.1 \pm .5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 3}) \\ &= (2.05 \pm .06) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 13}) \\ &= 4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 5}) \\ \\ k_{\text{NF}_3} &= (1.07 \pm .07) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{this work}) \\ &= (1.23 \pm .05) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 13}) \\ \\ k_{\text{SF}_6} &< 10^{-13} \text{ cm}^3 \text{ s}^{-1} \quad (\text{this work})\end{aligned}$$

Table II
Kr₂F* Decay Constants

Radiative Lifetime

$$\begin{aligned}\tau_{\text{rad}} &= 225 \pm 21 \text{ ns (this work)} \\ &= 165 \pm 41 \text{ ns (Ref. 3)} \\ &= 181 \pm 12 \text{ ns (Ref. 4)} \\ &= 200 \pm 18 \text{ ns (Ref. 12)} \\ &= 132 \text{ ns (Theory, Ref. 10)}\end{aligned}$$

Quenching Rate Coefficients

$$\begin{aligned}k_{\text{Kr}} &< 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ (this work)} \\ k_{\text{F}_2} &= (1.8 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (this work)} \\ &= (3.40 \pm 8.5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (Ref. 3)} \\ &= 1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (Ref. 5)} \\ k_{\text{NF}_3} &= (2.7 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \text{ (this work)} \\ k_{\text{SF}_6} &< 10^{-13} \text{ cm}^3 \text{ s}^{-1} \text{ (this work)}\end{aligned}$$

Figure Captions - Appendix

- Fig. 1 Schematic diagram of experimental setup for RGH trimer kinetics studies.
- Fig. 2 Comparison of the time dependence at low and high current densities of the (a) e-beam current, (b) ArF* fluorescence, and (c) Ar₂F* fluorescence. A 2.5 Torr F₂-1500 Torr Ar gas mixture was used.
- Fig. 3 Peak ArF* and Ar₂F* fluorescence signals vs average e-beam current density for a 5 Torr F₂-1500 Torr Ar gas mixture.
- Fig. 4 Peak KrF* and Kr₂F* fluorescence signals vs average e-beam current density for a 5 Torr F₂-750 Torr Kr gas mixture.
- Fig. 5 Comparison of the time dependence of the Kr₂F* fluorescence at low and high current densities for a 5 Torr NF₃-750 Torr Kr gas mixture. The average current densities were 2.2 A/cm² and 400 A/cm².
- Fig. 6 Comparison of the experimental and model trimer fluorescence signals at low current density Curve "E" is the experimental ArF* signal of Fig. 2(c), curve "T" the result of the analysis of Sect. IV.
- Fig. 7 Ar₂F* decay rate vs gas pressure for concentration ratios of (a) [Ar]/[F₂] = 300/1, (b) [Ar]/[F₂] = 600/1. The solid lines are the results of the linear regression analysis described in the text.

Fig. 8 Kr_2F^* decay rate vs gas pressure for concentration ratios of (a) $[\text{Kr}]/[\text{NF}_3] = 75/1$ and (b) $[\text{Kr}]/[\text{NF}_3] = 150/1$. The solid lines are the results of the linear regression analysis described in the text.

Fig. 9 Ar_2F^* formation rate α vs gas pressure for various gas mixtures and e-beam current densities: (a) Ar-F_2 , 11 A/cm^2 , $X = 0.5$; (b) Ar-F_2 , 33 A/cm^2 , $X = 1$; (c) Ar-NF_3 , 11 A/cm^2 , $X = 2$. The triangles and circles are results for mixtures with concentration ratios of argon to fluorine donor of 300/1 and 600/1, respectively.

Fig. 10 Kr_2F^* formation rate α vs gas pressure for various gas mixtures and e-beam current densities: (a) Kr-F_2 , 11 A/cm^2 , $X = 0.5$, (b) Kr-F_2 , 33 A/cm^2 , $X = 1$, (c) Kr-NF_3 , 2.2 A/cm^2 , $X = 2$. For (a) and (b) the triangles and circles are results for mixtures with concentration ratios of $[\text{Kr}]/[\text{F}_2]$ of 150/1 and 300/1, respectively. For (c) the triangles and circles are results for mixtures with concentration ratios of $[\text{Kr}]/[\text{NF}_3]$ of 75/1 and 150/1, respectively.

Fig. 11 Ar_2F^* quenching rates vs time obtained from analysis of the high current density data of Fig. 2. The sum of the radiative and heavy particle decay rates is τ^{-1} ; the excitation-dependent quenching rate is $\gamma(t)$.

Fig. 12 Current dependent Ar_2F^* quenching rate vs current density for gas mixtures of: (a) 2.5 Torr F_2 -1500 Torr Ar (Δ); (b) 5.0 Torr F_2 -1500 Torr Ar ($\diamond$); (c) 7.5 Torr F_2 -1500 Torr Ar (o). The solid lines are least square fits to the data for the given gas mixtures.

Fig. 13 Current dependent Kr_2F^* quenching rate vs current density for gas mixtures of: (a) 2.5 Torr F_2 -750 Torr Kr (Δ); (b) 5.0 Torr F_2 -750 Torr Kr ($\diamond$); (c) 7.5 Torr F_2 -750 Torr Kr (o). The solid lines are least squares fit to the data for the given gas mixtures.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

References - Chapter V

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Chapter VI

The Observation and Modelling of KrF Laser Action

A. Introduction

The previous five chapters have described the theoretical and experimental development of a kinetic model for the KrF laser system, including some comparisons of the model to the results of both fluorescence and absorption experiments. The acid test of this model however rests in the comparison of its predictions with the experimental observation of laser operation to which it specifically applies. In this chapter we present the results of some experiments on the variation of the performance of a KrF laser with gas mixture, and compare them with the predictions of our kinetics model.

In Section B. we describe the experimental setup used to produce and observe KrF laser action in e-beam excited gas mixtures. With the addition of U. V. mirrors, the gas cell described in Chapter V and used in that case for the generation of rare gas halide excimer fluorescence was converted into a laser cavity. Both the time dependence of the laser flux and the total energy output from the

laser were monitored. In addition, the time dependence of either the KrF^* or Kr_2F^* sidelight fluorescence during the laser pulse could be measured.

In the next section we describe the specific form of the kinetic model which we used to numerically calculate the predicted behavior for such a laser system. Specifically we discuss the complications introduced when the laser flux has to "boot-strap" itself up from the spontaneous emission of the medium. In cases where the time required for this buildup is longer than the excitation pulse it may happen that no measurable laser action occurs, even though the net gain of the cavity is always positive.

In Section D. we present our experimental results for the comparison with gas mixture of the performance of e-beam pumped Kr-F_2 laser gas mixes buffered with either helium or neon at both high ($\sim 430 \text{ A/cm}^2$) and intermediate current density ($\approx 160 \text{ A/cm}^2$) and compare them with the predictions of our kinetics model. The experimental and calculated values of both the total energy output from the laser and the time dependence of the laser flux were found to agree moderately well.

In Section E. we conclude with a discussion of what has been learned in the development of our KrF laser kinetics model. We list both the successes and the shortcomings of the present model, and point out the systems for which we feel it provides accurate predictions. Finally, we discuss some ways in which the model itself

might be improved, especially as concerns the heavy particle kinetics of helium buffered mixtures.

B. Experimental Technique

A schematic diagram of the apparatus used to produce and observe KrF laser action is presented in Fig. 1. The setup is essentially the same as that used for the fluorescence experiments of Chapter V and described in Section II of the appendix to that chapter. Modifications were made only in the configuration of the gas cell and in the diagnostic equipment used.

The length of the active volume of the cell (defined by the stainless steel insert) was increased to 10. cm. while its depth and height were held at 1.5 and 1.0 cm., respectively. This change allowed us to make use of the full lateral extent of the electron beam and thus provided the maximum possible small signal gain in the medium. The spatially averaged current density injected into this volume was measured with a suitably apertured Faraday cup, and was found to be only slightly smaller (<10%) than that observed for the 2.5 cm. long volume discussed in Chapter V.

The laser cavity was defined by placing circular front surface dielectric coated (on a MgF_2 substrate) U. V. mirrors at both ends of the 10. cm. long active region. The separation of the mirror surfaces from the lasing volume was small enough (<1 cm.) so that the

absorption due to F_2 in this dead region was negligible (<1%). At one end (facing a U. V. photodiode) we used a maximum-reflectivity mirror (reflectivity 99% at 249 nm.) throughout the experiment. At the other end of the cavity we used a 50% reflective mirror for the measurements with argon as the buffer gas; with helium as the buffer a 70% reflective mirror was used.

The active surfaces of the mirrors which faced the laser medium were concave with a 1 meter radius of curvature. The curved surfaces were aligned by superimposing their reflections of a helium neon laser beam directed down the center of the laser cavity with the incoming alignment beam itself. As noted in Fig. 1., the area of mirrors (each having a diameter of 2.7 cm.) was considerably larger than the $.8 \text{ cm}^2$ cross section of the output beam defined by the cell insert and the mirror edge. The off-axis mounting chosen allowed the laser to "see" less than one-fourth of the mirror area, and rotating the mirror mounts by 90° made a previously unexposed section of the mirrors available. The mirrors were rotated and re-aligned after each data set was completed (typically after about 25 shots); though the active regions of the mirrors appeared to be degraded when viewed in the visible after such use there was no apparent drop-off in their U. V. performance

The time dependence of the KrF laser signal was monitored using a CsTe-photocathode biplanar vacuum photodiode, 2.5 cm in diameter. Even though less than 1% of the intra-cavity flux was transmitted by

the mirror in the direction of the diode, the introduction of neutral density filters into the beam path was required to reduce the incident intensity to a level at which the diode was not saturated.

The energy output through the partially transmitting mirror at the other end of the cavity was measured using a Scientech Model 3602 laser power meter.¹ Since the duration of the laser pulse (≈ 50 ns.) was very much smaller than the characteristic cooling time (~ 1 s.) of the active area of the power meter, the output signal from its thermocouple (monitored on a chart recorder), extrapolated to the moment of the laser pulse, was directly proportional to the total energy in the output beam.

The power meter was calibrated for energy measurement by comparing its output signal to that from a specially constructed volume calorimeter for a set of identical input pulses at 249 nm.² In the latter case, the optical energy was incident on a thermally isolated cylinder of Pyrex 7740 glass, whose thickness (< 1 mm.) was sufficient to completely absorb the input beam. Its temperature increase was then measured (relative to a similar nearby reference piece of glass to minimize the effects of thermal drift); coupled with the specific heat of the sample this then determined the energy of each calibration pulse. The power meter was used in these experiments, because, once calibrated, it had much more sensitivity than the volume calorimeter (9.3 mV/J as opposed to 95 μ V/J).

The photodiode detector and laser power meter were aligned with the laser axis using the same helium neon laser beam as was used to position the cavity mirrors. In addition, the spatial extent of the laser output beam in the direction of the power meter was determined by placing Dylux paper in the beam path,^{1,3} and was found to be completely encompassed by the entrance aperture of the meter which insured that all of the output energy was captured.

The sidelight fluorescence from the center of the active volume of the cavity was monitored using a S-20 photodiode detector, whose line of sight into the gas cell was apertured to prevent any laser photons scattered off the sides of the exit hole from entering. Either the KrF^* or the Kr_2F^* fluorescence could be measured for a given excitation of the gas by the electron beam. We isolated the dimer signal using an interference filter having a bandwidth of 10 nm, centered at 250 nm and the trimer signal with a Corning 5-56 color filter.¹

The gas cell fill system and electron beam diode and beam transport into the cell were described in the appendix to Chapter V. Since the gas mixture generally varied from shot to shot the gases were combined in the gas cell itself. A lapse of 10 minutes between the filling of the cell and its excitation by the e-beam was sufficient to allow the gases to mix thoroughly. In these experiments, the laser gases were excited either with the full e-beam

pulse (at an average current density of 430 A/cm^2), or with an attenuated pulse at 160 A/cm^2 .

C. Laser Model

The bulk of the kinetic equations used to model the electron beam pumped KrF laser system have already been introduced in Chapters II and IV. In this section we treat the complications introduced by the requirement that the cavity flux arise from the amplification of spontaneous emission from the laser upper level, rather than being driven by an incident "seed" beam, as discussed in Chapter IV. Two results of this "bootstrapping" are the delay of the laser pulse relative to the beginning of the gas excitation and, in some cases, the absence of laser action even though the resonator shows a net positive gain.

Because of the small separation of the cavity mirrors relative to their radius of curvature (10 cm. vs. 1 m.), the standard resonator analysis found in several textbooks^{4,5} does not apply to our experimental setup. In particular, the waist of the lowest order Gaussian mode in this configuration is $<.2 \text{ mm.}$, much less than the transverse dimension ($\sim 1 \text{ cm.}$) of the active volume of the laser medium. This would imply that a large number of higher order modes should contribute significantly to the laser output. In point of fact, the laser flux fills the entire active volume, as indicated by images of the output beam on Dylux paper. In this case we have

developed a simple model which we believe at least qualitatively describes the buildup of the laser flux in the cavity.

As stated in the opening paragraph, we wish to model a system where the laser field builds up from the spontaneous emission from the laser upper state. It is clear, however, that only a certain fraction of the spontaneous radiation into a given solid angle will be amplified into the laser output, as those photons which are directed toward the cavity walls are absorbed by them. The time required to attain laser action in the cell depends critically on this solid angle fraction, and it is the purpose of our analysis to estimate its magnitude.

We begin our treatment of this problem by first considering the fluorescence geometry pictured in Fig. 2(a). The long, thin active region (length $\sim L$, width and height $\sim D$) is assumed to be populated with a steady-state density N of upper state molecules, each of which has a spontaneous radiative lifetime τ_r and stimulated emission cross section σ for photons in the frequency range of interest. We represent by $\rho(\Omega)$ the number density of photons directed in the solid angle $d\Omega$ travelling down the length of the medium. In a coordinate system moving with the photons, the rate equation determining the growth of $\rho(\Omega)$ in the absence of loss is simply

$$\frac{d}{dt} \rho(\Omega) d\Omega = \frac{Nd\Omega}{4\pi\tau_r} + Nc\sigma\rho(\Omega)d\Omega \quad (1)$$

During the amplification of the photon density to "laser" intensities, it has a negligible effect on the value of N , in which case Eq. 1 may be solved yielding

$$\rho(\Omega)d\Omega = \frac{d\Omega}{4\pi c \sigma \tau_r} (\exp(Nc\sigma t) - 1) \quad (2)$$

The rise of the photon density to "laser" levels is assumed to mean that it must reach a point where the stimulated decay of the upper state dominates all other decay processes, and in particular we must have

$$Nc\sigma\rho(\Omega)d\Omega \gg N/\tau_r \quad (3)$$

Inserting Eq. 2 into Eq. 3 yields an inequality relating $d\Omega$ and t

$$(d\Omega/4\pi)(\exp(Nc\sigma t) - 1) \gg 1. \quad (4)$$

For the geometry of Fig. 2(a), we see that we must have $L \geq ct$ for Eq. 4 to be applicable, in which case it implies that

$$(d\Omega/4\pi)(\exp(\alpha L) - 1) \gg 1 \quad (5)$$

where we have defined the small signal coefficient $\alpha = \sigma N$. For a given transverse dimension D , there is then a minimum length L and therefore a maximum value of $d\Omega$ ($d\Omega \approx (D/L)^2$) for which Eq. 5 remains

valid, which is set by the equation

$$\frac{(\alpha D)^2}{4\pi(\alpha L)^2} (\exp(\alpha L) - 1) \gg 1 \quad (6)$$

Equation 6 indicates that for the geometry of Fig. 2(a) there is a minimum length requirement for the system to be superfluorescent, i.e., having a power output proportional to N^2 rather than N , a result which can be found in a more esoteric form in the literature.⁶ We recall at this point that we have restricted ourselves in Chapter IV to consider only geometries in which the transverse gain is small, that is, with $(\alpha D) < 1$. With this limitation we find (as is illustrated in Table I), that the value of (αL) required for superfluorescence is relatively insensitive to the exact value of the transverse gain, and ranges about an average value of $(\alpha L) \approx 20$.

At first glance it would seem that the preceding analysis has little to do with a discussion of the resonator described in Section B., as the values of αL for the 10 cm. cell length indicated by the results quoted in Chapter IV are typically ≤ 1 . Looking at Fig 2(b), however, we see that the addition of mirrors to the ends of the cell is equivalent to lengthening it, while at the same time introducing an

effective loss coefficient

$$\gamma = (2 - R_1 - R_2)/2L_c \quad (7)$$

where R_1 and R_2 are the mirror reflectivities and L_c is the cavity length. In this case we may use the treatment above to define a minimum effective gain length L for laser action in the resonator provided that we replace α by

$$\alpha' = \alpha - (2 - R_1 - R_2)/2L_c. \quad (8)$$

Once a value for L is found we then have that the solid angle available for laser action is on the order of $d\Omega = (D/L)^2$ (where D is the transverse dimension of the active region, which equals about 1 cm.). This factor then determines the size of the spontaneous emission source for the laser field.

Though the above analysis is admittedly crude (neglecting among other things the small curvature of the mirrors), it does explain two important effects. Since the photons must travel a distance L in the gas before being amplified to laser intensities, we see that a finite buildup time $T = L/c$ is required for the laser oscillation. At a "typical" value (for the argon buffered mixtures) of $\alpha = .1 \text{ cm}^{-1}$, and with $R_1 \approx 1$, $R_2 = .5$, we would have $\alpha' \approx .075 \text{ cm}^{-1}$, $L \approx 270 \text{ cm}$. and $T \approx 9 \text{ ns.}$, comparable to but less than the excitation pulse width of about 50 ns. For cases where α is smaller, the buildup will take

even longer, and for extreme cases laser action may not occur either due to a negative value for α' , or due to the fact the the rise time T is significantly greater than the duration of the e-beam pulse. It is in fact for these very reasons that the 70% reflective mirrors had to be used to achieve laser action in the helium buffered mixtures with their smaller gain coefficients.

The end result of the above discussion is that the rise of the laser flux was modelled in the following manner. For a given gas mixture and electron beam current density the code CELLKIN described in Chapter IV was first run to determine the small signal gain coefficient which would appear in the cell in the absence of laser action. The solid angle $d\Omega$ for the laser flux was then calculated using the mirror reflectivities of interest, and a fraction $d\Omega/4\pi$ of the spontaneous emission was assumed to serve as the source of the laser signal in each direction. This ratio was then used as input to the computer program LASRES (listed in the microfiche at the end of this thesis), which is similar to CELLKIN but which tracks the full laser kinetics according to the methods described above in Chapter IV and in the above discussion. With regard to the photon transport, a single zone was found sufficient for the modelling, since in all cases $\alpha_L \leq 1$. The results of these calculations are to be found in the following section.

D. Results of Experiment and Calculation

(i) Introduction

We begin this section by noting that the experimental setup described in Section B. allows the variation of a large number of the quantities (e. g., the current density, mirror reflectivities, buffer gas, fluorine donor, etc.) which determine the laser output. A detailed study carried out over the entire relevant range of this multi-dimensional parameter space is well beyond the scope of this thesis. Rather, to reduce the problem to a tractable size it was necessary to fix most of these variables at somewhat arbitrary values, and investigate the functional dependence of the laser performance only over the remaining few.

Referring specifically to the results presented below, we applied the following restrictions:

Average current density: either 160 or 430 A/cm²;

Fluorine donor: molecular fluorine (F₂);

Buffer gas: either 1500 Torr of argon or
11,600 Torr of helium;

Mirror reflectivities: maximum reflectivity (99%) and
50% (70%) reflective mirrors with argon (helium) as
the buffer gas.

The values of the current density, choice of fluorine donor, and argon buffer gas pressure selected were typical of what is required

for KrF laser operation, The helium buffer pressure was selected to yield the same energy deposition from the 600 keV electron beam as would occur in the argon mixture, according to tabulated stopping powers.⁷ Finally, the output mirror for the laser cavity was chosen merely by the requirement that its selectivity was sufficient to achieve experimentally observable laser action at some time during the 50 ns. e-beam pulse.

Under the limitations described above, the laser efficiency (defined as the ratio of the output energy to the energy deposited by the e-beam in the laser medium) was experimentally optimized as a function of both the F_2 and krypton gas concentrations for both buffer gases at both current densities. In each case we first determined the optimum F_2 pressure at an arbitrary krypton pressure of 100 Torr; using this fluorine concentration the krypton density yielding the maximum laser efficiency was then sought out. Finally, the F_2 density was then varied to insure that at least a local optimum had been found in this two variable parameter space. In all cases the energy deposited in the laser gas was assumed to equal twice that for a single pass of the 600 keV electron beam, as was previously discussed in Section D. of Chapter IV.

Upon completion of the experimental work the KrF laser kinetics model described in Chapters II and IV, and in Section C. of this chapter, was used to predict the laser output from the gas mixtures and

laser configurations investigated experimentally. The comparison of the results of the model calculations with those observed experimentally is described in detail in subsections (ii) and (iii) below. In general the agreement between the model and experiment was better for the argon buffered mixtures than for those with helium as the buffer gas, and also for the more intensely pumped samples at 430 A/cm^2 as compared to those at 160 A/cm^2 . Possible reasons for this behavior will be discussed in Section E.

(ii) Argon Buffered Mixtures

The experimental optimization of the laser efficiency in argon buffered mixtures at both current densities is depicted graphically in Figs. 3 - 6, and the optimal gas pressures and maximum efficiencies are summarized in the first part of Table II. In Figs. 3 and 4 it is sufficient to show only the laser output energy, as the variation of the deposited energy with F_2 pressure was negligible. When the krypton pressure was varied this was obviously not the case as is apparent in Fig. 5 where the deposited energy changed by more than a factor of 2 over the range in krypton concentration.

The qualitative dependence of the laser output on the fluorine pressure exhibited in Figs. 3 and 4 is easily expressed as a competition between several processes. First, at the lower fluorine concentrations the KrF production rate suffers from a decrease in the density of its fluorine precursors (F^- and F_2), and the density of thermal electrons in the medium rises (since the primary loss process

for these electrons is dissociative attachment to F_2) causing an increase in the KrF dimer destruction rate. Both of these processes result in a fall-off in the output energy as the F_2 pressure is decreased; at the lowest fluorine concentrations both are magnified by the depletion of the initial F_2 density, causing a rapid decline in the laser output. Conversely, as the fluorine pressure is increased the surfeit of molecular F_2 results in an increased heavy particle quenching rate for the dimer, eventually causing a decrease in the output energy at the highest fluorine concentrations

The dependence of the laser output on the krypton pressure illustrated in Figs. 5 and 6 is the result of a similar competition. At the lowest krypton pressures the KrF production rate rises with the krypton concentration while its destruction rate remains essentially constant. At elevated krypton densities the heavy particle two- and three-body quenching of the laser upper state begins to rise faster than its creation rate, causing an eventual decrease in the laser signal.

The prediction of our laser kinetics model for the laser output energies is presented along with the experimental data in Figs. 3 - 5. In all of these calculations it was assumed that the energy deposition rate from the e-beam into the gas was equal to twice the value from a single pass as discussed above. The agreement between the experimental and calculated outputs at 430 A/cm^2 is quite

good with regard to both the absolute magnitude and shape of the two curves. In Fig. 4 at 160 A/cm^2 the result of experiment and calculation are qualitatively similar, but there is a definite shift in the position and magnitude of the peak signal between the two curves.

The absence of a plot of the predicted laser output for the experimental conditions of Fig. 6 is due to the fact that over most of the relevant range of krypton pressures (i. e., values significantly different from 100 Torr) the predicted output energy was essentially zero. As will be discussed more completely in Section E., we believe that the radical difference between the results of experiment and the model stems from an inherent inaccuracy in the application of the laser build-up approximation of Section C. in the case of laser operation near threshold.

This variation in the agreement between model and experiment is also evident in the time dependence of the laser output as illustrated in Figs. 7 and 8. The experimental output power in both cases was calculated by normalizing the time dependence of the signal measured by the photodiode through the maximum reflectivity mirror to the total energy exiting the output mirror. The degradation in the qualitative fit of the model to the experiment as the current density decreased is easily seen. While there is good agreement at 430 A/cm^2 , at the lower value of 160 A/cm^2 the magnitudes, shapes, and durations of the two curves all are different.

(iii) Helium Buffered Mixtures

Data from the experimental optimization of the laser efficiency with the krypton and fluorine gas pressures with helium as the buffer gas are presented in Figs. 9 - 12, and the final results are summarized in the second half of Table II. The magnitude of the output signal varied in the same qualitative manner as was seen above for the argon buffer mixtures, but the peak efficiencies were found to be lower at both values of the current density. This latter result has two apparent causes: the decreased energy efficiency for creating the KrF upper state with a helium buffer (due to the higher values for the energies of the excited and ionic states of helium as compared to those of argon), and the increased quenching of the KrF dimer present at the elevated helium pressures required to obtain the same energy deposition as in the lower pressure argon mixtures.

Due to the relative uncertainty in the kinetics of helium buffered KrF laser media (as compared to the wealth of data available for the argon buffered kinetics) we decided to also measure the KrF and Kr₂F sidelight fluorescence signals from the gas cell with the laser mirrors removed for the case of varying fluorine pressure as a test of our understanding of the processes involved. The results of these calculations are presented in Figs. 9 and 12 along with the corresponding laser output signals. At both values of the current density the dimer fluorescence signal and laser output energy peak at the same value of the fluorine concentration, as we would expect in the situation where the medium gain dominates the loss, and as is

predicted by the kinetics model. The occurrence of the peak of the trimer signal at a lower value of the fluorine pressure than that of dimer is explained by the fact that heavy particle quenching by F_2 is more important for Kr_2F as a result of its much longer radiative lifetime .

The predictions of the laser kinetics model for the laser output from mixtures pumped at 430 A/cm^2 are presented in Figs. 10 and 11. In order to obtain any agreement with the experimental results it was necessary to include in the kinetics a two-body quenching reaction for the KrF upper state by helium, with a rate constant of $2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. Because of the large helium concentrations required to achieve a significant deposition from the electron beam we would expect two-body quenching to be a much more important effect here than in the argon buffered mixtures. That this reaction proceeds at such a rate seems likely, in line with the measured reaction coefficient of $7.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for the destruction of KrF by krypton quoted in Chapter IV.

It is important to note at this point that reaction rate constants which require a full kinetic model calculation for their evaluation, as was the case for the two-body quenching coefficient above, should in general be held as suspect. It is quite possible that the disagreement between the model and experiment is the result of some other inaccuracy in the kinetic model. The rate constants used in the model for the various reactions should as a rule be the

product of experiments which unequivocally focus on the relevant subset of the full kinetics.

With this caveat in mind we see that while the predictions of the model at 430 A/cm^2 do not differ radically from the experimental values, the agreement between the two is obviously worse than was seen for the argon buffered mixtures of subsection (ii). This point is also evident in the match between the predicted and observed time dependence of the laser output, plotted in Fig. 13. The curve for the experimental output power was obtained by normalizing the corresponding photodiode signal, as discussed above. Though the total output energy was approximately the same for the two cases, the experimental signal was of longer duration and lower magnitude than predicted by the calculation.

At the lower value of the current density (160 A/cm^2) the problems with the model calculation mentioned above for the argon buffered mixtures were even more apparent. The calculated output energy was not appreciably different from zero for any of the mixtures considered. Here we feel that this is due both to inaccuracies in the kinetics model (which are more likely here because of the paucity of data for the helium buffered kinetics), and to the inapplicability of our laser build-up approximation in the region close to threshold. Because of the lower efficiencies for the helium buffered mixtures as compared to those using argon we would expect this latter problem to

be more important in the present case. Both of these difficulties will be discussed more thoroughly in the following section

E. Discussion

As evidenced by the comparisons of the experimental data and model predictions for KrF laser operation presented in Section D., the primary factor determining the quality of the fit between the two appeared to be the amount of gas excitation. At the larger value of the current density (430 A/cm^2) the fit was quite good for all the data from the argon buffered media and there was agreement between the predicted and observed output energies for the mixtures where helium was the buffer. At 160 A/cm^2 , however, the calculated values for the laser output differed quite radically from those actually observed, effectively equaling zero for most of the cases considered.

We believe that this failure of the kinetics model at the lower current density was actually due to an inaccuracy involved in using the laser flux build-up approximation of Section C. in the threshold regime (i. e., in situations where the intensity in the laser medium was always less than the saturation intensity). In the "boot-strap" model above we stated that laser operation was achieved when the photon density reached a point where stimulated emission by the laser upper level dominated all its other decay processes. We then estimated the angle $d\Omega$ inside which the spontaneous emission from the dimer could be amplified to such levels before hitting one of the

cavity walls. Finally, we assumed that only the radiation directed inside this range had to be considered in determining the laser output through the cavity mirrors. In situations where the net effective gain (including the mirror losses) was large enough for the radiation in the cone $d\Omega$ to grow to "laser" levels in a time short compared to the duration of the excitation pulse such an approach was valid because this "mode" rapidly saturated the laser transition and prevented the intensity directed in other directions from becoming appreciable. When the time required for the laser buildup exceeded the e-beam pulse width, however, no such domination of the KrF^* decay occurred and the flux into other solid angles could reach levels comparable to that directed in the limited range $d\Omega$.

A short calculation illustrates the magnitude of this effect for our experimental setup as the gain in the cell decreased. Due to the 50 ns. length of the pump pulse the maximum small signal gain achievable by the radiation in the gas cell at an effective gain coefficient of $.003 \text{ cm}^{-1}$ was ≈ 4.5 , and the solid angle inside which the spontaneous emission could experience this growth without striking the walls was about 1.5×10^{-6} sterad. In contrast, for the same parameters the solid angle for laser operation calculated according to Eq. 6 is 5×10^{-8} sterad., indicating that the buildup model above underestimated the energy output by at least a factor of 25.

We see that any method which is meant to accurately model the photon transport in the laser medium at low levels of excitation must

take into account the angular dependence of the amplified radiation, which is to say that it must involve at least a two-dimensional (spatial) calculation. Such a treatment is also required for any configuration for which the gain in directions other than the laser axis is appreciable. In this latter case amplified stimulated emission can present a significant loss mechanism for the KrF upper state and in addition cause a transverse variation in the gain profile.

Since such multi-dimensional calculations can be accomplished only at greatly increased calculational cost it is valuable to note that the one-dimensional model above is valid for those configurations where the distribution of amplified radiation is dominated by a single "mode". One situation where this assumption applies has been demonstrated above in the behavior of our laser resonator at high values of the effective gain coefficient. We would also expect our approximation to accurately treat the case of a single pass amplifier which is probed at an input intensity greater than the saturation intensity of the medium.

Limiting ourselves to the consideration of only those cases where our one-dimensional treatment of the radiation was valid, we have found that for argon buffered mixtures of krypton and fluorine the KrF laser kinetics model accurately predicted the experimental results over a wide range of excitation levels and gas pressures. For the mixtures where helium was used as the buffer, the agreement between the model and experiment was somewhat less clear. Although the

calculated magnitudes for the laser output were of the same approximate size as those observed experimentally, their variation with the gas pressures and time dependence leads us to suspect that there is room for improvement in our treatment of the helium buffered kinetics.

To see how this might be accomplished we refer back to Table II of Chapter IV, where we first note that for want of better values the rate constants for several of the reactions involving the transfer of excitation from helium to krypton were set equal to those for the corresponding reactions involving argon. The proper values of these rate coefficients could be determined simply by repeating the procedures by which the argon - helium data was obtained,⁸⁻¹⁰ substituting krypton for the argon gas component. A similar lack of experimental data forced us to assume that all of the reactions involving the excited states of fluorine proceeded at their gas kinetic values, an approximation which was justified by the fact that a negligible fraction of the gas excitation (<1%) typically passed through these channels. Nevertheless, this situation could be improved by an experiment analogous to the one in which Puestis et al. studied the quenching of F^* and F_2^* in e-beam excited mixtures of neon, xenon, and F_2 ,¹¹ again making the appropriate gas substitutions. Finally, with regard to the value for the rate coefficient for the two-body quenching of KrF by helium postulated in Section D., it should be possible to experimentally measure this quantity via a technique similar to that used by Rokni et al. to

determine the destruction coefficients for the dimer in e-beam excited Ar/Kr/F₂ gas mixes.¹²

We conclude by noting that in the introduction to this thesis we stated that it was our purpose to "develop a kinetic model for the KrF* laser system", and specifically for "electron beam pumped Kr - F₂ mixtures, buffered with either helium or argon." Computational complexity has forced us to consider only a limited set of laser configurations for which the distribution of amplified radiation is dominated by a single "mode". Within this restriction we believe we have fulfilled our original intentions with regard to the description of systems typical of KrF laser operation, though further future improvement in the model regarding helium kinetics is possible and awaits further experimentation.

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Table I

Small Signal Gain Required for Superfluorescence

Transverse Small Signal Gain (α_D)	Axial Gain Required (α_L)
<hr/>	<hr/>
.003	22.7
.01	20.0
.03	17.6
.1	14.8

(Note: The minimum required gain was found by setting the left-hand side of equation (6) equal to 10.)

Table II

Result of the Experimental Optimization of
the Laser Efficiency at Fixed Buffer
Gas Pressure and Current Density

Buffer Gas: 1500 Torr Argon

Average Current Density <u>(A/cm²)</u>	Maximum Laser Efficiency <u>(%)</u>	Krypton Pressure <u>(Torr)</u>	F ₂ Pressure <u>(Torr)</u>
160	.85	100	2.5
430	4.2	300	6.0

Buffer Gas: 11,600 Torr Helium

Average Current Density <u>(A/cm²)</u>	Maximum Laser Efficiency <u>(%)</u>	Krypton Pressure <u>(Torr)</u>	F ₂ Pressure <u>(Torr)</u>
160	.17	50	4.0
430	1.3	200	5.0

Fig. 1. Schematic illustration of the modifications to the MEG I gas cell used to produce and observe KrF laser action.

Fig. 2. (a) Geometry for the superfluorescence calculation of Section B.

(b) Demonstration of the "unfolding" of the laser cavity to resemble the superfluorescent geometry. The mirror reflectivities are R_1 and R_2 , respectively.

(N.B. In both (a) and (b) the transverse dimension (D) is greatly exaggerated)

Fig. 3. Laser output energy vs F_2 pressure from 1500 Torr Ar - 100 Torr Kr - F_2 gas mixtures at an average current density of 430 A/cm^2 : ($\triangle$) experimental; ($\circ$) calculated.

Fig. 4. Laser output energy vs F_2 pressure from
1500 Torr Ar - 100 Torr Kr - F_2 gas mixtures at
an average current density of 160 A/cm^2 :
(Δ) experimental; ($\circ$) calculated.

Fig. 5. Laser output energy and laser efficiency vs Kr pressure from 1500 Torr Ar - 6.00 Torr F_2 - Kr gas mixtures at an average current density of 430 A/cm^2 : (Δ) experimental; ($\circ$) calculated; ($\diamond$) experimental. (At 400 Torr Kr the calculated value is 165 mJ)

Fig. 6. Observed laser output energy and laser efficiency vs Kr pressure from 1500 Torr Ar - 2.50 Torr F_2 - Kr gas mixtures at an average current density of 160 A/cm^2 .

Fig. 7. Time dependence of the laser output from a 1500 Torr Ar - 100 Torr Kr - 5.00 Torr F_2 gas mixture pumped at an average current density of 430 A/cm^2 : (E) experimental; (C) calculated.

Fig. 8. Time dependence of the laser output from a 1500 Torr Ar - 100 Torr Kr - 5.00 Torr F_2 gas mixture pumped at an average current density of 160 A/cm²: (E) experimental; (C) calculated.

Fig. 9. Observed fluorescence signal (no mirrors) and laser output energy (with mirrors) vs F_2 pressure from 11,600 Torr He - 100 Torr Kr - F_2 gas mixtures at an average current density of 430 A/cm^2 .

Fig. 10. Laser output energy vs F_2 pressure from
11,600 Torr He - 100 Torr Kr - F_2 gas mixtures
at an average current density of 430 A/cm^2 ;
(Δ) experimental; ($\circ$) calculated.

Fig. 11. Laser output energy and laser efficiency vs Kr pressure from 11,600 Torr He - 5.00 Torr F_2 - Kr gas mixtures at an average current density of 430 A/cm^2 : (Δ) experimental; ($\circ$) calculated; ($\diamond$) experimental.

Fig. 12. Observed fluorescence signals (no mirrors) and laser output energy (with mirrors) vs F_2 pressure from 11,600 Torr He - 100 Torr Kr - F_2 gas mixtures at an average current density of 160 A/cm^2 .

Fig. 13. Time dependence of the laser output from a
11,600 Torr He - 100 Torr Kr - 5.00 Torr F₂ gas
mixture pumped at an average current density of
430 A/cm²: (E) experimental; (C) calculated.

References - Chapter VI

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Microfiche Listings of Computer Programs