Direct dissociation of F_2 in electron beam pumped excimer lasers: The effect on electron density

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The electron impact dissociation of molecular fluorine in XeF and KrF excimer lasers is examined. Two methods of dissociation are discussed: dissociative attachment and direct neutral dissociation by excitation to the dissociative electronic states $a^3\Pi_u$ and $A\,^1\Pi_u$. Computer models for the kinetics of the lasers are parameterized, and predictions of electron density are compared to experimental results for electron beam pumped Ne/Xe/F_2 gas mixtures [W. D. Kimura, D. R. Guyer, S. E. Moody, J. F. Seamans, and D. H. Ford, Appl. Phys. Lett. **50**, 60 (1987)]. To obtain agreement with experiment, the ratio of direct dissociation to dissociative attachment must be $\geqslant 2$. The implications of these results with respect to electron quenching and the validation of computer models are discussed.

Molecular fluorine is often used as the halogen donor in electron beam (*e*-beam) pumped XeF and KrF lasers.[1] The instantaneous density of F_2 is important to the generation and quenching of the upper laser level, and because it is an absorber at the laser wavelength. Collisions of excited rare gas species with F_2 directly generate the upper laser level through the harpooning reaction constituting the "neutral channel" (e.g., $Xe^* + F_2 \rightarrow XeF^* + F$). Dissociative attachment to F_2 generates F^- ions which by an ion-ion neutralization reaction populates the upper laser level through the "ion channel" (e.g., $Xe^+ + F^- \rightarrow XeF^*$). The density of F_2 is also important in determining the bulk electron density. In typical gas mixtures the initial F_2 mole fraction is 0.1–0.5%, and the loss of bulk electrons is dominated by dissociative electron attachment to F_2.[2] Even though the rate of excitation of the upper laser level depends only weakly on the bulk electron density, electron collision quenching of the upper laser level is directly proportional to it and can account for 20–50% of all quenching. The burnup of F_2 is therefore important because of heavy particle reactions which directly involve the molecular species and because of its effect on the electron density.

In this letter, we discuss contributions to the dissociation of F_2 by electron impact and its effect on electron density using results from computer models for KrF and XeF *e*-beam-pumped lasers. Two dissociation processes are studied: dissociative electron attachment ($e + F_2 \rightarrow F^- + F$) and direct neutral dissociation ($e + F_2 \rightarrow 2F + e$). Direct dissociation of F_2 is a result of excitation to the dissociative electronic states $a^3\Pi_u$ and $A\,^1\Pi_u$ (minimum threshold energy 3.16 eV).[3] By parameterizing rate constants for these processes used in the model and comparing the predicted electron densities to experimental measurements, the proportions of F_2 dissociation attributed to each process are estimated. We find that in typical *e*-beam-pumped XeF lasers, the majority of the dissociation of F_2 by electron impact is direct and not by dissociative attachment.

The dissociation of F_2 by electron impact in excimer laser plasmas has been investigated by Nighan[4,5] and Klimek *et al.*[6] Nighan calculated that in an *e*-beam sustained discharge KrF laser only 14% of F_2 dissociation resulted from dissociative attachment while 36% was direct, for a total of 50% by electron impact. The remainder resulted from dissociative excitation transfer (e.g., $Kr^* + F_2 \rightarrow KrF^* + F$). Since the average electron energy in an *e*-beam sustained discharge is higher than in an *e*-beam-pumped system, one might expect a higher proportion of dissociation to occur via the higher threshold process. In an *e*-beam-pumped KrF laser, Klimek *et al.*[6] also attributed $\approx 50\%$ of the total dissociation of F_2 to electron impact, though only by dissociative attachment.

Models of *e*-beam and discharge excited excimer lasers using F_2 do not, as a rule, include direct electron impact dissociation with an appreciable rate. Many models[7–11] do not include the direct process. Other models[12–14] use a direct rate constant, $k_d = 3\times 10^{-10}\ \text{cm}^3\,\text{s}^{-1}$, which is small compared to that for dissociative attachment, having a rate constant $\beta = 1\text{–}5\times 10^{-9}\ \text{cm}^3\,\text{s}^{-1}$. Only in analyses of discharge excited systems[15–17] is a comparably valued rate constant used.

To first order, the electron density in an *e*-beam-pumped excimer laser is determined by the balance between beam ionization and attachment to F_2, $n_e \approx P/W\beta[F_2]$, where n_e is the bulk electron density, P is the specific power deposition, and W is the energy/ion pair. The burnup of F_2 is determined by dissociative attachment, direct dissociation, and heavy particle excitation transfer.[18] The bulk electron density, though, does not directly affect the formation of the upper laser level other than by its relation to the density of F^-. Therefore, since the burnup of F_2 is proportional to the sum of the rates of dissociative attachment and direct dissociation, the proportion of F_2 burnup individually attributed to these two processes does not significantly affect predictions of gain or laser energy. In fact, predictions of extracted laser energy in optically saturated lasers are moderately insensitive to the precise value for the dissociative attachment rate constant β, provided that electron collision quenching does not dominate, as shown in Fig. 1. This condition results from the fact that deposited energy efficiently flows to the

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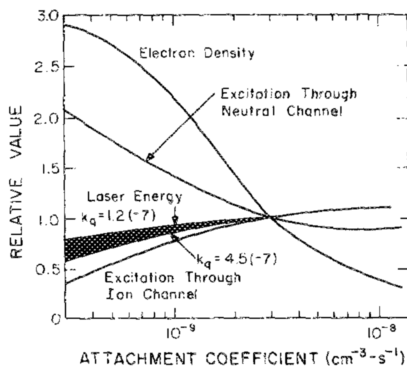

FIG. 1. Relative changes in the mode of excitation (neutral channel or ion channel), electron density, and laser energy in an e-beam-excited KrF laser as a function of the rate coefficient for dissociative attachment to F_2, β. The gas mixture is 1.32 atm $Ar/Kr/F_2$ = 89.73/10.0/0.27 with average power deposition of 125 kW cm^{-3} and a 500 ns pulse length. The darkened region shows the range of predicted laser output energy while varying the rate coefficient for electron collision quenching of the upper laser level, k_q, between 1.2×10^{-7} and 4.5×10^{-7} $cm^3\,s^{-1}$. These results were obtained with the model described in Ref. 17. The predicted laser energy is not sensitive to β due to the compensation in the dominant excitation channel (ion or neutral) provided that electron collision quenching is not important.

upper laser level through either the neutral or ion channels. A reduction in excitation through one channel is compensated by an increase in excitation through the other channel (see Fig. 1). Also, without significant direct dissociation of F_2, the burnup of F_2 is only weakly dependent on the value of β, as shown in Fig. 2. Therefore, quenching of the upper laser level by F_2 is also not sensitive to β. Because of these effects, models of e-beam-pumped excimer lasers which use values of β having a range of $1\text{–}5\times10^{-9}$ $cm^3\,s^{-1}$ all still satisfactorily predict laser output energy.[8,11–13,19–21] As power deposition and the electron density increase, though, this weak dependency ceases since electron collision quenching becomes a dominant loss.

One concludes that agreement of predicted laser output energy to experiments is not sufficient to validate the values of β and k_d used in a model. Other information is required, specifically the electron density. Recent measurements of the electron density in e-beam-pumped XeF lasers made by Kimura *et al.*[22] provide the data required to apportion the dissociation of F_2 between dissociative attachment and direct processes. The measurements are for e-beam-excited mixtures of 3.8 atm Ne/0.5% Xe/F_2 with initial halogen fractions of 0.05%–0.2%. With an average power deposition of 180 kW cm^{-3} and pulse lengths of 600 ns, the experiments span nominal to extreme halogen burnup.

Using a kinetics model for an e-beam-excited XeF laser[23] we parameterized the rate constants for dissociative attachment and direct dissociation of F_2, and compared the predicted electron densities with the results of Kimura *et al.* We found best agreement using $\beta = 1.43\times10^{-9}$ $cm^3\,s^{-1}$ and $k_d = 4.6\times10^{-9}$ $cm^3\,s^{-1}$, or a ratio of direct dissociation to dissociative attachment of ≈3, as shown in Fig. 3. This ratio is close to that found by Nighan ($k_d/\beta\approx2.6$) for an e-beam sustained discharge KrF laser. The actual values of β and k_d, though, are both sensitive to the bulk electron temperature T_e. β increases with decreasing T_e while k_d decreases. The ratio scales as $0.7\leqslant k_d/\beta\leqslant7.8$ for $1.5\leqslant T_e\leqslant2.5$. Our derived values for β and k_d agree very well with those one would obtain by convolving a Maxwellian electron distribution having $T_e = 2.0$ eV with electron impact cross sections for the processes.[3] This temperature is slightly higher than that calculated for comparable gas mix-

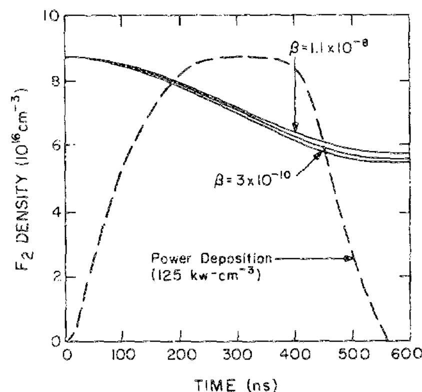

FIG. 2. Density of F_2 during e-beam excitation of a KrF laser as a function of the rate coefficient for dissociative attachment to F_2 (3×10^{-10} $cm^3\,s^{-1}\leqslant\beta\leqslant1.1\times10^{-8}$ $cm^3\,s^{-1}$). The conditions are the same as for Fig. 1. The burnup of F_2 is not sensitive to β if direct dissociation is not important.

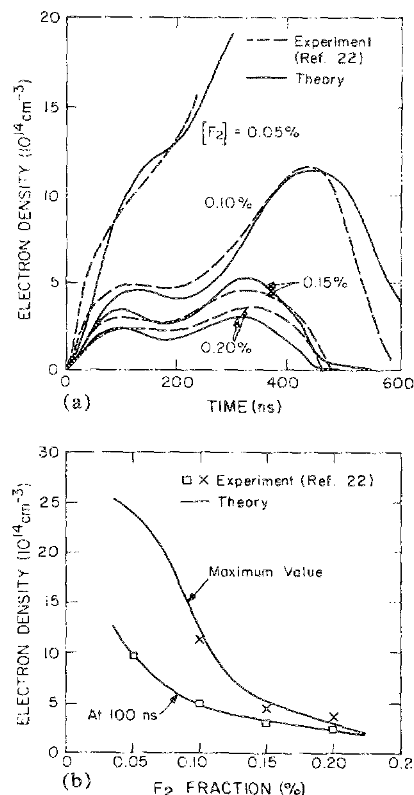

FIG. 3. Comparisons of predicted and measured (Ref. 22) electron densities in an e-beam-excited Ne/Xe 0.5%/F_2 gas mixture at 3.8 atm. The average power deposition is 180 kW cm^{-3}. (a) Time-dependent electron densities, (b) electron density as a function of F_2 mole fraction at 100 ns into the excitation pulse and the maximum electron density. The roll-over in the maximum density at fractions < 0.05% indicates almost total burnup of the halogen donor.

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tures.[2,23] The electron distribution, though, is a function of the instantaneous F_2 concentration, electron density, and rare gas metastable density.[2] This functionality, as well as the dependence of the attachment cross section on the vibrational state of F_2,[24] requires that β and k_d be obtained on a case by case basis as opposed to being considered fixed constants.

In conclusion, direct electron impact dissociation of F_2 in *e*-beam-pumped excimer lasers is competitive with dissociative attachment as a F_2 destruction mechanism. Good agreement was obtained between results from our model and experiment for electron densities in an *e*-beam-pumped XeF laser when we used rate constants for direct dissociation and dissociative attachment of $k_d \approx 4.6 \times 10^{-9}$ cm^3 s^{-1} and $\beta \approx 1.4 \times 10^{-9}$, respectively. Even including uncertainties in power deposition and experimental error of 15–20%,[22,25] and uncertainties of factors of 2 in some rate constants commonly used in excimer laser models,[1] our results still suggest that $k_d/\beta \gg 1$. Our results also suggest that the electron density predicted by models of *e*-beam-pumped excimer lasers which do not include direct electron dissociation are too small, perhaps by a factor of ≈ 2. Due to the efficiency of channeling deposited power to the upper laser level through either the neutral or ion channels, this discrepancy has a small effect on predicted laser energy for moderate to low power deposition where the electron density, and hence electron collision quenching of the excimer, is small. For higher power deposition ($k_{\text{quench}} n_e > 10^8$ s^{-1}) the discrepancy in electron density is important because electron collision quenching will be underpredicted.

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