Reassessment of the rate constant for electron collision quenching of KrF(B)

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The rate constant for electron collision quenching of KrF(B) has been reassessed by analyzing previous theoretical [A. Hazi, T. Rescigno, and A. Orel, Appl. Phys. Lett. **35**, 477 (1979)] and experimental [D. Trainor and J. Jacob, Appl. Phys. Lett. **37**, 675 (1980)] data. From this analysis we recommend that the rate constant for electron collision quenching of KrF(B), used for modeling electron beam and discharge excited lasers, should be $3\text{–}6\times 10^{-8}$ cm^3 s^{-1}.

Electron collision quenching of KrF(B) is an important process in electric discharge and electron beam (e-beam) excitation of the KrF($B\rightarrow X$) excimer laser (248 nm) at high levels of power deposition ($\gtrsim 0.5$ MW cm^{-3}).[1-6] Electron collision quenching (ECQ) is largely responsible for the increase in laser saturation intensity observed at high pump rates, a consequence of a shortening of the lifetime of the upper laser level by that process. ECQ is also partly responsible for the saturation of small-signal gain of the KrF($B\rightarrow X$) transition experienced at high pump rates.

The value of the rate constant for ECQ of KrF(B), k_q, has been previously investigated both theoretically and experimentally. Hazi *et al.*[1] calculated the cross section for ECQ using a modified impact parameter method with extensive *polci* (configuration interaction) wave functions. After convolving their cross section with a Maxwellian electron distribution function ($T_e = 1.5$ eV) they obtained $k_q = 2.8\times 10^{-8}$ cm^3 s^{-1}.

Trainor and Jacob[2] indirectly measured k_q by experimentally observing fluorescence from KrF(B) in an e-beam excited Kr/F$_2$ gas mixture as a function of the mole fraction of F$_2$. Under these conditions, the density of low-energy "bulk" electrons is inversely proportional to the mole fraction of F$_2$. This experimental technique is therefore a method whereby the bulk electron density may be varied at constant pump rate. The dependence of KrF(B) emission as a function of F$_2$ was then used to abstract the rate constant for ECQ using a Stern–Volmer plot. By doing so, Trainor and Jacob obtained the expression

$$k_q = 2.9\times 10^{-7}\ k_a/\tau, \tag{1}$$

where τ (s) is the radiative lifetime of KrF(B) and k_a is the rate constant for dissociative electron attachment to F$_2$. Using $\tau = 6.5$ ns and $k_a = 4.5\times 10^{-9}$ cm^3 s^{-1}, Trainor and Jacob obtained $k_q = 2.0\times 10^{-7}$ cm^3 s^{-1}. The theoretical and experimental values for k_q, therefore, differ by a factor of 8.

In spite of this disagreement in the values of k_q, there has been no further work on calculating or measuring its value. Kinetics models of KrF lasers[3-6] have tended to use the experimental value ($1.5\text{–}2.5\times 10^{-7}$ cm^3 s^{-1}). To mitigate the difference between the theoretical and experimental values for k_q, we have performed a reassessment of each. The reassessment of the experiments is aided by results from a Monte Carlo simulation for the slowing of e-beams in excimer gas mixtures, and a solution of Boltzmann's equation for the electron energy distribution including e–e collisions. The two codes can be linked to obtain a self-consistent solution for the electron energy distribution in discharge and e-beam excited lasers. The model is described in detail in Ref. 7.

A reexamination of the method used by Hazi *et al.* to calculate the ECQ cross section confirmed its accuracy to a factor of approximately 2. The theoretical rate constant quoted by Hazi *et al.*, however, was obtained by a convolution of their calculated cross section with a Maxwellian electron energy distribution (EED). It is well known that the EED in e-beam excited plasmas may be non-Maxwellian.[7,8] We therefore calculated the EED for the experimental conditions of Trainor and Jacob (Kr/F$_2$ = 99.5/0.5, 190 Torr, $P \approx 70$ kW/cm^{-3}). The effective electron temperature obtained from the calculation is 1.58 eV. By convolving the calculated EED with Hazi's cross section, we obtained $k_q = 3.0\times 10^{-8}$ cm^3 s^{-1}, which is close to the value obtained using a Maxwellian EED.

The value of k_a that we obtained from our calculation of the EED for Trainor and Jacob's conditions is 1.9×10^{-9} cm^3 s^{-1}, a factor more than two times smaller than that used by Trainor and Jacob in their analysis. As seen from Eq. (1) and discussed below, the value of k_a has a direct impact on the experimentally derived value of k_q. The values of k_a used in models of KrF lasers have ranged from 1 to 5×10^{-9} cm^3 s^{-1} (Ref. 9 and citations therein) and kinetics measurements or calculations of the rate coefficient ($T_e \approx 1$ eV) have yielded values of $(1.5\text{–}5.5)\times 10^{-9}$ cm^3 s^{-1} (Ref. 10 and citations therein). A portion of this variation in k_a can be attributed to the fact that the cross section for dissociative attachment, σ_a, depends on the vibrational state of F$_2$.[11] Therefore, k_a depends on the vibrational distribution of F$_2(v)$ as well as the EED, which is a function of gas mixture, and fractional ionization.[7,8] For example, the reduction in the density of low-energy electrons which results from their attachment F$_2$ can actually reduce k_a when the fraction of F$_2$ is increased.

Recent measurements of the electron density[12] in e-beam excited Ne/Xe/F$_2$ mixtures and a subsequent analysis of those measurements[9] resulted in derived values for k_a which are in the range $(1\text{–}2)\times10^{-9}$ cm^3 s^{-1}. Rozenberg *et al.*[8] measured and theoretically analyzed the rate constant for dissociative attachment to F_2 in *e*-beam excited gases for conditions similar to that of Trainor and Jacob. Their values for k_a are also $(1\text{–}2)\times10^{-9}$ cm^3 s^{-1}. In our analysis below, we therefore take $k_a = 2\times10^{-9}$ cm^3 s^{-1} as an upper bound, with the acceptable range being $1\times10^{-9} < k_a < 2\times10^{-9}$ cm^3 s^{-1}. Assuming a smaller value of k_a than that used by Trainor and Jacob implies the electron density for their conditions is higher than cited, since $n_e \sim ([F_2]k_a)^{-1}$. Therefore, the same level of experimentally observed quenching requires a smaller value of k_q. The larger value of n_e also implies that dissociative recombination of Kr_2^+ has a nonnegligible contribution to electron loss since this loss scales as $n_e^1 Kr_2^+$.

With these issues at hand, we repeated the analysis of Trainor and Jacob's experimental data using $k_a = (1\text{–}2)\times10^{-9}$ cm^3 s^{-1} and included dissociative recombination of Kr_2^+ as an electron loss ($k_r = 1.5\times10^{-7}$ cm^{-3} s^{-1}).[3] We also included the effect of quenching of KrF(B) by Kr in two [$\mathrm{KrF}(B) + \mathrm{Kr} \rightarrow 2\mathrm{Kr} + \mathrm{F}$, $k_1 = 2\times10^{-12}$ cm^3 s^{-1}] and three body [$\mathrm{KrF}(B) + 2\mathrm{Kr} \rightarrow \mathrm{Kr_2F^*} + \mathrm{Kr}$, $k_2 = 3.2\times10^{-31}$ cm^6 s^{-1}] processes.[3] The latter two processes reduce the effective lifetime of KrF(B) from the radiative value of 6.5 to 5.5 ns. We constructed a Stern–Volmer plot similar to Trainor and Jacob using these values. In so doing, n_e is not directly proportional to $[F_2]^{-1}$. By including these effects, the experimentally derived value for k_q is 6.5×10^{-8} cm^3 s^{-1} for $k_a = 2\times10^{-9}$ cm^3 s^{-1}, and 3.7×10^{-8} cm^3 s^{-1} for $k_a = 1\times10^{-9}$ cm^3 s^{-1}, significantly lower than the previous experimentally derived k_q. The agreement between experiment and theory for these values, though, is to within a factor of 2 or better. We therefore recommend that the rate constant for ECQ of KrF(B) in *e*-beam excited lasers to $(3\text{–}6)\times10^{-8}$ cm^3 s^{-1}. The rate constant for dissociative attachment to F_2 consistent with these values is $k_a \approx 2\times10^{-9}$ cm^3 s^{-1}.

The precise values of k_q which should be used in the analysis of KrF($B\rightarrow X$) lasers do, of course, depend upon the details of the electron energy distribution function. However, since the cross section for ECQ is relatively insensitive to electron energy above a few tenths of an eV, we expect that k_q will remain fairly constant for conditions covering a variety of discharge and *e*-beam excited lasers provided the average electron energy exceeds $\approx$0.5 eV. For example, using the cross section for ECQ from Hazi *et al.*, the rate constant k_q is plotted in Fig. 1 as a function of E/N in a He/Kr/F_2 = 99/1/0.1 mixture having $n_e/N = 10^{-5}$.[13] This mixture is typical for discharge excited lasers.[14] The value changes little over the range of $1\times10^{-17} \leqslant E/N \leqslant 50\times10^{-17}$ V cm^2.

According to Eq. (1), the experimentally derived value of k_q/k_a should be nearly constant. Therefore, one might conclude that the effect of ECQ on laser performance would be independent of k_q since $n_e k_q \sim (1/k_a)k_q$. This dependence, however, is only an artifact of the method of analyzing the experimental data. k_q and k_a are not fundamentally related other than by changes they may cause in the EED. To assess the impact of the value of k_q on the predicted small-signal gain and saturation intensity at 248 nm in an electron beam excited KrF laser, we parametrized a plasma kinetics

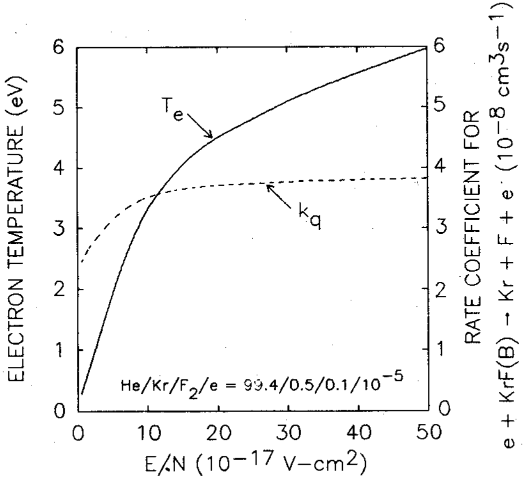

FIG. 1. Rate coefficient for electron collision quenching of KrF(B) as a function of E/N, and average electron energy in a He/Kr/F_2 = 99/1/0.1 mixture ($n_e/N = 1\times10^{-5}$).

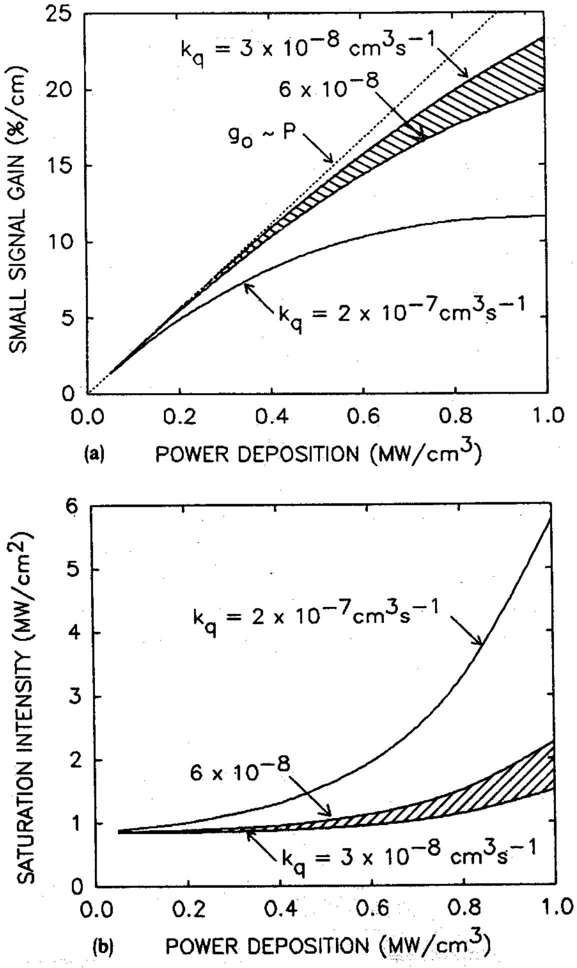

FIG. 2. Predicted (a) small-signal gain and (b) laser saturation intensity in an *e*-beam excited KrF laser (Ar/Kr/F_2 = 90/10/0.3) as a function of power deposition. The cross-hatched region shows results for our recommended range for k_q ($3\text{–}6\times10^{-8}$ cm^3 s^{-1}). The remaining curve is the result using the previous experimental value for k_q (2×10^{-7} cm^3 s^{-1}).

model for the laser, changing k_q while holding k_a constant (1.2×10^{-9} cm^3 s^{-1}). The results are shown in Fig. 2. The gas mixture is Ar/Kr/F_2 = 90/10/0.3 and the power deposition is 0.05–1.0 MW cm^{-3}. The model is described in Ref. 15. The effects of amplified spontaneous emission were ignored. The predicted small-signal gain g_0, obtained using $k_q = 2\times10^{-7}$ cm^3 s^{-1}, saturates at a pump power of $P\approx0.7$ MW cm^{-3} due to the high rate of ECQ. The "roll-off" of g_0 is accompanied by an increase in the saturation intensity I_s. These effects are largely mitigated when $k_q = 3\times10^{-8}$ cm^3 s^{-1}, the lower limit of our recommended range for k_q.

The validation of our recommended value for k_q requires systematic measurements of g_0 and I_s at elevated pump powers. Indirect validation can be found from the experimental results of Peters *et al.*[5] They found that at high pump power and low F_2 concentration (0.1%), their predicted laser power using $k_q = 2\times10^{-7}$ cm^3 s^{-1} terminated sooner than their experimental results. The cause was excessive ECQ of KrF(B) in the model resulting from the increase in n_e due to burnup of F_2. This was remedied by assuming that ECQ proceeded by dissociative attachment: $e + \mathrm{KrF}(B) \rightarrow \mathrm{Kr} + \mathrm{F}^-$. This has the effect of lowering n_e, and hence, reducing further ECQ, and "recirculating" the F^- to participate in the exciplex forming reaction: $\mathrm{Kr}^+ + \mathrm{F}^- \rightarrow \mathrm{KrF}(B)$. Both processes lengthen the laser pulse. Lengthening of the predicted laser pulse length could have equivalently been obtained by reducing the value of k_q without hypothesizing that ECQ proceeds by attachment.

Further validation of our proposed values of k_q can be obtained from the results of Kannari *et al.*[16] for laser efficiency in Ar/Kr/F_2 mixtures. They found laser efficiency to be nearly a constant for power deposition of up to 1.25 MW cm^{-3} and Kr concentrations of 10 to 99.7%. A value of k_q as large as 2×10^{-7} would have reduced laser efficiency at the high pump rate.

In conclusion, we have reassessed previous experimental and theoretical results for the electron collision quenching of KrF(B), and recommended that for conditions typical of e-beam excited KrF lasers, $k_q = (3\text{–}6)\times10^{-8}$ cm^8 s^{-1}. This reassessment shows that the theoretical value of k_q proposed by Hazi *et al.*, and the experiments of Trainor and Jacob are essentially in agreement.

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