

# High-temperature kinetics in He and Ne buffered XeF lasers: The effect on absorption

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Excimer lasers excited by electron or ion beams having energy deposition of 100's J//over many microseconds experience a temperature rise of hundreds of degrees (K). The increase in gas temperature may greatly impact both the kinetics and spectroscopic parameters. In this letter we discuss the high-temperature ( $\leq 900$  K) plasma kinetics and absorption in He and Ne buffered gas mixtures for particle beam pumped XeF lasers. We find both gain and absorption depend differently on gas temperature in these mixtures (absorption decreasing in He mixtures, increasing in Ne mixtures). The differences are attributed to a reduction in diatomic absorbing species with increasing temperature and differences in the temperature dependence of the optical absorption cross sections for  $\text{NeXe}^+$  and  $\text{Xe}_2^+$ .

Excitation of excimer lasers with an energy deposition of 100's J// results in gas heating of hundreds of degrees (K). As both the gas phase kinetics and spectroscopic parameters of excimer lasers are functions of gas temperature, the dependence of these quantities on energy deposition is important with respect to the efficiency of the laser. This is particularly true for the  $\text{XeF}(B \rightarrow X)$  laser (351 and 353 nm) whose spectrum and efficiency are functions of the initial gas temperature.<sup>1-3</sup>

In electron beam (*e*-beam) excited  $\text{XeF}(B \rightarrow X)$  lasers, neon or argon are typically used as the buffer gas due to their higher stopping power compared to helium. In fact, in experiments where helium was added to neon buffered mixtures in an *e*-beam pumped laser, performance degraded.<sup>4</sup> Nevertheless, helium buffered mixtures are interesting due to their use in discharge lasers and in heavy ion excited systems where the lower stopping power of helium is not as important a consideration. Also, in lasers pumped by fission fragments (i.e., heavy ion excitation) fissile  $^3\text{He}$  is often used as the buffer gas.<sup>5</sup> With equal power deposition, one should expect similar  $\text{XeF}(B \rightarrow X)$  laser performance in He buffered gas mixtures compared to neon. Helium is less reactive than neon in that there are no stable helium analogs to  $\text{NeXe}^*$ ,  $\text{NeXe}^+$ , or  $\text{Ne}_2\text{F}$  which either compete with  $\text{XeF}(B)$  formation, are quenching products of  $\text{XeF}(B)$ , or are absorbers. In fact, it is generally assumed that  $\text{HeXe}^+$  is very short lived or does not absorb at the laser wavelength, and therefore is not included as an absorber in models of  $\text{XeF}(B \rightarrow X)$  or  $\text{XeCl}(B \rightarrow X)$  lasers.<sup>6</sup> An exception to these arguments is that the net rate of quenching of  $\text{XeF}(B \rightarrow C)$  at room temperature is approximately three times larger by helium than by neon,<sup>7</sup> which may explain the detrimental effect of adding helium to neon buffered mixtures in XeF lasers.<sup>4</sup> The energies of the He metastable and ion are higher than those for Ne. One might then expect additional quenching reactions of precursors to XeF by these species. Since the analogous reactions with Ne are also exothermic, the differences in rate constants are not likely to be large.

Given the interest in high-energy deposition ( $> 100$ 's J/

//) in excimer lasers by either *e*-beams or heavy ions and in the use of He as a buffer gas, in this letter we compare high gas temperature ( $T_g \leq 900$  K) plasma kinetics and optical absorption in Ne and He buffered gas mixtures for  $\text{XeF}(B \rightarrow X)$  lasers. This study uses results from a plasma kinetics model for an  $\text{XeF}(B \rightarrow X)$  laser which has been previously described.<sup>8</sup> We examine *e*-beam pumping at the same power deposition for He and Ne buffered mixtures for periods exceeding many microseconds where there is an increase in gas temperature of 300–600 K. The nearly equivalent performance of *e*-beam and heavy ion beam pumping when compared on the basis of specific power deposition enables this work to be applied to heavy ion pumped systems as well.<sup>8</sup>

The first effect of increasing the gas temperature in *e*-beam pumped plasmas results from heavy particle reaction rate coefficients being functions of  $T_g$ . Two-body rate constants for exothermic processes typically scale as  $T_g^{1/2}$  to account for the increase in thermal velocity. Rate constants for exothermic three-body association reactions, though, typically have a negative temperature effect, scaling as  $T_g^{-n}$ , where  $1.5 \leq n \leq 3.5$ .<sup>9-12</sup> Therefore, one should expect a decrease in the relative number of, for example, diatomic ions at higher  $T_g$ . This effect may be offset by the negative temperature coefficients for the two dominant loss processes for diatomic ions; dissociative recombination and ion-ion neutralization. The rate coefficient for dissociation recombination typically scales as  $1 - \exp(-\epsilon_v/kT_g)$ , where  $\epsilon_v$  is the fundamental vibrational energy.<sup>13</sup> Positive ion-negative ion neutralization typically scales as  $T_g^{-1/2}$ .<sup>14</sup> These cited temperature scalings were generally used in the model where for three-body association reactions we used  $k \sim T^{-1.5}$ .

The gain and lasing spectra of  $\text{XeF}(B \rightarrow X)$  are also functions of gas temperature. Recent work by Burde *et al.*<sup>2</sup> examined the effect of increasing  $T_g$  on the distribution of rotational and vibrational states in  $\text{XeF}(B)$  and  $\text{XeF}(X)$ , and on the dissociation of  $\text{XeF}(X, \nu)$ . The change of the dominant laser line from 353 nm (300 K) to 351 nm ( $T_g > 400$  K) can be attributed to these changing distributions. Our model explicitly includes the vibrational distribu-

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tions of  $\text{XeF}(B, X)$  and the temperature dependence of dissociation of  $\text{XeF}(X, v)$  in the manner described by Blauer *et al.*,<sup>3</sup> and is able to reproduce the cited behavior. The temperature induced change of population in rotational and vibrational states also affects the optical absorption cross sections of molecular species, which is important since a large fraction of the absorption in excimer lasers is from molecular species. Although the dependence of these cross sections on  $T_g$  is not in general well known, theoretical and semiempirical studies have been performed for the cross sections of interest.<sup>3,15-19</sup> These values are listed in Table I with cross sections used in the model for atomic species. Some of these values were calculated assuming a vibrational distribution of the absorber which is in equilibrium with the gas temperature. We acknowledge that these species may have nonequilibrium distributions which could alter the cited temperature dependence. Note that the absorption cross section for  $\text{Xe}_2^+$  decreases with increasing  $T_g$  while that for  $\text{NeXe}^+$  increases.

We examined  $M/\text{Xe}/\text{NF}_3 = 99.38/0.5/0.125$  ( $M = \text{He}$  or  $\text{Ne}$ ) gas mixtures at 3 atm and with a power deposition of  $132 \text{ kW cm}^{-3}$ . These conditions (for  $\text{Ne}$ ) correspond to the experiments of Mandl and Hyman,<sup>16</sup> and Mandl and Litzenger<sup>4</sup> with whom we favorably compared to validate the model,<sup>8</sup> except that we extended the pulse length to  $7.5 \mu\text{s}$ . For a total energy deposition of  $\approx 900 \text{ J/l}$ ,  $T_g$  increases in both mixtures by  $\approx 580 \text{ K}$ .

Our results are sensitive to the disposition of  $\text{NF}_3$  with respect to burnup, attachment, and reassociation. Experiments indicate that  $\text{NF}_3$  reassociates from  $\text{NF}_2 + \text{F}$  rapidly enough so that the halogen burnup observed in  $e$ -beam pumped lasers using  $\text{F}_2$  does not occur.<sup>16,20</sup> We used the rate constant  $k = 1.0 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  for  $\text{NF}_x + \text{F} + M \rightarrow \text{NF}_{x+1} + M$  ( $x = 1, 2$ ) for both  $M = \text{Ne}$  and  $\text{He}$ , as measured for  $M = \text{Ar}$ .<sup>21</sup> We estimated that  $k \sim T_g^{-3/2}$ . The rate constant for dissociative attachment of  $\text{NF}_3$  was obtained from Ref. 22 ( $4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at 1.5 eV), and 0.1 that value was used for  $\text{NF}_2$  and  $\text{NF}$ . Although it is known that dissociative attachment may have a dependence on  $T_g$  this function is not known for  $\text{NF}_3$ , and was not included.

In Fig. 1 we show predicted absorption  $\alpha$  and net gain,  $g_0 - \alpha$ , for  $\text{XeF}(B \rightarrow X)$  in He and Ne buffered mixtures excited as described above. The gain in the He mixture is initially  $\approx 0.75$  that for the Ne mixture. The formation efficien-

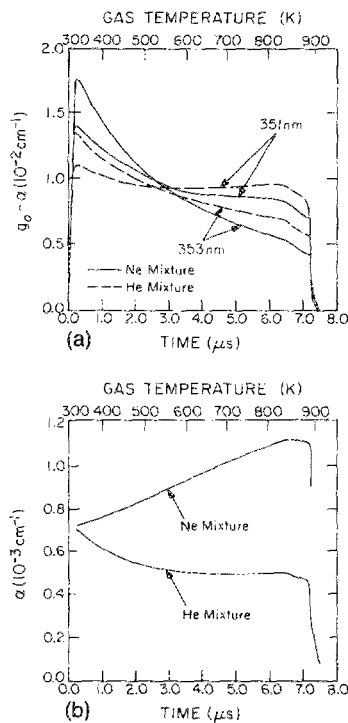


FIG. 1. Computed (a) net gain ( $g_0 - \alpha$ ) and (b) absorption ( $\alpha$ ) during a  $7.5 \mu\text{s}$  excitation pulse in an  $\text{XeF}(B \rightarrow X)$  laser for 3 atm He and Ne buffered gas mixtures ( $132 \text{ kW/cm}^3$ ). The gas temperature is shown on the top scale.

cies for  $\text{XeF}(B)$  in each case, though, are nearly identical. The differences in gain can be attributed largely to the increased net rate of quenching of  $\text{XeF}(B \rightarrow C)$  in helium ( $3.0 \times 10^{12} \text{ cm}^3 \text{ s}^{-1}$ ) compared to neon ( $1.0 \times 10^{17} \text{ cm}^3 \text{ s}^{-1}$ ).<sup>7</sup> Maximum gain is first at 353 nm and then, with the increase in  $T_g$ , changes to 351 nm. The overall decrease and leveling in gain is due to a combination of some burnup of  $\text{NF}_3$  ( $\approx 10\%$ ), an increase in the rate of quenching of  $\text{XeF}(B)$  due to the  $T_g^{1/2}$  scaling of these coefficients, and somewhat more favorable vibrational distribution for the 351 nm transition. At later times, gain in the He mixture exceeds that for the Ne mixture. This condition results, in part, from higher absorption in the Ne mixture (see below). Another factor is that with a higher rate of  $B \leftrightarrow C$  mixing in He mixtures, the reservoir of molecules in the (lower energy)  $C$  state is more accessible when  $T_g$  is sufficiently high to compensate for the activation energy barrier ( $775 \text{ cm}^{-1}$ ).

Absorption in each mixture, initially the same, evolves to be quite different. In the Ne mixture, absorption increases with gas temperature, while it decreases to a nearly constant value in the He mixture. This behavior can be explained by examining the ion and radical densities in Fig. 2, and the fractional optical absorption in Fig. 3. The dominant ions in the Ne mixture are initially  $\text{NeXe}^+$  and  $\text{Ne}_2^+$ ; however later in the pulse the dominant ion switches to  $\text{Ne}^+$ . This change to atomic ions results largely from the inverse temperature dependence ( $\sim T_g^{-3/2}$ ) of the three-body association rate constant. The  $\text{F}^-$  density also increases during the pulse since ion-ion neutralization rate constants decrease with temperature ( $\sim T_g^{-1/2}$ ). The increase in  $\text{F}^-$ , though, is smaller than expected because the dominant positive ion switches from  $\text{NeXe}^+$  to  $\text{Ne}^+$ , whose ion-ion neutralization

TABLE I. Absorption cross sections at 353 nm.<sup>a</sup>

Species	Cross section ( $\text{cm}^2$ )	Reference
$\text{Ne}_2^*$	$1.98 \times 10^{-13} T_g^{1.49}$	3
$\text{Ne}_2^+$	$8.20 \times 10^{-22} T_g^{1.38}$	3, 16
$\text{NeXe}^+$	$2.03 \times 10^{-22} T_g^{1.05}$	3
$\text{Xe}_2^*$	$1.00 \times 10^{-18}$	17, b
$\text{Xe}_2^+$	$4.96 \times 10^{-14} T_g^{1.1}$	3, 16
$\text{Xe}^{**}$	$1.00 \times 10^{-17}$	18
$\text{F}_2^*$	$8.35 \times 10^{-13} T_g^{2.3}$	3
$\text{F}^-$	$2.0 \times 10^{-17}$	19

<sup>a</sup>  $T_g$  = Gas temperature (K).

<sup>b</sup> The temperature dependence of absorption from  $\text{Xe}_2^*$  is not available; however, its fractional contribution is small.

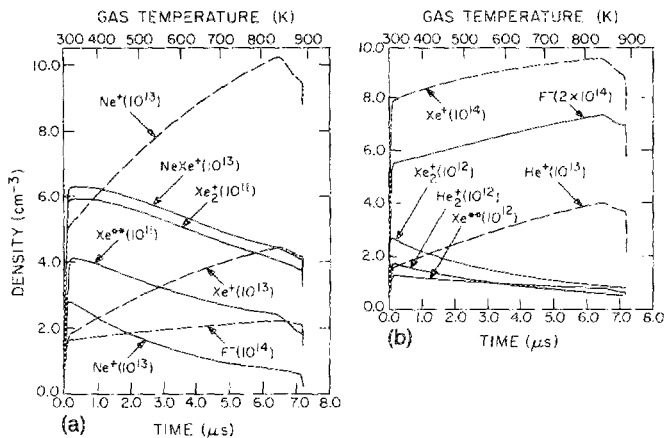


FIG. 2. Excited-state densities in (a) Ne and (b) He buffered gas mixtures for the conditions of Fig. 1. Excited diatomic densities decrease due to association rate constants scaling as  $T_g^{-3/2}$ . The  $F^-$  density increases due to ion-ion neutralization rates scaling as  $T_g^{-1/2}$ .

rate constant is more than twice as large. Similar trends are observed in the He mixture.

The absolute and fractional densities of absorbing molecular species decrease in both mixtures during the pump pulse. Accordingly, the density of atomic species which either do not absorb or weakly absorb, increases. One would expect, then, that optical absorption should decrease with increasing  $T_g$ . This is, in fact, observed in the He mixture where absorption decreases due to a decrease in the fractional contribution of  $Xe_2^+$  resulting from a smaller density and cross section (see Fig. 3). This decrease in absorption is somewhat offset by an increase in the density of  $F^-$ .

In the Ne mixture, though, absorption increases with increasing  $T_g$ . Absorption, initially dominated by  $F^-$ , is shared nearly equally by  $NeXe^+$  late in the pulse (see Fig. 3). The increase in fractional absorption by  $NeXe^+$  with increasing  $T_g$ , which accounts for the increase in total absorption, results from an increase in the absorption cross section at 353 nm which more than compensates for the decrease in the absolute density of  $NeXe^+$ . It has been recently suggested that the  $N_2$  buildup in  $NF_3$  gas mixtures degrades the laser performance by selective absorption by  $N_2^+$  at 353 nm.<sup>23</sup> Our predicted maximum  $N_2$  fraction is sufficiently small that we do not believe  $N_2^+$  absorption is important.

In conclusion, high gas temperature ( $T_g \leq 900$  K) plasma chemistry and absorption in the  $XeF(B \rightarrow X)$  laser have been investigated. The rate of quenching reactions generally increases with increasing  $T_g$  and therefore the small-signal gain is reduced. The rate constant for ion-ion neutralization decreases with  $T_g$ , so that the negative ion density and its absorption should increase. The rates of three-body association reactions, though, decrease with increasing  $T_g$ . Therefore, diatomic excited species and ions decrease in both fractional and absolute density with increasing gas temperature. This change in the dominant ion affects the negative ion density since the rates of ion-ion neutralization are functions of species. In general, optical absorption should decrease with increasing  $T_g$  since excited-state absorption is dominated by diatomic species. The temperature dependence of the

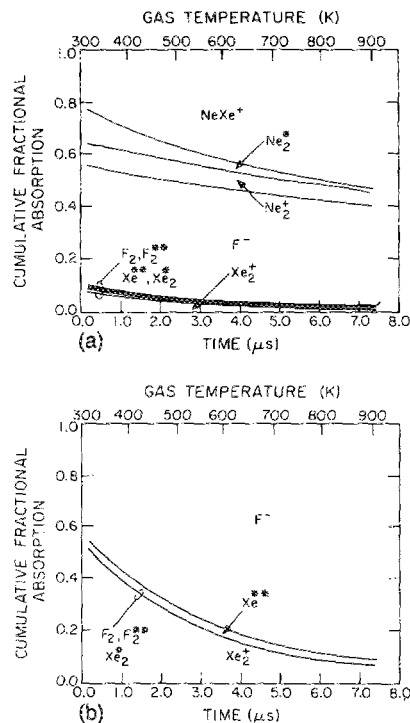


FIG. 3. Fractional cumulative absorption in (a) Ne and (b) He buffered gas mixtures for conditions of Fig. 1.

individual cross sections for these processes, though, may dominate over their change in number density.

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