Triatomic rare gas halide excimers

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ABSTRACT

The spectroscopy and kinetics of electron beam-pumped broadband triatomic excimers will be reviewed. Laser considerations such as gain and absorption effects will be discussed, with emphasis on Xe_2Cl

INTRODUCTION

The triatomic rare gas halides, Rg_2X^* were discovered in 1976 as broadband companion emissions from RgX^* laser media [1,2]. These trimer emissions are observed in all the rare gas halides at high pressure and are listed in Table 1. By careful choice of pressure conditions, it is possible to identify emissions of several mixed or unsymmetrical triatomic rare gas halides, $Rg Rg'X$ [3]. Figure 1 shows a calculated potential energy diagram for a typical Rg_2X exciplex, Xe_2Cl^*. Typical high pressure emission spectra obtained with electron beam excitation are shown in Fig. 2. The broad Rg_2X fluorescence with 50 to 120 nm spectral bandwidth offers the potential of tunable excimer lasers in the wavelength region from 230 nm (Ar_2Cl) to 670 nm (Xe_2F).

KINETICS ISSUES

The basic kinetic reaction pathways for dimer and trimer formation in argon buffered rare-gas halide mixtures are shown in Fig. 3. Deposition of electron beam energy occurs primarily in the dense Ar buffer and to a minor extent in the rare gas with subsequent build-up of RgX^*. Various processes for the formation of the trimer Rg_2X^* have been discussed in the literature. As indicated in Fig. 3, the principal reaction appears to be three-body clustering:

$$RgX^* + 2Rg \rightarrow Rg_2X^* + Rg$$
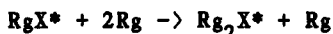
Alternative pathways for direct formation of Rg_2X^* via Rg_2^+ or Rg_2^* as precursors are also possible but are apparently less important.
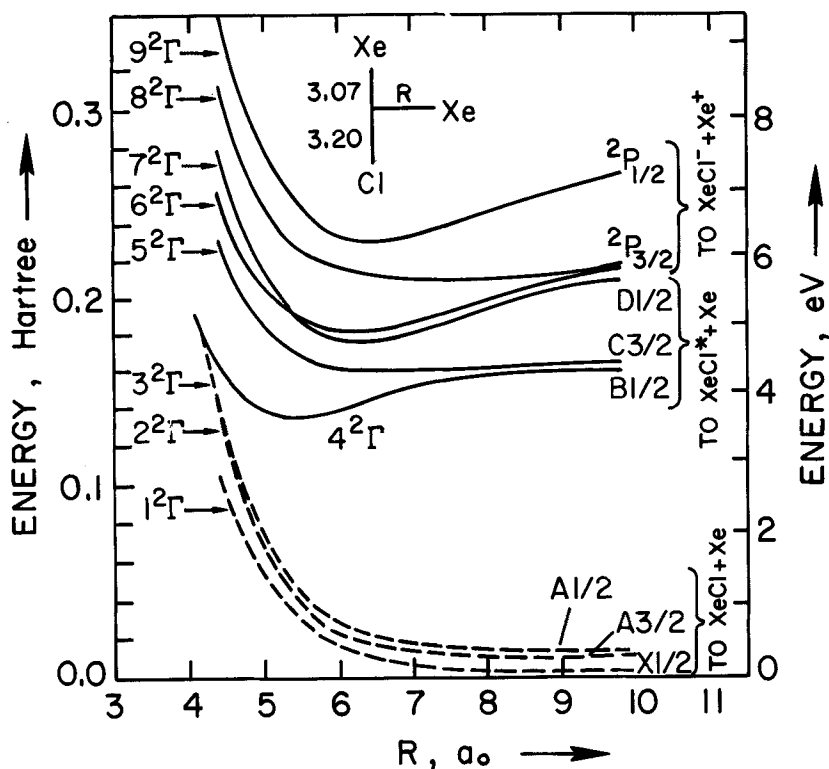
Fig. 1: Diatomics in molecules potential surfaces for Xe_2Cl leading to $Xe_2^+ + Cl^-$.

There is general agreement that production of the symmetrical trimers under typical pressure conditions (e.g. 6 atm Ar, 200 Torr Xe, 1 Torr halogen donor) occurs on a fast time scale. Typical three-body formation rates are in the range of 10^{-31} cm^6 s^{-1} to 10^{-30} cm^6 s^{-1} [4].

Studies of formation of the unsymmetrical trimers, e.g.

$$KrF^* + 2Ar \rightarrow ArKrF^* + Ar$$
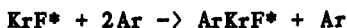
have been substantially less definitive in large part because the product is short lived as a consequence of displacement reactions of the type,

$$ArKrF^* + Kr \rightarrow Kr_2F^* + Ar.$$
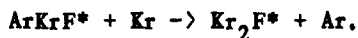
Thus the formation of the mixed trimers must be inferred from deconvolution of the pressure dependence of RgX^* decay and formation of the final Rg_2X^* product. In general it appears that the rates of formation of the unsymmetrical triatomics are significantly slower in comparison with their symmetrical counterparts.
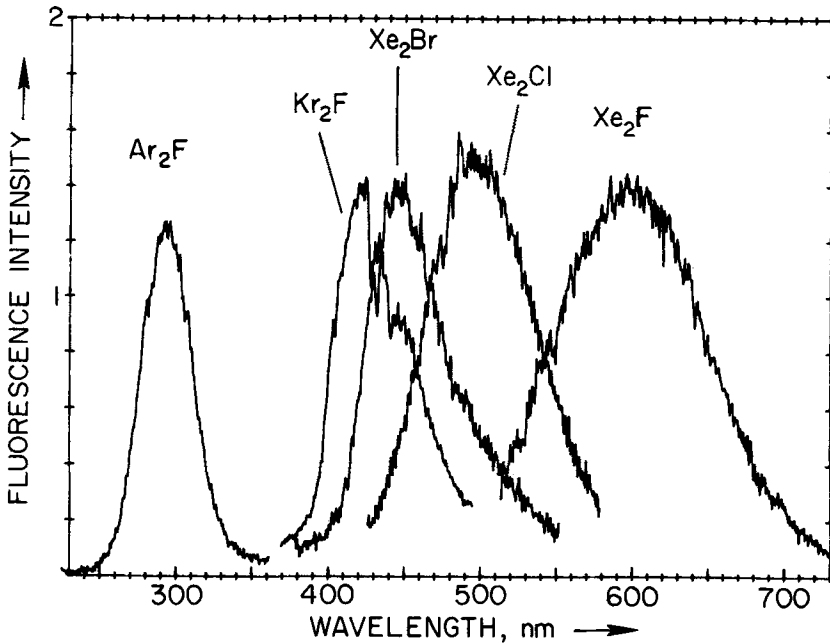
Fig. 2: Time-integrated fluorescence spectra of the trimers Ar_2F, Kr_2F, Xe_2Br, Xe_2Cl, and Xe_2F obtained with electron beam excitation of high pressure argon buffered rare gas halide mixtures.

The broadband nature of the Rg_2X^* emissions is accompanied by rather long radiative lifetime (130-330 nsec) as compared to the short (4-16 nsec) lifetimes of the $RgX^*(B \rightarrow X)$ transitions. The long spontaneous lifetime and the broad bandwidth of the trimer transitions have important implications for laser development. First they are responsible for a relatively small optical gain [4,5]. Furthermore, they make Rg_2X^* species vulnerable to quenching by the halogen donor. However, a long lifetime permits laser operation after the decay of absorption that may be dominant during the short excitation pulse.

The quenching behavior of both the diatomic precursor (e.g. $XeCl^*$) and the trimer (Xe_2Cl^*) by the halogen donor and the rare gases has been studied in detail. Typically the halogen donor is the most severe quencher of the Rg_2X^* emission with rates of the order of $10^{-10} \, cm^3 s^{-1}$. The optimum halogen donor in terms of fluorescence yield, quenching and chemical stability must be selected with care. Table 2 summarizes the relevant formation and quenching data for the triatomic excimer, Xe_2Cl.
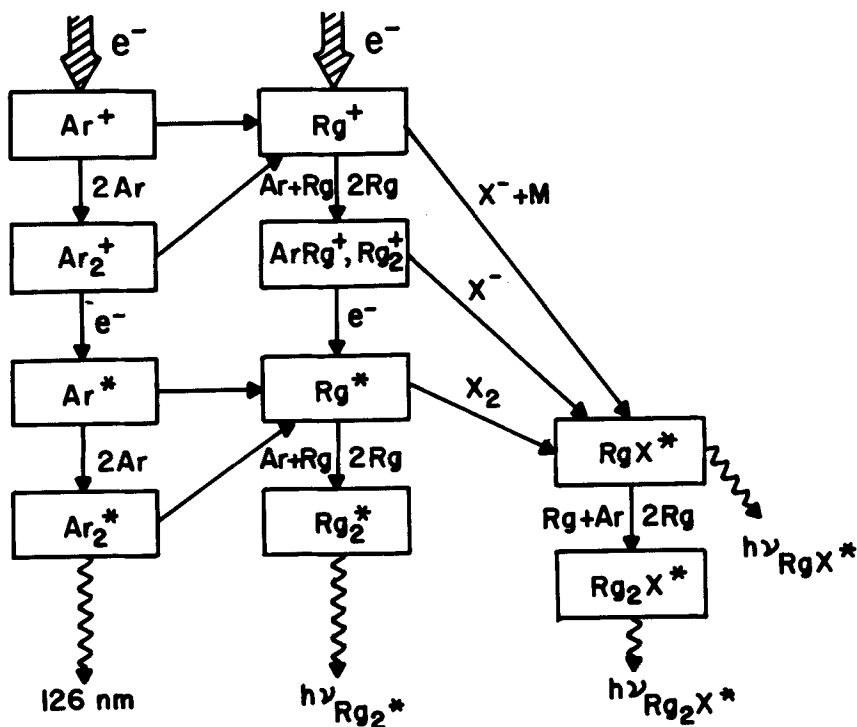
Fig. 3: Principal reaction pathways in high argon pressure buffered rare gas halide mixtures.

LASER CONSIDERATIONS

A critical issue of the performance of low gain electron beam-pumped Rg_2X lasers is the relationship between gain of the excimer transition and absorptions from excited molecular and atomic species. A compilation of the cross sections for stiumulated emission σ_e is given in Table 3, calculated by means of the equation:

$$\sigma_e \approx \frac{1}{8\pi\tau c} \frac{\lambda^4}{\Delta\lambda}$$

and the spectroscopic data in Table 1, where τ is the spontaneous decay time, c is the speed of light, $\Delta\lambda$ is the bandwidth (FWHM) and λ is the central fluorescence wavelength. In the absence of absorbers, the unsaturated gain coefficient is $g = \sigma N$, where N is the excited state population density in the upper laser level.

Electron beams and open discharge excitation have so far been the two most effective pumping techniques for fluorescence and laser studies of trimers. A typical electron-beam source, such as a Pulserad 110 delivers up to 120 J per ns duration pulse of 1 MeV electrons, resulting in a Rg_2X^*-concentrations of 10^{15} to 10^{16} cm^{-3}. Due to the relatively small cross-section for stimulated emission σ_e (10^{-18} $cm^2 \leq \sigma_e \leq 10^{-17}$ cm^2), this excited state concentration leads to gains of a few percent per cm. For the trimer Xe_2Cl^* typical gain values of 3% cm^{-1} have been determined experimentally [4].
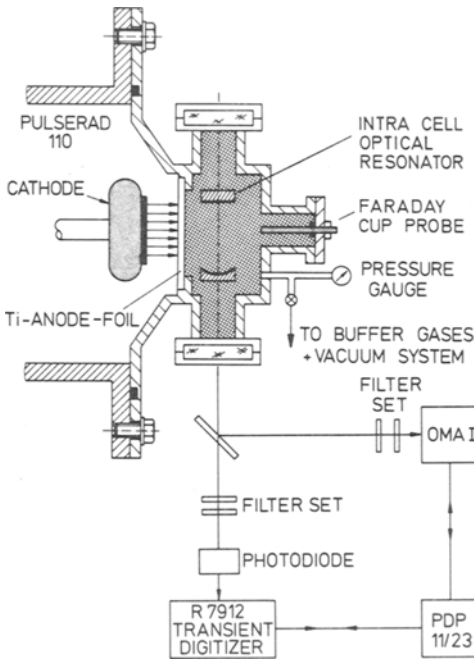
Fig. 4: Schematic diagram of transverse electron beam-pumped laser cell and associated instrumentation for time and spectrally resolved measurements.

Various molecular and atomic absorption processes in electron beam-pumped rare gas halides interfere severely with the performance of triatomic excimer lasers. Stimulated emission is both delayed by broadband absorbing species and influenced by a large number of intense absorption lines. The broadband absorbers have been identified as molecular in orgin [6] with typical cross-sections, $\sigma_a \leq 5 \cdot 10^{-17}$ cm^2 They absorb in the visible and UV principally due to positive ionic states such as Ar_2 and due to photo-ionization of rare gas excimers, such as absorptions by Ar_2, Kr_2 and Xe_2. The other source of absorption is due to transitions from metastable Xe* atoms to high lying Rydberg levels [4].

LASER EXPERIMENTS

Of the 10 trimers listed in Table 1, laser operation has so far been demonstrated for Xe_2Cl* [7], and Kr_2F* [8,9]. The basic experimental arrangement used in these experiments is shown in Fig. 4. It consists of the electron-beam excitation source, a high pressure cell with an externally adjustable optical resonator and various electrical and optical diagnostic instrumentation. Details of such a setup and the techniques employed are given in Ref. 4.

A typical Xe_2Cl laser spectrum is shown in Fig. 5. The diatomic XeCl (B -> X) transition at 308 nm, the Xe_2Cl* laser output spectrum, and, for comparison, Xe_2Cl* spontaneous fluorescence are depicted. The laser spectrum which has a center wavelength of 520 nm shows significant spectral narrowing from 70 nm (spontaneous emission) to 32
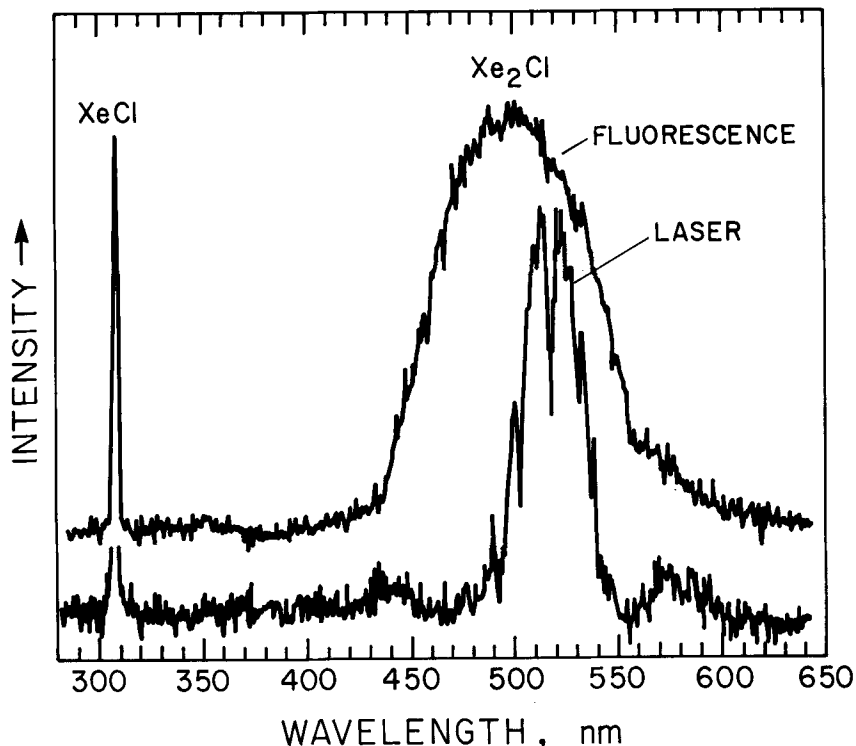
Fig. 5: Fluorescence and laser spectra of Xe_2Cl and XeCl(B->X) of an electron beam-excited mixture consisting of 6.5 atm Ar, 200 Torr Xe and 1 Torr CCl_4.

nm. In addition greatly enhanced intracavity absorption features can be observed. The laser output spectrum is red-shifted relative to the fluorescence spectrum by approximately 20 nm. This shift is due to both the λ^4 dependence of the stimulated emission cross section and to the long wavelength tail of the various rare gas absorbers, such as Xe_2^+ or Ar_2^+. A reduction in bandwidth from 31 nm (FWHM) to only 13 nm occurs as a consequence of tighter focusing cavity reflectors. Fig. 6 shows a typical normalized temporal composite of UV and visible fluorescence and Xe_2Cl laser output from a high pressure Ar-Xe-CCl_4 mixture. The 40 ns long laser pulse is considerably delayed with respect to the electron beam pump pulse due to induced buffer gas absorptions discussed below. Furthermore, the Xe_2Cl^* emission occurs delayed with respect to the UV fluorescence pulse, and the laser output reaches its maximum peak intensity later than the Xe_2Cl^* fluorescence peak as a consequence of the long ring up time of cavity oscillations.

Tuning experiments with intracavity dispersive tuning elements (i.e., a prism or grating) as demonstrated for the broadband diatomic XeF(C -> A) excimer [10] were unsuccessful. However, broadband tunability (over a 40 nm spectral range) could be demonstrated for Xe_2Cl by using two reflectors with different center wavelengths [11].
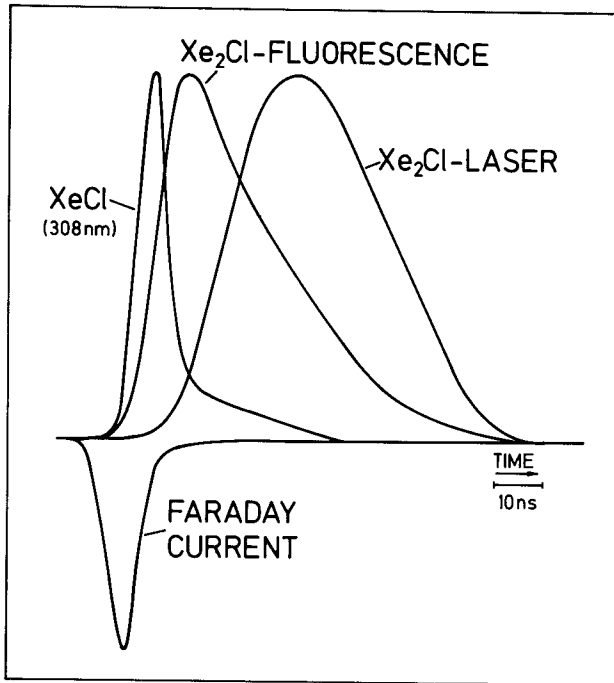
Fig. 6: Normalized temporal characteristics of Xe_2Cl laser and fluorescence, XeCl(B->X) fluorescence and the e-beam pump pulse.

Recent work reported in Ref. [12] suggests that the atomic metastable absorptions may be quenched by rapid transfer to N_2 when using photolytic excitation at 172 nm with an Xe_2^* radiation source. Various efforts have been made to study the role of Xe^* metastables on laser output characacteristics for e-beam excited gas mixtures. In a recent study [13] the influence of N_2 addition on Xe_2Cl^* fluorescence and laser behavior has been investigated. Considerable improvement of the Xe_2Cl laser output was observed when nitrogen was added to the gas mixture. A significant increase of the laser output power by a factor up to three was achieved by the addition of 200 Torr of nitrogen.

The role of N_2 as an additive to an $Ar/Xe/CCl_4$ mixture to enhance the Xe_2Cl laser performance can be best understood by consideration of the influence of N_2 on the production and loss by the primary absorbing species Xe^*, Xe_2^* and Xe_2. Assuming that the measured quenching coefficient of $1.9 \times 10^{-11} cm^3 s^{-1}$ for $Xe(^3P_2)$ by N_2 is also representative of the other Xe(6s) levels [4], a nitrogen pressure of 100 Torr results in Xe^* quenching time constant of about 20 ns, which is close to the observed delay for the onset of lasing. Since the dimer Xe_2^* is produced from Xe^*, it follows that the presence of N_2 will reduce both discrete and broadband absorption resulting from Xe^* and Xe_2^*.

Table 1:   Emission Features of the Rare-Gas Halides

Rg	X	RgX D1/2->X1/2	RgX B1/2->X1/2	RgX C3/2->A3/2	RgX B1/2->A1/2	Rg_2X
Ne	F	(106)[a]	108	(110)	(111)	(~145)
Ar	F	(185)	193	(203)	(204)	285 ± 25
Ar	Cl	–	175	–	–	246 ± 15
Kr	F	220	248	275	(272)	420 ± 35
Kr	Cl	200	222	240	–	325 ± 15
Kr	Br	–	207	222	228	~ 318
Xe	F	264	351	460	(410)	610 ± 65
Xe	Cl	236	308	345	(340)	490 ± 40
Xe	Br	221	282	300	320	440 ± 30
Xe	I	203	253	265	320	~ 375

[a] Wavelengths in nm, theoretical values in parenthesis.

SUMMARY

Electron beam-pumped broadband triatomic excimers, Rg_2X^* has been discussed in terms of their underlying spectroscopic and kinetic characteristics, emphasizing those that are relevant to laser performance. Because the triatomic rare gas halogens have a steeply repulsive potential energy curve in the ground state, the fluorescence is inherently broadband as compared to the narrow spectral linewidth of the diatomic excimer.

The energy transfer and excited state kinetics for trimers is complex. The detailed kinetic route by which the excimer is formed depends upon the particular trimer, the halogen donor, the excitation conditions and the partial pressures of the constituent gases. Trimers are produced principally by three-body clustering collisions involving the diatomic RgX* as precursors. Most of the three-body reaction rates are of the order of 10^{-31} to 10^{-30} $cm^6 s^{-1}$.

Unfortunately from the point of view of laser development, the broadband trimer emission is accompanied by long radiative lifetimes which implies low optical gain for these excimers. To date, two triatomic lasers Xe_2Cl centered at 520 nm and Kr_2F centered at 435 nm have been demonstrated. Electron beam pump-induced transient atomic and molecular absorption effects were found to severely limit the potential laser efficiency and usefulness of triatomic excimers.

Table 2: Summary of rate constants for reactions quenching XeCl* and Xe$_2$Cl*

Reaction	Rate coefficient	Reference
XeCl* + Ar + Xe -> products	$(3.8 \pm 0.2) \times 10^{-30}$ cm^{6}s^{-1}	[14]
XeCl* + Ar + Xe -> Xe$_2$Cl* + Ar	$(1.5 \pm 0.5) \times 10^{-31}$ cm^{6}s^{-1}	[15]
XeCl* + Ar + Ar -> products	$< 3 \times 10^{-33}$ cm^{6}s^{-1}	[14]
XeCl* + Xe + Xe -> products	7.3×10^{-31} cm^{6}s^{-1}	[16]
XeCl* + CCl$_4$ -> products	$(4.6 \pm 0.2) \times 10^{-10}$ cm^{3}s^{-1} 5.0×10^{-10}	[14] [66]
XeCl* + Cl$_2$ -> products	8.8×10^{-11}	[16]
XeCl* + Ar -> products	$< 2 \times 10^{-13}$ cm^{3}s^{-1}	[14]
XeCl* + Xe -> products	1×10^{-11} cm^{3}s^{-1}	[16]
XeCl* -> Xe + Cl + hν(308 nm)	41 ± 3 ns 11 ns 40 ns 27 ns	[17] [20,21] [16] [17]
XeCl* -> Xe + Cl + hν (345 nm)	53 ns for C state 133 ± 10 ns	[17] [21]
Xe$_2$Cl* -> 2Xe + Cl + hν (500 nm)	$135(\pm^{70}_{60}$ ns) 210 ± 20 210 ns 185 ns 120 ± 30 ns 330 ns	[15] [18] [16] [17] [5] [19]
Xe$_2$Cl*+CCl$_4$ -> quenching	$(6 \pm 1) \times 10^{-10}$ cm^{3}s^{-1}	[15]
Xe$_2$Cl*+Cl$_2$ -> quenching	4.5×10^{-10} 2.6×10^{-10}	[16] [17]
Xe$_2$Cl*+Ar -> quenching	$(3 \pm 1) \times 10^{-14}$ cm^{3}s^{-1}	[15]
Xe$_2$Cl*+Xe -> quenching	$< 5 \times 10^{-13}$ cm^{3}s^{-1} $< 4 \times 10^{-14}$ cm^{3}s^{-1} $< 6 \times 10^{-15}$ cm^{3}s^{-1}	[15] [16] [17]

Table 3: Stimulated emission cross sections for broadband transitions.

Rg_2X*	$\sigma_e(10^{-18}cm^2)$
Ar_2F*	0.95
Kr_2F*	3.28
Xe_2F*	14.05
Xe_2Cl*	4.56
Xe_2Br*	2.65

Other trimers with wide fluorescence bandwidths – Ar_2F at 290 nm, Xe_2Br at 420 nm and Xe_2F at 614 nm exhibited gains which were too small to achieve laser action in the 10 cm transversely pumped laser cavity used so far in these experiments.

Optimization of gas mixtures [13] and novel pumping schemes such as radiation transfer pumping [9,12] have been partially successful in minimizing quenching collisions of excited species, competing B -> X transitions and absorption effects. An important remaining technical challenge is the realization of a fast-discharge excited triatomic excimer laser. Such a development will require stable discharge conditions in a high pressure gas mixture which can be obtained with X-ray, UV-laser or electron-beam preionization.

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