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ABSTRACT

The field of UV/visible gas lasers has undergone a rapid expansion in the past three years since the discovery of the first rare gas monohalide excimer laser. There are now many new high power UV and visible lasers available with demonstrated efficiencies exceeding 1%. This review of the field emphasises the common properties of these laser systems and indicates their potential impact on commercial photochemical processes.

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1. INTRODUCTION

Major breakthroughs in laser development, many within the past few years, have revolutionised the field of UV lasers. A new generation of UV molecular gas lasers has appeared with demonstrated or realistically predicted efficiencies exceeding 1% and the capacity for high peak power (> 1 MW cm^{-2}) and/or high average power (> 1 kW) operation. Eleven of these lasers span the 175-360 nm UV region while five more operate in the blue/green region.

These advances in UV/visible lasers are opening up many new and exciting possibilities. The lower diffraction limited divergence of light at shorter wavelengths is of interest in such diverse fields as satellite communications and photolithography. More importantly, the inherent tunability of these molecular lasers associated with the vibrational structure of the upper and lower laser levels, coupled with the efficiency of stimulated Raman scattering to generate new UV laser wavelengths, will allow for the first time ultra-high resolution of the electronic structure of molecules, with biological molecules being of particular interest. From a commercial viewpoint, there are possibilities of practical applications in a vast array of photochemical processes of which isotope separation and the reprocessing of radioactive waste are discussed in section 8.

The UV/visible lasers considered here can conveniently be grouped into six 'classes'. These lasers are listed in Table 1 together with their operating wavelengths and the primary references to reports of laser action achieved in various modes of excitation. As indicated in Table 1, laser action has been achieved in plasmas created by high energy electron beams (e-beams), electrical discharges and e-beam/discharge combinations. In all cases the high excitation rates required for laser operation restrict their operation to a short ($\lesssim 1$ μs) pulse mode, although CW laser action is theoretically possible in several cases.

A most important characteristic shared by the lasers in Table 1 is the fact that their upper laser levels are populated in electronic excitation reactions. These reactions may be defined as ones in which one of the products is created in an electronically excited state. The reactions are selective because their reaction rates depend on the degree of electronic excitation in the product. Their importance is discussed in section 2, vis-a-vis UV gas laser development, and the reactions themselves are described in more detail in section 3. This common feature of new UV/visible lasers is emphasised in this review by discussing their performance as a whole, rather than individually. In keeping with this approach, sections 4, 5 and 6 group the performance of these laser systems in one or other of the three forms of excitation given in Table 1. Thus it is hoped that future developments in this rapidly expanding field can be judged in the context of the performance of existing lasers.

2. THE DEVELOPMENT OF UV GAS LASERS[30]

Prior to 1970 the majority of UV gas lasers were low efficiency, pulsed devices operating on transitions in ionized atoms excited in low pressure, high current discharges.[31] In these devices the upper laser level is populated from the neutral ground state atom through multiple electron excitation collisions. Because electron excitation is a non-selective process, these lasers are inherently low efficiency ($\lesssim 10^{-4}$) devices. Further, the power capability of these lasers is severely limited because electron de-excitation of the atom in the upper laser level becomes important in high current discharges and reduces the population inversion.[32]

One way of overcoming these limitations and achieving the highest efficiencies from discharge lasers is to exploit the long-lived species which are efficiently produced in a discharge. This may be illustrated by considering the discharge in a rare gas X containing a small quantity of some other gas Y which will be referred to as the seed gas. Rare gas ions and metastable atoms are the dominant species in such a discharge, but their store of internal energy can be efficiently transferred in certain (thermal energy) electronic excitation reactions as defined in section 1. In such a reaction one of the products emerges in a single electronic level (eg $(Y^+)^*$, XY^*) which becomes the upper laser level of a potentially efficient device.

The rare gas - metal vapour lasers, lasing on transitions in singly ionized metal atoms, were the first UV discharge devices to exploit electronic excitation reactions.[33] Their efficiencies were greater than those of earlier discharge UV lasers, although still less than 0.1%, permitting both pulsed and CW laser operation in many cases. However, the number of potential UV laser transitions in singly ionized atoms is small.[34] Electronic excitation reactions involving one of the dominant species in a discharge are limited in terms of the energy available for transfer, the maximum being 24.5 eV from a He^+ ion. This restricts the range of potential lasant species to neutral and singly ionized atoms and molecules. The consequences for UV atomic lasers are unfortunate, since the strongest UV transitions in neutral and singly ionized atoms generally terminate either on a ground level or on a level having a relatively long radiative lifetime (often lengthened by radiation trapping effects). Fortunately the same restrictions do not apply to molecules where UV transitions between electronic levels comprise many individual transitions between discrete vibrational states. The lifetime of these lower vibrational states is greatly reduced by collisional 'quenching' (ie collision-induced transfer of population to adjacent states) and/or by spontaneous or collision-induced dissociation of the molecule. Consequently, UV molecular lasers which rely on selective excitation reactions to create the population inversion represent an important class of laser, to which all of the lasers listed in Table 1 belong.

The transitions involved in molecular lasers can conveniently be divided into two categories according to the nature of the upper and lower electronic levels; bound-bound transitions associated with traditional level schemes in laser devices, and bound-free transitions where the lower level is dissociative ie it lies in a continuum of positive states.

To date, laser action on bound-free transitions has only been observed when the lower level is the ground level of the molecule, ie the molecule is an excimer. Although many chemists would restrict the definition of an excimer to specify homonuclear dimers with dissociate ground levels, common usage of the term 'excimer' by the laser community extends the term to refer to the general class of molecules with dissociative ground levels (when a clear distinction between homonuclear dimers and more complex molecules is important, the term 'exciplex' is used). Referring to Table 1, most of

the rare gas monohalides are seen to be excimers. The rapid decay of their ground states in $\sim 10^{-12}$s (one vibration period) makes them ideal lower laser levels and excimer lasers are thus unique in their potential for high efficiency, high power operation.

Bound-bound laser transitions are also of great interest. However, for high power, high efficiency laser operation it is clearly desirable to minimise 'bottle-necking' (ie build-up of population in the lower laser level) before and during laser action. For bound lower levels this can only be achieved by collisions which dissociate the molecule or redistribute population between the discrete vibrational states.

The major advance which pointed the way to the new UV/visible lasers was the discovery of the xenon dimer (Xe_2) laser.[35] This was the first excimer laser. It was also the first laser to demonstrate that efficient high power coherent operation in the UV ($\sim$ 173 nm) was a practical possibility. To date, laser operation has only been achieved by e-beam excitation of high pressure ($\gtrsim$ 1 atm) xenon gas or liquid xenon. The function of the e-beam is simply to provide ionization of the bulk gas; the dominant rare gas species produced in such a plasma are the same as those produced in a discharge excited plasma. However, the efficiencies for creating these species are considerably greater in an e-beam-produced plasma.[36] It was this observation in the xenon laser (inferred from measurements of fluorescence efficiencies for the laser transition, which approached 50% of the theoretical limit[37]) that encouraged the addition of seed gases to e-beam excited rare gas plasmas in the search for new efficient lasers based on selective excitation reactions. The result of this search has been the discovery of many new UV/visible lasers, mostly within the past three years. Of these new lasers, the rare gas monohalides have demonstrated the highest efficiencies and output powers.

3. ELECTRONIC EXCITATION REACTIONS IN THE NEW UV/VISIBLE LASERS

In each of the new UV/visible lasers, population inversion is achieved through selective excitation reactions in a rare gas plasma containing a small quantity of seed gas as discussed above. Creation of the plasma has

been accomplished both by electrical discharges and by e-beam excitation. Each leads to its own set of reactions by which energy is transferred to the plasma and then to the upper laser level. These differences are discussed more fully in sections 4 and 5; here we consider only the final step(s) in the reaction sequence.

The process of selective electronic excitation of the upper laser level is most readily demonstrated for the case of the rare gas monohalides. These molecules are similar in electronic structure to the alkali halides. In this regard, rare gas metastable atoms have similar chemical properties to the alkali ground state atoms (eg Kr* ≡ Rb). In particular, the rare gas monohalides are ionic in nature, possessing deeply bound ionic levels of which the lowest becomes the upper laser level.[38] It is this strong binding which accounts for the high selectivity in the formation reactions (1) and (2) below in exciting to the upper laser level.[39] Only the ArF, KrF, XeF and XeCl upper laser levels however are stable to predissociation[38] In the monohalides formed by the lighter rare gases and heavier halogens, predissociation is particularly rapid and accounts for their absence from Table 1.

Selective excitation of the rare gas monohalide upper laser level is known to occur primarily through two types of processes. The first is the so-called 'harpooning' reaction involving an excited rare gas atom X*[40] and may be written as

$$X^* + YR \rightarrow XY^* + R \qquad \ldots(1)$$

where R is a radical attached to a halogen Y.[39] In all cases, rates are large, $\sim 5.10^{-10}$ cm^3s^{-1}, and where YR is the Y_2 halogen molecule the reaction rate is largest and the selectivity of the process approaches unity.[38,39]

The second process is three body ion-ion recombination ie

$$X^+ + Y^- + M \rightarrow XY^* + M \qquad \ldots(2)$$

where M is some third body.[41] Rate-constants for this process are very large at low pressures, $\sim 10^{-25}$ cm^6s^{-1}, and reach a diffusion limited two body value of $\sim 1.10^{-6}$ cm^3s^{-1} at an optimum pressure between 1 and 3 atm.[42]

Ion-ion recombination involving X_2^+ ions is also believed to selectively populate the upper laser level.[43]

Both reactions (1) and (2) play an important role in populating the upper laser level in e-beam-produced and discharge plasmas. In the monofluorides, reaction (2) is probably dominant, due to the particularly rapid production of F^- ions by dissociative attachment. For example, for 1 eV electrons in fluorine at one Torr the reaction time for the process

$$F_2 + e \rightarrow F^- + F \qquad ...(3)$$

is only 10 ns.[44]

It might be supposed that increasing the halogen partial pressure would increase the population in the upper laser level of the rare gas monohalide as electronic excitation reactions compete with others (eg recombination or electron de-excitation) for the stored energy in the rare gas. However, the fluorescence efficiency (the fraction of the input energy absorbed by the laser gas and released as fluorescence) for the laser transition is typically observed to maximise at a relatively low pressure of seed gas, and this has been interpreted in terms of fast two-body 'quenching' of the upper laser level by the seed gas.[45] In the rare gas monofluorides for example, radiative decay and fluorine (F_2) quenching of the upper laser level are equal at a fluorine pressure of $\sim$ 6 Torr.[43,46,47] It follows that the upper laser level formation process must have a large cross-section as well as being selective in nature if high fluorescence efficiencies are to be achieved. These requirements are satisfied in the rare gas monohalides; in particular, intrinsic efficiencies of $\sim$ 25% are predicted for KrF and values up to 18% have been observed.[48]

By comparison, consider the selective excitation reaction between metastable argon atoms and nitrogen molecules which populates the upper laser level of the Ar/N_2 laser (listed in Table 1)

$$Ar^* + N_2 \rightarrow N_2^* + Ar \qquad ...(4)$$

The branching ratio for direct production of the upper laser level $N_2(C)$ by the above excitation transfer process is only 0.1, although this

rises to ~ 0.4 after collisional transfer from more highly excited N_2 molecules.[49] Further, in an e-beam plasma, the pressure of nitrogen required to transfer 40% of the Ar* excitation to N_2^* leads to 75% of the $N_2(C)$ molecules being collisionally quenched by N_2 before they radiate spontaneously.[4]

The kinetics of the other energy transfer laser listed in Table 1, the He-N_2 laser, are more favourable than those of the Ar-N_2 laser. The He-N_2 laser is the only known molecular ion laser and the electronic excitation (charge-transfer) reaction

$$He_n^+ + N_2 \rightarrow N_2^+(B) + nHe \qquad ...(5)$$

is some twenty times faster than reaction (4) at room temperature; it is also thought to be highly selective.[5] In reaction (5), n is believed to be 3.[51] In contrast to the Ar* species in reaction (4) which rapidly dimerises (and is then lost for $N_2(C)$ formation in reaction (4)) at the high pressures required by these lasers (see also sections 4 and 5), He_n^+ ions are relatively stable and do not undergo rapid dissociative recombination like the ions of the other rare gases. As a result, high helium pressures (upwards of 30 atm for e-beam excitation) are beneficial in optimising molecular ion formation.

The high efficiencies achieved for some of the rare gas monohalide lasers has encouraged the development of other laser systems in which the fast reactions (1) and (2) are employed, and in which the upper laser is ionic in nature and therefore selectively excited. These conditions are satisfied in the most recent additions to Table 1, the halogen dimer and mercury monohalide lasers. By analogy with the rare gas monohalides, the 'harpooning' reaction involving mercury metastable atoms or halogen atoms in low lying excited states (which are effectively metastable under laser conditions due to radiation trapping) is believed to proceed at about the same rate as for the rare gas metastable atoms.[38,52] However, at least in e-beam-produced plasmas, the dominant upper laser level excitation reaction has been tentatively assigned to three-body ion-ion recombination, which first requires the production of the appropriate positive ion, eg.

$$Ar^* + I_2 \rightarrow Ar + I^+ + I^- \qquad ...(6a)$$

$$Ar_2^* + I_2 \rightarrow 2Ar + I^+ + I^- \qquad ...(6b)$$

for a halogen ion[53] and Xe_2^+ charge transfer to mercury atoms to produce Hg^+ ions.[19,20,22]

The particular interest in the halogen dimer lasers arises from the high fluorescence efficiencies of $13 \pm 4\%$ which have been measured for reaction (6) in an e-beam-produced plasma.[53] Similar efficiencies have not yet been attained for Ar/Xe/Hg halogen mixtures, but the fluorescence efficiency will be severely limited by the 9.5% quantum efficiency for the laser excitation process[21] (see section 6).

Contrasting with other laser molecules considered above, the rare gas oxide molecule in the upper level is only weakly bound (~ 0.06 eV for XeO) and the excitation reaction is best described by the equilibrium

$$2X + O(^1S) \rightleftarrows XO(^1\Sigma) + X \qquad ...(7)$$

The development of these lasers follows the interest in oxygen (and other Group VI elements) as potential high efficiency, high energy storage amplifier media. Several photolytic processes exist for selectively producing $O(^1S)$ atoms for an atomic oxygen laser, but in e-beam excited rare gas/oxygen mixtures a two step electronic excitation process is believed to be responsible.[54] Very high pressures (10-20 atm) of rare gas are required to maintain comparable equilibrium densities of $O(^1S)$ and XO species,[55] and indeed the role of the rare gas in reaction (7) can equally well be considered as collisionally inducing radiation from the $O(^1S)$ level.[15,56]

4. LASER OPERATION UNDER E-BEAM EXCITATION

4.1 The Rare Gas Monohalides

The rare gas monohalides (with the exception of XeF and XeCl) are excimer molecules. In excimer lasers the dissociative nature of the lower laser level prevents it from 'bottle-necking'. This allows full use of

the upper laser level population to create laser photons. It also permits intracavity powers greatly exceeding the saturation value for the upper laser level[57] to be maintained during the laser pulse. In this way very high laser powers can be achieved and losses associated with collisional quenching of the upper laser level can be avoided. Even in XeF and XeCl, 'bottle-necking' is partially removed by rapid collisional quenching or dissociation of the lower laser level.

Of the rare gas monohalides, the best laser performance to date has been achieved with the rare gas monofluorides.[1,4,8,58,59,60] This may be largely attributed to the reduced electron attachment rates for the heavier halogens. Of the fluorides, KrF has the highest potential efficiency. High efficiency in XeF is limited primarily by absorption losses in the laser plasma and 'bottle-necking',[61] while in ArF collisional quenching of the upper laser level is a problem as discussed below.

Table 2 lists relevant laser parameters for the rare gas fluorides. Stimulated emission cross-sections at line centre (σ_o) are given for typical laser operating conditions, and quantum efficiencies (η_Q) are calculated assuming reaction (2) to be the dominant upper laser level formation process. There are some discrepancies in radiative lifetime data, and the values given should be taken only as provisional. Taking a small signal gain (α) of 2% cm^{-1} to produce the short laser build-up time (τ_{bu}) for efficient pulsed laser operation ($\tau_{bu} \sim 50$ ns for $\alpha = 2\%$ cm^{-1}) Table 2 also lists calculated values for the required minimum excited rates R_{min} ($cm^{-3}s^{-1}$) and power densities P_{min} for the most favourable conditions where the lower laser level population can be neglected and the dominant decay of the upper laser level is radiative. For these conditions, Table 2 also lists calculated values for the saturation power I^{sat}_{min}. The large I^{sat}_{min} values of these (and other rare gas monohalides) are characteristics of high power lasers, while the small τ_R values exclude their use as high energy storage amplifiers.

Using appropriate reaction rates given in section 3, the R_{min} values in Table 2 can readily be converted into particle density requirements. To achieve an excitation rate of $\sim 2.10^{22}$ $cm^{-3}s^{-1}$ (see Table 2), only a low fractional ionization is required for three body recombination (reaction

(2)) in the diffusion limited regime, corresponding to densities ~ 2.10^{14} cm^{-3} for both ion species. To achieve an equivalent excitation rate by harpooning collisions (reaction (1)) with the typical 4 Torr fluorine used in these lasers, an unusually high metastable density of some 3.10^{14} cm^{-3} would be required.

The minimum power density requirements outlined in Table 2 can readily be satisfied and greatly exceeded with conventional cold-cathode-type e-beam machines for pulse durations of $\lesssim$ 2 μs with gas pressures (for neon or heavier gases) $\gtrsim$ 1 atm.[68] Excitation power densities achieved with an e-beam scale linearly with gas pressure (until the beam becomes depleted) but two and three-body quenching of the upper laser level by the rare gas sets an upper pressure limit for efficient laser operation.[69] This quenching by the rare gas halves the lifetime of the upper laser level at pressures of 430 Torr Kr,[46] 220 Torr Xe[63,70] or 550 Torr Ar.[43] Fortunately with xenon or krypton monohalides argon or neon can be used as buffer gases, to absorb the energy from the e-beam. In these three-component mixtures, energy is transferred to the upper laser level but quenching rates for KrF* or XeF* by Ar or Ne are at least an order of magnitude smaller than for the Kr and Xe respectively.[48,63] The energy transfer processes are complex and are illustrated schematically in Fig.1 for production of XeF in an $Ar/Xe/F_2$ mixture with argon as the major constituent.[70] The dominant species produced directly by e-beam excitation are Ar^+ ions. Two separate reaction paths are indicated depending on whether or not Ar_2^+ formation (which becomes significant at pressures $\gtrsim$ 1 atm) is important. Both paths are efficient and the probability of producing an XeF* molecule from an Ar^+ ion is close to unity.[63]

Table 3 illustrates the wide range of operating conditions and laser performance achieved by the e-beam excited rare gas monofluorides. Where available, pulse energies and durations, laser efficiencies, specific energy extraction and laser gas conditions are given. Optimised parameters have been underlined. Efficiencies are given either in terms of total energy consumed by the laser ('wall-plug' efficiency) η_o, or in terms of energy deposited into the laser medium, η_l. Because of the rapid rate of development in this laser field, Table 3 is necessarily dated, but gives a useful

indication of the present capabilities of these lasers. In particular it illustrates the high power capability of these devices and the flexibility in laser pulse duration from a few tens of ns to $\gtrsim$ 1 μs.

The optimised gas conditions given in Table 3, reflect the result of other experimental and theoretical studies that the highest laser efficiencies and/or powers are typically achieved under plasma conditions where heavy-body collisional quenching of the upper laser level dominates over spontaneous radiative decay. This situation reflects a minimum gain requirement set by the need both for a rapid build-up of intracavity laser power and for a gain greatly exceeding the threshold set by absorption and scattering losses. Under these conditions, laser efficiencies approaching (and even surpassing) fluorescence efficiencies demand intracavity powers greatly exceeding the saturation value. This is highlighted in the case of the 100J pulses obtained from ArF and KrF (Table 3) where similar efficiencies were obtained for both lasers despite the larger quenching losses in the ArF laser. Efficiencies (η_1) approaching the 20-25% limit for KrF have been claimed by e-beam pumping of the gas using a coaxial geometry (see Table 3). The relatively poor efficiencies achieved using other pumping geometries may be attributed to non-uniformities in the e-beam energy deposition.

The limiting factor in achieving the high potential efficiencies of e-beam pumped rare gas monohalide lasers is usually absorption losses within the laser medium.[61,62,70,73,74] Such losses could be anticipated in multi-component molecular media, particularly since at the short operating wavelengths of these lasers many molecular species can be photodissociated. The major absorption losses have generally been attributed to photodetachment of the negative halogen ion,[75] photoexcitation of rare gas monohalide triatomics[62] (see section 7.2) and photoexcitation of rare gas dimer ions.[62,73] Direct absorption losses by a halogen seed gas can also be a serious loss,[62] and, for this reason, halogen donor molecules are often used eg NF_3 in place of F_2[76] (see Table 3).

Absorption losses in the XeF laser (by Xe_2^+ ions) are more serious than in the other rare gas monofluorides.[61,73,74] These losses, coupled with partial bottlenecking of the lower laser level account for the relatively

poor laser efficiencies of $\lesssim$ 3% achieved to date for XeF compared to the predicted upper limit of 14%.[61] However, it has recently been found that substituting neon for argon as the buffer gas has greatly improved the performance of the XeF (and also the KrF) laser.[74] This improvement can be attributed to reductions both in the absorption at the laser wavelength[74] and to collisional quenching of the upper laser level by the buffer gas.[70]

4.2 Other UV/Visible Lasers

To date, none of the other e-beam pumped UV/visible lasers has matched the rare gas monofluoride lasers in terms of efficiency, pulse power or energy. Disappointing performances of the Ar-N_2 and He-N_2 energy transfer lasers is significant, since the relevant kinetics are well understood and they were the first of the new UV/visible lasers to be reported. On the other hand, the halogen dimer and mercury monohalide lasers have only recently been reported and show considerable promise.

In the two energy transfer lasers, fluorescence on the laser transition is dominantly from the $v'' = 0$ vibrational state of the upper laser level to the (tightly bound) $v' = 0$, 1 or 2 states of the lower laser level. Neither rapid dissociation nor collisional quenching of these lower v' states occurs and, as a result, bottlenecking is severe.[49,78] This bottlenecking has not prevented peak powers of several MW[25,27,49,51] or pulse durations of $\gtrsim$ 1 μs[25,29] from being achieved, nor does it prevent these lasers from being capable of efficiencies exceeding 1%.[25,49,51] However, it does place a severe restriction on the duration of the e-beam pumping pulse for efficient laser operation. Thus a high repetition rate, high mean power operating mode is most suitable for these lasers.[68]

In contrast to the energy transfer lasers, bottlenecking is not a problem in the rare gas oxide lasers due to rapid predissociation of the lower laser level.[55,77] However, the performance of the rare gas oxide lasers to date has been disappointing.[13] This may be partly attributed to the experimental conditions, since the laser build-up times exceeded both the e-beam pump duration and the collisional lifetime of the upper laser level.[13] Of the new UV/visible lasers, the rare gas oxides have by far the smallest stimulated emission cross-sections ($\sigma_o \sim 2.5.10^{-19}$ cm^2 under

typical laser operating conditions for KrO,[79] nearly three orders of magnitude smaller than the values quoted in Table 2). This, combined with relatively slow $O(^1S)$ formation rate and a highly pressure and temperature sensitive equilibrium population in the upper laser level[55] (reaction (7)), places an inherent limitation on the performance capability of these lasers.

The halogen dimers are of particular current interest as potentially efficient lasers, in view of the high fluorescence efficiencies reported in section 3. These efficiencies are compatible with a 10-20% efficiency for production of the upper laser level.[52] Apart from favourable formation kinetics, bottlenecking of the lower laser level may not be a serious problem. This is a consequence of large Franck-Condon shifts which occur because of the different binding natures of the upper (ionic) and lower (covalent) laser levels. As a result, the strong components of the laser transition terminate on states with a typically large ($\nu' \sim 20$) vibrational quantum number.[16,80] From these states collisional de-excitation or dissociation can be rapid.[17,80] This favourable situation is also common to the mercury monohalides.[20,22]

High power outputs of up to 25 MW (at 1 J) have been reported for an e-beam pumped I_2 laser,[80] while the performance of the Br_2 and F_2 lasers has been much poorer.[14,15] The Cl_2 laser has yet to be made to operate, but it is believed to have a dissociative lower laser level.[81] While there have been too few reports of halogen dimer laser operation to generalise with confidence, optimum laser performance has so far been achieved only at pressures substantially in excess of those which produce the maximum fluorescence efficiency.[15,17] While collisional quenching can be overcome in laser systems where lower laser level bottlenecking can be removed, there have been indications (in the Br_2 laser[15]) that bottlenecking is indeed a problem.[16] Nevertheless, the major limitation to overall efficiency may be absorption of laser radiation by excited halogen dimers, which can be dissociated by the (energetic) laser photon.[16,38]

The mercury monohalide lasers are the latest additions to the new UV/visible lasers, and are the first of possibly a whole series of metal based molecular lasers (see section 7). To date, laser performance has been poor,[19,20,23] but the hope for these systems lies primarily in

discharge or e-beam sustained discharge excitation,[22] discussed in sections 5 and 6.

5. DISCHARGE EXCITED LASERS

One of the recent breakthroughs in rare gas monohalide development has been the operation of these lasers in a discharge plasma. To date, the rare gas monohalide lasers together with the He-N_2 laser are the only members of Table 1 to operate in a self-sustained discharge. The high excitation power densities given in Table 2 demand high pressure operation ($\gtrsim$ 1 atm)[82] while the addition of an electronegative (halogen) gas to the laser mixture in itself is a source of discharge instability.[83,84] In earlier devices, fast Blumlein circuitry with no preionization was employed to excite small gas volumes in pulses $\lesssim$ 10 ns in duration,[4,6,10,85,86,87] while later developments employing strong UV preionization of the laser gas have allowed stable discharge of duration $\sim$ 100 ns to be achieved with large volume excitation.[3,88,89,90,91]

E-beam produced plasmas are characterised by low plasma electron temperatures, which favour rapid recombination and high excited state populations. They differ from self-sustained discharge plasmas where electron temperatures must be sufficiently high for electron ionization to dominate over recombination and other electron loss processes.[34] Consequently discharge plasmas tend to produce ions rather than excited states, and this favours the fast electronic excitation reactions (2) and (5) which produce inversions in the rare gas halide and He-N_2 lasers. The mercury monohalide lasers should also operate well in a discharge device.

Broadly speaking, the operating conditions of rare gas monohalide discharge lasers are determined not by the kinetics and plasma absorption but by the requirements of plasma stability. For example despite large absorption losses in the discharge XeF laser ($\sim$ 2% cm^{-1},[92] principally due to fluorine and xenon species) energy outputs continue to rise up to almost the highest partial pressures of the active gases that can be tolerated before rapid arc formation occurs.[89] Successful discharge operation has been achieved only in a three component mixture with helium as the dominant

(buffer) gas, not with argon and only poorly with neon.[89] Unlike the situation in the e-beam plasma, rapid reactions transferring energy from discharge products of helium to the minority rare gas and halogen in the laser mixture are not known. However, helium participation as a heat 'sink' to minimise the vibrational temperature of the upper laser level and as a third body in the ion-ion recombination process is indicated.[92]

The performance of some self-sustained discharge rare gas monofluoride lasers is summarised in Table 4 using a similar format to Table 3. Also included where appropriate are PRF values. The high PRF capability of discharge devices is one of their principal advantages over e-beam devices, which are typically limited (except in a 'burst' mode) to $\lesssim$ 1 Hz operation.

A direct comparison of η_l efficiencies between Tables 3 and 4 (η_l values are approximately twice η_o values in discharge devices) clearly reflects the non-optimum plasma conditions in discharge devices. The effects of plasma photoabsorption at the laser wavelength may also be dramatic, as indicated from a computer simulation of the ArF and KrF discharge lasers where an improvement in laser output of a factor of four was predicted when all absorption losses in the plasma were set to zero.[93]

The energy output from these lasers is presently limited by plasma stability requirements, which limits the time during which energy can be fed into the plasma to $\lesssim$ 100 ns - even with good preionization. Taking a typical value for a UV preionized KrF laser of 80J/l.atm for the maximum energy deposition,[82] in laboratory size lasers (active volume $\sim 0.5\ell$) outputs of $\sim$ 1J can be achieved at a few atmospheres pressure. Up to the highest pressures for which an arc-free discharge has been achieved (see Table 2) these lasers have shown a rise in laser output energy with pressure.[88,91] However, in discharge lasers electron collisional quenching (first and second kind collisions) of the upper laser level[32] must eventually set an upper limit to the power capability per unit volume from these devices. This contrasts with e-beam plasmas where electron densities are relatively low due to the rapid attachment rate at the lower electron temperatures.[94]

The He-N_2 laser has also been operated in both fast discharge[26,95] and UV-preionized modes.[96,97] In this case, direct electron impact

ionization and excitation may dominate the formation kinetics under some conditions. As with the rare gas monohalide discharge lasers, optimum laser operation is achieved under high gain conditions, and output energy is observed to increase linearly with helium pressure up to the limit of 3 atm, at which these lasers have presently been operated.[97] However, because of the relatively long radiative lifetime of the upper laser level (78 ns) electron collisional quenching may set a low upper limit to the efficiency and power capability of this laser. To date maximum energies of $\sim$ 3 mJ have been obtained, with pulse durations of up to 35 ns.[97]

6. E-BEAM SUSTAINED/STABILISED DISCHARGE LASERS

In both e-beam-produced and discharge plasmas, the conditions favour the production of ions over metastable species. This situation can be changed by e-beam sustained discharge operation. The technique, applied successfully to many IR lasers, allows the applied discharge field to be reduced in order to optimise the net production rate of metastable atoms rather than of ions and electrons. This is achieved by means of a simultaneously applied e-beam which provides the auxiliary ionization rate within the plasma necessary to sustain the discharge. For those UV/visible lasers which can utilise electronic excitation reactions involving atoms rather than ions to populate the upper laser level, an improvement in laser efficiency can be achieved in principle. The technique would have many advantages for the mercury monohalide lasers where direct excitation of mercury metastable atoms rather than argon ions (see section 3) would improve the quantum efficiency from 9% for pure e-beam pumping to $\sim$ 45%.[23,24] For the rare gas monohalides the gains in efficiency by utilising reaction (1) instead of reaction (2) are significant but not large.[6,10]

It is not clear that any of the reported e-beam/discharge excitation lasers could be regarded as operating in a sustained mode in view of the low enhancement factors (ratio of energy deposited by the discharge to energy deposited by the e-beam) that have been achieved, usually less than three.[6,10,61,100] Also, for efficient rare gas metastable production, metastable densities must be kept $\lesssim 10^{-5}$ of the ground state atom density.[101]

It has been shown that under conditions necessary for the efficient production of metastable atoms the gains in KrF and XeF lasers are so low that plasma absorption losses (as discussed in section 3) seriously limit the overall laser efficiency and output energy.[6,10]

The most effective e-beam/discharge operation for the new UV/visible lasers can best be described as e-beam stabilised. The e-beam maintains a low impedance plasma which is resistant to arc formation when an auxiliary electric field is applied.[102] In this way, stable discharge operation has been achieved in KrF and XeF lasers even using argon instead of helium as buffer gas, in Ar/N_2[29] in HgCl[21,22] and in HgBr.[22] Similar operation in others of the UV/visible lasers should also be possible. To date, e-beam stabilised rare gas monohalide discharge lasers have performed both in terms of their efficiency (η_1) and output laser pulse characteristics in a manner very similar to their pure e-beam counterparts.[61,100] In all cases the laser output energy was found to improve up to the highest fields that could be applied while still maintaining a stable discharge. Discharge instabilities invariably set in when the e-beam was terminated. This mode of operation has the advantage over pure discharge operation that gas pressures and compositions can be better optimised to improve laser efficiency, and the discharge circuit characteristics can be efficiently matched to a reasonably constant plasma impedance. These improvements become in practice more important to plasma stability than the condition for bulk stability (ie a zero average growth of electron density). This latter condition can be satisfied if sufficient electron-attaching gas is present to maintain an electron attachment rate in excess of twice the ionization rate in the plasma,[103] but results in pure discharges indicate that the discharge is made not more but less stable by the addition of a halogen (attaching) gas. This has been borne out by recent attempts to operate a stable e-beam controlled discharge Br_2 laser in which arc-free operation could not be achieved over the duration of the e-beam pulse although laser action was observed.[16]

7. NEW EXCIMER LASERS

7.1 Introduction

The intrinsically high efficiency of these lasers has stimulated an interest in new excimer molecules not only to generate alternative laser wavelengths in the UV and visible region, but also to fill the requirement for a very efficient high energy, short pulse amplifier for laser fusion applications.[104] The range of excimer candidates extends from combinations of atoms with closed shell ground electronic configurations (ie the rare gas and GpII metals eg Ar_2 (130 nm), Hg_2 (335 nm), HgXe (275 nm), CdHg (470 nm)) to some open shell-closed diatomics (eg KrF (248 nm), CsXe (572 nm)). Some triatomics (eg Kr_2F (400 nm)) and more complex molecules (eg $Hg(H_2O)$ (290 nm), $Hg(NH_3)$ (350 nm)) may also be considered.

For a high energy amplifier (say 10^4- 10^5J) an inversion lifetime of $\gtrsim 10^{-6}$s is required to allow sufficient energy transfer time to the gain medium.[104] To minimise superfluorescence and parasitic oscillations the stimulated emission cross section should be small, but greater than 6.10^{-19}-6.10^{-20} cm^2 at 300 nm. This minimum cross section is set by the requirement that the saturation energy density be within the handling range of presently available window materials ($\sim$ 1-10 J/cm^{-2}). For short pulse amplification by an excimer molecule, the broad fluorescence linewidth associated with the dissociative nature of the lower laser level has the potential advantage of allowing the population of many vibrational states of the upper laser level to contribute to the amplification process.

It is clear that many excimer molecules do not satisfy high efficiency laser/amplifier requirements. Rapid predissociation of the upper laser level excludes some if not all of the alkaline earth dimers[105] as well as many of the lighter rare gas monohalides. Strong excimer absorption at the laser wavelength excludes the XeBr[106] and XeI monohalides, the rare gas dimers[36] and the Hg_2 510 nm ($A^3\Sigma_v^- \rightarrow X^1\Sigma_g^+$) transition.[107] The creation of a large thermal population in the lower laser level and the spread of upper laser level population among many excited vibrational states[36] are possible drawbacks to high temperature operation, and may exclude from consideration the excimers of less volatile metals.

In an energy storage amplifier, low collisional and radiative decay of the upper laser level during the excitation period is of utmost importance. In a laser, (where minimum gains of $\sim 1\%$ cm^{-1} may be required for high efficiency,) excited state-excited state collisions can also present a serious quenching loss. Such quenching losses clearly become increasingly important with smaller stimulated emission cross sections, and in the rare gas dimers ($\sigma_o \sim 1.4.10^{-17}$ cm^2 in Xe_2) Penning ionization eg

$$2Xe_2^* \rightarrow Xe_2^+ + 2Xe + e \qquad ...(8)$$

gives rise to the low efficiencies (η_1 typically < 1%) of these lasers.[36]

A final requirement for potential laser/amplifier candidates is the existence of a fast selective excitation reaction to provide the population inversion. For closed shell-closed shell excimers (eg rare gas dimers) this mechanism is inherently three body, and rapid excimer formation requires high pressures. In the closed shell-open shell excimers, two body mechanisms are possible (eg 'harpooning' collisions for the rare gas monohalides). However, while strong exchange interaction leads to modest covalent excited state binding energies in homonuclear excimers,[55] such energies are typically very small in heteronuclear dimers.[55] Here, a tightly bound ionic level in the excimer is required which is resistant to predissociation and which can be selectively excited with high efficiency. To date the principal interest in new excimer lasers appears to be in the rare gas monohalide triatomics and the mercury-based excimers. These are discussed in more detail below.

7.2 The Rare Gas Monohalide Triatomics

The rare gas monohalide triatomics (X_2Y, where X = rare gas, Y = halogen) come close to satisfying the requirements outlined above. The dominant formation mechanism for the potential ($4^2\Gamma$) upper laser level is believed to be three body quenching of the corresponding rare gas monohalide diatomic.[62] In diatomic rare gas monohalide laser gas mixtures, fluorescence attributed to the triatomic species increases up to high

pressures (~ 10 atm) while fluorescence on the diatomic laser transition decreases.[108] This fluorescence from the triatomic has been attributed to $4^2\Gamma \rightarrow 1^2\Gamma$ and $2^2\Gamma$ transitions.[109] The upper level is bound and ionic ($X_2^+ + Y^-$) and the lower level is dissociative and covalent ($X_2 + Y$).[109,110] Broad band emission has been observed from Xe_2Cl (450 nm), Kr_2Cl (325 nm), Ar_2Cl (246 nm), Kr_2F (400 nm) and Ar_2F (292 nm).[108]

Calculations[111] and experimental measurements[112] on Ar_2F and Kr_2F give upper level radiative lifetimes of ~ 180 ns, with corresponding stimulated emission cross sections (calculated here using reported fluorescence linewidths[108]) of 4.10^{-19} cm^2 and 1.10^{-18} cm^2. These molecules have clear potential as gain media for high power, high energy devices. To date, gains have been so small that laser action has not been achieved. However, fluorescence yields suggest that high laser efficiencies might be achieved at high pressures.[108]

7.3 Mercury-Based Excimers

A major attraction of group II metal excimers as lasers over rare gas excimers is the high efficiency and selectivity with which the metastable states of metal atoms can be excited by electrons in a discharge.[113] High efficiency e-beam sustained discharge operation of such lasers should therefore also be possible. Because mercury is the most volatile group II metal its excimers, notably Hg_2, HgCd and HgTh have been studied in detail. To date however, e-beam excitation has generally been employed in the search for new lasers.

The attraction of e-beam excitation is that high excitation power densities can readily be achieved without the stability limitations on gas pressure and metal composition otherwise imposed by discharge excitation. For metal excimer systems e-beam excitation offers the additional advantage of simplicity in the design of the high temperature vessel. However, e-beam plasmas create metastable atom levels chiefly through ion recombination, and the process of populating the metastable atoms levels by this process is much slower in pure mercury than in the rare gases (as evidenced by fluorescence decay measurements) even at high pressures,[114] and this may explain the present lack of success with these systems.

To date, gains have been reported of 0.65% cm^{-1} on the Hg_2 330 nm ($A^3\pi_u \rightarrow X^1\Sigma_u$) transition in e-beam excited mercury vapour,[115] and of 0.2% cm^{-1} near 460 nm in a flashlamp pumped Hg/Cd mixture.[116] However, these measurements have not been subsequently confirmed by reports of laser action. This failure may be due in part to the difficulty of producing a laser medium of sufficiently high optical quality at the high temperatures ($\sim 400^oC$) required. However both Hg_2 and HgCd show good potential for high energy laser/amplifier applications, as shown by their measured stimulated emission cross-section and lifetime values of $9.7.10^{-19}$ cm^{-2}, 220 ns and $2.9.10^{-19}$ cm^{-2}, 2.8 μs respectively.

8. LASERS FOR PHOTOCHEMICAL APPLICATIONS

Near UV photons are capable of electronically exciting or dissociating most molecules and many atoms. Consequently the availability of efficient, tunable high power UV laser sources has opened up many new possibilities in the field of photochemistry. The new UV/visible lasers are not only high power, high efficiency, tunable devices, but are also capable of both short pulse and quasi cw operation. Some of these properties are summarised in Tables 3 and 4. In particular, for the rare gas monohalides, e-beam excitation can provide both single-shot sub kJ pulses and also pulses of $\sim$ 1J at a pulse repetition frequency (PRF) of 1-10 Hz and with a 'wall-plug' efficiency of $\sim$ 1%. Discharge operation offers sub-joule pulses at PRF's $\lesssim$ 1 kHz and 'wall-plug' efficiencies $\sim$ 1%. Clearly, for many photochemical applications the prospect of efficient 1 kW mean power operation is extremely attractive, particularly in a discharge device with its inherent simplicity and reliability.

An important consequence of the characteristically high power and short operating wavelength of the rare gas monohalides is the efficiency with which the laser frequency can be shifted by Stimulated Raman Scattering (SRS). The UV wavelength of these lasers in particular permits near resonant scattering using highly allowed transitions in many atomic species.[118] A photon conversion efficiency approaching unity has been reported for SRS of XeF in barium vapour,[118] and in high pressure hydrogen up to sixth order Stokes wavelengths have been generated.[119] From the viewpoint of selective

excitation in molecules and atoms it is interesting to note that all of the 200-360 nm region can be covered using SRS combined with the inherent tunability of the rare gas monohalide lasers.

In a mixture of molecules, individual component molecules can be selectively photo-excited as a result of the differences in molecular absorption spectra.[120] This selectivity may be permanent if the excited molecule dissociates (either spontaneously or through collisions), undergoes a fast chemical reaction or is photo-dissociated by application of a second UV photon. An example of this approach of interest to the reprocessing of radioactive waste is the liquid phase separation of individual lanthanides from a mixture by chemical reaction following excitation by ArF or KrF lasers.[121] Another example is the single-step purification of silane (used in the manufacture of solar cells) by the photo-dissociation of impurities using an ArF laser.[122] In these examples the differences in the absorption spectra involved are so large that untuned lasers can be employed.

The most interesting field commercially at the moment is laser isotope separation (LIS).[123] LIS methods for many elements promise high separation factors, high efficiencies and relatively low running costs. In particular a successful LIS approach to uranium enrichment could have a significant economic impact. The techniques most discussed for LIS in the USA involve the simultaneous irradiation by two lasers, the first providing isotopically selective excitation, the second (UV) photon producing either photo-dissociation (in a molecular route)[124] or photo-ionization (in an atomic route).[125] The dissociation products can then be separated physically. There are relatively broad linewidth requirements for the second UV photon, the main specifications are efficiency (since this photon typically provides most of the energy of separation) and mean power. In the case of uranium the LIS requirements are exceptional, in view of the enormous throughputs of material required. Total average UV laser powers for a commercial plant could be tens of kilowatts. Even so, these requirements seem within the range of present rare gas monohalide lasers. The stated LASL uv requirements for uranium separation by a molecular route are $\eta_o > 1\%$, PRF 100 Hz - 5 kHz, pulse energy $\geq$ 1J and wavelength range

400-380 nm or 300-235 nm[124] and would seem to be met by a fast-flow KrF discharge laser with SRS shifting of the output frequency.

In the long term, one might envisage true cw operation of one of the new UV lasers, with particular view to photochemical processes requiring high throughputs of material (eg heavy water production) or involving the interaction of a laser with a fast flowing medium. However, there are some major obstacles that first need to be overcome as discussed below.

The high saturation power densities of the new UV/visible lasers (eg see Table 2) imply that round-trip laser cavity losses must be kept much less than 1% if efficiency considerations alone are not to dictate minimum cw laser output powers of kW's cm^{-2}. However the minimum power density needed tc be supplied to the laser gas mixture is dictated by absorption losses in the gain medium. These losses can presently be minimised to $\sim 0.1\%$ cm^{-1} for the KrF and XeF lasers[62,74] yet still imply that power densities greatly in excess of 1 kW cm^{-3} would be required to reach laser threshold. Ultra-high gas flows would therefore be necessary with fast and efficient clean-up of the gas in a closed loop configuration.[126] In essence therefore the development of gas excitation techniques will clearly determine the feasibility of cw lasers of this type. However, with the rapid evolution of the new UV lasers over the past few years, one may be cautiously optimistic about the future of the cw devices and the role of UV lasers generally in the photochemical industry.

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REFERENCES

1. HOFFMAN, J.M., HAYS, A.K., TISONE, G.C. - Appl.Phys.Lett.28 (1976) 538
2. BURNHAM, R., DJEU, N. - Appl.Phys.Lett.29 (1976) 707
3. WAYNANT, R.W. - Appl.Phys.Lett.30 (1977) 234
4. EWING, J.J., BRAU, C.A. - Appl.Phys.Lett.27 (1975) 350
5. SUTTON, D.G., SUCHARD, S.N., GIBB, O.L., WANG, C.P. - Appl.Phys.Lett. 28 (1976) 522
6. MANGANO, J.A., JACOB, J.H. - Appl.Phys.Lett.27 (1975) 495
7. MURRAY, J.R., POWELL, H.T. - Appl.Phys.Lett.29 (1976) 252
8. BRAU, C.A., EWING, J.J. - Appl.Phys.Lett.27 (1975) 435
9. BURNHAM, R., HARRIS, N.W., DJEU, N. - Appl.Phys.Lett.28 (1976) 86
10. MANGANO, J.A., JACOB, J.H., DODGE, J.B. - Appl.Phys.Lett.29 (1976) 426
11. KUDRYAVTSEV, YU A., KUZ'MINA, N.P. - Sov.J.Quant.Elect.7 (1977) 131
12. SEARLES, S.K., HART, G.A. - Appl.Phys.Lett.27 (1975) 243
13. POWELL, H.T., MURRAY, J.R., RHODES, C.K. - Appl.Phys.Lett.25 (1974) 730
14. RICE, J.K., HAYS, A.K., WOODWORTH, J.R. - Appl.Phys.Lett.31 (1977) 31
15. MURRAY, J., SWINGLE, J.C., TURNER, C.E. - Appl.Phys.Lett.28 (1976) 530
16. EWING, J.J., JACOB, J.H., MANGANO. J.A., BROWN, H.A. - Appl.Phys.Lett. (1976) 656
17. BRADFORD, R.S., AULT, E.R., BHAUMIK, M.L. - Appl.Phys.Lett.27 (1975) 546
18. EWING, J.J., BRAU, C.A. - Appl.Phys.Lett.27 (1975) 557
19. EDEN, J.G. - Appl.Phys.Lett.31 (1977) 448
20. PARKS, J.H. - Appl.Phys.Lett.31 (1977) 192
21. TANG, K.Y., HUNTER, R.O. Jnr., OLDENETTEL. J., HOWTON, C., HUESTIS, D., ECKSTROM, D., PERRY, B., McCUSKER, M. - Appl.Phys.Lett.32 (1978) 226

22. WHITNEY, W.T. - Appl.Phys.Lett.32 (1978) 239

23. PARKS, J.H. - Appl.Phys.Lett.31 (1977) 297

24. COLLINS, C.B., CUNNINGHAM, A.J., STOCKTON, M. - Appl.Phys.Lett.25 (1974) 344

25. COLLINS, C.B., CUNNINGHAM, A.J. - Appl.Phys.Lett.27 (1975) 127

26. ISHCHENKO, V.N., LISITSIN, V.N., RAZHEV, A.M., STARINSKY, V.N. - JETP Lett.19 (1974) 233

27. AULT, E.R., BHAUMIK, M.L., OLSEN, N.T. - IEEE J.Quant.Elect.10 (1974) 624

28. SEARLES, S.K., HART, G.A. - Appl.Phys.Lett.25 (1974) 79

29. NELSON, L.Y., MULLANEY, G.J., BYRON, S.R. - Appl.Phys.Lett.22 (1973) 79

30. For a review of UV gas lasers prior to 1974 see RHODES, C.K. - IEEE J.Quant.Elect.QE-10 (1974) 153

31. BRIDGES, W.B., CHESTER, A.N., HALSTED, A.S., PARKER, J.V. - Proc. IEEE 59 (1971) 724

32. WEBB, C.E. - 'The Fundamental Discharge Physics of Atomic Gas Lasers' in 'High Power Gas Lasers, 1975' Institute of Physics Conf.Series No.29, London (1976)

33. CW UV laser transitions have been observed in Cd^+ (SILFVAST, W.T. - Appl.Phys.Lett.15 (1969) 23), Ag^+ (McNEIL, J.R., JOHNSON, W.L., COLLINS, G.J., PERSSON, K.B. - Appl.Phys.Lett.29 (1976) 172), Cu^+ (McNEIL, J.R., COLLINS, G.J., PERSSON, K.B., FRANZEN, D.L. - Appl. Phys.Lett.28 (1976) 207), Al^+ (GERSTENBERGER, D.C., REID, R.D., COLLINS, G.J. - Appl.Phys.Lett.30 (1977) 466) and Au^+ (REID, R.D., McNEIL, J.R., COLLINS, G.J. - Appl.Phys.Lett.29 (1976) 666)

34. GREEN, J.M., WEBB. C.E. - J.Phys.B7, (1974) 1698

35. BASOV, N.G., DANILYCHEV, V.A., POPOV, Y.M. - Sov.J.Quant.Elect.1 (1971) 18

36. WERNER, C.W., GEORGE, E.V., HOFF, P.W., RHODES, C.K. - IEEE J.Quant. Elect.QE-13 (1977) 769

37. TURNER, C.E.Jnr. - Appl.Phys.Lett.31 (1977) 659

38. EWING, J.J. - 'Review of UV Excimer Lasers' SPIE 76 (1976) 132

39. LAIDLER, K.J. - 'Theories of Chemical Reaction Rates' McGraw-Hill, NY (1969)

40. At the rare gas pressures typical for laser conditions, strong radiative trapping makes all the low lying $np^5(n+1)s$ levels effectively metastable.

41. This process is proposed by analogy to the formation of the alkali halides eg. MANDL, A. - J.Chem.Phys.55 (1971) 2918

42. BATES, D.R., FLANNERY, M.R. - Proc.Roy.Soc.(London) A302 (1968) 367

43. ROKNI, M., JACOB, J.H., MANGANO. J.A., BROCHU, R. - Appl.Phys.Lett.31 (1977) 79

44. CHEN, H., CENTER, R.E., TRAINOR, D.W., FYFE, W.K. - J.Appl.Phys.48 (1977) 2297

45. By collisional 'quenching' of a level is meant its non-radiative decay induced by collisions. However, in relation to many measurements on the laser systems reported here, the collisional quenching rate of the upper laser level is a net rate which also includes the quenching of species that feed the level.

46. JACOB, J.H., ROKNI, M., MANGANO. J.A., BROCHU, R. - Appl.Phys.Lett.32 (1978) 109

47. EDEN, J.G., WAYNANT, R.W. - to be published in J.Chem.Phys. (1978)

48. MANGANO, J.A., JACOB, J.H., ROKNI, M., HAWRYLUK, A. - Appl.Phys.Lett. 31 (1977) 26

49. BRAUMIK, M.L. - 'New Approaches to High Power UV Visible Lasers' in 'High Power Gas Lasers, 1975' Institute of Phys.Conf.Series No.29, London (1976)

50. FEHSENFELD, S.C., SCHMELTEKOPF, A.L., GOLDEN, P.D., SHIFF, H.I., FERGUSON, E.E. - J.Chem.Phys.44 (1966) 408 and BOHME, D.K., ADAMS, N.G., MOSESMAN, M., DUNKIN, D.B., FERGUSON, E.E. - J.Chem.Phys.52 (1970) 5094

51. COLLINS, C.B., CARROLL, J.M., LEE, F.W., CUNNINGHAM, A.J. - Appl.Phys. Lett.28 (1976) 535

52. KRAUSE, H.F., JOHNSON, S.G., DATZL, S., SCHMIDT-BLEEK, F.K. - Chem. Phys.Lett.31 (1975) 577

53. McCUSKER, M.V., HILL, R.M., HUESTIS, D.L., LORENTS, D.C., GUTCHECK, R.A., NAKANO, H.H. - Appl.Phys.Lett.27 (1975) 363

54. HUESTIS, D.L., GUTCHECK, R.A., HILL, R.M., McCUSKER, M.V., LORENTS, D.C. - 'Studies in E-beam pumped Molecular Lasers' Report No. MP75-18 SRI International, Menlo Park, Ca. (1975)

55. LORENTS, D.C., HUESTIS, D.L. - 'Excimer and Energy Transfer Lasers', Proc. 2nd Int.Conf.on Laser Spectroscopy, Magèv, 23-27 June (1975) Pub. Springer-Verlag, NY (1975)

56. MURRAY, J.R., POWELL, H.T., RHODES, C.K. - 'The Oxygen Auroral Transition Laser System Excited by Collisional and Photolytic Energy Transfer' - ibid.

57. The Saturation Power is defined here as the intracavity laser power at which the rate of stimulated emission out of the upper laser level equals its combined rate of spontaneous radiative and non-radiative decay. Defined in this way, the saturation power is a useful concept when considering laser efficiency, and in an excimer molecule is identical to the saturation power as generally defined ie the power required to reduce the steady-state population inversion by a factor of two.

58. AULT, E.R., BRADFORD, R.S.Jnr., BHAUMIK, M.L. - Appl.Phys.Lett.27 (1975) 413

59. BHAUMIK, M.L., BRADFORD, R.S. Jnr., AULT, E.R. - Appl.Phys.Lett.28 (1976) 23

60. TISONE, G.C., HAYS, A.K., HOFFMAN, J.M. - Opt.Comm.15 (1975) 118

61. HSIA, J.C., JACOB, J.H., MANGANO, J.A., LOKNI, M. - 'One Metre KrF Laser System' Avco Everett Research Laboratory, Everett, Ma.USA, DARPA Order No.3125 (1978)

62. HAWRYLUK, A.M., MANGANO, J.A., JACOB, J.H. - Appl.Phys.Lett.31 (1977) 164

63. ROKNI, M., JACOB, J.H., MANGANO, J.A., BROCHU, R. - Appl.Phys.Lett.30 (1977) 458

64. LOREE, T.R. - Private communication to A.E. Greene and C.A. Brau

65. DUNNING, T.H., HAY, P.J. - Appl.Phys.Lett.28 (1976) 649

66. BURNHAM, R., SEARLES, S.K. - Paper AA-3 13th Annual Conf.Gaseous Electronics, Palo Alto Ca.USA (1977)

67. DUNNING, T.H., HAY, P.J. - 7th Winter Colloquium on High Power Visible Lasers, Park City, Utah USA (1977) unpublished.

68. BRADLEY, L.P. - 'Electron-beam Pumping of Visible and UV Gas Lasers' in 'High Power Gas Lasers, 1975' Institute of Physics Conf.Series No.29, London (1976)

69. It can readily be argued that direct two-body quenching of the upper laser level of an excimer by a rare gas atom will be negligibly small, and measured rates presumably correspond to the quenching of higher excited excimer states that would otherwise relax to the upper laser level.

70. ROKNI, M., JACOB, J.H., MANGANO, J.A., BROCHU, R. - Appl.Phys.Lett.32 (1978) 223

71. MAXWELL, H. - 7th Winter Colloquium on High Pressure Visible Lasers, Park City, Utah, USA (1977) unpublished.

72. CHAMPAGNE, L.F., EDEN, J.C., HARRIS, N.W., DJEU, N., SEARLES, S.K. - Appl.Phys.Lett.30 (1977) 160

73. WADT, W.R., CARTWRIGHT, D.C., COHEN, J.S. - Appl.Phys.Lett.31 (1977) 672

74. CHAMPAGNE, L.F., HARRIS, N.W. - Appl.Phys.Lett.31 (1977) 513

75. MANDL, A. - Phys.Rev.A3 (1971) 251

76. LA PAGLIA, S.R., DUNCAN, A.B.F. - J.Chem.Phys.34, (1961) 1003

77. GUTCHECK, R.A., HILL, R.M., HUESTIS, D.L., LORENTS, D.C., McCUSKER, M.V. - Report No.MP75-43 Stanford Research Institute, Menlo Park, Ca.USA (1975)

78. Earlier results claiming quasi-cw operation of the He-N_2 laser (ref.25) can alternatively by explained by a model in which 'bottle-necking' is indeed severe (ref.97)

79. Calculated from Eqn.(43) of Ref.68.

80. HAYS, A.K., HOFFMAN, J.M., TISONE, G.C. - Chem.Phys.Lett.39 (1976) 353

81. CHEN, O.H., PAYNE, M.G. - Appl.Phys.Lett.28 (1976) 219

82. In a pulsed glow discharge, it can readily be shown that the power density applied per molecule for a constant E/N scales as the pressure squared, and that using experimentally measured plasma parameters for a discharge KrF laser a minimum pressure of ~ 0.6 atm is required to achieve laser action. ROTHE, D.E., GIBSON, R.A. - Paper CA-7 13th Annual Conf.Gaseous Electronics, Palo Alto, Ca.USA (1977)

83. DOUGLAS-HAMILTON, D.H., MANI, S.A. - J.Appl.Phys.45 (1974) 4406

84. NIGHAN, W.L., WIEGAND, W.J. - Phys.Rev.A10, (1974) 922

85. WANG, C.P., MIRELS, H., SUTTON, D.C., SUCHARD, S.N. - Appl.Phys.Lett. 28 (1976) 326

86. WANG, C.P. - Appl.Phys.Lett.29 (1976) 103

87. GODARD, B., VANNIER, M. - Opt.Comm.18 (1976) 206

88. SARJEANT, W.J., ALCOCK, A.L., LEOPOLD, K.E. - Appl.Phys.Lett.30 (1977) 635

89. ROTHE, D.E., GIBSON, R.A. - Opt.Comm.22 (1977) 265

90. ANDREWS, A.J., KEARSLEY, A.J., WEBB, C.E., HAYDON, S.C. - Opt.Comm.20 (1977) 265

91. SARJEANT, W.J., ALCOCK, A.J., LEOPOLD, K.E. - IEEE J.Quant.Elect.QE-14 (1978) 177

92. GOWER, M.C. EXBERGER, R., ROWLEY, P.D., BILLMAN, K. - to be published

93. GREENE, A.E., BRAU, C.A. - J.Quant.Elect.(1978) to be published.

94. HSIA, J. - Appl.Phys.Lett.30 (1977) 101

95. ISHCHENKO, V.N., LISITSIN, V.N., RAZHEV, A.M., STARINSKII,V.N., CHAPOUVSKY, P.L. - Opt.Comm.13 (1975) 231

96. LAUDENSLAGER, J.B., PACALA, T.J., WITTIG, C. - Appl.Phys.Lett.29 (1976) 581

97. LITTLEWOOD, I.J. - Private communication.

98. ANDREWS, A.J., KEARSLEY, A.J., WEBB, C.E. - Private communication.

99. WANG, C.P. - Appl.Phys.Lett.32 (1978) 360

100. LACINA, W.B., COHN, D.B. - Appl.Phys.Lett.32 (1978) 106

101. JACOB, J.H., MANGANO, J.A. - Appl.Phys.Lett.28 (1976) 724

102. WEBB, C.E., - Private communication.

103. DOUGHERTY, J.D., MANGANO, J.A., JACOB, J.H. - Appl.Phys.Lett.28 (1976) 581

104. MURRAY, J.R., JOFFIN, P.W., - 'High Energy Lasers and their Applications' ed. S.F. Jacobs, M. Sargent III and M.O. Scully, Addison-Wesley, Reading, Ma.USA (1974)

105. FREEMAN, R.R., LIAO, P.F. - Paper JA-6, 13th Annual Conf.Gaseous Electronics, Palo Alto, Ca.USA (1977)

106. SEARLES, S.K. - Appl.Phys.Lett.28 (1976) 602

107. HILL, R.M., ECKSTROM, D.J., LORENTS, D.C., NAKANO, H.H. - Appl.Phys. Lett.23 (1973) 373

108. LORENTS, D.C., HUESTIS, D.L., McCUSKER, M.V., NAKONO, H.H., HILL, R.M. - 'Optical Emissions of Triatomic Rare Gas Halides', Report No. MP77-53R SRI International, Menlo Park, Ca.USA (1977)

109. WADT, W.R., HAY, P.J. - J.Chem.Phys. (1978) to be published.

110. HUESTIS, D.L., SCHLOTTER, N.E. - Paper AA-2, 13th Annual Conf.Gaseous Electronics, Palo Alto, Ca.USA (1977)

111. WADT, W.R., HAY, P.J. - Appl.Phys.Lett.30 (1977) 573

112. CHEN, C.H., PAYNE, M.G. - Appl.Phys.Lett.32 (1978) 358 and QUIGLEY, G.P., HUGHES, W.M. - Appl.Phys.Lett.32 (1978) 649

113. FOURNIER, G.R., McGEOCH, M.W. - J.Appl.Phys.49 (1978) 2651

114. The decay of excited rare gas atomic state fluorescence at high (~ 10 atm) pressures (see LORENTS, D.C. - Physica 82C (1976) 19) is nearly two orders of magnitude faster than the corresponding decay of mercury fluorescence at the same pressure (see GUTCHECK, R.A., HILL, R.M., HUESTIS, D.L., LORENTS, D.C., McCUSKER, M.V. - 'Studies of E-beam Pumped Molecular Lasers' SRI International, Menlo Park, Ca.USA (1972) November).

115. SCHLIE, L.A., GUENTHER, B.D., RATHGE, R.D. - Appl.Phys.Lett.28 (1976) 393

116. McGEOCH, M.W., FOURNIER, G.R. - J.Appl.Phys.49 (1978) 2659

117. McGEOCH, M.W., FOURNIER, G.R., EWART, P. - J.Phys.B 9 (1976) L121

118. DJEU, N., BURNHAM, R. - Appl.Phys.Lett.30 (1977) 473

119. Laser Focus, September 1977, 32

120. LETOKHOV, V.S. - Science 180 (1973) 451

121. DONOHUE, T. - Conf.on Chemical and Molecular Lasers, St.Louis, Miss.USA April 1977.

122. Laser Focus, September 1977, 24

123. For a comprehensive review see, for example, KARLOV, N.W., PROKOHOROV, A.M. - Sov.Phys.Usp.19 (1976) 285

124. O'HAIR, E.A., PILTCH, M.S. - SPIE 86 (1976) 147

125. GEORGE, E.V., KRUPKE, W.F. - SPIE 86 (1976) 140

126. JOHNSON, P.M., KELLER, N., TURNER, R.E. - Appl.Phys.Lett.32 (1978) 291

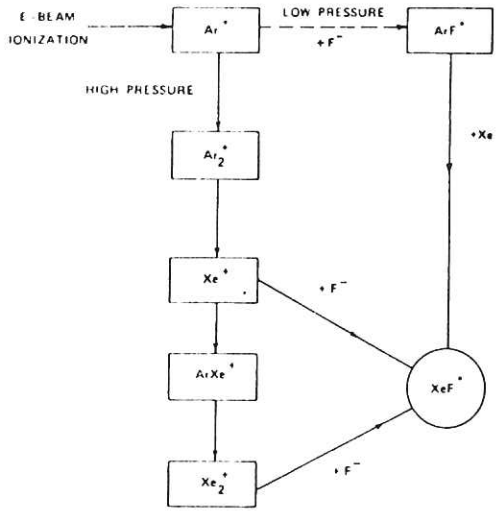

Fig. 1 Dominant XeF* formation processes in e-beam pumped $Ar/Xe/F_2$ mixtures.[70]

TABLE 1

THE NEW GENERATION OF UV/VISIBLE LASERS

Laser	Mean Operating Wavelength (nm)	Excitation*			Lower Laser Level
		E-beam	Discharge	E-beam/ Discharge	
Rare Gas Monohalides					
ArF	192	(1)	(2)	-	Dissociative
ArCl	175	-	(3)	-	"
KrF	248	(4)	(5)	(6)	"
KrCl	222	(7)	(3)	-	"
XeF	352	(8)	(9)	(10)	Bound
XeCl	308	(4)	(11)	-	"
XeBr	283	(12)	-	-	Dissociative
Rare Gas Oxides					
XeO	558	(13)	-	-	Bound
KrO		(13)	-	-	"
ArO		(13)			"
Halogen Dimers					
F_2	157	(14)	-	-	Bound
Br_2	292	(15)	-	(16)	"
I_2	342	(17),(18)	-	-	"
Mercury Monohalides					
HgCl	557	(19),(20)	-	(21)(22)	Bound
HgBr	502	(23)	-	(22)	"
Charge Transfer					
He-N_2	391,428	(24),(25)	(26)	-	Bound
Excitation Transfer					
Ar-N_2	358, 381	(27),(28)	-	(29)	Bound

* References given in parentheses

TABLE 2

PARAMETERS FOR THE RARE GAS MONOFLUORIDE LASERS

Parameter	KrF	XeF	ArF
Stimulated emission cross-section at line centre (σ_o cm^2)	$2.7.10^{-16}$ [62]	4.10^{-16} [63]	4.10^{-16} [64]
Radiative lifetime (τ_r ns)	7 [65]	15 [66]	4 [67]
Minimum saturation power (I_{sat}^{min} W/cm^{-2}) (= $h\nu/\sigma_o\tau_r$)	$4.2.10^5$	$9.4.10^4$	$6.5.10^5$
Quantum efficiency (η_Q)	.29	.23	.34
For a gain (α) of 0.02 cm^{-1}:			
Minimum excitation rate (R_{min} $cm^{-3}s^{-1}$) (=$\alpha/\sigma_o\tau_r$)	$1.1.10^{22}$	$8.3.10^{21}$	$1.3.10^{22}$
Minimum power density (P_{min} kW cm^{-3}) (= $h\nu R_{min}/\eta_Q$)	31	8.2	40

TABLE 3 Performance of some e-beam excited XeF, KrF and ArF lasers

Pump Configuration	Laser Pulse Characteristics E(joule)	τ (FWHM) ns	Laser Efficiency	Gas Pressure and Composition	Specific Energy Extraction (J/ℓ.atm)
Longitudinal	$KrF^{(1)}$ 108	57	η_l = 3%	F_2:Kr:Ar 1 25 325 1400 Torr	1.8
	$ArF^{(1)}$ 92	55	η_l = 3%	F_2:Ar 1 350 1400 Torr	1.5
	$XeF^{(1)}$ 35				
	$KrF^{(71)}$ 350*				
Coaxial,	$KrF^{(59)}$ 1.5	125	η_l = 15% η_0 = 1%	NF_3:Kr:Ar 1 130 1300 1700 Torr	6.7
	$XeF^{(58)}$ 0.08	100	η_l = 3%	NF_3:Xe:Ar 1 25 250 1300 Torr	0.5
Transverse	$XeF^{(72)}$ 0.3	1000	η_l = 0.5	NF_3:Xe:Ar 1 3 830 1900 Torr	0.3

* Largest energy reported for an excimer laser. No details available.

TABLE 4 PERFORMANCE OF SOME DISCHARGE EXCITED XeF, KrF AND ArF LASERS

Pump Configuration	Laser	Pulse Characteristics E(Joule)	Pulse Characteristics τ(FWHM)ns	Laser Efficiency	Gas Pressure and Composition	Specific Energy Extraction (J/ℓ.atm)	PRF(Hz)
Fast Discharge	$XeF^{(87)}$	0.017	6	η_o= 1%	NF_3 : Xe : He 1 4 100 500 Torr	11.6	100
	$KrF^{(87)}$	0.004	4	η_o= 0.4%	NF_3 : Kr : He 0.2 10 100 800 Torr	1.8	100
UV Preionized	$XeF^{(88)}$	0.29	20	-	NF_3 : Xe : He 1 3 2700 3600 Torr	0.34	~ 0.1
	$KrF^{(91)}$	0.61	20	η_o= 0.5%	F_2 : Kr : He 1 18 1500 4560 Torr	0.56	
	$ArF^{(91)}$	0.35	8	-	F_2: Ar : He 1 10 370 4560 Torr	0.32	
UV Preionized	$ArF^{(98)}$	0.33	15	η_o = 0.75%	F_2 : Ar : He 6 125 2170 2300 Torr	1.4	≲ 2
	$KrF^{(98)}$	0.36	15	η_o = 0.8%	F_2 : Kr : He 5 20 2275 2300 Torr	1.5	
	$XeF^{(98)}$	0.16	15	η_o = 0.35%	F_2 : Xe ; He 5 7 2290 2300 Torr	0.67	
UV Preionized, Fast Flow	$XeF^{(99)}$	0.003	60	η_o = 0.25%	NF_3 : Xe : He 5 15 1000 650 Torr	0.29	500