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THE EFFECTS OF CHEMICAL KINETICS AND STARTING MATERIAL REGENERATION
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ABSTRACT

A model of the chemical kinetics occurring in an iodine laser amplifier is presented and used to calculate the degree to which the starting material is consumed as a result of laser operation. The cost of purchasing new starting material is estimated and shown to be prohibitive. A scheme for regenerating the starting material from the species present in the amplifier after lasing is proposed. It is shown that the estimated efficiency of this chemical regeneration process is appreciably higher than the projected optimum efficiency of the pumping process.

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Section I

Introduction

The iodine laser is currently under consideration as a candidate for laser fusion applications. If this laser is to prove attractive, it must be shown to be capable of efficient operation in addition to having suitable optical output. This report discusses the role chemical reactions play in determining the overall efficiency of an iodine laser amplifier. Section II presents a simple model for predicting the performance of an iodine amplifier. The model is used to calculate the consumption of chemical starting material associated with amplifier operation. A simple treatment is given to show that replacement of the consumed chemicals through purchase of more starting material is an unattractive option. Section III presents a scheme for regenerating the starting material from the end products of amplifier operation. The energy expended in the regeneration process is estimated to be a minor component of the total energy required to operate an amplifier.

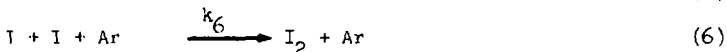
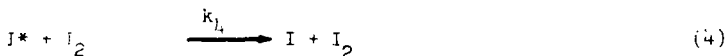
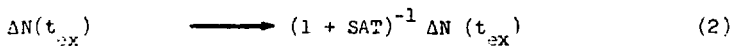
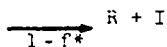
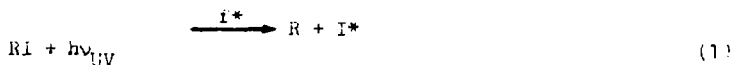
Section II

Predicted Amplifier Performance

The iodine laser operates on the $5^2P_{1/2} - 5^2P_{3/2}$ transition of the iodine atom. Excited atoms are produced by near ultraviolet photolysis of iodine bearing compounds, RI. Typically, the R group is C_nF_{2n+1} , that is, a perfluoroalkyl radical. These species are chosen because they yield on photolysis a large value of f^* , the fractional atomic excited state population, and because the collisional deactivation of the excited atoms I^* by R is slow. The working medium of a typical iodine laser amplifier¹ is a mixture of RI highly diluted in argon. The argon serves

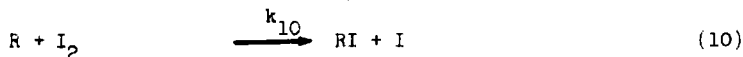
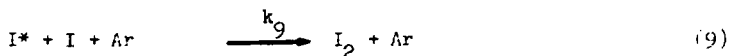
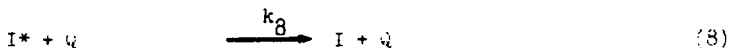
to pressure broaden the lasing transition and to minimize the temperature rise resulting from the absorption of the pumping radiation. Reference 2 summarizes much of the physics and chemistry of the iodine laser.

When pure RI is subjected to intense, unfiltered ultraviolet radiation from a high current flashlamp, a complicated mixture of reaction products is obtained.³ Use of a filter which blocks wavelengths less than 220 nm eliminates many undesirable effects of photolysis,⁴ and dilution of RI with Ar eliminates the pyrolytic decomposition of RI.² Only when the temperature of the working medium exceeds about 900°K are products other than RI, R₂, I₂ and buffer gas (if used) found in the working medium after photolysis.⁵ The temperature in the amplifier of the Sandia atomic iodine laser, SAII-1, does not exceed 400°K, and filters blocking short wavelengths are used. Thus, only a fairly simple set of chemical reactions needs to be considered. The amplifier model treated here is based on the following processes:



Process (1) represents the ultraviolet photolysis of the starting material RI. The photolysis pulse is of the form $I (t/\tau)^N e^{-t/\tau}$ where I governs the irradiation intensity, and N and τ are chosen to give the desired

pulse shape. A fraction f^* of the photolytically produced iodine atoms appears in the excited state. Reference 2 tabulates f^* for most of the compounds for which it has been determined experimentally. Process (1) represents the extraction of optical energy from the amplifier by a very short input pulse occurring at the time t_{ex} . For the cases discussed here $t_{ex} = 2 \Delta t_{pump}$, where the latter quantity is the temporal full-width-at-half-maximum intensity of the photolysis pulse. It is assumed that energy is extracted from both upper hyperfine levels with equal efficiency, governed by the parameter SAT. Processes (3) through (7) embody the kinetics considered here. The rate constants k_4 and k_6 are well known and are $k_4 = 3.6 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$,⁶ $k_6 = 6.7 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$.⁷ A survey of the literature⁸ indicates that k_3 , k_5 , and k_{RR} are well determined for at most only a few R groups. For the calculations reported here the following values were assumed: $k_5 = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, $k_3 = 1.5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$; k_{RR} is a variable parameter. The value of k_{RR} for a given R group is chosen by reference to the literature or by reasonable extrapolation. Processes (1) - (7) encompass most of those currently thought to be important in an iodine amplifier.² Calculations were performed for more extensive sets of kinetic processes by including



and by allowing k_3 , k_5 , and k_{10} to change as k_{RR} was varied. In (8) Q is a species in the working medium which quenches excited iodine atoms. Calculations utilizing expanded sets of kinetic processes gave results qualitatively similar to those reported here. These calculations did not

however fit the data on loss of RI associated with laser operation, reported by Fuss and Hohla,⁹ as well as those based on (1) - (7) only.

Figure 1 illustrates typical results obtained by numerical integration of the differential equations appropriate to the model discussed above, considering only (1) - (7). The quantity M, the number of molecules of RI consumed per laser output photon (or twice the number of R₂ or I₂ molecules thus formed), is plotted as a function of k_{RR} for three values of Δt_{pump} . There is a significant dependence of M on Δt_{pump} for $\Delta t_{\text{pump}} \approx 1 \mu\text{sec}$ because in this regime appreciable R - R association can occur during pumping if a long photolysis pulse is used. Labeled dots on the $\Delta t_{\text{pump}} = 1 \mu\text{sec}$ curve identify the estimated values of k_{RR} for several compounds of interest. M depends strongly on k_{RR} , but can be constrained to $M < 0.1$ for any photolysis pulse width considered if $k_{RR} \leq 4 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$.

Any RI consumed during laser operation must be replaced; if replacement is through purchase of additional RI, the following argument indicates that the replacement cost is not economically attractive. The current cost of C₃F₇I is about \$200 per mole in 10 kg lots; for simplicity this price is also assumed for t-C₄F₉I. Using the values of M displayed in Fig. 1 for $\Delta t_{\text{pump}} = 1 \mu\text{sec}$, the costs of replacing the RI lost in the generation of 1 kJ iodine laser output are: t-C₄F₉I, \$0.13; i-C₃F₇I, \$0.40; n-C₃F₇I, \$1.06. If an overall electrical efficiency of 1% is assumed for the laser and if the cost of electricity is \$0.01 per MJ, then the cost of the electricity required for 1 kJ of laser output is \$0.001. It is clear that chemical replacement cost strongly dominates electrical energy cost and would continue to do so even if chemical prices were reduced by a large factor.

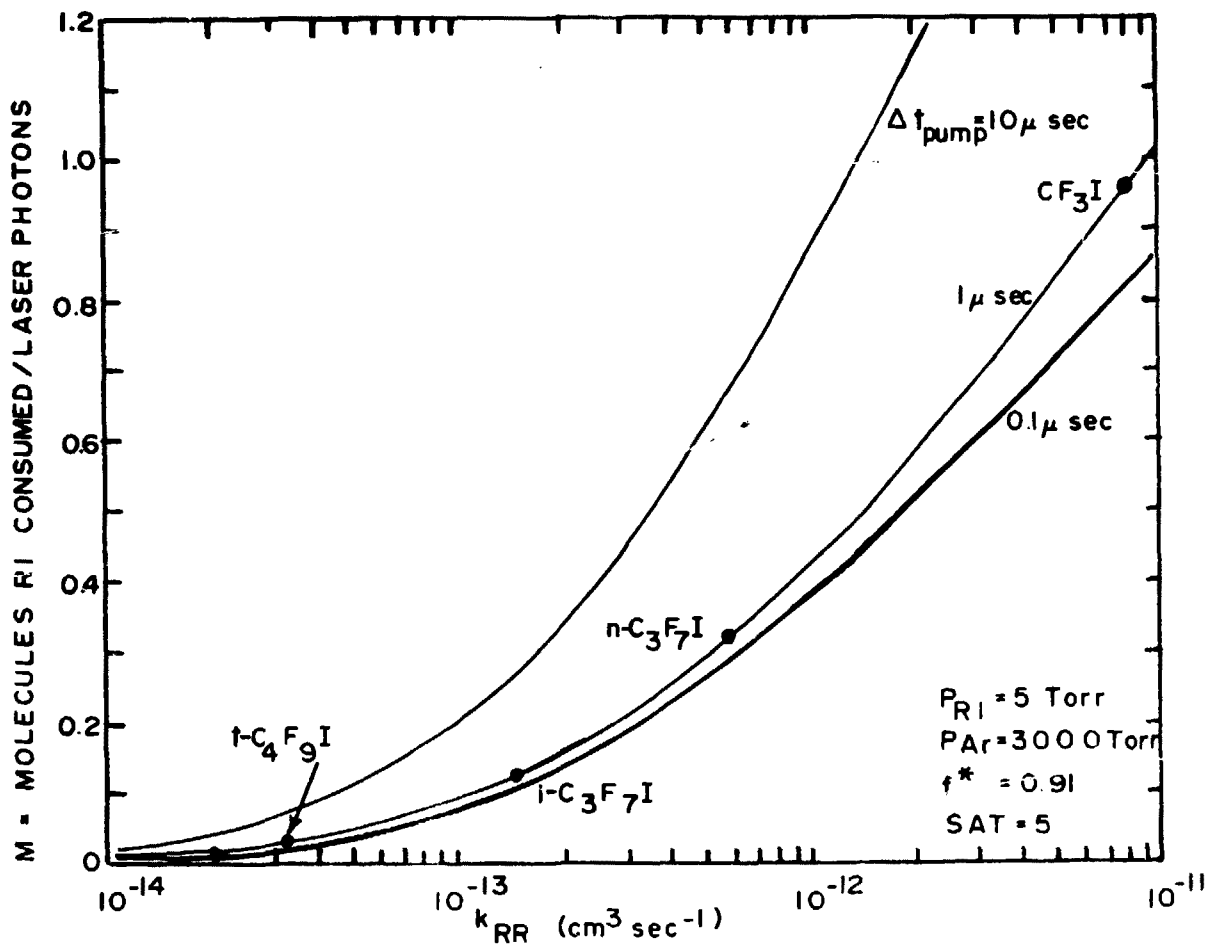
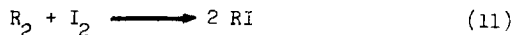


Figure 1 Effects of radical-radical association rate constant and photolysis pulse width (PAPM) on consumption of starting material in an iodine laser amplifier. Labeled dots identify estimated values of k_{RR} for several compounds of interest.

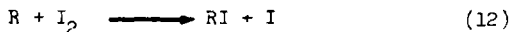
Section III

Chemical Regeneration Scheme

This section discusses two variants of a scheme for regenerating RI from R_2 and I_2 and estimates the efficiency of the regeneration process. Schemes for regenerating RI from species other than R_2 and I_2 are not discussed because, as was indicated in Section II, such species are not formed under typical amplifier operating conditions. The dissociation energies of C-C, I-I, and C-I bonds are 3.60 eV, 1.6 eV, and 2.4 eV, respectively. Thus the minimum energy expenditure for the process



is about 0.2 eV per molecule of RI produced. Unfortunately, no scheme for carrying out (11) with an energy expenditure approaching this minimum value has ever been devised. The difficulty in devising efficient schemes for carrying out (11) arises from the fact that R_2 is a per-fluoroalkane and these species are exceptionally stable, exhibiting virtually no chemical reactions. It presently appears that in order for (11) to proceed it is necessary to break the C-C bond uniting the two R groups. The reaction



will then proceed spontaneously.¹⁰ If the required C-C bond cleavage can be performed selectively, chemical regeneration can be made relatively efficient. If a nonselective technique such as pyrolysis is used to

break C-C bonds,¹¹ the overall efficiency of the regeneration process will be appreciably lower.

One conceptually simple scheme for carrying out (11) is the following two step process: Multiple photon dissociation of R_2 , followed by reaction of R with I_2 as described by (12). Specifically, a mixture of R_2 in an excess of I_2 is irradiated with an intense infrared laser pulse. During the pulse an individual R_2 absorbs enough photons that it can decompose unimolecularly. The overall pressure of the mixture is adjusted to such a value that, for the R_2 excitation level under consideration, decomposition through C-C bond breakage occurs on the average before the occurrence of collisions which might deactivate the excited R_2 . The R fragments then react with I_2 to form RI. This reaction occurs after the laser pulse is over, thus the RI formed will not be excited or decomposed by irradiation.

The calculations required to estimate the excitation energy required for a given R_2 unimolecular dissociation rate can be carried out easily under the assumption that excitation energy is randomly distributed in the R_2 molecule. RRKM theory yields the approximate relation:¹²

$$k_{C-C}^{uni}(\text{sec}^{-1}) = \nu_{vib} \left(\frac{\epsilon_{C-C}}{\epsilon_{C-C} + E_{C-C}} \right)^n \quad (13)$$

where k_{C-C}^{uni} is the dissociation rate through the desired C-C bond cleavage, ν_{vib} is an average molecular vibrational frequency, ϵ is the total internal energy in excess of the C-C bond energy E_{C-C} , and n may be taken to be the total number of vibrations in the molecule. (See Reference 12 for a more exact but only slightly different definition of n .)

The difference is inconsequential here.) The quantity ϵ_{C-C} is related to other energies by

$$\epsilon_{C-C} = E_{IR} + E_{thermal} - D_{C-C} \quad (14)$$

where E_{IR} is the amount of energy absorbed by a molecule from the infrared laser beam and $E_{thermal}$ is the average thermal excitation.

The expression for k_{uni}^{C-F} is analogous to (13) except that the C-F bond dissociation energy $D_{C-F}^{C-F} = 5.0$ eV, must be substituted for D_{C-C} , and the overall expression must be multiplied by the number of C-F bonds in R_2 .

Figure 2 displays calculated values of k_{uni}^{C-F} for the irradiation of C_2F_6 at an initial temperature of $300^\circ K$. The value of ν_{vib} was assumed to be $3 \times 10^{13} \text{ sec}^{-1}$. If the regeneration process is carried out at a total pressure on the order of 1 torr, k_{uni}^{C-F} must be of the order 10^6 sec^{-1} for C_2F_6 to dissociate to $2CF_3$ before any deactivating collisions occur. This requires that $E_{IR} \approx 5.7$ eV, and at this level of excitation $k_{C-C}^{uni} / k_{C-F}^{uni} > 10^7$. In general, the amount of energy which must be absorbed by R_2 molecules to regenerate the laser mixture is, per photon of laser carrier

$$E_R = M E'_{IR} / 2 \quad (15)$$

where M is discussed in Section II and E'_{IR} is the absorbed energy yielding the desired k_{C-C}^{uni} . For an amplifier using CF_3I and having $\Delta t_{pump} = 1 \mu\text{sec}$, the requirement $k_{C-C}^{uni} = 10^6$ yields $E_R = 2.7$ eV. The corresponding energies for operation with $n-C_3F_7I$, $i-C_3F_7I$, and $t-C_4F_9I$ are 2.1 eV, 0.77 eV and 0.33 eV, respectively. For comparison, the energy of an iodine laser photon is 0.94 eV. It must be mentioned that the regeneration scheme described here may not be appropriate for molecules such as C_6F_{14} or C_8F_{18} . The reason is that the required energies E'_{IR} are so high that C-C bonds other

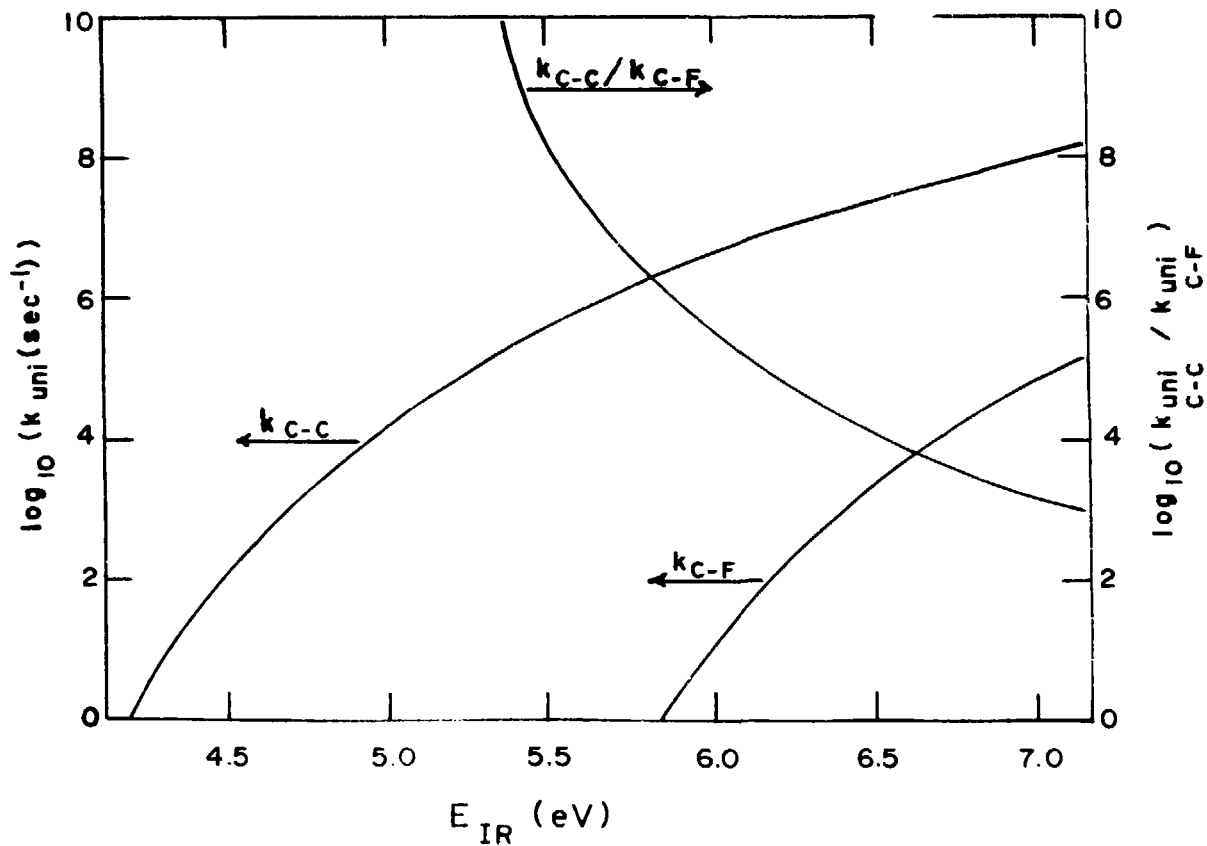


Figure 2 Dependence of unimolecular decomposition rate in C-C and C-F channels on infrared energy for the case of $^{12}C_2F_4$ irradiated at an initial temperature of 400 K.

than the one joining the two K groups may break at a rate comparable to the decay rate in the desired channel. The C-C bond joining two $i-C_2F_7$ or two $i-C_4F_9$ groups is expected to be the weakest bond in an K_2 molecule, but a quantitative determination of the difference between its strength and that of the other C-C bonds is not available. The difference may not be large enough to insure that the desired C-C cleavage occurs with nearly unit probability unless ϵ in (13) is small. A regeneration process with small ϵ is described below.

The pulsed laser scheme described above is analogous to dissociation schemes proposed for SF_6 ¹⁴ and other molecules^{14,15} for several years. It relies on the absorption of sufficient infrared quanta during a single laser pulse that decomposition occurs before collisional deactivation. The requirement of rapid dissociation leads to large ϵ . Recently the decomposition of ethane samples placed in the output beam of a CW CO_2 laser has been reported.¹⁶ Ethane does not absorb CO_2 radiation at 10.6 μm , and decomposition occurred only when SF_6 and C_2H_6 were mixed. No decomposition of SF_6 was observed. The experiment is not yet well enough understood that the detailed kinetics can be interpreted, but absorption of radiation by SF_6 will be considered below as a model for C_2H_6 since ϵ is small. The fact that the experiment is carried out in a CW rather than in a pulsed mode of operation removes the requirement of rapid unimolecular decay and allows for the possibility of small ϵ . Reference 16 reports that the absorbed energy per molecule of C_2H_6 decomposed was 3.8 eV under the best attainable experimental conditions and predicts that lower values would be obtained with higher power CO_2 laser excitation. $D_{C-C} = 3.6$ eV; thus, the above remarks and reference to (14) indicate that the CW decomposition scheme can indeed be used to dissociate molecules under conditions for which ϵ is small and selectivity is maintained.

There appears to be no reason why the technique discussed above should work only for C_2H_6 . C_2F_6 and other R_2 molecules have energy levels lying close to the appropriate levels in SF_6 and V-V energy transfer from SF_6 to R_2 should be an efficient process. Chemical regeneration using the energy transfer scheme could be carried out as follows. A mixture of SF_6 and R_2 diluted in Ar is flowed through the output beam of a CW CO_2 laser, resulting in dissociation of R_2 to $2R$. Immediately downstream of the excitation region I_2 is mixed into the stream to allow the regeneration of RI . The relation (15) may still be used to calculate E_R , but now $E'_{IR} \approx D_{C-C}$ for all species R_2 . This means that the CW regeneration process would be appreciably more efficient than the pulsed one.

It is now possible to estimate the efficiency of the chemical regeneration process, and to compare it to the estimated efficiency of the pumping process. Consider a figure of merit η , customarily called the efficiency, defined for closed loop amplifier performance as

$$\eta = \frac{\text{extracted laser energy}}{\text{total input energy}} \quad (16)$$

If several operational steps are involved, and η_i for step i is defined in a manner analogous to (16), then

$$\eta^{-1} = \sum_i \eta_i^{-1} \quad (17)$$

Only the pumping (electrical) figure of merit η_p and the chemical regeneration figure of merit η_R will be considered here. The value of η_R is related to E_R defined in (15) by

$$\eta_R = \frac{0.94 \eta_L \phi}{E_R (eV)} \quad (18)$$

where 0.94 eV is the energy of an iodine laser photon, η_L is the overall figure of merit of the infrared laser used in the regeneration process, and ϕ is the fraction of the infrared photons actually utilized. For purposes of evaluating η_R , it is assumed that the infrared laser used is a CO_2 laser (typical R_2 species absorb in the region of the CO_2 laser output¹⁷). The value of η_L is assumed to be 0.2. This value can be attained in either pulsed^{18,19} or CW²⁰ operation. The best current estimate of ϕ for pulsed experiments is 0.5; the data in reference 16 indicate that $\phi \approx 1$ for carefully conducted CW experiments. The numbers for η_L and ϕ given here together with values cited earlier for E_R and the information contained in Fig. 1 are used to construct Table 1.

TABLE 1

Tabulation of estimated figures of merit η_R for pulsed and CW Chemical regeneration processes. Assumed value of Δt_{pump} is 1 μ sec.

RI	Pulsed		CW	
	E_R (eV)	η_R	E_R (eV)	η_R
CF_3I	2.7	0.03	1.7	0.11
i- C_3F_7I	0.77	0.12	0.22	0.86
t- C_4F_9I	0.33	0.29	0.07	2.6

The data in Table 1 apply only for $\Delta t_{\text{pump}} = 1 \mu$ sec. Values of η_R for other photolysis pulse widths may be determined by using the appropriate data in Fig. 1. Values of η_R are given for both pulsed

and CW regeneration processes for comparison purposes, but the reservations expressed earlier concerning the use of the pulsed technique with large molecules should be remembered. The CW process is more efficient than the pulsed one by a factor that increases with increasing size of the RI molecule. The reason for this can be seen by inspecting (13). For a given value of k_{uni} , ϵ increases with n . Only when a low value of k_{uni} is acceptable can the dissociation process proceed with small ϵ , more or less independent of n . There is, of course, a lower limit on the value of k_{uni} which is acceptable in a given experiment, and actual values of η_R for large molecules regenerated in a CW process consequently may be smaller than those reported in Table 1.

Based on the foregoing material, it seems reasonable to predict that a chemical regeneration process with $\eta_R \approx 0.1-0.2$ can be found. It is instructive to compare this estimate to the expected pumping efficiency η_P . In the case of photolysis using conventional flashlamps, η_P is the ratio of energy extracted from the amplifier to energy stored in the flashlamp capacitor bank. It has been estimated²¹ that with conventional flashlamp pumping the maximum attainable electrical efficiency is $\eta_P \approx 0.01$. Experimentally determined efficiencies²²⁻²⁴ are a factor of two or more lower than this estimate. When estimated values of η_R and η_P are compared and considered in terms of (17), it is clear that the overall figure of merit for an iodine laser should not be strongly influenced by the requirement of chemical regeneration, if conventional flashlamp pumping is used. A much more efficient pump source would have to be found before η_R could become the limiting term in the overall operational figure of merit, if the above regeneration scheme is in fact successful.

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