HIGH-ENERGY VISIBLE AND ULTRAVIOLET LASERS

STANFORD RESEARCH INSTITUTE

PREPARED FOR
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

MARCH 1975

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: JSR-74-1

2. GOVT ACCESSION NO.:

3. RECIPIENT'S CATALOG NUMBER: AD-A009227

4. TITLE (and Subtitle): HIGH-ENERGY VISIBLE AND ULTRAVIOLET LASERS

5. TYPE OF REPORT & PERIOD COVERED: Technical Report JSR-74-1

6. PERFORMING ORG. REPORT NUMBER: SRI Project 3000

7. AUTHOR(s): Compiled from contributions by: C. G. Callan, Jr., R. L. Carman, J. I. Katz, P. L. Kelley, N. M. Kroll, D. C. Lorents, C. B. Moore, R. Novick, C. K. Rhodes

8. CONTRACT OR GRANT NUMBER(s): Contract DAHC15-73-C-0370

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Stanford Research Institute, Menlo Park, California 94025

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

11. CONTROLLING OFFICE NAME AND ADDRESS: Defense Advanced Research Projects Agency, 1400 Wilson Boulevard, Arlington, Virginia 22209

12. REPORT DATE: March 1975

13. NO. OF PAGES: 114

14. MONITORING AGENCY NAME & ADDRESS (if diff. from Controlling Office):

15. SECURITY CLASS. (of this report): UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

High-energy lasers
Visible and UV
Energy transfer
Chemical energy
Isotope separation
X-ray lasers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This study evaluated the scientific issues relevant to the development of visible or near-UV high-energy lasers. It is concluded that such lasers can be developed and that they will have applications of considerable consequence to the DoD. It is concluded that the basic knowledge required to design such lasers is lacking and this is impeding their development. It is recommended that a well coordinated and substantial research effort in selected areas of atomic and molecular physics be initiated to provide the needed data base. The relevant technical areas have been identified and specific recommendations were made.

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PREFACE

The participating members of the 1974 JASON summer study on High-Energy Visible and Ultraviolet Lasers are as follows:

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I SUMMARY[†]

In this study an evaluation was made of promising current and proposed research efforts directed at realizing high-energy lasers in the visible and UV spectral regions as well as certain other related areas such as X-ray generation, photochemistry, and isotope separation. The major objective of this study has been the appraisal of the scientific issues relevant to the development of high-energy lasers (HELs) operating on electronic transitions in the visible and near-UV portion of the spectrum. It became clear during this effort that the realization of these goals depends strongly on, and is limited by, a body of knowledge concerning atomic and molecular phenomena that is currently not available. The relevant area of concern can be broadly classified in the category of the physics and chemistry of electronically excited atoms and molecules. It is an area that has received insufficient attention in the past, but for which the tools of research either are available or are rapidly being developed. Therefore, it is our general conclusion that strong emphasis should be given to this area of research in the immediate future to serve as a technically sound, efficient and economical means of establishing the data base directly applicable to the ultimate goal of a visible HEL.

A major result of this study is the realization of the enormous impact that certain areas of atomic and molecular physics can have on the effort to develop an HEL. The specific topics that need to be addressed, together with the recommended research effort and priority, are listed in Table 1. Given an adequate data base it should be possible to successfully

[†]This section was prepared by D. Lorents and C. Rhodes.

Table 1

RECOMMENDED ANNUAL RESEARCH EFFORT AND PRIORITIES

Technical Area	Priority	Number of Personnel	Discussion (Report Section Number)	Conclusions (Report Section Number)
Excimer collisional and radiative transfer	1	20	III-A-1	IV-A
Triatomic structure	1	10	III-A-1	IV-B
Vibrational-to-electronic energy transfer	1	10	III-A-2-a-2	IV-C
Chemiluminescence (theory and experiment)	1	15	III-A-2-a-1	IV-D
Exothermic decomposition	1	10	III-A-2-a-3	IV-F
Nonlinear multiquantum processes	2	5	III-A-5	IV-G
Collisionally stimulated emission	2	5	III-A-1-d	IV-H

design large-scale HELs in a manner historically similar to the development of the CO_2 laser. The time scale for this development is estimated at 5 to 10 years. In order to minimize the time and cost expended, it is essential that the program operate as a cohesive, integrated and well planned effort designed to meet the objectives. The establishment of an organized laser program centered around reputable and well established atomic physics and laser technology groups should be seriously considered.

The main conclusions and recommendations of this study concerning the development of the HEL can be summarized as follows:

(1) There appears to exist little doubt that high-energy lasers operating in the visible or near-ultraviolet regions at

acceptable efficiencies will be developed once the pertinent atomic and molecular data are available.

(2) The time scale under which the required developments occur can be substantially reduced by increased and sustained effort on research in certain well defined areas of physics and chemistry. It is estimated that the time period of this development can be decreased by a factor of 2 with a coordinated program of sufficient scope.

(3) The relevant technical areas have been identified and are listed in Table 1, along with an assignment of priorities and an estimate of the minimum manpower required.

(4) The minimum scale of the total effort to achieve the objective of visible and near-ultraviolet high-energy laser development is estimated at a program of between $5 and $10 million per year for 5 to 10 years.

(5) A unified program of this nature should be initiated that addresses both DoD and AEC needs, and the bulk of this effort should be located at an appropriate major scientific institute.

Conclusions pertaining to X-ray generation, photochemistry and isotope separation, and free electron lasers are included in Sections V-E, V-I, and V-J respectively.

II INTRODUCTION†

In the 1971 JASON Summer Study on lasers, the broad aspects of laser applications and research were examined and a number of recommendations formulated. In the current study the focus was narrowed to an evaluation of current and proposed research directed at realizing high-energy lasers in the visible and ultraviolet spectral regions as well as certain related applications including X-ray generation, photochemistry, and isotope separation.

In the last two to three years the need for high-energy lasers in certain applications has come into much clearer focus. This is particularly true in the case of the laser-induced fusion, DoD applications, and isotope-separation areas. These applications in themselves will have a tremendous impact on the nation's energy supply in both the mid- and long-term future and are sufficient justification for a substantial effort to develop the required lasers. Obviously, these particular applications have substantial impact on military problems as well and are sufficient reason for DoD participation in the effort. In particular, it would appear that the rapid developments now occurring in the laser isotope-separation field may have significant military implications within a few years. In addition to these important areas there are potentially very significant applications of HELs in the weapons area, in the simulation of weapons effects, in X-ray lasers, in optical radar and communications, and in photochemical processing. These various applications require HELs operating at a variety of wavelengths from the IR through the visible and into the UV portion of the spectrum.

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†This section was prepared by D. Lorents.

The currently available and developing HELs are all in the IR region of the spectrum. Of these, the neodymium glass lasers have been most extensively developed and are being used for initial scaled-up pellet implosion experiments. Other laser media with demonstrated HEL promise are the CO_2 system at 10.6 μ, the I laser at 1.315 μ, the CO at 5 μ, and the HF at 2.7 μ. The salient characteristics of these lasers are listed in Table 2.

Table 2

LASERS FOR FUSION

Property	CO_2	Nd:Solid	I	CO	HF
Wavelength	10.6 μ	1.06 μ	1.32 μ	5 μ	2.5 μ
Efficiency	5%	0.1%	0.5%	50%	3.3% chemical 180% electrical
Energy density	15 J/ℓ (3 atm)	500 J/ℓ	30 J/ℓ	100 J/ℓ (100 Torr)	96 J/ℓ
Small-signal gain	0.045- 0.055 cm^{-1}	0.04- 0.08 cm^{-1}			
Pulsewidth	≥ 1 ns	≥ 20 ps	0.6 ns		
Demonstrated energy output	200 J (1 ns)	350 J (1 ns)	15 J (1 ns)	200 J (100 μs)	2.3 kJ (35 ns) 0.8 kJ (6 ns)
Scalability	Partially defined	Defined to 10^4 J			
Wavelength conversion	Not demonstrated	0.26% 1.9 μ (≥ 40% eff)	Similar to Nd:glass		
Average power capability	High (flow)	Very low	High (flow)	High (flow)	High

At the present time no HELs have been demonstrated for the visible or UV portion of the spectrum, and studies of the viable candidate media are just beginning. Nevertheless, it is the committee's view that such devices will be developed and will be capable of operation at reasonable efficiencies. It is equally clear that the pace of this development can be accelerated by an intelligently constructed research program designed to impact the critical scientific areas. This report is devoted to an identification and appraisal of the technical areas relevant to high-energy laser development.

One can list the general desired characteristics of HELs for various applications in the higher-frequency range, and these parameters are presented in Table 3. The implications that each of these criteria have for the characteristics of the laser medium are indicated in Table 4. Thus, one has a logical set of criteria against which to screen various candidate laser media in the search for practical HELs. The application of these screening criteria narrows the candidate field considerably, but is limited in many cases by an insufficient store of important fundamental information. Indeed, it would appear that one of the major tasks associated with the discovery and development of large-scale HELs is the improvement of the relevant data base of atomic and molecular physics.

Because of the magnitude of the engineering problems associated with multi-kilojoule lasers, it is essential that the basic design parameters be as well established as possible before any large-scale systems are designed. In the current state of knowledge, it is clear that an appropriate research effort should be directed at well coordinated efforts to obtain systematic analysis of promising candidate systems and thereby provide enough of the atomic and molecular physics of these systems to determine the scaling characteristics. In the case of the IR lasers, such as CO_2, this approach has been most successful.

Table 3

LASER PARAMETERS

Parameter	Desired Ranges
Wavelength (λ)	3000 $\mathring{A}$ - 10 μ
Energy (J)	10^5 - 10^6
Energy storage (kJ/liter)	0.1 - 1.0
Efficiency (η)	> 10%
Beam quality	~ Diffraction-limited
Pulse length (s)	1 - 10^{-10}

Table 4

IMPLICATIONS OF LASER CRITERIA

Average Power System	Peak Power System
Electronic and vibrational transitions	Electronic transition
$\Delta n^{\dagger} \geq 10^{17}$ cm^{-3}	$\Delta n^{\dagger} \geq 10^{17}$ cm^{3}
Gas (flow)	Gas (flow)
Allowed or forbidden transition	"Forbidden" transition
	$\sigma \sim 10^{-20}$ cm^2
Spectroscopic structure (atoms/molecule)	Sprectroscopic structure (atoms)

$^{\dagger}\Delta n$ = inversion density

Technically, we have formulated recommendations of specific theoretical and experimental areas that are likely to have the greatest impact on high-energy laser development as well as the related areas of isotope separation and X-ray lasers. These recommendations include priority assignments and manpower assessments that constitute an estimate of a total program addressing this area.

III TECHNICAL TOPICS

A. High-Energy Lasers

1. Electronic Energy Transfer and Collisional Systems†

a. General

Any high-peak-power visible or ultraviolet laser system involves the generation of substantial inverted energy density stored in the appropriate electronic states. Clearly all possible excited electronic states are not equally suitable; certain classes of electronically excited systems will obviously have preferred properties. Furthermore, the detailed nature of the required system will be dependent on several factors, including (1) the desired wavelength, (2) the stimulated emission cross-section, and (3) the time scale available to provide the excitation. Within the context of a given application, classes of eligible systems can be identified. Once their identity has been established it remains to explore and evaluate methods of excitation. In the discussion below, we examine the considerations relevant to these issues and state the conclusions derived by this analysis. In this way we are able to pinpoint various critical areas impacting high-power laser developments and to formulate recommendations based on these findings. Gas laser systems are stressed, because these seem most suitable for high-average-power applications.

Laser systems involve both the generation of excited species and the radiative properties of the inverted state population. We observe

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† This section was prepared by D. Lorents and C. Rhodes.

that collisional phenomena generally have a strong influence on both these processes and provide us with important mechanisms to control the properties (e.g., energy density, wavelength, lifetime, and cross section) of the laser system. It is these processes that we wish to emphasize.

We note the following important point concerning the status of our present technological position. The rare gas excimers (e.g., Xe_2^* and Kr_2^*) have the unique property of being able to <u>efficiently</u> convert energy deposited by an electron beam into energy stored in an electronically excited manifold of states. An example of this energy flow is given in Figure 1, which illustrates the energy pathways in xenon. The ionized and excited material is channeled directly into the $^1\Sigma_u^+$ and $^3\Sigma_u^+$ levels. Furthermore, the dynamics are such that the energy resides in a band of states with a Q of approximately 10. Thus, we have a convenient mechanism for efficiently channeling broadband energy into a relatively narrow band of electronic states. It is now reasonable to consider <u>selective</u> processes of energy transfer, either radiatively or collisionally, to an appropriate acceptor system that has the desired collisional and radiative properties. These mechanisms are explored below.

b. <u>Photolytic Energy Transfer</u>

General processes such as

$$\gamma + a \rightarrow a^* \quad \text{(direct)} \tag{1}$$

or

$$\gamma + ab \rightarrow a^* + b \quad \text{(dissociative)} \tag{2}$$

can efficiently couple radiative energy for the production of the appropriate class of excited species a^* (see Murray and Rhodes, 1973,[†]

[†] References are listed at the end of the report.

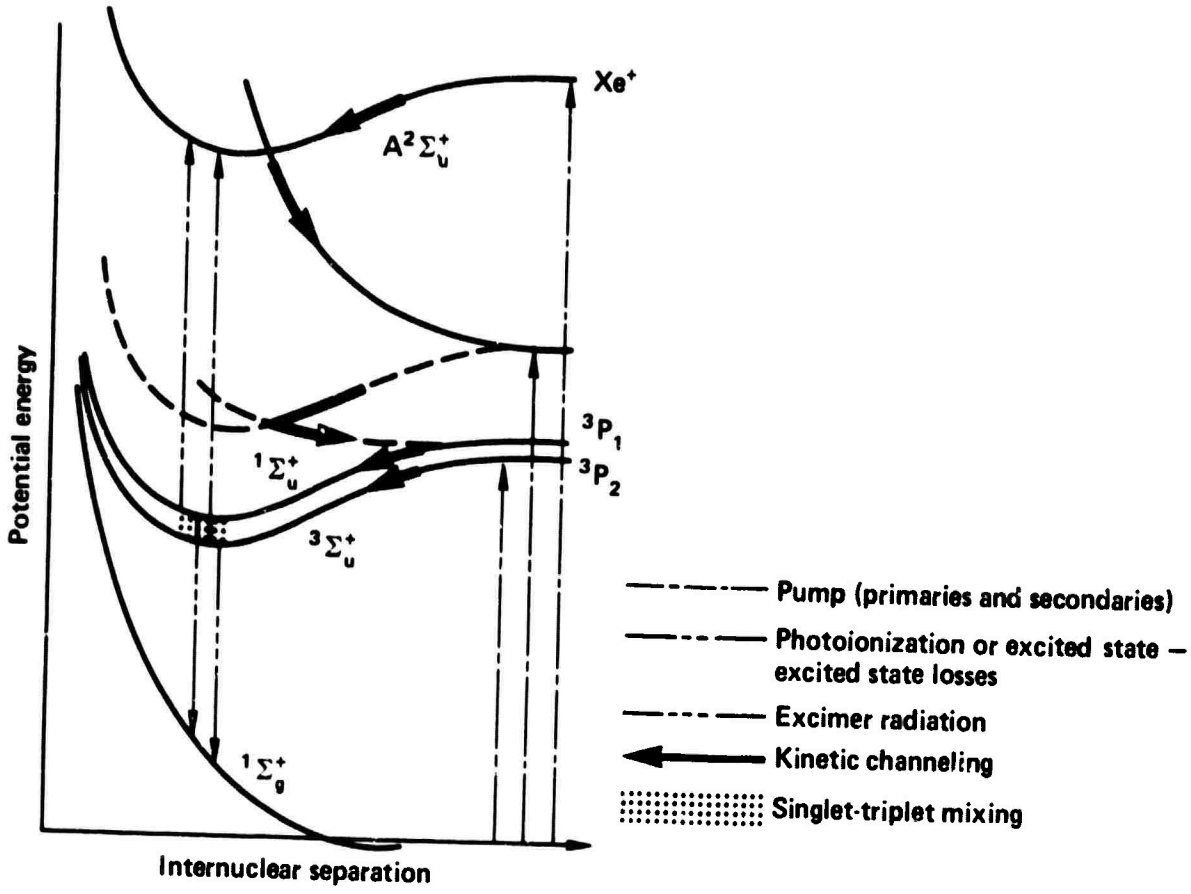

FIGURE 1 ENERGY PATHWAYS FOR THE XENON EXCIMER SYSTEM. The other rare gases, such as krypton and argon, are similar.

for analysis utilizing this type of process) An example of the dissociative process is

$$\gamma + N_2O(X) \rightarrow N_2(X) + O(^1S_0) \qquad (3)$$

which has recently been utilized (Murray et al., 1974) to generate copious densities of metastable $O(^1S_0)$ atoms.

The wavelength dependence and quantum yields of these photolytic reactions require reasonably detailed knowledge of the states of the molecular system ab, which may be a polyatomic molecule. Unfor-

tunately, our current data base for the important class of triatomics is severely restricted, in substantial contrast to the corresponding situation for diatomics, which is in much better condition. For illustration, Figures 2 and 3 exhibit the correlation diagrams believed to apply to N_2O for the linear and bent conformations, respectively. Notice the curve-crossing of the two $^1A''$ states induced by the transition from $C_{\infty v}$ to C_s symmetry (bent configuration), which furnishes a channel to the $O(^1S_0)$ state at an energy below the $4^1A''$, which arises from the $2^1\Sigma^+$ in linear geometry. We observe here that dynamical effects arising from curve-

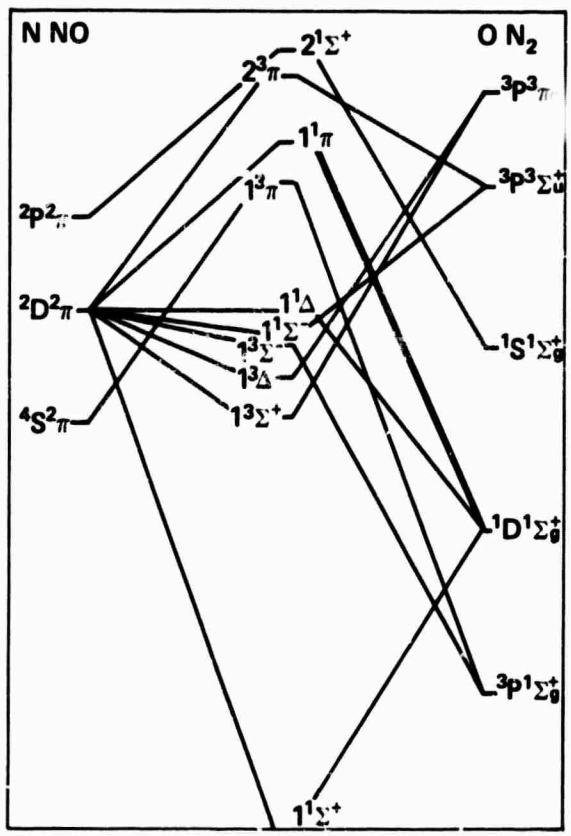

FIGURE 2 CORRELATION DIAGRAM FOR N_2O IN A LINEAR CONFIGURATION ($C_{\infty v}$). Courtesy of M. Krauss, NBS, Washington, D.C.

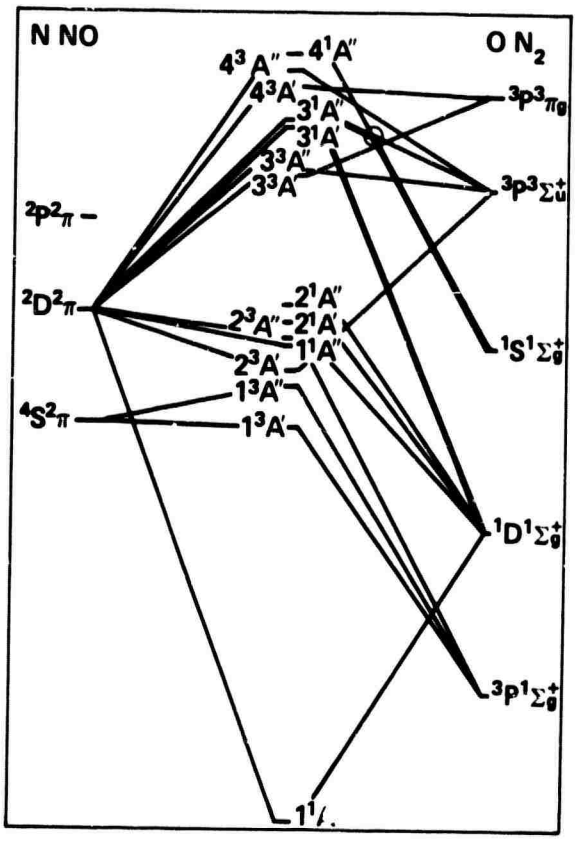

FIGURE 3 CORRELATION DIAGRAM FOR N_2O IN A BENT CONFORMATION (C_s). Note the crossing of the $4^1A''$ and $3^1A''$ surfaces. Courtesy of M. Krauss, NBS, Washington, D.C.

crossing phenomena constitute an important class of issues directly applicable to laser-related problems. Their significance is predicated on the fact that these sensitive collisional processes create selective energy pathways that enable efficient channeling of energy into a narrow band of excited states. Again, the picture for diatomic systems involving radial, rotational, and spin-orbit coupling appears satisfactory for current needs, but larger systems, and in particular triatomics, urgently need emphasis. In this case the problem is much more complex since these are described in terms of three-dimensional potential surfaces and the

couplings between such surfaces, as compared to the much simpler one-dimensional diatomic problem. Data of this type are required for a wide variety of molecular systems of which OCS, OCSe, OCTe, Cl_2O, and ClO_2 are a few good examples. Both experimental and theoretical techniques are applicable.

c. Collisional Energy Transfer from Metastable Species and Excimers

In analogy with the photolytic reactions (1) and (2), collisional mechanisms such as

$$M^* + a \rightarrow M + a^* \quad \text{(direct)} \tag{4}$$

or

$$M^* + ab \rightarrow M + a^* + b \quad \text{(dissociative)} \tag{5}$$

are also useful in transferring energy. An example of the successful use of collisional transfer is given by the Ar/Xe system (Rhodes, 1974). In our opinion the important and central consequence of the operation of the xenon ultraviolet laser through the energy-transfer process

$$Ar_2^* + Xe \rightarrow Ar + Ar + Xe^* \tag{6}$$

and subsequent xenon molecule formation by

$$Xe^* + Xe + Ar \rightarrow Xe_2^* + Ar \tag{7}$$

is the experimental demonstration that this electronic transfer can be achieved with modest losses and that the energy can be radiated coherently. It is immediately suggested that this technique can be extended to systems that radiate in a more favorable spectral region. We examine below the possible use of energy transfer from metastable species to appropriate acceptors in the generation of inversion densities in the near ultraviolet and visible range.

An example of a direct collisional transfer system--Eq. (4)--that has been recently studied is that of Ar - N_2 (Hill et al., 1974). The kinetic model that has been developed for this system shows the transfer occurring from both atomic and excimeric Ar. Interest has centered on the second positive emission arising from the $N_2(C)$ state, which is populated by transfer from metastable atoms. Unfortunately, this transfer is not as specific as desired because of the multiplicity of both donor and acceptor levels in this energy range. Because of the manifold of levels in the neighborhood of the $N_2(C)$, this state is also easily quenched to lower levels and the overall result is that the efficiency is $\leq$ 1%. Although this example illustrates some of the problems that must be avoided, the $N_2(A)$ state through which all of the electronic excitation flows is extremely efficiently populated and is an example of a system that is ideal in most respects. Unfortunately, the extreme metastability of the A-X transition and the relatively rapid self-quenching characteristics combine to exclude this system as a gas phase laser. Both of these undesirable characteristics, however, can be largely eliminated by going to low-temperature mixtures such as liquid Xe-N_2. In this case, the lifetime is shortened by 10^3, the self quenching is probably reduced by a similar factor, and the density is scaled up by a factor of 10^2 so that the possibility of obtaining a very efficient high-energy-storage laser on this transition appears promising. There exist also several other liquid-phase rare-gas energy-transfer systems that show real promise on the basis of existing data (see Table 5). This is an area where little research has been done, but considerable effort is warranted.

The scaling law favoring high-density systems can be simply formulated. Consider the example introduced earlier (Ar/N_2O) with the N_2O as the impurity constituent ($<$ 1%). An elementary analysis of the kinetics immediately discloses that the critical processes in the collisional energy transfer are the following:

Table 5

POSSIBLE LOW-TEMPERATURE MEDIA FOR ELECTRONIC TRANSITION LASERS

Host	Additive	Transition	Wavelength (Å)	Lifetime (s)	Stimulated Emission Cross Section (cm^2)	Energy density @ Gain of 1%/cm (joules/liter)	Reference
Ar	N_2	$A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$	(0,8) 3130 (0,9) 3352	0.38	$\sim 3 \times 10^{-23}$	2×10^5	Tinti and Robinson (1968)
Kr	N_2	$A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$	(0,8) 3130 (0,9) 3352	1.5×10^{-2}	$\sim 3 \times 10^{-22}$	8×10^3	Tinti and Robinson (1968)
Xe	N_2	$A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$	(0,8) 3130 (0,9) 3352	$\sim 10^{-3}$	$\sim 1 \times 10^{-20}$	6×10^2	Tinti and Robinson (1968)
Ar Kr Xe	O_2	$A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$	(0,8) 4183 (0,9) 4776 (0,7) 4220	$\sim 10^{-3}$	$\sim 5 \times 10^{-20}$	1×10^2	Shoen and Broida (1960) Lewis and Teegarden (1973)
Ar Kr	N_2O O_2	$O(^1S) \rightarrow O(^1D)$ $ArO(^1S) \rightarrow ArO(^1D)$ $ArO(^1S) \rightarrow ArO(^3P)$	5577 5100-5600 3010-3080	2.5×10^{-2} $10^{-3} - 10^{-6}$?	$\sim 10^{-19}$ -- ?	30 --	Shoen and Broida (1960) Lewis and Teegarden (1973) Murray and Rhodes (1973)
Ar	NO	$a^4\Sigma^- \rightarrow X^2\Pi$	(0,6) 3683 (0,7) 3930 (0,8) 4207	2.3×10^{-2}	1.5×10^{-22}	9×10^3	Frosch and Robinson (1966)
Kr	NO	$a^4\Sigma^- \rightarrow X^2\Pi$	(0,6) 3683 (0,7) 3930 (0,8) 4207	3.5×10^{-2}	1.2×10^{-21}	2×10^3	Frosch and Robinson (1966)
Ar	NO	$B^2\Pi \rightarrow X^2\Pi$	(0,7) 3050	$\sim 10^{-6}$	$\sim 10^{-17}$	--	Frosch and Robinson (1966)
Ar	S_2	$B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$	(0,7) 3740	$\sim 10^{-6}$	$\sim 2 \times 10^{-17}$	--	Brewer and Brabson (1966)
Ar	CO	$a^3\Pi \rightarrow X^1\Sigma^+$	(0,4) 2491	$\sim 10^{-3}$	$\sim 5 \times 10^{-21}$	1.6×10^3	Observation on gas phase Ar + CO mixtures at SRI

$$Ar^* + Ar + Ar \xrightarrow{K_1} Ar_2^* + Ar \tag{8}$$

$$Ar^* + N_2O \xrightarrow{K_2} Ar + N_2O^* \tag{9}$$

$$Ar_2^* + N_2O \xrightarrow{K_3} Ar + Ar + N_2 + O^* \tag{10}$$

$$Ar_2^* \xrightarrow{1/\tau_r} Ar + Ar + \gamma \quad . \tag{11}$$

The condition for energy transfer through the dimer chain [process (8) followed by reaction (10)] is then given as

$$\rho_{Ar}^2 \frac{K_1}{K_2} > \rho_{N_2O} > \frac{1}{\tau_r K_3} \tag{12}$$

where ρ_{Ar} and ρ_{N_2O}, respectively, denote the argon and nitrous oxide densities. We observe that a threefold increase in ρ_{Ar} allows a ninefold increase in ρ_{N_2O}. This favorable scaling condition (energy content rising quadratically with medium density) arises from the three-body reaction (8), with the conclusion that condensed media are indicated to maximize energy storage.

In several respects atomic radiators have the most desirable characteristics as energy-transfer acceptors. In particular, the collisional quenching is reduced, since fewer channels are available than in the case of molecular systems. If one considers the class of metal atoms, one has a very wide choice of acceptor and radiator levels in the visible range that can be pumped by the rare gases. For example, in reaction (6) the Xe might be replaced by a metal atom M. The possibility of finding a three-level atomic system in the visible-to-near-UV range in which the

lower laser level is collisionally removable appears good. This also improves the chance of finding transitions with lifetimes in desired ranges. The major limitation is the technological one of operation at high temperatures dictated by the generally low vapor pressures of the metal atoms. A large step toward the solution of this problem has occurred with the development of heat-pipe technology. Work in this area, which has been confined mainly to the alkalies and Hg, should be extended to other metals selected on the basis of their desired laser characteristics.

At this point we note that the argon/xenon example combines an energy-transfer process (6) with an associative reaction (7) to form the radiating system. Thus, it arises naturally to imagine schemes that represent the logical inverse--that is, mechanisms that combine energy transfer with dissociative amplitudes.† Consider the reaction (5) where M^* denotes the relevant metastable, ab is the acceptor system, a^* is an electronically excited fragment, and b is the corresponding remnant whose unspecified internal state is presumed to carry a negligible or vanishing excitation. Of course, in order for this process to be attractive for the production of a^*, the channel

$$M^* + ab \rightarrow M + a + b^* \tag{13}$$

as well as other deactivating reactions must be weak. Note that we have produced the excited system of interest a^* in a single process which, in comparison to the argon/xenon case, obviates the subsequent molecular association step analogous to reaction (7).

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† A well known example of energy transfer leading to inversions through dissociative excitation involves the production of excited oxygen atoms from oxygen molecules important in the 8446 Å oxygen laser transition. For details see Bennett et al. (1962), Rautian and Rubin (1965), and Feld (1967).

Considerable data exist for atomic metastables (Stedman and Setser, 1971)--e.g., Ar^*, Kr^*, and Xe^*--in collision with a multitude of molecules including N_2O, HN_3, C_2N_2, NOCl, NO_2, and CF_3NO among others producing a wide variety of excited fragments such as $NO(A^2\Sigma^+)$, $NO(B^2\pi)$, $CN(B^2\Sigma^+)$, and $NH(A^3\pi)$. Although efficiencies are unknown, intense emission has been observed originating from these molecular fragments.

In contrast to the situation of the atomic metastables, the data for molecular metastable systems are relatively scarce, with the exception of the important $N_2(A^3\Sigma_u^+)$ state (Wright and Winkler, 1968). In connection with the $N_2(A^3\Sigma_u^+)$ state, it is interesting to explore the possibility of chemical production of this state. This issue is examined in Section III-A-2. In particular, there is a manifest paucity of information concerning the important class of rare gas dimers (He_2^*, Ne_2^*, Ar_2^*, Kr_2^*, and Xe_2^*) which can be formed, as experiments demonstrate, in appreciable concentrations as the result of conversion of atomic metastables in high-density material. Although it is possible to formulate estimates of their collisional properties in some cases, it is obviously difficult to predict the preferred amplitudes with certainty. This is particularly true in situations involving exchange processes, since this generally implies an intimately coupled collisional complex. The necessary determinations are best deduced experimentally. Further data on these systems with possible application for high-energy density storage are urgently needed.

d. Collisional/Radiative Phenomena

Collisions modify the spectral width and radiative strength of atomic and molecular transitions. Collisional influence on the transition amplitude can be particularly striking for high-density systems involving forbidden transitions. Since the ratio of the

spontaneous radiation rate to the linewidth is an important determinant of the stimulated-emission cross section, which is an important parameter in a scalable laser system, an understanding of these phenomena enables us to controllably vary the coupling of the inversion density to the radiation field. Examples of collision-induced emission involving the oxygen atom (Hampson and Okabe, 1970) and the nitrogen molecule (Tinti and Robinson, 1968) are

$$O(^1S_0) + Ar(^1S_0) \rightarrow O(^1D_2) + Ar(^1S_0) + \gamma \qquad (15)$$

and

$$N_2(A^3\Sigma) + Xe(^1S_0) \rightarrow N_2(X^1\Sigma) + Xe(^1S_0) + \gamma \quad . \qquad (16)$$

Although analogous behavior is anticipated for states similar to the $O(^1S_0)$ such as $S(^1S_0)$ and $Se(^1S_0)$, it has not been observed thus far. Systems of this nature represent an important class of problems with an obvious impact on laser technology, and constitute an area that clearly needs considerable further attention.

e. Conclusions and Recommendations

The main conclusions and recommendations pertaining to this section are as follows:

(1) Since the details of the excited state structure of relatively simple polyatomics, particularly triatomics, play a generally important role in the dynamics of many laser systems, stronger experimental and theoretical effort should be applied to determine their relevant properties. Of special interest is the construction of excited-state correlation diagrams and surfaces, an appraisal of curve crossing and other excited-state coupling phenomena, and absolute photolytic

quantum yields. We recommend a level of effort of 10 men in the pursuit of these goals.

(2) Collisional and photolytic energy transfer from important excited species [e.g., $N_2(A^3\Sigma_u^+)$ and the rare gas atoms and dimers] has very promising direct application to a wide variety of electronic laser systems, and considerable experimental effort should be focused on an evaluation of their properties. In particular, the reactions (1), (2), (4), and (5) should receive emphasis. Of particular importance are the transfer of excitation to specific states, dissociative excitation, quenching mechanisms, and energy pooling. An important fundamental consideration in this case is the experimental demonstration that the rare gas dimers can be generated with high (~ 30%) efficiency in large volumes of high-density material. It is also essential that the kinetic mechanisms be understood for the dense environment (high-density gas or liquid phase) needed for the HEL medium. A level of effort of approximately 20 men is recommended to field the appropriate small-scale kinetic studies specifically designed to appraise the energy-transfer processes.

(3) Collisional processes of excited species leading to the emission of radiation is a topic that historically has not received adequate attention with regard to laser applications. A recommendation of 5 men for the support of an effort incorporating both experimental and theoretical components is suggested for this area.

2. Chemical Processes[†]

From the standpoint of laser technology, chemical processes can be examined in two contexts; one involves the conversion of chemical energy into coherent radiation while the other relates to the use of

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[†] This section was prepared by C. B. Moore and C. Rhodes.

radiation to influence chemical reactions. We also allow for the interesting possibility of overlap and simultaneous interplay of these two areas. From the standpoint of the former application, chemical energy is attractive on account of its potential of high energy-storage density.

a. Conversion of Chemical Energy to Coherent Radiation

The use of chemically stored energy could substantially reduce the size of a high-energy laser system. Of particular interest are chemical processes leading to the production of electronically excited radiators (e.g., BaO^* and SmO^*) as well as metastables such as $N_2(A^3\Sigma_u^+)$. In this section we explore three general topics: (1) chemiluminescent reactions, (2) vibrational-electronic energy transfer, and (3) exothermic decomposition leading to electronically excited fragments.

1) Chemiluminscent Reactions

In regard to the strongly radiating species, metal oxidation reactions have been found to generate strong chemiluminescence from electronically excited products (Jones and Broida, 1974; Huestis, 1974). The participating reactant metal atoms can be either free systems as in the Ba + N_2O and Sm + N_2O reactions, or bound systems as in the B_2H_6 + F_2 reaction (Gole, 1974). Under appropriate conditions the quantum yield of such chemical reactions can be impressive; 38% has been observed in the Sm + N_2O reaction, albeit at rather low density.

The sum of current experience indicates that the majority of chemical reactions lead directly to excited vibrational levels of the ground electronic state. Subsequent perturbations due to collisions or internal level crossings can provide the observed electronic excitations. Naturally, this complicates the process of energy extraction on an appropriate electronic transition in the visible or

near-ultraviolet spectral range. Additionally, even under circumstances where the kinetic pathways populate radiating electronically excited states, the resulting chemiluminescence generally occurs over an extremely large bandwidth that arises from a variety of vibrational sequences and progressions. It is characteristic of these reactions that the energy density is not well disciplined, and consequently it appears that substantially greater control of the state populations is necessary to render systems of this nature useful in the context of high-power lasers. Greater emphasis must be placed on the control of the reaction pathways.

The energy distributions of the product species are governed by the detailed structure of polyatomic surfaces. This includes excited configurations in which crossings play an important role as a mechanism of switching from a ground to an excited surface. It is interesting to note that these same factors concerning molecular structure were found to be important in Section III-A-1-b, entitled Photolytic Energy Transfer. Both areas would benefit generously from effort on this general problem. Experimental methods are an essential component of this analysis, and support of detailed studies of electronically chemiluminescent reactions should continue in order to expand the range of materials examined.

2) Vibrational-Electronic Energy Transfer

It is well known that a large variety of chemical reactions are efficient in the production of high densities of vibrationally excited material. The process of vibration-to-electronic energy transfer may provide an important mechanism to convert the vibrational excitation commonly produced in chemical reaction products to electronic excitation. In this way a substantial fraction of reaction exoergicity might be channeled to electronic inversion in a three-level atomic

system. The use of an atomic acceptor with a low density of states will enable the combined action of vibrational-vibrational (V-V) transfer and vibrational-electronic (V-E) transfer to channel the chemical energy selectively. A diagram of this mechanism is shown in Figure 4. The

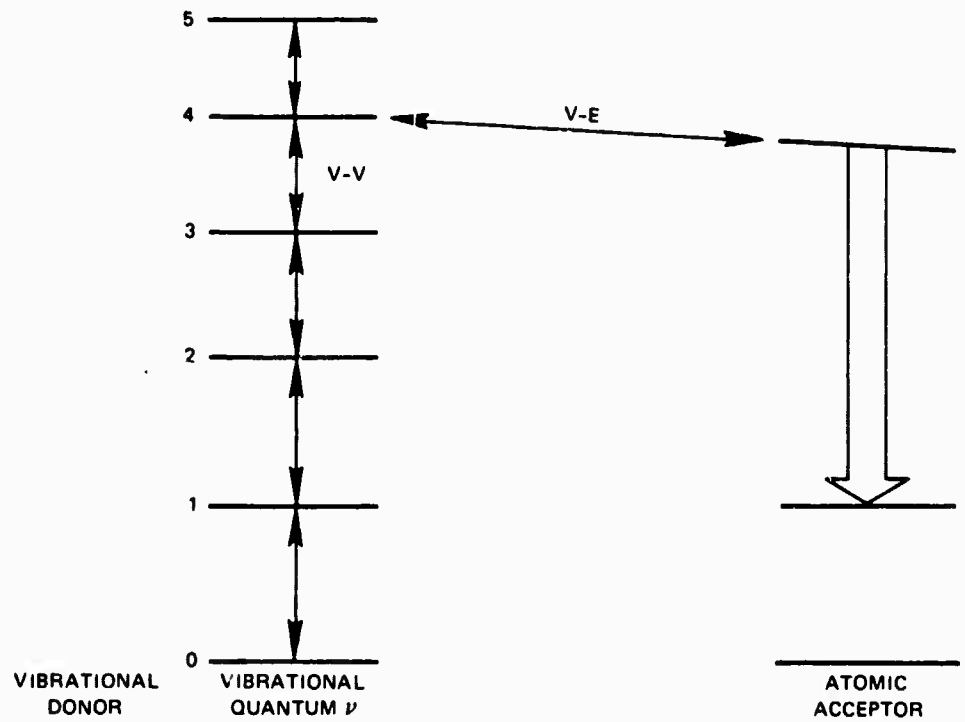

FIGURE 4 ENERGY-LEVEL DIAGRAM ILLUSTRATING VIBRATIONAL-ELECTRONIC AND VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER IN THE EXCITATION OF AN ELECTRONIC ACCEPTOR BY A CHEMICALLY PRODUCED VIBRATIONAL MANIFOLD

previously noted inherent difficulties of electronic chemical lasers would thus be overcome. Past research on (V-E) energy transfer, both theoretical and experimental, is much too limited to allow specific systems to be suggested at this time. Laser sources now make it possible to investigate this field extensively. New theoretical methods also show considerable promise. The problem of V-E energy transfer also influences the multiple quantum excitation scheme described in Section III-A-5.

3) Exothermic Decomposition

There is evidence that exothermic decomposition of complex molecular species (e.g., dioxetanes and azides) generates electronically excited products (Taylor, 1974; Turro et al., 1974). In some cases the electronic excitation is substantial, being ~ 80 kcal/mole. Furthermore, it is conceivable that these systems could operate at solid density. Visible luminescence, for example, has been observed (Deb and Yoffe, 1960) from solid TlN_3. In all cases, however, very little detailed and substantive information is currently available. Naturally, it would be desirable to orchestrate the release of the chemically stored energy density through the agency of an applied laser field. It appears that there exists no fundamental consideration precluding this possibility. Among other things, this calls for an analysis appraising the influence of intense radiation fields on the activation energies and reactive properties of the constituent systems. This is an area in which our present knowledge is at absolute zero.

At the present time far too little is known concerning the behavior and structures of this class of materials to formulate a realistic assessment of their possible application to laser devices. On account of their potential for unusually high energy-density storage, it seems advisable to establish a data base that would permit such an appraisal. Three areas of preliminary study that would provide important information are (1) kinetic studies on materials for which some information currently exists, (2) the determination of the spectral properties (infrared, visible, and ultraviolet) of available systems, and (3) the development of chemical synthesis procedures to enlarge the class of experimentally available materials.

b. Chemical Processing with Lasers

The possibility of bulk photochemical processing using laser sources has been suggested many times since 1960. In early studies with CO_2 lasers pyrolytic processes were observed. The specific vibrational excitation is degraded to thermal excitation on a time scale shorter than for reaction. Recently, several experiments in which vibrational excitation enhances the rate of reaction (e.g., excited ozone with NO) have been reported. A great deal more research will be necessary before practical systems can be developed. The utility of lasers for visible and ultraviolet photochemistry is similarly unevaluated. If relaxation to the lowest vibrational level of the lowest excited state in liquids is fast compared to reaction, photochemical products will not be wavelength-dependent. In gases and possibly solids it seems more likely that one can selectively excite an electronic-vibration state and thus favor one photochemical pathway over another.

A much more detailed knowledge is needed of the variation of chemical reaction rates with energy state of the reactants, of the rates of energy transfer, and of the competition between energy transfer and reaction. As such research develops we can expect to deliver on, or debunk, the promise of laser-selected chemical processing.

c. Conclusions and Recommendations

The main conclusions and recommendations of this section are as follows:

(1) Studies on exothermic chemiluminescent reactions involving both free and bound metal atoms should continue at essentially the current level of national support. Efforts that exhibit imagination and indicate well reasoned arguments concerning the channeling of the chemically liberated energy should be encouraged. Emphasis on the

control of the released energy is preferred over randomly selected flame studies. Although the current experimental effort appears adequate, the theoretical effort needs additional support. A level of effort of 15 men is recommended.

(2) Vibration to electronic energy transfer (V-E) processes in combination with rapid V-V processes affords the possibility for efficient conversion of chemically produced vibrational energy into electronic excitation of appropriate acceptor species. The current effort is far less than that required to adequately pursue this field. An effort of 10 men including roughly comparable theoretical and experimental components is recommended.

(3) The use of exothermic decomposition of complex molecular systems has exciting possibilities for applications to high-energy lasers. The data base on this class of systems should be expanded to allow a realistic assessment of their potential. We recommend an effort of approximately 5 men that stresses kinetic studies on currently available materials, the determination of their spectral properties under modest resolution (infrared through ultraviolet), and the development of synthesis procedures to enlarge the class of available materials.

(4) Work on vibrationally driven reactions in connection with vibrational transition HELs should be maintained. Emphasis on studies with the goal of determining reaction mechanisms should definitely be encouraged. Expansion of support over the current level should be encouraged only when important new results appear or when a particular application arises. Considering the availability of infrared systems in the 5-μ and 10-μ region, advances here could have a strong impact on isotope separation (Section III-B).

3. Nonlinear Radiative Extraction†

a. Technical Aspects

This section will consider the use of multiple quantum transitions for radiatively extracting energy from an inverted medium. The advantages for the case of two quantum transitions are that the pulse-width can be drastically reduced during amplification, energy can be extracted from otherwise radiatively metastable levels, and the frequency of the amplified light is different than the input laser light. This last advantage leads to the possibility that in some cases the output light frequency can be programmed in time over a large frequency interval, as well as to the possibility of using the change in light frequency for isolating the original laser from a target and its possible back reflections. We observe that this enables the frequency of the light to be changed in a process involving energy gain, which is in contrast to customary methods that normally introduce substantial losses. Finally, the kinds of transition that constitute good two-quantum amplifiers naturally involve metastable upper levels that can store high energy densities without complications arising from rapid superfluorescence decay.

The types of nonlinear process under discussion are the three illustrated in Figure 5. All three of these processes can compete in a system where two-quantum energy extraction is to be used.

A detailed analysis of the various cases using Maxwell's equations and the nonlinear Bloch equations has been carried out during the progress of this study and is contained in a paper prepared for publication (Carman, 1974). Briefly, the findings are that two different

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† This section was prepared by R. L. Carman.

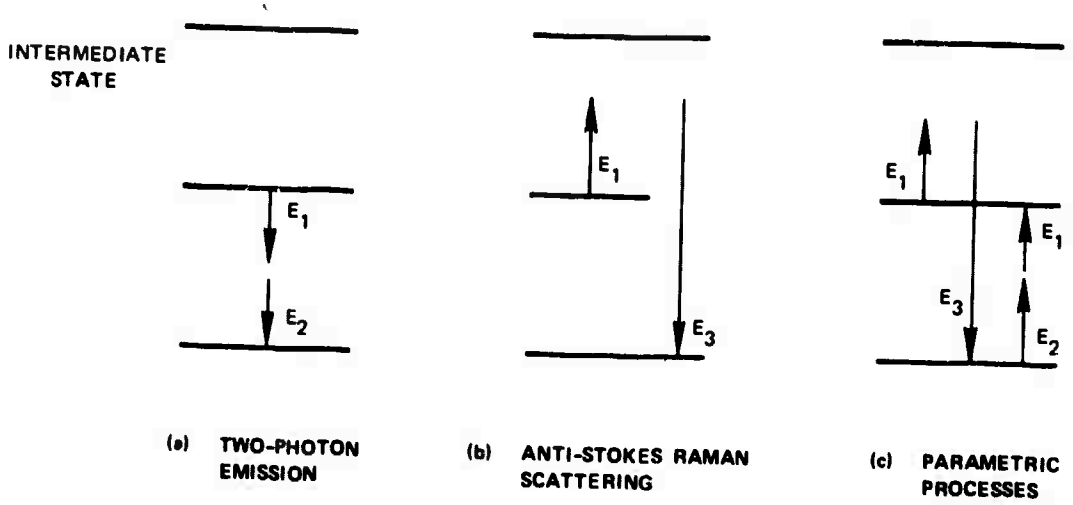

FIGURE 5 ENERGY-LEVEL DIAGRAMS ILLUSTRATING TWO-PHOTON PROCESSES

extraction schemes naturally evolve. Both involve optimizing two-photon emission [Figure 5(a)] during the initial growth phase. This assures that the resultant amplifier will have a reasonable energy gain. We observe that parametric processes [Figure 5(c)] lead only to frequency changes in the energy density and do not lead to any energy extraction, while anti-Stokes stimulated Raman scattering [Figure 5(b)] is limited by photon number conservation to an energy gain that equals the ratio of the output frequency to the input laser frequency. For the two-photon emission mode only energy storage limits the achievable energy gain. Further technical details of these processes are contained in Appendix A.

b. Conclusions and Recommendations

The main conclusions and recommendations concerning this section are provided below.

(1) The properties of stimulated two-photon emission and odd-harmonic generator response must be experimentally demonstrated. Current understanding seems to indicate that these studies are feasible

and should be carried out in atomic iodine produced by photolysis of CF_3I. Such work is currently underway at LASL and will require one to two man-years of effort. No further support is indicated.

(2) The theoretical analysis shows that two-quantum devices of this nature are impractical as amplifiers unless inversion densities $\sim 10^{18}$ cm^{-3} can be generated. This is roughly an order of magnitude greater than that listed previously (Table 4) for conventional amplifier systems. A kinetic analysis should be instituted with the goal of determining the limiting mechanisms and the feasibility of generating inversions of this magnitude with existing or anticipated pump sources. An effort of two man-years is estimated.

(3) Extraction of stored energy in a beam with good spatial coherence is an important issue that is complicated by the intrinsic nonlinearity of the radiative coupling. Computer studies should be carried out to simulate the propagation problem for a finite beam in space and for pulse durations short compared with T_1 and T_2. This effort should constitute about one man-year.

4. Solid State, Semiconductor, and Dye Laser Systems†

a. Technical Aspects

It is useful to consider briefly some visible or near-visible laser systems that are not examined in detail in the present study, but that are very efficient or have the potential of being very efficient. These include:

(1) Rare-earth solid-state lasers

(2) Semiconductor lasers

(3) Liquid and vapor-phase dye lasers.

We discuss the properties of these systems, including both their assets and liabilities, which are summarized in Table 6.

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† This section was prepared by R. L. Carman and P. L. Kelley.

Table 6

EFFICIENT SOLID-STATE AND DYE LASERS

Laser System	Assets	Liabilities
Rare earths	• High energy storage • Low gain	• Lack of narrowband efficient optical pump* • Thermal effects* • Nonlinear effects
Semiconductor laser	• High efficiency • Relatively high energy storage • Variety of pumping techniques	• High gain* • Small active regions* • Low damage threshold* • Lack of large crystals* • Thermal and nonlinear effects
Dye in solution	• High quantum efficiency	• High gain* • Low energy storage • Lack of efficient optical pump* • Thermal and nonlinear effects
Vapor-phase dye	• High quantum efficiency • Low-index nonlinearities	• High gain* • Lack of efficient pump*

*Potentially soluble problems.

The process used in obtaining inversion is a primary consideration. Only the semiconductor laser can be readily pumped by nonoptical methods--namely, by current injection at a junction or by using an electron beam. Electron-beam pumping of vapor-phase dyes has not been attempted, and it is doubtful if such a technique would be successful on account of dissociation and chemical reactions that are likely to occur in an intense electron beam. In the case of nonoptical pumping of semiconductors, quantum efficiencies of the order of 30% have been obtained. Radiative limitation on carrier diffusion near the junction,

mode confinement, optical damage threshold, and the need to suppress higher-order modes all combine to limit the active volume (and hence the energy output) of diode laser oscillators to about $1 \times 30 \times 100\ \mu m^3$. Electron-beam pumping is limited also to small volumes because of the small penetration depths of low-energy electrons. The use of high-energy electrons is precluded by radiation damage. The active volume of a semiconductor could be increased by using parallel amplifiers to eliminate spurious modes and to keep the intensity below the damage threshold.

All the lasers considered in this section can be optically pumped by relatively narrowband radiation ($Q \sim 10$ to 50) to give laser output at high quantum efficiency. Unfortunately, there are very few efficient narrowband sources that can be used as pumps (most of these are also themselves lasers). For example, the choice of particular rare earths for lasers is in part tied to the types of pump lamp available. Because of the typical low pumping efficiency associated with very broadband light sources, a great deal of heat is generated in the active medium, causing severe optical distortion and damage. Solid-state lasers that are pumped by other lasers do not suffer from this problem. While diode lasers are efficient and can pump (for example, a Nd glass or YAG laser), an impractically large array of diodes is required. On the other hand, an argon ion laser on xenon laser can be used to pump a ruby laser efficiently, but these gas lasers are themselves very inefficient. It is evident that the development of very efficient fluorescers, such as the excimers, Xe_2^*, Kr_2^*, $XeHg^*$, etc., could be very important to further advances in this field. The output wavelengths of such fluorescers will then dictate the type of solid-state or dye laser system to be developed.

A second question to address is energy storage. Most, but not all gas systems are limited by three-body collisional deactivation or other nonlinear pressure-dependent loss mechanisms to inversion

densities of about $10^{17}/cm^3$, corresponding to about 50 joules/liter of stored energy. In principle, a solid could allow for 100 or more times this storage density. For example, the Nd glass laser can store as high as 10^3 joules/liter or more. Typical energy storage densities are > 10 joules/liter for GaAs and ~ 1 joule/liter for a dye laser. The experimentally observed storage level in GaAs diode lasers is probably not the fundamental limit. Limits are set for junction lasers by ohmic losses and optical losses due to absorption in uninverted regions, but by clever design these problems can probably be minimized further. Semiconductor lasers and dye-solution lasers have extremely high gain and are therefore subject to parasitic mode losses. Systems can be designed that alleviate these difficulties. For example, one can conceive of face-pumping (optically or with an electron beam) a semiconductor crystal, over a large area and using the pumped face as one end of a cavity. By periodically introducing loss along the surface, parasitic modes within the plane of the surface are prevented and power densities do not reach damage thresholds. Perhaps the biggest limitation here is the availability of large crystals, which might necessitate the use of arrays of crystals.

Another important consideration in evaluating solids or dyes for high-energy laser applications is that materials at solid and liquid densities are subject to nonlinear optical instabilities (self-focusing, thermal blooming, stimulated scattering, etc.) when optical propagation occurs in the bulk. Furthermore, even with narrowband pumping, there will be some residual waste heat which will limit the average power obtainable from a given volume. Since they can be flowed, both gases and liquids suffer much less than solids from the heating problem. Experience with Nd glass lasers has indicated that both heating and the intensity-dependent refractive-index effects (self-focusing, self-phase-modulation, etc.) provide severe constraints on obtaining very high energies for either AEC or DoD purposes. While it may yet be

feasible to obtain 10^4 J in a usable beam within the pulse-duration range of 0.1-1 ns, for AEC applications the magnitude of these problems should not be underestimated. We note that the average power from Nd glass lasers is only a few watts on account of thermal cycling problems. While the heat conductivity of glass is not high, and blackbody flashlamps produce substantial unnecessary heating (despite some filtering of the blackbody spectrum), it is hard to conceive of raising with improved pumping this average power in solid-state materials by 10^6. Semiconductors may be useful for two-photon amplifiers (discussed in Section III-A). The third-order susceptibility for this process can be about five orders of magnitude greater in semiconductors than in high-pressure gases. The large gains and high storage densities, which are in principle obtainable, make these systems worth further examination.

b. Conclusions

We conclude that the prospects for high-energy ($\geq 10^4$ J) visible and ultraviolet lasers using solids and dyes are poor. This is not to say that novel approaches are not worth exploring, such as new pump geometries and techniques. Smaller efficient visible and ultraviolet lasers will of course be important for applications where high energies or high average powers are not needed. The development of efficient narrowband pumps is useful not only for solid-state and dye lasers but for systems considered elsewhere in this report. These conclusions may be summarized as follows:

(1) General problem areas

- Lack of efficient optical pumps
- Lack of scalability
- Lack of materials in suitable sizes.

(2) General conclusions

- Prognosis not good for 10^4 J or higher systems
- Lower-energy systems have wide DoD applications
- Novel pumping schemes should be tried
- There is a need for an efficient narrow-band optical pump.

5. Multiple-Infrared-Photon Processes[†]

a. Introduction

In this section we will focus our attention on the potential applications of multiple-photon interactions with molecular systems. Because the basic interaction between the photon and charged matter is very small, processes in which more than one photon are emitted or absorbed at a time usually have small rates. This ceases to be true when a very strong oscillating field of strength comparable to the fields holding the molecule together is present to stimulate the process. In favorable cases, lasers can produce peak fields of this order of magnitude, and it is therefore important to ask whether multiphoton processes offer new types of solutions to laser-related problems. We also point out that when energy surfaces are close, as in the neighborhood of a crossing, the laser power required to produce nonlinear behavior will be substantially reduced.

An important problem is the development of an efficient high-power visible laser. Since one already has an efficient high-power source of infrared photons and since $\sim$ 20 infrared photons are equivalent to one optical photon, one might wonder whether a mechanism exists for simultaneously converting $\sim$ 20 infrared photons into one optical photon.

[†]This section was prepared by C. Callan.

If such a multiple-photon process could be made to go with a sufficient rate, one could parlay the existing CO_2 laser into a high-power optical laser.

Another important problem is isotope separation. We shall see that the rate at which multiple-photon processes go is a very steep function of the stimulating field strength. That is, there is a threshold below which these processes essentially do not occur at all and above which they occur with substantial rate. Molecular species can of course be made to dissociate by exciting large amplitudes of nuclear vibration, a process involving the absorption of many infrared photons. Since the properties of molecular vibration in the electronic potential well depend on the nuclear mass, one might imagine carefully choosing the stimulating field strength so that only one isotope has a large dissociation probability. Thus, instead of tuning the laser frequency with very high accuracy, one might achieve isotopic separation by tuning both the laser power and frequency with modest accuracy.

Both of these interesting possibilities involve multiple-infrared-photon interactions with the nuclear vibrations in a fixed electronic potential well. In order to assess their merits we need more information about electromagnetic transition rates in such a system. Consequently, we now turn to a qualitative estimate of the relevant transition probabilities.

b. Qualitative Rate Estimates

We shall consider a model in which infrared photons interact with a single optically active vibrational mode. We regard the potential curve as fixed, no matter how strong the applied field (this will be wrong when the applied field is capable of disturbing the electronic structure). The energy levels of a typical molecular mode generally

involve many tens of discrete levels with gradually decreasing spacing followed by a continuum with a dissociation limit, D, of a few electron volts. A reasonably accurate formula for the discrete energy levels is usually

$$E(v) = \Delta v[1 - xv] \tag{17}$$

where Δ is on the order of 10^3 cm^{-1} and x, the anharmonicity, is usually on the order of 10^{-2}.

We are interested in dissociating the molecule, and could in principle require that the system be directly removed to the continuum. Furthermore, we require a mechanism that couples nuclear and electronic motions. This is obtained if there exists a dissociation pathway for which there is a curve-crossing such as that shown in Figure 6 for NH_3. The importance of such crossings in coupling nuclear and electronic motions arises in the following discussion (III-A-5-c). Then the levels in the neighborhood of the crossing will have a large width due to their finite probability of transferring to the other potential curve and escaping to infinity. We shall assume that this curve-crossing affects the levels in a small neighborhood of $v = v_o$, where v_o is on the order of a few tens. Our problem, then, is to compute the transition probability to these unbound levels from the ground state when the system is perturbed with a strong infrared photon field.

The perturbing Hamiltonian is then

$$H_I = eEr \sin \omega t \tag{18}$$

where e is the effective charge of the mode, r its coordinate, and E is the perturbing field strength. It will obviously be favorable to choose ω so that $\hbar\omega \approx \Delta$, since then the perturbing field is nearly in resonance

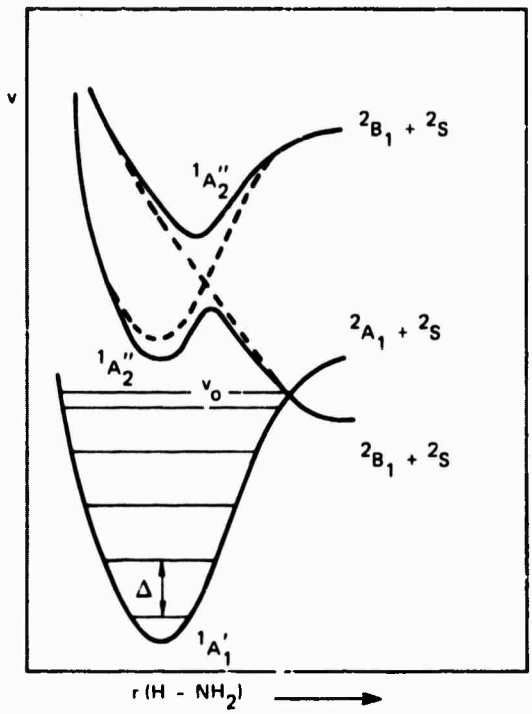

FIGURE 6 ENERGY-LEVEL STRUCTURE OF NH_3 ILLUSTRATING THE H-NH_2 COORDINATE. Note the crossing of the $^2A_1$ and $^2B_1$ surfaces at large r which provides a mechanism for coupling nuclear and electronic motions. The quantity Δ represents the fundamental vibrational spacing while v_o designates the vibrational level near the crossing.

with the basic vibration frequency of the well. If the unbound level v_o is reasonably narrow, then energy conservation requires that ω be adjusted so that

$$E(v_o) = N\hbar\omega \quad . \tag{19}$$

Then the dissociation energy can be supplied by precisely N infrared photons. If the anharmonicity parameter is small, $N \approx v_o$ and $\hbar\omega \approx \Delta$.

The standard formulas for the time-dependent perturbation theory give the transition amplitude for $v = 0 \rightarrow v = v_o$ as a sum over terms corresponding to specific sequences of photon absorption and

emission leading from the initial to the final state. The basic amplitude is proportional to eE and is normally small because e itself is small and the field E is small compared to normal molecular fields. Consequently, for small enough E, the term with the smallest number of steps will be the dominant one. In the situation we are considering, the leading term is easily seen to be

$$M = \frac{\langle v_o|A|v_o - 1\rangle \ \ldots\ \langle 1|A|0\rangle}{(\omega_{vo} - N\omega) \ \ldots\ (\omega_2 - 2\omega)(\omega_1 - \omega)} \tag{20}$$

where $A = eEr$ and $\hbar\omega_i = E(i)$. Consequently the rate, which is proportional to $|M|^2$, will be roughly proportional to

$$R \propto \left(\frac{P}{P_o}\right)^N \tag{21}$$

$$P_o \sim \frac{c}{4\pi}\left(\frac{\Delta E}{d}\right)^2 \tag{22}$$

where d is a mean value of the transition moment, $\langle n + 1|er|n\rangle$, and ΔE is a mean value of the energy denominators, $\hbar(\omega_n - n\omega)$, appearing in M. Crude estimates of such sums have been made by Pert (1973), and he claims that for favorable molecular parameters, P is on the order of 10^{10} W/cm^2, a value that may be reduced by as much as two orders of magnitude in the neighborhood of a crossing.

The important points to make about this result are these: The quantity P/P_o is the expansion parameter of the perturbation series. When it becomes comparable to 1, the lowest-order calculation is not accurate. On the other hand, P_o plays the role of a threshold. If N is large (say, on the order of ~30), then reducing P by a few percent makes an order-of-magnitude change in the transition rate. Consequently,

one can almost think of the process as not occurring at all for $P \lesssim P_o$, and happening with a large rate for $P > P_o$. The crude lowest-order calculation probably gives a good order-of-magnitude estimate of the location of this threshold. Finally, we should remark that P_o clearly must depend on the reduced mass, μ, governing the vibrations of the mode in question. The precise dependence on μ is not clear, but the distance scale of motions in the well, and hence the effective dipole moment, varies as $\mu^{-1/2}$. Then a 10% change in μ might lead to a 5% change in P_o and an order-of-magnitude cnange in transition rate, $(P/P_o)^N$ (holding P fixed and taking N = 20). Consequently, it would appear to be possible to selectively dissociate different isotopic species just by choosing the peak laser power correctly!

Finally, a word should be said about rotation. So far we have simply ignored the molecule's rotational coordinate, in effect assuming that the vibrational axis is aligned with the infrared field. If the axis makes an angle θ with the field direction, the effective forcing field is not E, but E cos θ, and the effective dissociation rate is $(\cos^2\theta P/P_o)^N$ rather than $(P/P_o)^N$. When N is large, and $P \sim P_o$, only molecules with just the right orientation will succeed in being dissociated. This need not pose a problem if collisions are sufficiently frequent to redistribute the molecules in orientation (but not sufficiently frequent to disturb the distribution in vibrational levels).

Last, but not least, substantial reductions in the threshold flux, P_o, can be achieved by supplying more than one infrared frequency. To get the maximum effect out of the stimulating field, its photon energy should match as closely as possible the energy difference between successive vibrational levels. The problem is that this difference decreases as we go up the well and it seems evident that the overall frequency match can be made better with two or perhaps several

appropriately chosen frequencies than with a single frequency. A classical calculation suggests that it may be possible in this manner to reduce the threshold flux, P_o, by between one and two orders of magnitude.

c. Potential Applications

1) Production of Electronically Excited States by Predissociation

Suppose that the vibrational mode we have been considering corresponds, for large values of the coordinate, r, to dissociation of the molecule into two species, A and B. We now recall the curve-crossing illustrated for the example of NH_3 in Figure 6. When the molecule is excited to $v = v_o$, it may remain on the ground-state surface $^1A_1'$ or transfer to the excited $^1A_1''$ curve. In the latter case the fragment (NH_2) may escape in an electronically excited state. The details of these processes depend strongly on the precise nature of the electronic surfaces near the crossing point. In order to produce inversion of the relevant electronic transition, it is necessary that the crossing avoidance be weak. If it is, this might be an efficient method of pumping a laser working on the transition $^2A_1 \rightarrow {}^2B_1$ of NH_2. Furthermore, the rate of pumping can be adjusted be adjusting the strength and frequency of the infrared laser field.

The type of potential curve called for here exists commonly in polyatomic systems. Therefore, one would have to regard this as a schematic representation of a common situation in suitable polyatomic molecules. There are known examples of (rather complicated) molecules that preferentially dissociate into electronically excited fragments when appropriately stimulated,† and it may be useful to consider stimulating this dissociation by multiple-infrared-photon absorption.

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†A good example is dioxetane. See Turro et al. (1974).

2) Isotope Separation

Here one is interested simply in dissociating the molecule. If N infrared quanta are required to dissociate the molecule, then the rate should go like $(P/P_o)^N$, where P is the laser power and P_o is characteristic of the molecule and depends on the reduced mass. Then the ratio of the dissociation rate for two different molecular species is $(P_o(\mu_1)/P_o(\mu_2))^N$. If N is large, a small percentage difference between μ_1 and μ_2 will lead to a large difference between the dissociation rates and a greatly altered isotopic distribution in the dissociated fragments.

The uncertainties in this scheme are manifold, including both the coupling of the radiation and the subsequent kinetics. The efficiency will be low if energy can be lost out of the mode in any other way than by dissociation. So collisions that exchange vibrational energy with kinetic energy would degrade this mechanism as would mixing with other vibrational modes in a polyatomic molecule.

3) Frequency Conversion

This scheme calls for a potential curve configuration similar to that provided by BaO. The intense infrared field is used to excite the vibrations of the lower well to the N^{th} level, which mixes strongly with the lowest vibrational level of the upper well (corresponding to a different electronic state). This level then has a strong transition matrix element back down to the v = 0 vibrational level of the lower well. We require the wells to be nested in this fashion so that the Franck-Condon factor for this transition is large.

If the system is initially in the ground state and then subjected to a fast, intense infrared pulse, an inversion will typically be produced. In a harmonic oscillator system, initially in the ground state and subjected to an oscillating electric field, the

distribution among the levels is

$$P(n) = \frac{M^n}{n!} e^{-N} \qquad (23)$$

where M varies with time such that $M\hbar\omega$ is the mean energy absorbed by the oscillator as a function of time (which, by the way, may be computed classically). The mean value of n is N and the variance is $\sqrt{M}$, so that, in effect, the system has been transferred to a small number of levels in the neighborhood of n = M, and the transition between n = M and n = 0, say, has been inverted. We expect similar behavior in our anharmonic well, although an actual calculation of the inversion one could produce this way would be difficult.

With the nested well configuration we have postulated, it should therefore be possible, with a sufficiently intense short infrared pulse, to transfer a finite fraction of the system from the v = 0 state of the lower well to the v = 0 state of the upper well, thereby inverting the corresponding electronic transition and making laser action possible at the optical frequency.

d. Recommendations

The important thing is to determine whether with real molecules and manageable infrared laser fluxes one can in fact excite very high vibrational modes. The work of Karlov et al. (1970) on BCl_3, Letokhov on BCl_3 and NH_3, and Rhodes (1974) on NH_3 suggest that one can. (These experimenters dissociate their molecules with intense infrared fields). It would be useful to see whether the qualitative theoretical predictions (e.g., value of threshold flux, and isotopic enrichment of dissociated fragments) are borne out by existing experiments. If they are, it would be useful to have a more detailed theory that attempts a

more accurate (no doubt numerical) evaluation of transition rates and seriously concerns itself with the effect of collisions and loss rates to other modes. With such information in hand it would be possible to decide whether any useful physical realizations of the schemes discussed here are possible.

A level of effort of approximately five men is recommended to pursue both the experimental and theoretical issues of this problem.

B. Isotope Separation and Selective Photochemical Processes[†]

1. Introduction

Isotope shifts occur in the spectra of atoms and molecules. The shifts allow the selective preparation of one isotopic species in an excited state in which, by further modification, it may be separated from the other isotopic species (Letokhov, 1973; Moore, 1973). These further modifications include the spontaneous change from a predissociative (autoionizing) to a dissociative (ionized) state as well as chemical reactions in the excited state. Alternatively, once the initial selective excitation process has occurred, further nonselective electromagnetic excitation can occur to dissociative (ionized) or predissociative (autoionizing) states. Processes that change physical properties of the molecule or atom without changing the chemical or electronic composition can also be considered.

Laser radiation is an appropriate excitation source because of its high spectral purity, spatial coherence, and polarization properties.

[†] This section was prepared by C. B. Moore and P. L. Kelley.

The spatial coherence available from a laser is important to simplify optical systems and to obtain beams of sufficient intensity to saturate single-photon transitions and to produce efficient multiphoton excitation.†

We now discuss several illustrative cases in more detail: (1) With varying degrees of difficulty and expenditure of energy we can make an atomic vapor of a given element. Selective excitation is produced in one of the isotopes between the ground state and a higher-energy bound state. A second photon produces a nonselective transition between the excited bound state and the continuum of ionized states. The ionized isotopic atom is then separated from the other un-ionized isotopes by electrostatic deflection (Levy and Janes, 1970). (2) Molecular gases containing an element whose isotopes we wish to separate can generally be produced at high room-temperature vapor pressures with reasonable expenditures of energy. Vibration-rotation spectra occur that show isotopic shifts; however, the electronic transitions become more complex and therefore selective electronic excitation becomes more difficult for heavy molecules as well as for those containing more than several atoms. A typical scheme consists of selective vibrational excitation coupled with photodissociation or photopredissociation (Ambartsumian et al., 1973; Rockwood and Rabideau, 1974). Alternatively, for simpler molecules, single-photon photopredissociation may be used (Yeung and Moore, 1972). (3) Momentum may be transferred to atoms or molecules containing a given isotope by repeated selective resonance absorption and fluorescence (Ashkin, 1970). Such deflection schemes are most appropriate in atomic

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†By minimizing the momentum transfer to an atom or molecule multiphoton absorption the Doppler effect can be reduced or eliminated, thereby increasing absorption and selectivity. This effect was first suggested by Vasilenko et al. (1970). Further information and additional references may be found in Chebotaev et al. (1974), and Kelley et al. (1974).

systems where oscillator strengths are large. Schemes for coherently re-emitting the radiation have been proposed so that more efficient use can be made of the energy in the radiation field (Szöke and Nebenzahl, 1974). (4) In Section III-B-4 we consider another method of separation in which photoexcitation is used to change the electrostatic and/or magnetostatic properties of neutral molecules or atoms. Field gradients are then used to separate the isotopic species. Table 7 lists laser isotope separation processes that have been studied experimentally.

A number of difficulties may occur in laser isotope separation processes that can cause a decrease in the degree of separation and in overall efficiency. The initial excitation process may not be sufficiently selective on account of the complexity of the spectra or the small fractional presence of the desired isotope. Once the initial selective excitation occurs, the selectivity may be lost due to energy-transferring collisions between isotopic species or the excitation may be lost to radiative decay or to nonradiative internal decay. Perhaps the most formidable difficulties occur after ionization dissociation or chemical change. In the case of ionization, for example, charge exchange may occur and high separation factors may be lost. Adverse molecular interchanges can occur in a wide variety of ways. The discussion of these potential adverse processes for a specific case of bromine isotope separation is given later in this report.

We next consider some of the reasons why efficient separation of isotopes may be desirable. It is worthwhile first to note that the minimum energy per particle of the desired isotope, assuming complete separation and isothermal conditions, is

$$\Delta u_{min} = -kT \left\{ \ln f + \left(\frac{1-f}{f} \right) \ln(1-f) \right\} \qquad (24)$$

Table 7

ISOTOPE SEPARATION EXPERIMENTS

Isotopes	Initial Molecule	Process	Comments	Reference
$^{79}Br - ^{81}Br$	Br_2	1-step excitation of electronic state plus collisionally induced dissociation	Didn't work	Tiffany et al. (1968)
$^{1}H - ^{2}H$	CH_3COOH	Vibrational absorption	Not reproducible	Mayer et al. (1970)
$^{1}H - ^{2}H$	H_2CO	1-step predissociation		Yeung and Moore (1972)
$^{14}N - ^{15}N$	NH_3	2-step dissociation		Ambartsumian et al. (1973)
$^{235}U - ^{238}U$	U	2-step ionization		Levy and Janes (1970); Tuccio et al. (1974)
$^{79}Br - ^{81}Br$	Br_2	1-step predissociation		Letokhov (1974)
$^{40}Ca - ^{n}Ca$	Ca	2-step ionization		Brinkman et al. (1974)
$^{138}Ba - ^{n}Ba$	Ba	Photodeflection		Leone and Moore (1974)
$^{10}B - ^{11}B$	BCl_3	2-step dissociation		Rockwood and Rabideau (1974)

where f is the initial fraction. As an example, for the complete separation at room temperature of ^{235}U initially in natural abundance (0.7%) we require about 1/6 eV per atom (1.6×10^4 J/mole or 5×10^{-3} kW-hr/mole). In contrast, diffusion plants require about a factor 5×10^7 more energy. It is estimated that with diffusion-plant technology about one hundred billion dollars must be spent in the next 15 to 20 years on uranium enrichment in order to meet expected U.S. electrical power needs. Clearly, a less expensive enrichment scheme would have a significant economic impact. Lighter isotopes (C, O, N), which are of interest in medicine and biology, are currently prepared in small quantities by distillation at an energy expenditure of the order of 10^4 kW-hr/mole. Reducing the cost of these isotopes could increase demand. A scheme in which most of the energy expenditure is in the absorption of visible or UV photons ($\sim$ 5 eV), then, will require about 5×10^5 J/mole or 0.15 kW-hr/mole. Even with typical laser efficiencies of about 10^{-3} the energy expenditure is much less than that of diffusion or distillation. This, of course, does not take into account expenditures of energy other than on the laser--for example, that used in heating a metal to obtain reasonable atomic vapor pressures.

2. Uranium Isotope Separation

It is apparent from the discussion in the introduction that efficient uranium isotope separation is of considerable economic significance. As a consequence, the U.S. AEC (principally at Los Alamos and Livermore), commercial enterprises such as the joint AVCO-EXXON venture, and a number of foreign organizations are actively pursuing laser isotope separation. In the fall of 1973 AVCO-EXXON announced the successful separation of ^{235}U with lasers, although details of the experimental results (including separation rates) were not given. AVCO-EXXON had earlier obtained a patent (Levy and Janes, 1970) for a process that involves vaporization in an oven of uranium metal to produce a beam of

atomic uranium, 2-step selective photoionization of ^{235}U, and magneto-hydrodynamic separation of the ionized atoms. Tuccio et al. (1974) gave experimental results on separation using a technique similar to that described in the AVCO-EXXON patent. Electrostatic deflection was used in the spatial-separation stage of the process. Recently, AVCO-EXXON workers have suggested electron-beam vaporization of uranium metal as the source for the atomic beam. There is considerable energy expenditure ($> 10^3$ eV) in vaporizing uranium metal to obtain an atomic beam. To achieve high throughputs, either very large systems or high vapor pressures are required. Vapor pressures are limited by adverse collisional processes such as the charge exchange reaction

$$^{235}U^+ + {}^{238}U \rightarrow {}^{235}U + {}^{238}U^+ . \qquad (25)$$

Finally, large values of the product of density and optical path are required because of low cross section for optical ionization. It should be noted that atomic deflection schemes also suffer from vapor-pressure limitations because of the adverse effect of velocity-changing collisons. In addition, if a quantum is used just once, only a small fraction ($h\nu/2\ mc^2$) of its energy goes into deflection and a considerable inefficiency results. Coherent absorption and re-emission processes have been suggested to overcome this difficulty--for example, adiabatic fast passage (Szöke and Nebenzahl, 1974).

Molecular techniques are also being considered for uranium isotope separation. A number of 5- and 7-atom molecules are known that have reasonable vapor pressures near room temperature. These spectra are expected to be exceedingly complex under normal conditions both for electronic transitions (visible and UV) and for vibration-rotation transitions (infrared). The photochemistry of these molecules is at best poorly understood and there is virtually no information on the isotopic selectivity of

these processes. A major advantage of many molecular schemes is the higher density, and therefore shorter path lengths than are possible with atomic processes.

3. Other Elements

The separation of isotopes of many elements at low cost can be expected to open up new applications for isotopes in research, medicine, and technology. Each possible application will have a cost threshold and cost demand curve. Applications for Calutron (mass spectrometer) separated material are very limited indeed. Prices are on the order of 10^6 dollars/mole and demand about 10^6 dollars/year. Laser methods requiring low vapor densities should have lower costs than Calutrons; photochemical and predissociation laser processes at high vapor densities will be considerably less expensive. However, each element is likely to require a method specific to its own chemistry and spectroscopy. It is important to evaluate the feasibility and economics of applications for separated isotopes to establish priorities for research and development work on separation-methods.

Experimental results have been reported for several separation schemes at pressures above 1 torr: D_2CO, photopredissociation (Yeung and Moore, 1972); BCl_3 (Rockwood and Rabideau, 1974) and $^{15}NH_3$, two-step photodissociation; ortho and para I_2 (Bernhardt et al., 1974), electronic photochemistry; and $^{81}Br_2$ (Letokhov, 1974),† collision-induced predissociation. In spite of the considerable quantity of new data in these reports, more fundamental spectroscopic, kinetic, and energy-transfer research is necessary before engineering design work may begin. The

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†O- and p- I_2 were separated by excitation of one species with an Argon laser. The excited molecules reacted with 2-hexene.

molecular bromine example (Leone and Moore, 1974) illustrates the research and development problems common to most of these separation schemes. Molecular bromine may be excited selectively in its resolved vibronic band spectrum. However, the overlapping continuum absorption is not selectively excitable.

$$^{n}Br_2 + h\nu \begin{cases} \xrightarrow{\text{bands}} {}^{81}Br_2^* & (26) \\ \xrightarrow{\text{continuum}} {}^{n}Br_2^* \quad . & (27) \end{cases}$$

Addition of a reactive second gas to this system dissociates the excited Br_2 and then reacts with the atoms to produce a chemical product:

$$^{81}Br_2^* + HI \rightarrow 2\,{}^{81}Br + HI \qquad (28)$$

$$HI + {}^{81}Br \rightarrow H{}^{81}Br + I \quad . \qquad (29)$$

Of course the mixed atoms, ^{n}Br, produced by continuum absorption give mixed-product $H{}^{n}Br$. Scrambling also occurs when

$$^{81}Br_2^* + {}^{n}Br_2 \rightarrow {}^{81}Br_2 + {}^{n}Br_2^* \qquad (30)$$

and

$$^{81}Br + {}^{n}Br_2 \rightarrow {}^{81}Br\,{}^{n}Br + {}^{n}Br \quad . \qquad (31)$$

Furthermore, the much slower processes

$$^{n}Br_2 + HI \rightarrow {}^{n}BrI + H{}^{n}Br \qquad (32)$$

$$I + {}^{n}Br_2 \rightleftarrows I{}^{n}Br + {}^{n}Br \qquad (33)$$

and perhaps

$$^{n}Br + H^{81}Br \rightleftarrows H^{n}Br + {}^{81}Br \qquad (34)$$

prevent the final collection of a separated product.

The rate constants for most of these processes are unknown and must be measured in a variety of experiments. In fact, the ideas for the separation scheme developed out of a basic research program to measure rates for reactions (29) and (34). The spectroscopy must also be studied in much more detail. This need for fundamental spectroscopic and kinetic data is typical of chemical schemes for isotope separation. Explorations of the effect of infrared radiation on chemical reaction rates have just begun. Much of this basic research impacts directly on the discovery and development of new high-energy laser mechanisms. Table 7 summarizes the current status of experimental isotope separation efforts.

4. The Possible Separation of Isotopes by Photoinduced Changes in the Electrostatic and Magnetostatic Properties of Atoms and Molecules[†]

Photochemical and photoionization methods have been proposed for isotope separation. Photodeflection has also been considered a means of isotope separation in which only transitions between bound states occur. We discuss here another method of separation in which photoexcitation is used to change the electrostatic and/or magnetostatic properties of bound molecules or atoms. The excitation process can change electric dipole moment, electric polarizability, magnetic dipole moment, and magnetic polarizability. Field gradients then exert forces on the molecule

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[†]This section was prepared by P. L. Kelley, N. Kroll, and C. Rhodes.

or atom. The forces can be particularly large when the first-order Stark or Zeeman effect exists or when Stark or Zeeman coupled energy levels are initially split by such small amounts that only modest field strengths are required to cause substantial changes in the level splittings. We will consider the situation in which the electrostatic or magnetostatic forces act perpendicular to an atomic or molecular beam and separation is achieved by the difference between the deflection of the excited molecules and the deflection of the unexcited molecules.

We show that a degree of separation approaching 100% can be obtained provided that the ratio of the achievable Stark or Zeeman shift difference to the transverse thermal energy is sufficiently large (say, ~ 5).

Let d_o be the initial beam diameter, u_T a measure of the transverse velocities, and τ the interaction time. Then the final beam diameter, d, is given by

$$d = d_o + u_T \tau \quad . \tag{35}$$

Separation is achieved provided that the deflection difference Δ for the two species is greater than or equal to d. For the electrostatic case, the force difference, δF, is approximately related to the Stark shift difference δE_s via the relation

$$\delta E_s = \mathcal{E} \cdot \delta\mu \cong \Delta \delta F \tag{36}$$

where δu is the electric dipole moment difference and $\mathcal{E}$ the applied electric field. We have assumed that the field gradient is of the order of $\mathcal{E}/\Delta$. Hence,

$$\Delta = \frac{1}{2} \frac{\delta F}{m} \tau^2 = \frac{1}{2} \frac{\delta E_s}{\Delta m} \tau^2 \tag{37}$$

or

$$\Delta = \sqrt{\frac{\delta E_s}{2m}}\,\tau \quad . \tag{38}$$

Now setting Δ equal to d yields

$$\tau = \frac{d_o}{\sqrt{\frac{\delta \mathcal{E}_s}{2m}} - u_T} \tag{39}$$

and since τ is intrinsically positive,

$$\delta \mathcal{E}_s > 2mu_T^2 \tag{40}$$

and

$$\frac{\Delta}{d_o} = \frac{1}{\sqrt{1 - \frac{2mu_T^2}{\delta E_s}}} \quad . \tag{41}$$

Taking $\mathcal{E} \sim 10^5$ V/cm as the maximum usable electric-field strength, one finds $\delta E_s/\delta \ell = 0.53 \times 10^{-3}$ eV/Debye, which implies a need for transverse temperatures less than 10°K and perhaps typically of the order of or less than 1°K. The required beam might be formed by expansion cooling through a nozzle followed by collimation to limit the transverse velocities. Multiple beams each having a small variation in transverse velocity could be formed from the output of a single nozzle. For less than nearly complete separation we may relax the condition that the dipolar energy exceed the transverse thermal energy.

To estimate throughput we note that the beam current J is given by $\pi/4\ d^2 \rho v_L$, where ρ is the particle density and v_L the longitudinal velocity. For a beam length L, longitudinal velicity spread Δv_L, and scattering cross section σ, collisions limit the density to

$$\rho = \frac{1}{\sigma L} \frac{v_L}{\Delta v_L} \quad . \tag{42}$$

Thus,

$$J = \frac{\pi d^2 v_L}{4\sigma L} \frac{v_L}{\Delta v_L} \cong \frac{\pi d u_T}{4\sigma} \frac{v_L}{\Delta v_L} \tag{43}$$

As typical values we take $v_L/\Delta v_L = 10$, $u_T \cong 10^3$ cm/s, $\sigma \cong 10^{-14}$ cm^2, and d = 1 cm to yield $J = 10^{18}$ s^{-1} per beam.

5. Recommendations

We recommend the following:

(1) That fundamental research in photochemistry, chemical kinetics, energy transfer, and spectroscopy related to isotope separation be broadly supported.

(2) That efforts to develop ^{235}U enrichment methods be as broad in scope as possible and that fundamental measurements be made for all promising schemes before efforts are narrowed to one or two large-scale engineering programs.

(3) That the feasibility of new applications of separated isotopes be carefully evaluated.

(4) That emphasis be given to development of tunable (both stepwise and continuous) high-intensity lasers with the ultimate goal of high efficiency. There is particular need for efficient sources both in the visible and near UV and the results of laser development programs suggested in the previous section can have considerable impact on laser isotope separation and photochemistry.

C. X-Ray and Gamma-Ray Lasers[†]

1. X-Ray Lasers

The distinction between X-rays and ultraviolet radiation is arbitrary, and so is the definition of an X-ray laser. For our current purposes it is useful to consider as X-rays photons with energies $h\nu \gtrsim$ 100 eV ($\lambda < 124$ Å). We begin by noting that the problems of producing a laser in the X-ray region are very different from those of the soft ultraviolet ($h\nu \lesssim 1$ Rydberg = 13.6 eV), visible, and infrared regions. At the lower photon energies the complexities of molecular physics, chemistry, and kinetics provide many opportunities for the experimentalist (or nature) to be ingenious in producing the necessary inversions. However, this complexity, and ignorance of cross section and rate coefficients for the numerous complex processes that occur, make theoretical calculations uncertain and difficult; this is true of chemical processes in general. In contrast, X-ray transitions occur between tightly bound states of highly ionized atoms. The properties of such states vary slowly along isoelectronic sequences. Since binding energies are much greater than a Rydberg, the wave functions are nearly hydrogenic and the cross section and rate coefficients for all important processes may be calculated. Finally, there are no molecules. The experimenter who attempts to construct an X-ray laser can control only a few parameters: the atomic number Z of the material, its initial density and geometry, and the time history of the applied energy source. Then it is possible to calculate the time-history of the various atomic state occupation numbers, and thus to determine whether a sufficient inversion occurs. The feasibility of ab initio calculations for X-ray laser systems means

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[†] This section was prepared by J. Katz.

that the approach to their design can, and must, be different from that of designing lower-frequency lasers. Only designs for X-ray lasers that have been shown to be promising by calculation justify experimental test. Many schemes fail by several orders of magnitude for well understood physical reasons; experimental tests of these are a waste of effort. Unfortunately, several experiments that have been done fall in this category. The situation resembles that in laser fusion, in that interesting and informative experiments require a great deal of calculation and careful preparation, while irradiation with available resources is easy, but useless. Both X-ray lasers and laser fusion make exacting demands on visible or near-visible lasers (the only energy source feasible for X-ray lasers, as will be seen), and the development of these lasers is an essential and difficult task.

The relative simplicity of X-ray lasers physics is offset by the demanding criteria for successful operation. The cross section of an atom in the excited state for stimulated emission at the peak of a line whose only width is its natural (spontaneous decay) width is given by

$$\sigma_o = \frac{\lambda^2}{2\pi} \tag{44}$$

at the center of a Breit-Wigner line profile. It is clear from this expression alone that as the wavelength becomes smaller it becomes harder to make a laser. Any inversion of a state with an excitation potential in the X-ray region will very rapidly relax as the spontaneous decay rate for allowed transitions usually scales as λ^{-2} and is about 10^{+13}/s at 10 Å. For this reason, and because efficient X-ray mirrors are difficult or impossible to produce, the most favorable design for an X-ray laser is a traveling-wave excitation device similar to the type developed by Shipman (1967). A region of population inversion, and net gain, moves along a column of laser medium at the speed of light. Instead of an

oscillator, the laser is a superradiant amplifier, which amplifies its own spontaneous emission. A pulse of radiation that moves along the column with the region of population inversion is amplified, and constitutes the laser output. For successful operation (and a reasonable design safety factor) this column must have a length of at least 100 small signal gain lengths. If losses are ignored, this gives the condition on the inversion density N^*:

$$N^* > 100 \frac{2\pi}{\lambda^2} \frac{\Delta\nu\tau_{SP}}{\ell} \tag{45}$$

where ℓ is the length of the lasing column, $\Delta\nu$ is the bandwidth of the transition, and τ_{SP} is its spontaneous lifetime. The bandwidth $\Delta\nu$ is large because of Stark and Doppler broadening (in hot matter) or the Auger effect (if the matter is cold enough so that outer-shell electrons remain bound). Consequently, $\Delta\nu\tau_{SP} >> 1$, the effective cross-section (averaged over the broadened line) for stimulated emission is very much less than σ_c, and large values of N^* are required. For example, at solid density for 1-keV photons with ℓ = 1 cm, $N^* > 10^{20}/cm^3$ results. Combining this inversion density and photon energy with a pulse length of 30 ps (the light travel time for a 1-cm column) gives a power density of about $10^{18.5}$ W/cm^3 to ionize the matter and produce the inversion. We have taken an efficiency of 10^{-4} because all the atoms, not only those inverted, must be ionized, and the energy of ionization per atom exceeds the energy of the lasing transition. The point of this very crude estimate is that the volume of inverted material must be very small. In a natural design the column of lasing material is only 1 μ in diameter, so the volume is 10^{-8} cm^3 and the required power is $10^{10.5}$ W. This power must be supplied for 30 ps for a 1-cm-long column, which gives a total pulse energy of 1 J. These numbers are only ballpark estimates, but

even so we see that the only feasible energy source for such a design is a near-diffraction-limited visible (or near-visible) laser. A major component of an X-ray laser development project must be the development of short-pulsed lasers, both to advance the technology in this area in general and to construct a laser to meet the specifications determined by a quantitive study of an X-ray laser design. Our estimates of the energy required are independent of the inversion density but depend on the inversion fraction; lower inversion fractions require larger ℓ or larger density and larger total energies. We have considered only one source of energy loss, and have ignored the inefficiency of conversion of the power source to ionization energy. The crude estimates of this paragraph are sufficient to point to designs involving traveling-wave excitation of a very thin fiber, with the power source a picosecond-pulsed laser. The general constraints summarized here were developed in detail by the LLL group (Wood et al., 1973; Wood et al., 1974) and in outline at NRL (Ali, 1974) and at MIT (Lax and Guenther, 1972).

We have discussed some necessary energetic constraints on an X-ray laser, but have not yet established that it is actually possible to produce a population inversion. This can be established only by a detailed numerical calculation of the populations of the various ionization and excitation states with time, including the processes of collisional and radiative ionization, recombination, excitation, and de-excitation, including dielectronic recombination and the Auger effect. Fortunately, rates for all these processes can be calculated for hydrogenic wave functions (an adequate approximation for highly ionized atoms). The calculation of the various state populations to the necessary accuracy is expected to be feasible with present-day large computers. The atomic physics calculations require as input the output of a hydrodynamic and energy-transport code that calculates the deposition of power from the external source, its transport, and the resulting hydrodynamics and

variations of temperature and density with time and space. The atomic physics code and the hydrodynamics code should run coupled together, since the hydrodynamics sets the boundary conditions on the atomic physics, and the atomic physics affects the equation of state and transport properties (especially the radiation rate) of the hydrodynamics.

One possible way of obtaining an inversion is to find an ion for which collisional excitation and radiative decay in steady state give an inversion. One example of such a scheme is due to Elton (1974a), who discusses the collisionally excited $2p3p\ ^3D \rightarrow 2p3s\ ^3P$ transitions of the carbon isoelectronic sequence. Unfortunately, the energy of this transition scales as the Z of the ion (the energy difference being a result of configuration interaction), and reaches 100 eV for $Z > 100$. Further, to avoid collisional de-excitation of the upper level requires low densities and very large systems; estimated gains are 0.1/cm. The resulting laser would have to be $\approx$ 10 m long, which presents enormous pumping problems. The system is very inefficient, because atoms have to be kept ionized to an ionization potential that scales as Z^2, to extract an energy that scales as Z. The inversion density is low ($\approx 2 \times 10^{-4}$ for $Z \approx 30$-40), which makes the system very sensitive to possible losses, such as photoionization from less completely ionized species; this is not calculated. A steady-state approximation is used but not justified. In many ways this paper is a good example of how not to design an X-ray laser, because many physical processes that must occur (hydrodynamics, radiative recombination, etc.) are ignored without justification in the interests of a tractable analytical calculation.

A scheme related to the preceding one involves the steady-state photoionization of inner-shell electrons (Stankevich 1970; Elton 1974b). A single hole in the K shell is an inverted population (with respect to holes in the L shell), and if L-shell holes decay fast enough the inversion may be maintained. Again, the problem with published calculations

is that most of the physics has been excluded from the discussion. For example, at the very high ionization rate required to overcome photoionization losses the matter heats and its ionization balance changes. Also, no photoionization source of suitable intensity and spectrum exists; the design of such a source would be the major part of the design of an X-ray laser in this scheme.

A different approach toward obtaining an inversion uses rapidly changing physical conditions to obtain rapidly changing steady-state ionization and excitation levels. The finite rate of relaxation of the actual ionization and excitation conditions to the steady state appropriate to the varying physical parameters leads to deviations from the steady-state occupation numbers and to possible inversion. One form of this scheme is that of Duguay and Rentzepis (1967), who use a rapidly rising pulse of X-ray radiation to create an inversion of K-holes with respect to L-holes [they do not rely on the rapid L-hole decay estimated by Stankevich (1970) and Elton (1974b)]. Another version (Wood, et al , 1973, 1974) uses the rapid adiabatic decompression (the time scale is 1 ps for a 1-μ fiber) and cooling of a laser-heated fiber to produce an inversion by collisional recombination. At high densities (this scheme would operate near solid density) collisional recombination, which preferentially populates upper states, dominates radiative recombination, which preferentially populates the lower states, and an inversion of n = 3 levels with respect to n = 2 levels may result. These schemes also have not been verified by a full computation.

Some general principles must guide the design of X-ray lasers, and these may be seen without detailed calculation. (1) As previously emphasized, the short wavelength requires a high inversion density, a high power density, and a high state of ionization. (2) The large Stark or Doppler line broadening means that for a metastable transition the bandwidth is independent of the spontaneous decay rate, so the required

inversion density increases inversely as the spontaneous decay rate. If the pumping rate is held fixed, and there are no other decay mechanisms, then the inversion density does increase at the required rate. However, if some competitive process occurs (as collisional de-excitation must occur), then the inversion density does not become that large, and gain is reduced. Consequently, metastable X-ray lasing transitions are probably not feasible. (3) Because radiative decay rates are rapid, upper-state occupation numbers tend to be very small. However, electrons will accumulate in the ground state. Therefore, it is very difficult to invert a resonance transition. (4) The distribution of ionization potentials will be very similar for all species. Therefore, although charge exchange and excitation transfer will occur (and may be important), pumping of highly excited levels by near-resonant charge exchange (Sobel'man, 1972) and the bulk-matter analogs of the beam-target scheme of Scully et al. (1973) are very unlikely to produce inversions. (5) The opacity of matter for soft X-rays is rather high. A lower bound is set by the electron scattering opacity of 0.2 cm^2/gm, but the photoelectric opacity may be much higher. This is in contrast to near-visible photons, for which opacities are often less than 10^{-3} cm^2/gm. The high soft-X-ray opacity means that inversion densities must be high to overcome these losses. Also, the useful length of an X-ray laser (amplifier) is limited to one absorption optical depth beyond the point where the gain has saturated. After that, further inversion energy does not appear in the output beam, but instead is reabsorbed within the laser.

We believe the following steps should be taken to convert the X-ray laser from speculation to hardware. A specific quantitative design must be developed that predicts an inversion and gain when calculated with the hydrodynamics and atomic physics codes. It is a prerequisite to this design study that the codes exist. The laser power-source requirements should be within the bounds that have been actually achieved with

such lasers, and preferably the laser energy required should not exceed 1 J. The first design should be for a very soft X-ray lasing frequency, with 100 eV < hν < 300 eV. Simultaneous with this work should be development of a picosecond-pulse laser system that can meet the specifications of the X-ray laser project. Once a design exists for which the codes predict X-ray lasing, this design must be experimentally tested. A clear test for X-ray lasing is the presence of an intense collimated (angular width ~ 0.1 mrad with the parameters we have been discussing) beam of monochromatic radiation directed along the fiber axis. Only such a beam is evidence of lasing. In the absence of lasing, the X-ray intensity is a minimum in this direction, due to projection-angle effects. The various reports in the literature of anomalous line ratios, bright emission lines, etc., are all evidence of the complexity of radiative transport, but do not imply lasing. It is important that the initial experiment be modest (use long wavelengths) and be conservatively designed. Only if it is successful is there reason to try to develop lasers at shorter wavelengths. Experiments that do not use carefully computed designs have very little possibility of success and do not justify support.

2. Gamma-Ray Lasers

Gamma-ray lasers present a problem even more exotic than X-ray lasers, and are definitely much more difficult to realize. The definition of a gamma ray is a photon emitted by a transition between internal states of a nucleus. With one exception, all known gamma rays have energies of at least several keV, and most transitions of interest for gamma-ray lasers have energies of several tens of keV. The exception is the 75-eV isomeric transition of U^{235}. However, this transition has only been observed by electron conversion from the P shell, and never as a photon (the conversion coefficient may be estimated from the Weisskopf electromagnetic transition rate expressions, and the observed half-life is between 10^{15} and 10^{20} s)

and is therefore of no interest to us. The possibility of gamma-ray lasers was first suggested shortly after the development of optical lasers (Vali and Vali, 1963) and has been revived several times since. Three different kinds of schemes have been proposed. These are discussed below.

Scheme 1. The laser medium is a hot plasma, in which a high nuclear inversion density has been produced by rapid neutron reactions [such as (n, γ), (n, p), etc]. The required intense neutron flux is produced by a nuclear explosion or a laser-produced micro explosion. This approach has been discussed by Wood and Chapline (1973), and by Wood et al. (1974), who find that it requires very favorable cross-sections, branching ratios, and rapid electromagnetic transition rates. These requirements are unlikely to be met. The detailed nuclear data required for quantitative evaluation of this scheme do not exist, and would require a major effort to obtain.

Scheme 2. The laser medium is a cold crystal, in which isomers of spontaneous half-life $\sim$ 1 μs undergo stimulated Mossbauer transitions. The isomers are produced by a burst of neutrons as in Scheme 1, but now the neutrons have been thermalized. This was suggested and discussed by Gol'danskii and Kagan (1973). The neutron fluxes required are enormous, and inconsistent with a cold crystal in which the Mossbauer effect takes place. These authors suggest a dilute alloy of beryllium and the species that undergoes neutron reactions in order to reduce the neutron heating effects, but the required dilutions are large and this scheme appears infeasible. In a later paper Gol'danskii et al. (1973), attempt to reduce the required neutron fluxes by proposing a method for concentrating the isomeric excitation of the first (dilute) target in a second target. The method is Mossbauer spontaneous emission and resonant absorption. Although this can concentrate the excitation, in a two-level system it can

never produce inversion in the second target, because in any region where the upper and lower state population (divided by their respective statistical weights) become equal, absorption ceases. Since some photoelectric absorption is always present, the gain in the second target must always be negative. Inversions may be produced in a three-level system, where the third level is a nuclear state intermediate in energy between the other two, or where an external RF field is used to alter the population of magnetic or hyperfine substates (very low temperature and large polarizing fields are required to produce an appreciable effect). Even when the inversion-concentration works, required neutron fluxes are extreme and this method of obtaining a gamma-ray laser is unpromising.

Scheme 3. Isomeric states of spontaneous half-life $\gtrsim$ 1000 sec are produced in a reactor or accelerator, and are separated to make a pure crystal, which produces coherent radiation by stimulated Mossbauer transitions. This was the original scheme of Vali and Vali (1963), and has been re-discussed by Wood and Chapline (1973) and by Wood et al. (1974). It must be remembered that even if this scheme is successful, the output pulse has a time duration of not very much less than the spontaneous half-life (due to the uncertainty principle and broadening of the levels by the stimulated emission rate). The pulse is highly directional, however, just as in X-ray lasers. For this scheme to work, it is necessary that extraordinarily narrow ($Q > 10^{22}$) Mossbauer transitions be obtained. The narrowest Mossbauer lines yet observed have $Q \sim 10^{15}$, in Zn^{67} and Ag^{107}. The latter isomer has a half-life of 63 s, and ideally $Q \sim 10^{21}$, but in fact the observation (Bizina et al., 1964) showed a line broadened by a factor of about 10^6 over its natural width. An early analysis (Ruby, 1963) showed that with this degree of broadening it is not possible to detect stimulated emission, much less produce a laser. The broadening has several sources--nuclear dipole-dipole coupling, chemical

impurities, and crystal dislocations. It is difficult to quantitatively estimate these effects. The need for chemical purity rules out isotopes and isomers that have appreciable α or β decay rates; this includes most interesting candidates. If there is no broadening, then for the pure isomeric material (complete inversion) a necessary condition for gain is

$$\sigma_{phot} < \frac{\lambda^2}{2\pi} \frac{f}{1+\alpha} \tag{46}$$

where σ_{phot} is the photoelectric absorption cross section per atom, f is the Mossbauer fraction (which may be close to 1), and α is the electron conversion coefficient (for which reliable calculations exist that may be looked up, if the transition type and multipolarity are known). The most promising isomers that are α and β stable fail to satisfy this criterion or do so only marginally. Dipole-dipole coupling introduces a width into the upper and lower states (unless a state has spin 0, in which case it is not broadened, but this can be the case for only one of the two levels) of the order of μ^2/r^3, where μ is a typical nuclear magnetic moment and r is the nearest-neighbor separation; this is typically a few kilohertz. This broadening has the effect of dividing the right-hand side of Eq. (46) by the factor $(\tau_{sp}\,\delta\nu)$, where τ_{sp} is the spontaneous lifetime of the isomer and $\delta\nu$ is the broadened width. This factor will be $\gtrsim 10^6$, and its inclusion clearly makes it impossible to satisfy Eq. (46). We know of no way to avoid this spin-spin broadening, and its presence makes the Mossbauer laser impossible to achieve.

We conclude that gamma-ray lasers do not appear to be possible within our present understanding. Work toward a better understanding of broadening processes in extremely narrow Mossbauer lines is interesting and appropriate; such work has other applications to Mossbauer studies. Aside from this, we do not consider work on gamma-ray lasers justified at the present time.

D. Free-Electron Lasers[†]

1. Introduction

The term "free-electron laser" refers to proposed amplification processes arising from the stimulation of emission in transitions between electron continuum states. These processes are variously identified as the stimulated Compton effect (Pantell et al., 1968), stimulated Brehmsstrahlung (Madey, 1971; Madey et al., 1973), stimulated Cerenkov radiation, and electron-beam-pumped parametric emission (Pantell, 1974). All the devices proposed depend on an electron beam for their operation and in all cases (except the stimulated-Compton-effect down-converter) the electron beam is the primary source of the energy.

A cursory inspection of many of the devices proposed discloses an evident similarity with conventional traveling-wave amplifiers. In particular, stimulated Cerenkov radiation would appear to correspond to the ordinary electron-beam traveling-wave amplifier, while the stimulated Brehmsstrahlung device proposed (Madey et al., 1973) appears to correspond to the undulator (Motz and Nalsurnura, 1960). An obstacle to this interpretation, noted (Madey et al., 1973) in connection with the undulator, resides in the fact that the classical traveling-wave small-signal gain formulas depend on $n_e^{1/3}$, where n_e is the electron number density, while gain via stimulated processes is characteristically proportional to n_e. The dependence on other parameters is also quite different in the two cases. Research currently in progress (McMullin and Kroll, 1974) has shown, however, that the difference resides in the fact that the classical calculations are carried out under the assumption $\frac{\delta v}{c} \ll \frac{\Gamma}{k}$, where δv is the longitudinal beam velocity spread, Γ the gain, and k the wavenumber; while the stimulated emission calculations have been carried out under the opposite assumption. It is a straightforward matter to extend either

[†] This section was prepared by N. Kroll.

calculation to the other domain and, in the cases examined, the results are then found to be identical. We conclude therefore that there is indeed no difference between these particular free-electron lasers and classical traveling-wave amplifiers (electron-beam-pumped parametric emission is an exception that will be discussed in Section III-D-3). The stimulated-emission point of view has been useful in identifying the previously overlooked $\xi v/c >> \Gamma/k$ regime, and in suggesting configurations (e.g., the stimulated Compton effect) that to the author's knowledge had not been previously proposed.

Another kind of parametric amplification process that may occur in sufficiently dense plasmas is the parametric conversion of a transverse electromagnetic wave into a lower-frequency transverse wave and a longitudinal plasma excitation (Goldman and Dubois, 1965). This process is often referred to as stimulated plasmon emission or as the plasma Raman effect. This process can also take place in a relativistic electron beam with backscattering of the incident radiation. On account of the Doppler shift of the backscattered radiation, the device becomes an up-conversion device with most of the energy coming from the kinetic energy of the electron beam. Strong submillimeter radiation has recently been observed from intense relativistic electron beams (Granatstein et al., 1974). It has been suggested that it arises from an analogous parametric conversion process (Sprangle and Granatstein, 1974). In these particular experiments an intense longitudinal magnetic field is present, which modifies the properties of the transverse waves, and the pump wave is close to the cutoff frequency. It is claimed that this circumstance significantly enhances the Raman process. More detailed discussion of these processes is deferred, pending the development of the relativistic theory.

2. The Stimulated Compton Effect

Backscattered Compton photons from relativistic electron beams have been successfully employed as a source of polarized monochromatic X-rays for research applications (Sinclair et al., 1969). It has been suggested that the stimulated version of this process might be achieved as a source of coherent radiation.

We consider an electron beam characterized as follows:

n_e = Electron density

p = z component of electron momentum

$F(p)$ = Distribution function in p normalized so that

$$\int_{-\infty}^{\infty} F(p)dp = 1.$$

The transverse momentum $\underset{\sim}{p}_\perp$ is assumed cylindrically symmetric and $\ll mc$. The distribution in p is also assumed to be narrow, about some mean value p_o, with energy γmc^2, and velocity $\beta = p_o/\gamma mc$.

An electron beam of frequency ω_1 is directed along the beam axis (as nearly as practical) in a direction opposite to the beam motion. There is then the possibility for amplification of a beam of frequency ω_2, directed along the beam direction. The gain Γ for this wave may be shown to be†

$$\Gamma = n_e \frac{d\sigma}{d\zeta}(\omega_1, p \to \omega_2, p') \frac{(2\pi)^3}{k_2^2} \frac{I_1}{\omega_1} \gamma m \frac{dF}{dp}\Bigg|_{p_r} \qquad (47)$$

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† Our formulas, Eqs. (47) and (50), differ from that of Pantell et al. (1968) by a factor of two because only one polarization should be included in the mode density formula [Eq. (6) of Pantell et al., 1968]. It is assumed that $|p-p'|$ is small compared to the width of the momentum distribution. Our equations are not restricted to the $\beta \approx 1$ region.

In Eq. (47), I_1 is the power per unit area in the frequency ω_1 beam, $k_2 = \omega_2/c$, the resonant momentum p_r satisfies $p_r = \beta_r mc/\sqrt{1 - \beta_r^2}$, and the resonant velocity $\beta_r c$ satisfies

$$\beta_r c = \frac{\omega_2 - \omega_1}{k_1 + k_2} \quad . \tag{48}$$

We see from Eqs. (47) and (48) that only the portion of the electron distribution that moves at the velocity of the beat wave between ω_1 and ω_2 participates in the process. The appearance of the derivative of the momentum distribution is a reflection of the fact that there is a competition between the gain process $(\omega_1, p_r \rightarrow \omega_2, p_r')$ and the inverse (loss) process $(\omega_2, p_r' \rightarrow \omega_1, p_r)$. Since we are assuming $\omega_2 > \omega_1$, then $p_r' = p_r - \hbar(\omega_2 - \omega_1) < p_r$. Gain occurs when the population at p_r is greater than that at p_r', corresponding to a position slope dF/dp.

Note that Eq. (48) may also be written

$$\frac{\omega_2}{\omega_1} = \frac{1 + \beta_r}{1 - \beta_r} = \gamma^2 \, (1 + \beta_r)^2 \tag{49}$$

so that a highly relativistic beam yields a large up-conversion. Down-conversion is of course also possible. If one chooses ω_2, ω_1 such that dF/dp is negative, then attenuation occurs at ω_2, but gain occurs at ω_1 and the electron beam gains energy. It should be recognized that whether a given process is an up-conversion or a down-conversion depends on the reference frame from which it is observed.

If ω_2', ω_1' are the frequencies as seen from the electron rest frame and, if $\hbar\omega_2'$, $\hbar\omega_1'$ are both small compared to mc^2, (as is the case for all remotely practical cases) then $d\sigma/d\Omega$ may be obtained by Lorentz transformation from the Thomson cross section and Eq. (47) becomes (for

parallel polarized beams)

$$\Gamma = n_e r_o^2 \frac{(2\pi)^3}{k_1 k_2} \frac{I_1}{\omega_1} m\gamma \frac{dF}{dp} \qquad (50)$$

where $r_o = e^2/mc^2$ is the classical electron radius. We note the absence of $\hbar$ in Eq. (50), which implies that the effect is entirely classical. To the author's knowledge, no classical derivation of the gain formula has been given previously, but research in progress (McMullin and Kroll, 1974) has led to Eq. (50) in the non-relativistic regime. A classical treatment is advantageous because it is simpler to take many important effects into account. These would include the effects of beam geometry, transient effects, and higher-order nonlinearities.

One important effect of beam geometry has been noted by Sukhatme and Wolff (1973). They point out that for finite beam length strict momentum conservation in the z direction no longer holds. As a result, electrons can interact over a velocity range given by

$$\Delta\beta_r = \frac{d\beta_r}{d(k_1 + k_2)} \Delta(k_1 + k_2) = \beta_r \frac{\Delta(k_1 + k_2)}{k_1 + k_2} \sim \frac{\beta_r}{k_2 L} \quad . \qquad (51)$$

The velocity width of the electron beam, $\delta\beta$, is related to the momentum width δp via

$$\delta\beta \sim \frac{\delta p}{mc\gamma^3} \quad . \qquad (52)$$

Equation (50) can be expected to hold only when $\Delta\beta_r < \sim \delta\beta$. When $\Delta\beta_r >> \delta\beta$ one expects the gain to be reduced from Eq. (50) because both positive and negative values of dF/dp can then contribute. Setting

$$\left|\frac{dF}{dp}\right|_{max} \cong \frac{1}{\delta p^2} = \frac{1}{(mc^2)\gamma^6 \Delta\beta_r^2} = \frac{k_2^2 L^2}{\beta_r^2 \gamma^6 (mc)^2} \tag{53}$$

we find,

$$(\Gamma)_{max} \sim n_e r_o^2 \frac{(2\pi)^3}{k_1 k_L} \frac{I_1 \gamma}{mc^2 \omega_1} \left(\frac{k_2 L}{\beta_r \gamma^3}\right)^2 \tag{54}$$

which, for the relativistic domain we rewrite as

$$(\Gamma)_{max} \sim \frac{n_e r_o^2 4(2\pi)^2}{\gamma^3} \left(\frac{I_1 L^2 \lambda_1}{mc^3}\right) \quad . \tag{55}$$

Equation (55) was derived under the assumption $\delta\beta \sim \Delta\beta_r$. It should give the correct order of magnitude, however, even when the velocity width of the beam is much narrower than $\Delta\beta_r$. One simply gets no additional advantage from the narrower distribution.

Equation (55) can no longer be expected to hold when Γ itself exceeds $1/L$. The reason is that under these conditions we expect $\Delta k \sim \Gamma$. To obtain an estimate we replace L by $1/\Gamma$ in Eq. (55) and solve for Γ to obtain

$$\Gamma \sim \frac{n_e^{1/3} r_o^{2/3} (4\pi)^{2/3}}{\gamma} \left(\frac{I_1 \lambda_1}{mc^3}\right)^{1/3} \quad . \tag{56}$$

We note that the $n_e^{1/3}$ dependence on the electron density is characteristic of classical electron-beam traveling-wave devices, which are usually discussed in terms of single-electron-velocity beams (so that $\Delta\beta_r > \delta\beta$ always holds). $\Gamma c\tau$ (τ is the pulsewidth) as well as ΓL must exceed one.

By comparison with the non-relativistic classical theory (McMullin and Kroll, 1974) we can infer the correct numerical coefficient for Eq. (56)--the missing numerical factor is $\sqrt{3}/(2\pi)^{1/3} \sim 0.93$. Hence,

$$\Gamma = \frac{2\sqrt{3} n_e^{1/3} r_o^{2/3} \pi^{1/3}}{\gamma} \left(\frac{I_1 \lambda_1}{mc^3} \right)^{1/3} . \qquad (57)$$

With the perhaps extreme values of $n_e = 10^{12}$ (a 5-kA/cm^2 beam), $I_1 = 10$ MW/cm^2, $\lambda_1 = 3$ cm, $\gamma = 10$, Eq. (6) yields $\Gamma = 0.05$ cm^{-1}, so that with a 1-m beam and some feedback, oscillation at 75 μ could be achieved. Because of the large power in the electron beam, large power outputs can be expected. The device also has the advantage of voltage tunability. It is to be noted that the gain is only weakly dependent on the wavelength. Hence, with the development of technology, a broad range of applicability cannot be ruled out.

3. Stimulated Brehmsstrahlung

Madey (1971), and Madey et al. (1973) have proposed a free-electron laser in which a relativistic electron beam is passed through a region where a spatially periodic transverse static magnetic field has been established. Assuming a sin(qz) spatial dependence for the external magnetic field, one easily finds that forward Brehmsstrahlung takes place at the angular frequency $\omega = \beta(1 + \beta)\gamma^2 qc$ ($\approx 2\gamma^2 qc$ for a highly relativistic beam), assuming $\hbar q \ll mc/\gamma(1 + \beta)$. Stimulation of the forward Brehmsstrahlung process leads to gain at frequency ω, which we find to be

$$\Gamma = \frac{\pi^2 r_o^2 B^2 m}{\beta(1 + \beta) q^3 \gamma} \frac{dF}{dp} \qquad (58)$$

where B is the static magnetic field. As in the case of the stimulated Compton effect, to which this process is closely analogous, the appearance of the derivative dF/dp of the momentum distribution function comes about as a result of the competition between stimulated Brehmsstrahlung and inverse Brehmsstrahlung. Again in analogy with the Compton effect, if $\delta p/mc \ll \gamma\Gamma/q(1+\beta)$, we set

$$\frac{dF}{dp} \sim \left[\frac{q(1+\beta)}{mc\gamma\Gamma}\right]^2 \quad , \tag{59}$$

insert in Eq. (58) and solve for Γ, to obtain

$$\Gamma = \left[n_e \pi^2 \frac{1+\beta}{\beta} \frac{r_o^2}{q\gamma^3} \frac{\beta^2}{mc^2}\right]^{1/3} \quad . \tag{60}$$

Equation (60) is in full agreement with the classical result of Motz and Nakamura (1960) as quoted by Madey et al. (1973) as far as its parametric dependence is concerned (there appears to be a numerical factor difference ~ 2.5, of as yet undetermined origin).

We conclude that there is no difference between this device and the classical undulator. The particular device proposed has been designed to produce a small gain at 10 μ. The principal motivation appears to be the experimental establishment of the "new" gain mechanism, and is in our view not well founded.

4. Electron-Beam-Pumped Parametric Emission

Pantell (1974) has pointed out that an electron beam passing through matter can emit two photons in the forward direction. That is, if one photon is in the visible region where the index of refraction $n \sim 1.5$, and the other in the X-ray region where we take $n \sim 1$ (and

ignore losses), then the emission of two photons in the forward direction with frequencies in the indicated regions becomes consistent with energy and momentum conservation. A parametric amplification process is therefore possible in which the electron beam plays the role of pump, photons of one frequency (say, the X-ray photons) play the role of signal, and photons of the other frequency (say, the visible photons) play the role of idler. The gain for such a process depends linearly on the electron density, and within some limits is independent of the electron distribution function. The idler spectrum is therefore incoherent and relatively broad. The absence of dependence on the derivative of the momentum distribution comes about because the process of two-photon absorption is less effective in canceling the gain than in the processes considered in the previous actions.

Even if the gain is too small to be interesting, parametric conversion--say, from visible to X-ray light--may, in principle, have significant amplitude. In this case, however, the X-ray emission is incoherent and relatively broad (in the context of lasers). This process bears a strong analogy with the backscattered spontaneous Compton scattering (Sinclair et al., 1969) referred to in Section III-D-2, and its potentiality can be most easily assessed by comparing the two processes.

Because the visible light is moving with a velocity c/n, in a reference frame in which the electrons are at rest, the direction of propagation of the visible light is reversed and the process becomes identical to backscattered Compton scattering (taking due account of the directional dependence of the index of refraction). Following the procedure suggested by this remark,[†] we find for the emission rate of the

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[†] Our analysis and results are in disagreement with those given by Pantell (1974). The treatment of the conversion process given by Pantell (1974) is erroneous.

upconverted photons, $dN_2/dtd\Omega$, in the beam direction,

$$\frac{dN_2}{d\Omega dt} = r_o^2 \frac{cE_1^2}{8\pi} \frac{(n\beta - 1)\gamma^2(1 + \beta)^2}{\hbar\omega_1} \tag{61}$$

$$= r_o^2 I_1 \frac{(n\beta - 1)\gamma^2(1 + \beta)^2}{n\hbar\omega_1} \tag{62}$$

where I_1 is the intensity of the visible light, and the frequency relation is

$$\omega_2 = (n\beta - 1)\gamma^2(1 + \beta)\omega_1 \quad . \tag{63}$$

To assess the value of this process we compare it with the alternative of omitting the transparent medium and producing backscattered photons at frequency ω_2, with incident photons at ω_1' and intensity I_1'. We find in this case

$$\left(\frac{dN_2}{d\Omega dt}\right)_{\text{Compton}} = r_o^2 I_1' \frac{\gamma^2(1 + \beta)^3}{\hbar\omega_1'} \tag{64}$$

with [from Eq. (49)]

$$\omega_2 = \gamma^2 (1 + \beta)^2 \omega_1' \quad . \tag{65}$$

Hence, with $n \sim 1.5$, $\beta \sim 1$,

$$\frac{\left(\frac{dN_2}{dtd\Omega}\right)_{\text{parametric conversion}}}{\left(\frac{dN_2}{dtd\Omega}\right)_{\text{Compton}}} = \frac{(n\beta - 1)^2}{n(1 + \beta)^2} \frac{I_1}{I_1'} = \frac{1}{24} \frac{I_1}{I_1'} \tag{66}$$

with

$$\omega_1 = \frac{(1 + \beta)}{(n\beta - 1)} \omega_1' \approx 4\omega_1' \quad . \tag{67}$$

The parametric conversion process appears therefore to have no region of utility.

We have also estimated the gain for the parametric amplification process and find

$$\Gamma = \frac{8\pi}{3} r_o^2 n_e \frac{n\beta - 1}{n} \approx 2.2 \times 10^{-25} n_e \text{ cm}^{-1} \quad (n_e \text{ in cm}^{-3}) \tag{68}$$

which is totally negligible.

5. Concluding Remarks and Recommendations

Experimental work with intense relativistic electron beams in the presence of a longitudinal magnetic field suggests the possibility that free-electron lasers may provide an important source of far-infrared radiation. Consequently, it would appear to be highly desirable to vigorously pursue this line of development. There is, however, no reason at present to be optimistic about the utility of this approach in the visible and shorter-wavelength regions. The possible utility of the stimulated Compton effect in such regions at some future time cannot, however, be totally ruled out.

Our brief investigation of this field has indicated a rather rudimentary level of theoretical analyses, a circumstance that handicaps the assessment of its possibilities. It is recommended that some effort be made to remedy this situation.

IV CONCLUSIONS AND RECOMMENDATIONS

In study an evaluation was made of promising current and proposed research efforts directed at realizing high-energy lasers in the visible and UV spectral regions and in certain related areas such as X-ray generation, photochemistry, and isotope separation. It became clear during th's effort that the realization of these goals is strongly dependent on, and limited by, the current unavailability of a body of knowledge in the atomic and molecular physics area. The area of concern can be broadly classified in the category of the physics and chemistry of electronically excited atoms and molecules. It is an area that has received insufficient attention in the past, but for which the tools of research either are available or are rapidly being developed. Therefore, it is our general conclusion that strong emphasis should be given to this area of research in the immediate future as the most efficient and economical means of removing these limitations and attaining the ultimate goal of HELs. The topics most urgently in need of attention have been defined in this report and are listed below together with a suggested level of effort.

A. Excimer Collisional and Radiative Transfer

Collisional and photolytic energy transfer from important excited species [e.g., $N_2(A^3\Sigma_u^+)$ and the rare gas atoms and dimers] has very promising direct application to a wide variety of electronic laser systems and considerable experimental effort should be focused on an evaluation of their properties. In particular, Reactions (1), (2), (4), and (5) in Section III-A-1 should receive emphasis. Of particular importance are

the transfer of excitation to specific states, dissociative excitation, quenching mechanisms, and energy pooling. An important fundamental consideration in this case is the experimental demonstration that the rare gas dimers are generated with high ($\sim 30\%$) efficiency in large volumes of high-density material. It is also essential that the kinetic mechanisms be understood for the dense environment (high-density gas or liquid phase) needed for the HEL medium. A level of effort of approximately 20 men is recommended to field the appropriate small scale kinetic studies specifically designed to appraise the energy-transfer processes.

B. Triatomic Structure

Since the details of the excited-state structure of relatively simple polyatomics, particularly triatomics, play a generally important role in the dynamics of many laser systems, stronger experimental and theoretical effort should be applied to determine their relevant properties. Of special interest are the construction of excited-state correlation diagrams and surfaces, an appraisal of curve-crossing and other excited-state coupling phenomena, and absolute photolytic quantum yields. We recommend a level of effort of 10 men in the pursuit of these goals.

C. Vibrational-to-Electronic Energy Transfer

Vibrational-to-electronic energy transfer (V-E) processes in combination with rapid V-V processes affords the possibility for efficient conversion of chemically produced vibrational energy into electronic excitation of appropriate acceptor species. The current effort is far less than that required to adequately pursue this field. An effort of 10 men including roughly comparable theoretical and experimental components is recommended.

Work on vibrationally driven reactions in connection with vibrational transition HELs should be maintained. Emphasis on studies with the goal of determining reaction mechanisms should definitely be encouraged. Expansion of support over the current level should be encouraged only when important new results appear or when a particular application arises. For example, considering the availability of infrared systems in the 5-μ and 10-μ region, advances here could have a strong impact on isotope separation (Section III-B).

D. Chemiluminescence (Theory and Experiment)

Studies on exothermic chemiluminescent reactions involving both free and bound metal atoms should continue at essentially the current level of national support. Efforts that exhibit imagination and indicate well-reasoned arguments concerning the channeling of the chemically liberated energy should be encouraged. Emphasis on the control of the released energy is preferred over randomly selected flame studies Although the current experimental effort appears adequate, the theoretical effort needs additional support. A level of effort of 15 men is recommended.

E. X-Ray and Gamma-Ray Lasers

It is recommended that work on X-ray lasers proceed cautiously and that experiments be designed on the basis of existing laser hardware using the most reliable hydrodynamics and atomic physics codes. Simultaneously the development of a picosecond-pulse laser system that can meet the specifications of a more ideal X-ray laser experiment should be undertaken. A level of effort of about 5 men is recommended for this project.

We conclude that gamma-ray lasers do not appear to be possible within our present understanding. Work toward a better understanding of

broadening processes in extremely narrow Mossbauer lines is interesting and appropriate; such work has other applications to Mossbauer studies. Aside from this, we do not consider work on gamma-ray lasers justified at the present time.

F. Exothermic Decomposition

The use of exothermic decomposition of complex molecular systems has exciting possibilities for applications to high-energy lasers. The data base for this class of systems should be expanded to allow a realistic assessment of their potential. We recommend an effort of approximately 10 men that stresses kinetic studies on currently available materials, the determination of their spectral properties under modest resolution (infrared through ultraviolet), and the development of synthesis procedures to enlarge the class of available materials.

G. Nonlinear Multiquantum Processes

The immediate question is to determine whether with real molecules and manageable infrared laser fluxes one can in fact excite very high vibrational modes. The work of Karlov et al. on BCl_3^*, Letokhov on BCl_3, and Rhodes on NH_3 suggest that one can. (These experimenters dissociate their molecules with intense infrared fields.) It would be useful to see whether the qualitative theoretical predictions (e.g., value of threshold flux, and isotopic enrichment of dissociated fragments) are borne out by existing experiments. If so, it would be useful to have a more detailed theory that attempts a more accurate (no doubt numerical) evaluation of transition rates and seriously concerns itself with the effect of collisions and loss rates to other modes. With such information in hand it would be possible to decide whether any useful physical realizations of the schemes discussed here are possible.

A level of effort of approximately 5 men is recommended to pursue both the experimental and theoretical issues of this problem.

H. Collisionally Stimulated Emission

Collisional processes of excited species leading to the emission of radiation are a topic that historically has not received adequate attention with regard to laser applications. A recommendation of 5 men for the support of an effort incorporating both experimental and theoretical components is suggested for this area.

I. Photochemistry and Isotope Separation

We recommend the following: (1) that fundamental research in photochemistry, chemical kinetics, energy transfer, and spectroscopy related to isotope separation be broadly supported; (2) that efforts to develop ^{235}U enrichment methods be as broad in scope as possible and that fundamental measurements be made for all promising schemes before efforts are narrowed to one or two large-scale engineering programs; (3) that the feasibility of new applications of separated isotopes be carefully evaluated; (4) that emphasis be given to development of tunable (both stepwise and continuous) high-intensity lasers with the ultimate goal of high efficiency. There is particular need for efficient sources both in the visible and near UV, and the results of laser development programs suggested in the previous sections can have considerable impact on laser isotope separation and photochemistry. Because of the substantial ongoing efforts in this area, particularly in isotope separation, no recommendation is made for additional effort

J. Free-Electron Lasers

Experimental work with intense relativistic electron beams in the presence of a longitudinal magnetic field suggests the possibility that free-electron lasers may provide an important source of far-infrared radiation. Consequently, it would appear to be highly desirable to vigorously pursue this line of development. There is, however, no reason at present to be optimistic about their utility in the visible and shorter-wavelength regions. The possible utility of the stimulated Compton effect in such regions at some future time cannot, however, be totally ruled out.

Our brief investigation of this field has indicated a rather rudimentary level of theoretical analyses, a circumstance that handicaps the assessment of its possibilities. It is recommended that some effort to remedy this situation be expended.

Appendix A

ANALYSIS OF NONLINEAR RADIATIVE EXTRACTION†

Further analysis of the two-quantum amplifier is presented below. In the most general case for which $\omega_1 \neq \omega_2$ (nondegenerate two-photon amplifier), both the optimization of energy gain and the early dominance of two-photon emission (TPE) dictate that ω_1 (the input laser field) $\ll \omega_2$. A further aid to optimizing two-photon emission is to locate an intermediate state between the upper and lower states of the transition, where the cross sections for radiative decay from the upper to the intermediate state are very small compared with the intermediate-to-lower-state cross section, and are comparable to the upper-to-lower-state cross section. Furthermore, since the parameteric process [Figure 5(c)] generates ω_3, it can override quantum fluctuations as the source for input to the anti-Stokes Raman scattering (ASRS) process [Figure 5(b)] leading to earlier domination of Raman scattering. Therefore, a large phase mismatch created by a large linear chromatic dispersion is highly desired.

With large gains achieved due to two-photon emission, a further amplification can then be realized by allowing anti-Stokes Raman scattering to occur. However, it would be desirable to allow not both ω_1 and ω_2 but only one of these to Raman scatter. Starting with an infrared laser, we thus arrive at a large flux of visible light with a frequency of either ω_2 or ω_3. Assuming that a programmed frequency versus time is desired, it can be achieved by first programming the input infrared laser frequency in time. A small frequency range in the infrared will then lead to a large frequency range in the visible.

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† This appendix was prepared by R. L. Carman.

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A second energy-extraction scheme involves making the input laser frequency correspond exactly to half that of the upper-to-lower-level frequency separation, or $\omega_1 = \omega_2$. Now, since initially $E_1 = E_2$, the parametric process is highly favored, where $\omega_3 = 3\omega_1$. Again, a large phase mismatch and resonant enhancement of two-photon emission allow the early domination of two-photon emission. However, as E_1 grows, we eventually reach an intensity where the coherence length for generating $3\omega_1$ becomes comparable to the conversion length. Then, the exponential gain at $3\omega_1$ due to stimulated anti-Stokes Raman scattering leads to a rapid conversion of ω_1 into ω_3. Similarly, the second anti-Stokes mode $\omega_5 = 5\omega_1$ will suddenly turn on as long as linear absorption can be neglected and the principal intermediate states are not equally displaced around the relevant virtual intermediate state, leading to a cancellation in the total cross section. Such a system is then describable as an odd-harmonic generator, where on account of the gain the intensity in high odd harmonics could be substantially higher than that of the input. Viewed simply as a "frequency chirping" technique, it is possible to discretely shift an infrared input laser in time from the infrared to the blue. A second slightly more speculative use is to then take this high-intensity light in the blue or vacuum UV and use a third-harmonic generation process similar to that of S. Harris of Stanford University to efficiently produce coherent soft X-rays. For example, an energy gain of ~ 100 into the 9th harmonic of a 1-μ laser combined with a conversion efficiency of 1% for third-harmonic generation from the 9th to the 27th harmonic leads to as much power at ~ 370 Å as is present in the 1-μ input to the two-photon amplifier.

While it is possible to use two-photon amplification to provide a high-power visible laser source of essentially one visible frequency, the consequence of producing light pulses whose center frequency changes simultaneously with its time evolution, either continuously or discretely,

has intrinsic excitement, and is best addressed in terms of laser-induced fusion. Such a pulse, if it can be generated to sweep its center frequency from the infrared to the UV, should have a very important impact, since by initiation and preliminary heating of the plasma with infrared light, many symmetry problems can be alleviated (Henderson, 1974). However, a progressive increase in the laser frequency during the hydrodynamic shock and adiabatic compression cycle of the implosion implies that laser energy should be deposited closer and closer to the supersolid-density core, minimizing the difficulties of energy transport and decoupling of the corona from the center of the pellet, as well as minimizing energy losses due to superthermal electrons and ions (Kidder et al., 1972; Ehler et al., 1974).

Having decided on the kind of extraction schemes that are interesting we can then use five very simple concepts to help us decide what range of experimental parameters and kinds of material properties are required to make such a system work.

As a first condition we recognize that the single-photon radiative loss rate must be sufficiently small so that the required energy storage can be achieved before superfluorescence de-excitation occurs. It is also desirable to be able to avoid complicated isolation schemes. Since a gain of $\sim e^7$ is usually accepted to be marginally stable in the absence of reflecting surfaces, we conclude that

$$N\sigma_I \Gamma < g_s \approx 7 \qquad \text{(A-1)}$$

where σ_I/Γ is the total single photon cross section, and Γ is the corresponding linewidth.

We note that the radiative depumping rate is scaling as the excited state density times the length of the medium, which is the same scaling as the total energy storage per unit beam area. Therefore, since large total energy storage per unit area implies low total loss rates, it is

equally important to examine nonradiative losses that scale with the excited state density N. However, since no simple expression of general applicability can be written, we will simply have to remember that there exists an upper bound to the achievable excited state density N.

In a system where the second-order Bloch equations apply, a steady-state response of the system implies that the minimum laser pulse duration is bounded (Kroll, 1965; Wang, 1969; Carman et al., 1970) and dependent on the magnitude of the nonlinear gain G_{NL}, representing TPE or ASRS--for example,

$$t_L \gtrsim (\ln G_{NL})/\Gamma \quad . \tag{A-2}$$

The origin of this condition is the desire to avoid higher-than-minimum intensity levels, as well as minimizing the length of the nonlinear medium.

In the system we must have sufficient energy stored per unit beam area so that the amplifier need not saturate at least until near the end of the last e-folding length, or

$$\text{System Energy Gain} \equiv G_E < 1 + \frac{\text{usable stored energy}}{\text{laser energy input}} \quad ,$$

leading to the condition

$$G_E < 1 + \frac{\hbar\omega_o N\ell}{I_L t_L (\ln G_{NL})} \quad . \tag{A-3}$$

The final empirical relationship relates the onset of laser-induced damage to components, breakdown in various gaseous media, large F-center production rates, etc. to the laser energy density--namely

$$I_L t_L G_E < \mu_{BKD}(\lambda) \tag{A-4}$$

where μ_{BKD} is a constant depending only on the relevant wavelength.

This condition is to be applied only over the pulse duration range 50 ps $< t_L <$ 3 ns. We are implicitly neglecting multiphoton-induced processes, such as self-focusing, which clearly dominate for very short pulse durations, and may also be important for the shorter wavelengths where two- or three-photon absorption leads either to resonances with states near ionization or to the ionization continuum, or at almost any wavelength in long pieces of solid material. By simply manipulating the above four conditions, we can immediately derive two conditions that must be satisfied.

$$\frac{(G_E - 1)\, I_L t_L (\ln G_{NL})}{\hbar \omega_o} < N\ell < g_s \Gamma / \sigma_I \tag{A-5}$$

$$(\ln G_{NL})\, \Gamma < t_L < \mathcal{F}_{BKD} / I_L G_E \tag{A-6}$$

We can further eliminate the center parameter in both above relationships to obtain two upper bounds on the laser intensity--namely

$$I_L < \begin{cases} \dfrac{\hbar \omega_o g_s \Gamma^2}{\sigma_I (G_E - 1)(\ln G_{NL})^2} \\ \dfrac{\mathcal{F}_{BKD}\, \Gamma}{G_E (\ln G_{NL})} \end{cases} \tag{A-7}$$

Which condition--either total energy storage or breakdown--dictates the limitation depends on the parameter, which we shall define as $\mathcal{F}_{sat} / \mathcal{F}_{BKD}$, being either less than or greater than one, respectively, where

$$\mathcal{F}_{sat} \equiv \frac{\hbar \omega_o g_s \Gamma}{\sigma_I (\ln G_{NL})} \tag{A-8}$$

While we have succeeded in obtaining bounds, those bounds are not in terms of only material parameters. We can go substantially further, however, if we assume the form of G_{NL}. We will demonstrate for the case of unsaturated steady-state anti-Stokes stimulated Raman scattering where

$$G_{NL} \equiv G_{AS} = \exp\left[\frac{16\pi^2 \frac{\partial\sigma_R}{\partial\Omega} I_L N\ell}{\hbar\omega_1 \Gamma k_3^2}\right] . \qquad \text{(A-9)}$$

Solving Eq. (A-9) for $N\ell$ and substituting we can immediately find the following two relationships

$$I_L > \frac{k_3^2 \hbar\omega_1 \sigma_I (\ln G_{AS})}{16\pi^2 \frac{\partial\sigma_R}{\partial\Omega}} \qquad \text{(A-10)}$$

$$t_L < \frac{\hbar\omega_o \Gamma k_3^2 \hbar\omega_1}{16\pi^2 \frac{\partial\sigma_R}{\partial\Omega} I_L^2 (G_E - 1)} \qquad \text{(A-11)}$$

Finally, Eq. (A-10) can then be used to eliminate I_L from all the other relationships, leading to a set of bounds on experimental parameters that are expressed solely in terms of material parameters. These are summarized in Table A-1.

We can even go one step further by eliminating the center parameter in any of the three relationships of Table A-1 to find an upper bound on the ratio of the single-photon cross sections to the two-photon cross sections--namely,

Table A-1

CONSTRAINTS FOR THE CASE OF ANTI-STOKES STIMULATED RAMAN SCATTERING
(UNSATURATED AND STEADY-STATE)

$$\frac{(G_E - 1)\, k_3^2\, \sigma_I (\ln G_{AS})^3}{16\pi^2 g_s \Gamma \frac{\partial \sigma_R}{\partial \Omega}} \left(\frac{\omega_1}{\omega_o}\right) < N\ell < \frac{g_s \Gamma}{\sigma_I}$$

$$\frac{k_3^2\, \hbar\omega_1 \sigma_I (\ln G_{AS})}{16\pi^2 g_s \frac{\partial \sigma_R}{\partial \Omega}} < I_L < \begin{cases} \dfrac{\hbar\omega_o g_s \Gamma^2}{\sigma_I (G_E - 1)(\ln G_{AS})^2} \\ \dfrac{\nu_{BKD} \Gamma}{G_E (\ln G_{AS})} \end{cases}$$

$$\frac{(\ln G_{AS})}{\Gamma} < t_L < \begin{cases} \dfrac{16\pi^2 g_s^2 \Gamma \frac{\partial \sigma_R}{\partial \Omega}}{(G_E - 1) k_3^2 \sigma_I^2 (\ln G_{AS})^2} \left(\dfrac{\omega_o}{\omega_1}\right) \\ \dfrac{16\pi^2 g \nu_{BKD} \frac{\partial \sigma_R}{\partial \Omega}}{k_3^2 G_E \hbar\omega_1 \sigma_I (\ln G_{AS})} \end{cases}$$

$$\frac{\left(\sigma_I/\Gamma\right)}{\left(\frac{\partial\sigma_R}{\partial\Omega}\right)} < \begin{cases} \dfrac{16\pi^2 g_s^2 \Gamma}{k_3^2 \sigma_I (G_E - 1)(\ln G_{AS})^3}\left(\dfrac{\omega_o}{\omega_1}\right) \\ \dfrac{16\pi^2 g_{s'BKD}^2}{k_3^2 \hbar\omega_1 G_E (\ln G_{AS})^2} \end{cases} . \qquad \text{(A-12)}$$

If breakdown is negligible this implies

$$\frac{\left(\sigma_I/\Gamma\right)^2}{\frac{\partial\sigma_R}{\partial\Omega}} < \frac{4 g_s^2 \lambda_3^2}{(G_E - 1)(\ln G_{AS})^3}\left(\frac{\omega_o}{\omega_1}\right) = 2 \times 10^{-11}\left(\frac{\omega_o}{\omega_1}\right)\lambda_3^2(\mu) \qquad \text{(A-13)}$$

$$= 2 \times 10^{-3} \frac{\bar{k}_o}{\bar{k}_1(\bar{k}_o + \bar{k}_1)^2} .$$

Thus, large ω_o and large ω_1 must be associated with small σ_I and large $\partial\sigma_R/\partial\Omega$ and vice versa, leading to the conclusion that infrared lasers and modest electronic transition energies will more readily satisfy the constraints.

From Table A-1, we note that the maximum pulse duration and the reciprocal of the minimum laser intensity scale in the same manner as indicated for $\sigma_I(\partial\sigma_R/\partial\Omega)^{-1}$, as shown in Eq. (A-13). This suggests that, for fixed material parameters, the optimum laser energy density required is probably nearly independent of wavelength. The reason to conclude this is that the minimum laser energy density scales as $\bar{k}_1(\bar{k}_o + \bar{k}_1)^2$ while the maximum laser energy density scales as $[\bar{k}(\bar{k}_o + \bar{k}_1)^2]^{-1}$.

In order to treat the nondegenerate two-photon emission problem, it is necessary to use the more complicated form of the gain

$$G_{NL} = G_{NDTP} = \frac{\exp B}{1 + \frac{2I_{10}}{I_L}\left(\frac{\alpha_{21}}{\alpha_{31}}\right)^2 \frac{k_1\omega_2^2}{k_2\omega_1^2}\,[1-\exp B]} \tag{A-14}$$

where B is given by

$$B = 16\pi^2 \frac{\partial\sigma_R}{\partial\Omega} \frac{I_L N\ell}{\hbar\omega_1\Gamma}\left(\frac{\alpha_{21}}{\alpha_{31}}\right)^2 \frac{\omega_2^2 k_2}{k_1 k_3^2 \omega_1^2} \quad . \tag{A-15}$$

This form of gain leads to very similar conditions on I_L, t_L, and $N\ell$, and can be obtained by replacing

$$G_{AS} \longrightarrow G_{NDTP}\left[\frac{1 + 2\frac{I_{10}}{I_L}\left(\frac{\alpha_{21}}{\alpha_{31}}\right)^2 \frac{k_1\omega_2^2}{k_2\omega_1^2}}{1 + \frac{2I_{10}}{I_L}\left(\frac{\alpha_{21}}{\alpha_{31}}\right)^2 \frac{k_1\omega_2^2}{k_2\omega_1^2}\, G_{NDTP}}\right] \tag{A-16a}$$

and

$$\frac{k_3^2}{16\pi^2} \longrightarrow \frac{k_3^2}{16\pi^2}\frac{k_2\omega_1^2}{k_1\omega_2^2}\left(\frac{\alpha_{31}}{\alpha_{21}}\right)^2 \tag{A-16b}$$

in Table A-1.

Since the degenerate two-photon amplifier does not involve exponential gain, but rather a more singular gain, we will examine this case more carefully. The gain expression is given by

$$G_{NL} \equiv G_{DTP} = \left(1 - \frac{32\pi^2 \left(\frac{\alpha_{11}}{\alpha_{31}}\right)^2 \frac{\partial \sigma_R}{\partial \Omega} I_L N\ell}{\hbar\omega_o \Gamma k_1^2} \right)^{-1} \qquad \text{(A-17)}$$

Now following the same procedure as for ASRS and tabulating the resulting bounds, we arrive at the results given in Table A-2. Note that both the minimum intensity and the minimum $N\ell$ product have been reduced by a factor of

$$\ln G_{AS} \left[1 - \frac{1}{G_{DTP}} \right] , \qquad \text{(A-18)}$$

which for $G_{DTP} \sim G_{AS} \sim e^{10}$ amounts to a factor of ~ 20. Furthermore, the maximum usable pulse duration has been increased by the same factor. This result is not inconsistent with the results of the previous discussion, however, because the anti-Stokes competition is so effective for the degenerate TPA primarily because of the efficient parametric generation of third harmonic which acts as an input to the exponential gain. Thus, we see that energy extraction for the degenerate TPE case involves much more desirable experimental parameters than the nondegenerate TPE case.

In Figure A-1 we have graphed the maximum achievable energy gain G_E versus wavelength for both TPE and ASRS for the $^2P_{\frac{1}{2}} \rightarrow {}^2P_{3/2}$ transition of atomic iodine. As indicated previously, we note that best performance is achieved for the degenerate TPE process or for long-wavelength inputs. The nonresonant character of this transition enables this simple set of curves to be plotted. For other systems, the intermediate states will usually complicate this type of plot.

In Tables A-3 and A-4, we have estimated the relevant material parameters and then used them to predict the bounds on experimental parameters. We note that while a CO_2 frequency upconverter using excited atomic iodine

Table A-2

CONSTRAINTS FOR THE CASE OF DEGENERATE TWO-PHOTON AMPLIFIER

$$\left[1 - \frac{1}{G_{DTP}}\right] \frac{(G_E-1)\, k_1^2\, \sigma_I (\ln G_{DTP})^2}{32\pi^2 g_s \Gamma \frac{\partial \sigma_R}{\partial \Omega} \left(\frac{\alpha_{11}}{\alpha_{31}}\right)^2} \left(\frac{\omega_1}{\omega_o}\right) < N\ell < \frac{g_s \Gamma}{\sigma_I}$$

$$\frac{\hbar\omega_1 \sigma_I k_1^2 \left[1 - \frac{1}{G_{DTP}}\right]}{32\pi^2 g_s \Gamma \frac{\partial \sigma_R}{\partial \Omega} \left(\frac{\alpha_{11}}{\alpha_{31}}\right)^2} < I_L < \begin{cases} \dfrac{\hbar\omega_o g_s \Gamma^2}{\sigma_I (G_E-1)(\ln G_{DTP})^2} \\ \dfrac{\alpha_{BKD} \Gamma}{G_E (\ln G_{DTP})} \end{cases}$$

$$\frac{\ln G_{DTP}}{\Gamma} < t_L < \begin{cases} \dfrac{32\pi^2 g_s^2 \Gamma \frac{\partial \sigma_R}{\partial \Omega} \left(\frac{\alpha_{11}}{\alpha_{31}}\right)^2}{k_1^2 \sigma_I^2 (G_c-1)(\ln G_{DTP})} \left(\frac{\omega_o}{\omega_1}\right) \left[1 - \frac{1}{G_{DTP}}\right]^{-1} \\ \dfrac{32\pi^2 g_s \alpha_{BKD} \frac{\partial \sigma_R}{\partial \Omega} \left(\frac{\alpha_{11}}{\alpha_{31}}\right)^2}{\hbar\omega_1 k_1^2 \sigma_I G_E} \left[1 - \frac{1}{G_{DTP}}\right]^{-1} \end{cases}$$

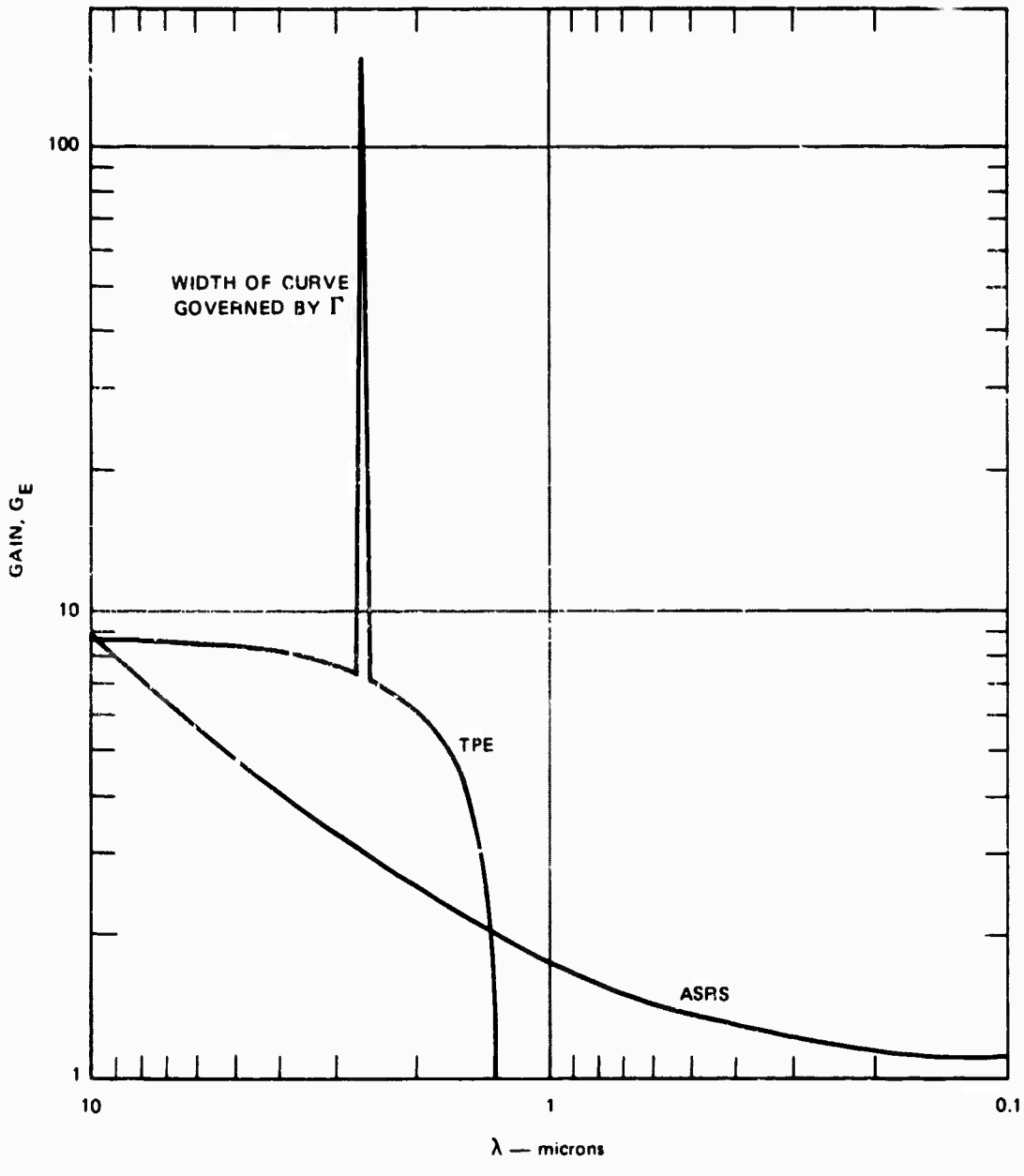

FIGURE A-1 PLOT OF THE THEORETICAL MAXIMUM ENERGY GAIN vs WAVELENGTH OF THE INCIDENT DRIVING LASER, FOR BOTH TWO-PHOTON AMPLIFICATION (limited by energy storage density and the high extraction intensity required) AND ANTI-STOKES RAMAN SCATTERING (limited by photon number conservation).

Table A-3

ESTIMATED VALUES OF MATERIAL PARAMETERS FOR VARIOUS PLAUSIBLE SYSTEMS

Parameter	$I^*(^2P_{\frac{1}{2}})$ and CO_2	$I^*(^2P_{\frac{1}{2}})$ and HF	Degenerate TPA $I^*(^2P_{\frac{1}{2}})$	Degenerate TPA $O^*(^1S)$	Degenerate TPA $S^*(^1S)$	N_2^* (A) and Nd Glass
λ pump ( )	10.6	2.75	2.63	1.12	1.485	1.06
λ TPE ( )	1.5	2.52	--	--	--	$\sim$ 0.33
λ AS ( )	1.17	0.89	0.877	0.371	0.195	0.2
λ_{2AS} ( )	1.051	0.67	0.526	0.224	0.297	$\sim$ 0.16
$(\alpha_{11}\ \alpha_{31})$	$\sim$ 1	1	1	1	$\sim$ 1	10^{-4}
σ_R	10^{-28}	10^{-28}	10^{-28}	$\sim 3 \times 10^{-29}$	10^{-29}	10^{-30}
Γ (s^{-1}) (pressure broadened with inert gas)	1.9×10^{11}	1.9×10^{11}	1.9×10^{11}	1.9×10^{11}	1.9×10^{11}	1.9×10^{11}
σ_I (cm^2)	2×10^{-19}	2×10^{-19}	2×10^{-19}	2×10^{-20}	$\sim 10^{-19}$	$\sim 3 \times 10^{-22}$
ϵ_I pump (J)	1.9×10^{-20}	7.3×10^{-20}	7.5×10^{-20}	1.77×10^{-19}	1.33×10^{-19}	1.9×10^{-19}
ϵ_{sat} (J)	1.5×10^{-19}	1.5×10^{-19}	1.5×10^{-19}	3.54×10^{-19}	2.66×10^{-19}	10^{-18}
G_E	10	7	100	100	10	5
G_{SL}	e^{10}	e^{10}	e^{10}	e^{10}	e^{10}	e^{10}
g_∞	7	7	7	7	7	7
ϵ_{EKD} (J/cm^2)	1	5	5	10	$\sim$ 10	$\sim$ 5

Table A-4

BOUNDS ON EXPERIMENTAL PARAMETERS DICTATED BY TABLE A-3

Parameter	$I^*(^2P_{\frac{3}{2}})$ and CO_2	$I^*(^2P_{\frac{1}{2}})$ and HF	Degenerate TPA $I^*(^2P_{\frac{1}{2}})$	Degenerate TPA $O^*(^1S)$	Degenerate TPA $S^*(^1S)$	$N_2^*(A)$ and Nd Glass
$I_L(W/cm^2) <$	1.5×10^9	1.5×10^9	10^8	2×10^9	4×10^9	2×10^{10}
$I_L(W/cm^2) >$	2×10^8	1.2×10^9	7×10^7	3×10^8	2×10^9	10^{10}
$t_L(ps) <$	300	100	72	400	95	100
$t_L(ps) >$	50	50	50	50	50	50
$N\ell(cm^{-2}) <$	5×10^{19}	3.5×10^{19}	3.5×10^{19}	3.5×10^{20}	7×10^{19}	2×10^{19}
$N\ell(cm^{-2}) >$	4×10^{18}	2×10^{20}	2.5×10^{19}	4×10^{19}	3.5×10^{19}	2×10^{19}
$\ell(cm) <$	$95\ d^2(cm)$	$365\ d^2$	$380\ d^2$	$892\ d^2$	$673\ d^2$	$943\ d^2$

($5^2P_{\frac{1}{2}}$) appears feasible, an HF upconverter with I^* does not appear interesting. Also while a degenerate two-photon amplifier using either I^* or excited atomic oxygen ($^1S_o - {}^1D_2$) appears interesting, the corresponding excited atomic sulfur ($^1S_o - {}^1D_2$) is not. Of greater interest is the possibility of using the $^1D_2$ state in the atomic oxygen, sulfur, or selenium systems as an intermediate state for two-photon emission between ^1S_o and the ^3P manifold.[+] Here an absolute inversion is required, however.

In the case of the atomic iodine proposals it is possible to go one step further for the case of the photolysis process, involving CF_3I, for example, as the production mechanism of I^*. This is because the optical absorption of flashlamp light at ~ 2650 Å is of a nonsaturable nature, leading to the following relationship between the diameter of the system and the density of initial gas:

$$d = \frac{2\eta}{N\sigma_{2650}} \qquad \text{(A-19)}$$

where η is the percentage of available iodine that is inverted to I^* (1% to 10%, typically) and $\sigma_{2650} \approx 5.4 \times 10^{-19}$ cm^2. Furthermore, we have a relationship guaranteeing that diffraction will not cause the beam of input diameter $d = 2a$ to get bigger than the tube after traveling through the inverted medium of length ℓ:

$$d^2 > 10\lambda\ell \qquad \text{(A-20)}$$

Equations (A-19) and (A-20) plus the conditions on the product $N\ell$ can be used to establish what minimum d and ℓ and maximum N are possible--namely,

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[+]This was first suggested by C. K. Rhodes.

$$d > \frac{5\lambda_1 (N\ell)_{MIN} \sigma_{2650}}{\eta} \qquad \text{(A-21)}$$

$$\ell > \frac{2.5(N\ell)^2_{MIN} (\sigma_{2650})^2 \lambda_1}{\eta^2} \qquad \text{(A-22)}$$

and

$$N < \frac{2\eta^2}{5(\sigma_{2650})^2 \lambda_1 (N\ell)_{MIN}} \qquad \text{(A-23)}$$

In Table A-5 we summarize the predictions for the cases of the CO_2 frequency upconverter, and degenerate two-photon amplifier for the situation considered in Tables A-3 and A-4 and where $\eta = 0.01$.

Table A-5

PREDICTED MINIMUM MEDIUM DIAMETER AND LENGTH AND MAXIMUM INVERSION DENSITY FOR THE CASE OF OBTAINING I^* FROM PHOTOLYSIS OF CF_3I AND $\eta = 1\%$

	CO_2	Degenerate TPA
$d \geq$	1.2 cm	1.8 cm
$\ell \geq$	124 cm	1200 cm
$N \leq$	$3.5 \times 10^{16}/cm^3$	$2.1 \times 10^{16}/cm^3$

Appendix B

SUMMARY OF SCHEDULED PRESENTATIONS

A summary of the scheduled presentations heard at the 1974 JASON Laser Summer Study is given below:

Participant	Topic	Date
R. Carman	Multiphoton Amplifiers	6/17/74
C. Rhodes	High Energy Lasers	6/18/74
P. Kelley	Isotope Separation	6/18/74
P. Kelley	Two-Photon Absorption	6/19/74
C. B. Moore	Isotope Separation (Br_2)	6/20/74
D. Lorents	Energy Transfer in Condensed Matter	6/21/74

Participant (Affiliation)	Topic	Date
D. Huestis (SRI) W. Stevens (LLL)	Molecular Structure Calculations and Chemical Processes	7/ 9/74
T. Bernhardt (LLL) G. Chapline (LLL) L. Wood (LLL)	X-ray Lasers and Isotope Separation	7/11/74
R. Olson (SRI)	Molecular Curve Crossings	7/12/74
R. Taylor (Phys. Sci.)	Electronic Chemical Systems	7/16/74
P. Robinson (LASL) D. Smith (Oak Ridge)	Isotope Separation	7/17/74
J. Gole (MIT)	Electronic Chemical Lasers	7/17/74
E. V. George (MIT) P. Hoff (LLL)	Plasma Properties of Lasers	7/18/74

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Participant (Affiliation)	Topic	Date
D. Judd (LASL) T. Dunning (LASL) R. Jensen (LASL)	Theoretical Studies and Electrically Excited Systems	7/19/74
J. Murray (LLL) H. Powell (LLL)	Experiments on Metastable Laser Systems	7/23/74
K. Boyer (LASL)	LASL Laser Program	7/25/74
R. Pantell (Stanford)	Interaction of Electron Beams and Photon Beams	7/29/74

The wrap-up presentation was given August 30, 1974 to ARPA officials and other invited guests by C. Rhodes, P. Kelley, C. B. Moore, and J. Katz.

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