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A FEASIBILITY STUDY OF PULSED CHEMICAL LASER IGNITION BY VERY RAPID INFRARED ABSORPTION HEATING

S. C. Lin and C. C. Chen

Xonics, Inc.

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July 1972

AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base
New Mexico

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FOREWORD

This report was prepared by Xonics, Inc., Van Nuys, California, under Contract F29601-71-C-0081. The research was performed under Program Element 62301D, Project 1256, and was funded by the Advance Research Projects Agency under ARPA Order No. 1256.

Inclusive dates of research were May 1971 through January 1972. The report was submitted 1 June 1972.by the Air Force Weapons Laboratory Project Officer, Lt John T. Slankas (LRT).

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This technical report has been reviewed and is approved.

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ABSTRACT

(Distribution Limitation Statement B)

The theoretical problem of pulsed chemical laser ignition by very rapid infrared laser absorption heating is investigated. It is found that for single-phase systems, the only hope for ever achieving energy gain appears to lie in the utilization of long or fast-branching chemical chains in the pumping reactions. For the hydrogen-halide system, the usable chain length is severely limited by the very rapid collisional de-excitation rate of the vibrational states by the reaction product molecules, making positive energy gain very unlikely. In two-phase systems, however, one may try to utilize the large amount of combustion energy release from burning of finely-dispersed, submicron size solid particles for generation of additional atoms required in the pumping of the laser reactions. The reduced input energy requirement for generating a fixed number of active atoms in such two-phase system may improve the prospect for achieving positive energy gain in multistage pulsed chemical laser applications.

CONTENTS

Section Page

I SUMMARY 1

1. TECHNICAL PROBLEM AND OBJECTIVE OF STUDY 1

2. GENERAL METHOD OF APPROACH 2

3. TECHNICAL RESULTS 3

4. DOD IMPLICATIONS 7

5. IMPLICATIONS FOR FURTHER RESEARCH 8

II DETAILED TECHNICAL RESULT 9

1. INTRODUCTION 9

2. SOME FUNDAMENTAL CONSIDERATIONS OF PULSED CHEMICAL LASER DESIGN AND OPERATION 11

3. METHODS OF INITIATION 15

a. Initiation by Pulsed Electromagnetic Wave Absorption 16

(1) Flashlamp Ignition 17
(2) Laser Ignition 18

b. Initiation by Electronic Processes 19

(1) Pulsed Electric Discharge Ignition 19
(2) Electron Beam Ignition 20

4. LASER IGNITION OF SINGLE-PHASE SYSTEMS 21

a. General Nature of Interaction Between an Intense Laser Beam and an Absorbing Gas 22

CONTENTS (Cont'd)

Section	Page
(1) The Governing Equations	23
(2) Thermal Defocusing	27
b. Gas-phase Absorption Processes Resulting in Dissociation	31
(1) Photodissociation	32
(2) Cascade Excitation of Vibrational Modes	33
c. Prospect of Pulse Energy Gain from Nonchain Reactions	33
d. Prospect of Pulse Energy Gain from Chain Reactions	34
(1) Prediction of Pulsed Chemical Laser Energy Output Based on Chain Reactions	35
(a) The Single Chain Reactions	35
(b) The Branched Reaction	37
(2) Kinetics of the HF Chemical Laser System	42
(3) "Inversion Boundary" for the Pulsed H_2-F_2 System	45
(a) Total Inversion	47
(b) Partial Inversion	55
(4) Estimate of Maximum Energy Gain Potential for Pulsed H_2-F_2 Laser Systems	58
5. LASER IGNITION OF TWO-PHASE SYSTEMS	61
a. Definition of Two-phase Pulsed Chemical Laser Systems	61
b. Optical Properties of Two-phase Systems	63

CONTENTS (Cont'd)

Section | Page

c. Solid Particles as Inert Catalyst for Chain Initiation and Chain Branching 72

d. Two-phase Systems Involving Solid Particle Combustion 82

(1) Energy Gain Potential 82
(2) Chemical and Thermal Stability of Two-phase Systems 88
(3) Rate of Heating of Solid Particles 89
(4) Burning Rate of Metal Powders 91
(5) Redistribution of Combustion Energy for Laser Pumping 94
(6) Matching of Molecular Diffusion Time and Collisional Deexcitation Time 98
(7) Simultaneous Matching of All Necessary Conditions 102

APPENDIX 1. RECOMMENDED RATE CONSTANTS FOR H_2-F_2 CHEMICAL LASER (From Ref. 47) 106

REFERENCES 109

ILLUSTRATIONS

Figure		Page
1	The idealized 3-level system used in Ref. 1	46
2	Inversion boundaries as functions of the translational temperature for single-phase, H_2-F_2 chemical laser systems	54
3	Extinction coefficient K as a function of wavelength for some ionic crystals	67
4	Refractive index and extinction coefficient as a function of wavelength for some metals and graphite near room temperature	68
5	Absorption cross section as a function of wavelength for some submicron size particles ($ka << 1$) of some ionic crystals, metals, and graphite	70
6	Particle volume fraction in a two-phase mixture which would yield an e-folding absorption length scale of 10 meters at room temperature for some ionic crystals, metals, and graphite as a function of wavelength, neglecting gas-phase absorption and assuming $ka << 1$ size particles	71
7	Initial rate of temperature rise, dT/dt, for some submicron size particles ($ka << 1$) suddenly heated by a laser beam of intensity I and wavelength λ, neglecting scattering and conductive heat loss	74
8	Geometry and nomenclature for the spherical diffusion problem	76
9	Normalized solution for transien spherical diffusion of chain center atoms from a catalytic particle surface located at radius a into a gaseous volume of interparticle separation distance 2ℓ, where $\ell/a = 10$	80

ILLUSTRATIONS (Cont'd)

Figure		Page
10	Normalized solution for transient spherical diffusion of chain center atoms from a catalytic particle surface located at radius a into a gaseous volume of interparticle separation distance 2ℓ, where $\ell/a = 100$	81
11	Diffusion flame model in classical vapor-phase combustion theory	93

TABLES

Table		Page
I	Observed Spectra from the Continuous Chemical Lasers	44
II	Comparison of Ignition Energy and Heat of Combustion for Some Solid Particles	85

SECTION I

SUMMARY

A summary of the essential findings of a 6-month theoretical study on the feasibility of pulsed chemical laser ignition by very rapid infrared absorption heating is presented. Specifically, the infrared source of particular interest is the output from another high-power laser, so that the subject of this investigation is, in effect, pulsed-chemical laser initiation by another laser. Detailed technical results from this investigation are presented in section II.

1. TECHNICAL PROBLEM AND OBJECTIVE OF STUDY

To make high-energy pulsed chemical laser operations feasible, it is necessary to obtain some multiplication factor of the input initiation energy. There are currently several methods of initiating a chemical laser --- flashlamp, spark discharge, and electron beam. All of these methods have potential limitations when applied to scaling of large pulsed laser systems. Among the problem areas are efficiency of initiation, volume uniformity of initiation, speed of initiation, and the required pulsed duration of the initiating system. One method which has not yet been investigated is the initiation of a pulsed chemical laser by another laser. In view of the current rapid development of high-power chemical and nonchemical lasers, and the many desirable characteristics of such lasers (e.g., rapid rise time, beam uniformity, adaptability to multiple staging, etc.) which suggest themselves as natural initiation sources for the later-stage power amplifiers in a pulsed chemical laser system, the feasibility of such initiation method merits exploration so that their potential usefulness can be further assessed.

The objective of the present investigation is, therefore, to determine the feasibility of initiating a pulsed chemical laser by the use of another laser. The main emphasis of this study is in the identification and definition of the physical and chemical conditions under which such initiation process would be favorable.

2. GENERAL METHOD OF APPROACH

Since this is a theoretical study involving the exploration of an original concept, our method of approach necessarily involves more than what is ordinarily required in a standard analytical program. Thus, in addition to literature search for relevant data and related previous works, it is necessary to carry out conceptual formulation involving consideration of many alternatives before detailed formulation and numerical computation can begin. In areas where no experimental data or prior knowledge exist, it is also necessary to consult experts in related fields so that meaningful extrapolations from existing knowledge can be made and the probable uncertainties in the resultant order-of-magnitude estimates can be assessed.

Because of the extremely short duration of the contracted study, opportunity for in-depth investigation is severely limited, and breadth coverage of many pertinent subjects is, at best, highly selective. A best effort has been made, however, in striking a proper balance between breadth and depth coverage within the time and resources available so that the most important features and inherent limitations of the pulsed chemical laser initiation problem can be brought out and some preliminary conclusions can be drawn regarding the feasibility of the laser initiation process.

3. TECHNICAL RESULTS

From a pragmatic point of view, the use of one laser to initiate or "trigger" another laser will be meaningful only if one or more of the following functions could be accomplished: (a) Power or energy amplification, (b) frequency shift to facilitate beam propagation and/or energy coupling to target, and (c) pulse shaping for the same purposes. However, because the energy output per unit volume or per mole of reactants from current pulsed chemical lasers, by whatever means of initiation, is generally minuscule in comparison with their true potential, achievement of significant energy amplification have, therefore, been considered our most important immediate objective.

It may be noted that all chemical laser systems which have been studied or under active investigation as reported in the published and unpublished literatures up to the time of commencement of the present research (May 1971) were "single-phase" systems. That is, the lasing medium from which chemical energy was to be extracted and converted into coherent radiation energy was either all in the gas-phase or all in the liquid-phase. In fact, the most energetic chemical laser systems discovered to date have been, and apparently still are, purely single-phase systems involving only gaseous mixtures (e.g., the hydrogen-halogen systems). For this very reason, the proposed feasibility study was originally intended only for single-phase pulsed chemical laser systems. This is reflected in the contractual work statement (Section I).* However, soon after the commencement of the contracted study, we discovered that artificial enhancement of infrared absorption in a laseable gas mixture can, in principle, be achieved by the addition of finely-dispersed, submicron size solid particles (or liquid droplets) into the gaseous medium. Furthermore, the addition of such solid particles of suitably chosen chemical properties into a laseable gas mixture may greatly improve the energy gain potential of the resultant "two-phase system."

The consideration of more than one phase of matter in a lasing medium clearly represents an additional complication which one wishes to avoid, if at all possible. However, we feel that in any search for potentially high gain and/or high-power laser systems in the conceptual stage, there appears to be no good a priori reason for limiting oneself to the consideration of only single-phase systems. Accordingly, with the consent of cognizant personnel at the Air Force Weapons Laboratory (AFWL)

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*Air Force Special Weapons Center (PMRA), contract number F29601-71-C-0081, 5 May 1971, pp. 25-26.

and at the Advanced Research Projects Agency/Strategic Technology Office (ARPA/STO), we have broadened the scope of our theoretical study of pulsed chemical laser initiation to include the consideration of "two-phase systems" -- with no increase in the contracted leve of effort

The major conclusions which we have arrived at by the end of the 6-month period are as follows:

A. Initiation of a pulsed chemical laser by another laser is generally feasible.

B. In single-phase pulsed chemical laser systems, the only hope for ever achieving energy gain appears to lie in the utilization of long or fast-branching chemical chains in the pumping reactions.

C. For the hydrogen-halide system, which is about the only chemical laser system that has been demonstrated to be capable of operating at high-power density in continuous wave (CW) application, the usable chain length appears to be severely limited by the very rapid collisional de-excitation rate of the vibrational states by the reaction product molecules [e.g., de-excitation of HF(v) by HF(0)]. The chain-branching rate in the single-phase hydrogen-halide system also appears to be too slow to be of any help.

D. If long chemical chains cannot be utilized, and the energy required for generating active atoms for the pumping of the lasing reactions must come from the external energy source, the laser output energy will always be smaller than the inpuc energy supplied by the external source and hence a positive energy gain will not be possible. The fact that all pulsed chemical laser experiments using flashlamp and electric discharge initiation in hydrogen-halogen mixtures failed to yield any significant laser output energy in relation to the initiation energy is, perhaps, a good indication of this situation.

E. In two-phase systems, one may try to make use of the large amount of combustion energy release from burning of finely-dispersed, submicron size solid particles for generation of dissociated atoms in the hot flame zone surrounding the particles. If the combination of rate constants and experimental parameters were right, there is a good chance that frozen-diffusion of dissociated atoms from the hot flame zone into the bulk of the inter-particle space would lead to efficient conversion of the dissociation energy into laser energy through nonchain rearrangement reactions.

F. The heat of combustion of some metal and solid compound is often two orders of magnitude greater than the energy required to heat the same mass of metal or compound up to their respective ignition temperature, there exists a good possibility for achieving positive energy gain in the two-phase systems.

G. Our present knowledge about the burning rate of submicron size particles in laseable gas mixtures and about the chemical kinetic and/or de-excitation rates of their reaction products is too incomplete to allow any quantitative prediction of two-phase pulsed chemical laser performance. In fact, we do not even know the initial chemical stability (or time-dependent explosion limit) of any of the energetically attractive two-phase mixtures to allow an assessment of their suitability for premixed pulsed laser operation at this time.

4. DOD IMPLICATIONS

Existing DOD/ARPA pulsed chemical laser programs at the Aerospace Corporation, Avco Everett Research Laboratory, and at other contractor locations all involve single-phase systems (i. e., all gas mixtures). Initiation mechanisms for these single-phase systems are either (a) flashlamp initiation, (b) electrical discharge initiation, or (c) electron beam initiation. So far, no work on two-phase pulsed chemical laser appears to have been done.

In view of the positive energy gain potential indicated for the two-phase pulsed chemical laser system involving solid particle combustion, it appears that a sufficient level of effort should be mounted by DOD in the exploration of this potential so that its eventual development would not represent a technical surprise. The problem of laser ignition of single- and two-phase pulsed chemical laser systems also merits further exploration since it may lead to convenient multiple staging of the power (or energy) amplifiers within such systems.

5. IMPLICATIONS FOR FURTHER RESEARCH

The present investigation of the feasibility of pulsed chemical laser ignition by very rapid infrared absorption heating clearly points to the need for further research in the following areas of chemical physics so that the energy gain potential of two-phase systems can be more quantitatively assessed:

A. Chemical and thermal stability of two-phase mixtures with laser potential.

B. Optical properties of solid particles which are energetically attractive when used in two-phase chemical laser systems.

C. Ignition process and the rate of combustion of submicron size particles in laseable gas mixtures.

D. Emissivity of the products of reaction in two-phase chemical laser systems involving solid particle combustion.

E. Energy transfer mechanisms during solid particle combustion in two-phase systems.

F. Excitation and de-excitation processes in heterogeneous, nonsteady chemical reactions.

SECTION II

DETAILED TECHNICAL RESULT

1. INTRODUCTION

The potential of chemical lasers as efficient, high specific energy coherent radiation sources has been well demonstrated by the recent works of Airey and McKay,[1] Cool, Stephens et al.,[2-5] and Spencer, Jacobs, et al.[6-9] Among the different single-phase chemical lasers studied, the deuterium fluoride (DF) and the deuterium fluoride-carbon dioxide (DF-CO_2) systems within the hydrogen-halide group appear most promising, both from the point of view of energy conversion efficiency and that of atmospheric propagation. Of these two systems, the pure DF laser, with strong lines lying within the $3.5 \sim 4.2\mu$ atmospheric window, offers one possible advantage over the DF-CO_2 system in terms of higher breakdown threshold (by a factor of about 8 according to frequency-square scaling). On the other hand, the DF-CO_2 system, being a mixed gas system involving vibrational energy transfer to a chemically inert diluent (i.e., CO_2) of variable concentration, may offer the advantage of being more flexible in pulse-shaping.

While all of the recent works reported in the literature[1-9] have been concentrated in the study of CW chemical laser operation and performance, corresponding effort in the basic study of pulsed chemical lasers appears to be lagging. In addition to the problem of inversion kinetics, there is the additional important problem of initiation in the pulsed operation. To make high-energy pulsed operations feasible it is necessary to obtain some multiplication factor of the input energy. There are currently several methods of initiating a chemical laser - spark discharge, flashlamp, and electron beam. All of these systems have potential limitations when applied to scaling of large pulsed laser systems. Among the problem areas are efficiency of initiation, volume uniformity of initiation, speed of initiation and the required pulsed duration of the initiating system. One method currently not being investigated is the initiation of a pulsed laser with another laser.

The objective of this study is, therefore, to determine the feasibility of initiating a pulsed chemical laser by the use of another laser. The main emphasis of this study is to define the physical and chemical conditions under which such initiation would be favorable.

The most penetrating theoretical analysis of single-phase chemical laser operation applicable to pulsed hydrogen-halide systems involving chain chemical reactions to date appears to be that of Oraevskii,[10] even though the analysis was limited to linear systems involving very few rate-limiting reactions. Theoretical and experimental study of nonchain pulsed chemical lasers in single-phase, hydrogen-halide systems initiated by flash photolysis have also been reported by Airey.[11]

2. SOME FUNDAMENTAL CONSIDERATIONS OF PULSED CHEMICAL LASER DESIGN AND OPERATION

As explained by Spencer et al.[8] and Cool et al.,[3] laser action in the continuous-flow DF and the DF-CO_2 systems is caused by population inversion among the first few vibrational levels of DF, and that between the $(10^00)/(02^00)$ and the (00^01) levels of CO_2, respectively. For both systems, the chemical pumping energy was derived mainly from the pair of chained rearrangement reactions

$$F + D_2 \rightarrow DF(v) + D \qquad \Delta H = -31.7 \text{ kcal/mole} \tag{1}$$

$$D + F_2 \rightarrow DF(v) + F \qquad \Delta H = -106.7 \text{ kcal/mole} \tag{2}$$

in which a large fraction of the respective chemical energy released (i.e., negative value of the heat of formation ΔH) ended up in the vibrational excitation of the newly formed DF molecules. In the experimental arrangement of Spencer et al.,[8] only reaction (1) was involved and the free fluorine atoms needed in the chained rearrangement reaction was supplied by thermal decomposition of SF_6, using arc-heated nitrogen as an external heat source. In the experimental arrangement of Cool et al.,[3-5] reactions (1) and (2) were allowed to proceed simultaneously in a mixing flow consisting of one stream of partially dissociated F_2 and another stream of D_2-CO_2 mixture. Partial dissociation of the F_2 gas in the primary stream was accomplished either by a high-frequency electrical discharge or by an auxiliary hypergolic reaction of the type

$$F_2 + NO \rightarrow NOF + F \qquad (3)$$

It is important to note that in the continuous flow chemical lasers of the types described by Cool et al.[2-5] and by Spencer et al.,[6-9] the chemical pumping rate was actually limited by the rate of molecular mixing between the active reactants when the initially segregated streams were brought together, and not by the chemical kinetic rates for the corresponding homogeneous gas-phase reactions. The de-excitation rate, on the other hand, was controlled by vibrational relaxation of the respective lasing molecular species.

The use of heterogeneous stream mixing as a means for controlling the chemical reaction and laser pumping rates by the above cited investigators were probably necessitated by the fact that a premixed gas containing substantial concentrations of very active chemicals like F_2 and D_2 has a tendency of being easily detonated by a fast chemical chain formed by a close coupling between reactions (1) and (2), and is therefore too difficult to handle in a continuous flow system.

Because the maximum output power per unit active volume for any laser system is directly proportional to the population inversion density, an obvious direction for increasing the chemical laser output power density is to increase the reactant mass density within the mixing reactor while trying to maintain a fixed inverted population ratio between the upper and the lower lasing states. However, rapid mixing of initially heterogeneous gas streams of high-mass densities generally necessitates the use of high intensity turbulent flows. Furthermore, operation at high gas densities also tends to shorten the vibrational relaxation time for de-inversion of the laser levels. This tends to limit the available streamwise dimension of the active region. Thus, one of the major problems in future development of high power-density, continuous-wave chemical lasers of good optical quality may well lie in the area of controlling the spatial homogeneity and temporal stability of high Reynolds number compressible turbulent flows with strong chemical reactions -- a well known unsolved problem in contemporary gas dynamics!

In the conceptual design of high-energy pulsed chemical lasers of relatively short pulse duration (say, of the order of 10^{-4} sec or less), the introduction of convective flow motion appears to offer no particular advantage, except for the purpose of gas sample replacement within the active volume for repetitive operations. The argument is simply that: (a) if a premixed reactant mixture (e.g., a stoichiometric mixture of D_2 and F_2 gases at standard temperature and pressure) were used in a continuous-flow arrangement through the active laser volume, the danger of accidentally detonating the entire reactant storage and supply system by the pulsed chemical reactions would be too great; (b) if an un-premixed flow system were used to bring the reactants into the active laser volume in a continuous fashion, molecular mixing of the reactants may not have time to reach completion during the intended pulse period, resulting in a loss of effective lasing volume or an undesirable stretching out of the laser pulse, or both. Furthermore, one would have to face the same problem of controlling the homogeneity of the reacting mixture as in the case of a continuous-wave chemical laser considered in the preceding paragraph; (c) if the reactants were brought into the active laser volume in an intermittent manner, then there appears to be no compelling reason for initiating the pulsed chemical reaction before most of the residual fluid motions have subsided.

The above argument then leads one to the tentative conclusion that a high-energy pulsed chemical laser would most likely consist of the following essential elements:

(a) An explosion-proof pulsed chemical laser reactor, with infrared window (or windows) and other necessary optical elements for coupling out the laser energy. The internal surfaces of the reactor, of course must be suitably passivated so as to reduce the probability of prematurely detonating the reactants by surface-catalysed reactions to a minimum.

(b) Explosion-proof and fast-acting gas filling and evacuation systems for loading of reactants into, and removal of reaction products out of, the pulsed reactor within certain desired pulse repetition period. If the reactants were not to be premixed, the gas filling system must be suitably designed to ensure uniform mixing of the reactants within the allocated time period (i. e., some fraction of the pulse repetition period).

(c) Provisions for igniting the pulsed chemical reactions uniformly over the active volume of the laser reactor.

The provision of items (a) and (b) appears relatively straightforward. It is only a matter of degree to which various mechanical performance parameters demanded of the laser system can actually be satisfied (e. g., maximum operating pressure, maximum pulse repetition rate, etc.). The last provision (c), on the other hand, is expected to be the most crucial. It is precisely the suggestion of a new method for homogeneous ignition of pulsed chemical lasers, together with an exploration of its potential, that provided the initial motivation for the present study.

3. METHODS OF INITIATION

Let us now consider the crucial question of uniform ignition of a detonable mixture like D_2-F_2, or H_2-F_2, in a pulsed chemical laser system. The conventional method of point-ignition (e. g., use of spark-plugs, as in the case of internal combustion engines) is bound to be unsatisfactory.

From elementary physics considerations, there appear to be only two general methods for effecting simultaneous (or "nearly" simultaneous when measured against the characteristic time scale of the chemical reaction) ignition over an extended volume, namely: (a) pulsed electromagnetic wave absorption; and (b) fast particle injection. We will briefly consider the essential difference between these two methods here:

a. Initiation by Pulsed Electromagnetic Wave Absorption

This method can, in principle, be used whereve. here exists a strong absorption coefficient in the laseable mixture over the frequency range of the source of electromagnetic radiation. The resultant spatial homogeneity of the ignited mixture is expected to depend on the initial spatial homogeneity of the radiation source, and of the mixture absorption coefficient. Obviously, in order to achieve nearly homogeneous volume absorption from an external radiation source (or sources) introduced through the boundary surfaces of the reactive volume, the absorption coefficient must not be too strong so as to cause excessive attenuation of the incident radiation. On the other hand, in order to achieve simultaneity of ignition over the reaction volume, the combination of absorption coefficient and incident radiation intensity must be sufficiently high so that the characteristic time for mixture heating remains short in comparison with the characteristic time for the laser-pumping chemical reaction.

According to the nature of the source of electromagnetic radiation, this method can further be subdivided into two or more classes:

(1) Flashlamp Ignition. The most common method for initiating a pulsed chemical laser generally employs an electronic flashlamp as the source of electromagnetic radiation. Since the emission spectrum of high intensity flashlamps usually peaks in the near ultraviolet, the incident radiation can be used for direct generation of chain centers (e.g., halogen atoms in hydrogen-halide systems) through photodissociation of the reactant molecules in most of the chemical laser systems studied to date. This method of initiation is, therefore, also called the method of flash photolysis initiation.

Since the process of flash photolysis is capable of selective dissociation of the desired chemical species through proper matching of the flashlamp emission spectrum and the species photodissociation spectrum, the principal advantage of this method of initiation is in its ability to generate a relatively high concentration of active atoms without excessively heating up the laseable mixture. A secondary advantage of this method is that electronic flashlamps are readily available and of relatively low cost (say, in comparison with a laser light source of comparable pulse energy).

The principal disadvantage of this method of initiation, on the other hand, is the limitation of radiation flux density (or light intensity) that can be obtained from any electronic flashlamp operating at a finite plasma temperature. This limitation imposes an upper bound on the rate of photolysis, and also a requirement for large window areas for coupling in of the initiation energy to the reactive volume. A secondary disadvantage of this method of initiation is that flashlamps are inherently inefficient devices for conversion of electrical input energy into light output energy (say, in comparison with the 10% or higher conversion efficiency that has been demonstrated for some infrared electrical and chemical lasers). Such low conversion efficiency tends to increase the size and mass of the electrical energy storage (e.g., capacitor bank or flywheel generator) required to deliver a given initiation pulse energy -- which is, of course, a serious disadvantage for any portable system!

(2) Laser Ignition. This is the subject of the present investigation about which we have much more to say later. At this point, it suffices to say that, potentially, laser ignition offers the same principal advantage as does flashlamp ignition, but without many of the latter's inherent limitations. Furthermore, since the input and output radiation are of the same nature (i.e., both are coherent laser radiation), this method of initiation readily renders itself to the possibility of multiple staging in which the laser output from one power amplifier stage can be used both as the initiation energy source and as the input coherent beam for further amplification in the next power amplifier stage.

b. Initiation by Electronic Processes

Electron-molecule collisions at sufficiently high-electron energy generally lead to dissociation as well as vibrational and electronic excitation of the molecules. Thus, passage of an electric current is a well proven method for initiating a chain chemical reaction. However, achievement of spatial homogeneity for the resultant chemical reaction is not an easy matter since the local concentration of reaction chain centers (e.g., dissociated atoms) would be proportional to the local electron current density, and the achievement of uniform current density distribution in a gaseous medium is not at all trivial, especially at high gas pressures.

According to the way in which the initiating electron current is introduced into the reaction volume, this method can further be subdivided into two or more classes:

(1) Pulsed Electric Discharge Ignition. In recent development of transversely excited atmospheric (TEA) CO_2 lasers,[12-17] it has been demonstrated that relatively uniform pulsed electrical discharges in diatomic and polyatomic gas mixtures at pressures comparable to, or somewhat higher than, the standard atmospheric pressure (760 torr) can be achieved either through the use of multiple, individually ballasted electrodes, or through the use of double-discharge with carefully contoured electrodes. While the degree of spatial homogeneity so achieved has been found to be satisfactory for electrical pumping of chemically-passive molecular lasers,

one does not know at this time if it would also be adequate for the initiation of chemical lasers. At any rate, for the initiation of those chemical lasers involving chain chemical reactions, the discharge current must be uniformly distributed over the bulk of the reaction volume in a time scale that is short in comparison with the characteristic chain propagation time so as to avoid the formation of detonation waves. This tends to impose a more stringent requirement on the discharge geometry and method. (For example, helical discharges[15] which leaves a major fraction of the reaction volume devoid of discharge current are bound to be unsatisfactory. The use of double discharge[17] may also be inhibited by prematured detonation considerations.)

(2) Electron Beam Ignition. The possible use of high-energy electron beam as a means for uniform pumping of CO_2-N_2 lasers at moderately high pressure was suggested by the principal investigator to one of his graduate students in 1966.[18] The advantage of using high-energy electrons is that multiple scattering of the primary beam and rapid spreading of the secondary electron-ion pairs in the target gas tend to make the current distribution much more uniform than would be possible in ordinary electrical discharges. The only disadvantage of using high-energy electron beam is that relatively high voltage would be needed in the generation of such beam, and that relatively thin windows made up of low-Z (i.e., low atomic number) material would have to be employed as

partition between the beam generation chamber and the laser gas excitation chamber.

The predicted superiority of high energy electron beam over that of conventional electrical discharge as a means for the pumping of electrical lasers has since been demonstrated by recent works at the AVCO Everett Research Laboratory[19] and elsewhere.[20] Purely from the point of view of spatial homogeneity, one may expect that the use of high-energy electron beam would also be superior to the use of conventional electrical discharge for the purpose of igniting a chemical laser. However, on absolute term, and in actual application, there are other factors to be considered. For example, it is not clear at this point to what extent would the presence of free electrons be detrimental to the maintenance of vibrational population inversion in an ignited chemical laser mixture. (According to the principle of detailed balance, electron impact processes that are efficient in vibrational excitation would also be efficient in vibrational de-excitation.) Such questions, of course, cannot be answered without further investigation -- and investigation into such problems is quite outside the scope of the present study.

4. LASER IGNITION OF SINGLE-PHASE SYSTEMS

Let us now turn to the main subject of the present investigation, namely, laser ignition. In this subsection, we will consider only single-phase chemical laser systems. In particular, we will focus our attention on the hydrogen-halide systems since such systems appear to be the only ones that have been demonstrated to be capable of yielding relatively high power density among all presently known chemical lasers.

a. General Nature of Interaction between an Intense Laser Beam and an Absorbing Gas

Interactions between a laser beam and an absorbing medium are governed by the electromagnetic wave propagation equations; the mass, momentum, and energy conservation equations of the medium; the equation of state which relates the local stress (including the hydrostatic pressure) to the local strain and other thermodynamic state variables (such as mass density and translational temperature) of the medium; the constitutive equations which relate the local macroscopic electromagnetic properties of the medium (such as the refractive index, the absorption coefficients, etc.) to the local thermodynamic state of the medium; the relaxation equations (including all relevant chemical kinetic rate equations); and also the boundary conditions for the interaction medium. The general problem is therefore very complex, and, in fact, open-ended.

For the purpose of studying the chemical laser initiation problem in a gaseous medium, one may ignore all quantized field effects and adopt the semiclassical treatment of electromagnetic radiation as an approximation. Furthermore, the processes of absorption and refraction can be considered independently, with the ray curvature determined entirely by refractive index gradient as in a lossless dielectric medium. The refractive index gradient, in turn, is determined by the non-uniform heating effects caused by intial beam inhomogeneity, and non-uniformity in the spatial distribution of absorption coefficient, if any. This is reasonable since absorption occurs along the path length and has little effect on bending the rays except indirectly through localized heating, which changes the refractive index distribution.

(1) The Governing Equations. Within the above stated approximation, the radiation field associated with the laser beam can be represented by a slightly-curved, nearly-monochromatic electromagnetic wave of local electric and magnetic field vectors

$$\vec{E} = \vec{E}_o\, e^{-i\omega t} \tag{4}$$

$$\vec{H} = \vec{H}_o\, e^{-i\omega t} \tag{5}$$

The vector field amplitudes $\vec{E}_o$, $\vec{H}_o$, in turn, are governed by the source-free Maxwell's equations, such that[18, 21, 22]

$$\vec{\nabla}\times \vec{H}_o + i k_o \epsilon \vec{E}_o = 0 \tag{6}$$

$$\vec{\nabla}\times \vec{E}_o - i k_o \mu_m \vec{H}_o = 0 \tag{7}$$

$$\vec{\nabla} \cdot \mu_m \vec{H}_o = 0 \tag{8}$$

$$\vec{\nabla} \cdot \epsilon \vec{E}_o = 0 \tag{9}$$

where ϵ and μ_m are the local dielectric constant and magnetic permissivity as defined by the constitutive equations

$$\vec{D}_o = \epsilon \vec{E}_o = \text{electric displacement} \tag{10}$$

$$\vec{B}_o = \mu_m \vec{H}_o = \text{magnetic induction} \tag{11}$$

and $k_o = 2\pi/\lambda_o = \omega/c$ is the magnitude of the vacuum propagation vector. After substitution of Eq. (7) into (6) and applying (9), one gets

$$\nabla^2\vec{E}_o + \epsilon\mu_m k_o^2 \vec{E}_o + \vec{\nabla} \log \mu_m \times (\vec{\nabla} \times \vec{E}_o) + \vec{\nabla}(\vec{E}_o \cdot \vec{\nabla} \log \epsilon) = 0 \tag{12}$$

For propagation through gaseous media, it is reasonable to assume μ_m = constant = 1, such that (12) becomes

$$\nabla^2\vec{E}_o + n^2 k_o^2 \vec{E}_o + 2\vec{\nabla}(\vec{E}_o \cdot \vec{\nabla} \log n) = 0 \tag{13}$$

where $n = \sqrt{\epsilon}$ is the ordinary index of refraction.

In a gas, $n = 1 + \Delta n$ where $\Delta n << 1$, and hence the ratio of the third term to the second term in Eq. (13) is of the order of magnitude[23]

$$\frac{E_o k_o \Delta n/\ell}{E_o n^2 k_o^2} = 2\Delta n/(n^2 k_o \ell) \tag{14}$$

where ℓ is the smallest scale of variation of the refractive index. It can always be assumed that $\lambda << \ell$, hence $2\Delta n/n^2 k_o \ell << 1$ and therefore Eq. (13) reduces to

$$\nabla^2\vec{E}_o + n^2 k_o^2 \vec{E}_o = 0 \tag{15}$$

Next, let us assume that

$$E_o(r, z) = A(r, z)\ e^{i[k_o z - \omega t + k_o \rho(r, z)]} \tag{16}$$

is a component of the laser beam electric field where $A(r, z)$ and $\rho(r, z)$ are slowly varying functions of the axial coordinate z and rapidly varying functions of the radial coordinate r. Substituting Eq. (16) into (15), equating real and imaginary parts, and making the eikonal approximation with $k_o \to \infty$, one obtains

$$\frac{\partial A^2}{\partial z} + q \frac{\partial A^2}{\partial r} + A^2 \left(\frac{q}{r} + \frac{\partial q}{\partial r} \right) = 0 \tag{17}$$

$$\frac{\partial q}{\partial z} + q \frac{\partial q}{\partial r} = - \frac{1}{n_o} \frac{\partial n}{\partial T} \frac{\partial T}{\partial r} \tag{18}$$

where $q \equiv \frac{\partial \rho}{\partial r}$. The condition $q = 0$ implies that phase fronts are moving in the z direction or that the ray paths are not diverging. Equations (17) and (18) show that the amplitude and phase of the laser radiation are not independent. The effect of absorption can be taken into account by modifying[22] Eq. (17) to include the absorption term αA^2, such that

$$\frac{\partial A^2}{\partial z} + q \frac{\partial A^2}{\partial r} + A^2 \left(\frac{q}{r} + \frac{\partial q}{\partial r} \right) + \alpha A^2 = 0 \tag{19}$$

where α is the absorption coefficient which may be a function of the spatial coordinates. Thus, for the simplest case of a nondivergent beam with $q = 0$, Eq. (19) reduces to

$$\frac{\partial A^2}{\partial z} + \alpha A^2 = 0 \qquad (20)$$

which is the radiative transfer equation[24] applied to a parallel beam propagating in the z direction with no source term.

Neglecting convection and relaxation effects, the local gas temperature T is related to the electric field amplitude by the energy equation in a constant volume absorption process

$$\rho C_v \frac{\partial T}{\partial t} = \nabla \cdot (K \nabla T) + \alpha I \qquad (21)$$

where $I = I(r, z)$ = local beam intensity = $\langle c/8\pi \, \mathrm{Re}(E \times H^*) \rangle = c/8\pi A^2$ with the $\langle\ \rangle$ brackets indicating a time average, C_v is the specific heat at constant volume, and K is the heat conduction coefficient of the gaseous medium. Thus, if the absorption coefficient α were known, neglecting convection and relaxation effects, Eqs. (18), (19), and (21) constitute three equations and three unknowns q, A^2, and T. These equations are difficult to solve[21, 22] in general and therefore the usual procedure is to solve the equations assuming $q = 0$ (i. e., negligible beam divergence) and then determine thermal defocusing effects in an iterative manner. This is a reasonable procedure only when the beam divergence effect is weak (i. e., either weak absorption, or small initial beam inhomogeneity, or both). When the beam divergence effect is strong, Eqs. (18), (19), and (21) must be solved simultaneously together with the appropriate boundary conditions, including wall reflection and scattering to the extent that they are present.

(2) Thermal Defocusing. Once the temperature distribution is determined as indicated above for $q = 0$, the ray paths of the laser beam can be calculated within the eikonal approximation assuming propagation through a lossless dielectric medium with a known temperature dependence of the refractive index $n = n(T)$. The problem would, of course, be much more complicated if relaxation effects were present. In the case, the refractive index would also be a function of time, and so would be the absorption coefficient α.

The eikonal approximation[25] to Maxwell's equations assumes that the time independent part of the electric and magnetic field is described by

$$\vec{E}_o = \vec{\mathcal{E}}(\vec{r})\, e^{ik_o \zeta(\vec{r})} \tag{22}$$

$$\vec{H}_o = \vec{\mathcal{H}}(\vec{r})\, e^{ik_o \zeta(\vec{r})} \tag{23}$$

where $\zeta(\vec{r})$ is the scalar eikonal term.

If Eqs. (22) and (23) are substituted into Eqs. (6), (7), and (8) and going to the geometric optics limits where $k_o \to \infty$ one obtains the eikonal equation.

$$(\vec{\nabla}\zeta)^2 = n^2(\vec{r}) \tag{24}$$

Also, $\vec{S}$ = time averaged Poynting vector = $c/8\pi \, \mathrm{Re}(\vec{\mathcal{E}} \times \vec{\mathcal{H}}) = c/8\pi \, (\vec{\mathcal{E}} \cdot \vec{\mathcal{E}}^{*}) \vec{\nabla} \zeta$. Thus, in the geometric optics limit, the gradient of the eikonal has the same direction as the Poynting vector or the energy flux vector. Therefore,

$$\vec{\nabla} \zeta = n \vec{s} = n \frac{d\vec{r}}{ds} \tag{25}$$

where $\vec{s}$ is a unit vector in the direction of $\vec{S}$ and $\vec{r}(s)$ is a positive vector along the ray path. As the laser beam propagates through an absorbing gas, self heating effects create radial temperature gradients. These temperature gradients induce radial gradients in the refractive index which cause the beam to diverge and reduce the centerline intensity. If wall reflection and scattering were absent, the reduction in intensity due to divergence of the rays is determined from the condition

$$\vec{\nabla} \cdot \vec{S} = \vec{\nabla} \cdot (I \vec{s}) = \vec{\nabla} \cdot [(I \vec{\nabla} (\zeta / n))] = 0 \tag{26}$$

where I is the local intensity. The intensity ratio at any two points of a diverging ray is therefore given by

$$I_2 / I_1 = (n_2 / n_1) \exp \left[- \int_{s_1}^{s_2} \frac{\vec{\nabla} \cdot (n \vec{s})}{n} \, ds \right] \tag{27}$$

The local curvature of a ray is related to the variation in the refractive index by use of Eq. (25). Thus,

$$\frac{d}{ds}\left(n\,\frac{d\vec{r}}{ds}\right) = \frac{d}{ds}\,(\vec{\nabla}\zeta) = \vec{\nabla} n \tag{28}$$

the curvature

$$\vec{\kappa} \equiv \frac{d^2\vec{r}}{ds^2} = \frac{1}{\rho_\kappa}\,\vec{\Upsilon} \tag{29}$$

is therefore from Eq. (32) given by

$$n\vec{\kappa} = \vec{\nabla} n - \frac{dn}{ds}\,\vec{s} \tag{30}$$

$$\frac{1}{\rho_\kappa} = |\vec{\kappa}| = \vec{\Upsilon} \cdot \vec{\nabla}(\log n) = \frac{d\theta}{ds} \tag{31}$$

where θ is the angular deflection of the ray. For the special case where the radial gradients in the refractive index are much greater than in the z direction, Eq. (31) reduces to

$$\theta_{z_2} - \theta_{z_1} = \int_{z_1}^{z_2} \frac{1}{n}\,\frac{\partial n}{\partial r}\,dz \tag{32}$$

gives the angular divergence of a ray propagating in the z direction. To first order, therefore, Eqs. (27) and (32) determine thermal defocusing effects as discussed by Gordon et al.[26] and D. C. Smith[27] for a given temperature distribution.

An alternate formulation which eliminates the iteration procedure is to use the energy equation for the electromagnetic field. Thus, the energy equation is

$$\nabla \cdot (I\vec{S}) + \alpha I = \vec{\ } \cdot \vec{\nabla} I + I\vec{\nabla} \cdot \vec{\ } + \alpha I = 0 \tag{33}$$

which reduces to the radiative transfer equation

$$\frac{dI}{ds} + \alpha I = 0 \tag{34}$$

for the case $\vec{S}$ = constant. The term $\vec{\nabla} \cdot \vec{S}$ means that the intensity is reduced by beam divergence as well as absorption. The divergence effect is determined from the eikonal approximation

$$\vec{\nabla} n = \frac{d}{ds} (n\vec{S}) \tag{35}$$

and the energy equation for the fluid such as Eq. (21) when convection effects are neglected. The refractive index $n = n(T)$ is assumed a known function. Then Eqs. (21), (33), and (35) give five equations and five unknowns I, T and $\vec{S}$ which must be solved simultaneously. This is more difficult than the previously discussed iteration procedure where there are only two unknowns I and T.

Using the above formulation, numerical calculations on the time-dependent temperature and beam intensity distributions in the strong thermal interaction region of a suddenly turned on CO_2 laser beam propagating through a pure CO_2 gas confined in a cylindrical chamber of inside diameter much larger than that of the laser beam with a Gaussian initial intensity distribution have been carried out by R. A. Chodzko,[18, 28] using the finite-difference method. In Chodzko's calculations, relaxation effects were neglected, and the temperature-dependent absorption coefficient was calculated according to the assumption of local equilibrium population of the CO_2 vibrational and rotational states. While not directly applicable to the present problem of interest (where the reactive gas container diameter is likely to be comparable to, or even somewhat smaller than, the incident beam diameter in order to avoid excessive nonuniform heating), Chodzko's results clearly showed that at high beam intensities, nonlinear heating effects caused by the temperature-dependence of the absorption coefficient are often dominant in determining the time-dependent temperature and beam intensity distributions within the absorption region.

The finite-difference code developed by Chodzko[18] can readily be adopted for the calculation of transient heating of any chemically passive gas mixture of known $\alpha(T)$ and $n(T)$ for any desired container diameter and initial beam intensity distribution. With suitable modifications, it can also be used for the calculation of other interaction effects, such as optical-acoustic coupling[29, 30] and internal pressure wave excitation. However, these have not been carried out in the present study due to the very limited time and resources available.

b. Gas-phase Absorption Processes Resulting in Dissociation

When a laser beam is used as an energy source for the initiation of a chemical laser, the most ideal absorption process would be one in which most of the absorbed energy is spent in the generation of active atoms which contribute to the chemical pumping of the laser states. This means not only that very little energy would be wasted in translational/rotational heating and in other unwanted internal excitations, but also that most undesirable interaction effects such as thermal defocusing, optical-acoustic coupling, nonuniform heating, etc., would accordingly be minimized.

In gas-phase absorption, there are two known processes which could approach the above cited ideal when the incident laser beam frequency is in the right range.

(1) Photodissociation. It is well known that most halogen molecules, such as F_2, Cl_2, I_2, etc., have strong dissociation continua in the near ultraviolet.[31] Thus, high-power pulsed lasers operating in the near ultraviolet region could conceivably be utilized as efficient initiation sources for hydrogen-halide lasers through direct photodissociation of the halogen molecules. However, recently discovered coherent quantum effects, such as self-induced transparency (SIT),[32, 33] may limit the applicability of photodissociation of such gases by coherent laser sources to relatively high gas pressures or relatively low incident beam intensity.

Even if coherent quantum effects does not turn out to be a serious impediment to the photodissociation process, the feasibility of laser ignition through direct photodissociation would still hinge on the availability of efficient, high-energy pulsed laser sources operating in the near ultraviolet part of the spectrum, as well as on the kinetics problem common to all methods of initiation.

(2) Cascade Excitation of Vibrational Modes. In contrast to the uncertain availability of efficient, high-energy pulsed near ultraviolet lasers, recent progress in gas laser technology has made near-term availability of efficient, high-energy pulsed infrared lasers a certainty.[19] Thus, in the laser ignition problem, it would be most fruitful to look for selective infrared absorption processes which may lead to preferential dissociation of the participating molecules. The cascade excitation dissociation of BCl_3 molecules by CO_2 radiation as recently observed by Karlov et al.[34] appears to be just one of such processes. Even though it is not clear at this time if such selective dissociation process can proceed in laseable gas mixtures, its possible usefulness as an initiation step certainly deserves further exploration.

c. Prospect of Pulse Energy Gain from Nonchain Reactions

Pulsed chemical laser actions involving nonchain reactions of the type

$$Cl + HBr \rightarrow HCl + Br + 15.5 \text{ kcal/mole} \tag{36}$$

$$Cl + HI \rightarrow HCl + I + 32.0 \text{ kcal/mole} \tag{37}$$

have been reported by Airey[11] and by Polanyi et al.[35,36] In these experiments, electronic flashlamps were used as the energy source for generation of the active atoms through photodissociation of Cl_2. In such nonchain reactions, the laser output energy that can be extracted from each mole of Cl atoms consumed is at most some fraction of the exothermicity, namely, 15.5 kcal/mole for reaction (36), and 32.0 kcal/mole for reaction (37). On the other hand, the dissociation energy of Cl_2 is about 57 kcal/mole, so that the energy required for generation of each mole of dissociated Cl atoms is at least 28.5 kcal. Thus, if a laser is used as the energy source for the generation of the active atoms for the pumping of the nonchain chemical laser reactions of the type (36) and (37), the required laser input energy would most certainly be greater than the resultant chemical laser output energy. Therefore, one can quite safely conclude that the prospect of achieving pulse energy gain from any single-phase, nonchain chemical laser driven by another laser is always negative.

d. Prospect of Pulse Energy Gain from Chain Reactions

When a laser is used as an initiation energy source for a pulsed chemical laser based on chain reactions of the type

$$F + H_2 \rightarrow HF + H + 31.7 \text{ kcal/mole} \qquad (38)$$

$$H + F_2 \rightarrow HF + F + 106.7 \text{ kcal/mole} \qquad (39)$$

or their isotopic equivalent, reactions (1) and (2), the prospect of energy gain appears to be much better since each chain center atom generated by the initiation source can now be recycled many times before the chain terminates. However, in pulsed systems where the reaction produce molecules (e.g., HF or DF from reactions (38), (39), (1) and (2) cannot be physically removed from the lasing region within the pulse period, the maximum laser energy output that can be extracted through the consumption of each chain center atom would be governed by the collisional de-excitation rate of the upper laser state as well as by the reaction chain length. We shall examine these points in more details in the sub-sections that follow, since these points are quite crucial in any quantitative prediction of single-phase pulsed chemical laser performance, using whatever method of initiation.

(1) Prediction of Pulsed Chemical Laser Energy Output Based on Chain Reactions. As mentioned in the introductory section, the most penetrating theoretical analysis of single-phase pulsed chemical laser operation involving chain chemical reactions to date appears to be that of Oraevskii,[10] even though the analysis was limited to linear systems involving very few rate-limiting reactions. Oraevskii's analysis can be summarized briefly as follows:

(a) The Single Chain Reaction

An idealized three-level system is considered here (see Fig. 1). Let us consider the following chain process,

$$\text{(i)} \qquad A_2 + Q \xrightarrow{k} 2A \qquad \text{(Chain initiation)}$$

$$\left.\begin{array}{ll} \text{(ii)} & A + B_2 \xrightarrow{k_0} AB(0) + B \\ \text{(iii)} & B + A_2 \xrightarrow{k_2} AB(2) + A \end{array}\right\} \qquad \text{(Chain propagation)}$$

$$\text{(iv)} \qquad AB(2) + M \xrightarrow{k_1} AB(1) + M \qquad \text{(Relaxation process)}$$

where A_2 and B_2 are the initial reactants, AB(2) is a molecule in the upper laser level, AB(1) is a molecule in the lower laser level, AB(0) is a molecule in the ground state, Q is the energy supplied to dissociate one of the reactants to form the chain centers, and M is any one of the reactants. And k, k_0, k_2, and k_1 are respectively the rate constants for the reactions (i), (ii), (iii) and (iv). If the initiation of the reaction is by light, then k is proportional to the photon density and the photodissociation cross section. The rate equations describing the forward reactions of these processes can be written down for the concentrations of AB(2), AB(1), A, B, A_2 and B_2, i.e., [AB(2)], [AB(1)], [A], [B], $[A_2]$, and $[B_2]$. However, $[A_2]$ and $[B_2]$ are assumed constant to permit a linear approximation of the equations. Introducing the following dimensionless variables,

$$\begin{array}{llll} x_2 = \dfrac{[AB(2)]}{[B_2]_0} , & & x_1 = \dfrac{[AB(1)]}{[B_2]_0} & \\[2ex] u = \dfrac{[A]}{[B_2]_0} , & & v = \dfrac{[B]}{[B_2]_0} & \\[2ex] \tau = k_2[B_2]_0 t , & & \sigma = \dfrac{k_0[B_2]}{k_2[B_2]_0} & \qquad (40) \\[2ex] \sigma_1 = \dfrac{k_1[M]}{k_2[B_2]_0} , & & \gamma = \dfrac{k[A_2]}{k_2[B_2]_0} & \end{array}$$

the rate equations can be written as

$$\frac{dx_2}{d\tau} = v - \sigma_1 x_2 \quad , \quad \frac{dx_1}{d\tau} = \sigma_1 x_2$$

$$\frac{du}{d\tau} = v - \sigma u + \gamma \quad , \quad \frac{dv}{d\tau} = -v + \sigma u \tag{41}$$

With initial conditions such as $x_2 = x_1 = u = v = 0$ at $\tau = 0$, and the assumptions that the excitation short pulse duration τ_0 is much less than the relaxation time and that $1 + \sigma >> \sigma_1$, the following expression for the maximum value of population inversion is obtained

$$(x_2 - x_1)_{max} \approx \nu \int_0^{\tau_0} \gamma(\tau') \, d\tau' \tag{42}$$

where $\nu = \frac{(1 - \ln 2)}{\sigma_1} \frac{\sigma}{1 + \sigma}$ is the chain length. It is obvious from Eq.(42) that the maximum inversion density is proportional to the absorbed number of pump quanta. Therefore, even for long effective chain length $\nu_{eff} = \frac{\sigma}{1 + \sigma} \frac{1}{\sigma_1}$, the output power of the chemical laser based on a simple chain reaction will be determined by the pump intensity.

(b) The Branched Reaction

From chemical kinetics point of view, the branched reactions give grounds for supposing that the number of active particles obtained in the final stage is independent of the energy initiating the reaction since it has been shown for such reactions[37] that the rate grows exponentially with time.

To obtain a population inversion in the system, a number of limitations on the rates of the elementary reactions of a branched chemical process are derived.

First, the following branching scheme is assumed,

$$\text{(v)} \qquad AB(2) + RA \xrightarrow{k_2'} AB(1) + R + A$$

where RA is some additional reagent that dissociates upon collision with AB(2). By incorporating reaction (v) into Eq. (41), the following system of equations are obtained

$$\frac{dx_2}{d\tau} = v - (\sigma_1 + \sigma_2)\,x_2 \ , \qquad \frac{dx_1}{d\tau} = (\sigma_1 + \sigma_2)\,x_2$$
$$\frac{du}{d\tau} = v - \sigma u + \sigma_2 x_2 + \gamma \ , \qquad \frac{dv}{d\tau} = -v + \sigma u \tag{43}$$

where $\sigma_2 = \dfrac{k_2'[RA]}{k_2[B_2]_0}$, and k_2' is the rate constant for reaction (v). The solution to x_2 may be written as

$$x_2 = A e^{s\tau} \tag{44}$$

where A is a constant which depends on the intensity of illumination, and s is the positive root of the equation

$$s^3 + s^2(1 + \sigma + \sigma_1 + \sigma_2) + s(1 + \sigma)(\sigma_1 + \sigma_2) - \sigma\sigma_2 = 0 \tag{45}$$

and it follows from Eq. (43) that

$$x_1 = \frac{\sigma_1 + \sigma_2}{s} A e^{s\tau} \tag{46}$$

The condition of exponential growth of the inverted population, i.e. $(x_2 - x_1) > 0$ implies the following inequality

$$s > \sigma_1 + \sigma_2 \tag{47}$$

Therefore a general condition which imposes a limitation on the partial densities of the reactants and the rate constants of the reacting mixture is obtained.

To be more specific, consider the following case of low branching rates such that $\sigma_2 \ll \sigma$, and also $\sigma \ll 1$. From Eq. (45), we obtain

$$s \simeq \sigma \sigma_2 / \sigma_1 \tag{48}$$

Thus, the inequality (47) becomes

$$\sigma \sigma_2 > \sigma_1^2 \tag{49}$$

Equation (49) can then be written as

$$\frac{(1 + \eta + \xi)^2}{\eta \xi} < \frac{k_0 k_2'}{k_1^2} \tag{50}$$

where

$$\xi = \frac{[RA]}{[B_2]}, \quad \text{and} \quad \eta = \frac{[A_2]}{[B_2]} .$$

Now Eq. (50) implies that ξ must satisfy the following inequality,

$$\xi_- < \xi < \xi_+ \tag{51}$$

where ξ_- and ξ_+ are the roots of the quadratic equation

$$\xi^2 + 2\left(1 + \eta - \eta\,\frac{k_0 k_2'}{2k_1^2}\right)\xi + (1+\eta)^2 = 0 \tag{52}$$

Since physically $\xi > 0$, therefore from (50)

$$\frac{k_0 k_2'}{k_1^2} \geq \frac{1+\eta}{\eta} \tag{53}$$

Similar conclusions can be drawn on η since it is obvious in Eq. (10) that both η and ξ are symmetrical.

Now, if the branching scheme is the following

(vi) $AB(2) + B_2 \rightarrow 2B + AB(0)$

then following similar analysis as before, we obtain the following:

$$\eta_- < \eta < \eta_+ \tag{54}$$

where η_- and η_+ are the roots of the equation

$$\eta^2 + \left[2 - \frac{k_0 k_2'}{k_1^2}\right] \eta + 1 = 0$$

and we must have

$$\frac{k_0 k_2'}{k_1^2} \geq 4 \qquad (55)$$

And if the branching of the reaction is due to the dissociation of A_2 molecules:

(vii) $AB(2) + A_2 = 2A + AB(0)$ (56)

then it is necessary that

$$\frac{k_0 k_2'}{k_1^2} > 1 \qquad (57)$$

and

$$\eta_- < \eta < \eta_+ \qquad (58)$$

where η_- and η_+ are the roots of the equation

$$\eta^2 \left(1 - \frac{k_0 k_2'}{k_1^2}\right) + 2\eta + 1 + 1 = 0 \qquad (59)$$

It can be observed that conditions (53), (55), and (57) all indicate that in order to have exponential growth of the inverted population with time in the initial stage of a branched chain reaction, the effective reaction rate of production of the active chain centers $(k_0 k_2')^{1/2}$ must be greater than the relaxation reaction rate k_1 (for reaction iv).

A numerical solution of a model problem is solved with arbitrarily selected rate constants demonstrating the independence of the maximum inversion on the intensity of initiation of reaction. This independence could be expected from the exponential growth of inversion at the initial moments of time.

(2) Kinetics of the HF Chemical Laser System. Experimental observations of laser action of hydrogen fluoride was first reported in 1967 by Kompa and Pimental.[38] They observed this laser action in the flash photolysis of uranium hexfluoride/hydrogen (deuterium) mixtures. Since then several other fluoride/hydrogen mixtures were used in the production of hydrogen fluoride laser by flash photolysis.[39-43] The first continuous-wave HF chemical laser was reported by Spencer, Jacobs, Mivels and Gross.[6, 7] They used a supersonic nitrogen jet, containing a dilute concentration of F atoms, flowing into an ambient hydrogen atmosphere and past an optical cavity. Molecular hydrogen was then injected through perforated tubes transverse to the jet. Diffusion of H_2 into the jet produces HF^* which lases in the optical cavity.

The spectral lines observed from continuous HF and DF laser outputs are given in Table I reproduced from Ref. 9. From the intensities of the lines shown in Ref. 9, it is found that $P_2(5)$ transition at 2.795 μ and $P_1(6)$ transition at 2.707 μ are the strongest in HF laser. It is also seen that all the lines are in the P branches of the various bands. This observation is confirmed by their calculations of the zero-power gain coefficients of the transitions in a given band. The calculations show that the P-branch lines generally have greater gain coefficients and the R-branch coefficients do not even have positive values unless the total inversion in the populations of two vibrational states is quite significant.

The proposed chemical chain reaction used for the $H_2 - F_2$ system proceeds as follows:

$$\begin{array}{ll}(\text{viii}) & F_2 + M \rightleftarrows 2F + M\end{array} \quad \text{(Chain-initiation step)}$$

$$\left.\begin{array}{ll}(\text{ix}) & F + H_2 \rightleftarrows HF(v) + H \\ (\text{x}) & H + F_2 \rightleftarrows HF(v) + F\end{array}\right\} \quad \text{(Chain-propagation step)}$$

$$\begin{array}{ll}(\text{xi}) & HF(v) + M \rightleftarrows HF(v-1) + M \\ (\text{xii}) & HF(v) + HF(v') \rightleftarrows HF(v+1) + HF(v'-1)\end{array}$$

$$\left.\begin{array}{ll}(\text{xiii}) & H + H + M \rightleftarrows H_2 + M \\ (\text{xiv}) & F + F + M \rightleftarrows F_2 + M\end{array}\right\} \quad \text{(Chain-termination step)}$$

Reaction (viii) represents the dissociation of fluorine molecule by collision

Table I

OBSERVED SPECTRA FROM THE CONTINUOUS CHEMICAL LASERS

HF Identification vibrational band	Line	Wave-length (μ)	DF Identification vibrational band	Line	Wave-length (μ)
1 - 0	P(4)	2.640	1 → 0	P(8)	3.680
	P(5)	2.673		P(9)	3.716
	P(6)	2.707		P(10)	3.752
	P(7)	2.744		P(11)	3.790
2 → 1	P(4)	2.760		P(12)	3.830
	P(5)	2.795	2 → 1	P(8)	3.800
	P(6)	2.832		P(9)	3.838
	P(7)	2.871		P(10)	3.876
				P(11)	3.916
				P(12)	3.957
			3 → 2	P(8)	3.927
				P(9)	3.965
				P(10)	4.005
				P(11)	4.046

with M, a collision partner. In reactions (ix) to (xii), a particular vibrational level of HF is indicated by v. Reactions (ix) and (x) are the excitation processes of HF molecules; reactions (xi) are the vibration-translation (V-T) transfer equations with single quantum steps only; vibration-vibration (V-V) exchange of a single quantum is represented by reactions (xii).

Different excitation and de-excitation rates for the H_2-F_2 system were also reported.[44-47] In fact, a detailed list of reactions considered for the rate equations of the vibrational levels of HF molecule together with selected rate constants prepared by the Aerospace group[47] is presented in Appendix 1.

(3) "Inversion Boundary" for the Pulsed H_2-F_2 System. Due to the complexity of the chemical reactions involved in the HF chemical laser (H_2-F_2 system), it is very difficult to solve the resulting non-linear chemical rate equations without resorting to numerical techniques. The simplified treatment of Ref. 10 on chemical lasers cannot be applied directly to the HF laser without making much more elaborate analyis because the HF laser is not a simple 3-level system as depicted in Fig. 1, and many more reactions are involved (Appendix 1). Therefore, the "inversion boundary" of HF laser is defined here as the dividing line in the n_{HF} and n_F plane which indicates the possible extent as to how the HF laser may progress. (Here n_ζ denotes the number of type-ζ molecule or atom per unit volume at any given instant.)

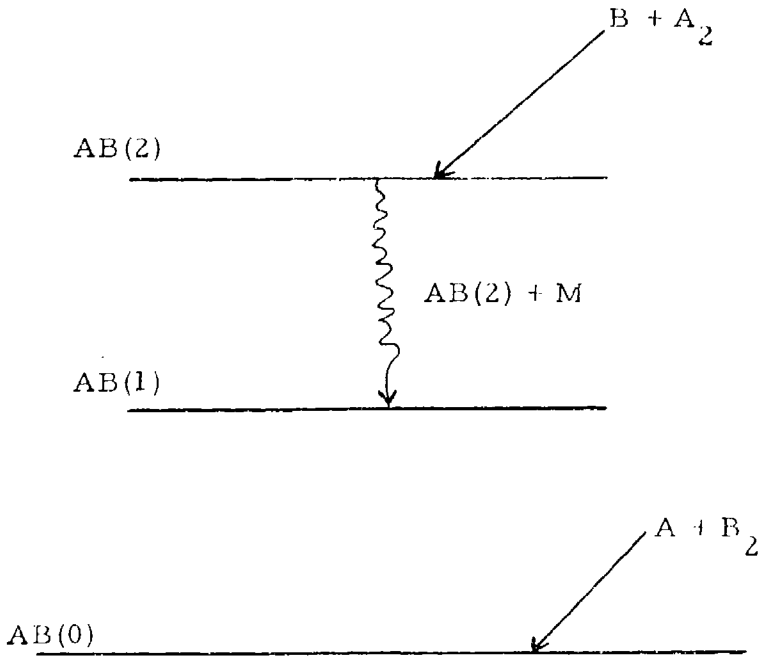

Fig. 1. The idealized 3-level system used in Ref. 1.

It has been reported[6-8, 38-43, 48] that the main laser actions of the HF chemical laser are between the second and the first (and also between the first and the ground) vibrational states of the HF molecules. For the sake of simplicity, let us only consider laser action between the second and the first vibrational states of the HF molecules. Since all the reaction rates are supposed to be known (Appendix 1), the detailed rate equation for the first and the second vibrational state population can be written down respectively. These two equations will generally involve the following unknowns: the various vibrational state number density of the HF molecule, $n_{HF(v)}$, $v = 0, 1, 2, 3, \ldots$, the hydrogen atom and molecule number density n_H, n_{H_2}, respectively, the fluorine atom and molecule number density n_F, n_{F_2}, respectively. By setting $\frac{dn_{HF(2)}}{dt} = \frac{dn_{HF(v)}}{dt}$, an algebraic equation results. With some simplification, this algebraic equation can be reduced to one involving only n_{HF} and n_F. This equation can then be represented by a curve in the $n_F - n_{HF}$ plane using n_F as the independent variable. Such a curve is what we call the "inversion boundary" of the system.

(a) Total Inversion. In the initial stage of the overall reaction, reaction (ix) is responsible for the vibrational excitation of the HF molecule. It can be accordingly expressed as

$$F + H_2 \rightarrow HF(v) + H\,, \qquad \text{where} \quad v = 0, 1, 2, 3 \tag{60}$$

The laser action occurs approximately at 3μ (see Table I), therefore, it requires about 9.6 kcal/mole to excite the HF molecules from their existing vibrational levels to the next higher vibrational levels. The heat of reaction for (38) or (60) can excite vibrational levels up to $v = 3$ for the HF molecule. It is then assumed that only $v = 0, 1, 2, 3$ vibrational levels of HF molecule are excited in the following formulation of the rate processes for the first and second vibrational levels of the HF molecule.

Now the rate equations for the first and second vibrational levels of the HF molecule can be written down according to the reactions listed in Appendix 1.

$$\begin{aligned}\frac{dn_{HF(1)}}{dt} = {} & k_{4(1)} n_F n_{H_2} + k_{5(1)} n_H n_{F_2} + k_{7a(1)} n_{HF(2)} n_{HF(0)} + k_{7a(2)} n_{HF(2)} n_{HF(2)} \\ & + k_{7b(2)} n_{HF(2)} n_{HF(3)} - k_{7b(1)} n_{HF(1)} n_{HF(2)} - k_{7a(1)} n_{HF(1)} n_{HF(1)} \\ & - k_{7a(2)} n_{HF(1)} n_{HF(3)} - k_{7c(1)} n_{HF(1)} n_{HF(3)} - k_{6a(1)} [n_{HF(1)} n_{HF} \\ & + n_{HF(1)} n_{H_2}] + k_{6a(2)} n_{HF(2)} (n_{HF} + n_{H_2}) \\ & - k_{6b(1)} n_{HF(1)} n_F + k_{6b(2)} n_{HF(2)} n_F - k_{6c(1)} n_{HF(1)} n_{F_2} \\ & + k_{6c(2)} n_{HF(2)} n_{F_2} - k_{6f(1)} n_{HF(1)} n_H + k_{6f(2)} n_{HF(2)} n_H \qquad (61)\end{aligned}$$

$$
\begin{aligned}
\frac{dn_{HF(2)}}{dt} = {} & k_{4(2)} n_F n_{H_2} + k_{5(2)} n_H n_{F_2} - k_{7a(1)} n_{HF(2)} n_{HF(0)} - k_{7a(2)} n_{HF(2)} n_{HF(2)} \\
& - k_{7b(2)} n_{HF(2)} n_{HF(3)} - k_{7b(1)} n_{HF(1)} n_{HF(2)} + k_{7a(1)} n_{HF(1)} n_{HF(1)} \\
& + k_{7a(2)} n_{HF(1)} n_{HF(3)} + k_{6a(2)} \left[n_{HF(2)} n_{HF} + n_{HF(2)} n_{H2} \right] \\
& - \oplus k_{6c(2)} n_{HF(2)} n_{F_2} + k_{6c(3)} n_{HF(3)} n_{F_2} - k_{6f(2)} n_{HF(2)} n_H \\
& + k_{6f(3)} n_{HF(3)} n_H
\end{aligned}
\qquad (62)
$$

where all $n_{HF(v)}$ can be related to $n_{HF} = \sum_v n_{HF(v)}$ by the following relationship,

$$\frac{n_{HF(v)}}{n_{HF}} \cong \frac{k_{4(v)}}{\sum_v k_{4(v)}} \qquad (63)$$

By using the values of rate constants in Ref. 7, we have

$$
\begin{aligned}
n_{HF(0)} &\cong 0.0552 \; n_{HF} \\
n_{HF(1)} &\cong 0.111 \; n_{HF} \\
n_{HF(2)} &\cong 0.555 \; n_{HF} \\
n_{HF(3)} &\cong 0.2775 \; n_{HF}
\end{aligned}
\qquad (64)
$$

The atom conservation equations for the hydrogen and fluorine atoms can be written as,

$$n_H = 2n_{H_2(t=0)} - 2n_{H_2} - n_{HF} \qquad (65)$$

$$n_F = 2n_{F_2(t=0)} - 2n_{F_2} - n_{HF} \qquad (66)$$

where $n_{H_2(t=0)}$ and $n_{F_2(t=0)}$ are the initial number densities of hydrogen and fluorine molecules. Since $\dfrac{n_H}{n_{H_2(t=0)}} \ll 1$, and $\dfrac{n_F}{n_{F_2(t=0)}} \ll 1$, we have approximately,

$$n_{HF} + 2n_{H_2} \cong 2\, n_{H_2(t=0)} \qquad (67)$$

$$n_{HF} + 2n_{F_2} \cong 2\, n_{F_2(t=0)} \qquad (68)$$

Thus, if $n_{H_2(t=0)} = n_{F_2(t=0)}$, then $n_{F_2(t)} \cong n_{H_2(t)}$, and consequently, $n_{H(t)} \cong n_{F(t)}$.

With the initial condition that $n_{H_2(t=0)} = n_{F_2(t=0)}$, we can introduce the following dimensionless quantities into Eqs. (61), (62), (64), (65), (66):

$$x = \frac{n_F}{n_{F_2(t=0)}} = \frac{n_H}{n_{H_2(t=0)}}$$

$$y = \frac{n_{HF}}{n_{F_2(t=0)}} = \frac{n_{HF}}{n_{H_2(t=0)}}$$

$$y_v = \frac{n_{HF(v)}}{n_{F_2(0)}}$$

$$z = \frac{n_{H_2}}{n_{H_2}(t = 0)} = \frac{n_{F_2}}{n_{F_2}(t = 0)}$$

Then Eqs. (61), (62), (65), and (66) become,

$$\begin{aligned}\frac{dy_1}{dt} = {} & k_{4(1)}\, xz + k_{5(1)}\, xz + k_{7a(1)}\, y_1 y_0 + k_{7a(2)}\, y_2 y_2 + k_{7b(2)}\, y_2 y_3 \\ & - k_{7b(1)}\, y_1 y_2 - k_{7a(1)}\, y_1 y_1 - k_{7a(2)}\, y_1 y_3 - k_{7c(1)}\, y_1 y_3 \\ & - k_{6a(1)}\, (y_1 y + y_1 z) + k_{6a(2)}\, (y_2 y + y_2 z) - k_{6b(1)}\, y_1 x + k_{6b(2)}\, y_2 x \\ & - k_{6c(1)}\, y_1 z + k_{6c(2)}\, y_2 z - k_{6f(1)}\, y_1 x + K_{6f(2)}\, y_2 x \qquad (69)\end{aligned}$$

$$\begin{aligned}\frac{dy_2}{dt} = {} & k_{4(2)}\, xz + k_{5(2)}\, xz - k_{7a(1)}\, y_1 y_0 - k_{7a(2)}\, y_2 y_2 - k_{7b(2)}\, y_2 y_3 \\ & - k_{7b(1)}\, y_1 y_2 + k_{7a(1)}\, y_1 y_1 + k_{7a(2)}\, y_1 y_3 - k_{6a(2)}\, y_2 (y + z) \\ & + k_{6a(3)}\, y_3 (y + z) - k_{6b(2)}\, y_2 x + k_{6b(3)}\, y_3 x - k_{6c(2)}\, y_2 z \\ & + k_{6c(3)}\, y_3 z - k_{6f(2)}\, y_2 x + k_{6f(3)}\, y_3 x \qquad (70)\end{aligned}$$

$$z = 1 - \frac{1}{2}(x + y) \qquad (71)$$

By setting $\frac{dy_2}{dt} = \frac{dy_1}{dt}$, we have

$$\bar{k}_4\, xz - \bar{k}_7 y^2 - \bar{k}_6\, f(y, z) = 0 \qquad (72)$$

where

$$\bar{k}_4 = k_{4(2)} + k_{5(2)} - k_{4(1)} - k_{4(2)}$$

$$\bar{k}_7 = 0.597\, k_{7a(1)} + 0.5564\, k_{7a(2)} - 0.0308\, k_{7c(1)} + 0.308\, k_{7b(2)}$$

$$\begin{aligned}\bar{k}_{6f}(y,z) = y^2 [1.11\, k_{6a(2)} - 0.2775\, k_{6a(3)} - 0.111\, k_{6c(1)}] \\ + yz\,[1.11\, (k_{6a(2)} + k_{6c(2)}) - 0.2775\, k_{6a(3)} + k_{6c(3)}) - 0.111\, (k_{6a(1)} + k_{6c(1)})] \\ + yx\,[1.11\, (k_{6b(2)} + k_{6f(2)}) - 0.111\, (k_{6b(1)} + k_{6f(1)}) - 0.2775\, (k_{6b(3)} + k_{6f(3)})]\end{aligned}$$

By substituting Eq. (71) into Eq. (72), there results,

$$y^2 + \frac{(\bar{k}_4 + 2\,\overline{k_{6bf}} - \overline{k_{6ac}})\,x + 2\,\overline{k_{6ac}}}{[2(\bar{k}_7 + \overline{k_{6a}}) - \overline{k_{6ac}}]}\,y + \frac{\bar{k}_4}{[2(\bar{k}_7 + \overline{k_{6a}}) - \overline{k_{6ac}}]}\,x^2 - 2\,\frac{\bar{k}_4}{[2(\bar{k}_7 + \overline{k_{6a}}) - \overline{k_{6ac}}]}\,x = 0 \qquad (73)$$

where

$$\overline{k_{6a}} = 1.11\, k_{6a(2)} - 0.2775\, k_{6a(3)} - 0.111\, k_{6a(1)}$$

$$\overline{k_{6ac}} = 1.11\,[k_{6a(2)} + k_{6c(2)}] - 0.2775\,[k_{6a(3)} + k_{6c(3)}] - 0.11\,[k_{6a(1)} + k_{6c(1)}]$$

$$\overline{k_{6bf}} = 1.11\,[k_{6b(2)} + k_{6f(2)}] - 0.2775\,[k_{6b(3)} + k_{6f(3)}] - 0.111\,[k_{6b(1)} + k_{6f(1)}]$$

where

$$\bar{k}_4 = k_{4(2)} + k_{5(2)} - k_{4(1)} - k_{4(2)}$$

$$\bar{k}_7 = 0.597\ k_{7a(1)} + 0.5564\ k_{7a(2)} - 0.0308\ k_{7c(1)} + 0.308\ k_{7b(2)}$$

$$\begin{aligned}\bar{k}_{6f}(y,z) = {} & y^2\left[1.11\ k_{6a(2)} - 0.2775\ k_{6a(3)} - 0.111\ k_{6c(1)}\right] \\ & + yz\left[1.11\ (k_{6a(2)}+k_{6c(2)}) - 0.2775\, k_{6a(3)}+k_{6c(3)}) - 0.111\ (k_{6a(1)}+k_{6c(1)})\right] \\ & + yx\left[1.11\ (k_{6b(2)}+k_{6f(2)}) - 0.111\ (k_{6b(1)}+k_{6f(1)}) - 0.2775\ (k_{6b(3)}+k_{6f(3)})\right]\end{aligned}$$

By substituting Eq. (71) into Eq. (72), there results,

$$y^2 + \frac{(\bar{k}_4 + 2\,\overline{k_{6bf}} - \overline{k_{6ac}})\,x + 2\,\overline{k_{6ac}}}{\left[2(\bar{k}_7 + \overline{k_{6a}}) - \overline{k_{6ac}}\right]}\,y$$

$$+ \frac{\bar{k}_4}{\left[2(\bar{k}_7 + \overline{k_{6a}}) - \overline{k_{6ac}}\right]}\,x^2 - 2\,\frac{\bar{k}_4}{\left[2(\bar{k}_7 + \overline{k_{6a}}) - \overline{k_{6ac}}\right]}\,x = 0 \tag{73}$$

where

$$\overline{k_{6a}} = 1.11\ k_{6a(2)} - 0.2775\ k_{6a(3)} - 0.111\ k_{6a(1)}$$

$$\overline{k_{6ac}} = 1.11\left[k_{6a(2)}+k_{6c(2)}\right] - 0.2775\left[k_{6a(3)}+k_{6c(3)}\right] - 0.11\left[k_{6a(1)}+k_{6c(1)}\right]$$

$$\overline{k_{6bf}} = 1.11\left[k_{6b(2)}+k_{6f(2)}\right] - 0.2775\left[k_{6b(3)}+k_{6f(3)}\right] - 0.111\left[k_{6b(1)}+k_{6f(1)}\right]$$

In Eq. (73), all the rate constants k are known functions of temperature; therefore, once the temperature of the system is given, Eq. (73) can be represented by a curve in the x-y plane. This curve is the "inversion boundary" for the HF chemical laser we sought.

In Fig. 2, the HF inversion boundary for three different values of the translational temperature, T = 300°K, 500°K, 1200°K are presented. It can be seen from the figure that in the region under the inversion boundary, $dn_{HF(2)}/dt$ is greater than $dn_{HF(1)}/dt$ because the pumping rate by n_F is faster than the de-excitation rate by n_{HF}. In this region, population inversion in the system is most likely (i. e., assuming reasonably favorable past history). Whereas in the region above the inversion boundary, the opposite is true. As expected, the inversion boundary moves upward as the translational temperature increases from 300°K to 500°K; but the upward move decreases as the temperature increases further from 500°K to 1200°K. These phenomena are because the excitation rate constants are much steeper functions of temperature than the de-excitation rate constants in the temperature range from 300°K to 500°K. As temperature increases further from 500°K to 1200°K, the temperature dependence of both the rate constants are comparable. In other words, as the temperature increases from 500°K to 1200°K, the de-excitation rate constants of the HF chemical laser catch up slowly with the excitation rate constants. In fact, for $n_F/n_{F_2(t=0)} \geq 10^{-2}$, it is seen from Fig. 2 that

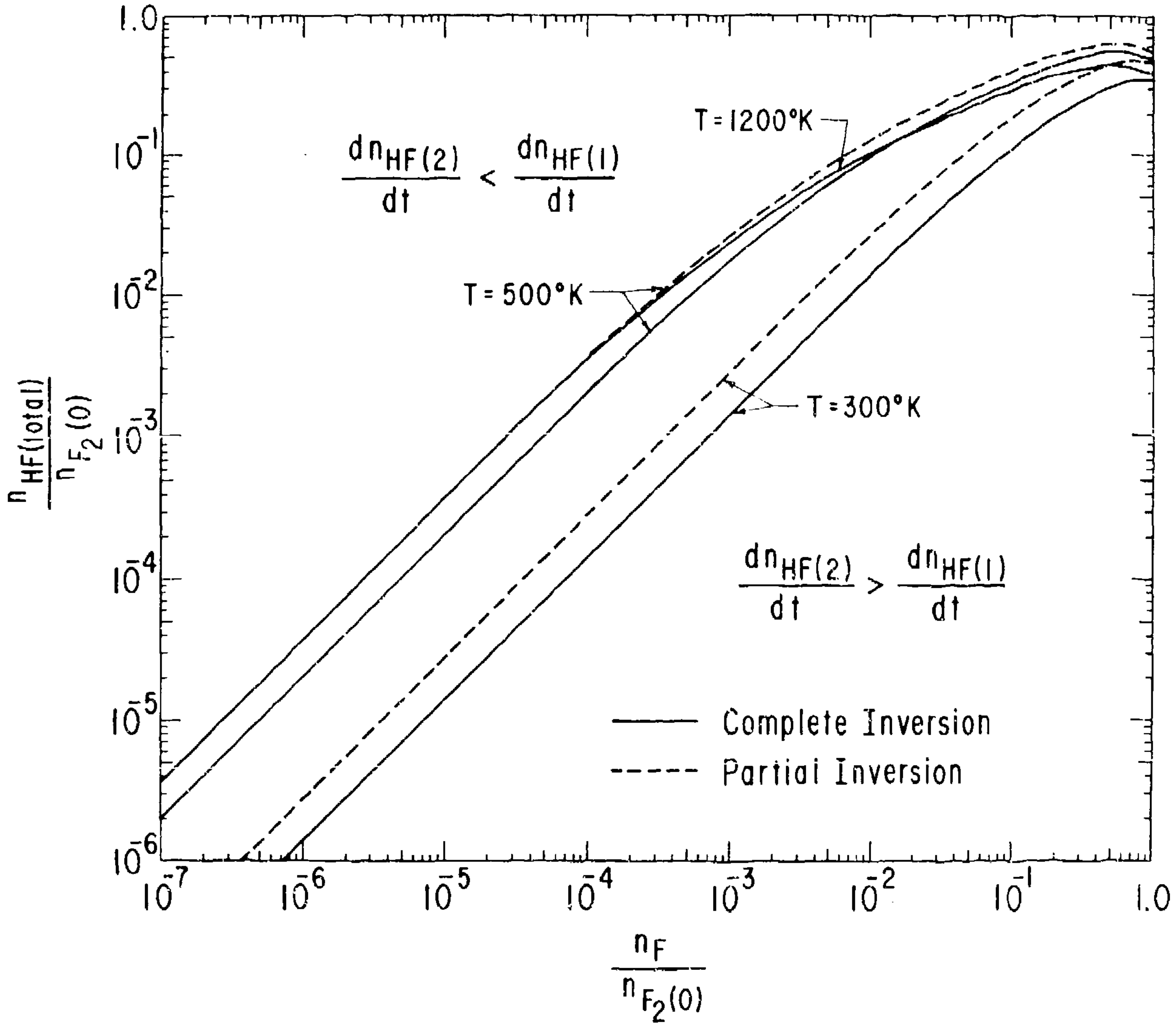

Fig. 2 Inversion boundaries as functions of the translational temperature for single-phase, H_2-F_2 chemical laser systems.

the inversion boundary at 1200° K is actually lower than the inversion boundary at 500° K.

(b) Partial Inversion. So far, we have only discussed the case of complete inversion (or vibrational inversion) in the HF chemical laser system, i. e., $n(v')$ and $n(v)$ are the number densities of the upper and lower vibrational states v' and v of a two-level laser system.

In fact, it is not always necessary to have complete inversion to ensure laser action between two levels of the same vibrational mode in a molecule. Laser action may be obtained also if there is only partial inversion[48-50] (vibration-rotational inversion), i. e.,

$$n(v', j') - \frac{g(j')}{g(j)} n(v, j) > 0 \qquad (74)$$

and

$$n(v') - n(v) \leq 0$$

where $n(v, j)$ is the number density of the specified vibrational state v and rotational state j, and $g(j)$ is the rotational degeneracy, $2j+1$. From statistical mechanics, we know that if the rotational states are in equilibrium among themselves at temperature T_r, $n(v, j)$ would be given by

$$n(v, j) = n(v)\, g(j)\, Q_{rot}^{-1}\, e^{-E_0(j)/kT_r} \qquad (75)$$

The rotational partition function Q_{rot} and the energy of the rotational state j, $E_0(j)$ can be expressed as

$$Q_{rot} = \frac{kT_r}{hc\,B}$$

$$E_0(j) = hc\,B\,j(j+1) \quad \text{(relative to } j=0 \text{ state of that same vibrational level } v\text{)}$$

where $n(v) = \sum_j n(v,j)$ is the total number density of the specified vibrational state v, k is the Boltzmann constant, h is the Planck constant, c is the speed of light, and B is the rotational constant. The rotational temperature T_r may be assumed to be equal to the translational temperature T.

Now in order to find the "partial-inversion boundary," we have to use the following condition:

$$\frac{dn(v',j')}{dt} = \frac{g(j')}{g(j)}\,\frac{dn(v,j)}{dt} \tag{76}$$

Assuming that the temperature is independent of time, we differentiate Eq. (75) with respect to time for both $n(v',j')$ and $n(v,j)$

$$\frac{dn(v',j')}{dt} = \frac{dn(v')}{dt}\,g(j')\,Q'^{-1}_{rot}\,e^{-E_0(j')/kT_r} \tag{77}$$

$$\frac{dn(v,j)}{dt} = \frac{dn(v)}{dt}\,g(j)\,Q^{-1}_{rot}\,e^{-E_0(j)/kT_r} \tag{78}$$

By substituting Eqs. (77) and (78) into Eq. (76), we obtain the following equation for the "partial-inversion boundary,"

$$\frac{dn(v')}{dt} \frac{1}{Q'_{rot}} e^{-E_0(j')/kT_r} = \frac{dn(v)}{dt} \frac{1}{Q_{rot}} e^{-E_0(j)/kT_r} \qquad (79)$$

A numerical example is chosen to compare the "partial-inversion boundary" with the "complete inversion boundary" in the HF chemical laser. For the strong HF laser line P(5) of the vibrational band 2 → 1,[9] we have

$$\left.\begin{array}{lll} v' = 2 , & j' = 4 & B' = 19.0335 \text{ cm}^{-1} \\ v = 1 , & j = 5 & B = 19.7883 \text{ cm}^{-1} \end{array}\right\} \text{(Ref. 51)}$$

By substituting these values into Eq. (39), there results

$$\frac{dn(v = 2)}{dt} = 1.04 \, e^{-307/T} \frac{dn(v = 1)}{dt} \qquad (80)$$

An algebraic equation similar to Eq. (73) can be obtained with different coefficients by substituting Eqs. (69) and (70) into Eq. (80).

The "partial-inversion" boundary for the HF chemical laser are calculated for three different temperatures, T = 300° K, 500°K and 1200° K, for comparison with the "complete-inversion" boundary. These are the dotted curves in Fig. 2. It is seen that the "partial-inversion" boundary is generally higher than the "complete-inversion" boundary. That is to say, under identical conditions, it is easier to obtain partial population inversion than complete population inversion. But the increase is not very substantial; at $T = 300°K$, the increase is about a factor of 2, at $T = 500°K$, the increase is about a factor of 1.3, and at $T = 1200°K$, the increase is only about a factor of 1.1. Actually, this is obvious from Eq. (80) because of the Boltzmann factor $e^{-307/T}$. As the temperature increases, the effect of the Boltzmann factor drops off exponentially. In other words, at high temperatures, complete inversion is as easy to obtain as partial inversion. But the effect is much more pronounced at low temperatures where partial inversion is much easier to obtain than the complete inversion.

(4) Estimate of Maximum Energy Gain Potential for Pulsed H_2-F_2 Laser Systems. The "inversion boundary" of the HF chemical laser just presented can be related to the maximum efficiency or energy gain potential of the laser system in the following way. The inversion density Δn is defined as

$$\Delta n \equiv n_{HF(2)} - n_{HF(1)} \leq n_{HF(2)} < n_{HF} \tag{81}$$

where $n_{HF} = \sum_{v} n_{HF(v)}$ is the total number density of the HF molecule. Now the total pulse energy up to time t is

$$E(t) = h\nu \int_0^t \frac{d(\Delta n)}{dt} dt < h\nu \int_0^t dn_{HF} \tag{82}$$

We want to define $\tau_{g=0}$ as the time when the gain of the laser system is zero, i.e., $t = \tau_{g=0}$, when $\Delta n = 0$, and τ_1 as the time when $\frac{d(\Delta n)}{dt} = 0$. Therefore, the total pulse energy of the laser is

$$E(\tau_{g=0}) = h\nu \int_0^{\tau_{g=0}} \frac{d(\Delta n)}{dt}\, dt < h\nu \int_0^{\tau_{g=0}} dn_{HF} = h\nu\, n_{HF}(\tau_{g=0}) \tag{83}$$

$n_{HF}(\tau_1)$ can be related to $n_{HF(\tau_g = 0)}$ in the following way,

$$\frac{n_{HF(\tau_1)}}{n_{HF(\tau_{g=0})}} \approx \frac{\tau_1}{\tau_g} \tag{84}$$

Since τ_1 is the time when $d(\Delta n)/dt = 0$, it is reasonable to assume that τ_1 is proportional to the excitation time of HF(2), τ_{ex}. And $\tau_{g=0} = \tau_1 + \tau_2$, where τ_2 is the time duration starting from $d(\Delta n)/dt = 0$ until $\Delta n = 0$; thus τ_2 is assumed to be proportional to the fastest relaxation time q HF(2), τ_{rel}

$$\begin{aligned} \tau_1 &\approx \tau_{ex} \cong \frac{n_{HF(2)}}{k_{4(2)}\, n_F n_{H_2}} \\ \tau_2 &\approx \tau_{rel} \cong \frac{1}{k_{6a(2)}\, n_{H_2}} \end{aligned} \tag{85}$$

Thus,

$$\frac{n_{HF}(\tau_{g=0})}{n_{HF}(\tau_1)} \approx \frac{\tau_g}{\tau_1} + 1 + \frac{\tau_1}{\tau_2}$$

$$\approx 1 + \frac{k_{4(2)}\, n_F}{k_{6a(2)}\, n_{HF(2)}}$$

$$\approx 1 + 1.8\, \frac{k_{4(2)}}{k_{6a(2)}}\, \frac{n_F}{n_{HF}} \qquad (86)$$

Now we want to define the maximum laser efficiency or energy gain potential as

$$\eta_{max} \equiv \frac{\text{laser output}}{\text{max. chem. energy input}} \approx \frac{1}{3}\, \frac{n_{HF}(\tau_{g=0})}{n_{F_2(0)}}$$

$$\approx \frac{1}{3} \cdot \frac{n_{HF}(\tau_{g=0})}{n_{HF}(\tau_1)}\, \frac{n_{HF}(\tau_1)}{n_{F_2(0)}} \qquad (87)$$

where $n_{HF}(\tau_1)/n_{F_2(0)}$ as a function of $n_F/n_{F_2(0)}$ is the curve in the "inversion boundary" plot of Fig. 2. Therefore, the maximum laser efficiency η_{max} is directly proportional to $n_{HF(\tau_1)}/n_{F_2(0)}$. For most of the operational HF lasers, the ratio of the free fluorine atom concentration to the hydrogen molecule concentration is about 4%, i.e. $n_F/n_{F_2(0)} \approx 4\%$. From the rate constants compiled in Appendix 2 and the "inversion boundary" plot, it can be shown that for $n_F/n_{F_2(0)} \leq 4\%$,[7, 40] at T = 300°K

$$\frac{n_{HF(\tau_{g=0})}}{n_{HF(\tau_1)}} \approx 2.8 \quad , \quad \eta_{max} \approx 0.9 \frac{n_{HF(\tau_1)}}{n_{F_2(0)}}$$

at T = 500°K

$$\frac{n_{HF(\tau_{g=0})}}{n_{HF(\tau_1)}} \approx 3 \quad , \quad \eta_{max} \approx \frac{n_{HF(\tau_1)}}{n_{F_2(0)}}$$

at T = 1200°K

$$\frac{n_{HF(\tau_{g=0})}}{n_{HF(\tau_1)}} \approx 9 \quad , \quad \eta_{max} \approx 3 \frac{n_{HF(\tau_1)}}{n_{F_2(0)}}$$

Thus, the "inversion boundary" plot can serve as an approximate maximum laser efficiency plot as a function of $n_F/n_{F_2(0)}$.

5. LASER IGNITION OF TWO-PHASE SYSTEMS

a. Definition of Two-phase Pulsed Chemical Laser Systems

For the purpose of the present study, we define a two-phase pulsed chemical laser system as a pulsed chemical laser system in which the lasing medium is made up of a reactive gas mixture plus some finely-dispersed, submicron size solid particles or liquid droplets. The apparent advantages of two-phase systems over the commonly considered single-phase systems (i.e., gaseous mixtures only) are many:

(1) The absorption of infrared and visible radiation by small particles is generally broad-band, which allows a wide selection of the chemical and surface properties of the absorber.

(2) By suitable choice of particle size and surface properties, the heated particles may be used to provide a large catalytic surface area for chain initiation and for subsequent chain branching without the need for grossly heating the entire gas mixture during the initiation process.

(3) By suitable choice of chemical properties, the heat of reaction from combustible particles may be utilized for generation of a high concentration of active atoms essential for efficient pumping of most known chemical laser systems.

Point (3) is especially attractive from the point of view of potential laser energy amplification due to the very large ratio between the heat of combustion of most metals and the energy required to heat the same metals to their corresponding ignition temperature, starting from room temperature condition. Point (1) is helpful when infrared lasers are to be used as initiation sources in view of the generally narrow-band nature of the absorption process. (For example, the cascade excitation dissociation process reported in Reference 34 was a resonant absorption process, and hence required accidental matching of the incident laser frequency and the molecular vibrational frequency.) Point (2) could be useful if long chains could be utilized for chemical laser pumping and if the rate of chain initiation in the otherwise purely gas-phase reaction were too slow.

We shall demonstrate these points in the subsections that follow.

b. Optical Properties of Two-phase Systems

The absorption and scattering properties of finely-dispersed, submicron size particles (or liquid droplets) at infrared frequencies can be calculated according to classical electromagnetic theory. According to such theory,[52] the total extinction cross-section Q_{ext} for a particle of equivalent spherical volume $V = 4\pi a^3/3$ and with mean radius a smaller than the radian wavelength $ƛ \equiv \lambda/2\pi \equiv 1/k$ of the incident radiation can be represented by an asymptotic series:

$$\frac{Q_{ext}}{\pi a^2} = -\,\mathrm{Im}\left\{ 4x\,\frac{m^2-1}{m^2+2} + \frac{4}{15}\,x^3 \left(\frac{m^2-1}{m^2+2}\right)^2 \frac{m^4+27\,m^2+38}{2m^2+3} \right\} + x^4\,\mathrm{Re}\left\{ \frac{8}{3}\left(\frac{m^2-1}{m^2+2}\right)^2 \right\} + \cdots \tag{88}$$

where Re and Im denote taking real and imaginary part, respectively, $x = ka = a/ƛ$ is the radius-to-wavelength ratio, and m is the complex index of refraction of the material that makes up the particle. The first term is the main absorption term, and the second term is the main scattering term which gives rise to the Rayleigh scattering formula when m is a real constant. By writing $m = n - i\kappa$, where n denotes the ordinary index of refraction and κ denotes the bulk extinction coefficient of the material, one obtains from Eq. (88) the following expressions for the absorption and scattering cross sections of the particle in the long wave limit (i.e., $\bar{\lambda} \gg a$, or $x \ll 1$),

$$\frac{Q_{abs}}{\pi a^2} \cong \frac{24\, n \kappa}{(n^2 - \kappa^2 + 2)^2 + 4 n^2 \kappa^2}\, ka \tag{89}$$

$$\frac{Q_{scat}}{\pi a^2} \cong \frac{f(n \kappa)}{[(n^2 - \kappa^2 + 2)^2 + 4 n^2 \kappa^2]^2}\, (ka)^4 \tag{90}$$

where

$$f(n, \kappa) = \frac{8}{3}\, (n^2 + \kappa^2)^4 + 2(n^2 - \kappa^2)[(n^2 + \kappa^2)^2 - 2]$$
$$- 3 n^4 - 46\, n^2 \kappa^2 - 3 \kappa^4 + 4$$

If the particle material is a low-loss dielectric (e.g., quartz, glass, ionic crystal, water, etc.), the extinction coefficient is generally much smaller than the index of refraction (i.e., $\kappa \ll n$). For such particles, the two cross sections become approximately,

$$\frac{Q_{abs}}{\pi a^2} \cong \frac{24\, n \kappa}{(n^2 + 2)^2}\, ka \tag{91}$$

$$\frac{Q_{scat}}{\pi a^2} \cong \frac{8(n^8 + 2n^6 - 3n^4 - 4n^2 + 4)}{3(n^2 + 2)^4}\, (ka)^4 \tag{92}$$

For metallic particles, n and κ are nearly identically given by

$$n \cong \kappa \cong \frac{\sigma \lambda}{c}^{1/2} \tag{93}$$

where σ is the electrical conductivity of the metal expressed in Guassian units, λ is the wavelength, and c is the velocity of light in vacuum. (Note that one M.K.S. unit of conductivity, i.e., 1 mho/meter, is equivalent to 9×10^9 Gaussian units of conductivity, which has the dimension of $\sec^{-1}$.) For a typical good conductor, such as aluminum, the numerical value of σ at room temperature is typically $3 \times 10^{17} \sec^{-1}$. Thus, at a typical infrared frequency $f = c/\lambda = 3 \times 10^{13} \sec^{-1}$ (corresponding to $\lambda = 10\ \mu$), the numerical value of n and κ for a good conductor is of the order of 10^2, which is much greater than unity. Accordingly, the absorption and scattering cross sections for submicron size metallic particles at infrared frequencies are approximately given by

$$\frac{Q_{abs}}{\pi a^2} \cong \frac{6}{n^2}\, ka = \frac{6c}{\sigma\lambda}\, ka \tag{94}$$

$$\frac{Q_{scat}}{\pi a^2} \cong \frac{8}{3}\,(ka)^4 \tag{95}$$

It is interesting to note that, since Q_{abs} is proportional to the first power of ka while Q_{scat} is proportional to the fourth power of ka, the scattering cross section decreases much more rapidly with particle size than the absorption cross section, so that at sufficiently small values of ka, the scattering cross section will become insignificant in comparison with the absorption cross section. In other words, a two-phase mixture composed of very fine suspended particles will essentially behave like a good absorbing medium rather than a strong scattering medium at infrared frequencies. From Eqs. (91) and (92), it is seen that for dielectric particles, the scattering cross section begins to fall below the absorption cross section when $ka < 3\,\kappa^{1/3}$. (Note that $n = 1.4$ for most dielectric material at infrared frequencies.) Similarly, from Eqs. (94) and (95), one may deduce that the scattering cross section for metallic particles will fall below the absorption cross section when $ka < 1.3\,(c/\sigma\lambda)^{1/3}$.

Another interesting point to note from Eqs. (91) and (94) is that, if we divide these equations through by the mean particle radius a, one obtains

$$\frac{Q_{abs}}{\pi a^3} = \begin{cases} \dfrac{48\,\pi\,n\kappa}{(n^2+2)^2\,\lambda} & \text{for dielectric} \\[2ex] \dfrac{12\,\pi\,c}{\sigma\,\lambda^2} & \text{for metal} \end{cases} \qquad (96)$$

which states that the absorption cross section for very small particles is proportional to the volume of the particle at a given frequency, no matter what kind of particle material.

Using handbook values, the extinction coefficient κ and index of refraction n are plotted in Figs. 3 and 4 as functions of the incident electromagnetic wavelength λ (in vacuum) over the infrared region for some ionic crystals and metals. From these values of n and κ, the absorption cross section for very small size particles made up of these materials (i.e., $ka \ll 1$) has been calculated according to Eq. (96) as a

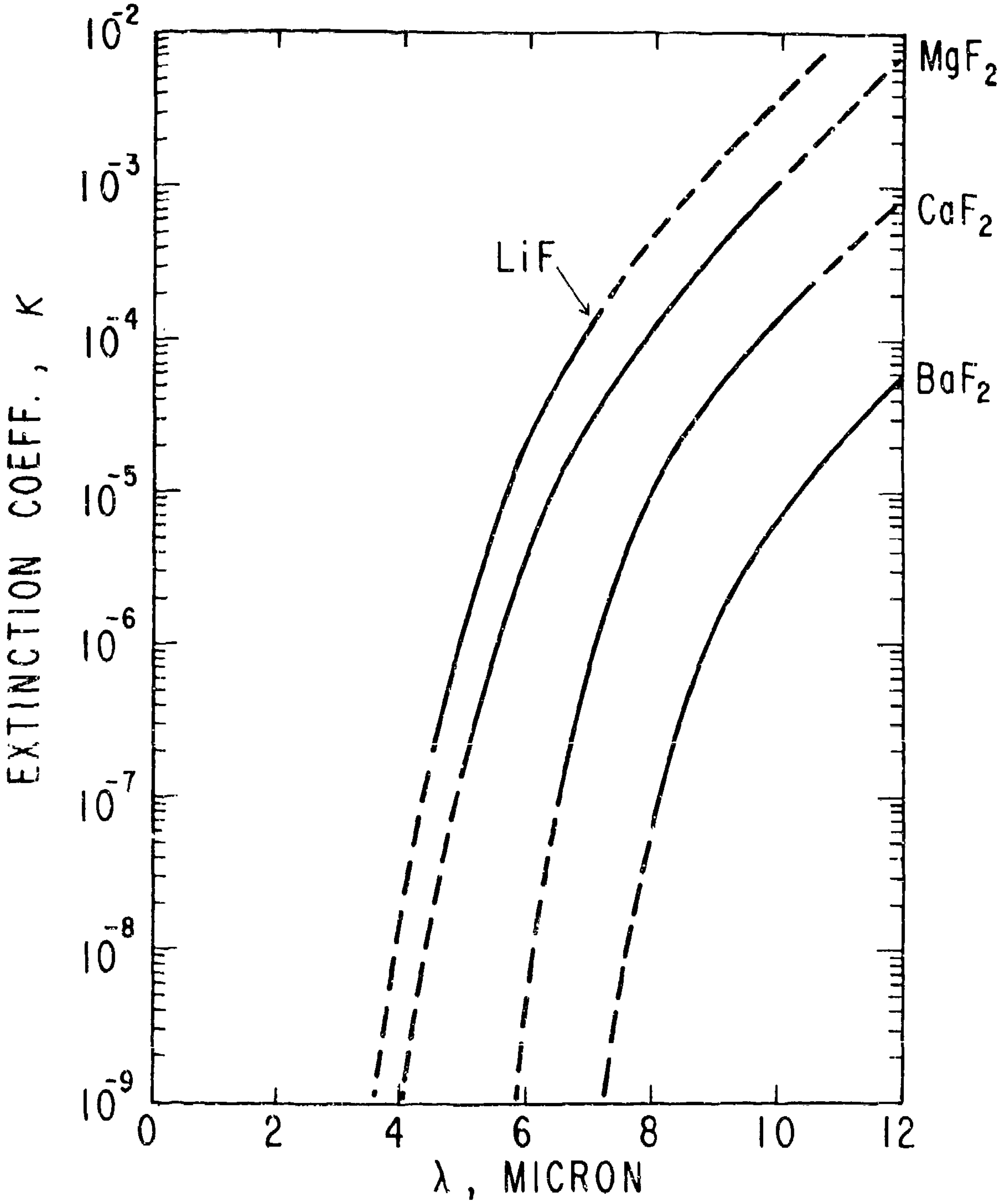

Fig. 3 Extinction coefficient K as a function of wavelength for some ionic crystals. The index of refraction n for these crystals has a nearly constant value of 1.4 in the infrared range of frequency.

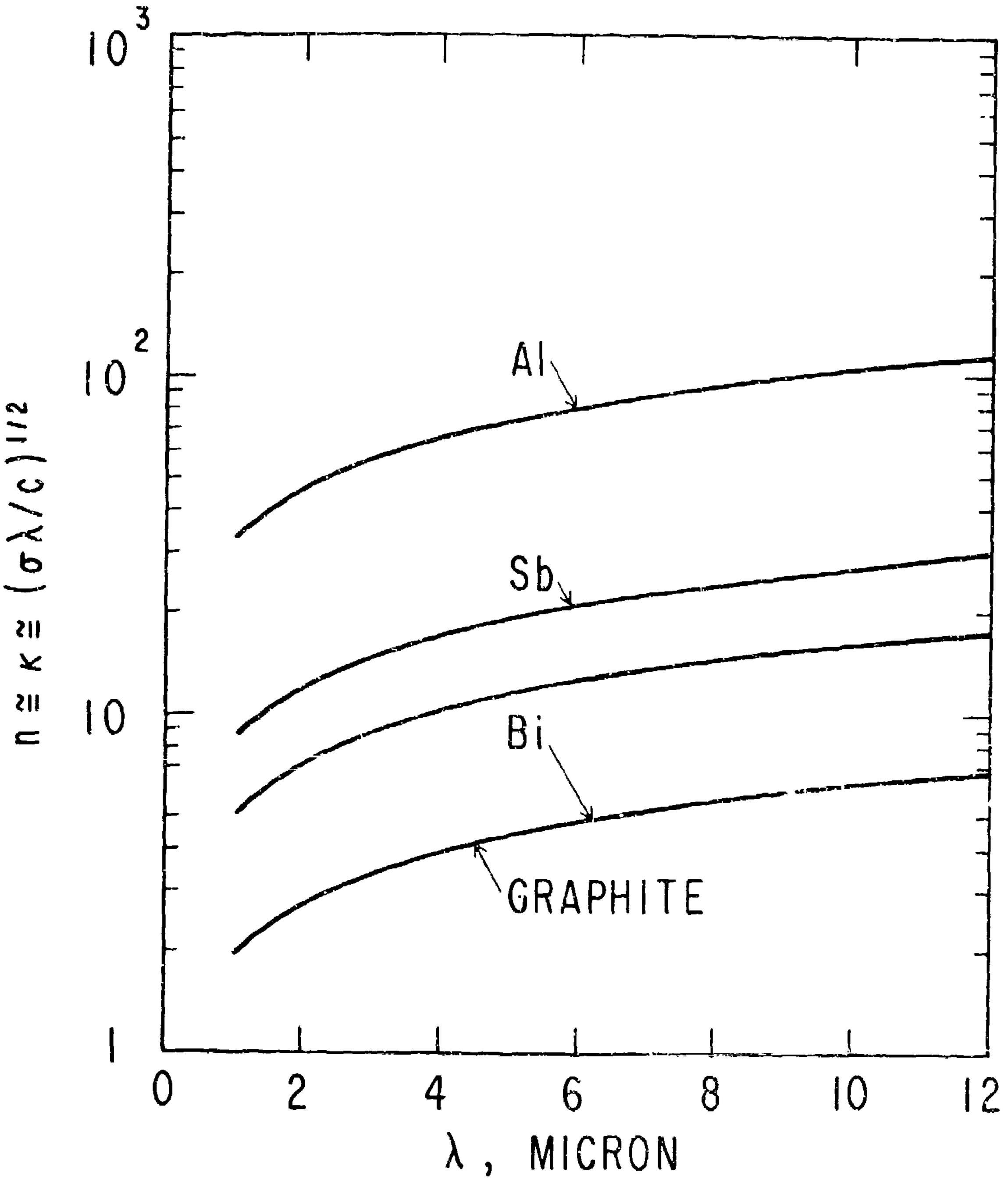

Fig. 4 Refractive index and extinction coefficient as a function of wavelength for some metals and graphite near room temperature.

function of incident wavelength. The results are plotted in Fig. 5. From these values of the absorption cross section, one can readily calculate the e-folding absorption length scale for a monochromatic beam of electromagnetic radiation propagating through a two-phase mixture consisting of a transparent gas-phase component, and a finely-dispersed solid-phase component of n_p particles per unit volume,

$$L_{abs} = \frac{1}{n_p Q_{abs}} \tag{97}$$

Since the volume fraction of solid particles, ϕ_p, in such a two-phase mixture is simply given by the product of n_p and the volume per particle $V = 4\pi a^3/3$, and the absorption cross section per particle is proportional to the particle volume according to Eq. (96), one can subsequently calculate the value of ϕ_p for yielding a desired absorption length scale, such that

$$\phi_p L_{abs} = \frac{4\pi a^3}{3 Q_{abs}} = \begin{cases} \dfrac{(n^2+2)^2 \lambda}{36\pi n \kappa} & \text{for dielectric} \\ \dfrac{\sigma \lambda^2}{9\pi c} & \text{for metal} \end{cases} \tag{98}$$

The value of ϕ_p so determined for an absorption length scale $L_{abs} = 10$ meter in two-phase mixtures containing the indicated solid particles is plotted in Fig. 6. Since the bulk density of most solids is typically 10^{-1} mole/cm^3 while the standard density for any perfect gas at room temperature and atmospheric pressure is about 4×10^{-5} mole/cm^3, the curves

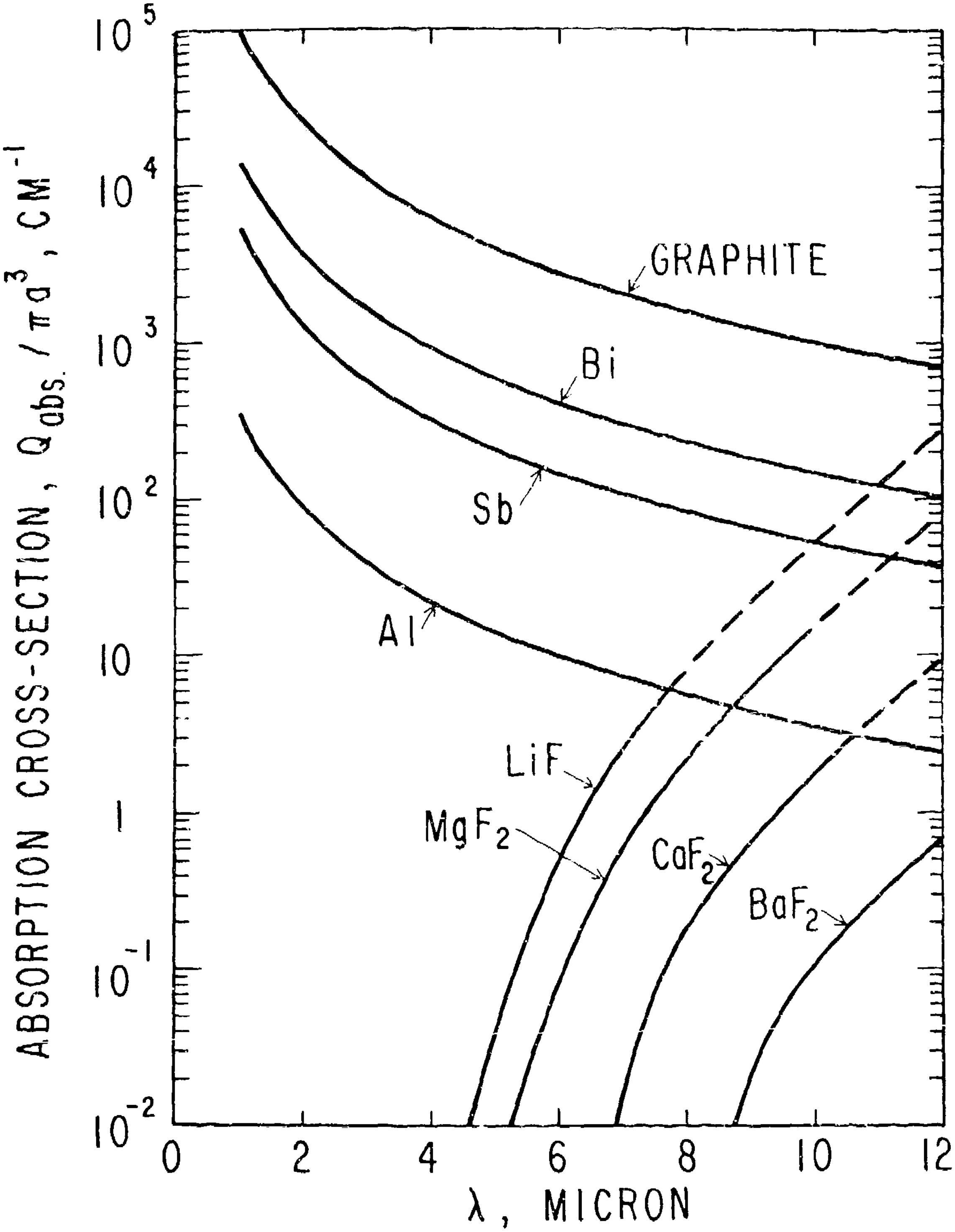

Fig. 5 Absorption cross section as a function of wavelength for some submicron size particles (ka << 1) of some ionic crystals, metals, and graphite.

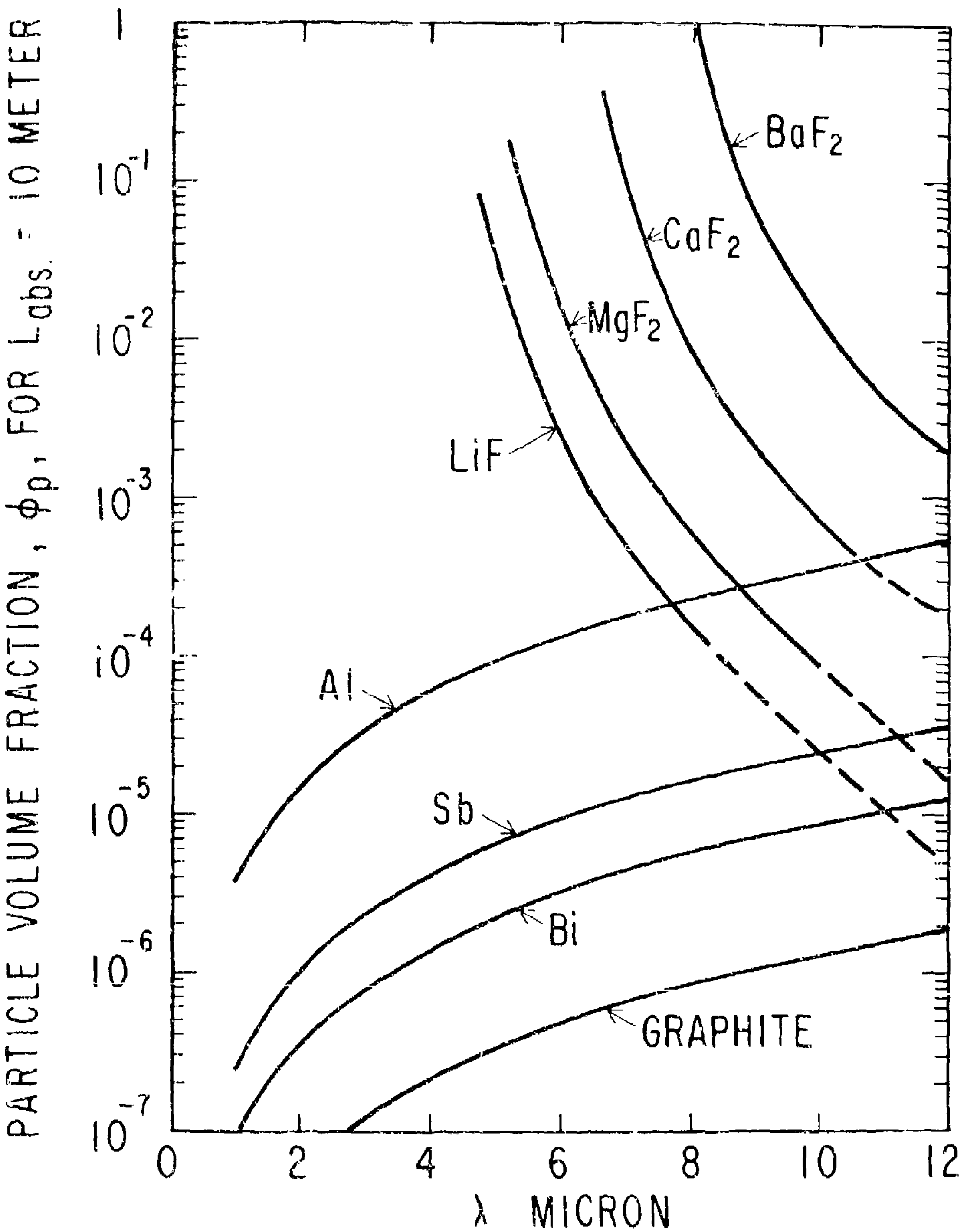

Fig. 6 Particle volume fraction in a two-phase mixture which would yield an e-folding absorption length scale of 10 meters at room temperature for some ionic crystals, metals, and graphite as a function of wavelength, neglecting gas-phase absorption and assuming ka << 1 size particles.

shown in Fig. 6 indicate that at the CO_2 laser wavelength of 10.6 μ, the mole fraction of solid particles required to yield an absorption length scale of 10 meter in a two-phase mixture at standard atmospheric pressure and temperature is about unity when the particles are made of highly conducting metals, such as aluminum and magnesium.

c. Solid Particles as Inert Catalyst for Chain Initiation and Chain Branching

It is well known that hot solid surfaces can act as catalytic surfaces for dissociation of gaseous molecules. Dissociation of H_2 by heated tungsten is just one of the examples. In general, one may expect that the rate of dissociation or catalytic efficiency would be a sensitive function of the solid surface temperature, as observed in the dissociation of H_2 by tungsten.[53] Thus, the large surface area provided by suddenly heated, finely-dispersed solid particles in a two-phase mixture can conceivably be utilized as a catalyst for chemical chain initiation and branching in the gas-phase component. Of course, in order to utilize such catalytic effect in a pulsed chemical laser system, the solid surface must be initially passive and inert so that the two-phase mixture would be stable before initiation.

Detailed calculation of the surface-catalized chain initiation and chain branching rate would require a specification of the particle heating rate as well as adequate knowledge about the temperature-dependent catalytic properties of the surface of interest. While such catalytic properties may be difficult to get, especially for particular combinations of gases and surfaces that have not yet been studied. The initial rate of heating of the solid particles by a suddenly turned on beam of electromagnetic radiation, on the other hand, is relatively easy to calculate. For example, by neglecting scattering, re-emission, and conductive heat loss, one can readily write down the energy balance equation for the small solid particles of individual volume $V = 4\pi a^3/3$ and of bulk specific heat per unit volume ρC_v during the passage of a laser beam of local intensity I,

$$\rho C_v V \frac{dT}{dt} + IQ_{abs} = 0 \tag{99}$$

Thus, the rate of temperature rise per unit beam intensity is simply given by

$$\frac{1}{I}\frac{dT}{dt} = \frac{Q_{abs}}{\rho C_v V} = \frac{3}{4\rho C_v} \cdot \frac{Q_{abs}}{\pi a^3} \tag{100}$$

The initial particle heating rate so calculated for the various particle material and absorption cross section shown in Fig. 5 is plotted here in Fig. 7. It is seen that for 10.6 μ radiation, the heating rate for aluminum particles by a beam of 10^6 watts/cm^2 would be about 1°K/μsec, whereas for graphite, the corresponding heating rate would be 300°K/μsec. At solid-state laser frequencies ($\lambda \sim 1\ \mu$), the heating rate would be about 50 times faster.

Avcter the chain center atoms are generated by the heated solid particles through surface catalysis, the problem of subsequent chain center

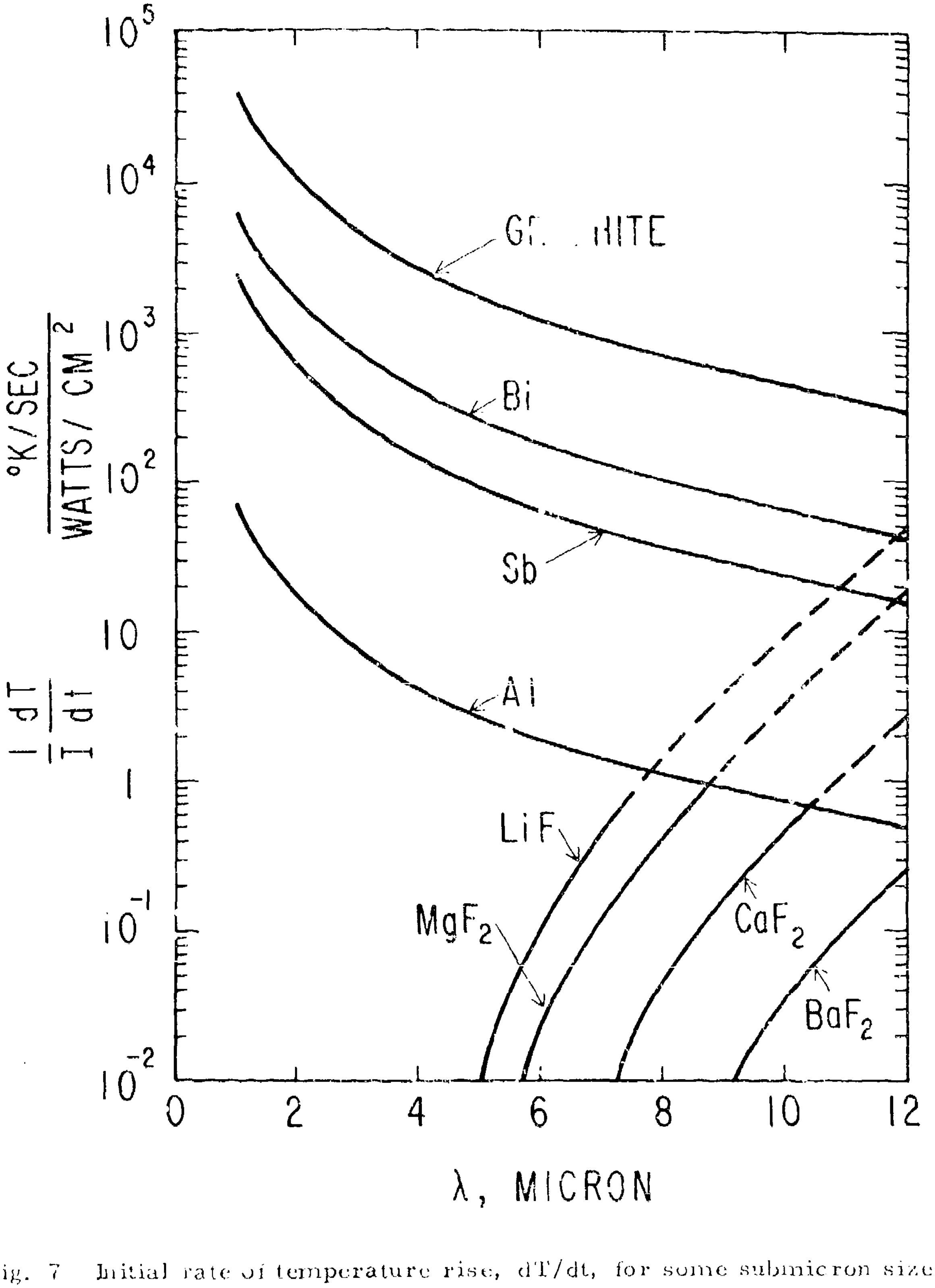

Fig. 7 Initial rate of temperature rise, dT/dt, for some submicron size particles (ka << 1) suddenly heated by a laser beam of intensity I and wavelength λ, neglecting scattering and conductive heat loss.

diffusion into the gas-phase mixture which fills up the interparticle space can be treated as a problem of spherical diffusion involving conserved passive scalar quantities (since the chain center atoms are simply being recycled during the chain propagation step in nonbranching, nonterminating chain reactions): It can be shown[54] that the three-dimensional spherically symmetric diffusion equation with constant diffusion coefficient may be written in the following way,

$$\frac{\partial}{\partial t}(r\,n) = D\,\frac{\partial^2}{\partial r^2}(r\,n) \tag{101}$$

where r is the radial distance, n is the concentration, and D is the binary diffusion coefficient.

Consider now some small spherical particles distributed randomly in a medium of detonable gas mixture such as H_2/F_2. When the surface of any one of the particles is uniformly heated to some temperature T_a instantaneously, dissociation of F_2 will take place on the surface at some value of T_a. Equation (101) with some appropriate initial and boundary conditions may be used to describe approximately the diffusion process both in time and space of the fluorine atom concentration on the particle surface. This approximation is based on the "equivalent sphere" concept which assumes that spherical symmetry is valid in this case up to a certain point in space for each particle. A schematic diagram of the problem is illustrated in Fig. 8.

Assuming that the concentration of the fluorine atom on any spherical

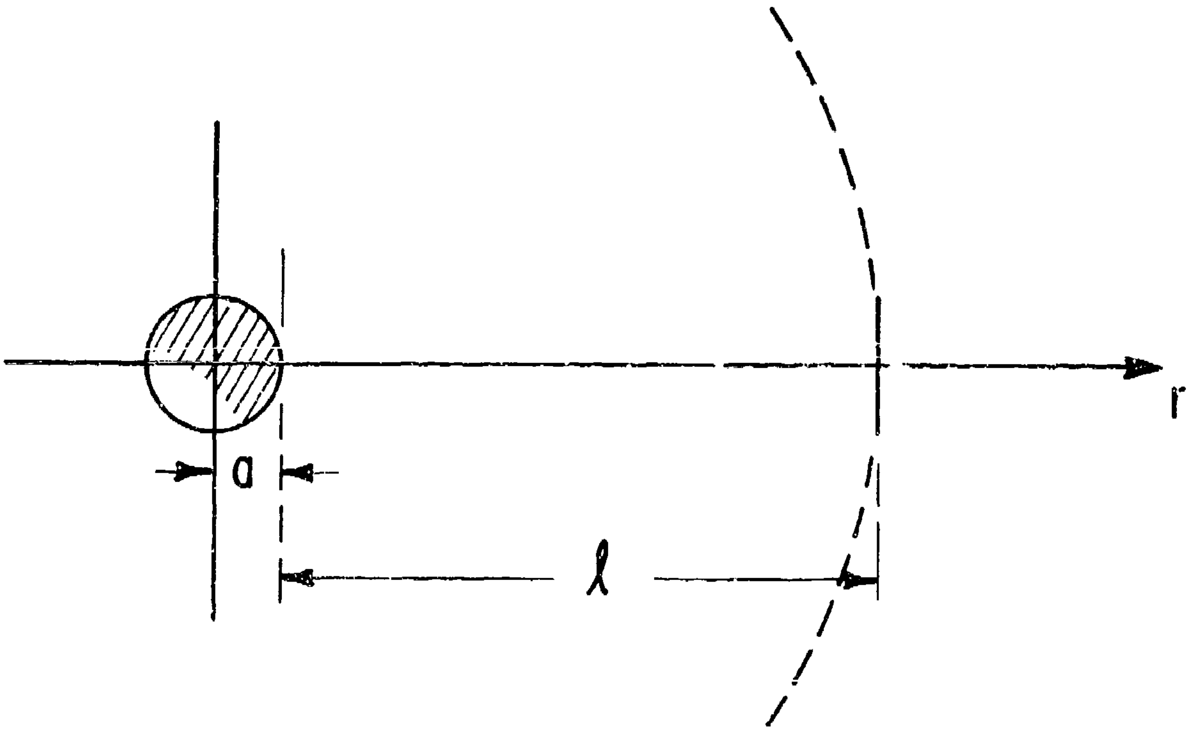

Fig. 8 Geometry and nomenclature for the spherical diffusion problem.

surface remains constant, and that there is no flux at the imaginary outer spherical boundary, we can set up the proper boundary conditions as follows,

$$
\begin{aligned}
&n_F(t,\ r) = n_{Fa} && \text{at } r = a \text{ for all } t \\
&\frac{\partial}{\partial r}\, n_F(t,\ r) = 0 && \text{at } r = \ell + a \text{ for all } t
\end{aligned}
\qquad (102)
$$

And the initial condition that there is no fluorine atom concentration anywhere in space at $t = 0$ can be represented as

$$
n_F(t,\ n) = 0 \qquad \text{at } t = 0 \text{ for all } r \qquad (103)
$$

Similar solution of the problem can be obtained if the following dimensionless quantities are introduced,

$$
\begin{aligned}
&\xi = \frac{r - a}{\ell}\ , && \bar{t} = \frac{Dt}{\ell^2} \\
&n'_F(\xi\ ,\ \bar{t}) = \frac{n_F(r,\ t)}{n_{Fa}}
\end{aligned}
\qquad (104)
$$

By substituting the expression in Eq. (104) into Eqs. (101), (102) and (103), we obtain the following nondimensional equation and its initial and boundary conditions,

$$
\frac{\partial}{\partial \bar{t}} \left[\left(\xi + \frac{a}{\ell} \right) n'_F \right] = \frac{\partial^2}{\partial \xi^2} \left[\left(\xi + \frac{a}{\ell} \right) n'_F \right] \qquad (105)
$$

with

I. C. $$n_F'(\bar{t}, \xi) = 0 \qquad \text{at } \bar{t} = 0 \text{ for all } \xi \tag{106}$$

B. C. $$\left(\xi + \frac{a}{\ell}\right) n_F' = \frac{a}{\ell} \qquad \text{at } \xi = 0 \text{ for all } \bar{t}$$

$$\left(\xi + \frac{a}{\ell}\right) \frac{\partial n_F'}{\partial \xi} = 0 \qquad \text{at } \xi = 1 \text{ for all } \bar{t} \tag{107}$$

This may be transformed into a problem involving diffusion in a plate of unit thickness (the "equivalent plate") under specific boundary conditions by making the substitution $u = \left(\xi + \frac{a}{\ell}\right) n_F'$. Then Eqs. (104), (105), and (106) become

$$\frac{\partial u}{\partial \bar{t}} = \frac{\partial^2 u}{\partial \xi^2} \tag{108}$$

with

I. C. $$u(\bar{t}, \xi) = 0 \qquad \text{for } 0 < \xi < 1 \quad \text{at } \bar{t} = 0 \tag{109}$$

B. C. $$u(\bar{t}, \xi) = a/\ell \qquad \text{at } \xi = 0 \quad \text{for all } \bar{t}$$

$$\frac{\partial u}{\partial \xi} - \frac{u}{\left(\xi + \frac{a}{\ell}\right)} = 0 \qquad \text{at } \xi = 1 \quad \text{for all } \bar{t} \tag{110}$$

Notice here that the second boundary condition that there is no flux at the outer boundary in the original problem becomes a radiation boundary condition (in the sense of Ref. 54) after the transformation. According to Ref. 54, the solution to the problem represented by Eqs. (108), (109), and (110) is

$$\frac{u}{a/\ell} = \frac{1 + L(1 - \xi)}{1 + L} - \sum_{n=1}^{\infty} \frac{2(\beta_n^2 + 1^2)\sin(\beta_n \xi)}{\beta_n(L + L^2 + \beta_n^2)} e^{-\beta_n^2 \bar{t}} \qquad (111)$$

where

$$L = -\frac{1}{1 + \frac{a}{\ell}}$$

and β_n are the positive roots of

$$\beta \cot \beta + L = 0 \qquad (112)$$

Therefore, the fluorine atom concentration is obtained,

$$n_F'(\xi, \bar{t}) = 1 - \frac{a/\ell}{\xi + \frac{a}{\ell}} \sum_{n=1}^{\infty} \frac{2(\beta_n^2 + L^2)\sin(\beta_n \xi)}{\beta_n(L + L^2 + \beta_n^2)} e^{-\beta_n^2 \bar{t}} \qquad (113)$$

Numerical solutions of n_F' for $\ell/a = 10, 100$ with different values of $\bar{t}$ are shown in Figs. 9 and 10. It should be remarked here that for large values of $\bar{t}$, the infinite series in Eq.(113) converges very rapidly. But for small values of $\bar{t}$, more and more terms in the series have to be used; in our case, for $\bar{t} = 0.01$, six terms of the series are used. Fortunately, for even smaller values of $\bar{t}$, we can approximate this diffusion problem with finite boundaries by the semi-infinite diffusion problem. Physically, for the case of small values of $\bar{t}$, the concentration does not have time to diffuse out far enough to "feel" the presence of the outer

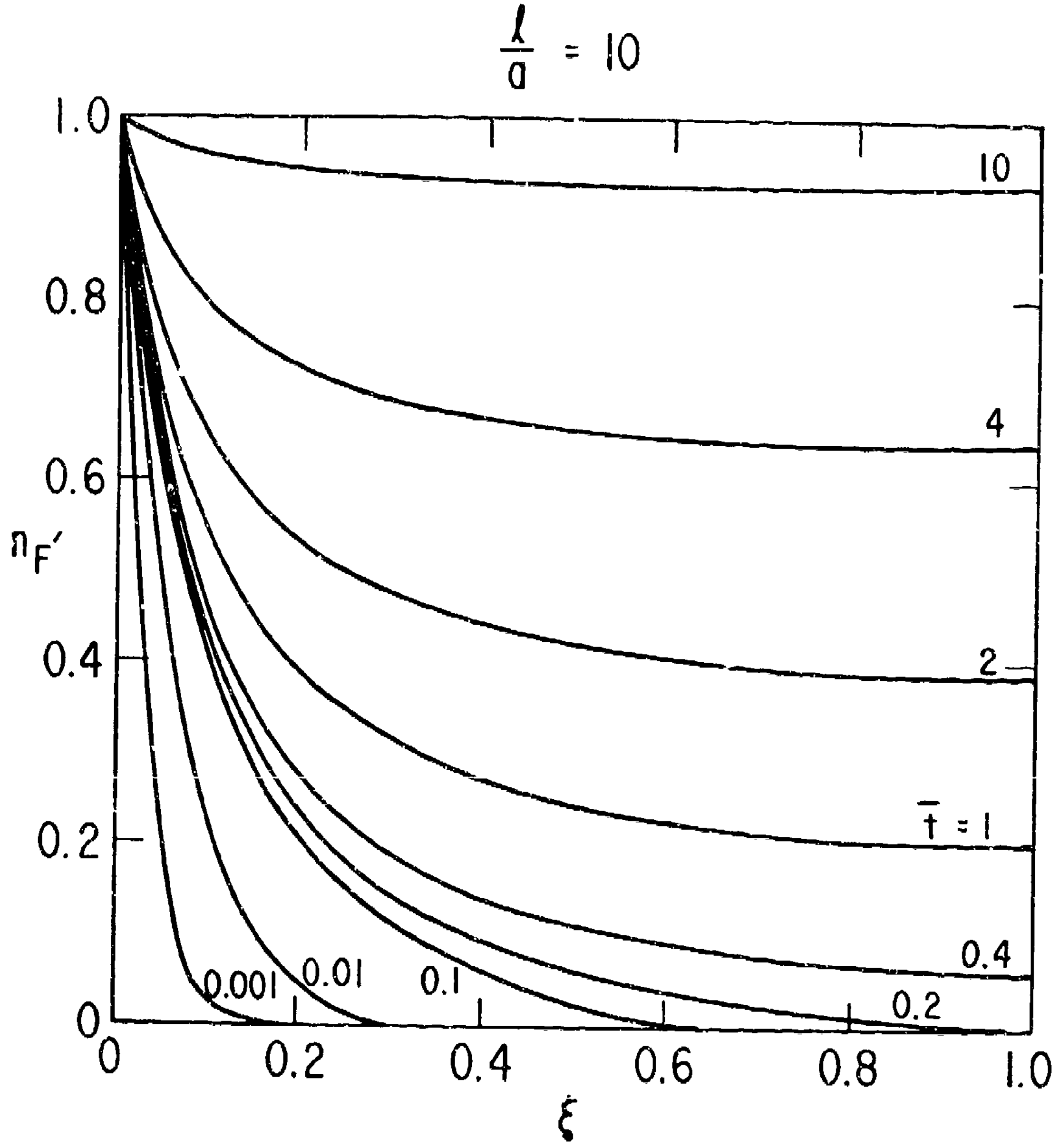

Fig. 9 Normalized solution for transient spherical diffusion of chain center atoms from a catalytic particle surface located at radius a into a gaseous volume of interparticle separation distance 2ℓ, where ℓ/a = 10. Other nomenclature:

$n_{F'} \equiv \frac{n_F}{(n_F)_a}$ ≡ normalized chain center concentration

$\xi \equiv \frac{r - a}{\ell}$ ≡ normalized radial coordinate

$t \equiv \frac{t}{\ell^2/D}$ ≡ normalized time ($D \equiv$ diffusion coefficient)

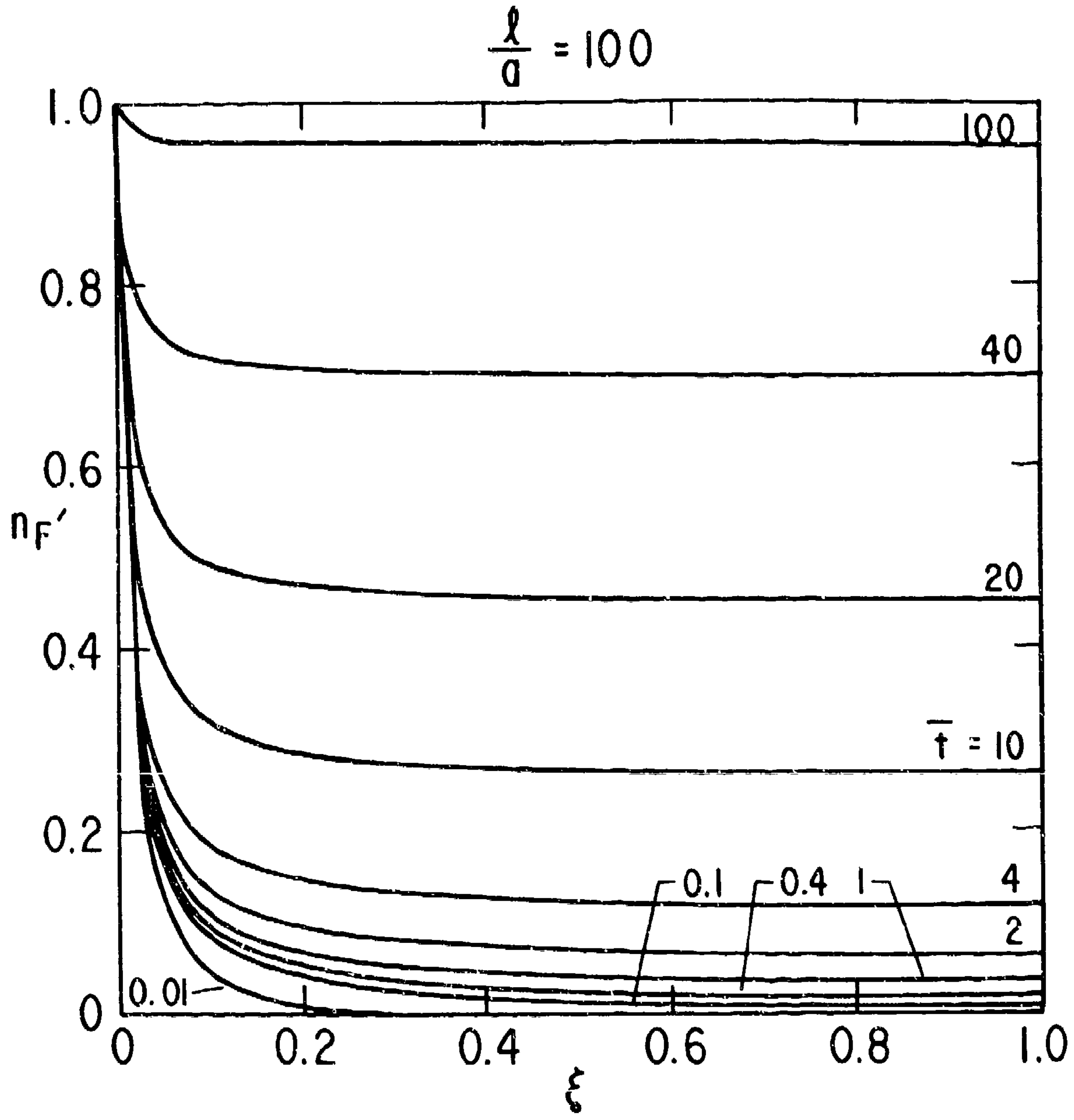

Fig. 10 Normalized solution for transient spherical diffusion of chain center atoms from a catalytic particle surface located at radius a into a gaseous volume of interparticle separation distance 2ℓ, where $\ell/a = 100$. Other nomenclature:

$$n_{F'} \equiv \frac{n_F}{(n_F)_a} \equiv \text{normalized chain center concentration}$$

$$\xi \equiv \frac{r-a}{\ell} \equiv \text{normalized radial coordinate}$$

$$t = \frac{t}{\ell^2/D} \equiv \text{normalized time } (D \equiv \text{diffusion coefficient}).$$

boundary. This is verified by taking the solution of the semi-infinite diffusion problem at $\bar{t} = 0.01$ to compare with the solution given by Eq.(113). And the comparison shows very little difference between the two solutions. Thus, for $\bar{t} << 1$, we have

$$n_F'(\bar{t}, \xi) \cong \frac{1}{1+\xi} \text{ erfc } \left(\frac{\xi}{2 \frac{\ell}{a} \sqrt{\bar{t}}} \right) \tag{114}$$

where erfc(x) is the complementary error function of argument x.

d. Two-phase Systems Involving Solid Particle Combustion

(1) Energy Gain Potential. When the heated particles in a two-phase chemical laser system is used simply as an inert catalyst, the energy gain potential of the two-phase system is not very different from that of a single-phase system using the same gas-phase reactive mixture. The reason is that the energy required to generate the dissociated atoms must still be supplied by the initiation source, so that the pulsed energy gain potential would still be governed by collisional de-excitation and useable chain length considerations as discussed in subsections 3.c and 3.d.

If the solid particles suspended in the two-phase system can be made to burn and the subsequent release of combustion energy could be utilized for further chemical pumping of the laser reactions, the prospect of energy gain appears much better. The improved prospect of energy gain derives from the fact that the heat of combustion of most metals and some solid compounds is often much greater than the energy required to heat the same mas of metal or compound to their respective ignition temperature, starting from room temperature. This is illustrated in Table 2 in which some known ignition temperature T_c for various solid dust particles in air,[55] the heating energy per mole ΔE_c for raising the solid temperature from $T_0 = 300°K$ to T_c, and the heat of combustion H_c per mole of the initial solid in O_2, F_2, and Cl_2 are listed.[56] Even though the ignition temperature for these solids in F_2 and Cl_2 are not known, they are likely to be lower than those corresponding to the air case. Thus, the heat of combustion of the more energetic solid fuel such as aluminum and boron in fluorine is generally greater than the energy required to bring the solid particles up to ignition temperature by a factor of about 100. For combustion in chlorine, the energy ratio is of the order of 30.

The dissociation energy for F_2 and Cl_2 is about 31 and 57 kcal/mole, respectively. Thus, the heat of combustion from 1 mole (or 27 grams) of Al in an F_2-rich mixture could generate up to 10 moles of F-atom (after due allowance is made for the enthalpy change associated with raising the gas temperature to 1, 700°K, which corresponds roughly to the temperature for complete dissociation of F_2 under thermodynamic equilibrium condition at standard density). Similarly, the heat of combustion from 1 mole of Al in a Cl_2-rich mixture could generate up to 2. 4 moles of Cl-atom. The corresponding maximum F-atom and Cl-atom yield from burning of 1 mole (or 24. 3 grams) of Mg in an F_2-rich or a Cl_2-rich mixture is about 6 and 1. 6

moles, respectively. If the F-atom or Cl-atom so generated can be utilized for direct pumping of such exothermic hydrogen-halide laser reactions as[8, 11]

$$F + H_2 \rightarrow HF + H + 31.7 \text{ kcal/mole} \qquad (115)$$

$$F + HBr \rightarrow HF + Br + 45.8 \text{ kcal/mole} \qquad (116)$$

$$F + HI \rightarrow HF + I + 62.3 \text{ kcal/mole} \qquad (117)$$

$$Cl + HI \rightarrow HCl + I + 32 \text{ kcal/mole} \qquad (118)$$

and assuming that only 12% of the exothermicity can be extracted as laser energy,[8] then combustion of 1 mole of aluminum could generate as much as 38, 55, and 75 kcal of HF laser energy from reaction (115), (116), and (117), respectively; or 9.2 kcal of HCl laser energy from reaction (118). Comparing these with the ignition energy $\Delta E_c \leq 4$ kcal/mole indicated for Al in Table II, it is seen that a potential energy gain by a factor of somewhere between 2 and 20 is quite possible through a laser-ignition process in a two-phase system. When a conventional flashlamp instead of a pulsed laser is used to initiate the ignition process, the potential energy gain is even more significant since the minimum energy required for direct photodissociation of 10 moles of F_2 is 310 kcalories and absorption of flashlamp energy by solid particles is likely to be more efficient than by a dissociating gas.

In order to make use of the heat of combustion from solid particles for efficient pumping of chemical lasers in two-phase systems, a number of physical and chemical conditions must be simultaneously satisfied. The

Table II

COMPARISON OF IGNITION ENERGY AND HEAT OF COMBUSTION FOR SOME SOLID PARTICLES. (Values taken from Refs. 55 and 56. Heat of combustion in parentheses includes heat of condensation of combustion product.)

Solid	Melting Point T_m, °K	Spontaneous Ignition Temp. of Dust in Air T_c, °K	Energy ΔE_c to Raise Solid Temp. from T_o to T_c kcal/mole	Heat of Combustion Hc, kcal/mole of Solid in		
				O_2	F_2	CL_2
Al	933	918	4.0	(200)	286 (385)	139
Mg	923	793	3.4	-4 (144)	175 (268)	100
Ti	2,003	603	1.9	15 (182)	156	72 (124)
Zr	2,118	293	0	21 (262)	147 (230)	78 (128)
B	2,573	1,003	2.9	100 (152)	270	96
C	3,813	883	2.5	94	220	26
LiH	959	Not known			123	54

more important of these conditions are: (a) The system must be initially stable, or at least quasi-stable to the extent that no significant spontaneous conversion of the reactants into products takes place in the time scale required to prepare the two-phase mixture for ignition within the laser cavity (a time scale which needs not be much greater than the typical gas-filling time of a few milliseconds, depending on the size and geometry of the cavity). (b) The intensity of the initiating radiation source must be sufficiently high so that the solid particles can be brought up to ignition temperature without excessive heat loss, and that ignition of all the particles will be nearly simultaneous in order to maintain a high degree of spatial homogeneity for the resulting laseable medium. (c) The burning rate of the solid particles must be sufficiently fast in comparison with the rate of de-excitation of the reaction product so that a high population inversion density can be maintained for laser generation. (d) The heat of combustion generated in the flame zone surrounding the solid particles must be transferred out, either through radiation or through molecular transport, into the interparticle space and redistributed among the gas-phase reactants in a time scale shorter than, or at most comparable to, the characteristic time for de-activation of the resultant gas-phase reaction products. (e) The processes of combustion energy redistribution and subsequent gas-phase reactions must favor the production of the upper laser state over that of the lower states.

It may be noted that condition (a) is actually a prerequisite for any true (i.e., premixed) pulsed chemical laser operation, and the satisfaction of which is just a matter of finding compatible mixtures. Satisfaction of condition (e) is also somewhat automatic if the gas-phase reaction chosen were one of the principal pumping reactions in single-phase chemical lasers like reactions (115) through (118), and that redistribution of the heat of combustion favors the generation of active atoms which participate in such principal pumping reactions. Condition (b) is common to all initiation process, and the satisfaction of which depends only on the availability of an initiation source of sufficiently high intensity.

Even though much of the basic chemical kinetics information required for quantitative analyses of processes related to the satisfaction of conditions (c) and (d) is not yet available, order-of-magnitude arguments based on extrapolation of existing knowledge about metal powder combustion in air or in other oxygen-laden gas mixtures does not indicate that these conditions cannot be satisfied. In fact, if the unknown rate constants for exothermic gas-phase reactions of the type

$$Al + F_2 \rightarrow AlF + F + 117.5 \text{ kcal/mole} \qquad (119)$$

$$LiH + Cl_2 \rightarrow HCl + LiCl + 108.0 \text{ kcal/mole} \qquad (120)$$

were anywhere comparable to those for the halogen-hydride reactions (1) through (4) cited in the introductory section, one could even become optimistic about the prospect of efficient two-phase chemical laser operation. We will demonstrate this point through the following discussion of various critical problems related to such prospects.

(2) Chemical and Thermal Stability of Two-phase Systems. If the mixing of finely-dispersed metal powders, such as Al and Mg, with active gas mixtures, such as F_2-H_2, Cl_2-HI, Cl_2-HBr, F_2O-H_2, etc., were strongly hypergolic (i.e., spontaneous ignition temperature equal to or below room temperature, with very rapid combustion rate), no ignition system will be necessary. For such hypergolic mixtures, the only possible mode of pulsed laser operation will be that of an intermittent-flow (i.e., blow-down type) mixing laser in which the reactive components are instantly introduced into the laser cavity in much the same way as reactants are introduced in any single-phase mixing laser system.[8] The efficiency of such two-phase mixing laser system will be governed by a competition among the rates of reactants mixing, combustion, halogen-atom generation, active molecule formation and collisional de-excitation of the active molecules.

If the two-phase mixture were stable or only weakly hypergolic (in the sense that the rates of reaction at room temperature remains so low that no significant conversion of reactants into products takes place in the time scale required to prepare the two-phase mixture and to send it through the laser cavity), genuine pulsed operation with premixed reactants would be possible. Economy of the initiation process would then be governed by the specific heat of the solid particles and the ignition temperature of such particles in the active gas mixture. The efficiency for subsequent conversion of chemical energy into laser energy is then governed by a competition among the rates of combustion, active-atom generation and diffusion, excited molecule formation, and collisional de-excitation of the active molecules.

(3) Rate of Heating of Solid Particles. To minimize the energy required for bringing the surface temperature of the solid particles up to ignition temperature without grossly heating the gaseous components in a two-phase system, it would be desirable to heat up the solid particles as rapidly as possible, i.e., in a time scale that is short in comparison with the characteristic time τ_D for diffusion of heat in the gas phase over the averaged inter-particle distance ℓ (see subsection c above).

$$\tau_D = \frac{\ell^2}{D} \tag{121}$$

The thermal diffusivity D is generally a function of gas density, temperature and chemical composition.[57] However, for the purpose of the present discussion, it suffices to consider D to be identical to the averaged molecular diffusivity with a typical value $D_0 \cong 0.25$ cm^2/sec for all gas mixtures of interest at standard density ρ_0 (defined here as the density at which the total number density of molecules in the gas phase is equal to $2.5 \times 10^{19}/\text{cm}^3$). Thus, at any given gas density ρ, the characteristic interparticle diffusion time is given by (when ℓ is measured in microns),

$$\tau_D = \frac{\ell^2}{D_0} \frac{\rho}{\rho_0} \cong 4 \times 10^{-8} \ell^2 \frac{\rho}{\rho_0} \text{ second} \tag{122}$$

It is seen that for a typical inter-particle distance of 50 microns, the characteristic diffusion time is about 100 μsec at standard density.

The rate of heating of very small particles by a suddenly turned on source of electromagnetic radiation was discussed earlier in subsection b, and the calculated rate of temperature rise per unit radiation intensity was plotted in Fig. 7. As noted earlier, for the heating of aluminum particles, in order to obtain a temperature rise of 1,000°K in a time scale of 10^{-5} sec., an intensity of 10^6 watts/cm^2 would be needed at 1 laser wavelength, or 10^8 watts/cm^2 would be needed for 10.6 radiation. For the heating of graphite particles, the intensity requirements for providing the same rate of temperature rise is reduced to 2.2×10^3 watts/cm^2 at $\lambda = 1\,\mu$ and 2.2×10^5 watts/cm^2 at $\lambda = 10\,\mu$. These intensities, though very high, appear to be well within current pulsed laser technology. For example, a commerically available* glass laser with a 9-joule energy output, 30-nsec pulse width, and a beam diameter of 12-mm would provide a peak intensity of about 3×10^8 watts/cm^2 at 1.06-μ wavelength. The same range of intensity at 10.6-μ wavelength can also be reached by mild focussing of the output beam from Transverse Electrically-excited Atmospheric-pressure (TEA) CO_2 lasers of performance characteristics comparable to those reported in the recent literature.[58,59]

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*E.g., American Optical Corp. Model No. A0-30P as listed in the Laser Focus 1971 Buyers' Guide, pp. 120-121.

When a flashlamp instead of a pulsed laser is used as the initiation source, the maximum intensity available for solid particle heating will be limited by the apparent brightness temperature of the flashlamp. Thus, for a flashlamp operating at a peak brightness temperature of 15,000 °K, the maximum intensity will be limited to about 3×10^5 watts/cm^2. However, since the light output from such a flashlamp would have a broad spectral distribution which peaks around 3,000 A, it appears that such an intensity would be quite adequate for heating up highly conductive metal powders, such as aluminum and magnesium, to their respective ingition temperature in a time scale of the order of 10^{-5} sec.*

(4) Burning Rate of Metal Powders. The rates of combustion of metal powders, such as Al, Mg, B, Ti, Zr, etc., in gases such as F_2, Cl_2, NF_3, F_2O, CO_2, etc., are generally not known. Hence, one can only infer such rate from experimental data published in the literature for burning of metal powder in air and in oxygen-laden gas mixtures.

According to the recent paper of Wilson and Williams,[60] the characteristic time τ_B for combustion of aluminum particles in oxygen-laden gases from all published experiments can be represented by the formula

---

*It may be noted that in order to calculate the heating rate by a flashlamp properly, equations should be suitably modified to take into account the broad spectral distribution of the flashlamp, as well as any resonance absorption effect near $\lambda = 2\pi a$.

$$\tau_B = \frac{\alpha_0^2}{\beta p(O_2)} \qquad (123)$$

where α_0 is the initial radius of the aluminum particle, $p(O_2)$ is the particle pressure of O_2 expressed in units of the standard atmosphere, and β is a constant which depends only on the dilution ratio of the oxygen-laden gas mixture for any given diluent. For combustion of aluminum particles of initial radius ranging between 10 and 300 micron in O_2/Ar mixtures, the value of β was found to be 4×10^{-3} cm^2/sec for pure O_2, and 9×10^{-4} cm^2/sec for a 10% O_2-90% Ar mixture of total pressure ranging between 1 and 5 atmospheres. The characteristic time τ_B is defined here as the time it takes the combustion process to reduce the initial radius of the aluminum particle by a factor of 2 (and hence, its volume by a factor of 8). Thus, according to these experimental data, the burning time for aluminum particles of 10 micron initial radius in pure oxygen at standard atmospheric pressure is about 2.5×10^{-4} sec.

As noted by Wilson and Williams,[60] the α_0^2 dependence of the characteristic burning time τ_B as indicated by Eq. (123) is consistent with what one would predict from the classical quasi-steady vapor-phase combustion theory (see Fig. 11) in which the diffusion flame geometry is assumed self-similar and the rate of release of combustion energy from the reaction zone is assumed to be governed by local equilibrium chemistry. Since the chemical kinetic rates never entered such a theoretical model of solid particle

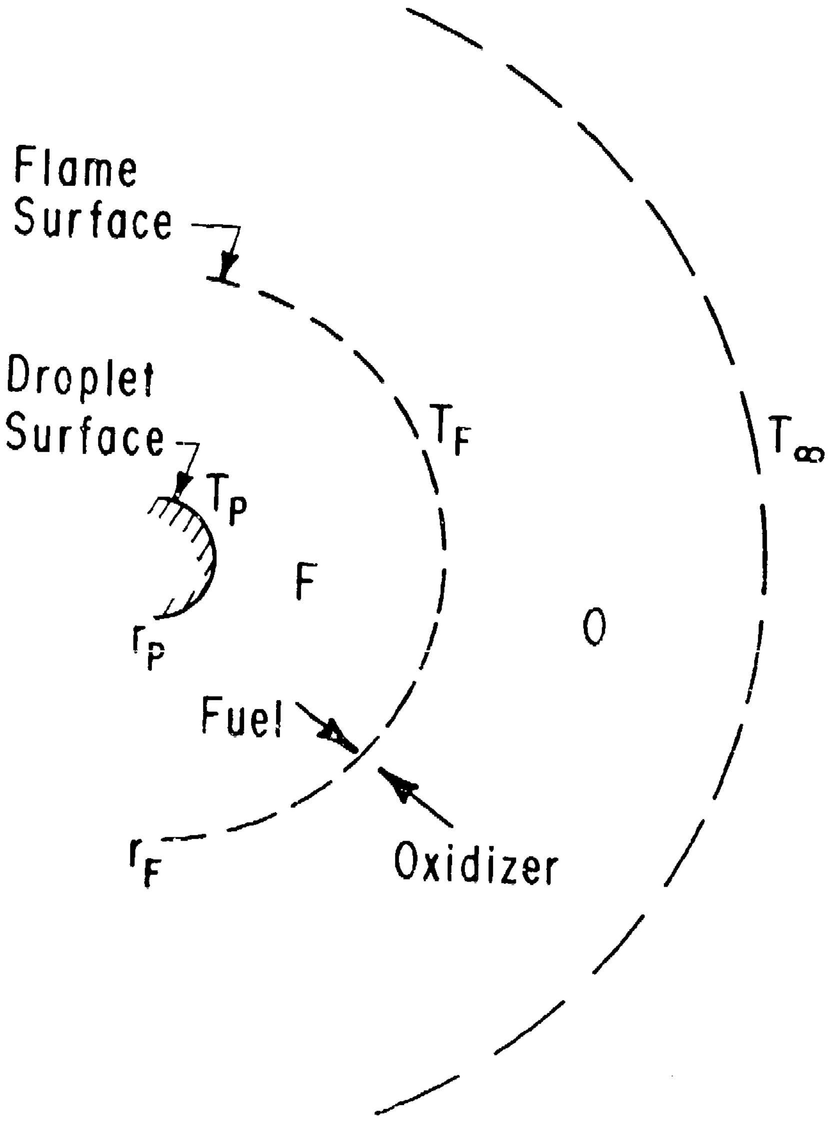

Fig. 11 Diffusion flame model in classical vapor-phase combustion theory.

combustion, there is no size limit on the applicability of the theory as long as the molecular mean-free-path remains sufficiently small in comparison with the particle diameter so that the continuum treatment was justified. However, from elementary considerations, it would be unrealistic to expect that the empirical formula (123) could be extrapolated indefinitely for prediction of the burning time for very small particles (i.e., $\alpha_0 \ll 10\ \mu$) due to the eventual onset of finite-rate chemistry and free molecule flow. (Note that the viscosity mean-free-path for air at standard density is about 0.06 μ.)

At this juncture, if one assumes that the rates of combustion of metal powders, such as Al, Mg, B, Ti, Zr, etc., in gases such as F_2, Cl_2, F_2O, etc., are at least as fast as that found for combustion of aluminum in O_2, and that the particle-size-dependence of the characteristic burning time as indicated by Eq. (123) can be extrapolated down to α_0 of the order of 1 μ, then metal powder burning time of the order of 10^{-6} sec appears reachable in two-phase ignition systems operating at standard density.

(5) Redistribution of Combustion Energy for Laser Pumping. For efficient conversion of combustion energy into laser energy in two-phase systems, it is essential that the heat of combustion generated in the flame zone surrounding the solid particles be transferred out into the interparticle space and redistributed among the gas-phase reactants in a time scale which is shorter than, or at most comparable to, the characteristic time for collisional de-activation of the lasing molecules. In chemical systems which make use of dissociated atoms for pumping of the upper laser states through

reactions of the type represented by Reactions (115) through (118), redistribution of the combustion energy must result in a preferential dissociation of the halogen-rich gases such as F_2, Cl_2, NF_3, F_2O, etc. over that of the hydrogen-containing molecules such as H_2, HBr, HI, etc. Alternatively, if redistribution of the combustion energy were to result in a preferential dissociation of the hydride molecules, the H atoms so generated may be utilized for pumping of hydrogen-halogen lasers through "hot reactions" of the type

$$H + F_2 \rightarrow HF + F + 101.5 \text{ kcal/mole} \qquad (124)$$

$$H + Cl_2 \rightarrow HCl + Cl + 45.1 \text{ kcal/mole} \qquad (125)$$

The worst situation one can imagine is that re-distribution of the combustion energy leads to simultaneous decomposition of all gas-phase reactants at about the same rate, but such a situation is probably not very likely.

Redistribution of the combustion energy from the hot flame zone cut to the cold gas occupying the bulk of the interparticle space will proceed radiatively as well as through molecular transport. If the flame zone were strongly chemiluminescent and the emitted light were to have a spectral range which overlaps that for photodissociation of the halogen-rich molecules, then direct conversion of a significant fraction of the combustion energy into dissociated halogen atoms could take place instantaneously throughout the interparticle space. In other words, the burning metal powder could act like an "internal flashlamp" for generation of active atoms in much the same way that active atoms are generated by external light sources in the conventional flashlamp initiation process for single-phase chemical lasers.

Visible light generated from burning of fine magnesium wires or powder in oxygen (or air) has long been utilized as a convenient light source in flash photography. Likewise, one may expect that the blue and near-ultraviolet end of the emission spectrum from the flame zone associated with burning of aluminum and magnesium powders in halogen-rich gases can also be utilized for photodissociation of F_2 and Cl_2, which are known to have strong dissociation continua in the spectral range $2,000 \leq \lambda$ 4,000 A.[58] (Photodissociation of H_2 from its ground electronic state is not very likely since the dissociation continua lie in the far ultraviolet.) According to Pearse and Gaydon,[59] AlF and AlCl are known to have strong electronic bands emitting in this spectral range of interest. In addition, continua emission resulting from molecular complex formation such as $(AlF_3)_n$, $(AlCl_3)_n$, or from condensation of such reaction products into very small refractory solid particles near the high-temperature flame zone may well extend into this near ultraviolet region. However, one must say at this time that we do not yet know enough about the probability of excited electronic state formation within the flame zone of burning metal powders, nor do we know the oscillator strengths associated with such excited electronic states of reaction products so formed, to make any quantitative prediction about the efficiency of such photo processes. For this reason, we suggest that some shock-tube experiments be carried out to collect quantitative information on chemiluminescence from burning metal powders that would be useful for further analysis of this particular problem.

In contrast to the photodissociation processes, which can be considered instantaneous for all practical purposes, redistribution of combustion energy into the bulk of the interparticle space through molecular diffusion and/or heat conduction would be much slower. Even though the detailed kinetic steps related to the burning of metal powders are not known (not even for burning of aluminum powder in oxygen, according to experts in the field of combustion theory[61]), one may postulate that gas-phase combustion of metal vapors, such as Al and Mg, in diatomic gases such as F_2 and Cl_2, is likely to proceed according to sequences of the type

$$\begin{aligned} &Al + F_2 \rightarrow F + 117.5\ \text{kcal/mole} \\ &AlF + F_2 \rightarrow F + 87.1\ \text{kcal/mole} \\ &AlF_2 + F_2 \rightarrow F + 106.0\ \text{kcal/mole} \end{aligned} \qquad (126)$$

$$\begin{aligned} &Al + Cl_2 \rightarrow AlCl + Cl + 53.1\ \text{kcal/mole} \\ &AlCl + Cl_2 \rightarrow AlCl_2 + Cl + 35.3\ \text{kcal/mole} \\ &AlCl_2 + Cl_2 \rightarrow AlCl_3 + Cl + 35.5\ \text{kcal/mole} \end{aligned} \qquad (127)$$

Out of the 310.6 kcal/mole generated from sequence (126), or the 123.9 kcal/mole generated from sequence (127), only 70.4 kcal/mole would be needed for vaporization of the aluminum solid. The remaining 240.2 kcal/mole from sequence (126) or 53.5 kcal/mole from sequence (127), would either be radiated out into the inter-particle space or deposited in the reaction products AlF, AlF_2, AlF_3, F, or AlCl, $AlCl_2$, $AlCl_3$, Cl, in the form of vibrational and translational/rotational energies. In the case of sequence (126), outward diffusion of the energetic reaction products into the inter-particle space may well lead to further dissociation of the ambient F_2 through reactions of the type

$$AlF(v) + F_2 \rightarrow AlF(0) + F + F \qquad (128)$$

$$AlF_2(v) + F_2 \rightarrow AlF_2(0) + F + F \qquad (129)$$

$$AlF_3(v) + F_2 \rightarrow AlF_3(0) + F + F \qquad (130)$$

$$F + F_2 \rightarrow F + F + F \qquad (131)$$

For sequence (127), however, the residual energy from none of the three steps appears high enough for further dissociation of Cl_2, but by the end of step 3, three moles of atomic Cl would already have been produced from burning of one mole of aluminum.

(6) Matching of Molecular Diffusion Time and Collisional Deexcitation time. If chemiluminescence were weak and the photodissociation processes were completely ineffective in redistributing the combustion energy, one must then rely on diffusion of the active atoms and/or the

energetic molecules for such energy redistribution.

Again, going back to the example of the hydrogen-halide systems cited in the preceding section, one may readily note that, concurrent with the diffusion of the F or Cl atoms into the interparticle space, laser pumping reactions, such as Reactions (115) through (118) will take place. The excited laser molecules, such as HF(v) or HCl(v), which are formed earlier (i.e., closer to the flame zone) will also be subjected to more de-excitation collisions as the outward diffusion of active atoms and energetic molecules progresses. Thus, in order to maintain a positive gain over the bulk of the inter-particle volume, it is essential that the characteristic diffusion time τ_D be kept shorter than, or at most comparable to, the characteristic collisional deexcitation time

$$\tau_C = \left(\sum_j k_{cj}\, n_j \right)^{-1} \tag{132}$$

where k_{cj} denotes some averaged rate constant for collisional de-excitation of the upper laser state by a type-j molecule over the interparticle space, n_j denotes the corresponding averaged number density of type-j molecules, and the summation is to be carried over all types of molecules present in the gas mixture filling the interparticle space. By writing

$$n_j = 2.5 \times 10^{19} \, [M_j] \, \frac{\rho}{\rho_0} \ \mathrm{cm}^{-3} \tag{133}$$

where $[M_j]$ denotes some averaged mole fraction of type-j molecules (appropriately normalized with respect to the initial molar concentration of the total gas-phase mixture before combustion and dissociation took place), and ρ/ρ_0 is the actual gas density divided by the standard gas density as defined earlier. The characteristic collisional de-excitation time may be expressed in the form

$$\tau_C = \left\{ 2.5 \times 10^{19} \frac{\rho}{\rho_0} \sum_j k_{cj} [M_j] \right\}^{-1} \text{ second} \tag{134}$$

if k_{cj} is given in units of cm^3/molecular-sec.

By equating Eq. (122) and Eq. (134), one therefore obtains the following expression for matching the characteristic diffusion time τ_D with the characteristic collisional de-excitation time τ_C

$$\ell \frac{\rho}{\rho_0} = 10^{-6} \left\{ \sum k_{cj} [M_j] \right\}^{-1/2} \tag{135}$$

where ℓ is the averaged interparticle distance measured in microns. The collisional de-excitation rate constant k_{cj} depends, of course, strongly on the type of laser molecule and the particular upper laser state under consideration. It may also depend strongly on the chemical type of the collision partner M_j, and on the translational/rotational temperature. For example, the value of k_{cj} for collisional de-excitation of the v = 1 level of HF at T = 500°K is about 8×10^{-17} cm^3/molecule-sec when the collision partner is Ar or F_2; and about 2.5×10^{-12} cm^3/molecule-sec when the collision partner is another HF. At a temperature of 1,500°K, the corresponding value of k_{cj} becomes 7×10^{-15} cm^3/molecule-sec for collision with Ar or F_2, and 1.7×10^{-12} cm^3/molecule-sec for collision with another HF, respectively. On the other hand, the value of k_{cj} for collisional de-excitation of the $v = 1$ level of HCl at $T = 500$°K is about 1.7×10^{-14} cm^3/molecule-sec, whether the collision partner were Cl_2, H_2, H, or another HCl molecule at ground vibrational level. At a temperature of 1,500°K, the value of k_{cj} becomes 4×10^{-13} cm^3/molecule-sec for the same set of collision partners.

By taking typical value $\Sigma k_{cj} [M_j] = 10^{-12}$ cm^3/molecule-sec for collisional de-excitation of HF vibrations, and 10^{-14} cm^3/molecule-sec for collisional de-excitation of HCl vibrations, respectively, Eq. (135) indicates that matching of τ_D and τ_C can be achieved for $\ell \rho/\rho_0 \cong 1$ micron in an HF system, and for $\ell \rho/\rho_0 \cong 10$ micron in an HCl system. Thus, at standard density, the characteristic diffusion time τ_D can be made shorter than the characteristic collisional de-excitation time τ_C if the averaged inter-particle distance ℓ is kept shorter than about 1 micron in an HF system, and 10 microns in an HCl system. At one-tenth the standard density (i.e., $\rho/\rho_0 = 0.1$, the corresponding value for ℓ should be kept shorter than 10 micron in an HF system, and 100 microns in an HCl system, in order to make the diffusion time shorter than the collisional de-excitation time of 4×10^{-7} sec for HF, and 4×10^{-5} sec for HCl, respectively.

(7) Simultaneous Matching of All Necessary Conditions. After matching the molecular diffusion time τ_D with the collisional de-excitation time τ_C in accordance with Eq. (135), one must now go back and re-examine all other constraints that may have been imposed, either directly or indirectly, on the product $\ell\, \rho/\rho_0$ through the requirement for matching of other characteristic time scales discussed earlier, and then see if they are all compatible.

The averaged interparticle distance ℓ is related to the number of solid particles per unit volume, n_p, such that $\ell = n_p^{-1/3}$ (since the averaged volume occupied by each particle is n_p^{-1}). The initial volume fraction of solid particles ϕ_p is given by n_p times the initial volume per particle $4\pi a_0^3/3$, so that

$$\phi_p = \frac{4\pi}{3}\left(\frac{a_0}{\ell}\right)^3 \tag{136}$$

The volume fraction of solid particles ϕ_p to be used in a two-phase system, in turn, is related to the mole ratio between the solid-phase particles and the gas-phase reactants, such that

$$X_p = \frac{\text{No. of moles of solid particles per unit volume}}{\text{No. of moles of gas-phase mixture per unit volume}}$$

$$= \phi_p \frac{\text{molal volume of gas-phase mixture at standard density}}{(\rho/\rho_0)\ \text{molal volume of solid}}$$

$$= \frac{2.24 \times 10^4\, \phi_p}{(\rho/\rho_0)\, V_p} \tag{137}$$

By combining (136) and (137), one obtains

$$\frac{\alpha_0}{\ell} = 2.2 \times 10^{-2} (V_p X_p)^{1/3} (\rho/\rho_0)^{1/3} \tag{138}$$

The molal volume V_p for most metals of interest to the present problem is of the order of 10 cm^3 (e.g., V_p = 10.0 cm^3 for Al, 14.0 for Mg, 10.6 for Ti, 14.3 for Zr, 4.3 for B, etc.), while the desired mole ratio X_p between solid and gas is expected to be of the order 0.1. Therefore, one may let $(V_p X_p)^{1/3} \cong 1$ for all practical purposes. The required ratio between the initial particle radius and the averaged interparticle distance is therefore, approximately

$$\frac{\alpha_0}{\ell} = 2.2 \times 10^{-2} (\rho/\rho_0)^{1/3} \tag{139}$$

Thus, if one denotes the value of $\ell \rho/\rho_0$ which satisfied the matching condition (135) by the symbol $(\ell \rho/\rho_0)^*$, Eq. (139) requires that the initial radius of the particles must satisfy the following inequality in order to keep $\tau_D \leq \tau_C$

$$\alpha_0 \leq 2.2 \times 10^{-2} \frac{(\ell \rho/\rho_0)^*}{(\rho/\rho_0)^{2/3}} \tag{140}$$

In the preceding section, we estimated that $(\ell \rho/\rho_0)^* = 1$ micron for the HF system, and $(\ell \rho/\rho_0)^* = 10$ micron. Accordingly, Eq. (140) requires that the particle radius be kept smaller than 2.2×10^{-2} and 0.22 micron for normal density operation in HF and HCl systems, respectively. For operation at $\rho/\rho_0 = 0.1$, the initial particle radius requirement becomes $a_0 \leq 0.102$ and 1.02 micron for HF and HCl systems, respectively.

If the particle burning time formula (123) can be extrapolated to burning of aluminum particles down to the sub-micron region in F_2 and Cl_2, then using the value of $\beta = 4 \times 10^{-3}$ cm^2/sec previously obtained for Al-O_2 combustion, one obtains a burning time $\tau_B = 1.2 \times 10^{-9}$ and 1.2×10^{-7} sec for burning of 2.2×10^{-2} and 0.22 micron particles, respectively, at normal density. For burning at 0.1 normal density, the burning time so obtained becomes 2.6×10^{-7} and 2.6×10^{-5} sec for burning of 0.102 and 1.02 micron radius aluminum particles, respectively. Since the collisional de-excitation time at $\rho/\rho_0 = 0.1$ has been estimated to be 4×10^{-7} sec and 4×10^{-5} sec for HF and HCl respectively, these estimated burning times appear quite satisfactory. However, as we discussed earlier, we do not really know if the burning time formula (123) can be extrapolated to burning of aluminum powder in halogen gases, nor do we know how far it can be extrapolated in the direction of decreasing particle radius beyond those covered by previous experiments.

From preceding discussion of the rate of heating of solid particles in subsection (3), we concluded that heating time scale of the order of 10^{-5} sec appeared quite feasible, but further compression of the heating time scale to values much shorter than 10^{-5} sec would cause undue strain on the requirement of radiation source intensity (unless the absorbing particles were made of much poorer conductors than aluminum). This additional constraint accordingly further limits the feasible range of two-phase pulsed hydrogen-halide lasers to initial gas-phase density somewhat below the standard atmospheric density (say, $\rho/\rho_0 \sim 0.1$). However, comparing this to the accessible density range of existing single-phase hydrogen-halide systems, the present estimated feasible gas density (for undiluted gas-phase reactants) $\rho/\rho_0 \sim 0.1$ already represents a very significant potential for improvement.

APPENDIX I

RECOMMENDED RATE CONSTANTS FOR H_2-F_2 CHEMICAL LASER (From Ref. 47)

A detailed list of reaction considered for the rate equations of the first and second vibrational levels of the HF molecule together with selected rate constants is presented here (only forward reactions are considered).

Excitation Reactions

$$F + H_2 \xrightarrow{k_{4(1)}} HF(1) + H \qquad k_{4(1)} = 1.8 \times 10^{13-1.6/\theta}$$

$$F + H_2 \xrightarrow{k_{4(2)}} HF(2) + H \qquad k_{4(2)} = 9 \times 10^{13-1.6/\theta}$$

$$H + F_2 \xrightarrow{k_{5(1)}} HF(1) + F \qquad k_{5(1)} = 6 \times 10^{12-2.4/\theta}$$

$$H + F_2 \xrightarrow{k_{5(2)}} HF(2) + F \qquad k_{5(2)} = 9 \times 10^{12-2.4/\theta}$$

Deexcitation Reactions

(1) V-T transfer

$$HF(1) + HF \xrightarrow{k_{6a(1)}} HF(0) + HF \qquad k_{6a(1)} = 10^{6.23}T^{1.77} + 10^{16}T^{-1.43}$$

$$HF(1) + H2 \xrightarrow{k_{6a(1)}} HF(0) + H2$$

$$HF(2) + HF \xrightarrow{k_{6a(2)}} HF(1) + HF \qquad k_{6a(2)} = 2k_{6a(1)}$$

$$HF(2) + H2 \xrightarrow{k_{6a(2)}} HF(1) + H2$$

$$HF(3) + HF \xrightarrow{k_{6a(3)}} HF(2) + HF \qquad k_{6a(3)} = 3\ k_{6a(1)}$$

$$HF(3) + H2 \xrightarrow{k_{6a(3)}} HF(3) + H2$$

$$HF(1) + F \xrightarrow{k_{6b(1)}} HF(0) + F \qquad k_{6b(1)} = 1.5 \times 10^{10-1.1/\theta}\ T$$

$$HF(2) + F \xrightarrow{k_{6b(2)}} HF(1) + F \qquad k_{6b(2)} = 2 \times k_{6b(1)}$$

$$HF(3) + F \xrightarrow{k_{6b(3)}} HF(2) + F \qquad k_{6b(3)} = 3 \times k_{6b(1)}$$

$$HF(1) + F2 \xrightarrow{k_{6c(1)}} HF(0) + F2 \qquad k_{6c(1)} = 5.45 \times 10^{-4}\ T^{4.056}$$

$$HF(2) + F2 \xrightarrow{k_{6c(2)}} HF(1) + F2 \qquad k_{6c(2)} = 2 \times k_{6c(1)}$$

$$HF(3) + F2 \xrightarrow{k_{6c(3)}} HF(2) + F2 \qquad k_{6c(3)} = 3 \times k_{6c(1)}$$

$$HF(1) + H \xrightarrow{k_{6f(1)}} HF(0) + H \qquad k_{6f(1)} = T(1.5 \times 10^{10-1.9/\theta})$$

$$HF(2) + H \xrightarrow{k_{6f(2)}} HF(1) + H \qquad k_{6f(2)} = 2 \times k_{6f(1)}$$

$$HF(3) + H \xrightarrow{k_{6f(3)}} HF(2) + H \qquad k_{6f(3)} = 3 \times k_{6f(2)}$$

(2) V-V exchange

$$HF(1) + HF(1) \xrightarrow{k_{7a(1)}} HF(0) + HF(2) \quad k_{7a(1)} = 2(10^{8}\ T^{1.5})$$

$$HF(1) + HF(2) \xrightarrow{k_{7b(1)}} HF(0) + HF(3) \quad k_{7b(1)} = 3(5 \times 10^{7}\ T^{1.5})$$

$$HF(1) + HF(3) \xrightarrow{k_{7c(1)}} HF(0) + HF(4) \quad k_{7c(1)} = 4(2 \times 10^{7}\ T^{1.5})$$

$$HF(1) + HF(3) \xrightarrow{k_{a(2)}} HF(2) + HF(2) \quad k_{7a(2)} = 6(10^{8}\ T^{1.5})$$

$$HF(2) + HF(0) \xrightarrow{k_{7a(1)}} HF(1) + HF(1)$$

$$HF(2) + HF(2) \xrightarrow{k_{7a(2)}} HF(1) + HF(3)$$

$$HF(2) + HF(3) \xrightarrow{k_{7b(2)}} HF(1) + HF(4) \quad k_{7b(2)} = 8(5 \times 10^{7}\ T^{1.5})$$

where $\theta = 2.3\ RT/1000$ kcal/mole, R is the universal gas constant, T is the temperature in °K, and the rate constants k are in units of cc/mole-sec.

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13. ABSTRACT

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The theoretical problem of pulsed chemical laser ignition by very rapid infrared laser absorption heating is investigated. It is found that for single-phase systems, the only hope for ever achieving energy gain appears to lie in the utilization of long or fast-branching chemical chains in the pumping reactions. For the hydrogen-halide system, the usable chain length is severely limited by the very rapid collisional de-excitation rate of the vibrational states by the reaction product molecules, making positive energy gain very unlikely. In two-phase systems, however, one may try to utilize the large amount of combustion energy release from burning of finely dispersed, submicron size solid particles for generation of additional atoms required in the pumping of the laser reactions. The reduced input energy requirement for generating a fixed number of active atoms in such two-phase system may improve the prospect for achieving positive energy gain in multistage pulsed chemical laser applications.

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