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HANDBOOK OF CHEMICAL LASERS

Edited by

R. W. F. GROSS

J. F. BOTT

**The Aerospace Corporation
Los Angeles, California**



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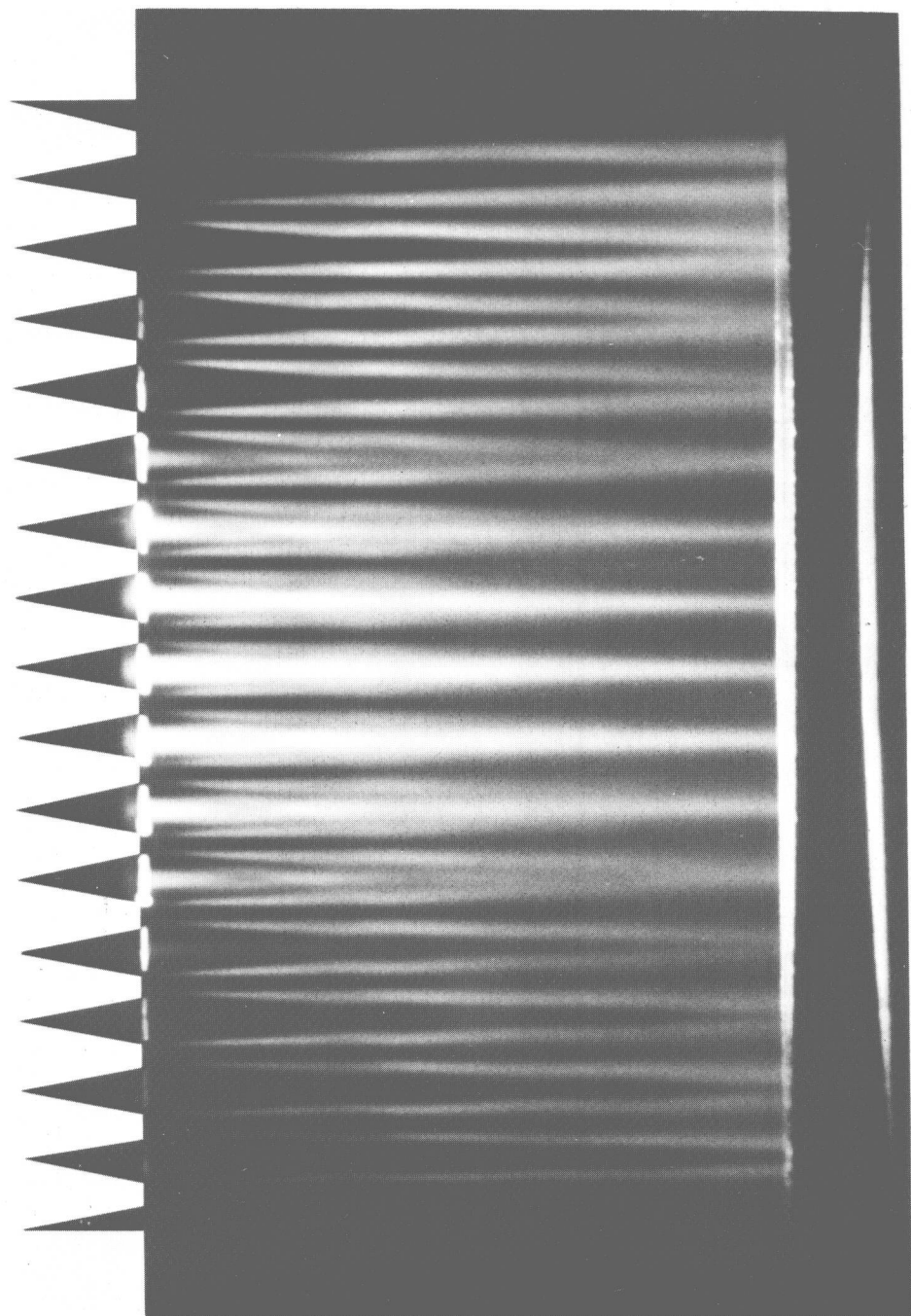


Plate 1

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PREFACE

In September 1964 an illustrious group of chemists, physicists, and laser specialists convened in San Diego, California to discuss the possibilities of nonequilibrium excitation and chemical pumping of lasers. The conference started out entirely speculative, since no chemical lasers existed at that time. At the end of the meeting, a young graduate student from Berkeley got up and claimed that he had observed the first laser pulses produced by a chemical reaction. The laser was the flash-photolysis iodine laser, and the student, Jerry Kasper from George Pimentel's group. With this dramatic event, chemical lasers were born. In the following ten years, the people who wrote this book have had the rare and exciting experience to be the participants in the development of an entirely new field from its basic inception to technical maturity.

This book collects the pieces of this work for the first time. We feel that we are at another turning point in the development of chemical lasers. Much of the basic scientific research, at least as far as the major chemical lasers HF, CO, and iodine are concerned, appears to be concluded. In the future, this work will pass on to the engineer, who will develop the large laser systems required for technical applications in laser chemistry, laser fusion, and materials processing.

To unlock the full possibilities of chemical lasers, three disciplines had to be combined: chemical kinetics of nonequilibrium reactions, gas dynamics of reactive flows, and laser physics of high-gain media. People working in any one of these fields are often unfamiliar with the "language" of the other two. It has, therefore, been our goal to make this book a kind of dictionary for the communication between these disciplines and a handbook for the future laser-systems engineer. It is not a basic textbook, but it attempts to equip the gas dynamicist with an understanding of kinetics and the physics of unstable cavities, the kineticist with a grasp of the all important gas dynamics of chemical lasers, and the laser

expert with a feel for the parameters of their unusual media to enable them to accomplish their task together.

In keeping with this objective, the book starts with basic reviews of the three fundamental fields. The ability to control the kinetics and thermodynamics of highly exothermic reactions by fast supersonic flows places gas dynamics into a central role. This subject is thoroughly explored in the chapter by Grohs and Emanuel. The following three chapters review the work on pulsed chemical lasers, transfer lasers, and numerical modeling of chemical lasers. Chapters 9 and 10 are devoted to the theory of reactive collision mechanisms leading to the nonequilibrium vibrational excitation of the molecules that constitute the active medium of chemical lasers. A new, detailed review of the CO chemical laser and the first comprehensive collection of the work on the high power iodine laser are given in Chapters 11 and 12. Reed Jensen concludes the book with a description of the work on metal-atom oxidation lasers at Los Alamos.

There is a long list of colleagues, supporters, and friends who have contributed to this field and to this book and who do not appear by name. It is only just to acknowledge our debt to them in the beginning. Foremost are our present and former colleagues at Aerospace Corporation: D. Durran, W. Gaskill, R. R. Giedt, J. Herbelin, T. A. Jacobs, M. Kwok, H. Mirels, R. Varwig, and W. Warren. Without their encouragement, work, and patience this book could not have been written. We are also aware of a great debt to the U.S. Air Force and to DARPA, not only for financial support of much of the work on chemical lasers described in this book, but also for the personal encouragement, drive, and vision in the ups and downs of this research—in particular to M. Berta, P. Clark, E. Gerry, J. McCallum, R. Oglukian, J. Rich, M. Rogers, and L. Wilson. Finally the editors owe their gratitude to Kathleen Bregand for performing the tremendous task of editing the original manuscripts with charm and devotion.

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1. WHAT IS A CHEMICAL LASER?

Chemical lasers now have nearly a 10-year history. The first meeting on the subject, in 1964, was organized by the American Optical Society and was filled with high hopes for a rapid development of this field. Chemical-laser emission was then experimentally realized for the first time in 1965 by Kasper and Pimentel¹ at Berkeley. The emission occurred in a photolytically initiated hydrogen-chlorine explosion. Predating this discovery, the first photodissociation laser was described by the same authors in 1964.² This laser is based on the formation of excited iodine atoms in the photoinduced bond rupture of alkyl iodides.

Such lasers have since provided a fruitful avenue for the study of elementary reaction dynamics and have stimulated the investigation of collisional energy-transfer processes. Most recently, chemical lasers have also been put to use as specialized excitation sources for spectroscopic and kinetic work.

Interest in the technical development of chemical lasers only appeared around 1970. This is, in part, due to their complicated theoretical background. Not only is their multilevel pumping scheme complex, but also the gain and spectral distribution change rapidly with time because of efficient collisional deactivation processes. Thus before progress could be made in either the theory or the technology of chemical lasers, concepts from various disciplines had to be combined. However, beginning about 1969, increasing numbers of technically oriented papers on chemical lasers have appeared in the literature. There have already appeared some general reviews.³⁻⁶ Continuous chemical lasers based on several reactions are now in operation, and pulsed chemical lasers have been scaled up in power to a technically interesting regime. Most of the information needed to assess the potentials of chemical lasers is now available.

This book, then, addresses itself to physicists, physical chemists, and

laser engineers interested in chemical lasers. The general thrust is towards application-oriented physics and laser engineering with some consideration of the chemical background. For the purposes of this audience, we shall define a chemical laser as a *laser operating on a population inversion produced—directly or indirectly—in the course of an exothermic chemical reaction*. Furthermore, our definition shall extend to all types of chemiluminescent excitation, which include, for example, pumping in the course of photoinduced or even electron-impact-induced chemical bond rupture as well as by the radiative association of atoms or molecules. Finally, we shall also consider lasing action that occurs in an admixture to which the chemical energy is transferred prior to lasing.

In its simplest approach, the energy partitioning in exothermic reactions may be considered with reference to the usual picture of a reaction profile, as illustrated in Fig. 1.

It is apparent that a product molecule that has just emerged from the activated complex will not be at thermal equilibrium. It contains excess energy that can be given off either in *radiative* or in *collisional* processes, which are always in competition. The key question, though, is whether

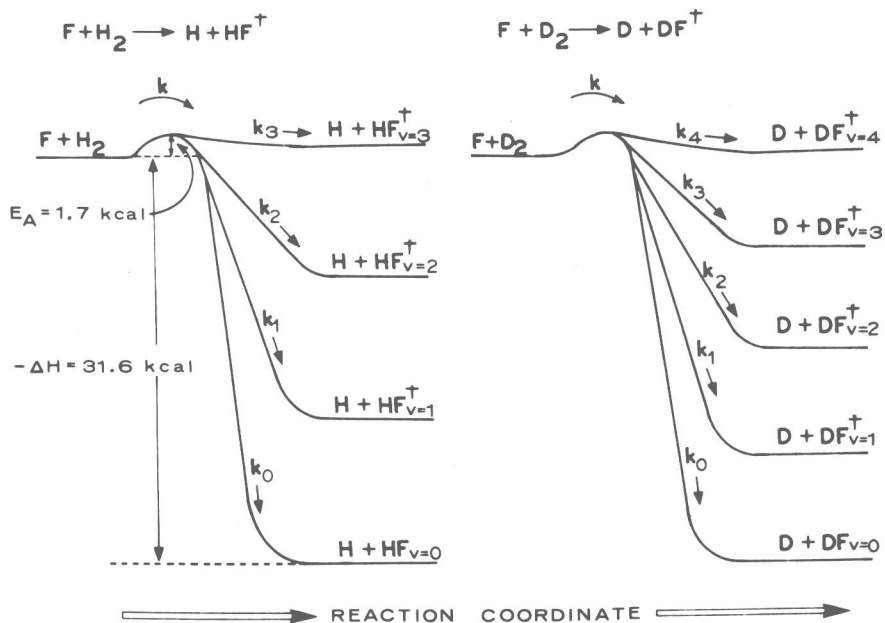


Fig. 1. Energy profiles for the reactions $F + H_2$ and $F + D_2$ (k_v is the rate constant into v th vibrational state).

the reaction selectively channels part of the energy into one or more higher product states to create a population inversion. This can happen when some dynamical constraint in the course of the reaction prevents a purely statistical distribution of the energy.

A molecule can store energy in the electronic, vibrational, rotational, and (although of no concern here) translational degrees of freedom. However, the probability that energy will accumulate in these various degrees of freedom and then lead to chemical laser action differs considerably. Beside the need for a population inversion, the production of laser gain also depends upon the cross-section for stimulated emission, which is simply related to the Einstein coefficient of stimulated radiation B_{12} and the line width $\Delta\nu$ of the transition

$$\sigma = \frac{B_{12}}{\Delta\nu c} = \frac{\lambda^2}{8\pi \Delta\nu \tau}$$

Thus the chance that laser emission may dominate over collisional relaxation varies with the square of the emission wavelength and inversely with the spontaneous lifetime τ of the emitting state and the line width $\Delta\nu$.

These factors seem to be more favorable for chemical lasers based on electronic excitation than for those based upon vibrational excitation; electronic transitions involve smaller wavelengths and, in most cases, much shorter lifetimes [$I^*(^2P_{1/2} \rightarrow ^2P_{3/2})$ is an exception]. Yet, chemically pumped vibrational lasers are common, and the electronic counterparts are rare. Of course, the energy required to excite transitions in the visible spectral region is high compared to typical chemical-reaction heats, that is, between 41 kcal/mol (700 nm) and 71 kcal/mol (400 nm). However, there are many chemical reactions that are sufficiently exothermic and, indeed, are known to produce chemiluminescence.

Plainly, loss mechanisms must be considered as well as gain factors. For vibrational excitation, collisional deactivation is the most significant; whereas, for electronic transitions, large A factors, which raise the gain, can also limit the growth of population inversion through spontaneous emission.

Still, favorable reactions are known (for instance, some reactions where polyatomic molecules or small molecules containing metal atoms are involved), and success in the chemical pumping of electronic states can be expected. Nevertheless, only in the related group of photodissociation lasers has emission from electronic states been realized. Laser emission based on rotational transitions has also been observed,^{7,8} but in no case has it been established definitively that chemical reactions provide the population inversion that caused the laser emission.

2. REACTION TYPES IN CHEMICAL LASERS

At this time, a relatively small number of chemical reactions are being intensively studied because they are the pumping reactions in efficient, high-energy lasers. The subsequent chapters will focus attention on these important systems. First, however, it is appropriate to review the range of reaction types that have successfully been used to pump chemical lasers, without regard to their possible applicability.

Table 1 lists the reaction types, following the categorization proposed by Pimentel.⁹ For each of these types, prototype examples are discussed, a comprehensive listing is included, and generalizations are noted.

Table 1. Reaction types in chemical lasers

Name	Prototype examples	Year	References
Three-atom Exchange	$\text{H} + \text{Cl}_2 \rightarrow \text{HCl}^\dagger + \text{Cl}$	1965	1
	$\text{F} + \text{H}_2 \rightarrow \text{HF}^\dagger + \text{H}$	1967	11
	$\text{O} + \text{CS} \rightarrow \text{CO}^\dagger + \text{S} \quad (?)$	1966	12
Abstraction	$\text{F} + \text{CH}_4 \rightarrow \text{HF}^\dagger + \text{CH}_3$	1968	13
	$\text{O} + \text{CS}_2 \rightarrow \text{CO}^\dagger + \text{S}_2 \quad (?)$	1966	12
Photodissociation	$\text{CF}_3\text{I} + h\nu \rightarrow \text{CF}_3 + \text{I}(^2\text{P}_{1/2})$	1964	2
	$\text{ClNO} + h\nu \rightarrow \text{NO}^\dagger + \text{Cl}$	1966	14
Elimination			
Radical combination	$\text{CH}_3 + \text{CF}_3 \rightarrow \text{HF}^\dagger + \text{CH}_2\text{CF}_2$	1968	15
Insertion	$\text{O}(^1\text{D}) + \text{CH}_n\text{F}_{4-n} \rightarrow \text{HF}^\dagger + \text{OCH}_{n-1}\text{F}_{3-n}$	1971	16
Addition	$\text{NF} + \text{H}_2\text{C}=\text{CH}_2 \rightarrow \text{HF}^\dagger + \text{CH}_3\text{C}\equiv\text{N}$	1972	17
Photoelimination	$\text{H}_2\text{C}=\text{CHCl} + h\nu \rightarrow \text{HCl}^\dagger + \text{HCCH}$	1969	18

2.1. Three-Atom Exchange Reactions

The reaction between an atom *A* and a diatomic molecule *BC* will be exothermic if the *AB* chemical bond is stronger than the *BC* chemical bond. Such free radical reactions are generally extremely fast because the activation energies are small and there are no significant restrictive geometrical requirements for a collision to be reactive.

The first two chemical lasers based upon such three-atom exchange reactions used the $\text{H} + \text{Cl}_2$ ^{1,10} and the $\text{F} + \text{H}_2$ reactions:¹¹



The energy available to the reaction products ($-\Delta H + E_A$) is enough to excite HCl to $v = 6$ in Reaction (1) and HF to $v = 3$ in Reaction (2). The

Table 2. Vibrational rate constants at room temperature

	H + Cl ₂ ^a	F + H ₂ ^b	F + CH ₄ ^c	F + HI ^c	Cl + HI ^d
ΔH	-45.1	-31.5	-32.6	-62.6	-32
E_A	1.8	1.7	1.2	1.4	2
%($-\Delta H + E_A$)					
In vibration	39	66	68	56	65
	h			h	
k_6	0.005 ^e	—	—	1.07	—
k_5	0.05 ^e	—	—	1.69	—
					h
k_4	0.1	—	—	1.27	2.29
		h	h		
k_3	0.92	0.47	0.23	1.05	3.00
k_2	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
k_1	0.28	0.31	0.33	0.83	0.57
k_0	—	0.0 ^f	0.0 ^f	0.4 ^f	—
		0.06 ^g			

^a Ref. 19.^b Ref. 20.^c Ref. 21.^d Ref. 22.^e Ref. 23.^f Estimated, see Ref. 21.^g Private Communication, M. J. Berry; also, Ref. 24.^h Energy insufficient to excite higher levels.

actual distribution among the vibrational states is expressed in terms of relative rate constants k_v in Table 2. These vibrational rate constants channel, on the average, 39% of the available energy into vibration in Reaction (1)¹⁹ and 66% in Reaction (2).²⁰ In each case, the highest population is formed in the $v = 2$ state, which provides highest laser gain in $v = 2 \rightarrow v = 1$ V-R transitions.

The observed laser emission from either of these reactions depends upon the populations initially determined by these k_v 's but as subsequently modified by rotational equilibration and vibrational deactivation processes. Usually, rotational equilibration is so rapid that the primitive rotational occupancies are not influential in the laser performance. In contrast, the role of vibrational-relaxation reactions varies greatly and

depends upon operational conditions. In pulsed lasers vibrational relaxation can be entirely negligible,²⁵ whereas, it is always important in cw lasers. This dependence derives from the high deactivation efficiencies of certain collision partners, which can be associated with attractive forces (e.g., hydrogen bonding) or with a close energy match between the vibrational levels of the two molecules involved, or both.^{26,27}

Despite the vibrational-deactivation problems, quite a number of exothermic three-atom reactions have been used to initiate chemical-laser emission. The reason for this success is illustrated in Table 2, particularly by the $F+HI$ and $Cl+HI$ reactions. In each case, vibrational excitation is observed up to the highest level that is thermodynamically possible in more than 15% of the reactive collisions. Even the $H+Cl_2$ reaction, the least efficient of the well-studied three-atom reactions, channels 39% of its exothermicity this way. It is a useful empirical generalization that *in exothermic three-atom reactions involving free radicals, a large fraction of the energy appears in vibrational excitation of the new bond formed.*

Table 3 lists 13 three-atom exchange reactions that have been used to pump chemical lasers. The various initiation techniques—pulsed photolysis, pulsed discharge, and continuous flow—are referenced separately. In each case, the earliest references are included, but, for later references, no attempt at completeness is made. Particularly for the $F+H_2$ pumping reaction, a complete list of references would be very long.

Table 3. Three-atom reactions for which chemical-laser emission has been observed^a

Reaction Initiation Method:	Pulsed photolysis	Pulsed discharge	Continuous flow
$H+Cl_2 \rightarrow HCl^+ + Cl$	1, 28, 29	30, 31, 32	33
$F+H_2 \rightarrow HF^+ + H$	11, 34, 35, 36, 37	30, 36, 38, 39, 40, 41, 42, 43	44, 45, 33, 46
$Cl+HI \rightarrow HCl^+ + I$	47	48	33, 46
$F+HX \rightarrow HF^+ + X$ $X = I, Br, Cl$	49, 50	51	47, 33, 46
$Cl+HBr \rightarrow HCl^+ + Br$	52	—	46
$Br+HI \rightarrow HBr^+ + I$	49	—	33 ^b
$H+F_2 \rightarrow HF^+ + F$	—	42	33
$H+Br_2 \rightarrow HBr^+ + Br$	—	31, 53	33 ^b
$O(^3P)+CH, CF, CN \rightarrow CO+H, F, N$	54	—	—
$O+CS \rightarrow CO^+ + S$ (?)	12	55, 56	57

^a The numbers refer to the list of references.

^b Experiment attempted, no laser emission observed.