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TRAINING COLLEGE ON PHYSICS AND CHARACTERIZATION OF LASERS AND OPTICAL FIBRES

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HIGH-POWER CHEMICAL LASERS

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1. – Introduction.

The most familiar ways of achieving population inversions are by optical pumping or by using a gas discharge. The first laser, using a ruby as the medium, was operated by shining pulses of radiation from a flash lamp. On the other hand, the first gas laser was run continuously as a gas discharge. However, there are several other very interesting possibilities; those based in some ways or other on the principles of fluid mechanics and chemical kinetics will be of particular interest here [1-6].

The high energy density that can be released in exothermic chemical reactions has led to the interest in converting chemical energy to coherent optical energy. If we could use the energy of this reaction directly to obtain a population inversion, we could build compact powerful lasers. Chemical lasers are a powerful tool for studying the kinetics of some reactions as well [7].

The possibility of using inversion subsequent to chemical reactions is particularly interesting specially for producing high power output. In this seminar, the term chemical laser will mean that the levels involved in the stimulated emission processes are inverted directly as a result of chemical reaction, and are energy levels of one of the reaction products. Such lasers do exist since fifteen years, although continuous production has been achieved for some of them only recently.

A closely related class of lasers also works because a chemical reaction produces excited species. However, the vibrational energy is transferred by resonant energy exchange to another species (usually CO_2), thereby providing inversion in the second species. The chemical reaction does not have to give a product with a population inversion [8].

One advantage of chemical lasers is that they will provide radiation output

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with no electrical input. This characteristic, and the fact that very high gain can be achieved, explain why much work is being spent developing such devices.

The first chemical-reaction laser was realized by KASPER and PIMENTEL in 1964 [9-11]. In their laser the active molecule was vibrationally excited hydrogen chloride, formed by the reactions

$$(1a)\qquad \mathrm{Cl}+\mathrm{H}_2 \rightarrow \mathrm{HCl}^{\dagger}(v=n)+\mathrm{H}\,,$$

$$(1b)\qquad \mathrm{H}+\mathrm{Cl}_2 \rightarrow \mathrm{HCl}^{\dagger}(v=n)+\mathrm{Cl}\,.$$

The initial chlorine atoms were produced by flash photolysis according to the reaction

$$(1c)\qquad \mathrm{Cl}_2 + h\nu \rightarrow 2\mathrm{Cl}\,.$$

The output of this laser is at several frequencies $\sim 3.7\ \mu\mathrm{m}$, corresponding to several rotation lines associated with the $v'=2 \rightarrow v=1$ vibrational transition of the HCl molecule.

This laser illustrates two aspects of chemical laser systems quite well. First, it is generally necessary to have a source of free atoms or free radicals that can react with other atoms or molecules to form an excited-state reactant. The development of chemical lasers is dependent on the ability to generate free atoms or free radicals. Second, long chain reactions, such as the one that produces the hydrogen and chlorine atoms, are of significant value, because they limit the rate of external production of free radicals. We need a strongly exothermic long chain reaction to be able to use efficiently the total energy available in a chemical reaction.

Since the HCl laser breakthrough, there has been a rapid advance in the development of chemical laser systems, although the chemical reactions utilized have been largely limited to the formation of hydrogen halides and CO in a reaction between oxygen and carbon disulfide. Many pulsed and continuous lasers based on the hydrogen isotopes and the halogenes have been developed, some with average powers of some kilowatt. In most of these systems some external means such as flash photolysis, electrical discharge or shock heating start the reaction, but COOL and STEPHENS [12, 13] developed the first purely chemical laser about ten years ago. Their laser was based on the reactions

$$(2a)\qquad \mathrm{F}_2+\mathrm{NO} \rightarrow \mathrm{NOF}+\mathrm{F}\,,$$

$$(2b)\qquad \mathrm{F}+\mathrm{D}_2 \rightarrow \mathrm{DF}^{\dagger}(v=n)+\mathrm{D}\,,$$

$$(2c)\qquad \mathrm{D}+\mathrm{F}_2 \rightarrow \mathrm{DF}^{\dagger}(v=n)+\mathrm{F}\,,$$

$$(2d)\qquad \mathrm{DF}(v=n)+\mathrm{CO}_2(00^00) \rightarrow \mathrm{DF}^{\dagger}(v=n-1)+\mathrm{CO}_2^{\dagger}(00^01)\,.$$

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In the first reaction F_2 is dissociated by a chemical means into free fluorine atoms. The fluorine atoms then mix rapidly with D_2 and CO_2 forming vibrationally excited DF. The excited DF transfers its energy to the CO_2 and laser action occurs at 10.6 μm.

2. – Physical principles.

Most chemical lasers operate on vibrational rotational transitions in a diatomic molecule. The energy levels of such a molecule are approximately represented by the allowed energy states of a rotating Morse vibrator described by a potential [14]

$$V(r) = D_e\{1 - \exp[-\beta(r - r_e)]\}^2 . \tag{3}$$

Here D_e is the dissociation energy referred to the potential minimum as zero. The approximate solution of the relative wave equation [15] then gives for the term values expressed in wave numbers

$$\frac{E}{hc} = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + \\ + B_e J(J+1) - \alpha_e\left(v + \frac{1}{2}\right) J(J+1) - D_e J^2(J+1)^2 \;(\text{cm}^{-1}), \tag{4}$$

where $\beta = (\omega_e x_e/4B_e)^{\frac{1}{2}}$. The eigenfunctions are given by

$$\psi_n(x) \propto \exp[-z/2]\, z^{(k-1)-n/2} L^{k-2n-1}_{k-n-1}(z) \tag{5}$$

with $k = 4D_e/\hbar\omega_e$ and $z = k\exp[-\beta r_e x]$ and $L^b_a(z)$ being the generalized Laguerre polynomial.

The strongest laser transitions involve a vibrational change $\Delta v = -1$ and a rotational change $\Delta J = +1$ [16].

Figure 1 shows a crude «billiard ball» picture of the reaction between a fluorine atom and a hydrogen molecule. The fluorine atom approaches the hydrogen molecule, and sometime during the collision the chemical bond is shifted from the hydrogen to the fluorine. After the collision, the fluorine is bounded to one of the hydrogen atoms, and the other hydrogen atom departs alone.

The process described above can be divided into three stages: 1) the approach of an atom A to a complex BC, 2) an intermediate stage when this approach continues but the bond B-C begins to stretch, 3) the separation of the reaction products AB and C. Let us assume that E_1, E_2 and E_3 are the energies evolved during these three stages. It has been shown [4] that the energy E_1 is evolved mainly in the vibrational form and E_3 mainly in the

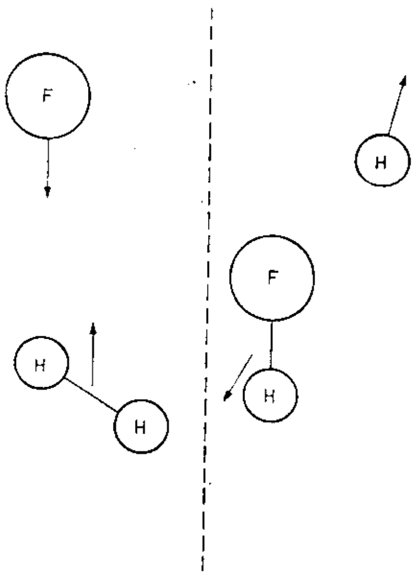

Fig. 1. – Schematic of a reactive collision.

kinetic form. The fraction of E_2 transformed into the vibrational energy of the molecules increases with the relative mass of atom A compared with the atoms B and C.

A more detailed analysis of the reactive scattering in molecular collisions can be carried out in the simplest case of collinear motion of particles when the potential energy depends only on two variables: $V = V(x_{AB}, x_{BC})$. The

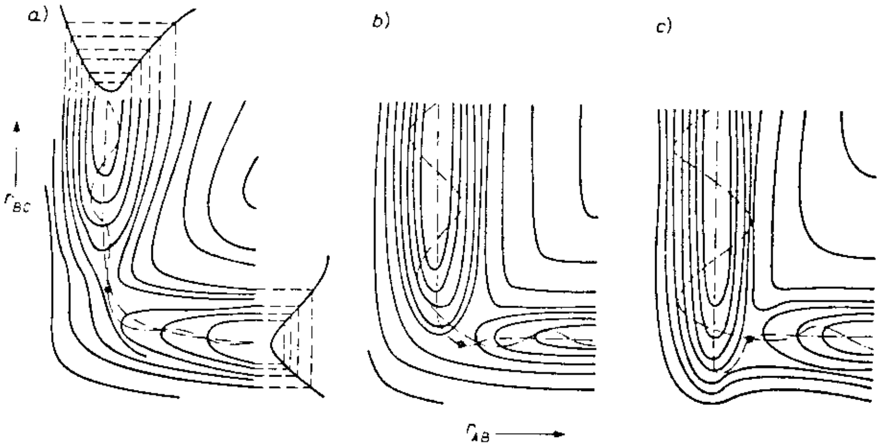

Fig. 2. – Potential surfaces of a system of collinear atoms: *a*) repulsive potential, *b*) mixed potential, *c*) attractive potential.

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potential surfaces of a system of atoms calculated by means of the London-Polanyi-Sato (LPS) method are sketched in fig. 2 [17]. The continuous curves represent the constant-energy lines, and the dashed curves show the possible trajectories of the motion of the system in the process described by $A + BC \to AB + C$. Early qualitative discussion suggested a simple relation between the partitioning of the reaction exothermicity and the form of the potential-energy surface. This applies to an $A + BC \to AB + C$ reaction without appreciable activation energy. If the surface is of the attractive or « early downhill » type, in which most of the exothermicity is released as the reactants approach rather than as the products separate, strong vibrational excitation of the newly formed AB bond is expected, whereas for a repulsive or « late downhill » surface most of the exothermicity is expected to appear in translational recoil of AB and C. The energy partitioning has been thoroughly examined in the Monte Carlo studies and found to obey this criterion, although in extreme cases other features of the surface have some effects also [18-23].

From the physical standpoint, we may use the following intuitive picture. When the chemical bond shifts from BC to AB, the electron jump occurs when the A and B atoms are farther apart than they would be in equilibrium in an AB molecule. Thus, the AB molecule is formed with a « stretched » molecular bond, containing potential energy. Then, as the AB and C separate, this stretch is converted into vibration in the newly formed bond.

According to the electron jump model the hydrogen-halide reactions are ion recombination reactions, as

$$A + B\text{-}C \to A^+ \dots B^- \dots C \to A^+B^- + C \,. \tag{6}$$

Polanyi suggested the picturesque term *harpooning* for this process: the attacking fluorine atom tosses out its valence electron, hooks the hydrogen, and hauls it in using their mutual Coulomb attraction [24].

Relative rate constants k_v for formation of vibrationally excited states of lasing molecules have been obtained by several authors. Parker and Pimentel [7], studying HF lasers, found $k_2/k_1 \sim 5.5$. Polanyi and Tardy, using [25-30] chemiluminescence techniques to study the $F+H_2$ reaction, determined k_v ($v = 0, 1, 2, 3$) and the relative rate constants into individual rotational states of each vibrational state. More sophisticated experiments have been carried out resorting to crossed-molecular-beam techniques [31].

The reaction energy disposal into the different vibrational levels has been analysed in the framework of the so-called « information-theoretic approach », particularly by Levine, Bernstein, Ben-Shaul and Kompa [32]. They have shown that the vibrational distribution resulting from exchange or abstraction reactions can be described by the distribution function

$$P(f_v) = Q_v^{-1} P_0(f_v) \exp[-\lambda_v f_v] \,, \tag{7a}$$

where the *a priori* distribution function P_0 reduces to

$$P_0(f_v) \sim \tfrac{2}{5}(1-f_v)^{\frac{3}{2}} \tag{7b}$$

in the rigid-rotator harmonic-oscillator approximation (RRHO), $f_v = E_v/E$ with E being the total energy released during the collision, λ_v is the « vibrational temperature » parameter (ranging from -5 to -10 for the reactions of laser interest), and Q_v is the partition function. For some reactions the vibrational-rotational joint distributions $P(f_v, J)$ have been shown to be represented by the formula

$$P(f_v, J) = Q_v^{-1}(2J+1)\{1-f_v-f_J(v)\}^{\frac{1}{2}}\exp[-\lambda_v f_v]\,, \tag{7c}$$

discussed by BEN-SHAUL, HOFACKER and KOMPA, or by

$$P(f_v, J) = Q_{vr}^{-1}(2J+1)\{1-f_v-f_J(v)\}^{\frac{1}{2}}\exp[-\lambda_v f_v - \theta_r f_r/(1-f_v)]\,, \tag{7d}$$

as proposed by LEVINE *et al.* [33].

3. – Chemical-reaction systems.

In 1964, KASPER and PIMENTEL reported the first chemical laser. An early search for vibrational excitation of CF_3 fragments from CF_3I photolysis was diverted by the discovery that the iodine atom is born almost exclusively in the $^2P_{\frac{1}{2}}$ excited state [9]

$$CF_3I + h\nu \to CF_3 + I^*(^2P_{\frac{1}{2}})\,. \tag{8}$$

The $^2P_{\frac{1}{2}} \to {}^2P_{\frac{3}{2}}$ transition gave stimulated-emission light pulses up to the kilowatt range with a duration of a few microseconds. The frequency is 7604 cm^{-1}, wavelength 1.315 μm. A similar behaviour was quickly discovered for a variety of alkyl iodides and perfluoroalkyl iodides. The CF_3I system displayed gain in excess of 100 dB m^{-1} and demonstrated the potentiality of chemical processes for high population inversion. Later on this system has been used by KOMPA and HOHLA for laser fusion applications [34, 35].

During 1966, POLLACK added a photodissociation laser based upon photolysis of nitrosyl chloride. Nitric oxide produced from ClNO emits in the 6 μm region [36, 37].

In concurrent research DEUTSCH discovered that nitrosyl chloride in a pulsed electrical discharge also produces nitric-oxide laser emission in the 6 μm region [38].

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$H + Cl_2 \to HC$
$Cl + HI \to HC$
$F + H_2 \to HI$
$F + HCl \to HI$
$F + HI \to HI$
$H + F_2 \to HI$
$F + D_2 \to DI$
$F + DI \to DI$
$D + F_2 \to DI$
$H + Br_2 \to HI$
$O + CS \to CC$

With OCS in a pulsed discharge, DEUTSCH found laser emission due to vibrationally excited carbon monoxide. He attributed this excitation to the dissociation of electronically excited OCS

$$\text{OCS} \to \text{CO}^{\dagger} + \text{S}\,. \tag{9}$$

The elucidation of the CF_3I photodissociation laser provided the key to previously confusing, but intense infra-red emissions from hydrogen chlorine explosions observed by KASPER and PIMENTEL using rapid-scan infra-red techniques. These emissions were then readily identified with laser emission from the secondary chemical reactions that occur in photolytically induced H_2-Cl_2 explosion [39, 40],

$$\left\{\begin{array}{l} \text{Cl}_2 + h\nu \to 2\text{Cl}\,, \\ \text{Cl} + \text{H}_2 \to \text{HCl}^{\dagger} + \text{H}\;, \\ \text{H} + \text{Cl}_2 \to \text{HCl}^{\dagger} + \text{Cl}\,. \end{array}\right. \tag{10}$$

Table I lists some of the chemical laser systems that have been operated since the first chemical laser. The separate listing of the D_2-Cl_2 and H_2-Cl_2 may seem redundant, but it makes an important point. Despite the apparent similarity of the H_2-Cl_2 and the D_2-Cl_2 explosion lasers, significant factors act

TABLE I. – *Chemical laser reactions.*

Reaction	Energy release (kcal/mol)	Laser wavelengths (μm)
$H + Cl_2 \to HCl^{\dagger} + Cl$	45	3.5 ÷ 4.1
$Cl + HI \to HCl^{\dagger} + I$	32	3.5 ÷ 4.1
$F + H_2 \to HF^{\dagger} + H$	32	2.5 ÷ 3.0
$F + HCl \to HF^{\dagger} + Cl$	33	2.5 ÷ 3.0
$F + HI \to HF^{\dagger} + I$	64	2.5 ÷ 3.2
$H + F_2 \to HF^{\dagger} + F$	98	2.5 ÷ 3.4
$F + D_2 \to DF^{\dagger} + D$	31	3.5 ÷ 4.1
$F + DI \to DF^{\dagger} + I$	64	3.5 ÷ 4.3
$D + F_2 \to DF^{\dagger} + F$	99	3.5 ÷ 4.5
$H + Br_2 \to HBr^{\dagger} + Br$	36	4.0 ÷ 4.7
$O + CS \to CO^{\dagger} + S$	75	5.0 ÷ 5.8

to lower the gain of the DCl laser relative to the HCl laser. Most obvious is the effect of the increase in the moment of inertia. Since rotational equilibration can be expected, the density of rotational states dilutes the inversion density of any particular rotational transition for a given vibrational transition. The mass effect has a second deleterious effect in increasing the density of the vibrational states.

The CS_2-O_2 flash-initiated explosion laser is of special interest as the second chemical system that displayed laser emission. The mechanism of the chemical pumping has been shown to be as follows:

$$(11)\qquad \left\{\begin{array}{ll} O+CS_2 \rightarrow CS+SO + 23\ \text{kcal}\,, \\ O+CS \ \ \rightarrow CO^{\dagger}+S + 75\ \text{kcal}\,, \\ S+O_2 \ \ \ \rightarrow SO+O + 6\ \text{kcal}\,. \end{array}\right.$$

The most popular chemical laser uses the HF molecule obtained from H_2-F_2, SF_4-H_2, UF_6-H_2, C_3H_8-F_2, to quote the most common reactions. The H_2-F_2 reaction is of particular importance because it has been studied in great detail,

$$(12)\qquad \left\{\begin{array}{l} F_2+h\nu \rightarrow 2F\,, \\ F+H_2 \rightarrow HF^{\dagger}\,(v>3) + H + 31.6\ \text{kcal}\,, \\ H+F_2 \rightarrow HF^{\dagger}\,(v>6) + F + 98\ \text{kcal}\,. \end{array}\right.$$

In the presence of dissociated hydrogen or fluorine H_2 and F_2 can react rapidly through the $F+H_2$ and $H+F_2$ reactions, which together form a chain reaction. The $F+H_2$ is called the « cold » reaction, because it releases less chemical energy than the « hot » reaction $H+F_2$.

Considerable interest has been focused on HCl and DF lasers emitting in the 3-5 atmospheric window. The DF laser has received the most attention because of the greater ease in producing large flows of vibrationally excited molecules. The reaction between H_2 and Cl_2 is not sufficiently rapid at room temperature. Recently, ARNOLD *et al.* [41, 42] have reported the successful operation of a 4 W purely chemical HCl laser using the reaction of NO with ClO_2 as a Cl atom source and the fast reaction $Cl+HI \rightarrow HCl^{\dagger}\,(v>4)+I$ as the laser pumping reaction,

$$(13)\qquad \left\{\begin{array}{l} NO+ClO_2 \rightarrow NO_2+ClO\,, \\ NO+ClO \ \ \rightarrow NO_2+Cl\,, \\ Cl+ClO_2 \ \ \rightarrow 2ClO\,. \end{array}\right.$$

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Chemical pumping of laser oscillation at 285.55 cm^{-1} from flash photolysis of $H_2:O_3$ mixtures has been reported. Laser lines have been assigned by DOWNEY and ROBINSON [43] to chemically excited water vapour $H_2O^{\dagger}$ produced by the reaction

$$(14)\qquad \left\{\begin{array}{ll} O_3+h\nu & \rightarrow O(^1D)+O_2(^1\Delta_f)\,, \\ O(^1D)+H_2 & \rightarrow OH+H\,, \\ H+O_3 & \rightarrow OH+O_2\,, \\ OH+H_2 & \rightarrow H_2O^{\dagger}+H\,. \end{array}\right.$$

Another important class of chemical lasers makes use of metal oxidization for obtaining partial inversion. It has been known since the pioneristic chemiluminescence experiments carried out by POLANYI in the thirties that alkali metal atoms, while abstracting halogen atoms, deposit much of the energy in the vibrational degrees of freedom. By using exploding wire and films, the Rice's group at Los Alamos has observed lasing from CO, TiO, VO, ZrO, MoO, TaO, WO, UO, LiF, CF, MgF, AlF, TiF, VF, FeF, NiF, CuF, ZnF, ZrF, MoF, AgF, TaF, WF, PtF, AuF and UF [44].

Starting from the experimental evidence that many metal atom oxidization reactions exhibit strong visible emission, a search for visible and near-IR laser action resulting from electronic excitation and inversion is being actively conducted in several laboratories. Some guidelines for this search have been suggested by SUTTON and SUCHARD [45] through the use of a computer code that calculates the minimum reactive branching ratio required for the abstraction reactions. Alkaline-earth oxides (*e.g.* BaO), carbon group molecules (*e.g.* CN), nitrogen group oxides, transition metal halides have been recommended as the best candidates for exhibiting laser action [46, 47].

Among the most promising reactions for use as potential chemically pumped electronic transition laser systems are those reactions that produce group IV oxides, halides and nitrides. In particular, CN has attracted the attention of many investigators. An interesting device for producing excited CN has been recently reported. It consists of an electric arc through which room temperature N_2 gas is passed, thus producing active nitrogen at roughly 6000 K. The mixture of vibrationally and electrically excited N_2 is expanded through a plug nozzle into a reaction chamber at velocities on the order of 10^6 cm/s for a 10 Torr reaction chamber pressure; the dwell time is about 10 microseconds. The hydrocarbon is injected at right angles into the expanding nitrogen flow, which results in the production of a bright flame. Two strong band systems have been identified in the flames produced in the reaction chamber, falling in the blue and near-ultraviolet regions extending from approximately 500 to 900 nm [48].

Before concluding, it is worth reporting the chemical-laser classification proposed by PIMENTEL, based on the different reaction types utilized [49-51]

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\left\{\begin{array}{lll}
\textit{Type} & \textit{Example} & \\
\text{Photodissociation} & CF_3I+h\nu & \rightarrow I^{\dagger}(^2P_{\frac{1}{2}})+CF_3\,; \\
\text{Three-atom} & H+Cl_2 & \rightarrow HCl^{\dagger}+Cl\,, \\
\text{exchange} & F+H_2 & \rightarrow HF^{\dagger}+H\,, \\
 & O+CS & \rightarrow CO^{\dagger}+S\,; \\
\text{Abstraction} & F+RH & \rightarrow HF^{\dagger}+R\,, \\
 & F+CH_4 & \rightarrow HF^{\dagger}+CH_3\,; \\
\text{Elimination} & CH_3+CF_3 & \rightarrow HF^{\dagger}+CH_2CF_2\,; \\
\text{Photoelimination} & CH_2CHX+h\nu & \rightarrow HX^{\dagger}+C_2H_2\,.
\end{array}\right. \tag{15}
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Another current classification of chemical lasers refers to the reaction initiation characteristics as follows:

flash initiation,
continuous wave,
thermal explosion (HN_3, ClN_3),
electronic transitions (?).

4. – High-energy and high-power chemical lasers.

Chemical chain reaction lasers are of interest because the laser output energy can be much greater than the energy required to initiate the reactions. For the HF system using a mixture of F_2 and H_2, the hot and cold reactions form a chain which proceeds until all available F_2 or H_2 is extinguished.

The achievement of high-energy laser pulses on a nanosecond time scale requires high pressures of H_2 and F_2 as well as a fast high-energy source to produce atomic fluorine and hydrogen. In experiments carried out at Sandia an intense electron beam (2 MeV, 50 kA, 70 ns FWHM) has been used to initiate room temperature H_2/F_2 mixtures in a large volume. The laser cell is a stainless-steel cylinder 14.9 cm diameter and 1.67 m long. The electrons from the REBA accelerator were drifted 16.5 cm at low pressure and then passed through a diaphragm into the laser cell. The laser output came through a hexagonal array of seven 4.3 cm diameter sapphire windows. A maximum laser energy of 2.3 kJ has been reported with a gas mixture of 360 Torr F_2, 140 Torr O_2, 100 Torr SF_6 and 100 Torr H_2. The oxigen was used to prevent spontaneous explosion of the mixture. The electrical efficiency (laser energy/deposited energy) was of 178%.

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GERBER *et al.* have obtained 228 J from a superradiant HF laser using a mixture of 400 Torr SF_6 and 40 Torr of C_2H_6. An axial e-beam has been used for dissociating the SF_6 and producing atomic fluorine [52],

$$(16)\qquad \begin{cases} SF_6+e \rightarrow SF_5+F+e\,, \\ SF_6+e \rightarrow SF_4+2F+e\,. \end{cases}$$

The key issue in using this sort of laser for generating very short and intense light pulses is the energy extraction scheme. In fact, the high gain makes very hard to achieve a good mode control. To overcome this difficulty and to control amplified spontaneous emission and parasitics, the laser must operate with a saturating optical field present during the pump cycle. By using this scheme, spatial and temporal control of energy extraction from a 1.3 m long amplifier filled with SF_6 and C_2H_6 excited by a 50 mm diameter Pulserad e-beam has been obtained at Los Alamos [53-56].

The development of these lasers has triggered a great deal of work for efficient generation of short pulses. SIMONIS [57] has achieved mode-locking of a single-line HF laser by using an unstable cavity and low-pressure HF gas as saturable absorber. Pulses 5 ns long have been obtained.

5. – Continuous-flow combustion lasers.

Two major classes of continuous-flow combustion lasers can be identified: gas-dynamic lasers (GDL) and chemical-mixing lasers (CML).

An inherent requirement for CW laser emission from these CML devices is the continuous generation of atoms. In the early research, COOL and coworkers [58, 59], AIREY and MEINZER *et al.* demonstrated such techniques. Based on these approaches high-power CML have been evolved consisting of a high-temperature, high-pressure, nonstoichiometric combustor yielding a sufficient concentration of free atoms at thermochemical equilibrium [60-66], a rapid-expansion supersonic nozzle to exhaust the combustion products thereby freezing the free-atom concentration, gas injectors to intermix the secondary reagent into the low-temperature, low-pressure, supersonic flow where the laser pumping reaction proceeds and a transverse optical resonator to sustain laser emission on the newly formed reaction products.

The kilowatt CW HF chemical-mixing laser developed by the Aerospace Co. and TRW typifies this approach. A thermal DC arcjet is used to generate free fluorine atoms from SF_6. MEINZER *et al.* demonstrated a pure combustion route to high concentrations of F atoms via F_2-rich H_2/F_2 combustion. The active medium formed in the mixing reacting supersonic flow was held at low temperature (400 K) and low pressure ($(2\div5)$ Torr) to minimize the normally rapid collisional decay of HF. Peak laser output greater than 2 kW has been reported.

The pumping of chemical-laser emission via chain reactions has been observed or suggested in flame lasers, for example CO laser pumped by the CS_2+O_2 system. The CO flame laser burns mixtures of CS_2 and O_2 to produce excited CO molecules, emitting in the 5 μm region. The flame is self-sustaining requiring no external energy source and burns at rather low pressures ((10÷40) Torr).

6. – Laser modelling.

Chemical-laser modelling has attracted the attention of several authors since the first attempt by COHEN *et al.* [67], who modelled the HCl laser of Corneil and Pimentel. A detailed account of the codes used to investigate a model of the kinetics, the optical energy extraction and the energy transfer processes, including the mixing models for CW lasers, can be found in the review paper by EMANUEL [68]. Among others, it is worth mentioning the RESALE, SPIKE, BLAZER and RICE codes [69].

In the large field of laser modelling we will limit ourselves to point at four classes of problems of particular relevance for basic physics, namely: dipole moment calculation for vibrational-rotational transitions in diatomic molecules, collision broadening in polar gases, information-theoretic approach to chemical excitation rates of vibrational levels and to energy transfer, extension of laser theory including cascade effects and population relaxation.

The radiation intensity gain α_ν per unit length is given by

$$\alpha_\nu = \frac{hB_{u\to l}}{4\pi}\,\nu\,\Delta N_u^l\,\Phi(\nu-\nu_0)\ (\text{cm}^{-1})\,, \tag{17}$$

where ν is expressed in cm^{-1}, $\Delta N_u^l = N_u - N_l g_u/g_l$ is the population inversion, $\Phi(\nu-\nu_0)$ is the unity normalized line shape factor and $B_{u\to l}$ is the Einstein coefficient of induced emission defined in terms of an isotropic intensity, which is related to the matrix elements of the dipole moment $\mathcal{M}$ for the transition $u\to l$,

$$B_{u\to l} = \frac{16\pi^4}{3h^2cg_u}\sum_{i,k}|\mathcal{M}_{ui}^{lk}|^2\,, \tag{18}$$

where the summation is over all the states belonging to the upper and lower levels. For a vibrational rotational transition v', $J'\to v$, J, this equation reduces to

$$B_{u\to l} = 4\pi\ 3.1414\cdot 10^{57}\,\frac{J'+J+1}{2J+1}\,|\mathcal{M}|^2\ (\text{Js}^{-1})\,. \tag{19}$$

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6'1. *Electric dipoles for diatomic molecules.* – In the Born-Oppenheimer approximation an electric-dipole moment function $\mu(r)$ may be defined by averaging the dipole operator with respect to the electronic co-ordinates of the wave function. As a result, it can be shown that

$$|\langle v'\,J'|\mu(r)|vJ\rangle|^2 = |m|\left|\int_0^\infty r^2\,\mathrm{d}r\,\psi^*_{v'J'}\,\mu^2\,\psi_{vJ}\right|^2, \tag{20}$$

where $m = J + 1$ for a R-branch and $m = -J$ for a P-branch. To evaluate these matrix elements the wave functions are needed. As a first approximation the wave functions of the Morse oscillator (see eq. (5)) have been used. MEREDITH and SMITH [70] have used the Rydberg-Klein-Rees empirical potential in the calculation of dipole moment matrix elements. By using the RKR potential, the classical turning points of the vibrational motion are determined directly from the observed energy level transitions of a particular molecule.

To evaluate the r.h.s. of eq. (20), it is necessary to take account of the fact that the variation of the dipole moment with internuclear distance is not strictly linear,

$$\mu(r) = M_0 + M_1(r - r_e) + M_2(r - r_e)^2 + \dots . \tag{21}$$

For very large and very small internuclear distances the dipole moment must approach zero except when the molecule dissociates into ions.

Substituting Morse eigenfunctions and the r.h.s. of (21) into (20) yields

$$\langle 0|\mu(r)|1\rangle = \frac{M_1}{\sqrt{2\alpha}}\,\frac{\sqrt{1-3x_e}}{1-2x} - M_2\,\frac{2x_e}{\beta^2}\,\frac{1}{1-2x_e}\sqrt{\frac{1-3x_e}{x_e}}\,\ln(1-5x_e/2)\,. \tag{22}$$

The M_i parameters have been determined for the HF molecule from the experimental parameters

$$\left|\begin{aligned} &\langle 0|\mu|0\rangle = 1.819\cdot 10^{-10}\ \text{esu cm}\,,\\ &\langle 1|\mu|0\rangle = 9.850\cdot 10^{-20}\ \text{esu cm}\,,\\ &\langle 2|\mu|0\rangle = -1.253\cdot 10^{-20}\ \text{esu cm}\,,\\ &\langle 3|\mu|0\rangle = 1.628\cdot 10^{-21}\ \text{esu cm}\,,\end{aligned}\right. \tag{23}$$

thus giving

$$\mu(r) = 1.7892 + 1.522(r - r_e) - 0.2335(r - r_e)^2 - 1.0958(r - r_e)^3\,. \tag{24}$$

As a result the Einstein coefficients $A(v', v)$ for HF are

$$(25)\qquad \begin{cases} A(1, 0) = 189.2\ \text{s}^{-1}\,, \\ A(2, 1) = 322.5\ \text{s}^{-1}\,, \\ A(3, 2) = 406.1\ \text{s}^{-1}\,, \\ A(4, 3) = 446.3\ \text{s}^{-1}\,. \end{cases}$$

In the limit $r \to 0$ the dipole moment must approach zero as the third power of the internuclear separation.

Analogous calculations have been carried out for CO, HCl and DF and the relative Einstein coefficients can be found in the papers by EMANUEL, HERBELIN and COHEN [67-76].

6·2. *Line width and resonance broadening.* – There are three main processes that contribute to the formation of the lasing transition: *a*) natural broadening, *b*) Doppler broadening, *c*) collision broadening. Stark broadening due to collision with electrons and ions is negligible. In a CW laser, which operates at low pressure, less than 10 Torr, collision broadening may be ignored. In pulsed lasers, where one cannot get along without the use of foreign gases, the contribution due to Lorenz broadening prevails over Doppler broadening. Pulsed HF lasers typically operate at cavity pressures greater than 30 Torr, where line widths are dominated by pressure broadening.

Many collision-broadening calculations have been based on billiard-ball interactions. The Fourier integral theory developed by LORENTZ, LENZ and WEISSKOPF assumes that no transitions are caused by collisions. Then the effect of a collision is equivalent to a relative phase shift of the radiation before and after the collision, with no amplitude change.

ANDERSON has given a complete treatment of pressure broadening of the collision type which allows for collisions which induce transitions based on the following assumptions: i) colliding molecules follow definite classical paths, ii) the duration of the collision is short compared with the time between collisions, iii) the collision operators are smooth functions of the collision parameter [77].

Anderson theory, subsequently amplified by TSAO and CORNUTTE [78] and modified by FIUTTAK and VAN KRANENDONK [79], resulted from detailed quantum-mechanical calculations of the probabilities of nonradiating transitions induced by the combined effects of all the intermolecular forces acting on the radiating molecules [80]. Many calculations for the broadening of HF, HCl and DF have shown a good agreement with experiments, thus giving support to the Anderson theory for a dipole-dipole interaction between polar diatomic species [81-85].

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The collision-broadened half-width γ of a vibration rotation line is

$$\gamma = \frac{n\bar{v}}{2\pi c} \sum_{J_k} \varrho_{J_k} \sigma(J_k) \,, \tag{26}$$

where $\bar{v}$ is the mean relative collision velocity and n is the number of molecules per cm³ at one atmosphere and at temperature T. The function $\sigma(J_k)$ is the collision cross-section of each rotational state J_k of the perturbing molecule and is expressed in terms of the development of the interaction time as follows

$$\sigma(J_k) = \int_0^\infty 2\pi b S(b)\, \mathrm{d}b \,. \tag{27}$$

Here b is the impact parameter and $S(b)$ contains the details of the collision. Typically the perturbing species are in rotational equilibrium and the population distribution is of the Boltzmann type. In the case of the chemical laser the rotational equilibrium may not be valid and the cross-sections σ_J would be weighted differently, thus resulting in an altered value of γ and a different optical-gain coefficient.

If it is assumed that the perturbations are due to the interactions involving the electric dipole μ_0 and quadrupole moment Q of colliding molecules, $S(b)$ may be written as

$$S(b) = \sum_{J_i J_f} \left[C_1 b^{-4} \sum_n g_{1n} f_1(k) + C_2 b^{-6} \sum_n g_{2n} f_2(k) + C_3 b^{-8} \sum_n g_{3n} f_3(k) \right] , \tag{28}$$

where

$$\left| \begin{array}{ll} C_1 = \dfrac{4}{9} \mu_0^4/(h\bar{v})^2 \,, & C_2 = \dfrac{4}{45} \mu_0^2 Q^2/(h\bar{v})^2 \,, \\ C_3 = \dfrac{1}{25} Q^4/(h\bar{v})^2 \,, & k = \dfrac{2\pi c b}{\bar{v}} \, |(\Delta E)_{s,l}| \,, \end{array} \right. \tag{29}$$

and the $g_{s,l}$ coefficients are functions of the Clebsch-Gordan coefficients.

In the Anderson theory the scattering probability is taken as unity for all impact parameters less than the kinetic-theory diameter b_0. In the van Kranendonk approximation the scattering probability for all impact parameters less than b_0 is assumed equal to $S(b_0)$. As a result of this choice, the line widths predicted by the latter theory are often narrower than those predicted by the former one.

The widths and shifts of HCl spectra have been adequately explained by HERMAN and TIPPING by applying the quantum-mechanical impact theory of Baranger, Kolb and Griem (BKG) originally developed for atomic line shape calculations. The BKG theory furnishes a line shape

$$\Phi(\nu - \nu_0) = \frac{\text{const}}{w^2 + (\nu - \nu_0 - \Delta\nu)^2}, \tag{30}$$

where the width w and shift $\Delta\nu$ of a single line are proportional to the real and imaginary parts of the reduced line space resolvent operator Φ_{if}

$$\Phi_{if} = N\int_0^\infty v f(v)\,\mathrm{d}v\int_0^\infty 2\pi b[U_f(\infty, -\infty)\,U_i^*(\infty, -\infty) - 1]\,\mathrm{d}b, \tag{31}$$

where N is the number density of perturbers, v is the relative velocity of the perturber-molecule pair, $f(v)$ is the velocity distribution, b is the impact parameter and $U(\infty, -\infty)$ is a time development operator acting on internal radiator states, with U_i and U_f regarded as acting indipendently upon the initial or final manifold of states.

Where model calculations of the H_2-F_2 laser have been compared with experimental data, some have shown fairly good agreement in the prediction of the pulse shape. However, predictions of laser energy over broad ranges of operating conditions have not shown good agreement. This discrepancy has been attributed to the assumption of constant pressure-broadened line widths for different rotational levels. The specific information regarding the v and J dependence of the broadening cross-sections and the distinguishing broadening characteristics of various species in the gas must be included in theoretical calculations in order to achieve good agreement with experiments, both in the prediction of total energy and in the discrimination of spectral content.

Lorentz broadening in the modelling of the HF laser has been reviewed by HOUGH. As a result of a survey of pressure-broadening data pertaining to species present in the H_2-F_2 chemical laser [85], γ is shown to strongly depend on the vibrational and rotational quantum numbers as well as on the partners used as diluent in the gas mixture. A detailed model for line broadening has been included in the SPIKE code developed by the Aerospace Corporation.

Line widths have been measured and calculated by many authors [81-85]. Recently [86], BONCZYK has reported a precise measurement of γ for the P-branch of the $v = 1$-0 band of the DF molecule, carried out by using a CW DF laser as a continuously tunable light source. The values of γ obtained are in excellent agreement with corresponding theoretical values. The use of a laser as a source has permitted the elimination of the instrumental modifications of the spectra occurring in earlier measurements done with large-band light sources. In fact, by measuring absorption at low pressure, the strength and width of single lines can be determined directly, thus getting rid of the overlapping of adjacent lines occurring with high absorber pressure.

6'3. *Information-theoretical approach.* – The time evolution of the population in a molecular gas is described by the master equation [87-90]

$$\frac{\mathrm{d}P(v,t)}{\mathrm{d}t} = -\sum_{v'} k(v\to v')P(v,t) + \sum_{v'} k(v'\to v)P(v',t)\,. \tag{32}$$

An explicit solution of the master equation is possible only when all the required rate constants are known. One often has only a rather incomplete input, say the time dependence of a few population distribution moments. To determine the population distribution at any instant in time, we seek a distribution P that does account for the magnitude of those moments that are known, but is otherwise as much independent as possible. The completely time-independent distribution is the equilibrium one $P^0(v)$. Hence, we seek the distribution $P(v,t)$ which is as close to $P^0(v)$ as possible while being consistent with the bulk data available on the system at time t.

As a measure of the deviation of the population of the state v at time t from its equilibrium value LEVINE and BERNSTEIN use the surprisal

$$I(v,t) = -\ln\frac{P(v,t)}{P^0(v)} \tag{33}$$

and find for microscopic and macroscopic disequilibrium that the v-dependence of the surprisal is simpler than the similar dependences of the actual probabilities. The surprisal is essentially synonymous with independent data that are required to uniquely specify the disequilibrium state of the system. Thereby, it identifies the variables whose average values suffice to characterize the system at the time t.

By using this approach PROCACCIA and LEVINE have shown the validity of an exponential gap law

$$k(v\to v';\,t) = A(T)\,k^0(vv';\,T)\exp\left[-\lambda_v|E_v - E_{v'}|/kT\right] \tag{34}$$

for the detailed rate constants. $A(T)$ is a temperature-dependent factor and $k^0(v\to v';\,T)$ is the so-called prior rate constant which can be calculated from phase-space theory. The vibrational surpisal parameter λ_v is a measure of the deviation of k from k^0.

Analogous results have been obtained for the energy disposal of reactive molecular collisions (see sect. **2**, eqs. (7)) pumping chemical lasers [91-94] and electronic transition lasers [95].

6'4. *Laser theory: cascade and relaxation effects.* – A quantum-mechanical multilevel cascade model has been discussed by NAJMABADI *et al.* [96]. They have analysed an anharmonic oscillator by neglecting rotation and vibration-

vibration collisions. They have assumed that only one cavity mode is resonant with any given transition of the cascade chain. By solving numerically the equation of motion of the density operator and retaining the third-order approximation, the mutual aid in cascading processes is evident. In particular, a slight increase in the intensity of the upper transition occurs whenever a new lower mode starts to oscillate. By filtering out the middle transition, they have broken the cascade chain, thus letting the upper and lower modes to lase as independent chains.

Gain saturation and Lamb-dip formation have been considered by several authors [97-100]. The influence of collisions on the saturation characteristics of vibration rotation transitions has been analysed by a suitable relaxation form of the Boltzmann equation and by treating the radiation by the equation of radiative transfer [97],

$$\begin{aligned}(35)\qquad \frac{\mathrm{D}P^u_J}{\mathrm{D}t} &= \Gamma^u_J M - R_2 P^u_J + \sigma^u_J(N^u_J M - P^u_J) + \\ &+ \sigma^u_J \chi\left[\frac{N^u_J}{N^u} N^u M - P^u_J\right] - 4\pi A_{u_J, l_{J+1}} P^u_J - A_{u_J l_{J+1}} Q_{u_J l_{J+1}} (P^u_J - P^l_{J+1})\,.\end{aligned}$$

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