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TRAINING COLLEGE ON PHYSICS AND CHARACTERIZATION OF LASERS AND OPTICAL FIBRES

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CHEMICAL LASERS

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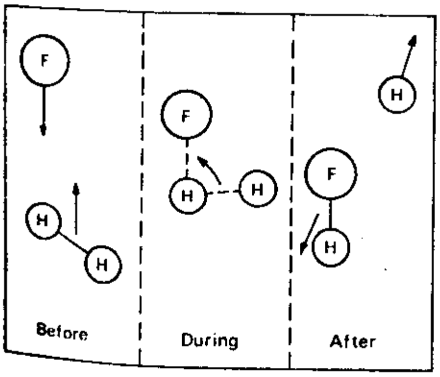
Chemical lasers open up a whole new field of laser research with the whole gamut of chemical reactions to be investigated. Professor Solimeno reviews the current state of the art

Figure 1 Schematic of a reactive collision



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

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 such reactions directly to obtain a population inversion, we could build compact powerful lasers. Chemical lasers may also become a powerful method of studying the kinetics of chemical reactions.

The possibility of using inversion subsequent to chemical reactions is particularly interesting, specially for producing high power output. In this article, 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 exist, although continuous wave production was achieved 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.

One advantage of chemical lasers is that they will provide radiation output with no electrical input. This characteristic, and the fact that very high gains (amplification) can be achieved, explain why much money and work are being spent developing such devices.

The first chemical reaction laser was realized by Jerome V Kasper and George C Pimentel in 1964. In their laser the active molecule was vibrationally excited hydrogen chloride, formed by the reactions

$$Cl + H_2 \rightarrow HCl^*(v = n) + H \cdot$$
$$H + Cl_2 \rightarrow HCl^*(v = n) + Cl.$$

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

$$Cl_2 + h\nu \rightarrow 2\,Cl.$$

The output of this laser is at several frequencies between 3·7 and 3·8 μm, corresponding to several rotational lines associated with $v = 2 \rightarrow v = 1$ 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 at present dependent on the ability to generate free atoms or free radicals. Second, long chain reactions, such as the one that produces hydrogen and chlorine atoms, are of significant value because they limit the rate of external production of free radicals. We will need strongly exothermic long chain reactions 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 to the formation of CO in a reaction between oxygen atoms and carbon disulphide. Many pulsed and continuous lasers based on the hydrogen isotopes and the halogens have been developed, some with average powers of some kilowatts. In most of these systems some external means such as flash photolysis, electrical discharge or shock heating start the reaction, but Terril Cool and Ronald Stephen (Cornell University) have developed a purely chemical laser. This laser is based on the reactions:

$$F_2 + NO \rightarrow NOF + F$$
$$F + D_2 \rightarrow DF^*(v = n) + D$$
$$D + F_2 \rightarrow DF^*(v = n) + F$$
$$DF^*(v = n) + CO_2(00°0) \rightarrow$$
$$\rightarrow DF^*(v = n - 1) + CO_2(00°1).$$

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.

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 vibrator. The strongest laser transitions involve a vibrational change $\Delta V = -1$ and a rotational change $\Delta J = +1$.

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 schematically 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 ε_1, ε_2 and ε_3 are the energies evolved during these three stages. It has been proved that the energy ε_1 is evolved mainly in the vibrational form and ε_3 mainly in the kinetic form. The fraction of ε_2 transformed into the vibrational energy of the molecules increases with the relative mass of atom A compared with 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 potential surfaces of a system of atoms are shown in figure 2. 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 $A + BC \rightarrow AB + C$. Early qualitative discussions suggested a simple relation between the partitioning of the reaction exothermicity and the form of the potential energy surface. This applies to an $A + BC \rightarrow AB + C$ 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.

Table 1 Chemical laser reactions

Reaction	Energy release (kcal mol⁻¹)	Laser wavelengths (μm)
$H + Cl_2 \rightarrow HCl^* + Cl$	45	3·5–4·1
$Cl + HI \rightarrow HCl^* + I$	32	3·5–4·1
$F + H_2 \rightarrow HF^* + H$	32	2·5–3·0
$F + HCl \rightarrow HF^* + Cl$	33	2·5–3·0
$F + HI \rightarrow HF^* + I$	64	2·5–3·2
$H + F_2 \rightarrow HF^* + F$	98	2·5–3·4
$F + D_2 \rightarrow DF^* + D$	31	3·5–4·1
$F + DI \rightarrow DF^* + I$	64	3·5–4·3
$D + F_2 \rightarrow DF^* + F$	99	3·5–4·5
$H + Br_2 \rightarrow HBr^* + Br$	36	4·0–4·7
$O + CS \rightarrow CO^* + S$	75	5·0–5·8

From a 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 further 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

$$A + B - C \rightarrow A^+ \ldots B^- \ldots . C \rightarrow A^+ B^- + C.$$

Michael 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.

Relative rate constants k_v for formation of vibrationally excited states of lasing molecules have been obtained by several workers. Parker and Pimentel, studying HF lasers, found $k_2/k_1 \sim 5{\cdot}5$. Polanyi and Tardy, using chemiluminescence techniques to study the $F + H_2$ reaction determined $kv(v = 0, 1, 2, 3)$ 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. The results of some results obtained by Schaffer *et al* are reported in figure 3.

Chemical reaction systems

In 1964, Kasper and Pimentel reported the first chemical laser involving electronic excitation. 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

$$CF_3I + h\nu \rightarrow CF_3 + I^*(^2P_{\frac{1}{2}}).$$

The $^2P_{\frac{1}{2}} \rightarrow {}^2P_{\frac{3}{2}}$ 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. Similar behaviour was quickly discovered for a variety of alkyl iodides and perfluoroalkyl iodides. The CF_3I system displayed gains in excess of 100 dB m⁻¹ and demonstrated the potentialities of chemical processes for high population inversion. In fact, this system has been exploited by Kompa, Holah and Hora for making a 1 kJ laser for laser fusion studies (called Asterix III). During 1966, Pollack (Bell Laboratories) added a photodissociation laser based upon photolysis of nitrosyl chloride. Nitric oxide produced from ClNO emits laser transitions in the 6 μm region.

In concurrent research, Tom Deutsch (Raytheon) discovered that nitrosyl chloride in a pulsed electrical discharge also produces nitric oxide laser emission in the 6 μm region.

With OCS in the pulsed discharge, Deutsch found laser emission due to vibrationally excited carbon monoxide. He attributes this excitation to the dissociation of electronically excited OCS*

$$OCS^* \rightarrow CO^* + S.$$

The elucidation of the CF_3I photodissociation laser provided the key to previously confusing, but intense infrared emissions from hydrogen chlorine explosions observed by Kasper and Pimentel using rapid scan infrared techniques. These emissions were then readily identified with laser emission from the secondary chemical reactions that occur in a photolytically induced H_2–Cl_2 explosion.

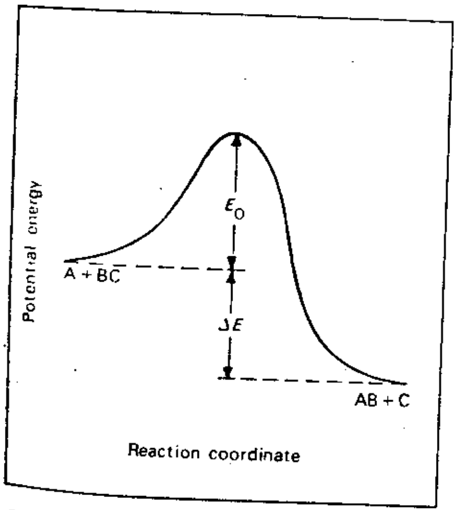
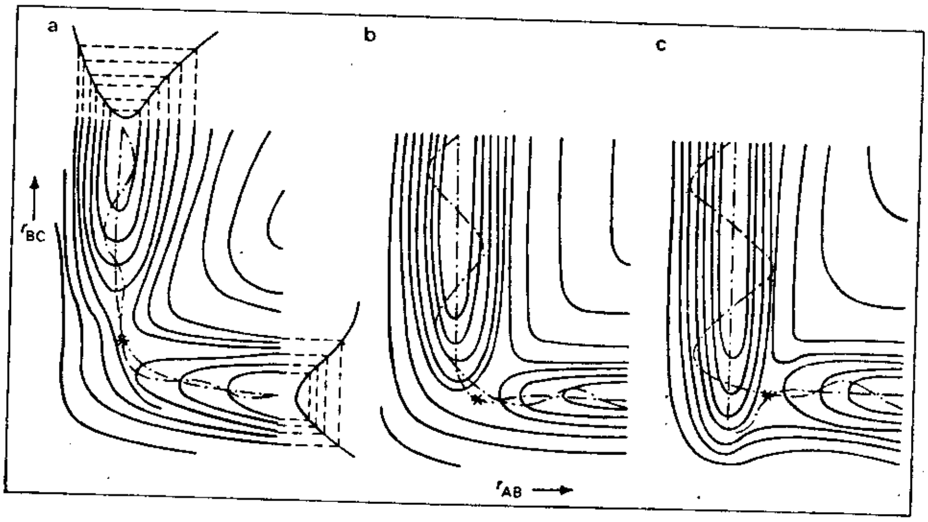


Figure 2 Potential surfaces of a system of colinear atoms. a repulsive potential, b mixed potential, c attractive potential



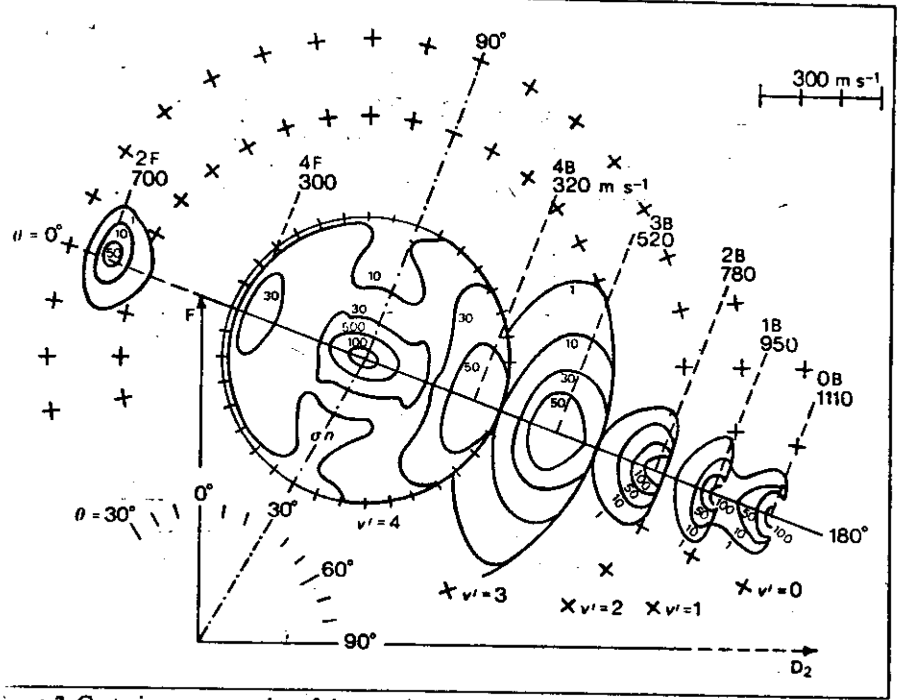


Figure 3 Cartesian contour plot of the reaction products (vibrationally excited DF molecules) of two molecular beams (D_2 and F) colliding at right angles. The dashed circles denote the largest DF velocity for each vibrational state allowed by energy conservation (from Schafer T P *et al* 1970 *J. Chem. Phys.* **53** 3385)

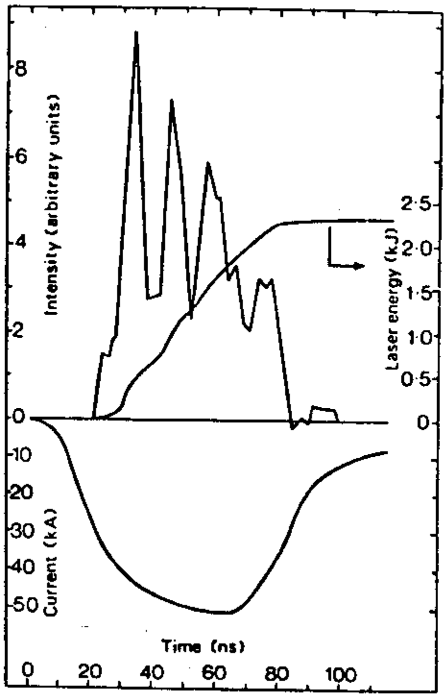


Figure 4 Reproduction of the electron beam current and photodetector signal in the electron beam initiated 2 kJ HF laser developed at the Sandia Laboratories

$$\begin{aligned}
&Cl_2 + h\nu \rightarrow 2\,Cl\\
&Cl + H_2 \rightarrow HCl^* + H\\
&H + Cl_2 \rightarrow HCl^* + Cl.
\end{aligned}$$

Table 1 lists the chemical laser systems that have been operated since the first chemical laser. The separate listing of the H_2–Cl_2 and HD–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 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. There was, until recently, some disagreement on the mechanism of the chemical pumping of the vibrationally excited CO. Recent studies showed the mechanism to be as follows:

$$\begin{aligned}
&O + CS_2 \rightarrow CS + SO + 23\ \text{kcal}\\
&O + CS \rightarrow CO^* + 2 \quad + 75\ \text{kcal}\\
&S + O_2 \rightarrow SO + O + 6\ \text{kcal}.
\end{aligned}$$

The most popular chemical laser uses the HF molecule obtained from H_2–F_2, SF_6–H_2, UF_6–H_2, C_2H_6–F_2, to quote the most common reactions. The H_2–F_2 reaction is of particular importance because it has been studied in some detail.

$$\begin{aligned}
&F_2 + h\nu \rightarrow 2F\\
&F + H_2 \rightarrow HF^*(v \leqslant 3) + H + 31{\cdot}6\ \text{kcal}\\
&H + F_2 \rightarrow HF^*(v \leqslant 6) + F + 98\ \text{kcal}.
\end{aligned}$$

H_2 and F_2 do not undergo a rapid direct reaction. However, in the presence of dissociated hydrogen or fluorine they can react rapidly through the $F+H_2$ and $H+F_2$ reactions, which together form a 'chain' reaction. The $F+H_2$ reaction is commonly called the 'cold' reaction because it releases less chemical energy than the 'hot' reaction $H+F_2$.

Before concluding, a current classification of chemical lasers refers to the reaction initiation characteristics as follows: (1) flash initiation, (2) cw, (3) electrical initiation, (4) thermal explosion (HN_3, ClN_3), (5) electronic transitions.

High energy and power chemical lasers

Chemical chain reaction lasers are interesting 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 'cold' and 'hot' reactions form a chain which proceeds until all available H_2 or F_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. Owing to recent advances in mixing room temperature F_2 and H_2 at high pressures as well as achievements in using intense relativistic electron beams to initiate lasers these experiments can be now performed.

In a recent experiment carried out at Sandia by Gerber *et al* an intense electron beam (2 MeV, 50 kA, 70 ns, FWHM) was used to initiate room temperature H_2/F_2 mixtures in a large volume. The laser cell was a stainless-steel cylinder 14·9 cm diameter and 1·67 m long. Electrons from the REBA accelerator were drifted 16·5 cm at low pressure and then passed through a stainless steel diaphragm into the laser cell. The laser output came through a hexagonal array of seven 4·3 cm diameter sapphire windows. An axial magnetic field of 0·079 T was externally applied to improve the transport of electrons through the laser cell.

A maximum laser energy of 2·3 kJ was obtained with a gas mixture of 360 Torr F_2, 140 Torr O_2, 100 Torr SF_6, and 100 Torr H_2. The oxygen was used to prevent spontaneous explosion of the mixture.

Time correlated electron beam current and a laser detector signal are shown in figure 4. An electrical efficiency (laser energy/deposited energy) of 178% was obtained.

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, Airey and Meinzer *et al*, demonstrated such techniques. Based on these approaches high power CML devices have been evolved consisting of a high temperature, high pressure, nonstoichiometric combustor yielding a sufficient concentration of free atoms at thermochemical equilibrium, 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 secondary reaction products.

The kilowatt cw HF chemical mixing laser reported by Spencer *et al* typifies this approach (see figure 5). In their studies a thermal DC arcjet was 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 (400–500 K) and low pressure (2–5 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 lasing 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 laser output in the 5 µm region. The flame is self sustaining requiring no external energy source and burns at rather low pressures (10–40 Torr). The most recent flame laser results have been reported by Linevsky and Carabetta. They obtained 25 W output with 13 J of laser output per gram of fuel consumed, representing a chemical conversion efficiency of 2·5%. The flame laser is likely to find promising applications where an external simple laser source is desired which requires no electrical input during operation.

Iodine laser

Among the most promising pulsed chemical lasers for fusion applications, the iodine laser is in the most advanced state of development. Its performance has been investigated for many years by Hora, Kompa, Holah and their colleagues of the Max Planck Institute for Plasma Physics in Garching.

The reaction used has been discussed above. Therefore, a few operative considerations will be reported here.

The iodine laser is a photochemical dissociation type, optically pumped at about 280 nm and emitting at 1·315 µm, a wavelength corresponding to the transition from the $^2P_{\frac{1}{2}}$ state to the $^2P_{\frac{3}{2}}$ ground state of iodine. Total efficiency to 0·5% has been reported.

Experiments indicate that 66% of the stored energy can be extracted. The cross section for stimulated emission is adjusted by adding a buffer gas to the laser medium. In this way the gain can be finely controlled. The principal limitation on efficiency seems to be the spectral width of the ultraviolet absorption of the parent alkyl iodides and the energy output of the flashlamp in the absorption region.

A subkilojoule system, called Asterix II has delivered 60 J in 0·7 ns pulses. The system consists of an oscillator, a pulse-cutting system and two amplifiers.

Currently a kilojoule system called Asterix III is being constructed. This system has a design similar to Asterix II except for optical isolation between amplification stages. The second amplifier is 10 m long with active diameter 20 cm ■

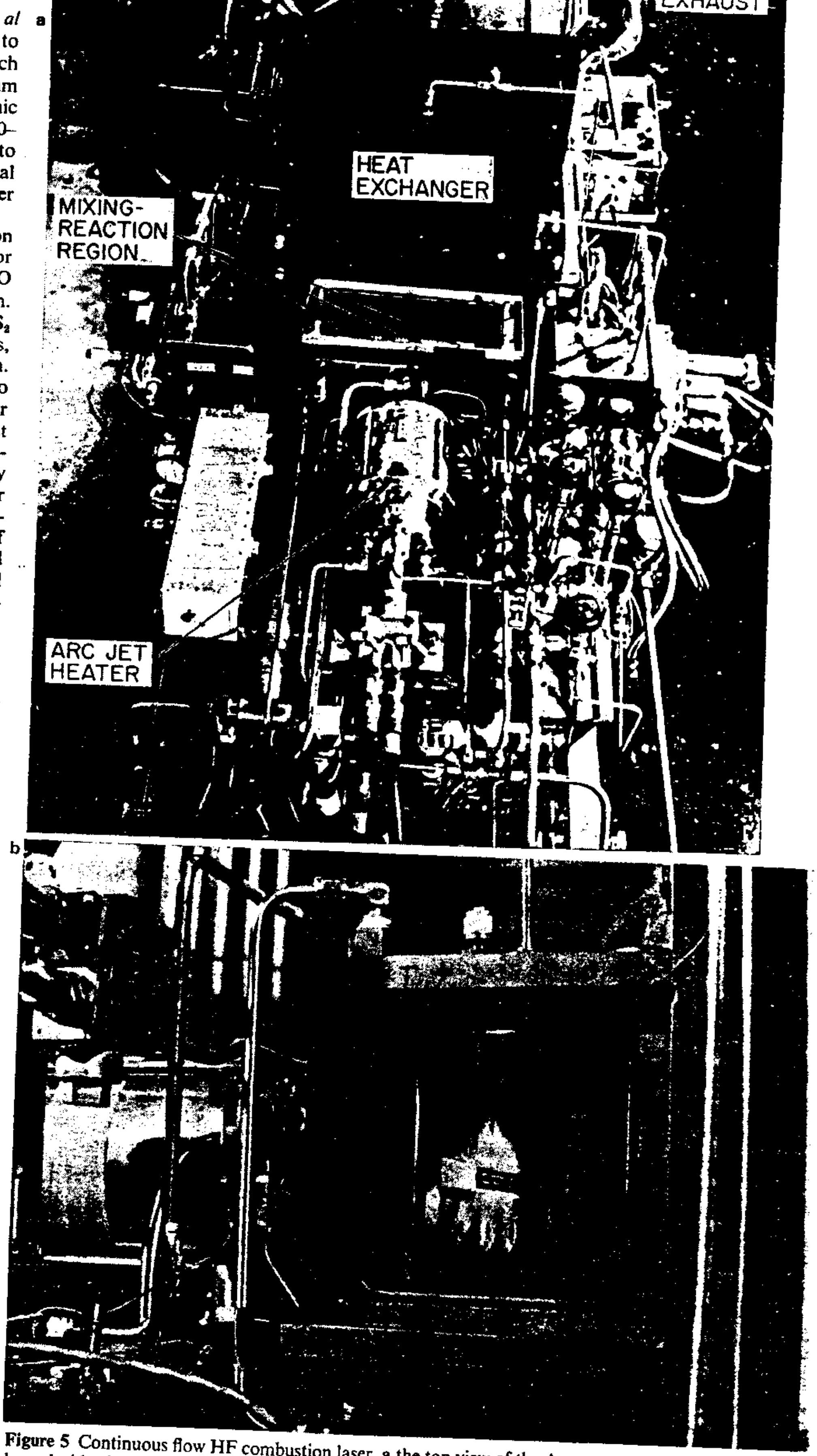


Figure 5 Continuous flow HF combustion laser. a the top view of the Aerospace Corporation laser, b side view of the laser

Acknowledgment

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Further reading

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