

Chemical Lasers and Kinetics

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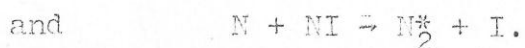
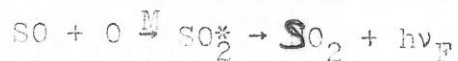
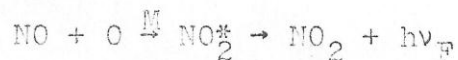
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Introduction

A chemical laser is a laser system in which the excitation energy and population inversion is supplied by means of some appropriate chemical reaction. As early as 1961 J. C. Polanyi suggested that laser action might occur in HCl^\ddagger that is vibrationally and rotationally inverted as a result of the chemical reaction between H atoms and Cl_2 .¹ Pimentel and Kasper observed the first chemical laser action in HCl^\ddagger formed by the flash photolysis of $\text{H}_2\text{-Cl}_2$ mixtures.²

Photodissociation lasers, in which the excited products that lase are directly formed from the primary photolysis, are not considered as chemical lasers, but rather in a class by themselves. In many cases, flash photolysis or pulsed electrical discharge is used to create radicals or excited species which then react to produce the excited species in which the laser action occurs. This latter type is considered to be a "pure" chemical laser.

Electronically and/or vibrationally excited states are known to be formed as products in many highly exothermic reactions. Some examples of reactions leading to electronically excited states are



However, to date, no chemical laser utilizing an electronic

transition has been developed, most emitting in the infrared and corresponding to various vibrational transitions. The hydrogen halides were among the first reactions investigated, due to their relatively high exothermicity. Table 1 lists some reactions that lead to laser action along with the ΔH_{rxn} . Unfortunately, the efficiency of conversion of vibrational quanta to emitted photons is low due to relaxation and the competing processes of vibration-vibration (V→V) and vibration-translation (V→T) energy transfer reactions which are often rapid enough to deplete the excited state in such a manner as to destroy any possible laser action.

Details of Laser Action

The importance of the role kinetics plays in determining whether or not lasing action occurs in a chemical system can be seen more clearly by examining the physical situation in more detail.

As light passes through a medium with extinction coefficient per unit length k , the absorption can be described by a Beer's Law type equation:

$$I/I_0 = e^{-kx}$$

or in differential form,

$$-\frac{1}{I} \frac{dI}{dx} = k.$$

Under ordinary photochemical conditions one can define k as $k = \sigma n$ where σ = absorption cross-section in $\text{cm}^2/\text{particle}$

TABLE 1

<u>Reaction</u>	<u>ΔH_{rxn} (kcal/mole)</u>
$\text{H} + \text{Cl}_2 \rightarrow \text{HCl}^\ddagger + \text{Cl}$	-47
$\text{Cl} + \text{HI} \rightarrow \text{HCl}^\ddagger + \text{I}$	-34
$\text{H} + \text{Br}_2 \rightarrow \text{HBr}^\ddagger + \text{Br}$	-43
$\text{H} + \text{F}_2 \rightarrow \text{HF}^\ddagger + \text{F}$	-90
$\text{Cl} + \text{HBr} \rightarrow \text{HCl}^\ddagger + \text{Br}$	-16
$\text{H} + \text{ClNO} \rightarrow \text{HCl}^\ddagger + \text{NO}$	-65
$\text{SO} + \text{CS} \rightarrow \text{CO}^\ddagger + \text{S}_2$	-53
$\text{H} + \text{ClN}_3 \rightarrow \text{HCl}^\ddagger + \text{N}_3$	-66
$\text{CH} + \text{O} \rightarrow \text{CO}^\ddagger + \text{H}$	-176
$\text{CH} + \text{NO} \rightarrow \text{CO}^\ddagger + \text{NH}$	-105

and n = number of particles/cm³. However, for cases where the excited state may be populated to an appreciable extent, the correct form for k is given by

$$k = \bar{\sigma} \left(n_1 - \frac{g_1}{g_2} n_2 \right)$$

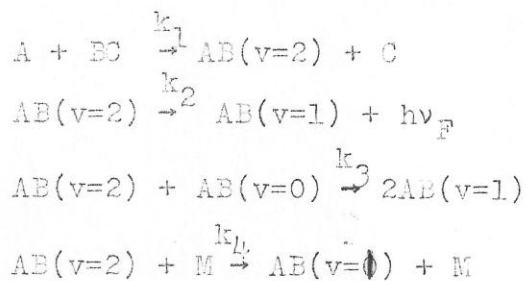
where $\bar{\sigma}$ is the absorption cross section averaged over the band in question, n_2 = number of particles in the upper state, n_1 = number of particles in the lower state, and g_2, g_1 are the corresponding degeneracies. Also,

$$\bar{\sigma} = \frac{h\nu}{c\Delta\nu} B$$

where ν = frequency of transition, $\Delta\nu$ = band width, and B is the Einstein coefficient for stimulated absorption or emission.³ It is easily seen that if the condition $\frac{n_2}{g_2} > \frac{n_1}{g_1}$, holds, then k is a negative number and one gets a condition of negative absorption or gain. That is, the intensity of light increases as it passes through the laser medium due to the effect of stimulated emission from the population inverted excited state. Consider the case of laser transitions occurring between two vibrational levels. The degeneracy of a vibrational level is one and that of a rotational level is $(2J + 1)$. Even though one can have $n_1 > n_2$, laser action can occur in P branch transitions since $(2J_2 + 1) < (2J_1 + 1)$. This effect was predicted by Polanyi¹, and is observed in almost all chemical laser transitions, since the rapid vibrational relaxation makes it difficult to

achieve absolute population inversions. In a system where the gain is greater than the optical losses in the system, self-sustaining laser action can occur. Obtaining the population inversion and maintaining it is a direct result of the kinetics of the system. The number in the excited state n_2 is determined by the rate of formation of excited state by reaction and the loss rates through emission, relaxation, and energy transfer. Most chemical lasers operate in a pulsed mode since there is a buildup in time of n_1 with resulting cessation of laser action. By varying pressure and other parameters and looking at how the intensity of laser emission (and therefore the systems gain) one can potentially ~~get out~~ ^{extract} data on the rate constants of the system in question.

As a simplified example consider the reaction scheme:



The first step is the pumping reaction producing the excited species. The second step is radiative transition that can lead to laser action under the appropriate conditions. Steps three and four are competing reactions that deplete the concentration of the state $AB(v=2)$ by vibration-vibration

and vibration-translation energy transfer respectively.

The rate equations for this system are as follows:

$$\frac{d[AB(v=2)]}{dt} = k_1[A][IC] - k_2[AB(v=2)] - k_3[AB(v=2)][AB(v=0)] - k_4[AB(v=2)][M]$$

$$I = \frac{+dh\nu_F}{dt} = k_2[AB(v=2)]$$

$$\frac{d[AB(v=1)]}{dt} = 2k_3[AB(v=0)] + k_2 [AB(v=2)] + k_4 [AB(v=2)] [M]$$

Assuming that the initial concentrations of A and IC are known and that the effective concentration of the quenching body M are known, this can be solved to give $[AB(v=2)]$ as a function of time. Qualitatively, the concentrations of the $v=0$, $v=1$ states are small initially and the concentration of the $v=2$ state builds up until a high enough concentration of this state exists to allow an observable laser action. As the lower vibrational levels become populated however, two things happen. The first is that depletion of the $v=2$ state becomes more rapid, and the second is that the ratio of $v=2$ to $v=1$ concentrations diminishes so that the population inversion is destroyed and laser action ceases primarily because of this reason.

Real systems are much more complicated, for example, the $v=1$ level will also be depleted by collision. The pumping mechanism also in general populates all the energetically allowed vibrational levels in the

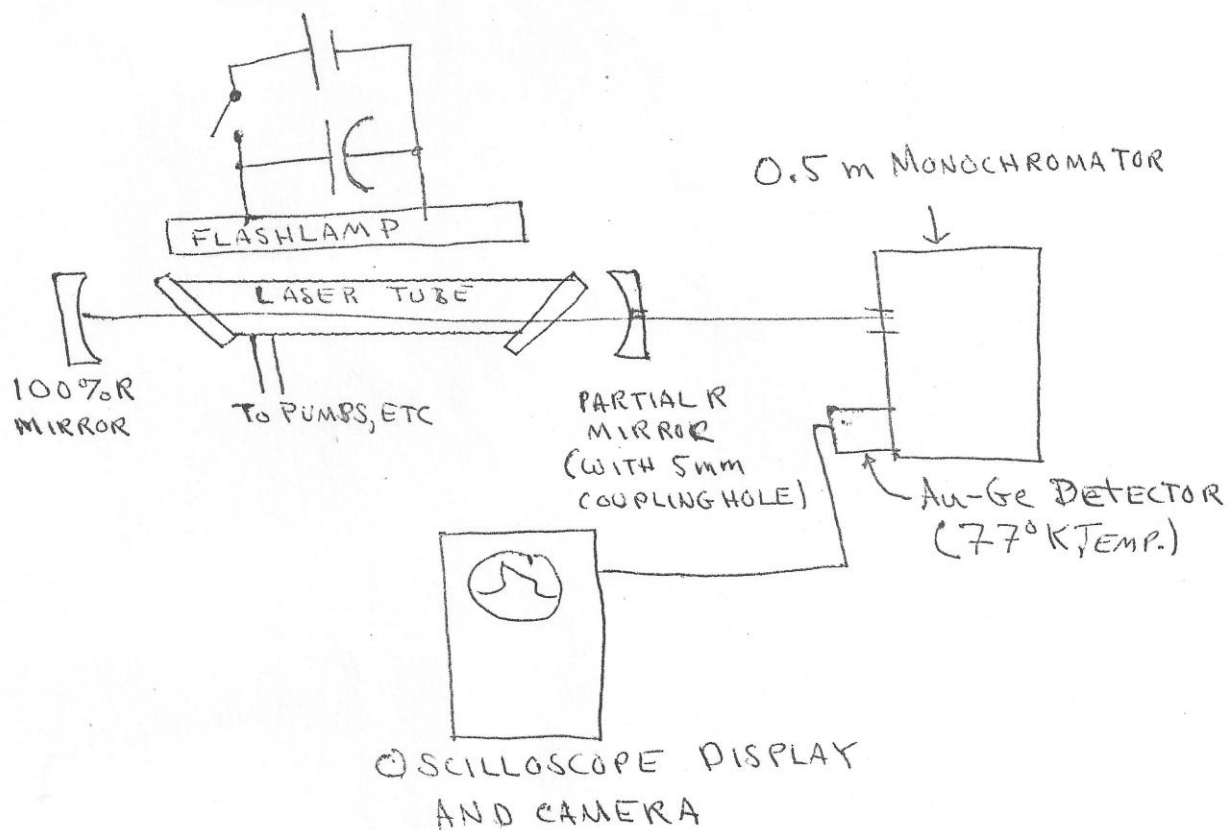
product molecule so that assumption that the concentration of the $v=1$ state is zero is invalid. In the H_2-Cl_2 explosion about 25% of the HCl product is in the $v=2$ state and 10% in the $v=1$ state.⁴ Naturally one expects the population inversion to be very difficult to maintain for a fairly long period of time. (Under the conditions of 1-25 torr pressure, with flashlamp excitation, pulse durations are in the order of 10-100 microseconds.)

As can be seen from the above simplified example, time-resolved measurements of the pulse intensity, and measurement of the total pulse emission as a function of reactant concentrations can yield specific and valuable information on the rate constants k_1 through k_4 . Knowledge of one or more of these simplifies the problem, but in a real system this information is often difficult to extract in a quantitative manner.

Specific Chemical Systems

At this point, a discussion of some specific chemical systems, the experimental conditions and the interpretation of the results may prove useful.

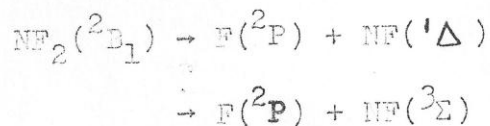
The first system discussed will be chemical lasers formed by flash photolysis of various N_2F_4 and RH mixtures. These were examined by M. C. Lin of the Naval Research Laboratory.⁵ See Fig. 1 for experimental arrangement.



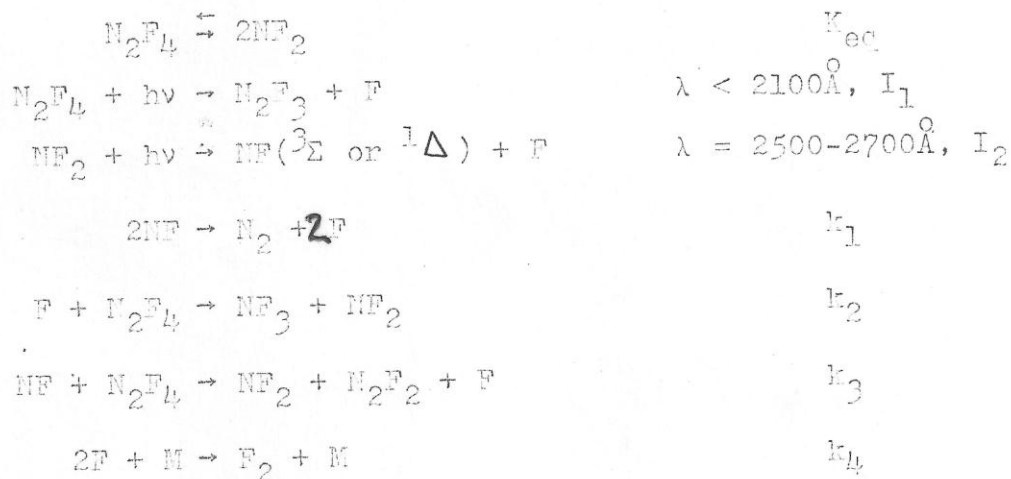
EXPERIMENTAL ARRANGEMENT OF LIN.

FIG. 1

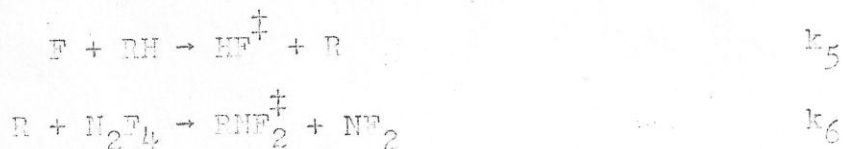
The lasing emission was found to occur on several vibrational-rotational levels of NF_2 . N_2F_4 at room temperature is in equilibrium with the free radical NF_2 . The NF_2 has an absorption in the region of 2500-2700 Å and is the light absorbing species, which can dissociate via two pathways

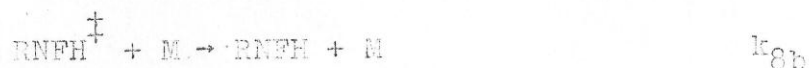
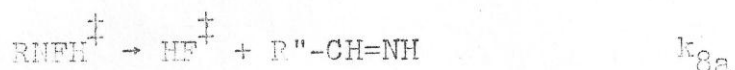
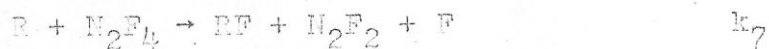
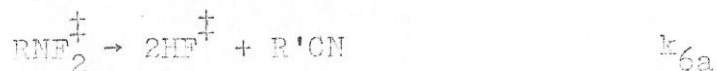


In order to account for the products found by mass spectrometric analysis, the following mechanism for pure N_2F_4 photolysis was proposed.



In the presence of RH however the hydrogen abstraction by F dominates and the last four reactions are minimized in effect. The mechanism proposed is then:

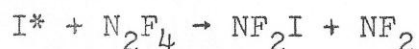




Reaction 5 has been studied by many authors and is known to be a rapid and efficient source of HF^\ddagger . Reaction 6 has been studied and is fast and is very efficient towards elimination of HF^\ddagger by 6a once enough activation energy is provided (about 90% eliminate HF^\ddagger). The presence of the other steps is supported by Lin's mass spectrometric analysis which indicated the presence of the products formed.

The HF^\ddagger can be produced by three of the reactions mentioned 5, 6, and 8. It is believed that reaction 5 is the principal pumping reaction. The reasons for this are that for the case $\text{RH}=\text{H}_2$ the population inversion $N_2/N_1 = 3.2$, $N_1/N_0 \rightarrow 1$ (we get an absolute population inversion with high potential gain) whereas reaction 6 as studied gives $N_1/N_0 = 0.35$ (with low maximum gain).⁶

The results of this experiment discussed above were that among the various RH species used, HCl and CH_3F vibrationally relaxed the HF^\dagger rapidly, setting a lower limit to those rate constants. In the case of $\text{RH} = \text{C}_2\text{H}_5\text{I}$, the flash also dissociated $\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{I}^*$. That no 1.3μ emission from the I^* was observed implies that the collisional quenching, or a chemical reaction such as

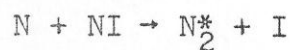


are faster than the time required to reach laser buildup conditions, again setting a lower limit to the rate constants.

Running off a series of closely related compounds, rather than the fairly different ones Lin ran may have yielded data more readily interpretable in terms of a trend.

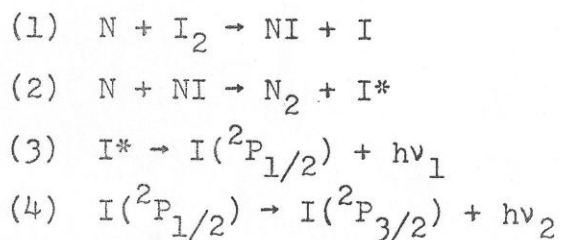
As can be seen, getting readily interpretable data out of such a system is difficult, and care must be taken in designing the experiment for maximum results.

As a sort of digression, consider the application of kinetics to designing a chemical laser. Previously mentioned was the fact that the reaction



can yield an electronically excited N_2 molecule (which is in the $\text{A}^3\Sigma_u^+$ metastable state). Phillips has studied the reaction of active nitrogen with I_2 and deduced a mechanism to explain the formation of the N_2^* , energy

transfer to I_2 with subsequent bright blue fluorescence.^{7,8} The reaction is about 189-191 kcal/mole exothermic, and the possibility of I^* (in the $6^2P_{3/2}$) state being formed with subsequent emission of the non-resonance $2062 \overset{\circ}{\text{A}}$ line. This line was not observed to any great extent in any experiments, but in work done during January term, I measured the $2062 \overset{\circ}{\text{A}}$ line as being by an order of magnitude the strongest emission by a reaction tube where the N atoms and I_2 are mixed. This brings up the possibility of an electronic chemical laser in a region very close to the vacuum ultraviolet. A reaction scheme such as follows:



might be proposed. Assuming constant concentration of N atoms from the condensed discharge and of I_2 one can solve this system for I^* and $I(^2P_{1/2})$ as functions of time. (One can also do this including quenching steps 3a, 4a where the two excited states are quenched by a body M assumed to be of constant concentration.) From earlier considerations we see that if

$$\frac{N(I^*)}{gI^*} > \frac{N(I^2P_{1/2})}{gI^2P_{1/2}}$$

at any time t, laser action could possible occur since there is a gain in the system.

$$g_{I^*} = 2J + 1 = 4$$

$$g_I^2 P_{1/2} = 2J + 1 = 2$$

We need therefore a situation where

$$N(I^*) > 2N(I^2 P_{1/2})$$

in order to get the right population inversion. Under the actual conditions, no laser action is observed, but if one could find some sort of "resonance" quenching reaction that more or less selectively depopulates the $^2P_{1/2}$ level of I then there is potential to get a continuous operation laser. As is, if the N and NI can be generated in a pulsed manner, then the possibility of a pulsed laser operating with pulse durations shorter than the lifetimes of the I* still exist.

Conclusion

Chemical lasers are related to kinetics in two manners. Firstly, a knowledge of the kinetics of systems allows one to predict the possibility of a chemical laser. Here kinetics is the tool of the person making the laser. On the other hand, kinetic data, particularly that relating to energy transfer and energy distributions in reaction products, can be gotten from analysis of laser emission data as a function of various parameters. However, getting unambiguous results is difficult as the system are often very complex. Also, to date the number of systems that can be studied is fairly small.

References

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