Application of Radiation Fronts in Chemical Lasers

Idealized case: no motion, no recombination, one frequency.

The concept of a radiation front may best be explained by considering a constant, unidirectional, monochromatic photon flux F_o(photons/cm^{2}sec) impinging upon some gas of N_o(particles/cm^3) and absorption cross section, α(cm^2). Upon absorption of a photon the particles become ionized, dissociated, or excited and thereafter are transparent to the radiation. In the approximation that there is no motion and no recombination (or de-excitation) one may easily show (Zuzak,1968) that a radiation front will be formed and propagate with a velocity, v_F

$$v_F=(F_o/N_o)/(1+F_o/cN_o) \quad , \qquad (1)$$

and that the structure of the radiation front is given by

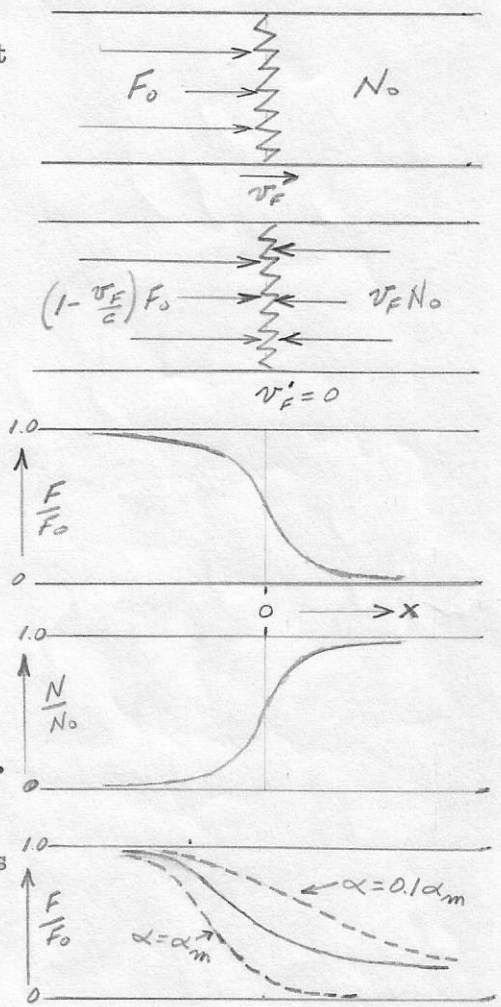
$$\frac{F(x,t)}{F_o}=(1+e^{+\alpha N_o(1+F_o/cN_o)x-\alpha F_o t})^{-1} \quad , \qquad (2)$$

and

$$\frac{N(x,t)}{N_o}=(1+e^{-\alpha N_o(1+F_o/cN_o)x+\alpha F_o t})^{-1} \quad , \qquad (3)$$

where $F/F_o=N/N_o=0.5$ when $x=0$, $t=0$ and where F_o/cN_o is a relativistic correction which is usually negligible. These profiles are illustrated in the diagrams on the right. The thickness of the front in which N/N_o varies between 0.1 and 0.9 is

$$\delta x=4.40/(\alpha N_o(1+F_o/cN_o)) \quad . \qquad (4)$$



(a) Continuous $F(\nu)$ and $\alpha(\nu)$.

The case of constant continuous radiation $F(\nu)$ and absorption cross section $\alpha(\nu)$ is defined by an equation of the form

$$F(\nu,x,t)=F(\nu,0,t)\exp\left\{-\alpha(\nu)N_o(1+F_o/cN_o)\int_o^{x'}(N(x',t)/N_o)dx'\right\} \quad . \qquad (5)$$

This equation may be integrated numerically to give similar profiles as for the ideal case above (see last diagram above). Notice that photons with small absorption

penetrate much deeper than photons with the maximum absorption cross section α_m leading to a stratification of the radiation.

(b) With motion, no recombination.

Motion in the above cases may be taken into account by working in Lagrangian co-ordinates. The problem reduces to a transformation from one co-ordinate system to another.

To see under what circumstances motion may be neglected consider the one-dimensional momentum equation

$$Du_x/Dt = \partial u_x/\partial t + u_x(\partial u_x/\partial x) = \rho^{-1}(\partial P/\partial x) \quad , \tag{6}$$

where u_x is the particle velocity, P is the pressure, ρ is the density and D /Dt represents the Lagrangian derivative. Let us rearrange eq'n(6) in terms of differentials

$$\Delta u_x = \rho^{-1}(\Delta P/\delta x)\, \Delta t \quad . \tag{7}$$

There are thus four ways to make Δu_x small:

(1) Make Δt small - either by performing the experiment before motion can start or have a very fast moving front, $v_F=F_o/N_o$ (i.e. a large photon flux to particle density ratio).

(2) Make $\delta x \gg L$, where L is the dimension of the container and δx is given by eq'n(4).

(3) Make the pressure jump across the front small, $\Delta P=P_1-P_o \ll P_o$. The pressure behind the front is roughly given by

$$P_1 = P_o+(\rho/M)\Delta(kT) = P_o+(\rho/M)(\langle h\nu\rangle-D)(\gamma_1-1)/2\gamma_1 \quad , \tag{8}$$

where $\Delta(kT)$ represents the temperature increase behind the front, $\langle h\nu\rangle$ the average energy of the photon, D the ionization, dissociation, or excitation energy and γ_1 is a fudge factor related to the ratio of specific heats of the gas behind the front. Thus, using $P_o=N_o kT_o$, $\rho=N_o M$, we obtain

$$\Delta P/P_o = (\langle h\nu\rangle-D)/kT_o\ (\gamma_1-1)/2\gamma_1 \quad . \tag{9}$$

(4) Make ρ large by using heavy particles ($\rho=N_o M$) or by using a buffer gas.

Substituting eq'n(9) into eq'n(7) and writing $\Delta t=L/v_F=LN_o/F_o$, we obtain

$$\Delta u_x = ((\gamma_1-1)/8.8\gamma_1)(\langle h\nu\rangle-D)\, \alpha N_o{}^2 L/MF_o \quad . \tag{10}$$

This equation illustrates the dependence of the motion on the various parameters even better than eq'n(7). To make $(\langle h\nu\rangle-D)$ small one must find a gas which absorbs radiation at an energy near its ionization, or dissociation energy (of course, $(\langle h\nu\rangle-D)=0$ for excitation).

(c) With recombination, no motion.

For the case in which there is recombination but no motion we obtain a stationary solution in which the number of recombinations (or de-excitations) per unit time is equal to the number of photons absorbed per unit length (provided the temperature doesn't change such that the recombination coefficients don't change). The exact structure depends upon the recombination (or de-excitation) law. For example, for two and three body recombination, we have

$$\partial F/\partial x = -\alpha NF = -\beta_2(T)N_i N_e - \beta_3(T)N_i N_e^2 \quad , \tag{11}$$

where we have neglected radiation from two body recombination.

(d) With recombination and with motion - General case.

So far we have been considering idealized cases. In the general case one will have both non-steady motion and non-steady reactions. One must consider the flow and reactions as a function of time. The evolution and structure of a dissociation front in oxygen has been considered by Zuzak,1968 and Zuzak and Ahlborn,1969. Here we shall consider an example which has chemical laser applications and show how external radiation may be used to enhance the capabilities of chemical lasers.

Laser action has been observed from the second vibrational state of hydrogen fluoride (Kompa,1970, Basov et al,1969). The exothermic reaction chain in H_2 and F_2 may be started by photo-dissociation of F_2 with 2900 Å radiation (absorption cross section, $\alpha = 10^{-20}$ cm^2). The equations are

(1) $F_2 + h\nu_{2900A} \longrightarrow 2F$

(2) $H_2 + F \longrightarrow FH^* + H$ $\qquad k_{H_2+F} = 2 \times 10^{-10} e^{-1000/RT}$ (cm^{3}sec^{-1})

(3) $H + F_2 \longrightarrow HF^* + F$ $\qquad k_{F_2+H} = 2 \times 10^{-10} e^{-2400/RT}$ (cm^{3}sec^{-1})

(4) $(HF^* + F_2 \longrightarrow HF + 2F)$

(5) $HF^* \rightleftharpoons HF + h\nu^*$

The concentration of each particular species in the chain at any time and position is described by a reaction rate equation of the form

$$\frac{\partial N_F}{\partial t} + \frac{\partial uN_F}{\partial x} = 2\left|\frac{\partial F}{\partial x}\right|_{2\to 1} + k_{H+F_2} N_H N_{F_2} + 2k_{HF^*+F_2} N_{HF^*} N_{F_2} - k_{H_2+F} N_{H_2} N_F \quad , \tag{12}$$

where we have chosen the fluorine atom as an example.

The intriguing aspect of these reaction equations is that if one had a sufficiently intense source of 2900 Å radiation one could dissociate all the fluorine molecules before collisional de-excitation of the vibrational level could occur (i.e. reactions 3 and 4 could be completely eliminated). In order to achieve this the time to photodissociate the fluorine molecules must be less than time for reaction 3 (or reaction 2) to occur. From the relation

$$\partial N_{H_2}/\partial t = kN_F N_{H_2} \quad , \tag{13}$$

we obtain a typical reaction time (assuming $N_{F_2}=N_{H_2}=10^{16}\,cm^{-3}=0.5N_F$, $k=2\times10^{-10}\,cm^3/sec$)

$$\Delta t = \Delta N_{H_2}/kN_F N_{H_2} = (kN_F)^{-1} = 0.25\ \mu sec \quad , \tag{14}$$

which is obviously an extreme case. If we are pumping a cylindrical cavity of radius r=1 cm filled with $10^{16}\,cm^{-3}$ F_2 molecules, then by equating the photons available to the total number of particles, $\int F_o 2\pi rh\,dt = N_{F_2}\pi r^2 h$, we find that we need 2×10^{22} photons passing into each unit area of the cylinder per second;

$$F_o \geq 0.5rN_{F_2}/\Delta t = 0.5rkN_F N_{F_2} \quad . \tag{15}$$

This is a substantial photon flux not easily attainable in the narrow wavelength range required.

Although the above scheme might not be easily attainable, it nevertheless illustrates the principle that selected external radiation may be used to either quench unwanted or enhance desired reactions in chemical lasers. In fact there has been recent interest in so-called "induced chemistry" where two particles recombine in the presence of an electromagnetic (photon) field and give off the excess energy in the form of a photon (i.e. in the case above, $H+F+nh\nu \rightarrow HF + (n+1)h\nu$). This certainly seems to be an idea worthy of investigation.

In concluding, we should point out that although we have stressed the non-dynamical aspects of radiation fronts, the dynamical effects may be made to be substantial (Ahlborn and Zuzak,1969; Zuzak,1968). Inthis way one could compress or rarify the reactants as well as irradiate them. Perhaps this could be used to advantage in dynamical chemical laser systems.

References:

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