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Formation of Compression Waves
in Photolysis Experiments

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Abstract:

In photolysis tubes of large dimensions filled with an absorbing gas of high concentration n_1 and absorption cross section α , compression waves are formed due to inhomogeneous absorption. A characteristic time t_c and an absorption depth x_c can be calculated as function of n_1 , α and the net energy absorbed, describing the growth of such compression waves. In the case of oxygen photolysis, where measurements and detailed calculations of the compression wave are available, t_c and x_c are sufficiently small compared to the time and distance where the compression wave actually reaches its maximum strength, so that these characteristic values for practical purposes define the region in which the photolysis is undisturbed by gasdynamical effects. For example the characteristic time for a photolytically pumped CF_3I laser of $n_1 = 4 \cdot 10^{18} \text{ cm}^{-3}$ initial density is $t_c = 15 \text{ /usec}$ and the characteristic distance measured from the edge of the absorbing volume is $x_c = 1.2 \text{ cm}$.

Introduction

In a photolysis experiment or an optically pumped chemical laser (eg. the HCL laser, see example below) light of the frequency ν_p is absorbed, distroying or helping to form some molecule. As a result of this absorbtion the heat of reaction Q is released or spent per photolysed particle and the reaction product may be exited to emit (laser) light of the frequency ν_e . The photolysed gas therefore must absorb the net energy q per gram

$$q = \frac{n_r}{\rho} [Q + h(\nu_p - j\nu_e)] \quad (1)$$

where h is the Planck constant, ρ (g/cm^3) is the total density of the reaction products, n_r the number of photolysed particles, and j the number of photons added to the laser radiation by each exited particle. Q is the sum of photodissociation energy spent and heat of reaction released per photolysed particle.

If q is high, the related temperature increase $\Delta T = q/c_v$ (with c_v = total specific heat after the photolysis) will change the equilibrium constants of the reaction ¹ and lead to thermal conduction effects ^{2,3,4}. The increase of temperature most often is reduced by addition of some inert gas (thermal bath) which increases ρ and thereby keeps q small. But such addition may not be wanted for physical reasons ⁵ (line broadening).

It has been assumed so far that the photons are absorbed homogeneously throughout the cylindrical absorption cell, which implies that the absorption length L , or e-folding distance of the absorbed radiation, is large compared with the radius r of the absorption tube.

$$r \ll L = 1/n_1 \alpha \quad (2)$$

where α , measured in cm^2 is the cross section of the absorbing particles which have a number density n_1 .

In order to optimize the number of photolytic reactions one will have to find a compromise between vessel radius and absorber density which most likely means approaching optical thick absorption, a condition which also guarantees the most effective use of the pumping light. But optically thick, or inhomogeneous absorption gives rise to the generation of density inhomogenities and compression-or sound waves, as observed by Burns and Hornig ⁶, Cross and Ardila ⁷ and theoretically studied by Burns ⁸ and Zuzak and Ahlborn ⁹. Under the influence of sufficiently intense pump light these waves may steepen into shock waves or detonations ^{10,11}, and a variety of sub and supersonic waves with compression as well as expansion of the reaction products may be produced ¹².

Qualitatively the inhomogeneous absorption causes pressure gradients which propel the gas away from the light source. For pump light of sufficient duration in a large absorbing volume, a "radiation front" or bleaching wave will develop and propagate into the absorbing gas at a velocity v_R which

can approximately be determined from the equation of conversion of energy. Neglecting the thermal energy and the kinetic energy compared to the photodissociation energy one finds

$$v_R \approx I_0/n_1 \quad (3)$$

This relation is often used to describe the propagation of ionizing radiation fronts¹³. It shows that the radiation front velocity can be varied by the choice of the pump light intensity I_0 (photons absorbed per second in one cm^2 of the front) and by the initial density n_1 (cm^{-3}).

If v_R is small compared to the speed of sound, a compression wave or even shock wave will develop ahead of the photolysed gas. The photo absorption then takes place in a gas which is receding from the light source and has increased density and pressure. The density may be six times above the initial value n_1 . The radiation energy absorbed in the bleaching wave reduces the increased pressure by about a factor 2 decreases the density below the initial value n_1 and decelerates the gas, so that it is at rest when the subsonic radiation front has passed¹².

If the bleaching wave velocity v_R is much higher than the speed of sound in the hot photolysed gas, no shock wave precursor can be set up and the absorption takes place in material of the initial density. The radiation front then heats and compresses (by not more than a factor 2) the gas and

pushes the photolysed material away from the light source. This subsonic motion of the gas is stopped when the moving particles are passed by the expansion wave which always develops behind such a supersonic radiation front.

A gradual transition exists between these extreme types of sub and supersonic radiation fronts. One particular case is a radiation front which behaves exactly like a steady Chapman Juguet detonation ¹².

The development of these waves is of course a gradual process. The compression neither appears instantaneously at the beginning of the flash light, nor do motion and compression reach a maximum value at the edge of the absorbing volume. Therefore the absorber density can be considered constant and gas dynamical effects can be neglected in a certain region at the beginning of the photolysis experiment in spite of inhomogeneous absorption. The extent of this "undisturbed" region in time and space is closely related to the point of formation F of the compression wave. If it is possible to give the time t_F and the position x_F where the compression wave has reached maximum strength, then for times $t \ll t_F$ and distances $x \ll x_F$ the photolysis will take place under undisturbed conditions.

Detailed calculations of the compression waves induced by inhomogeneous absorption require a considerable mathematical effort and may even not be possible due to uncertainties about the individual reaction steps and reaction constants.

Furthermore a single formation "point" is not really defined, since the wave amplitude grows steadily. One should therefore rather talk about a formation region where the wave reaches its maximum strength. In this paper we will show that it is relatively easy to calculate a time t_C and a distance x_C which are characteristic for the development of the compression wave but where the wave has not yet reached maximum strength. x_C and t_C are derived as function of n_1 , α , and q , using such approximations that the characteristic values x_C and t_C are with certainty smaller than the real formation times t_F and distance x_F of a compression wave in a photolysis tube.

Formation model

Suppose the absorbing gas is confined behind a plane window, Fig.1a, and is exposed to a short flash pulse of intensity I_0 at the time $t=0$. The light penetrates instantaneously into the gas and the intensity decays exponentially according to the absorption law

$$I(x) = I_0 \exp(-\alpha n_1 x) \quad (4)$$

Pressure p and temperature T in the gas are raised by the locally absorbed power $E(\text{erg/cm}^3 \text{ sec}) = h\nu \cdot dI/dx = \alpha n_1 \cdot h\nu \cdot I_0 \exp(-\alpha n_1 x)$, so that p and T and the speed of sound after a short time Δt will have distributions as shown in Fig.1b. Everywhere in the absorption region the pressure gradient will now produce small compression waves which travel with the local sonic speed in $+x$ direction.

Since the sound velocity is not constant, Fig.1b, these compression wavelets propagate with different absolute velocities and the fastest perturbation, generated at $x=0$ will gradually catch up to all other wavelets, increasing the amplitude steadily. The wave reaches the maximum strength, when the farthest wavelet, issued from the toe of the absorption region (at $x \approx 3L$), is overtaken and swallowed. This happens in the formation region, which for simplicity is given as the point F with the coordinates t_F and x_F . From there on the disturbance travels as a sound or blast wave into the unphotolysed gas. Fig.1c shows a space-time diagram with the path of several wavelets, the formation "point" F and the disturbed region where gasdynamical effects have reached their final strength.

In order to determine a characteristic point C, we make the following assumptions.

- 1) The wavelet generated at $x=0$ travels with the fastest speed possible, namely the sonic speed a_2 in the completely photolysed gas

$$a_2 = (\gamma p_2 / \rho_2)^{1/2} \approx (\gamma p_2 / \rho_1)^{1/2} =: \tan \beta_2 \quad (5)$$

where $p_2 = n_2 kT_2$, $T_2 - T_1 = q/C_p$, γ = adiabatic exponent, and q is defined by eq.(1). The path of the fastest wavelet is shown in Fig.1c as the broken line OC. It makes the angle β_2 with the t -axis.

- 2) The light penetrates only to the e-folding distance $L = \frac{1}{n_1 \alpha}$ into the gas. The wavelet generated at $x = L$ therefore must

travel with the slowest speed possible, the sound velocity in the cold gas $a_1 = (\gamma p_1 / \rho_1)^{1/2} =: \text{tang } \beta_1$, broken line LC.

We now define the characteristic point C as the point where the fastest wavelet (OC) of the model has caught up to the slowest wavelet. The coordinates of point C are found with the length L and the angles β_1 and β_2 in the triangle OCL.

$$x_C = L / (1 - a_1/a_2) \quad (6)$$

$$t_C = L / (a_2 - a_1) \quad (7)$$

Due to the approximations of this model the characteristic point C lies closer to the origin of the x-t plane than the real formation region F. The reasons are 1) the fastest wavelet does not travel with the maximum velocity a_2 , since the equilibrium temperature T_2 is not instantaneously reached. 2) The separation L of the origin of the fastest and the slowest wavelet of the model is pessimistically small comparing the real decay of intensity I as shown in Fig.1b. 3) Due to this deep penetration of light of low intensity, the slow wavelet from $x = L$ travels through already preheated material and therefore propagates with higher velocity than a_1 .

A pessimistically small L, the largest possible a_2 and the lowest possible a_1 obviously yield the smallest values for the coordinates of the characteristic point C. Both the x_C and t_C grow if a_1 is made larger. This raises the possibility of increasing the undisturbed zone by admixture of an inert gas with high speed of sound, so that the sonic speed in the cold gas mixture becomes large.

The usefulness of the easily obtainable characteristic point C is now demonstrated in two ways. Firstly we show by comparison with measurements ⁹ that the characteristic distance x_C is smaller than the observed formation distance x_F (as expected on the basis of the approximation), and that x_C and x_F both grow proportional with $1/n_1$. Secondly by comparison with detailed calculations of oxygen photolysis ⁹, we obtain the density variation accumulated at the instant t_C and the position x_C . It will be seen that the compression is still negligible small at the point C. Therefore in this particular case the characteristic point C lies so much closer to the origin than the formation point F that x_C and t_C can in fact be used to define the undisturbed region in this photolysis experiment.

Comparison of the formation model with other results

The oxygen photolysis experiment of Zuzak and Ahlborn (1969) ⁹ was carried out with an absorption tube with plane LiF window and a constricted arc as light source. The flash had a half time of 5 μ sec, and a spectral distribution of a black body of about 60,000 K. The pressure of the oxygen could be varied. Compression waves are generated due to the photolytic reaction



In this case the net heat Q is negative and equal to the dissociation energy D . No laser radiation is generated. For a pump light of $\lambda_p \approx 1500 \text{ \AA}$ the released energy per unit mass is

$$q = (-D + h\nu_p) / m_{O_2} = 10^{11} \text{ erg/g}$$

With a specific heat of $1.1 \cdot 10^7 \text{ erg/g } ^\circ K$ (average value taken at $T = 2000 \text{ } ^\circ K$ from ref. ¹⁴) one finds $\Delta T = q/c_p = 10^4 \text{ } ^\circ K$. We have used the specific heat at constant pressure since the gas is free to expand while the heat is added in the small region near the window. The associated speed of sound is $a_2 = 2.5 \cdot 10^5 \text{ cm/sec}$ ¹⁵ and $a_1 = 3.3 \cdot 10^4 \text{ cm/sec}$. For the absorption cross section we choose a conservative number of $\sigma = 5 \cdot 10^{-18} \text{ cm}^2$ which is about 1/3 of the maximum value measured by Metzger and Cook ¹⁶. x_c is now calculated by means of equation (7) and displayed in Fig.2. The measured positions of the appearance of a pressure disturbance x_F in oxygen from ref. ⁹ are also shown in the diagram ⁺) and it is noticed that the calculated x_c falls well below the measurements, while both have a similar run with initial density.

⁺) These measurements were taken with a large surface area (0.3 cm^2) piezo probe of high sensitivity. Later measurements with probes of reduced area (0.01 cm^2) and reduced sensitivity ⁷ did not yield one single significant formation point.

The detailed calculations of ref. ⁹ were carried out for an initial pressure of $p_1 = 0.1$ atm. They show, as expected, a gradual increase of the density ρ and growth of particle motion. The density is displayed in Fig.3 as function of x , and t . The maximum density variation of $\rho_{\max}/\rho_1 \approx 2$ is reached at $x = 0.6$ cm, $t = 14$ μ sec, and the maximum particle motion $u_{\max}/a_1 \approx 0.94$ is reached at $x = 0.4$ cm and $t = 8$ μ sec. A single formation point is not defined but the compression has reached 90% of its maximum value at $x \approx 0.5$ cm and $t \approx 10$ μ sec. For the same conditions the model yields the characteristic distance $x_C = 0.006$ cm and the characteristic time $t_C = 0.3$ μ sec, shown in Fig.3. At this instant, the density has only changed by about 1 %, the particle motion is still well below 5% of the maximum value and the conditions $x_C \ll x_F$ and $t_C \ll t_F$ are satisfied. Up to the point C the photolysis therefore takes place under practically undisturbed conditions.

In the particular case of oxygen photolysis with inhomogeneous absorption, gas dynamical effects can be neglected for times and distances smaller than x_C and t_C . In the absence of better knowledge we further conclude that the characteristic point C is generally a useful limit to determine the undisturbed region for photolysis experiments with inhomogeneous absorption.

Magnitude of the Fully Developed Perturbation

Besides knowing a characteristic point for the formation of a compression wave, the magnitude of the perturbation is

also of interest. The macroscopic motion u of the photolysed gas is due to the inhomogeneous absorption which creates concentration and pressure gradients. The local velocity change is described by the momentum equation

$$\rho \frac{du}{dt} = -\text{grad } p$$

The particles are accelerated only during the time interval Δt in which they are exposed to the pressure gradient. The end velocity u is therefore

$$u = \int du = \int_0^{\Delta t} \frac{1}{\rho} \text{grad } p \, dt \approx \frac{1}{\rho} \frac{\Delta p}{\Delta x / \Delta t}$$

where $\rho = \sum_i n_i m_i$ is the total density of the gas in the photolysed region. $\Delta x / \Delta t$ can be interpreted as the velocity v_R of the radiation front, which propagates into the laser medium, gradually photolysing the whole volume. $\Delta p = p_2 - p_1$ is the total pressure difference across this radiation front. The final pressure p_2 results from the release of heat and possibly from the increase of the total number density of particles in the photolysed material. p_2 depends on the energy of the absorbed photons but is independent on the intensity I_0 of the radiation.

With equation (3) the particle end velocity becomes

$$u = \frac{\Delta p}{\rho \cdot I_0 / n_1} \quad (8)$$

This relation has the surprising consequence that the motion will become small if the pump light is very intense, an effect predicted for supersonic¹² radiation fronts. A large average mass also helps to keep the motion small.

The unexpected result of vanishing motion for high pump light intensities or radiation front velocities respectively becomes more reasonable considering that the material has no time to react to pressure gradients, if the particles "see" the gradient for a very short time only. In the upper limit the radiation front can travel with the speed of the light and the acceleration time then reduces to about $\Delta t = \frac{L}{c} \approx 10^{-10}$ sec, for absorption length L of the order of 1 cm. The particle motion of course also becomes negligible for very low pump light intensities. A maximum of the particle motion and compression is expected if the radiation front velocity v_R is about equal to the speed of sound in the photolysed gas. In that case the radiation front will act as a travelling wave (surfboard effect) and accelerate and compress the photolysed gas to the largest possible values. This maximum compression will appear as a spike¹² in pressure and density just when the supersonic radiation front with decaying pump light intensity changes into a subsonic radiation front, giving birth at the same time to a preceeding shock front.

During the characteristic time of the compression wave t_c the radiation front will propagate the distance

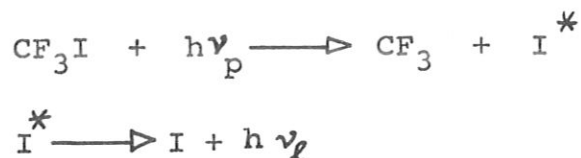
$$x_m = v_R \cdot t_c = \frac{L}{a_2 - a_1} \frac{I_0}{n_1} = \frac{I_0}{n_1^2} \frac{1}{\alpha (a_2 - a_1)} \quad (9)$$

material which is further away from the window than x_m , will be photolysed at a time when the compression wave has already become important.

Examples

The characteristic time and distance is now calculated for two well known photolytically pumped chemical lasers.

Firstly, the CF_3I laser of Kasper and Pimentel¹⁷ is considered, in which CF_3I is dissociated to generate electronically excited iodine

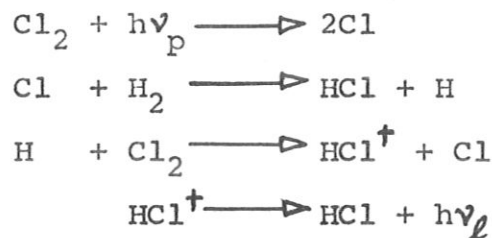


The pump light of $\lambda_p \approx 2700 \text{ \AA}$ is absorbed with $\alpha \approx 2.7 \cdot 10^{-19} \text{ cm}^2$ ¹⁸. Laser radiation is emitted at $\lambda_\ell = 1.3 \text{ }\mu\text{m}$. Assuming that the gas is fully dissociated near the tube wall, a total energy per unit mass of $q = 2 \cdot 10^{10} \text{ erg/g}$ is released. With a specific heat of $5 \cdot 10^6 \text{ erg/g}^\circ$ the temperature rise will be $4 \cdot 10^3 \text{ }^\circ\text{K}$. Therefore $a_2 = 8.1 \cdot 10^4 \text{ cm/sec}$ and $a_1 = 1.2 \cdot 10^4 \text{ cm/sec}$.

For an initial pressure of $p_1 = 100 \text{ torr}$ ¹⁹ one finds $L = 1.08 \text{ cm}$, $x_c = 1.2 \text{ cm}$ and $t_c = 15 \text{ }\mu\text{sec}$. The characteristic time is hence of the order of the duration of a typical pump flash τ_p . A typical photon flux of the pump light has an intensity of $I_0 = 1.5 \cdot 10^{22} \text{ photons/cm}^2 \text{ sec}$ ²⁰ so that the radiation front propagates at $v_R = I_0/n_1 \approx 4 \cdot 10^3 \text{ cm/sec}$ and it could bleach the laser gas completely up to a depth of $x_m \approx 0.5 \text{ mm}$. Since the penetration depth L is much larger than x_m it is obvious that the gas is only very incompletely dissociated. Therefore the real temperature rise and the speed of sound near the walls

will be much smaller than estimated above and the calculated values of x_C and t_C are safe lower limits to define the region in which gasdynamical effects can be neglected.

As a second example the HCl laser is considered, which results from the sequence



the net heat of reaction is 41.6 kcal/mole and the pumping light is absorbed with $\alpha = 1.08 \cdot 10^{-19} \text{ cm}^2$ at the wavelength $\lambda \approx 3300 \text{ \AA}$.¹⁶ Laser radiation is observed at $\lambda \approx 3.8 \text{ } \mu\text{m}$.²¹ Suppose the initial density is $n_{\text{H}_2} = n_{\text{Cl}_2} = 5.10^{17} \text{ cm}^{-3}$ and the number of photons in the pump light $\int_0^\infty I_0 dt$ allows to dissociate 1/4 of all Cl_2 molecules in the reaction tube so that $n_r = n_{\text{Cl}_2}/4$. The heat release per gram is then

$$q = \frac{1}{4(m_{\text{Cl}_2} + m_{\text{H}_2})} \left\{ 2.9 \cdot 10^{-12} + 6.6 \cdot 10^{-27} (21.98) 10^{14} \right\} \text{ erg/g}$$

to yield a temperature increase of 2300 °K with $c_p = 7.4 \cdot 10^6 \text{ erg/g}^\circ$.¹⁴ The speed of sound is $a_1 = 3.10 \cdot 10^4$ and $a_2 = 9.2 \cdot 10^4 \text{ cm/sec}$ respectively. We find $L = 18.5 \text{ cm}$, $x_F = 28 \text{ cm}$ and $t_C = 3.10^{-4} \text{ sec}$. With such a large characteristic distance x_C , the formation of compression waves may safely be neglected in a typical absorption tube of 2 cm diameter.

Conclusion

Macroscopic motion and compression waves are generated if the pumping light in a photolysis experiment is inhomogeneously absorbed due to high absorber concentration or large vessel dimensions. After qualitatively describing a region of formation $F(x_F, t_F)$ of such waves a characteristic time $t_C < t_F$, and a characteristic distance $x_C < x_F$ were defined, which can be calculated as function of the variables of the photolysis experiment α , n_1 and q . Motion and density variation are still negligible in the region $x \leq x_C$ and $t \leq t_C$, in the case of oxygen photolysis. The characteristic point C is therefore at least in this particular example a useful measure for the region where photolysis experiments are unaffected by gasdynamical effects in spite of inhomogeneous absorption of the pumping light. Both x_C and t_C grow if the speed of sound in the unphotolysed gas is raised. It is therefore suggested to enlarge the undisturbed region by admixture of an inert gas of high sonic speed so that the compound speed of sound is increased in the cold gas.

Acknowledgment

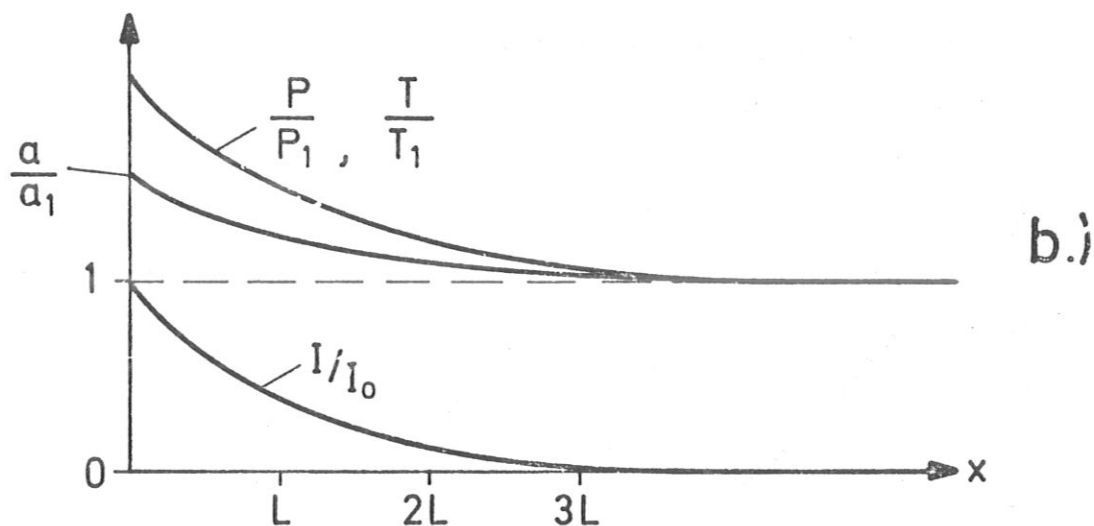
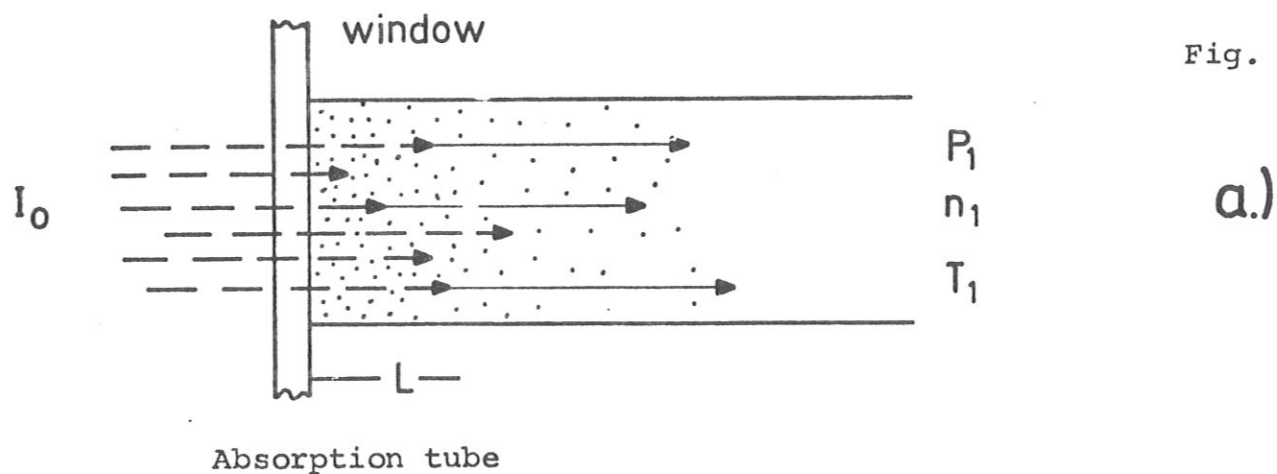
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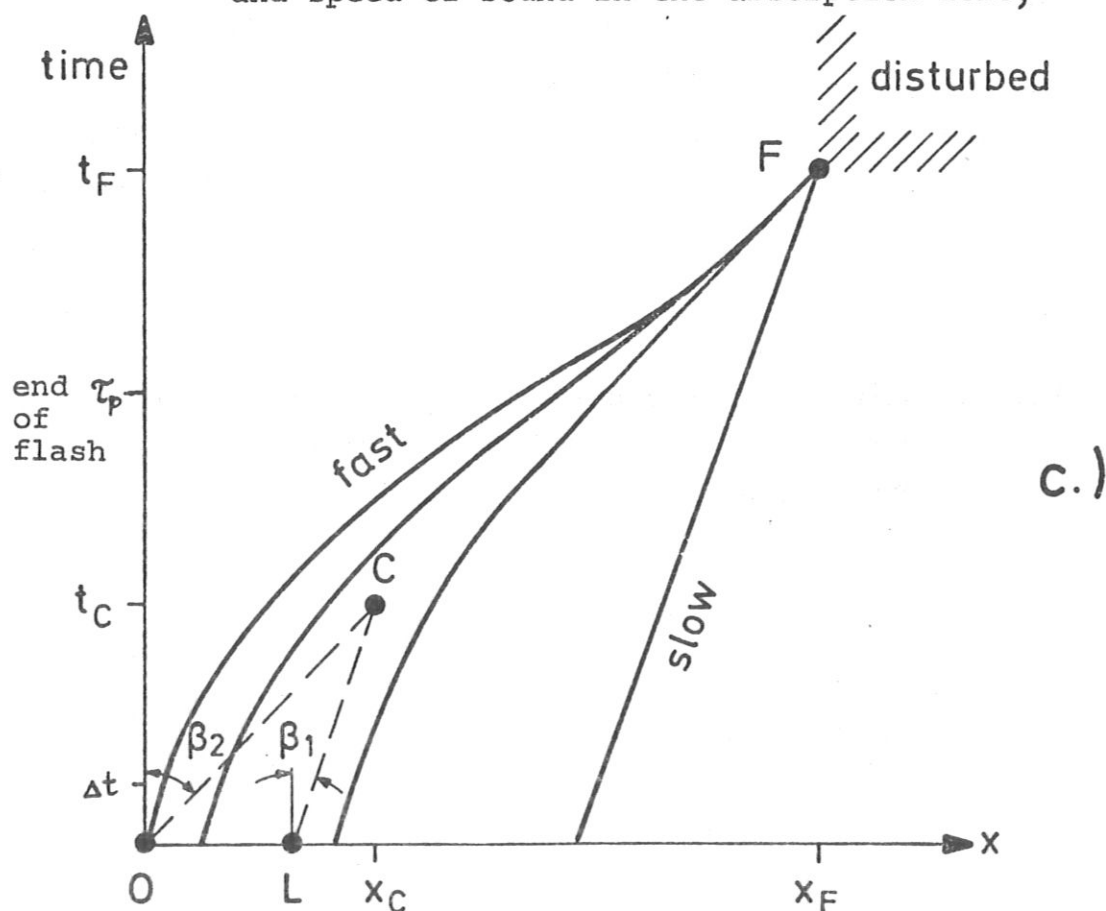
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Fig. 1



Distribution of intensity, pressure, temperature and speed of sound in the absorption zone, at $t = \Delta t$



Space time diagram. Characteristic point C, formation "point" F.

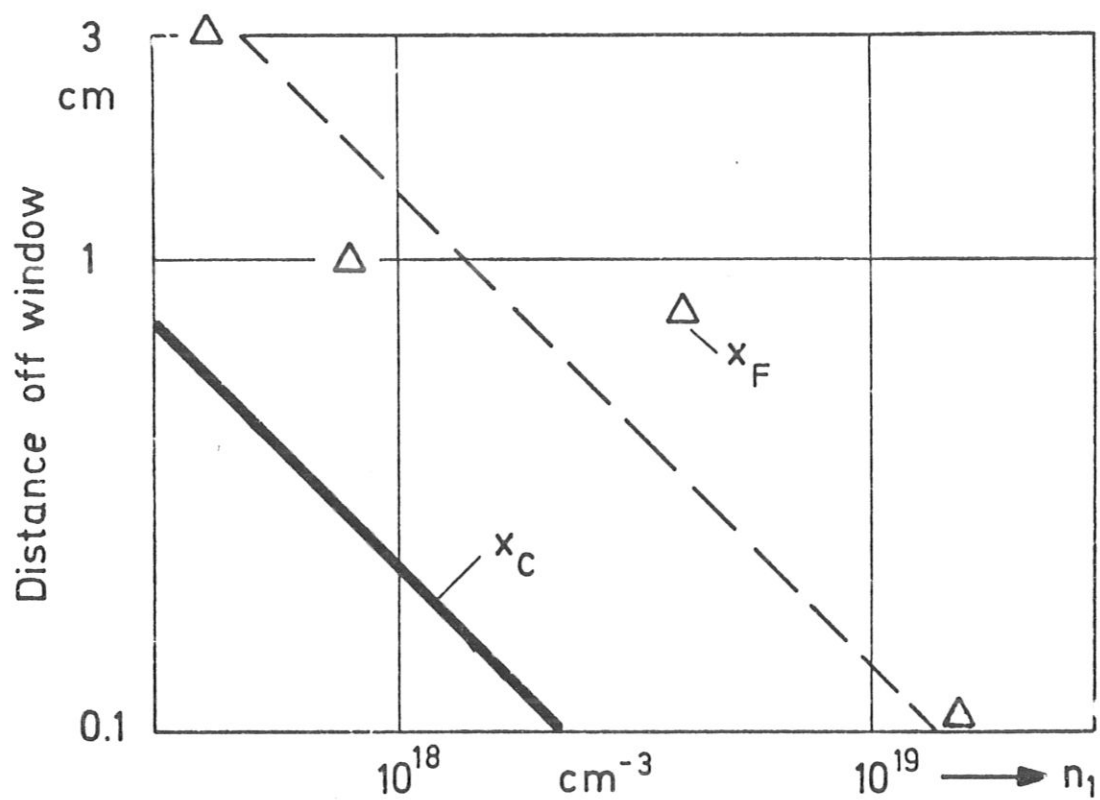


Fig. 2 Characteristic distance x_c as function of initial density n_1 . Measured formation distances x_F from ref. ⁹: Δ .

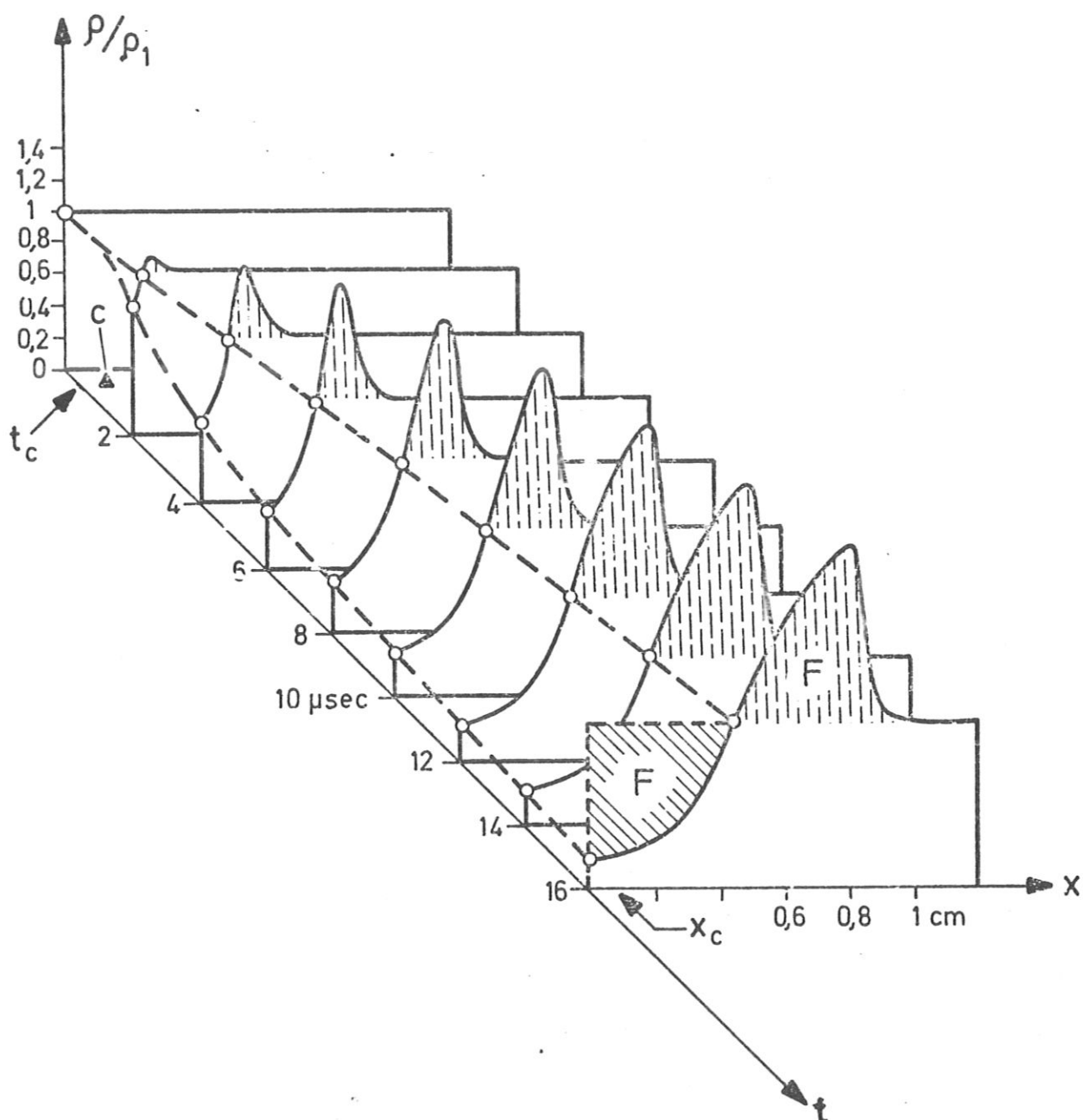


Fig. 3 Growth of compression wave in oxygen of room temperature and 0.1 atm pressure. Characteristic time t_c , characteristic distance x_c . Density ρ/ρ_1 plotted with data from ref. ⁹.