Photochemical decomposition waves

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Photochemical decomposition waves in an absorbing molecular gas are studied on the basis of the solution of the radiation transfer and particle number balance equations. The analysis is carried out for a light flux of arbitrary spectral composition and arbitrary directivity, taking the real molecular absorption bands into account. The resulting analytic expressions allow us to estimate the velocity and width of the photochemical decomposition wave and the effective frequency band for various shapes of the absorption bands. The possibility of stationary propagation of the photochemical decomposition wave is studied. The conditions for appearance of inverse level populations are considered for the case in which one of the photodecomposition products is in the excited state. It is shown that the conditions for inversion are qualitatively different in the regions of nonstationary and stationary photochemical decomposition wave propagation.

One comes into contact with wave phenomena that arise in absorbing media under the action of light in a number of fields of physics, ranging from astrophysics,[1] and radiative heat transfer[2] to laser physics[3] and laser plasma.[4,5] All these phenomena are described by equations that are similar in structure and have much in common. In the present work, photochemical decomposition waves in an absorbing molecular gas are considered on the basis of the equations of radiative transfer and particle number balance. The analysis is carried out for a light flux of arbitrary spectral composition with arbitrary directivity and with account of the real absorption bands of the molecules.

Gasdynamic motions that arise as a consequence of the evolution of heat on the decomposition of a substance can exert a significant influence on the process of photochemical decomposition. This transfer of matter can be neglected if the condition

$$v^2 \gg 2(\gamma^2 - 1)q,$$

is satisfied, where v is the photochemical decomposition wave velocity to be introduced below, γ the Poisson adiabatic exponent of the heated gas, q the heat released as a result of photochemical decomposition (calculated per unit mass). In the right side of the equation is the square of the velocity of the shock wave which arises in the material if a reaction occurs in it with specific heat release equal to q.

Let the half-space x > 0 be filled with AB molecules, which decompose under the action of light:[1)]

$$AB + h\nu = A + B. \tag{1}$$

The region of photochemical decomposition has dimensions of the order of $1/k$ (k is the light absorption coefficient) and, if the products of the reaction (1) do not absorb light and do not recombine into the initial material, a bleaching wave will propagate through space—the photochemical decomposition wave. We now consider the structure of this wave in more detail.

The interaction of the light with matter is described by the equations of radiative transfer and particle number balance:

$$\cos\theta \frac{\partial I_\nu}{\partial x} = -\sigma(\nu) I_\nu N, \tag{2}$$

$$\frac{\partial N}{\partial t} = -2\pi N \int_0^\infty \int_0^{\pi/2} \sigma(\nu) I_\nu \cos\theta \sin\theta \, d\theta \, d\nu, \tag{3}$$

where $I_\nu = I_\nu(\Omega, x)$ is the spectral light intensity in the direction of the unit vector Ω at the point x, ν is the frequency of the light, $\sigma(\nu)$ the absorption cross section of the AB molecules at the frequency ν, θ the angle between the normal to the surface x = 0 and the direction of propagation of the light, and N the concentration of AB molecules at the point x. The initial and boundary conditions are:

$$N(x, t=0) = N_0, \quad I_\nu(x=0) = I_\nu^0(\Omega). \tag{4}$$

In the general case, the solution of the system of equations (2)—(4) can be represented only in the form of quadratures (see below). For the particular case in which

$$\sigma(\nu) = \begin{cases} \sigma & \text{for } \nu_1 < \nu < \nu_2 \\ 0 & \text{for all the rest} \end{cases}$$

and a collimated light flux I_0 is incident on the medium, system (2)—(4) does not formally differ from the equations which have already been considered[3] in the study of illumination waves in two-level media. In this particular case, the solutions have the form

$$N(x,t) = N_0[1 + e^{-\sigma N_0 x}(e^{\sigma I_0 t} - 1)]^{-1}, \tag{5}$$

$$I(x,t) = I_0 e^{\sigma I_0(t-x/v)}[1 + e^{-\sigma N_0 x}(e^{\sigma I_0 t} - 1)]^{-1}, \tag{6}$$

where $v = I_0/N_0$.

It follows from (5) and (6) that for $x \gg (\sigma N_0)^{-1}$ or $t \gg (\sigma I_0)^{-1}$, the solutions have a wavelike character: $N = N(t - x/v)$ and $I = I(t - x/v)$, i.e., after the time for establishing the wave $t_{est} \sim (\sigma I_0)^{-1}$, a constant concentration profile of the initial molecules begins to move through space at velocity v.

In order to analyze the character of the photochemical decomposition wave, we introduce the following notation:

$$\tau = \sigma_0 \int_0^x N \, dx, \quad S = \int_0^\infty \int_0^{\pi/2} 2\pi (I_\nu - I_\nu^0) \cos^2\theta \sin\theta \, d\nu \, d\theta,$$

$$A = \int_0^\infty \int_0^{\pi/2} 2\pi \sigma(\nu) I_\nu^0 \cos\theta \sin\theta \, d\nu \, d\theta, \tag{7}$$

$$\bar{\sigma} = \frac{1}{S} \int_0^\infty \int_0^{\pi/2} 2\pi \sigma(\nu)(I_\nu - I_\nu^0) \cos\theta \sin\theta \, d\nu \, d\theta,$$

where $\sigma_0 = \max \sigma(\nu)$.

Using (2), (3) and (7), we can obtain a system of equations for S and N:

$$\frac{\partial S}{\partial x} = -\bar{\sigma}NS - AN, \qquad \frac{\partial N}{\partial t} = -\bar{\sigma}NS - AN \qquad (8)$$

with the initial and boundary conditions

$$S(x=0) = 0, \quad N(t=0) = N_0.$$

We note (this follows from (2)) that the functions S and $\bar{\sigma}$ are functions only of τ, and are known functions.

Changing in (8) to the variables τ and x, we obtain

$$N/N_0 = S/S(t=0),$$

$$S(\tau) = -\frac{1}{\sigma_0}A\exp\left(-\int_0^\tau \frac{\bar{\sigma}}{\sigma_0}d\tau'\right)\int_0^\tau \exp\left(\int_0^{\tau'}\frac{\bar{\sigma}}{\sigma_0}d\tau''\right)d\tau',$$

whence follows the equation for τ:

$$\frac{1}{N_0}\frac{\partial\tau}{\partial x} = \frac{1}{S(\sigma_0 N_0 x)}\frac{\partial\tau}{\partial t},$$

the general solution of which has the form

$$\tau = \Phi\left[e^{-At}\int_0^{\sigma_0 N_0 x}\exp\left(\int_0^\tau \frac{\bar{\sigma}}{\sigma_0}d\tau'\right)d\tau\right]. \qquad (9)$$

The form of the function Φ is determined from the initial conditions:

$$\sigma_0 N_0 x = \Phi\left[\int_0^{\sigma_0 N_0 x}\exp\left(\int_0^\tau \frac{\bar{\sigma}}{\sigma_0}d\tau'\right)d\tau\right]. \qquad (10)$$

Differentiating (9) with respect to x, we find

$$N = \frac{1}{\sigma_0}\frac{\partial\tau}{\partial x} \doteq N_0\Phi'e^{-At}\exp\left(\int_0^{\sigma_0 N_0 x}\frac{\bar{\sigma}}{\sigma_0}d\tau\right). \qquad (11)$$

Equations (9)–(11) are the exact solution of the initial system of equations. The form of the function Φ is found in the following way: $\bar{\sigma}(\tau)$ is calculated, after which we find the function

$$u(x) = \int_0^{\sigma_0 N_0 x}\exp\left(\int_0^\tau \frac{\bar{\sigma}}{\sigma_0}d\tau'\right)d\tau$$

and construct its inverse $x(u)$: then $\Phi(u) = \sigma_0 N_0 x(u)$.

For arbitrary dependence of $\sigma(\nu)$ on the frequency and for an uncollimated light flux, the integrals (9)–(11) are calculated only numerically. However, the velocity of the photochemical decomposition wave, the band of frequencies effectively used, and other characteristics can be estimated even without carrying out such calculations.

In the given problem, it is more convenient to follow not the profile of the density of the molecules, but the profile of the optical thickness τ. For the width of the wave, we can take the dimension Δx over which τ changes within prescribed limits, say from 0.2 to 2. We now find the velocity of displacement through space of the point which corresponds to a constant value of τ. For this purpose, we set τ = const in (9) and differentiate with respect to time. We obtain

$$v_\tau = \frac{dx}{dt}\bigg|_{\tau=\text{const}} = -\frac{S(\sigma_0 N_0 x)}{N_0}. \qquad (12)$$

It follows from (12) that the velocity of motion of the point τ = const does not depend on the value of τ. The following statement is obvious: if v_τ = const irrespective of the value of x, then the photochemical decomposition wave is stationary in the sense that the profile $\tau(x)$ remains unchanged in time. Constancy of the profile $\tau(x)$ is equivalent to constancy of the profile $N(x)$ since $N = \sigma_0^{-1}\partial\tau/\partial x$. Thus, the necessary condition for the existence of a steady state is

$$S(\sigma_0 N_0 x) = \text{const}. \qquad (13)$$

In physical meaning, S is equal to the rate of absorption of photons at the initial instant in a layer of gas of thickness x. It is therefore clear that the condition (13) can be satisfied only asymptotically for sufficiently large x, if the absorption band occupies a sharply limited portion of the spectrum (or the photodecomposition is brought about by light whose spectrum is limited). If there is an infinitely long wing on the absorption band (for example, a Lorentzian line), then the total number of absorbed photons increases with increasing x due to absorption of photons with frequencies corresponding to small values of $\sigma(\nu)$. Therefore $dv_\tau/dx > 0$ and the steady state is impossible. In this case, the curves $\tau(x)$ will become flatter with the passage of time, which corresponds to spatial broadening of the wave.

Let us consider specifically the case of a collimated light flux and two shapes of the absorption lines: for lines consisting of n rectangular steps and for a Lorentzian line.

1. Photochemical decomposition wave for an n-step absorption line. Let a rectangular step with value of cross section σ_k correspond to the intensity I_k^0 of the light. For definiteness, we assume that

$$\sigma_1 > \sigma_2 > \ldots > \sigma_n.$$

The mean cross section $\bar{\sigma}(\tau)$ for large τ, when $\sigma_n\tau \gg 1$, is equal to

$$\bar{\sigma}(\tau) = \sum_k I_k^0\sigma_k \bigg/ \sum_k I_k^0 = \bar{\sigma}(\infty) = \text{const}.$$

Therefore, for those x for which $\sigma_n N_0 x \gg 1$, we can obtain

$$v_\tau = C\exp[-\bar{\sigma}(\infty)N_0 x] + \sum_k I_k^0/N_0,$$

where $C > 0$ is a constant. Thus, for sufficiently large x, the photochemical decomposition wave goes into a steady regime and travels with velocity

$$v = \sum_k I_k^0/N_0.$$

The distance over which the steady state is established depends on the ratio of the quantities I_k^0 and σ_k.

2. Photochemical decomposition wave for a Lorentzian absorption line. The shape of the absorption line is given by the expression

$$\sigma(\nu) = \sigma_0\pi\Delta\nu f(\nu), \qquad f(\nu) = \frac{1}{\pi}\frac{\Delta\nu}{(\nu-\nu_0)^2+(\Delta\nu)^2}.$$

For large τ, for which

$$\int\sigma(\nu)\left[1-\exp\left(-\frac{\sigma(\nu)}{\sigma_0}\tau\right)\right]d\nu \approx \int\sigma(\nu)d\nu = \pi\Delta\nu\sigma_0,$$

the mean absorption cross section is equal to

$$\bar{\sigma} \approx \pi\sigma_0/2\sqrt{\tau}.$$

Therefore, for large x,

$$v_\tau = \frac{2I_0\Delta\nu}{N_0}(\sigma_0 N_0 x)^{1/2}. \qquad (14)$$

As was to be expected, in the case of a Lorentzian absorption line there is no steady-state propagation regime for the photochemical decomposition wave. Equation (14) shows that at a distance x from the boundary of the material, light radiated in a spectral interval

which exceeds the width of the Lorentzian line by a factor $(\sigma_0 N_0 x)^{1/2}$ takes part in the formation of the photochemical decomposition wave. Nor does a stationary spatial width of the photochemical decomposition wave exist for the Lorentzian absorption line. Using (14), we can show that the width of the photochemical decomposition wave increases linearly with time.

If one of the reaction products of (1) is in an excited state, then a wave of inverted level populations can arise in the medium. An example of such a molecule is CF_3I, on photodecomposition of which atomic iodine is formed in the excited state.[6,7] The investigation of the space-time structure of generation in a photodissociation laser is one of the most effective methods of verification of the laws obtained here and of the determination of the photochemical and molecular kinetic constants.

The expressions obtained for the photochemical decomposition waves permit us to find the conditions for the development of inversion in the medium. Starting out from the relations (5) and (6), we can show two regions where the conditions for the generation of inversion are qualitatively different: these are the transitional region and the region of stationary propagation of the photochemical decomposition wave. In the transitional region ($\sigma N_0 x \ll 1$), the rate of excitation $Q = -\gamma N/\partial t$ increases instantly from zero to the value $\sigma N_0 I_0$ and then falls off slowly. As is known, in instantaneous switching on of the pump source, inversion always appears, but exists only for a time approximately equal to the relaxation time τ_r of the excited state (it is assumed that the lifetime of particles on the lowest level of the laser transition is greater than τ_r).

In the region of stationary propagation ($\sigma N_0 x \gg 1$) the rate of excitation

$$Q = \sigma N_0 I_0 e^{-\sigma N_0(x-vt)}[1 + e^{-\sigma N_0(x-vt)}]^{-2}$$

increases exponentially with time of growth $(\sigma I_0)^{-1}$. The inversion of level population appears here only in the case

$$\tau_r > (\sigma I_0)^{-1}. \tag{15}$$

Thus, a situation can arise in optically dense layers of matter in which an inversion of level populations exists in the external layers and is absent in the internal ones.

On a gradual switching on of the pumping source, the opposite situation can arise: inversion of populations is absent in the external layer and exists in the internal ones. Such a picture will be observed if a sufficiently steep photochemical decomposition wave profile is formed in external layers of the material of thickness

$$l \approx \frac{1}{N_0}\int_0^{t_{ph}} I_0\,dt,$$

where t_{ph} is the characteristic time of switching on of the source and $t_{ph} > \tau_r$, and the duration of this wave proves smaller than τ_r (the condition (15) is satisfied).

In the general case of arbitrary shape of the absorption bands of the working sample and an arbitrary spectral composition of the pumping source, the analysis is more difficult; however, numerical calculations give a physically intelligible result—inversion appears where the characteristic time of growth of the excitation is shorter than the relaxation time, provided that the lower, ground level has not been filled at the stage of slow growth of the rate of excitation.

[1)]A and B can be either atoms or radicals.

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