Pyrolysis-induced transparency wave

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The profiles of the photodissociation wave that is stopped by recombination of the products into the original molecules are calculated and analyzed. The recombination limit imposed on the velocity of the dissociation wave, and the heating of the absorbing gas by the radiation, can bring about a new phenomenon, namely waves of transparency induced by pyrolysis. Approximate formulas are derived for the propagation of these waves, and the conditions for the formation of photodissociation and induced-transparency waves in CF_3I vapor are analyzed.

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A number of relatively recent papers[1-3] are devoted to the development of the concept of the so-called photodissociation waves (PW). According to these concepts, PW are produced when the absorption of photons by molecules leads to photodissociation of the latter and consequently to the transparentization of the absorbing medium.[1)] A typical example considered in these papers is the propagation of PW in CF_3I, the molecules of which dissociate under the influence of ultraviolet radiation into an iodine atom and the radical CF_3.

Borovich et al.[3] pointed out the possibility of slowing down or accelerating the PW by the chemical reactions that accompany the photolysis. They did not consider, however, concrete mechanisms of these actions.

There is also a series of studies by Oraevskiĭ and co-workers (see, e.g.,[4,5], in which they consider in detail the singularities of the propagation of PW in a two-component medium in which unbranched[4] and branched[5] chain reactions take place. These waves are characterized by much higher propagation velocities and can apparently be realized in the active media of certain chemical lasers. At the same time, the possibility of realizing "pure" PW free of the influence of chemical reactions and propagating with a velocity[2)] $v_{ph} = I_0/n_0$ (where I_0 is the flux density of the absorbed photons as they enter the absorbing medium and n_0 is the initial concentration of the absorbing molecules)[1] will be shown below to be quite limited.

If no conditions are provided for "bleaching" chain reactions, the PW can either slow down until they are completely stopped (if we neglect gasdynamic processes that are mainly of thermal origin), or go over into pyrolysis transparentization waves (PTW). The former case can be realized when the absorbing gas is diluted enough by a non-absorbing and chemically-noninteracting gas, while the latter case is more typical of conditions of an undiluted absorbing gas.

This paper deals with the influence of recombination on the motion of PW, an analysis of the conditions for the formation of PTW, and a derivation of approximate expressions for the stationary velocity and profile of the wave.

RECOMBINATION SLOWING DOWN OF PHOTODISSOCIATION WAVE

Usually the direct products of photodissociation are radicals (R) or atoms (A). In the simplest case they vanish by recombination. If the initial molecule is of type R_2 or A_2, then there is only one possible recombination process, which leads to regeneration of molecules of the initial form. In the case of photodissociation of molecules of the type RA, R′R″ or A′A″ with formation of free radicals (R, R′, R″) and (or) atoms (A, A′, A″), other recombination channels are possible, which do not lead to regeneration of the molecules of the initial type.

We consider initially the first case. The corresponding balance equation

$$dn/dt=-\gamma n+{}^1/_2kr^2, \tag{1}$$

where[3)] $\gamma = \sigma I$, r is the concentration of the radicals (or atoms), σ is the photon absorption cross section, and k is the (second-order) recombination coefficient,[4)] when account is taken of the fact that I is constant and of the condition for the conservation of the number of particles

$${}^1/_2r+n=n_0 \tag{2}$$

has as its solution

$$n=n_0\frac{\sqrt{\alpha+1}+1+(\sqrt{\alpha+1}-1)\exp\{t\gamma\sqrt{\alpha+1}\}}{\sqrt{\alpha+1}-1+(\sqrt{\alpha+1}+1)\exp\{t\gamma\sqrt{\alpha+1}\}} \tag{3}$$

where $\alpha = 8kn_0/\sigma I$.

As the PW moves, the region behind its front, where the photons are absorbed by the molecules produced through recombination, increases in size (we assume that the radical absorption bands do not overlap the working absorption band of the molecules). Therefore the motion of the PW slows down, and at any duration of the radiation pulse the PW will ultimately stop. Neglecting gasdynamic and diffusion phenomena we can derive (in implicit form) an expression for the profile of the stopped PW. In the one-dimensional case (plane wave) we can use for this purpose the equation

$$\partial I/\partial x=-\sigma nI, \tag{4}$$

where x is the coordinate. Putting $t = \infty$ in Eq. (3) and substituting the value of n_∞ obtained from (3) in (4), and then integrating (4) with respect to x under the boundary condition $I(0) = I_0$, we obtain

$$\ln\varphi+\varphi=\ln\varphi_0+\varphi_0-{}^1/_2\sigma n_0x; \tag{5}$$

here

$$\varphi=(\sqrt{\alpha+1}+1)/\alpha,\quad \varphi_0=\varphi(\alpha_0),\quad \alpha_0=8kn_0/\sigma I_0.$$

Equation (5) describes in implicit form the profile $I_\infty(x)$ of the stopped wave. Using Eq. (3) we easily obtain for $t = \infty$ the corresponding profile for $n_\infty(x)$ (Fig. 1). It is curious to note that, in contrast to the profile $I_\infty(x)/I_0$, the profile $n_\infty(x)/n_0$ does not depend on α_0 and has a clearly pronounced region with high gradients $n_0^{-1}\partial n_\infty/\partial x$, which moves into the interior in correspondence with the value of α_0.

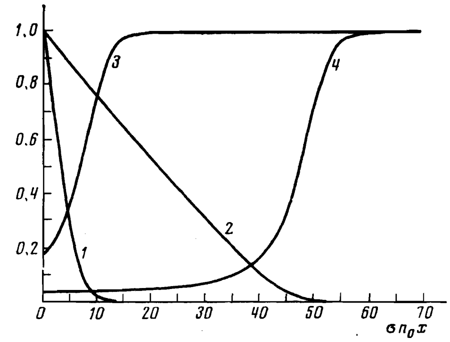

FIG. 1. Profiles of the "stopped" photodissociation waves $I_\infty(x)/I_0$ (curves 1 and 2) and $n_\infty(x)/n_0$ (curves 3 and 4) at $\alpha_0 = 1$ (curves 1 and 3) and $\alpha_0 = 0.1$ (curves 2 and 4).

Equating $n_\infty(x) = n_0(1 - 2\varphi + 4\alpha^{-1}) = n_0/2$, we obtain $\alpha = 8$ and get from (5) an expression for the distance traversed by the PW prior to stopping (at the level $n = n_0/2$), i.e., for the thickness $x_n = x|_{n_\infty = n_0/2}$ of the increased-transparency layer in which $n(x) \lesssim n_0/2$ at $t = \infty$:

$$x_n = 2(\sigma n_0)^{-1}[\varphi_0 + \ln(2\varphi_0) - {}^1/_2]. \tag{6}$$

From Eq. (6) we easily obtain also an expression for $x_I = x|_{I_\infty = I_0/2}$, i.e., for the thickness of the layer in which the radiation intensity lies in the range $I_0 \geq I(x) \geq I_0/2$. In this case $\alpha = 2\alpha_0$ and the value of x_I is determined by the formula

$$x_I = \frac{2}{\sigma n_0}\left\{\ln\left[\frac{2\sqrt{1+\alpha_0}+1}{\sqrt{1+2\alpha_0}+1}\right] + \frac{\sqrt{1+\alpha_0}+1}{\alpha_0} - \frac{\sqrt{1+2\alpha_0}+1}{2\alpha_0}\right\}. \tag{7}$$

Comparing (6) and (7) we can see that $x_n = x_I = 1.56(\sigma n_0)^{-1}$ at $\alpha_0 = 4$, which corresponds to $\gamma = \sigma I_0 = 2kn_0 = \tau^{-1}$ (τ is the lifetime of the radicals (atoms) for complete dissociation of the molecules). It is obvious that an appreciable advance of the PW corresponds to cases when $\alpha_0 \ll 4$. From a comparison of (6) and (7) it is also seen that in the region $\alpha_0 < 4$ (and, accordingly $\gamma > \tau^{-1}$) we have $x_I < x_n$ everywhere. It is easy to show that in the case of "pure" monochromatic PW we always have $x_I = x_n$.

We consider now the second case (molecules of the type RA, R′R″, and A′A″). The increased transparency of CF_3I vapor and of similar molecules belongs to just this case, if we disregard the slight complication that arises because photodissociation of these molecules produces directly metastable iodine atoms, which recombine in the main only after they become deactivated.

As shown in[6], the rather rapid rates of the recombination processes of the type $2R \to R_2$ and $2A \to A_2$ lead to the establishment of quasistationary concentrations of these particles, which have the same variation as the concentration of the RA molecules. Using the expressions obtained in[6] for these concentrations, we arrive at the following equation describing the change of the concentration of the RA molecules:

$$dn/dt = -\gamma n C_1,$$

$$C_1 = \frac{2\eta'}{1+2\eta'}\frac{k'}{k'+k''}, \quad \eta' = \frac{\sqrt{k_r k_a}}{k_{ra}}. \tag{8}$$

The rate constants of second order k_r, k_a, k_{ra}, k', and k'' correspond (in the same sequence) to the processes

$$2R \to R_2,\ 2A \to A_2,\ R+A \to RA,\ A^*+R \to A+R,\ A^*+R \to RA;$$

A^* denotes an atom in the metastable state. The factor $k'/(k' + k'')$ in (8) vanishes if the photodissociation yields electronically unexcited products.

Equation (8) is valid under the following assumptions: 1) the constants k_r, k_a and k_{ra} are large enough to ensure smallness of the concentration of R and A in comparison with the concentration of the initial molecules; 2) these constants depend weakly enough on the change of the chemical composition and the temperature of the gas (it is important to take this condition into account in the case of trimolecular recombination); 3) no secondary processes occur (either chemical or quenching processes) other than those listed above, nor does photodissociation of the final molecules of the type[5)] R_2 and A_2 take place; 4) the heat released is insufficient for an appreciable heating of the gas (see below). Integrating jointly Eqs. (4) and (8) we can readily establish that under the foregoing assumption there is produced a stationary PW that propagates with a velocity

$$v_{\text{ph}} = C_1 I_0/n_0. \tag{9}$$

The quantity C_1 is always smaller than unity. In view of the dependence of k_{ra} and especially k_a on the concentration of the particles, it depends somewhat on the gas pressure. In the case of CF_3I, even if it is assumed that the factor $k'/(k' + k'')$ (which has not been determined to date) is equal to unity, the value of C_1 does not exceed 0.2 to 0.3 if the CF_3I vapor is strongly diluted by a buffer gas (for example, 0.1 atm of CF_3I and 3 atm of CO_2 correspond to a value $\eta' \approx 0.2$[6]). This means that under the assumptions made the influence of the recombination leads to an appreciable lowering of the stationary velocity of the PW (by a factor 3–5 in the case of strong dilution with a buffer gas, and possibly by dozens of times in the case when no dilution is used).

In fact, in contrast to the considered model, the fourth assumption is more frequently not satisfied, i.e., the heating of the gas is appreciable and leads to the onset of a PTW that moves with a velocity

$$v_{\text{p}} = C_2 I_0/n_0, \tag{10}$$

where the factor C_2, as will be shown below, can exceed unity.

FORMATION OF PYROLYSIS TRANSPARENTIZATION WAVES

The inverse of recombination of atoms or radicals into molecules is thermal dissociation of molecules. The main factor that determines the direction of the recombination-dissociation process is the temperature (the influence of the pressure is much weaker). Heating of the gas when the radiation is absorbed by the molecules and photodissociation of the molecules can cause the vibrational temperature of the remaining molecule to become high enough to reverse the direction of the recombination process. This can lead to the formation of PTW under the condition that the high-temperature chemical reactions do not lead to the formation of products that absorb in the same region of the spectrum as the initial molecules.

The possibility of formation of PTW follows from the system of the following equations[7]:

$$dn/dt = -nF(\gamma + Ae^{-E/kT}), \tag{11}$$

$$\frac{dT}{dt}=\frac{n}{n_0C_v}(H_{\mathrm{ph}}\gamma-H_{\mathrm{p}}Ae^{-E/kT}) \tag{12}$$

and from Eq. (4). Here H_{ph} and $-H_p$ represent the effective thermal absorption of one photon and the pyrolysis,

$$n_0C_v\approx n_0(C_v^{(n)}+C_v^{(b)}b/n_0) \tag{13}$$

is the specific heat of the gas ($C_v^{(n)}$ and $C_v^{(b)}$ are the specific heats of the molecules of the absorbing and buffer gases, b is the concentration of the molecules of the latter). It is assumed that the dissociation of the molecules and the change of the temperature do not influence strongly the value of n_0C_V. A is the pre-exponential factor in the Arrhenius expression for the pyrolysis rate constant,[6)] depends on the gas pressure in the case of diatomic molecules and molecules with few atoms, but depends relatively little on the temperature, E is the activation energy, T is the absolute temperature, and k is Boltzmann's constant.

In contrast to the analogous equations given in[7], we have introduced in the right-hand side of (11) the factor $F = 1 - f_{ra} - f_{ra}^*\varphi'$, which is equal to C_1 in the case when the concentrations of the radicals (r) and of the atoms (a) are quasistationary. It is easy to verify that in this case $f_{ra} + f_{ra}^*\varphi' + f_r + f_a = 1$, with $f_r = f_a$. (Here f_{ra}, f_{ra}^*, f_r, and f_a are the effective quantum yields of the recombination processes, defined by the relations

$$f_{ra}/k_{ra}ra=f_r/k_rr^2=f_a/k_aa^2=[n(\gamma+Ae^{-E/kT})]^{-1},$$
$$f_{ra}^*=k''ra^*/\gamma n,\quad \varphi'=\gamma/(\gamma+Ae^{-E/kT});$$

at $T < T_p$ (see below) we have $\varphi' \approx 1$.) On the other hand, if the concentrations of at least some of the labile types of particles cannot be made quasistationary then, generally speaking, $f_{ra} + f_{ra}^*\varphi' + f_a + f_r \neq 1$ and the quantities f_{ra}, f_{ra}^*, f_r, and f_a can depend on the time.

An analysis of the system (4), (11) and (12), is best carried out under the assumption that all these quantities are constant. In this case, depending on the recombination characteristics of the gas (mainly x_n or η'), it is necessary to assume for F the values zero (in the case of molecules of type A_2 and R_2, and also RA, R′R″, and A′A″ if $f_{ra} + f_{ra}^*\varphi' \sim 1$), unity (in the case $\sigma n_0x_n \gg 1$), or C_1 (in the particular case of recombination of molecules of type RA, R′R″, and A′A″, when $\sigma n_0x_n \ll 1$, the concentrations of the radicals and the atoms are quasistationary, and $f_{ra} + f_{ra}^*\varphi' < 1$). Without changing the character of the problem, these assumptions enable us to explain its main features. (The intermediate cases are more difficult to analyze and are not considered in this paper).

The effective thermal absorption of one photon H_{ph} can be represented in the form

$$H_{\mathrm{ph}}=fH_0+f^*H_0^*+f_{ra}H_{ra}+f_{ru}^*H_{ra}^*+f_rH_r+f_aH_a+f_a^*H_a^*.$$

Here H_0 and H_0^* are the energies released directly in the photodissociation of the molecules RA with formation of atoms A and A* (kinetic, vibrational, and rotational energy of the products), H_{ra}, H_{ra}^*, H_r, and H_a are the thermal effects of the corresponding recombination processes, $H_a^* = H_{ra}^* - H_{ra}$ is the energy of the electron excitation of the atom A*, f and f* are the quantum yields of the atoms A and A* in the photodissociation of the molecules RA (it is assumed that f + f* = 1), f_a^* is the effective quantum yield of the process of the deactivation of the atom A*, defined as $k'a^*r/\gamma n$ and assumed constant, just as are f_{ra}, f_{ra}^*, f_r, and f_a.

The quantity Θ″ introduced in[7] corresponds in (12) to the quantity $-H_p/n_0C_V$, where

$$-H_{\mathrm{p}}=-[H_{ra}(1-f_{ra})-f_rH_r-f_aH_a]=-f_{\mathrm{p}}H_{ra},$$

and the factor $f_p < 1$ takes into account the possibility of the release of heat in the reactions of the pyrolysis products. We shall assume that $f_p > 0$ at least at a sufficiently high temperature $T \sim T_p$ (see below). In the quasistationary case this is reached if $2H_{ra} \gtrsim H_r + H_a$. At $T \sim T_p$, however, all the recombination processes become weaker to one degree or another, and the values $f_p > 0$ are apparently the most probable.

In view of the fact that the activation energies E are usually close to the molecule dissociation energies, we have as a rule $E/kT \gg 1$ for stable molecules at gas temperatures close to room temperature (T ~ 300°K). This is the cause of the exceedingly high sensitivity of the Boltzmann factor to changes of temperature. In this situation, at sufficiently low temperatures, the growth of the temperature is determined exclusively by the first term of (12). The action of the second term manifests itself exceedingly rarely,[7)] and since it plays the role of an inertialess negative feedback (if $f_p > 0$), its "turning-on" leads to rapid establishment of a quasistationary pyrolysis gas temperature T_p, which is determined from the condition $dT/dt = 0$ and is equal to

$$T_{\mathrm{p}}=(E/k)[\ln(AH_{\mathrm{p}}''/\gamma H_{\mathrm{ph}}'')]^{-1}. \tag{14}$$

To improve somewhat the accuracy of the analysis that follows we shall distinguish from now on between the values of F, H_{ph} and H_p averaged over the temperature range from the initial value (T_0) to T_p (F', H_{ph}', H_p'), and their values at $T = T_p$ (F'', H_{ph}'', and H_p''). The F(T), $H_{ph}(T)$, and $H_p(T)$ dependences follow from the possibility of thermal dissociation of the products A_2 or R_2 at $T < T_p$ and the relatively weak influence of the temperature on the values of the recombination rate constants. As a rule they are insignificant in comparison with $e^{-E/kT}$. In accord with Eq. (12), the value $T \approx T_p$ should be maintained, with the accuracy determined by the gasdynamic and diffusion processes), until the reserve of molecules is exhausted.

The problem of determining the steady-state PTW velocity (v_p) is easily solved if it is assumed that the region filled with the gas is divided into two parts by a plane boundary that moves with velocity v_p in the radiation direction x, and, for the sake of argument, perpendicular to this direction; in region I, which is on the side of the unperturbed gas, the concentration of the initial molecules and the gas temperature vary in accord with Eqs. (11) and (12) without the second terms, while in region II, on the side of the planar radiation source (which is homogeneous and of constant intensity), the gas temperature is constant and equal to[8)] T_p, while the molecules dissociate in accordance with the fully written out Eq. (11). In the described approximation, we can write down Eq. (11) for region I in the form

$$\partial n/\partial t=-F'\sigma In. \tag{15}$$

The possible values of the constant F′ were determined above. For region II, Eq. (11) can be transformed into

$$\partial n/\partial t=-\Phi\sigma In, \tag{16}$$

where $\Phi = F''(H_{ph}'' + H_p'')/H_p''$.

In a Lagrangian coordinate system (x', y', z', t') with origin in the plane that separates regions I and II, where $x' = x - v_p t$, $y' = y$, $z' = z$, and $t' = t$, while x, y, and z are the Euler coordinates, we can easily obtain with the aid of (15), (16), and (4), and with allowance for the obvious equality $\partial n/\partial t' = 0$, the following equations: in region I

$$\frac{\partial n}{\partial x'} = -\frac{F'\sigma}{v_p} In, \tag{17}$$

in region II

$$\frac{\partial n}{\partial x'} = -\frac{\Phi\sigma}{vp} In, \tag{18}$$

and in both regions

$$\partial I/\partial x' = -\sigma In. \tag{19}$$

Integrating them with allowance for the boundary conditions $n = 0$ and $I = I_0$ at $x' = -\infty$; $n = n(0)$, $I = I(0)$ at $x' = 0$ and $n = n_0$, $I = 0$ at $x' = \infty$, we obtain expressions describing the PTW in region I:

$$I = I_0'[1 + G' \exp(\sigma_1 n_0 x')]^{-1}, \tag{20}$$

$$n = n_0 G' \exp(\sigma_1 n_0 x')[1 + G' \exp(\sigma_1 n_0 x')]^{-1} \tag{21}$$

and in region II:

$$I = I_0[1 + G \exp(\sigma_2 n_0 x')]^{-1}, \tag{22}$$

$$n = n_0(\sigma_2/\sigma_1) G \exp(\sigma_2 n_0 x')[1 + G \exp(\sigma_2 n_0 x')]^{-1}. \tag{23}$$

Here $G' = -1 + I_0'/I(0)$, $I_0' = I_0 C_2/F'$, $\sigma_1 = \sigma$, $G = -1 + I_0/I(0)$, $\sigma_2 = \sigma\Phi/C_2$; C_2 was defined earlier in (1). Putting $z' = 0$ in (21) and (23) and eliminating I(0) from the resultant equations, we find that

$$C_2 = \left[\frac{1}{F'} + \frac{n(0)}{n_0}\left(\frac{1}{\Phi} - \frac{1}{F'}\right)\right]^{-1}. \tag{24}$$

The quantity n(0) can be easily obtained by integrating with respect to t in the region I (from $t = -\infty$ to $t = 0$) Eq. (12) with allowance for (11) (in the assumed approximation the pyrolysis term in these equations is equal to zero). This yields

$$\begin{gathered} n(0)/n_0 = 1 - \Theta F', \\ \Theta = C_v \Delta T/H_{ph}', \quad \Delta T = T_u - T_0, \quad T_0 = T|_{t=-\infty}. \end{gathered} \tag{25}$$

Using (25), we also find that

$$\frac{I(0)}{I_0} = \frac{\Theta\Phi}{1 + \Theta(\Phi - F')}.$$

Substituting (25) in (24) we determine the value of C_2 in terms of the recombination and thermal characteristics of the gas:

$$C_2 = \frac{\Phi}{1 + \Theta(\Phi - F')} = \frac{F''(1 + H_{ph}''/H_p'')}{1 + \Theta[(F'' H_{ph}''/H_p'') + F'' - F']}. \tag{26}$$

Thus, the velocity of the stationary PTW is determined on the basis of (10). As seen from (17) and (18), in the assumed approximation the derivative $\partial n/\partial x'$ at $x' = 0$ experiences a discontinuity. In fact, in place of the discontinuity there is obviously a narrow region of increased values of the derivative $\partial^2 n/\partial x'^2$. What is typical of the PTW, as seen from Fig. 2, is the asymmetry of the profile and its shortening in comparison with the PW profile, since $\sigma_2/\sigma = 1 + \Theta(\Phi - F') \geq 1$. (there is no shortening if $T_0 = T_p$).

The PTW is inevitably accompanied by gasdynamic motion of the gas, the possibility of which was not taken into account in the derivation of formula (26). Assuming (in the case least favorable for the formation of a "pure" PTW), that the temperature, the density ρ, and the pressure p behind the front of the produced waves are respectively equal to T_p, ρ_0, and $p_0 2T_p/T_0$ (where T_0, ρ_0, and p_0 are the values of these quantities ahead of the front), we can obtain for the shock-wave velocity

$$D_p = \left[\frac{Nk}{\mu}((\varkappa + 1)T_p + \varkappa(\varkappa - 1)T_0)\right]^{1/2}, \tag{27}$$

in which κ is the Poisson effective adiabatic exponent, N is Avogadro's number, and μ is the effective molecular weight.

Recognizing that T_p usually does not exceed $(1-2) \times 10^3$ °K, we arrive with the aid of (27) at the conclusion that D_p usually does not exceed several hundred meters. For example, for CF_3I (without dilution) at $T_p \sim 10^3$ °K, $\mu = 196$, $\kappa = 1.1-1.5$, and $T_0 = 300$°K we obtain $D_p = 300$ to 350 m/sec. It follows therefore that at values of v_p on the order of several km/sec or higher the formula (21) is accurate enough, and consequently the influence of the gasdynamic motion on the PTW profile is small.

We consider in conclusion the conditions for the formation of PW and PTW in CF_3I vapor. For PW to become possible, it is desirable to have strong dilution with a buffer gas, so as to decrease v_p (the PW can appear if $v_{ph} > v_p$ or, equivalently $F' > C_2$). Using (9), (10), and (26) and recognizing that in the case of CF_3I we have $F' = C_1$, $1 - F'/F'' \ll H_{ph}''/H_p''$, and $H_{ph}' \approx 110$ kcal/mole,[8,9], we readily obtain the corresponding condition for C_v:

$$C_v > \frac{H_{ph}'}{C_1 \Delta T} \approx \frac{1.1 \cdot 10^5 \text{ kcal/mole}}{0.3 \cdot 700\text{K}} = 520 \text{ cal/mole K},$$

where it is assumed that $C_1 = 0.3$ (see above) and $\Delta T = 700$°K. In accord with (13), the value $C_v = 520$ corresponds, for example, to a 25-fold dilution by a buffer gas with molar specific heat $C_v^{(b)}$ equal to $C_v^{(n)}$ (for example, a gas such as CF_4). The condition for the formation of a real PW in CF_3I vapor (and similar molecules) is even more difficult to satisfy if the quantity $k'/(k' + k'')$ which enters in the expression for C_1 is much smaller than unity, and if we use the ordinary plasma source of radiation, which impedes the establishment of quasistationary concentrations of radicals and atoms as a consequence of the photodissociation of the molecular gas (in the spectral region ~500 nm).[10]

The table lists the values of C_2 and v_p/v_{ph} calculated from (9) and (26) in four cases, which cover to a consid-

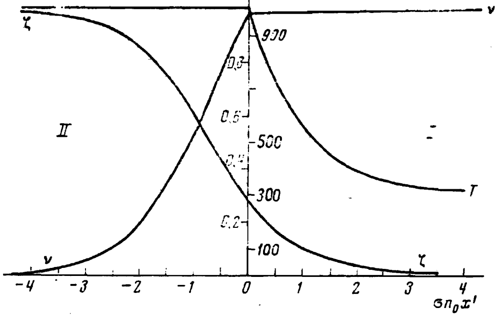

FIG. 2. Profile of purolysis transparentization was $\zeta = I(x')/I_0$, $\nu = n(x')/n_0$, and T in the assumed approximation for the case of CF_3I vapor (see the table, case 4).

Case	F'	F''	Θ	H'_{ph}	H''_{ph}	H''_p	C_2	v_p/v_{ph}
				kcal/mole				
1	0.1	0.2	0.128	109	103	6	2.7	27
2	0.1	1.0	0.128	109	103	6	5.5	55
3	0.1	1.0	0.128	109	54	54	1.6	16
4	0.114	0.57	0.222	110	73	36	1.3	11

erable degree the range of the uncertainty in the behavior of the quantities F, H_{ph}, and H_p due to the insufficient knowledge of the recombination and other rate constants at $T \sim T_p$, and also to the experimental conditions. It was assumed in all cases that $C_v^{(n)} = 20$ cal/mole-deg, $\Delta T = 700°K$, $f = 0$, $f^* = 1$, $f^*_{ra} = 0$ ($k'' = 0$), $f^*_a = 1$, and the thermal effects are equal to (in kcal/mole): $H^* = 3a$, $H^*_a = 22$, $H_{ra} = 54$, $H_r = 96$, and $H_a = 36$. The assumed value of $F' = C_1 = 0.1$ corresponds approximately to undiluted CF_3I vapor.

Case 1 is typical of a large (10%) deviation of all the labile particles from quasistationarity at $T = T_p$ (it is assumed that $f_{ra} + F^*_{ra}\varphi' + f_r + f_a = 0.9$). In case 2, when the temperature rises to $T = T_p$, only the effectiveness of the recombination of the radicals is preserved in full measure ($2R \rightarrow R_2$). In this case $f_r = 0.5$ in accord with the stoichiometric ratio, and the remaining recombination processes at $T = T_p$ are assumed to be ineffective ($f_{ra} = f^*_{ra} = f_a = 0$). In case 3, at $T = T_p$ all the recombination processes are assumed to be ineffective ($f_r = f_{ra} = f^*_{ra} = f_a = 0$). Case 4 is intermediate with respect to the conditions at $T \sim T_p$. The values of F′ and Θ are typical of a five-fold dilution of the CF_3I vapor by an inert gas. It is difficult to state at present which case (of the first three) is the most realistic. However, all cases point to a more than tenfold increase of v_p over v_{ph}, and also to a noticeable excess of v_p over the value I_0/n_0 to which the velocity v_{ph} would be equal in the absence of recombination.

It is seen from these data that the main difficulty in the realization of PW (in comparison with PTW) in CF_3I vapor (and apparently in other fluor-alkyl-iodides) is that at a given propagation velocity in the case of the PW (of course, at the required rather strong dilution of the absorbing gas), the radiation source would have to be stronger by C_2/C_1 times ($C_2/C_1 \gtrsim 10$ in the case of CF_3I) than in the PTW case. In view of the foregoing, the conclusion that the concepts developed in [1-3] for PW are applicable to CF_3I vapor call for a thorough revision.

The slowing down and damping of the PTW can be observed in the case when the processes that take place in the heated gas lead to stable or metastable products that are not photodissociated but are absorbed in the same spectral region. In the case of CF_3I these products may turn out to be the metastable radicals CF_2.[8]

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[1] Only gaseous media are considered.

[2] It is assumed throughout that $v_{ph} \ll c$, where c is the speed of light.

[3] For simplicity, we neglect here effects connected with the nonmonochromaticity of the radiation, since they do not change the gist of the matter. As applied to ordinary PW, they have been considered in [2,3]. For the same purpose, we assume that the radiation is collimated within a small angle β for which $\cos\beta \sim 1$.

[4] Frequently, and in the case of atom recombination as a rule, the recombination is a third-order process. For the sake of simplicity, this fact is not reflected in Eq. (1), which describes recombination correctly under the condition that the main contribution to the recombination is made by the components whose concentration does not change (i.e., the diluting gas).

[5] We use here a notation corresponding to the case of photodissociation of molecules of type RA. Our analysis can be easily extended to the case when the initial molecules pertain to types R′R″ and A′A″. When considering PTW, we also confine ourselves to the case of molecules of type RA (with allowance for the finite quantum yield of the metastable atoms upon photodissociation of these molecules), since the more general cases do not seem to be of practical interest.

[6] Here and below we use the term "pyrolysis" to denote only thermal dissociation of molecules. Cases of pyrolysis with the radical (chain) mechanism of destruction of the initial molecules are not considered here.

[7] The concept that the temperature dependence of the pyrolysis has a threshold seems to be of little use when the gas pressure is insufficient to prevent the molecule decay rate from being limited by the activation rate.

[8] In view of the fact that $\gamma(x)$ in (14) is under the logarithm sign, and we always have $A \gg \gamma$ and $H_p/H_{ph} \sim 1$, we can neglect the $T_p(x)$ dependence in region II, assuming for example $\gamma = \sigma I_0$ in (14).

[9] The inaccuracy is determined by the unknown and non-constant ratio of the recombination rates in the two possible recombination channels: 1) $R + A \rightarrow RA$ ($H'_{ph} = 107$ kcal/mole), 2) $2R \rightarrow R_2$ and $2A \rightarrow A_2$ ($H'_p = 119$ kcal/mole).

[10] The possibility of photodissociation of molecular iodine was not taken into account in [6]. As a result (in the case of a non-selective plasma pump source), and also in view of the inverse temperature dependence of the constant for the quenching of the iodine atoms by the iodine molecules, the onset of the iodine mechanism of shutting down the generation, which is considered in [6], is even more strongly limited than it follows from [6].

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