

## PHOTODISSOCIATION WAVES IN A GAS

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We investigate theoretically a new type of supersonic disturbances in a gas; these disturbances are connected with a wavelike photodissociation of the molecules under the influence of a quasimonochromatic radiation pulse of frequency  $\nu_{ph}$ . The effect takes place at high optical density of the gas at this frequency:  $D \gg 1$ . The density of the photon flux and the density of the excited atoms, the transitions in which can be used to generate the stimulated emission, depend on the argument  $t - x/v_{ph}$ , where  $v_{ph}$  is the velocity of the photodissociation wave. Estimates show that the effect of the photodissociation wave can be realized with the aid of pulses from plasma radiation sources, and also laser pulses. The velocity of the dissociation wave can exceed by several orders of magnitude the sound velocity in the gas, and comes close the velocity of light.

THE photodissociation of molecules<sup>[1-3]</sup> as a method of exciting the active medium of gas lasers was proposed by Rautian and Sobel'man<sup>[4]</sup>. This mechanism, which is discussed also in<sup>[5]</sup>, turned out to be effective, since it permits excitation of large volumes of active medium in a relatively broad spectral interval and to obtain stimulated-emission pulses of appreciable power and energy<sup>[6-10]</sup>. We consider below the process of excitation of a layer of gas in the photodissociation of molecules under the influence of a quasiharmonic radiation pulse. It is shown that if the optical density of the layer is large ( $D \gg 1$ ), the photodissociation process can have a wavelike character. An analogy is noted between the effect of the photodissociation wave, which leads to excitation of the gas, and the effect of the population-inversion wave in condensed media containing three-level absorbing centers<sup>[11,12]</sup>. The photodissociation wave is a new type of supersonic disturbance in the gas, with a velocity determined by the radiation flux density, and capable of approaching the velocity of light. The possible existence of the photodissociation-wave effects was noted in our earlier paper<sup>[12]</sup>.

## 1. QUALITATIVE CONSIDERATIONS

There is a significant difference between the photodissociation processes in the cases  $D \lesssim 1$  and  $D \gg 1$ . In the former case, which is realized for example in pulsed photolysis<sup>[2]</sup>, proposed by Norrish and Porter, the photodissociation process is spatially homogeneous. In the latter case, when  $D \gg 1$ , which so far has been investigated neither theoretically nor experimentally, an important role is played by the spatial inhomogeneity of the photon flux density in the medium.

Let the elementary act correspond to one of the reactions typical for photodissociations<sup>[2-10]</sup>  $RA + h\nu_{ph} \rightarrow R + A^*$ , in which the molecule  $RA$  breaks up under the influence of quasimonochromatic pump radiation corresponding to the spectral region of continuous absorption into a radical  $R$  and an excited complex, in particular an atom  $A^*$ , the transitions in which ensure generation of stimulated emission at a frequency  $\nu_g$ :  $A^* \rightarrow A + h\nu_g$ . We denote by  $\sigma_{ph}(\nu)$  and  $N_{RA}$  respectively the photodissociation cross section and the

equilibrium density of the molecules  $RA$  in the gas. We shall assume that the dependence of  $\sigma_{ph}$  on  $\nu$  in the pump-pulse frequency interval  $\Delta\nu_{ph}$  can be neglected. We neglect also the pump-photon losses not connected with photodissociation.

Using these premises, let us consider the process of photodissociation in a layer of gas of thickness  $l$  for the case of large optical densities ( $D = \sigma_{ph}N_{RA}l \gg 1$ ), at first qualitatively. The volume of the gas in which all the molecules are dissociated is transparent to the pump radiation during a time  $\tau_{rec}/2$ , where  $\tau_{rec}$  is the characteristic recombination time in the gas, during which products absorbing radiation of frequency  $\nu_{ph}$  are produced. When the gas is excited under equilibrium conditions, radiation is absorbed in a layer whose thickness is determined by the absorption coefficient at the frequency  $\nu$ :  $k_{ph}(\nu) = \sigma_{ph}(\nu)N_{RA}$ . As the molecules disintegrate, this layer becomes transparent and the radiation penetrates into the next layer. The region in which photodissociation takes place moves continuously inside the medium, and the process has a wavelike character. When the photodissociation wave is in the steady state, the particle density  $n_i$  ( $i = RA; R; A^*$ ) and the density  $\Phi$  of the pump-photon flux into the medium depend only on the argument  $t - x/v_{ph}$ , where  $v_{ph}$  is the velocity of the photodissociation wave.

The quantity  $v_{ph}$  at small photon flux densities  $\Phi_0$  on the boundary of the layer can be estimated from the condition of the balance of the number of absorbing centers in a plane-parallel layer of thickness  $\Delta x \approx 1/k_{ph}$  with transverse cross section  $S$ , and the pump-photon flux  $N_{RAS}\Delta x = \Phi_0 S \Delta t$  which enters the layer within a time  $\Delta t$ . Thus, the displacement velocity of the plane front of the photodissociation wave, leading to the bleaching of the gas in the frequency interval  $\Delta\nu_{ph}$ , is<sup>1)</sup>

$$v_{ph} = \Phi_0 / N_{RA}. \quad (1)$$

The foregoing qualitative picture is valid at dis-

<sup>1)</sup>If the radiating surface has the form of a cylinder of radius  $r_0$ , then the velocity of propagation of a photodissociation wave with a cylindrical front depends on the radius  $v_{ph} = \Phi_0 r_0 / N_{RA} r$ .

tances much larger than the molecule mean free path  $l^{(0)}$ , subject to additional assumptions connected with the influence of the relaxation and diffusion processes in the gas on the propagation of the photodissociation wave. The recombination of the molecules behind the wave front will lead to additional absorption of the radiation and, consequently, decrease the velocity of the wave. To exclude the influence of this factor, it is necessary to require satisfaction of the condition

$$l \lesssim v_{pl} \tau_{rec} / 2. \quad (2)$$

The diffusion of the unexcited molecules and dissociation products will lead to a stretching of the wave front. The influence of diffusion can be neglected if  $(D_{dif}/k_{ph}v_{ph})^{1/2} \lesssim k_{ph}^{-1}$ , where  $D_{dif}$  is the largest of the diffusion coefficients for the particles in the gas. The latter condition can be written in the form

$$\frac{1}{3} \frac{\bar{v}}{v_{ph}} D^{(0)} \lesssim 1, \quad (3)$$

where  $\bar{v}$  is the largest of the mean-square velocities of the molecules and atoms on the wave front, and  $D^{(0)}$  is the optical density of the gas layer over the mean free path  $l^{(0)}$ .

Photodissociation causes an increase in the number of particles in the bleached volume, and consequently a gradient of pressure exists on the wave front. The pressure drop produced in this manner can propagate in the gas in the form of a shock wave. Such a weak shock wave, with velocity  $v_{sh}$ , should arise when the velocity of the photodissociation wave decreases to values close to the velocity of sound  $v_s$ . The generation of the shock wave takes place at time intervals corresponding to the passage of the trailing edge of the pump pulse through the gas layer or when the photon flux is attenuated as a result of losses in the bleached region. In order for the kinetics of the shock waves not to distort the photodissociation wave front, it is necessary to satisfy the condition

$$v_{sh} < v_{ph}. \quad (4)$$

From relations (2)–(4) we can estimate the minimum energy flux densities at which the influence of recombination, diffusion, and shock waves can be neglected. The ratio of these quantities is

$$P_{rec} : P_{dif} : P_{sh} = 2l / \tau_{rec} : \bar{v} D^{(0)} / 3 : v_s q, \quad (5)$$

where the dimensionless coefficient  $q > 1$  is connected with satisfaction of condition (4), and  $v_s$  and  $v$  are of the same order of magnitude.

## 2. KINETICS OF PHOTODISSOCIATION WAVE

We now consider the bleaching resulting from photodissociation in the balance-equation approximation, assuming conditions (2)–(4) to be satisfied. In this case the kinetics of the photodissociation is described by the system of equations

$$\frac{\partial n_{RA}}{\partial t} = -\sigma_{ph} u c n_{RA}, \quad \frac{\partial u}{\partial t} + c \frac{\partial u}{\partial x} = -\sigma_{ph} u c n_{RA} \quad (6)$$

with initial and boundary conditions  $n_{RA}(x, t = 0) = N_{RA}$  and  $u(x = 0, t) = u_0$  respectively for the density of the absorbing molecules and for the density of the pump photons. Equations (6) coincide, apart from constant factors, with the equations describing the

kinetics of bleaching of optically dense media with two- and three-level absorbing centers<sup>[11–13] 2)</sup>.

The solutions of the system (6) in the case of a pulse of constant intensity have, deep inside the layer of gas at  $D \gg 1$ , a clear-cut wave-like form<sup>[12]</sup>:

$$n_{RA}(x, t) = N_{RA} \{1 + \exp[(t - x/v_{ph})\sigma_{ph}u_0c] - \exp(-D)\}^{-1}, \quad (7)$$

$$u(x, t) = u_0 \{1 + \exp[-(t - x/v_{ph})\sigma_{ph}u_0c] - \exp[-(t - x/c)\sigma_{ph}u_0c]\}^{-1}, \quad (8)$$

with the expression for the velocity of the photodissociation wave

$$v_{ph} = u_0 c (N_{RA} + u_0)^{-1} \quad (9)$$

agreeing with the estimate (1).

The photodissociation wave is formed on a finite distance  $x_1$  from the boundary of layer. The quantity  $x_1$  is determined by the condition  $\exp[-\sigma_{ph}N_{RA}x_1] \ll 1$ . In accordance with the solution (8), the width of the wave front, determined from the condition that the initial flux density of the photons be reduced by one order of magnitude, is  $l_f \approx 5/k_{ph}$ . The photodissociation wave covers this distance within a time  $\tau_{ph} \approx 5/\sigma_{ph}u_0c$ . The figure shows the profiles of the photodissociation wave, plotted in accordance with relations (7) and (8), for a mixture of the molecules RA with a buffer gas B in a coordinate system connected to the wave.

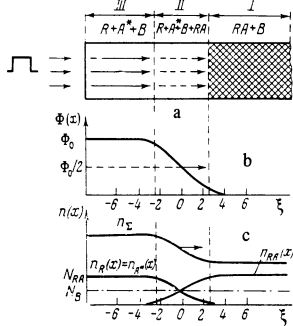
The applicability of solutions (7) and (8) on the wave front is limited by the condition  $D^{(0)} = \sigma_{ph}N_{RA}l^{(0)} \ll 1$ , which is connected with the balance-equation approximation, and the optical thickness of the medium over the mean free path  $l^{(0)}$  is determined, in order of magnitude, by the relation  $D^{(0)} \approx \sigma_{ph}/\sigma_{gas}$ , where  $\sigma_{gas}$  is the smallest of the gas-kinetic cross sections of the photodissociation products. The photodissociation cross section in the region of continuous absorption is  $\sigma_{ph} \lesssim 5 \times 10^{-18} \text{ cm}^2$ , whereas  $\sigma_{gas} \gtrsim 10^{-16} \text{ cm}^2$ , therefore  $D^{(0)} \lesssim 5 \times 10^{-2}$ . Thus, the condition for the applicability of solutions (7) and (8) on the front of the photodissociation wave is satisfied with a large margin, and the minimum value of the density of the quasi-monochromatic fluxes, necessary to excite the wave, is determined in accordance with the relation (5) by the larger of the quantities  $P_{rec}$  or  $P_{sh}$ .

It should be noted that the wavelike mechanism of photodissociation can take place also when the spectral interval  $\Delta\nu_{ph}$  corresponds to a discrete (line-band) spectrum and the decay of the molecules is by the induced predissociation mechanism. In this case the molecules absorb a quantum of energy  $h\nu_{ph}$  and decay as a result of collisions.

## 3. ESTIMATES OF THE DISSOCIATION WAVE PARAMETERS

Let us estimate the parameters of the photodissociation wave for two types of gaseous media containing iodine atoms: 1) a mixture of  $I_2$  with a buffer gas B; 2) a mixture of molecules RI with a buffer gas B. In both cases, we assume that the buffer gas does not absorb in the spectral region  $\Delta\nu_{ph}$ .

<sup>2)</sup>Analogous equations arise also in the problem of the amplification of a pulse of monochromatic radiation in an inverted medium (see, e.g. [14]).



Profiles of the photodissociation wave for the case of a rectangular radiation pulse in a layer of an optically dense gas consisting of molecules RA and atoms (molecules) of a buffer gas B. a – Three main regions occurring upon excitation of the photodissociation wave: I – unperturbed gas; II – region of front of the photodissociation wave, its optical density is  $\sim 5$ ; III – region of dissociated gas; b – density profile of flux of quasimonochromatic photons; c – density profiles of RA molecules, of the photodissociation products R and A\*, and also of the summary density  $n_\epsilon = n_{RA} + n_R + n_{A^*} + n_B$ , where  $n_B$  is the density of the particles of the absorbing buffer gas,  $\xi = \sigma_{ph} N_{RA} x$  is the optical thickness. The origin is located at the point for which  $\Phi = \Phi_0/2$ . The ratio of the partial pressures of the components in the initial mixture,  $p(B)/p(RA) = 0.5$ , corresponds to the case of photodissociation waves in the system  $I_2 + He$ , considered in Sec. 3. The arrows in cases b and c indicate the direction of wave motion.

The photodissociation processes in the system  $I_2 + B$  were thoroughly investigated by pulsed photolysis methods under conditions  $D(\nu) \lesssim 1$  by Norrish, Porter, et al.<sup>[15-16]</sup> (see also the review in the monograph by Kondrat'ev<sup>[2]</sup>).

The  $I_2$  absorption band connected with the photodissociation  $I_2 = h\nu_{ph} \rightarrow I(^2P_{3/2}) + I^*(^2P_{1/2})$  corresponds to wavelengths  $\lambda < \lambda_{lim}(I_2)$ , where  $\lambda_{lim}(I_2) = 4995 \text{ \AA}$  (<sup>[2]</sup>, p. 372), the half-width of the band in the continuous absorption region is  $\Delta\lambda_{ph} = 280 \text{ \AA}$ , and the photodissociation cross section, estimated in accordance with the data of Rabinowich and Wood<sup>[17]</sup>, is  $\sigma_{ph} = 2.2 \times 10^{-18} \text{ cm}^2$ . The recombination of atomic iodine is determined by the triple collisions  $I + I + X \rightarrow I_2 + X$ . The role of the third particle X is assumed most effectively by the molecule  $I_2$ <sup>[2, 15, 16]</sup>, and in this case the rate of recombination of the iodine atoms in the ground and excited states is the same<sup>[9, 15]</sup>.

The recombination kinetics for a medium of the first type is described by the equations

$$dn_{I_2}/dt = 1/2[k_B n_B + k_{I_2} n_{I_2} + k_I n_I] n_{I_2}^2; \quad (10)$$

$$2n_{I_2}(t) + n_I(t) = 2n_{I_2}^{(0)} + n_I^{(0)},$$

where  $n_I(t=0) = n_I^{(0)}$ ,  $n_{I_2}(t=0) = n_{I_2}^{(0)}$  are the initial densities of I and  $I_2$ ,  $n_B$  is the density of the buffer-gas particles,  $k_B$ ,  $k_{I_2}$ , and  $k_I$  are respectively the coefficients of trimolecular recombination in which the particles B,  $I_2$ , and I take part;  $n_X = a(T)p(X)$ ,  $a(T) = 3.54 \times 273T^{-1} \times 10^{16} [\text{cm}^{-3} (\text{mm Hg})^{-1}]$ , and  $p(X)$  is the pressure of the component X.

Am implicit solution of (10) is given by

$$t = \left[ \left( \frac{1}{2} + \alpha \right) k_I n_I^{(0)2} \right]^{-1} \left\{ \frac{n_I^{(0)}}{n_I} - 1 + \frac{1-2\beta}{1+2\alpha} \ln \left[ \left( 1 + \frac{1-2\beta}{2\alpha+\beta} \left( 1 - \frac{n_I}{n_I^{(0)}} \right) \right) \frac{n_I^{(0)}}{n_I} \right] \right\}, \quad (11)$$

where

$$\alpha = \frac{k_B n_B}{k_{I_2} n_{I_2}^{(0)}} + \frac{n_{I_2}^{(0)}}{n_I}, \quad \beta = \frac{k_I}{k_{I_2}}.$$

It follows from the solution (11) that the expression for the lifetime of the iodine atoms, determined from the condition  $n_I^0/n_I = e$ , can be written in the form  $\tau_{rec} = A/p^2(I_2)$ , where  $p(I_2)$  is the pressure of  $I_2$  prior to the excitation of the gas, and the quantity A does not depend on  $p(I_2)$  at a fixed ratio  $p(B)/p(I_2)$ . In the case of the mixture  $I_2 + He$  at  $T = 293^\circ \text{K}$  we have  $k_{I_2} = 760\kappa$ , and  $k_{He} = 0.84\kappa$ , where  $\kappa = 10^{-32} \text{ cm}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$ <sup>[15]</sup>. At small pressures  $p(I_2) \lesssim 1 \text{ mm Hg}$ , no noticeable contribution of collisions of the type  $X = I$  to the kinetics of trimolecular recombination were observed in the experiment. Assuming the photodissociation to be complete and putting  $p(B) = 0.5 p(I_2)$  and  $k_I = 0.1 k_{He}$ , we obtain a lower bound for  $\tau_{rec}$ , and with it  $A = 5.7 \times 10^{-4} \text{ sec} (\text{mm Hg})^{-2}$ .

The photon flux density necessary to excite the photodissociation wave can be realized with the aid of a gas-discharge radiation pulse. Let us estimate the effective temperature  $T_{eff}$  of the discharge, neglecting the contribution of the line spectrum and assuming that the radiation of the discharge in the spectral region  $\Delta\lambda_{ph}$  used for the photodissociation is described by the absolute black body model. Assuming that  $P_{rec}$  corresponds to the flux density of the gas-discharge radiation in 1 steradian, we obtain an estimate relating the effective temperature of the discharge with the parameters of the gas in which the photodissociation takes place:

$$T_{eff} = \frac{hc}{k\lambda_{ph}} \left[ \ln \left( 1 + \frac{\sigma_{ph} c \tau_{rec} \Delta\lambda_{ph}}{D\lambda_{ph}^4} \right) \right]^{-1}. \quad (12)$$

Using the values of  $\Delta\lambda_{ph}$ ,  $\sigma_{ph}$ , A, and T given above for the  $I_2 + He$  mixture at  $D = 10$ ,  $\lambda_{ph} = \lambda_{lim}$ , and  $p(I_2) = 1 \text{ mm Hg}$ , we obtain

$$P_{rec} = \frac{2h\nu_{ph} D p^2(I_2)}{\sigma_{ph} A} = 6.4 \cdot 10^3 \text{ W/cm}^2, \quad v_{ph} = \frac{2Dp(I_2)}{a\sigma_{ph} A} = 4.8 \text{ km/sec},$$

The foregoing value of  $v_{ph}$  is larger by one order of magnitude than the speed of sound in the unexcited mixture, and exceeds the velocity of the shock wave produced in the presence of a particle density discontinuity of the type  $I + I + He/I_2 + He$ . In accordance with (12) we have  $T_{eff} = 2.9 \times 10^4 \text{ K}$ .

Let us estimate the parameters of the photodissociation wave in gaseous media of the second type, used in photodissociation lasers under the condition  $D \lesssim 1$ . For different organic molecules RI ( $R = CH_3$ <sup>[6-8]</sup>,  $CF_3$ <sup>[6-10]</sup>,  $C_3F_7$ <sup>[8-10]</sup>, etc.), the maximum of the continuous absorption band, connected with the elementary photodissociation act  $RI + h\nu_{ph} \rightarrow R + I^*(^2P_{1/2})$  lies in the region  $\lambda_{ph} \approx 2500-2600 \text{ \AA}$ <sup>[18, 19]</sup>. The generation of the stimulated emission takes place at  $\lambda_g = 13150 \text{ \AA}$ , and is connected with allowed magnetic-dipole transitions  $I^*(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + h\nu_g$ . Owing to the chemical reaction that are excited in the gas under pulsed photolysis, the initial composition is not restored completely. Besides the recombination processes of the type  $R + I$  and  $I + I + X \rightarrow I_2 + X$ , there takes place the rapid bimolecular recombination reaction of the type  $R + R \rightarrow R_2$ , the coefficients of which are  $k(CH_3) = 3.7 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ <sup>[20]</sup> and  $k(CF_3) = 2.2$

$\times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ [21]. The radicals of the  $\text{CH}_3$  type produced in photodissociation, and also the products of recombination of  $\text{C}_2\text{H}_6$ , etc., practically do not absorb in the spectral photodissociation region  $\Delta\lambda_{\text{ph}}$  of the RI molecules [18,22].

Thus, the photon losses in the spectral interval  $\Delta\lambda_{\text{ph}}$  behind the front of the photodissociation wave will be determined by the formation of the RI molecules and possible  $\text{I}_2$ . For the gas  $\text{CF}_3\text{I}$ , the maximum value of  $\sigma_{\text{ph}}$  corresponds to  $\lambda = 2650 \text{ \AA}$ , and the half-width of the continuous absorption band, connected with the photodissociation, is  $\Delta\lambda_{\text{ph}} = 330 \text{ \AA}$  [10]. From the data of the same paper [10], the cross section for photodissociation in this region  $\Delta\lambda_{\text{ph}}$  is equal to  $5.4 \times 10^{-19} \text{ cm}^2$ , the lifetime of the iodine atoms at an initial-gas pressure  $p(\text{RI}) \lesssim 10 \text{ mm Hg}$  amounts to  $\sim 100 \mu\text{sec}$  [6]. At  $D = 10$  and  $p(\text{CF}_3\text{I}) = 5 \text{ mm Hg}$  we get  $P_{\text{rec}} = 3 \times 10^5 \text{ W/cm}^2$ ,  $v_{\text{ph}} = 20 \text{ km/sec}$ , and  $T_{\text{eff}} = 7 \times 10^4 \text{ K}$ . The obtained values of  $T_{\text{eff}}$  are estimates of the upper values of the effective temperatures, sufficient for the excitation of photodissociation waves in the systems  $\text{I}_2 + \text{B}$  and  $\text{RI} + \text{B}$ . The presently known pulsed plasma sources make it possible to obtain  $T_{\text{eff}} \approx 7 \times 10^4 \text{ K}$  in the visible region of the spectrum [23-25]. The indicated energy flux densities in the spectral intervals  $\Delta\lambda \lesssim 300 \text{ \AA}$  in the visible and ultraviolet regions can be obtained also with the aid of different types of pinch effects. Thus, for both types of gaseous media the effect of the photodissociation wave is observable upon excitation with radiation sources of the plasma type.

Let us consider the features of obtaining an inverted state in media of the first and second types. The ground and excited levels of the field belong to the split main term  ${}^2\text{P}^0$ , and the ratio of the statistical weights of these states is  $g({}^2\text{P}_{1/2})/g({}^2\text{P}_{3/2}) < 1$ . Therefore in excitation of a medium of the first type ( $\text{I}_2 + \text{B}$ ) and inverted state can appear<sup>3)</sup>. An excited medium of the second type corresponds to a fully inverted three-level system. Thus, the photodissociation wave in a gas medium of the type  $\text{RI} + \text{B}$  is analogous to the population-inversion wave in condensed media containing three-level centers [11,12].

#### 4. CONCLUSION

In addition to the shock wave, to the detonation wave, and to the absorption wave investigated by Raizer [26], the photodissociation wave is an independent type of supersonic disturbance in a gas. The features of each type of disturbance can be characterized by the propagation velocity, the wave front width  $l_f$ , and by the ratio  $n_-/n_+$ , where  $n_-$  is the density of the particles behind the front of the wave and  $n_+$  is the particle density ahead of the wave front. In the case of a photodissociation wave,  $n_-/n_+$  exceeds unity slightly.

<sup>3)</sup> Attempts to obtain generation with this system have so far been unsuccessful [8], a fact that can be explained, in view of the large lifetime of the excited state  $\text{I}^*({}^2\text{P}_{1/2})$  with respect to spontaneous transitions  $\sim 0.1 \text{ sec}$  [9,15], as being due to the effective quenching of the  $\text{I}^*$  atoms, determined by the resonant character of the energy transfer and by the short lifetime of the excited state of the molecule  $\text{I}_2$ . Such an assumption is indirectly confirmed by the fact that addition of  $\text{I}_2$  to systems of the type  $\text{RI} + \text{B}$  leads to suppression of the generation [8,10].

Such small values of  $n_-/n_+$  occur in weak shock waves having velocities close to that of sound [27]. In the case of shock waves, the particle density discontinuity occurs at distances on the order of the mean free path  $l^{(0)}$ . For a photodissociation wave  $l_f/l^{(0)} \approx 5\sigma_{\text{gas}}/\sigma_{\text{ph}} \gtrsim 100$ . The velocity of the photodissociation wave is determined by the density of the exciting radiation flux, and can exceed by several orders of magnitude the velocity of a shock wave on whose front the particle-density drop is the same as in the case of the photodissociation wave. Because of this, the weak shock wave can be overtaken by the photodissociation wave<sup>4)</sup>. With this, besides a change in the state of the gas, the parameters of the shock wave also change.

The limiting velocities of the photodissociation waves are determined by the multiphoton processes that take place at large energy flux densities. In this case, besides the wave-like single-photon photodissociation, there will take place competing processes - multiphoton excitation, photoionization, and multiphoton dissociation. Because of these processes, the photodissociation wave will go over into a Raizer absorption wave [28]. The direction of motion of such a wave is opposite the direction of motion of the photodissociation wave.

Notice should be taken of the possibility of excitation of photodissociation waves with the aid of monochromatic laser pulses. The emission the fourth harmonic by a neodymium-glass laser ( $\lambda_4 = 2650 \text{ \AA}$ ) corresponds to the region of photodissociation of molecules of the RI type. According to the data of Leblanc et al. [28], it is possible to obtain at the wavelength  $\lambda_4$  pulses with power  $2.5 \times 10^7 \text{ W}$ .

In accordance with expression (9) at  $p(\text{CF}_3\text{I}) = 1 \text{ mm Hg}$ ,  $T = 293^\circ \text{ K}$ , and emitting surface of area  $6 \text{ cm}^2$  [28], we obtain at the indicated value of the power

$$v_{\text{ph}} = c \left( 1 + \frac{ahc^2p}{P\lambda_{\text{ph}}} \right)^{-1} = 0.1c \quad \text{at } P = 4 \cdot 10^6 \text{ W/cm}^2$$

Thus, it becomes possible to realize experimentally conditions under which the front of the photodissociation wave moves with subluminal velocity.

In the elementary photodissociation act, an increase takes place in the kinetic energy of the reaction products compared with the initial kinetic energy of the molecule. This means that when the photodissociation wave passes the Maxwellian velocity distribution is disturbed. As a result, relaxation will take place in the gas to a new quasiequilibrium state. Thus, the photodissociation wave corresponds to a "Maxwellization wave" of the distribution function, behind the front of which a state of dissociated gas with temperature exceeding the temperature of the initial undissociated gas is established and exists for a time on the order of  $\tau_{\text{rec}}/2$ .

In conclusion we note two possible applications of the effect of the photodissociation wave. This effect makes it possible to excite weak shock waves, which are produced when the photodissociation wave is decelerated. The possibility of obtaining a photodissociation wave with close velocities  $v_{\text{ph}}$  and the selectivity of the action of the quasimonochromatic radiation flux,

<sup>4)</sup> When a shock wave passes through a gas, vibrational degrees of freedom of the gas molecules can become excited, and consequently a change can take place in the value of  $\sigma_{\text{ph}}$  in the spectral region  $\Delta\lambda_{\text{ph}}$ .

make it possible to use the predicted effect for the investigation of molecular parameters and the kinetics of rapidly occurring processes in gases. Notice should also be taken of the possible realization of the photo-dissociation wave effect in astrophysical and geophysical conditions at small gas pressures.

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102