SOVIET PHYSICS JETP VOLUME 31, NUMBER 3 SEPTEMBER, 1970

THEORY OF A STIMULATED RADIATIVE CHEMICAL REACTION IN GASES AND THE POSSIBILITY OF ITS USE IN LASERS

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Submitted April 26, 1969

Zh. Eksp. Teor. Fiz. 58, 854–864 (March, 1970)

The contribution to the complex dielectric constant of a gas mixture due to a radiative chemical reaction between the gases is calculated. The optical properties of a reacting mixture of gases are determined, including the coefficient of absorption or amplification of light, the intensity of chemiluminescence, and their frequency dependence. The formation of diatomic molecules from atoms is quantitatively analyzed.

Self-stimulation of a radiative reaction by the light emitted during the reaction is considered. It is shown that the reaction can be divided into two stages: 1) a comparatively long period of accumulation of photons associated with a very slow chemical reaction, and 2) a subsequent short time period of rapid chemical reaction. The possibility of using a self-stimulated reaction to make a chemical laser, which was proposed in[8], is considered. According to estimates, in such a laser with an initial concentration of 10^{19} atoms per cm^3, a coefficient of light amplification between 1 and 10 dB/cm is obtained, the pulse time of the reaction $\sim 10^{-9}$ sec, and the power per cm^3 $\sim 3 \times 10^9$ W.

AT the present time chemical lasers, in which excited gas molecules appear as the result of a chemical reaction and their de-excitation serves as the basic mechanism of the laser, are well known.[1-7] In this connection a radiative transition of the electrons is accomplished in a molecule without its chemical change. However, as noted by one of the authors,[8] other cases when a photo-transition is accomplished during the time of an elementary event of the chemical reaction itself are also of interest. Precisely such cases will be theoretically investigated in the present article.

Let us assume that there are two types of molecules in the gas which are able to participate in an exothermal chemical reaction. The latter represents a change of the electronic state during the collision and strong interaction of these molecules. Usually the excess energy is given to a third molecule, or else it is carried away by the molecules of the reaction products. However, another competing radiative reaction mechanism also exists in which the above-mentioned change of the electronic state is a photo-transition, and the excess energy luminesces. The first, i.e., the thermal-reaction mechanism, dominates most frequently. But in the presence of a sufficiently intense light wave, a stimulated photo-transition may turn out to be the dominant radiative mechanism.[8] The goal of the present work is a calculation of the rate of a stimulated radiative reaction and an investigation of the feasibility of its use in a laser.

A quantitative calculation will be carried out for the simplest model—a model of monatomic molecules. The results may be used for estimates even in the case of molecules containing many atoms.

In the first place the imaginary part of the dielectric constant of a reacting gas will be calculated. From it we determine the coefficient of amplification (absorption) of the light wave that stimulates the reaction, and the number of elementary reaction events per unit time.

1. DERIVATION OF A GENERAL EXPRESSION FOR THE IMAGINARY PART OF THE DIELECTRIC CONSTANT OF A REACTING GAS

Let us assume that the concentrations of the first and second types of atoms entering into the reaction are n_1 and n_2, and the concentration of the reaction product is negligible. We are interested in the frequency range of the radiation that appears in connection with the chemical reaction. Let us assume that this range does not overlap with the absorption spectra of isolated atoms. Then only pairs of adjacent, reacting, unlike atoms will absorb light. This absorption is cancelled if the concentrations n_1 or n_2 vanish. Therefore a phenomenological expansion of the imaginary part of ϵ in powers of the concentrations has the form

$$\operatorname{Im} \varepsilon = a n_1 n_2 + \dots . \tag{1}$$

In order to determine the coefficient a, it is sufficient to calculate Im ϵ for a single pair of atoms of different type.

One can obtain a general expression for Im ϵ by using the density matrix method:[9] [1)]

$$\operatorname{Im} \varepsilon = \frac{4\pi e^2}{\hbar\omega^2} \operatorname{Re} \lim_{\eta \to +0} \int_{-\infty}^{0} e^{(-i\omega+\eta)t} \times \operatorname{Sp} R \left(v_x e^{iHt/\hbar} v_x e^{-iHt/\hbar} - e^{iHt/\hbar} v_x e^{-iHt/\hbar} v_x\right) dt. \tag{2}$$

Here ω denotes the frequency of the light, H is the energy operator of the system unperturbed by the light, R is the density operator of the unperturbed system, and $\mathbf{v} = \sum_i \mathbf{v}_i$, where $\mathbf{v}_i$ denotes the velocity operator of the i-th electron.

[1)] Our formula (2) differs somewhat from the one obtained in [9] since we have used a more exact expression for the energy of interaction between the system and the electromagnetic wave, $V = -(e/c) \sum_i \mathbf{v}_i \cdot \mathbf{A}_i$ (A denotes the vector potential of the wave). The expression $V = -\mathbf{p} \cdot \mathbf{E}$ is used in [9] (p denotes the dipole moment, E is the electric field), which is suitable in the case of a potential field.

We choose the origin of coordinates at the center of mass of a pair of atoms, we denote the relative coordinate of the two nuclei by r, the reduced mass by μ, the total set of coordinates of all electrons by ρ, and we shall calculate the trace over the total system of orthogonal functions $\varphi_{gm}(\rho, r) = \Phi_{gm}(r)\psi_g(\rho, r)$ where $\psi_g(\rho, r)$ denotes the wave function of the electrons calculated in the adiabatic approximation, i.e., for a fixed value of r, notably

$$H = -\frac{\hbar^2}{2\mu}\Delta_r + \mathscr{H}(\rho, r), \quad \mathscr{H}(\rho, r)\psi_g(\rho, r) = U_g(r)\psi_g(\rho, r). \tag{3}$$

Here $\mathscr{H}(\rho, r)$ includes the kinetic energy of the electrons and the potential energy of their interaction among themselves and with the nuclei, but also includes the Coulomb interaction of the nuclei; $U_g(r)$ denotes the potential energy of the nuclei when the electrons are found in the state g.

According to the adiabatic approximation $\psi_g(\rho, r)$ is a slowly varying function of r. Therefore, introducing the notation $H_g = -(\hbar^2/2\mu)\Delta_r + U_g(r)$, we have approximately

$$H\Phi_{gm}(r)\psi_g(\rho, r) \cong \psi_g(\rho, r)H_g\Phi_{gm}(r) = E_{gm}\Phi_{gm}(r)\psi_g(\rho, r). \tag{4}$$

Here $\Phi_{gm}(r)$ is the wave function describing the translational relative motion of the atoms, m is the total set of quantum numbers determining this motion, and E_{gm} denotes the energy of the translational motion of the atoms, which coincides with the total energy of the system.

We shall define the density operator R in terms of its matrix. We require that the matrix R be diagonal in the energy representation, but arbitrary otherwise. In the adiabatic approximation this means that the matrix R is diagonal for the basis $\varphi_{gm}(\rho, r)$. Introducing the notation $\langle g|R|g'\rangle = \delta_{gg'}R_g(H_g)$, one can rewrite Eq. (2) in the adiabatic approximation in the form

$$\operatorname{Im}\varepsilon = \frac{4\pi e^2}{\hbar\omega^2}\operatorname{Re}\lim_{\eta\to+0}\int_{-\infty}^{0} e^{(-i\omega+\eta)t}\sum_{gg'}\operatorname{Sp}_r[R_g(H_g) - R_{g'}(H_{g'})]$$
$$\times|v_{x_{gg'}}|^2\exp\left(\frac{i}{\hbar}H_{g'}t\right)\exp\left(-\frac{i}{\hbar}H_g t\right)dt. \tag{5}$$

It was assumed above that the population of bound states of the atoms is negligible. This means that for the bound states one should set $R_g(E_{gm}) = 0$. For dissociated states $R_g(E_{gm})$ is proportional to the inverse volume of the gas. If this volume is set equal to unity, then formula (5) will express the quantity (1) when $n_1 = n_2 = 1$, i.e., the coefficient a.

2. CALCULATION OF THE IMAGINARY PART OF THE DIELECTRIC CONSTANT, THE COEFFICIENT OF AMPLIFICATION OF A LIGHT WAVE, AND THE RATE OF STIMULATED CHEMICAL REACTION FOR QUASICLASSICAL MOTION OF THE NUCLEI

For quasiclassical motion of the nuclei, the terms Δ_r and $U_g(r)$ in the operator H_g should be assumed to approximately commute. Therefore, in Eq. (5) one can replace the product of exponential functions by $\exp(i\Omega_{g'g}t)$, where

$$\Omega_{g'g}(r) \equiv \frac{1}{\hbar}[U_{g'}(r) - U_g(r)]. \tag{6}$$

After this in Eq. (5) one can integrate over t, as a result one obtains

$$\operatorname{Re}\lim_{\eta\to+0}\int_{-\infty}^{0} e^{i(\Omega_{g'g}-\omega)t+\eta t}\,dt = \pi\delta[\Omega_{g'g}(r) - \omega]. \tag{7}$$

It is now convenient to calculate the trace in formula (5) for the complete system of Fourier functions $e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$, where V is the volume of periodicity. Then with Eqs. (1), (6), and (7) taken into account, one obtains from Eq. (5)

$$\operatorname{Im}\varepsilon = \frac{16\pi^3 e^2}{\omega^2}\sum_{gg'j}[P_g(r_j) - P_{g'}(r_j)]\,|v_{x_{gg'}}(r_j)|^2\frac{r_j^2 V n_1 n_2}{|F_g(r_j) - F_{g'}(r_j)|}, \tag{8}$$

where the r_j are the distances between the nuclei at which the argument of the δ-function in Eq. (7) vanishes, $F_g(r) \equiv -\partial U_g/\partial r$ is the force acting between the nuclei, and

$$P_g(r) \equiv \frac{1}{V}\sum_{\mathbf{k}} R_g\left(\frac{\hbar^2\mathbf{k}^2}{2\mu} + U_g(r)\right). \tag{9}$$

According to the well known properties of the diagonal elements of the density matrix R_g, $P_g(r)dxdydz$ is the probability that the projections of the relative coordinate r will have values in the following intervals: from x to (x + dx), y to (y + dy), and z to (z + dz); the potential energy of the interaction between the nuclei is equal to $U_g(r)$.

In order to clarify how one should choose R_g, as an example let us consider the case when $U_g(r)$ has the form shown in Fig. 1. On it some of the curves of $U_g(r)$ vanish asymptotically as $r \to \infty$. Other curves (one of them is shown in the figure) here asymptotically tend to a constant positive value $U_2(\infty)$ where among the curves of the second type there are some which intersect curves of the first type. Such a type of $U_g(r)$ is often encountered, for example, when the molecule is heteropolar in the ground state (the curve $U_2(r)$), and for large values of r the energy is lower in the states of the neutral atoms (the curves $U_1(r)$ and $U_3(r)$). Thus, for the interaction between a hydrogen atom and a chlorine atom, the diatomic molecule possesses an appreciable dipole moment in its ground state. But as $r \to \infty$ the state consisting of neutral atoms has a much lower energy since the separation of an electron from a Cl^- ion uses up an energy of 3.7 to 3.8 eV, but upon the neutralization of the H^+ ion 13.6 eV of energy is released. Thus, $U_2(\infty)$ is of the order of +10 eV.

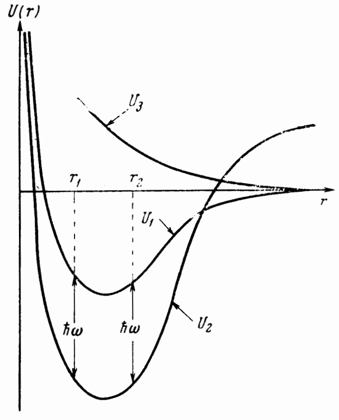

FIG. 1

Going on to the choice of the average population R_g according to the assumption made at the beginning of Sec. 1, we shall assume that no bound molecules at all are present in the gas, i.e., the corresponding $R_g = 0$; in the case shown in Fig. 1, $R_2 = 0$. We assume an equilibrium Gibbs distribution with a certain temperature T for the populations of all dissociated states of the atoms. Therefore we assume

$$R_g = C\Theta(H_g)e^{-H_g/T},$$

$$\Theta(x) = \begin{cases} 1 \text{ for } x \geqslant 0 \\ 0 \text{ for } x < 0 \end{cases} \qquad C^{-1} = \sum_g \int R_g\, d^3r. \tag{10}$$

Here H_g is the classical expression for the total energy of the relative motion of the nuclei. From Eqs. (9) and (10) one obtains

$$P_g(r) = \frac{1}{VG}\begin{cases} e^{-U_g/T} & \text{for } U_g(r) > 0, \\ 2\pi^{-1/2}\sqrt{-U_g/T} + [1 - \Phi(\sqrt{-U_g/T})]e^{-U_g/T} & \text{for } U_g(r) < 0 \end{cases}$$

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\, dt. \tag{11}$$

From the normalization condition one obtains $C = (GV)^{-1}(2\pi\hbar^2/\mu T)^{3/2}$. Here G denotes the number of electronic states (the number of values of the index g) for which $U_g(\infty) = 0$. For all other electronic states we assume $U_g(\infty) \gg T$, and for them the population $R_g = 0$.

We note that at first glance the right hand side of Eq. (8) appears to be equal to zero because of the antisymmetry of the expression which is summed over the indices g and g′. This is actually not so since r_j also depends on g and g′; however these indices for r_j are omitted in order to simplify the notation.

From Im ε one can easily find the imaginary part of the index of refraction n of light in the gas, $\text{Im}\, n \approx (1/2)\text{Im}\, \epsilon$. If the intensity of the light wave increases in space according to the law $I(x) = I(0)e^{\alpha x}$, then we obtain for the gain α

$$\alpha = -\frac{\omega}{c}\text{Im}\, \varepsilon. \tag{12}$$

We define the rate W of formation of diatomic molecules from atoms by a chemical reaction stimulated by light as the number of elementary reaction events per cm^3 per sec. One can easily calculate W by comparing the energy given to the light wave by the electrons per cm^3 per sec, $W\hbar\omega$, with the divergence dI/dx of the intensity of the wave. As a result one obtains

$$W = \frac{\alpha}{\hbar\omega}I(x). \tag{13}$$

Now let us present a criterion for the validity of the quasiclassical treatment of the motion of the nuclei, which was used above. It is necessary and sufficient that the inequality $(\hbar\mu F_g(r_j)/p^3)^2 \ll 1$ be satisfied at the points r_j, where p denotes the larger of the quantities $\sqrt{-2\mu_g(r_j)}$ or $\sqrt{2\mu T}$. A derivation of this criterion is given in article[10].

In the case when $U_g(r_j)$ is of the order of 1 eV, the criterion for the quasiclassical nature of the process is always well satisfied. However, if $U_g(r_j) < T$, then the criterion is satisfied only at sufficiently high temperatures. For example, if $F_g(r_j)$ is of the order of 10^8 eV/cm and $\mu = 4 \times 10^{-23}$ g, then the temperature must appreciably exceed 300°K.

3. ESTIMATES OF THE COEFFICIENT OF AMPLIFICATION OF THE LIGHT WAVE AND OF THE STIMULATED CHEMICAL REACTION RATE

In general there are both positive and negative terms in the summation over g and g′ in Eq. (8). The first type causes light absorption; the second causes amplification. The ratio of the magnitudes of these terms may be very different. In order to obtain an estimate, let us consider the case when one term corresponding to amplification dominates in the summation, for example, the transition $g' = 1 \rightarrow g = 2$ shown in Fig. 1. Here the sum over j contains two negative terms. Let us estimate one of them.

Let us assume $U_1(r_j) = 1$ eV, $T = 0.025$ eV (300°K), $G = 2$, $|v_{x_{12}}(r_j)| = \omega \times 10^{-8}$ cm/sec, $r_j = 10^{-8}$ cm, $|F_1(r_j) - F_2(r_j)| = 10^8$ eV/cm, $\omega/c = 10^5\ cm^{-1}$, and $n_1 = n_2 = 10^{19}\ cm^{-3}$. In this connection one obtains $P_1 = 3.6/V$, $P_2 = 0$, and $\alpha = 0.25\ cm^{-1}$.

Cases are possible in which $F_1(r_j) = F_2(r_j)$ at a certain frequency ω_0. In fact, if one determines r_j^0 from the last equality, then the corresponding frequency ω_0 is determined by the equation $\omega_0 = \Omega_{12}(r_j^0)$. In this case in Eq. (8) the denominator of the term with $g' = 1$, $g = 2$ cancels, which means $\alpha = \infty$. It is obvious that in this case the approximations used to derive Eq. (8) are inadequate. It is necessary to take into account the finite nature of the linewidth of the radiation for a fixed value of r, the finite width being due to the fact that U_1 and U_2 are not the exact energy levels of the electronic subsystem (the perturbation due to the non-adiabatic nature of the process and other effects have been neglected). A more general calculation, taking account of the nonstationary nature of the levels U_1 and U_2 (which we do not cite in this article) leads to the following changes: on the right hand side of Eq. (7) one should write $\Gamma_{12}/\pi\{[\Omega_{12}(r) - \omega]^2 + \Gamma_{12}^2\}$ instead of $\delta[\Omega_{12}(r) - \omega]$, where Γ_{12} is the sum of the reciprocal lifetimes of the initial and final states of the system with respect to thermal transitions to any other state. As a result of such a generalization a term of the quantity (8) remains finite for arbitrary values of the difference $|F_1(r_j) - F_2(r_j)|$.

In particular, in the case $F_1(r_j^0) = F_2(r_j^0)$ mentioned above one obtains the following value for the gain α_0 upon taking account of the dominant term in the sum (8):

$$\alpha_0 = \frac{16\pi^3 e^2 P_1(r_j^0)(r_j^0)^2 V n_1 n_2}{c\hbar\omega_0}|v_{x_{12}}(r_j^0)|^2\left(\Gamma_{12}\left|\frac{\partial^2\Omega_{12}}{\partial r^2}\right|_{r_j^0}\right)^{-1/2}. \tag{14}$$

One can use formula (8) as long as the value of $|F_1(r_j) - F_2(r_j)|$ is not too small so that here the resulting $\alpha \ll \alpha_0$.

In order to estimate the value of α_0 we use the same values of all parameters as were used above in order to estimate α. But instead of the quantity $|F_1(r_j) - F_2(r_j)|$ which appeared in the expression for α, the quantity $\hbar\sqrt{\Gamma_{12}|\partial^2\Omega_{12}/\partial r^2|_{r_j^0}}$ enters into α_0, and one must estimate its value. In order to estimate this quantity let us assume that the point r_j^0 is located in a region where the curves $U_1(r)$ and $U_2(r)$ can be approximated by parabolas, we assume that the infrared frequencies of the vibrations of the nuclei in the states 1 and 2 are equal to ω_i

in order of magnitude, and the difference between the squares of the frequencies in these states will be of the order of $(1/2)\omega_i^2$.

In order to estimate Γ_{12} let us assume that the lifetime of the system in state 1 or state 2 is equal to s periods of the infrared vibrations. Thus, $\Gamma_{12} = \omega_i/2\pi s$. As a result one obtains

$$\hbar\sqrt{\Gamma_{12}\left|\partial^2\Omega_{12}/\partial r^2\right|_{r_j^0}} \sim \sqrt{\mu\hbar\omega_i^3/4\pi s}. \tag{15}$$

For a numerical estimate of this quantity, let us take $\mu = 4 \times 10^{-23}$ g and $\hbar\omega_i = 0.1$ eV. In order to estimate s, let us assume that a thermal transition of the system from state 2 (or state 1) to any other state g takes place near a point of intersection or close approach of the curves $U_2(r)$ and $U_g(r)$. For each passage of the system through this point we assume the probability of a thermal transition to be equal to 10^{-2};[11] thus s = 50. As a result a value for (15) on the order of 1.6×10^{-5} g cm/sec² is obtained. Here $\alpha_0 = 2.5$ cm^{-1}, i.e., the gain is very large.

Now let us go on to an estimate of the rate of a chemical reaction stimulated by light. It is determined by formula (13). If the gas is irradiated by light from an extraneous source with $I = 10^5$ W/cm², then for $\hbar\omega = 2$ eV and $\alpha = 0.25$ cm^{-1} ($n_1 = n_2 = 10^{19}$ cm^{-3}) one obtains $W = 10^{23}$ cm$^{-3}\cdot$sec^{-1}. Therefore, all of the initial atoms are combined into molecules after 10^{-4} sec.

It is of interest to determine the reaction rate under conditions when the gas is located in a reflecting container and the reaction is stimulated by the light created during the course of the reaction. Let us assume for simplicity that the mirror surfaces possess 100 percent reflectivity, and that at the instant of time t = 0 light of intensity I_0, exceeding the threshold of the laser regime, already exists in the space. Let $n_1 = n_2 = n$ be the concentrations of the gas atoms which have not reacted. The kinetics of the stimulated reaction is described by the equation

$$\frac{\partial n}{\partial t} = -W \equiv -\beta I n^2, \quad I = I_0 + (n_0 - n)\hbar\omega c, \tag{16}$$

where $\beta \equiv \alpha/\hbar\omega n_1 n_2$ is a constant which does not depend on n_1 or n_2 (see Eqs. (8) and (12)). If n_0 denotes the concentration of atoms which have not reacted at the moment t = 0, the initial photon concentration $q_0 = I_0/\hbar\omega c$, $\tau^{-1} = \beta\hbar\omega c(n_0 + q_0)^2$, and if we introduce the dimensionless concentration of atoms $z = n/(n_0 + q_0)$, then the solution of Eq. (16) has the form

$$\frac{1}{z} + \ln\left(\frac{1}{z} - 1\right) = \frac{t}{\tau} + \text{const.} \tag{17}$$

This dependence is shown in Fig. 2, on which it is necessary to choose the point t = 0 to be that place where z corresponds to the initial concentration n_0.

The first of Eqs. (16) does not take into account the absorption of light by the diatomic molecules which are produced as a result of the reaction, which corresponds to the assumption of infinitely rapid removal of these molecules. If such a removal actually does not occur, then the dependence shown in Fig. 2 is valid only at not too small values of z. The largest reaction rate W_{max} is reached for z = 2/3. It is given by $W_{max} = 4(n_0 + q_0)/27\tau$.

The reaction is characterized by two effective times:

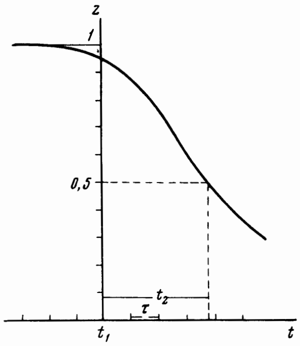

FIG. 2

1) a time t_1 of an accumulation of photons, during the course of which their concentration increases by many orders of magnitude, but the concentration of atoms decreases by only 1 to 5%, $t_1 = \tau\ln(n_0/q_0)$; 2) a subsequent period t_2 of rapid change of the concentration, during the course of which z changes from 0.95 to 0.5; $t_2 = 4\tau$.

Let us consider a numerical example: $n_0 = 10^{19}$ cm^{-3} and $\alpha = 0.25$ cm^{-1}. Here one obtains $\tau = 1.3 \times 10^{-10}$ sec, $W_{max} = 10^{28}$ cm$^{-3}\cdot$sec^{-1}, and $t_2 = 5.2 \times 10^{-10}$ sec. For $q_0 = 100$ photons/cm³ in a single mode one obtains $t_1 = 5.2 \times 10^{-9}$ sec. Thus, a stimulated reaction will bear the nature of an explosion.

Now let us estimate the time of the same reaction, but taking place in connection with spontaneous phototransitions. αc photons are radiated in each mode per cm³ per sec. In the interval of frequencies $d\omega$ there are $(\omega^2/\pi^2c^3)d\omega$ modes. Therefore, the reaction rate associated with spontaneous transitions is given by

$$W_{sp} = \frac{1}{\pi^2c^2}\int \alpha(\omega)\,\omega^2\,d\omega \sim \frac{\alpha_m\omega_m{}^2}{\pi^2c^3}\Delta\omega, \tag{18}$$

where $\Delta\omega$ is the effective width of the band of spontaneous radiation of light, and α_m and ω_m are the values of these quantities at maximum intensity of the radiation.

For $\alpha = 2.5$ cm^{-1}, $\Delta\omega = 0.1\,\omega_m$, $\hbar\omega_m = 2$ eV, one obtains W_{sp} of the order of 7.5×10^{23} cm$^{-3}\cdot$sec^{-1}. Here the reaction time is of the order of 10^{-5} sec. This time is appreciably larger than the time t_1 during which the stimulated reaction occurs. Thus, spontaneous transitions cannot compete with stimulated transitions.

4. FEASIBILITY OF CONSTRUCTING A LASER THAT OPERATES BY USING A STIMULATED CHEMICAL REACTION

Let the distance between the laser mirrors be L and let all the space between the mirrors be occupied by atoms of the first and second types. Let $1 - r$ denote the fraction of the light energy which is lost during propagation of the light from mirror to mirror, including reflection from one of the mirrors. Then, as usual, the condition for amplification of the light wave has the form $re^{\alpha L} > 1$. In order to maintain a large value of α, an inversion of the populations of the levels is required, i.e., a predominance of the concentrations of the atoms over the concentration of bound molecules. One can guarantee this, for example, by a sufficiently rapid "blowing out" of the gas through the space between the mirrors.

For L = 100 cm and r = 0.9 one obtains $\alpha > 10^{-3}\ \mathrm{cm}^{-1}$ from the criterion cited above. For the values of the parameters used above in order to estimate α_0, this criterion is satisfied for $n > 2 \times 10^{17}\ \mathrm{cm}^{-3}$.

Let us consider in more detail the case when the reaction product has not moved away completely, the reaction takes place as a pulse and is damped when the concentration of the bound molecules becomes comparable with the concentration of atoms. The kinetics of such a reaction (with the exception of its last damping phase) is described by formula (17) and Fig. 2. The energy radiated spontaneously will be small in comparison with the stimulated-radiation energy radiated if t_1 is much smaller than n_0/W_{sp}. This reduces to the inequality

$$\ln\frac{n_0}{q_0} \ll \frac{\pi^2 c^3 n_0}{\omega_m{}^2 \Delta\omega}. \tag{19}$$

Here α does not appear at all. Inequality (19) is already satisfied at the threshold concentrations n_0, even if one sets $\Delta\omega = \omega_{\mathrm{m}}$.

The light energy released during the duration of a pulsed reaction, referred to a unit volume of the gas, is of the order of $\hbar\omega n_0/2$, which for $\hbar\omega = 2$ eV and $n_0 = 10^{19}\ \mathrm{cm}^{-3}$ is equal to 1.6 J/cm^3. The average power of the light energy radiated per cm^3 is equal to $\hbar\omega n_0/2t_2 = (1/8)c\beta(\hbar\omega)^2 n_0^3$, which amounts to $3 \times 10^9\ \mathrm{W \cdot cm^{-3}}$ for $\hbar\omega = 2$ eV, $n_0 = 10^{19}\ \mathrm{cm}^{-3}$, and $\alpha = 0.25\ \mathrm{cm}^{-1}$.

For given values of $\alpha(\omega)$ and $r(\omega)$ the theory of a laser may be developed without choosing a specific model for the working substance. Therefore, in the case under consideration the theory of the laser will have the same form as in all other cases.

It was assumed above that during the time t_1 the light wave is able to traverse the distance between the mirrors many times. However, the opposite case $t_1 c < L$ is also possible, in which case the mirrors cease to play a role. This case will be separately considered in the following Section.

5. REACTION IN THE REGIME OF MULTIMODE SUPERLUMINESCENCE

Let us assume that the linear dimensions of the space occupied by the gas exceed $t_1 c$ in all directions, i.e., during the time of the reaction the radiation is not able to escape beyond the limits of the gas. In this case one can use the approximation of an infinite gaseous medium and an isotropic, coordinate-independent intensity of the light. One can relate the calculation to a unit volume of the gas. Let us assume, just as above, that the concentration of the bound molecules being generated is negligible.

Let q_ω denote the concentration of photons in any of the modes possessing a frequency ω. This concentration is determined from the equations

$$\frac{\partial q_\omega}{\partial t} = c\alpha(\omega)(q_\omega + 1) \equiv c\beta(\omega)\hbar\omega n^2 (q_\omega + 1), \tag{20}$$

$$\frac{\partial n}{\partial t} = -cn^2 \sum \beta(\omega)\hbar\omega(q_\omega + 1) \quad \text{or} \quad \sum q_\omega = n_0 - n, \tag{21}$$

where Σ denotes a sum over all modes and over the two polarizations of light. It is assumed that no radiation is present in the volume at t = 0. Just as in Sec. 3, one can divide the reaction into two stages: 1) a period of accumulation of photons associated with an almost unchanged value of n with an effective time t′, and 2) a subsequent period involving a rapid change of n with an effective time t″.

During the course of the first period, in Eq. (20) we assume $n = n_0$ and we obtain

$$q_\omega + 1 = \exp\{c\beta\hbar\omega n_0{}^2 t\}. \tag{22}$$

We determine the value of t′ from the condition that $0.05\ n_0$ of the atoms react during the first period: $\Sigma q_\omega(t') = 0.05\ n_0$. In order to evaluate this sum, we expand $\alpha(\omega)$ near its maximum in powers of $\omega - \omega_{\mathrm{m}}$: $\alpha(\omega) = \alpha_{\mathrm{m}} - \gamma(\omega - \omega_{\mathrm{m}})^2$. As a result the following equation is obtained for t′:

$$\frac{e^u}{\sqrt{u}} = \frac{\pi^{3/2} c^3}{\omega_m{}^2} 0{,}05 n_0 \sqrt{\frac{\gamma}{\alpha_m}}, \quad u \equiv c\alpha_m t'. \tag{23}$$

The spectral distribution of the intensity of the radiation approximately coincides with the distribution of the quantity (22). The half-width of this distribution is given by $\delta\omega = 2\sqrt{(c\gamma t)^{-1}\ln 2}$, i.e., the radiation band narrows with time.

Passing to an examination of the second stage of the reaction, let us assume that at the moment t′ the quantity $\delta\omega$ is considerably smaller than the half-width of the curve $\alpha(\omega)$. In this case, in the first of the formulas (21) one can take $\omega\beta(\omega)$, as a slowly varying function of ω, outside of the summation sign at the point ω_{m}. As a result this formula coincides with Eq. (16) in which one should set $I_0 = q_0 = 0$ and $\beta = \beta(\omega_{\mathrm{m}})$. The solution of this equation is given by formula (17) and is shown in Fig. 2. Thus, the duration of the second stage of the reaction, at the end of which $n = n_0/2$, is $t'' = 4\tau$, in the same way as in Sec. 3 but in the expression for τ one should set $q_0 = 0$ and $\beta = \beta(\omega_{\mathrm{m}})$.

In order to determine $q_\omega(t)$ during the second stage of the reaction, we eliminate $n^2 dt$ from Eqs. (20) and (21). One can easily integrate the obtained equation, and as a result one obtains

$$\frac{q_\omega + 1}{q_\omega{}' + 1} = \left(\frac{1 - z}{1 - z'}\right)^{\alpha(\omega)/\alpha_m}, \tag{24}$$

where q'_ω and z′ denote the concentrations of photons and atoms at the moment t = t′. Having substituted z′ = 0.95 and q'_ω from formula (22) into Eq. (24), we obtain

$$q_\omega + 1 = \left[\frac{e^u}{0{,}05}(1 - z)\right]^{\alpha(\omega)/\alpha_m}. \tag{25}$$

This formula determines the time dependence of q_ω if one substitutes z(t) from Eq. (17) or from Fig. 2 into it.

The moment of time t′, dividing the two periods in which different approximations were used above in order to solve Eqs. (20) and (21), was to a considerable extent chosen arbitrarily. Therefore, the obtained results are only valid in that case when they are slightly sensitive to the choice of t′. We show that this is actually so upon consideration of numerical examples.

It was assumed above that near its maximum $\alpha(\omega)$ is an even function of $\omega - \omega_{\mathrm{m}}$. However, if the maximum of α is located at a point ω_0 corresponding to a transition to a configuration r_j^0 for which $\Omega_{12}(r)$ has an extremum, then $\alpha(\omega)$ is extremely asymmetric in the neighborhood of the maximum: if $\Omega_{12}(r)$ has a minimum at $r = r_j^0$ then

$$\alpha(\omega) = \alpha_0 - \gamma(\omega - \omega_0)^2 \text{ for } \omega > \omega_0, \quad \alpha(\omega) = 0 \text{ for } \omega < \omega_0. \tag{26}$$

If $\Omega_{12}(r)$ has a maximum at $r = r_j^0$, then

$$\alpha(\omega) = \alpha_0 - \gamma(\omega - \omega_0)^2 \text{ for } \omega < \omega_0, \quad \alpha(\omega) = 0 \text{ for } \omega > \omega_0. \tag{27}$$

In this case it is necessary to introduce the following changes in the formulas obtained above. The right hand side of Eq. (23) should increase by a factor of two. One should use the formula $\delta\omega = \sqrt{(c\gamma t)^{-1}\ln 2}$ for the half-width of the spectral distribution of the intensity of the radiation.

If the maximum of $\alpha(\omega)$ is located at the point ω_0, then the parameter γ entering into Eqs. (26) and (27) can be approximately related to Γ_{12} which has been encountered above. In order to do this, one can identify the half-width of the curve $\alpha(\omega)$ obtained by two methods: 1) as the deviation of the frequency from ω_0, for which Eqs. (8) and (12) give a value for α which is two times smaller than (14) (this deviation turns out to be equal to $|\omega - \omega_0| \equiv \Delta\omega = 8\,\Gamma_{12}$[2)]); 2) as the deviation in the frequency from ω_0, for which Eqs. (26) and (27) give $\alpha(\omega) = \alpha_0/2$ (here $\Delta\omega = \sqrt{\alpha_0/2\gamma}$). Equating the two indicated quantities, we obtain

$$\gamma \sim \alpha_0 / 128\Gamma_{12}^2. \tag{28}$$

For numerical estimates we shall use this formula and the previous values $\Gamma_{12} = 5 \times 10^{11}$ sec^{-1}, $\hbar\omega_0 = 2$ eV, and $n_0 = 10^{19}$ cm^{-3}. In this connection, from Eq. (23) but with the right hand side doubled, one obtains $u = 16.3$. Hence for $\alpha_0 = 2.5$ cm^{-1} one obtains $t' = 2.1 \times 10^{-10}$ sec and $t'' = 5.2 \times 10^{-11}$ sec. The half-width of the curve $\alpha(\omega)$ is given by $\Delta\omega = 4 \times 10^{12}$ sec^{-1}; the half-width of the spectral distribution of the intensity at the moment t' is given by $\delta\omega = 1.1 \times 10^{12}$ sec^{-1}.

If the duration of the first stage of the reaction is redefined so that the coefficient 0.01 stands on the right hand side of Eq. (23) instead of 0.05, then in this connection the coefficient associated with $(1 - z)$ in the square brackets of formula (25) decreases by only 5%. Hence the small sensitivity of the results to the arbitrary choice of z' is evident.

The results obtained above indicate that it is possible to make lasers in which a stimulated photo-transition occurs during the elementary chemical reaction event itself and accelerates the rate of the latter. Such a laser may possess a large gain and a large power of outgoing radiation. On the other hand, the system under consideration is also of interest from the point of view of accelerating the chemical reaction and controlling it. Thus, a quantitative calculation has confirmed the estimates made by one of the authors,[8] and the advantages mentioned there of the type of lasers under consideration.

It is of interest to compare the stimulated reaction in the multi-mode regime, which was considered in Section 5, and the reaction in the single-mode regime, which was considered in Sec. 3. For multimode superluminescence the maximum of the intensity of the radiation spectrum coincides with the maximum of $\alpha(\omega)$ at ω_m. For the single-mode regime the emission is monochromatic and its frequency is determined by the frequency of the original radiation with intensity I_0. For identical values of α and n_0 the rate of the fast stage of the reaction turns out to coincide in both cases; the duration of the slow stage of the reaction turns out to be several times longer in the single-mode regime. The radiated power is the same in both cases, but in the single-mode regime it is concentrated in a very narrow range of frequencies and directions of propagation.

[2)] It should be taken into consideration that near r_j^0 there are two values of r_j at which an identical frequency ω is emitted. Therefore in Eq. (8) in the sum over j one should keep two terms which are almost identical in magnitude.

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Translated by H. H. Nickle
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