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RECOMBINATION RADIATION OF ATOMS (RADICALS) AND THERMAL LASERS

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Recombination radiation of atoms or radicals in conjunction with rapid cooling is shown to be a feasible method of producing laser inversion.

1. A number of chemical reactions emit a photon according to the equation[1]

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

A typical characteristic of these reactions is the fact that the emission of a photon is not the consequence but the necessary condition of the elementary act (1). Just as any spontaneous radiative process has a "stimulated" analog, so can process (1) under suitable conditions be used for the amplification and generation of photons.

Pekar[2] considered a number of problems bearing on the use of the chemical photorecombination process for the generation of coherent radiation. Further analysis shows however that the method of producing stimulated photorecombination by the fusion of reagents, each of which having a different chemical stability, as proposed in [2], is hardly possible in practice.

2. Let the collision of A and B result in an excited unstable complex AB* that can be stabilized either by collision with a third particle that receives the excess energy or by the emission of a photon. We consider the kinetics of the latter case. Let the concentrations of initial reagents be the same. If N is the density of AB* complexes and n is the density of A(B) particles, then

$$\frac{dN}{dt} = \langle\sigma v\rangle n^2 - \frac{1}{\tau}N - wN, \tag{2a}$$

$$\frac{dn}{dt} = -\langle\sigma v\rangle n^2 + \frac{1}{\tau}N, \tag{2b}$$

where w is the probability of photon emission by complex AB*, τ is the lifetime of this complex relative to the decay into initial component elements, and σ is the collision cross section of particles involving the formation of AB*. The order of magnitude $\tau = \sigma^{1/2}/v$ is very small: 10^{-12}–10^{-13} sec for simple formations and $\sim 10^{-10}$ sec for polyatomic complexes. Therefore it is entirely valid to replace (2a) by

$$\langle\sigma v\rangle n^2 = (1/\tau + w)N$$

and to obtain (assuming that $w\tau \ll 1$) the following equation for n

$$dn/dt = -w\langle\sigma v\rangle\tau n^2. \tag{3}$$

The solution of (3) is

$$\frac{n}{n_0} = \frac{1}{1 + w\langle\sigma v\rangle\tau n_0 t}, \tag{4}$$

where n_0 is the initial concentration of A particles.

In the order of magnitude the value of $\langle\sigma v\rangle\tau$ equals volume V of complex AB*. Assuming that $w = 10^6$ sec^{-1}, $V = 10^{-23}$ cm^3, $n_0 = 10^{19}$ cm^{-3} (as is done in [2]), practically one-half of the molecules will react in time $t_0 = 10^{-2}$ sec. Superradiance can considerably reduce this time.

3. In the case of diffusive mixing of two substances in time $t_0 = (wVn_0)^{-1}$, they are mixed in a layer whose thickness is

$$a = \sqrt{D(wVn_0)^{-1}} = \sqrt{\frac{d}{wV}\frac{1}{n_0}}, \tag{5}$$

where $D = d/n_0$ is the diffusion coefficient. This means that the total number of the mixture particles in a volume that has one dimension determined by the diffusion layer thickness is

$$n_{\text{total}} = S\sqrt{d/wV} \tag{6}$$

and does not depend on the density of initial reagents (S is the area of interface between the diffusing gases). We assume that the laser is designed so that amplification occurs in a plane normal to the direction of diffusion. Generation along the diffusion layer requires a minimum thickness of that layer determined by a number of factors and ultimately by the diffraction divergence of the beam generated in a thin layer.

The laser excitation condition for a layer a thick and L long and for mirrors with reflection coefficient r can be written in the form

$$\varkappa \geqslant (1 - r + l_D)/L, \tag{7}$$

where κ is the gain of the medium and l_D are diffraction losses depending on the generated wavelength λ:[3]

$$l_D = 0{,}103(\lambda L/a^2)^{3/2}.$$

The right-hand side of (7) as function of L has a minimum that is equal to $4(1 - r)^{1/3}\lambda/a^2$. For the stimulated analog of (1)

$$\varkappa = \frac{1}{4}\frac{\lambda^2}{\Delta\omega}Vwn_0^2$$

($\Delta\omega$ is the width of the luminescence spectrum); this together with (7) leads to

$$\frac{\lambda}{\Delta\omega} > 16\left(\frac{1 - r}{d}\right)^{1/3}. \tag{8}$$

Condition (8) is distinguished by the fact that it does not depend on reagent density and probability of process (1), and imposes a lower limit on the wavelength in generation along the diffusion layer. For r = 0.99 the value of $d \approx 3 \times 10^{18}$ cm^{-1} sec^{-1}, $\Delta\omega = 10^{14}$ Hz, and $\lambda > 10^{-4}$ cm.

Let us estimate the generation across the diffusion layer (in the direction of diffusion). The necessary generation condition is

$$\varkappa am > \ln r^{-1}, \tag{9}$$

where a is the thickness of the diffusion layer and m is the number of diffusion layers. If a is determined by (5) the quantity κa increases linearly with increasing density of the mixing reagents and (9) can in principle be satisfied for reasonable densities of reacting mixtures.

The orderly analysis of the direct use of (1) to generate light must take into account the triple collision process as the reaction mechanism

$$A + B + M \rightarrow AB + M, \tag{10}$$

where M is any particle of the reacting mixture. The reaction rate of (10) is proportional to Kn_0^2, where K is the rate constant of (10). Simple kinetic analysis shows that the number of nonreacted mixture products is time dependent according to

$$n / n_0 = (1 + 2Kn_0^2 t)^{-1/2}, \tag{11}$$

and hence the characteristic time of material depletion due to the triple collision reaction is $t_0 = 3/2Kn_0^2$. This dependence of t_0 on concentration determines the decrease of the total number of particles in the diffusion layer with increasing density (as $\sqrt{n_0}$) (compare with (6)). Amplification within the diffusion layer thickness still increases with increasing density but only as $\sqrt{n_0}$. Then for $\lambda = 0.5\,\mu$, $d = 3 \times 10^{18}$, and $r = 0.95$, condition (9) is transformed into the inequality

$$n > 10^{67} \frac{K}{w^2 m^2}. \tag{12}$$

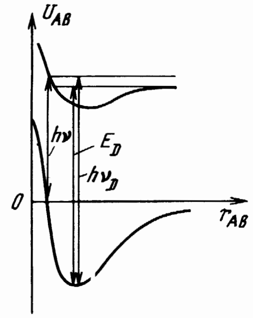
This means that for $w = 10^5$–10^6, the necessary reagent density is $\sim 10^{18}$ and there must be 10^2–10^4 diffusion layers.

These results would seem to be encouraging. In our view, however, the principal difficulty with lasers based on (1) where each reagent has a different chemical stability consists in the fact that the value of w is much less than 10^6 sec^{-1} for such reagents and it is not easy to reach the excitation conditions.

Consequently the use of the photorecombination process for generation of coherent emission by fusion of reagents with different chemical stability encounters the following problems: (a) only infrared emission can be generated along the diffusion layer (see (8)); (b) triple collisions reduce the total number of particles per unit diffusion layer with increasing density of the reacting materials; (c) the probability of recombination of chemically stable compounds is very low.

Atoms or radicals that as a rule are chemically unstable have a sufficiently high photorecombination probability. This means that they should be obtained either by external excitation or in the course of a chemical reaction.

4. For example, the emission of quanta has been well studied in the recombination of iodine, bromine, chlorine,[1,4] nitrogen,[5] etc. However, in the normal state, these elements exist in molecular form. Therefore the following method of laser excitation suggests itself: gas molecules are heated up to a temperature where dissociation becomes significant and then rapidly cooled by techniques described in [6], for example.



We evaluate the necessary cooling of heated and partially dissociated gas of AB molecules in order to produce inversion. Let the reaction rate of (1), leading to the emission of a quantum with frequency ν be $K_\nu^{em} n_a n_b \Sigma_{ab}^{-1}$, and the rate of the absorption process be $K_\nu^{abs} n_{M\nu}$, where n_a and n_b is the number of atoms A and B; $n_{M\nu}$ is the number of molecules absorbed at frequency ν; and $\Sigma_{ab}(T)$ is the statistical sum of colliding atoms. The amplification condition requires that

$$K_\nu^{\text{em}} \frac{n_a n_b}{\Sigma_{ab}(T_{\text{f}})} > K_\nu^{\text{abs}} n_{M\nu}, \tag{13}$$

where T_f is the final temperature of the working medium.

If cooling is fast and occurs in time shorter than that required to establish equilibrium dissociation then

$$\frac{n_a n_b}{n_M} = \frac{1}{kT_{\text{i}}} K_{\text{e}}(T'_{\text{i}}), \tag{14}$$

where T_i is the initial temperature and $K_e(T_i)$ is the dissociation equilibrium constant. If also the equilibrium in the vibrational-rotational spectrum of the AB molecule is established in time shorter than the time required to establish dissociation equilibrium, we can say that

$$n_{M\nu} = \frac{n_M}{\Sigma_M(T_{\text{f}})} \exp\left\{-\frac{h(\nu_D - \nu)}{kT_{\text{f}}}\right\},$$

where Σ_M is the statistical sum of the molecules, $h\nu_D$ is the energy of dissociation of the molecule into atoms A and B whose states are capable of recombining into a molecule with the emission of a light quantum of frequency ν; $h\nu_D \geq E_D$; and E_D is the dissociation energy of the molecule (see drawing).

The relation between K^{em} and K^{abs} can be found from the principle of detailed balancing written for the temperature T_i:

$$K_\nu^{\text{em}}(n_\nu + 1) \frac{n_a n_b}{\Sigma_{ab}(T_{\text{i}})} = K_\nu^{\text{abs}} n_\nu \frac{n_M}{\Sigma_M(T_{\text{i}})} \exp\left\{-\frac{h(\nu_D - \nu)}{kT_{\text{i}}}\right\},$$

where n_ν is the Planck distribution function. Considering (14) we find

$$K_\nu^{\text{abs}} = K_\nu^{\text{em}} \frac{\Sigma_M(T_{\text{i}})}{\Sigma_{ab}(T_{\text{i}})} \frac{K_{\text{e}}(T_{\text{i}})}{kT_{\text{i}}} \exp\left\{\frac{h\nu_D}{kT_{\text{i}}}\right\}. \tag{15}$$

Taking into account the values of the equilibrium constant K_e, the partition functions, and (15), inequality (13) can be written in the form

$$\exp\left\{-\frac{h\nu_D}{kT_{\text{i}}}\right\} > \exp\left\{-\frac{h(\nu_D - \nu)}{kT_{\text{f}}}\right\}, \tag{16}$$

which is equivalent to

$$(T_i - T_f)/T_i > \nu/\nu_D. \tag{17}$$

We assume that (16) is satisfied with room to spare so that

$$\varkappa_\nu = \frac{1}{c} K_\nu^{\mathrm{em}} \frac{n_a n_b}{\Sigma_{ab}}.$$

Applying the reasoning presented in [1] we can write for κ_ν an expression in terms of the coefficient of absorption due to photodissociation

$$\varkappa_\nu = \varkappa_\nu^{\mathrm{em}} \frac{r_0^2}{s} \frac{h}{m} \left(\frac{8\pi m}{kT_f} \right)^{1/2} n_a n_b, \tag{18}$$

Here s = 1 for a molecule consisting of different atoms, s = 2 for a molecule of the same atoms, m is the reduced mass of recombining atoms, and r_0 is the equilibrium distance between centers of atoms in the AB molecule.

The excitation condition $\kappa_\nu L > \ln r^{-1}$ together with (14) allow us to determine the initial heating temperature and initial concentration n_M.

The small vibrational quantum makes the establishment of thermal equilibrium faster than that of recombination equilibrium. This makes it possible to use halides for generation by the heating-cooling method. If iodine data [1] are used in (18): $\kappa_\nu^{ab} = 14$ cm^{-1}/atm, $r_0 = 2.26$ Å, s = 2, m = 10^{-22} g, then for $n_a = 3 \times 10^{18}$ cm^{-3} we have $\kappa_\nu = 10^{-2}$–10^{-3} cm^{-1} which is quite sufficient to produce excitation when the amplifying medium is ~10 cm long. The necessary initial number of iodine molecules is 6×10^{18} cm^{-3}.

An interesting generation medium is nitrogen whose atoms recombine into a molecule with the emission of a photon

$$N + N \rightarrow N_2 + h\nu \tag{19}$$

at the rate of [5]

$$w' = 0.6 \cdot 10^{-17} (300/\kappa T)^{0.9} N^2 \text{ [photon/sec]}. \tag{20}$$

The N_2 molecule obtained from the recombination of nitrogen atoms is in the $B^3\pi$ state. Photons are emitted from the transition

$$N_2(B^3\pi) \rightarrow N_2(A^3\Sigma) + h\nu.$$

Although $A^3\Sigma$ is not the ground state it would seem at first that this would not be useful since $A^3\Sigma$ is metastable with a long lifetime. Nevertheless it was shown in [7] that state $A^3\Sigma$ can be effectively depleted by collisions of $N_2(A^3\Sigma)$ with nitrogen atoms:

$$N_2(A^3\Sigma) + N \rightarrow N_2(X^1\Sigma) + N.$$

As a result of this act the molecule drops down to ground state $X^1\Sigma$ at the rate of [7]

$$w'' = 5 \cdot 10^{-11} N.$$

For a concentration of atoms N ~ 10^{13} cm^{-3} this process may be faster than the population of level $A^3\Sigma$ by radiation.

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