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POPULATION INVERSION OBTAINED BY THERMAL DISSOCIATION OF MOLECULES IN A SHOCK WAVE

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It is shown, with the N_2O molecule as an example, that population inversion can be produced by thermal dissociation of molecules in a shock wave. The kinetics of the processes, determining the population of the energy levels of the working medium, is considered.

IT was shown in an earlier paper[1] that thermal dissociation of several molecules can be used to obtain population inversion. Examples of such molecules are N_2O and CO_2, the ground state of which is the $^1\Sigma$ state, whereas the ground state of the oxygen atom is ^3P. This makes possible the following schemes of thermal dissociation of these molecules:

$$\text{a) } N_2O \rightarrow N_2 + O(^1D), \qquad \text{b) } CO_2 \rightarrow CO + O(^1D), \quad (1)$$

which takes place alongside the usual decay process

$$\text{a) } N_2O \rightarrow N_2 + O(^3P), \qquad \text{b) } CO_2 \rightarrow CO + O(^3P). \quad (2)$$

It is possible to produce here conditions such that the rate of processes (1) exceed that of processes (2). We present below an analysis for the conditions necessary to obtain self-excitation in N_2O gas heated by a shock wave.

It is known that to obtain self-excitation in a laser it is not necessary to satisfy the inequality

$$\frac{1}{8\pi^2}\lambda^2\frac{A_{21}}{\Delta\nu}\frac{L}{\ln(1/r)}\left(N_2\frac{g_1}{g_2}-N_1\right)>1, \quad (3)$$

where $\Delta\nu$ is the half-width of the spectral line, A_{21} the probability of spontaneous radiative transition between the working energy levels, λ—the radiation wavelength, r the reflection coefficient of the mirrors, and g_1 and g_2 the statistical weights of the energy levels. For the $^1D \rightarrow {}^3P$ transition, we have $g_1 = 9$ and $g_2 = 5$; N_1 and N_2 are the energy level population densities and L is the laser length. The transition of oxygen atoms from the state ^1D to the ground state ^3P is accompanied by radiation of light of wavelength $\lambda \approx 6300$ Å.[2] For this transition $A_{21} = 73 \times 10^{-4}$ sec^{-1}.[2]

The nominal value of the initial line width is determined by the Doppler effect

$$\Delta\nu_D = 0.74\,\bar{v}/c,$$

$\bar{v}$ is the average thermal velocity of the atom. When $T \approx 3000°$ K the width is $\Delta\nu_D \approx 2 \times 10^9$ cps. Substituting all the necessary values in (3) and assuming that $N_2 \gg N_1$, we find that when $r = 0.98$ and $L = 100$ cm, the excited-particle density necessary for self-excitation of the generator is

$$N_2 \approx 10^{18}\,\text{cm}^{-3}. \quad (4)$$

At such a high density of the medium, the line width $\Delta\nu_c$ due to the collisions of the particles with one another can exceed $\Delta\nu_D$, so that it is necessary to substitute in (3) $\Delta\nu_c$ in lieu of $\Delta\nu_D$. Introducing the effective cross section σ of the collisions that lead to line broadening ($\Delta\nu_c = \sigma\bar{v}N$), we can rewrite condition (3) with inclusion of the foregoing concrete values of A_{21}, λ, g_i, and r, in the form

$$0.33\cdot10^{-10}\frac{L}{\sigma\bar{v}}\frac{N_2}{N} > 1. \quad (5)$$

N is the total number of particles per cubic centimeter of working medium. There are no reliable published data on the cross section σ for the $^1D \rightarrow {}^3P$ transition in oxygen. However, it can hardly exceed 10^{-14} cm^2. In this case for $L = 100$ cm it is necessary to have $N_2/N > 0.4$.

According to the data given in the book by Glasstone et al.,[3] the disintegration of nitrous oxide in accordance with the scheme (2) has a rate

$$k = 4.2\cdot10^9\exp(-53\,000/RT). \quad (6)$$

This reaction is accompanied by a change in the multiplicity of the state of oxygen. Therefore its transmission coefficient χ is small, on the order of 10^{-4}. Since the dissociation energy of the N_2O molecule is in accordance with the scheme (1a) equal to ~90,000 cal/mole, the rate of reaction

(1a) is

$$k^* = k\chi^{-1} \exp(-37\,000 / RT). \tag{7}$$

In order for the reaction to proceed predominantly via the excited state of oxygen in accordance with the scheme (1a), it is necessary to satisfy the condition

$$k^* \gg k, \tag{8}$$

which, with allowance for (7), leads to the relation

$$\exp(-37\,000 / RT) \gg \chi. \tag{9}$$

Assuming condition (8) to be satisfied if $k^* = 10k$, we obtain for the necessary heating temperature of the N_2O gas

$$T \approx 2700^\circ \mathrm{K}. \tag{10}$$

At this temperature the rates of reactions (1a) and (2a) are respectively

$$k^* = 2 \cdot 10^6 \ \mathrm{sec}^{-1}; \qquad k = 2 \cdot 10^5 \ \mathrm{sec}^{-1}. \tag{11}$$

The heating of a dense gas ($N \gtrsim 10^{18}$ cm^{-3}) can be realized with the aid of a shock wave.[4] It is known that the temperature of a gas T behind the front of a powerful shock wave is given by the relation[5]

$$T = \frac{49}{320} M^2 T_0, \tag{12}$$

where T_0 is the initial gas temperature and M is the Mach number. If the initial gas temperature is $T_0 \approx 300^\circ$ K, then to heat the gas to a temperature 2700° we need $M = 8$. Since the initial temperature is $T_0 = 300^\circ$ K, the rate of propagation of the shock wave corresponding to $M = 8$ is $\sim 3 \times 10^5$ cm/sec. For a laser tube 1 cm^2 in diameter the time to heat the system $\tau_h \approx 3 \times 10^{-6}$ sec. This is longer than $\tau = 1/k^*$.

Since the propagation of the shock wave is a relatively slow process, metastable levels must be used to accumulate in the system a sufficiently large number of excited atoms. It is precisely the ^{1}D level of the oxygen atom which satisfies this requirement. As follows from the given value of A_{21}, the time of its radiative decay is $\tau_c \approx 140$ sec, so that the condition necessary for accumulation of a sufficiently large number of excited atoms

$$\tau_c > \tau_h \tag{13}$$

is satisfied with a large margin.

Consequently the metastable levels of other atoms, with a considerably smaller radiative decay time, down to $10^{-4} - 10^{-5}$ sec, can prove to be perfectly suitable. It must be borne in mind here, however, that with decreasing τ_c the deactivation time of the excited atoms τ_d also decreases, due to collisions of atoms with atoms and with other particles.[1] Estimates show that for the ^{1}D level of oxygen this time can hardly be shorter than 10^{-3} sec at pressures on the order of several atmospheres. The deactivation due to collisions is insignificant up to values on the order of $10^{-5} - 10^{-6}$ sec, since at longer deactivation times the principal role is played by various chemical reactions.

Estimates of the rates of the chemical reactions show that an appreciable role is played, within the time of passage of the shock wave ($\sim 3 \times 10^{-6}$ sec), by the following chemical processes:

$$\text{a) } N_2O \to N_2 + O^*, \quad \text{b) } O + O + M \to O_2 + M,$$

$$\text{c) } N_2O + O \to \begin{cases} N_2 + O_2 \\ 2NO \end{cases} \tag{14}$$

The symbol M denotes any particle, and $O^* \equiv O(^1D)$. Therefore to calculate the number of excited oxygen atoms, it is necessary to use the equations

$$\begin{aligned} d[O^*]/dt &= k^*[N_2O] - 2k_1[M][O^*]^2 - k_2[N_2O][O^*], \\ d[N_2O]/dt &= -k^*[N_2O] - k_2[N_2O][O^*], \\ d[M]/dt &= k^*[N_2O] - k_1[M][O^*]^2, \end{aligned} \tag{15}$$

where the symbol [. . .] denotes the concentration of the corresponding component, and k^*, k_1, and k_2 are the specific rates of reactions (14a), (14b), and (14c). We neglect here the concentrations of the oxygen atoms in the state ^{3}P, assuming $k^* \gg k$.

Equation (15) will be reduced, for convenience in the analysis, to dimensionless form, by introducing the notation

$$\tau = k^* t, \quad x = [O^*] / [N_2O]_0, \quad y = [N_2O] / [N_2O]_0,$$

$$z = [M] / [N_2O]_0, \quad \chi_1 = \frac{k_1}{k^*}[N_2O]_0^2, \qquad \chi_2 = \frac{k_2}{k^*}[N_2O], \tag{16}$$

where $[N_2O]_0$ is the density of the nitrous oxide prior to the start of dissociation. In this notation, Eqs. (15) take the form

$$dx/d\tau = y - 2\chi_1 x^2 z - \chi_2 xy,$$

$$dy/d\tau = -y - \chi_2 xy, \quad dz/d\tau = y - \chi_1 x^2 y. \tag{17}$$

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[1] It must be noted, however, that with decreasing τ_c it is possible to satisfy the self-excitation condition at a lower particle density in the system. By decreasing the density of the medium one can increase the deactivation time of the excited atoms.

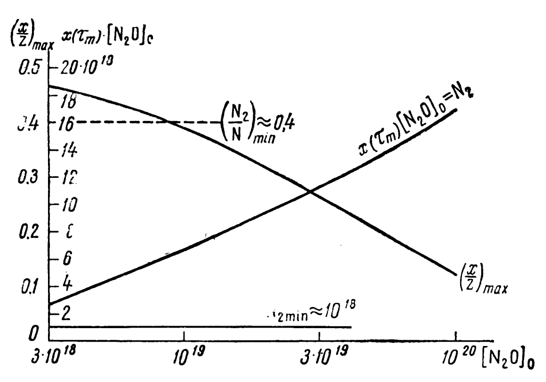

FIG. 1

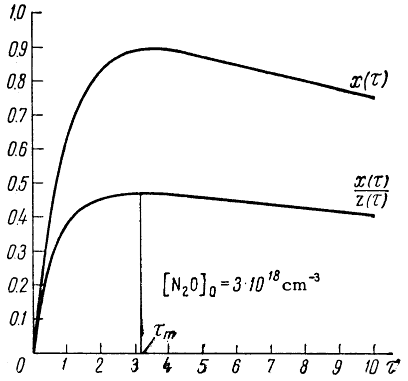

FIG. 2

For the investigation of these equations it is necessary to know the values of the constants χ_1 and χ_2. The recombination rate of the oxygen atoms in the temperature interval 2000—4000° K is described by the formula[5]:

$$k_1 = 6\cdot10^{21}T^{-2}\ \text{cm}^6/\text{mole}^2\ \text{sec}, \qquad (18)$$

if the third particle is an oxygen molecule. A recombination rate of the same order is obtained if the third particle is an oxygen atom. There are no grounds for assuming that the recombination of oxygen into a molecule occurs at a faster rate if the third particle is N_2O.[2)] It follows from (18) that at $T \sim 3000°$ K we get $k_1 \approx 8 \times 10^{14}$ cm^6/mole^2 sec. Therefore $\chi \approx 1$ for $[N_2O]_0 \approx 2 \times 10^{19}$ cm^{-3}. An increase in density leads to a quadratic increase in χ_1.

Johnston[6] has shown that reaction (14c) has an activation energy on the order of 1400—2400 cal/mole. An estimate of the rate of this reaction by the activated complex method[3,5] leads to a value

$$k_2 \lesssim 10^{-14}\ \text{cm}^3/\text{sec}. \qquad (19)$$

Equation (17) with account of (18) and (19) makes it possible to calculate the function $x(\tau)$. It is obvious that $x(\tau)/z(\tau)$ has a maximum at a certain value $\tau = \tau_m$.

Figure 1 shows a plot of $(x/z)_{max}$ and $x(\tau_m)$ against the value of $[N_2O]_0$. At larger densities, $(x/z)_{max}$ decreases, since the rate of recombination of the oxygen atoms into molecules increases. Therefore $[N_2O]_0$ should be such as to satisfy condition (5) (inasmuch as $N_2/N \equiv x/z$). At the same time, the initial density $[N_2O]_0$ cannot be small, for in accordance with (4) we must have

$$N_2 = [N_2O]_0 x(\tau) \gtrsim 10^{18}\ \text{cm}^{-3}$$

It can be verified that conditions (4) and (5) can be satisfied simultaneously. It is necessary to take into account here the fact that the density behind the front of a sufficiently strong shock wave exceeds by a factor of 8 the initial density of the unperturbed gas.[5]

In order to make the entire volume of the quantum-generator medium work uniformly, it is necessary that the entire time of passage of the shock wave through the working volume be equal to or even smaller than τ_m. An investigation of the system (17) shows that τ_m increases with decreasing χ_1. Consequently, it is necessary to choose $[N_2O]_0$ as small as possible but compatible with conditions (4) and (5). On the other hand, with increasing τ, the density of the active particles decreases relatively slowly. As can be seen from Fig. 2, when $\tau = 10\tau_m$, $x(\tau)$ decreases only by 15% compared with x_{max}. One can therefore switch on the cavity Q not at the instant τ_m, but somewhat later, so that the shock wave propagates over a larger region.

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[5] Ya. B. Zel'dovich and Yu. P. Raĭzer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavleniĭ (The Physics of Shock Waves and High-temperature Hydrodynamical Phenomena), Fizmatgiz, 1963, pp. 290, 347, and 352.

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[2)] The recombination rate of O + O + M is smaller than k_1, determined by (18) from [5], if $M \equiv N_2$, N, and NO.