DYNAMICS OF GAS-TEMPERATURE ESTABLISHMENT IN VIBRATIONALLY EXCITED OZONE

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1. Introduction. The establishment of the gas temperature in a vibrationally excited gas is fairly complicated, primarily (if we ignore macroscopic transport processes) because all the relaxation processes (V—V, V—V', R—T, V—T, etc.) are nonresonant ones in a real gas. Therefore, the establishment of quasiequilibrium on any internal degree of freedom may be accompanied by positive or negative changes in the gas temperature.

The dynamics of gas-temperature establishment (thermalization) for a nonequilibrium system may be examined in relation to radiation propagation, laser photochemistry, and as an independent technique for determining characteristic relaxation times.

A fair amount of attention has now been given to such topics [1-6]; for example, there are detailed experimental and theoretical studies of the cooling of gases containing CO_2 by the radiation from a CO_2 laser [1-3]. It has been found that the dominant part is played by vibrational—translational (V—T) and vibrational—vibrational (V—V') transfers. A prediction has been made [5] of the scope for kinetic cooling during nonresonant rotational—translational (R—T) exchange in a molecular gas that absorbs laser radiation in the P branch of the vibrational transition. This effect has been observed by experiment [6].

Here we present a detailed theoretical study of the thermalization in O_3 resonantly excited by IR laser radiation. Ozone is of interest because it plays an important part in the physicochemical processes in the atmosphere. It was found that the process is not monotonic in time and that to describe it one has to consider nonresonant R—T, V—V, V—V', and V—T processes as well as the parameters of the laser pulse (intensity and pulse shape, and frequency and width of the radiation line).

2. Theoretical Model. The following model was used to describe the thermalization of the excited O_3.

1. The ground electronic state of O_3 was represented as a set of vibrational levels, whose scheme [7] is given in Fig. 1. Here we incorporated the actual rotational structure of the $O_3(000) \to O_3(001)$ vibrational transition in mode ν_3, which is responsible for the absorption of the IR pumping range in the 9.6 μm region [8].

2. It was assumed that the ozone was excited by the radiation from a CO_2 laser in the 9.6 μm band, where ozone has a high absorption coefficient of $\sim 10^{-5}$-10^{-4} $Pa^{-1} \cdot cm^{-1}$ [9, 10]. The rotational structure of the absorption spectrum in the $O_3(000) \to O_3(001)$ vibrational transition is shown in Fig. 2. The points are from the measurements of [8]. The numbers on the curves are values of K_{-1} for the transitions. The P, Q, and R branches are seen. The structure of the branches is similar to that for the absorption band of a symmetrical fork, since the ozone molecule is a slightly unsymmetrical fork with asymmetry parameter $\varkappa = -0.968$ for the ground state [8]. We show below measurements of the absorption cross sections of ozone for various (P(8)-P(40)) lines in the 9.6 μm band of a CO_2 laser [9, 10]. It must first be emphasized that the exact laser frequency determines whether the P, Q, or R branch of the (000—001) transition is mainly pumped, and secondly that several rotational sublevels of the ground vibrational state are actually in resonance with the CO_2 laser line (the lines for the sublevels are shown broken in Fig. 1). Calculations [9] and comparison with experiment have shown that ozone lines >0.15 cm^{-1} from the CO_2 laser line make no appreciable contribution (within the error of measurement) to the absorption spectrum of ozone on laser lines. This means that not more than five or six rotational sublevels of the 000 state are

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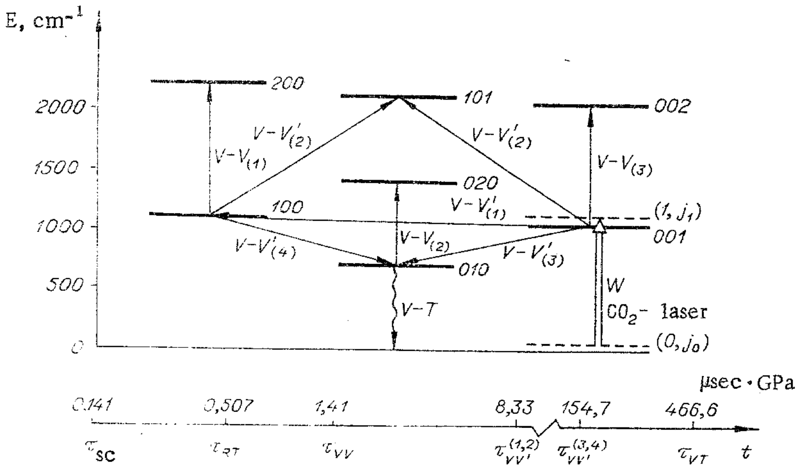


Fig. 1

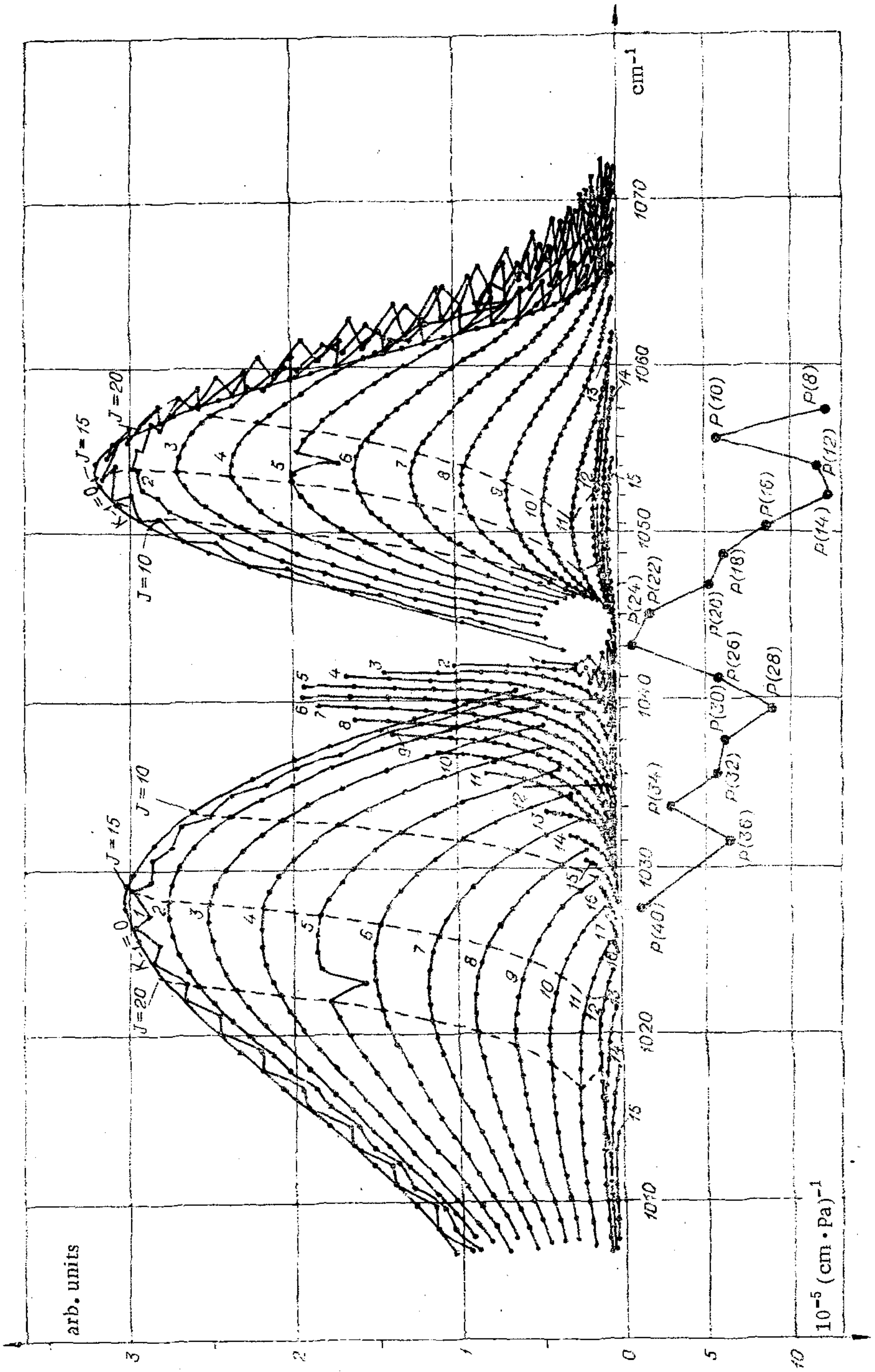
involved in the laser radiation absorption (or 1-2 sublevels for the transitions used in our calculations). Therefore, if no special measures are taken to broaden the laser line (real widths $\sim 10^{-2}$-$5 \cdot 10^{-3}$ cm^{-1}), the absorption will be based on $\sim 10^{-2}$-10^{-3} of the ground-state molecules, and the (000)—(001) transition will be saturated at laser intensities of $\sim$100 kW/cm^2-1 MW/cm^2. This is why the gas temperature change is small within the characteristic times of the relaxation processes (a fraction of a degree, as will be seen below).

3. The time course of the gas temperature was considered on the basis of R—T relaxation in the O_3(000) and O_3(001) vibrational states and also V—V, V—V', and V—T relaxation, as indicated by arrows in Fig. 1, where we also show the values of the characteristic times used in the calculations that were measured in [11]. The time of the R—T process for ozone given in Fig. 1 was estimated from $\tau_{RT} = 3.6\ \tau_{st}$, which is applicable for the O_2 molecule [12], where τ_{st} for O_3 was taken from [11].

Qualitative analysis of this model shows that there is competition between the processes that reduce and raise the gas temperature within the times of the order of the R—T, V—V and V—V' relaxations. The kinetic cooling is due to the R—T processes [5] in the 000 and 001 levels of the P branch (rotational cooling) together with the endothermic $V{-}V'_{(1)}$ process between the 001 and 100 levels, since this V—V' process is the most rapid intermode one in the ozone molecule (vibrational cooling). There is competition with these processes from the fast V—V and slower $V{-}V'_{(3-4)}$ processes, which release heat.

At large times ($t > \tau_{VV'}^{(3-4)} \gg \tau_{VV'}^{(1)}$) most of the excited molecules will have passed to the lower 010 vibrational level, from which they relax slowly to the 000 ground (V—T process) with the release of a considerable amount of heat, which results in uniform heating, which is the slowest process in the system (Fig. 1).

A closed system of kinetic equations for the populations of the vibrational levels of O_3, the rotational sublevels that interact with the radiation, and the gas temperature was used in quantitative description of this scheme in accordance with sections 1-3 above on the model. The rotational relaxation was considered in the framework of the strong-collision model[5]. The turning points in the gas temperature occur in a relatively short time interval ($t \lesssim \tau_{VV'}$), so the calculations did not incorporate the dissociation of ozone under UV radiation. Detailed theoretical studies [13] have shown that under these conditions (a short radiation pulse, intensity $\lesssim 10^6$ W/cm^2, excitation of only the first level of the IR-active mode of ozone, and only small proportions of the particles participating in the absorption) only a small percentage of the ozone will decompose in time $t \lesssim \tau_{VV'}$. Also, the temperature changes are small, so we neglect the dependence of Landau—Teller type on the rates of the relaxation processes on the gas temperature. Also, we neglected the excitation of the rotational sublevels of the ν_1 mode by the pumping radiation on account of the strong Coriolis interaction with certain rotational sublevels of the ν_3 absorbing transition, since the accompanying coefficient for the absorbing rotational (001) transitions to the (100) transitions are less than 1% for the CO_2 laser lines used in the calculations [8]. The direct excitation of ν_1 can be neglected because the absorption coefficient of this band is very weak by comparison with that of ν_3.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P(34)
P(36)
P(40)

Fig. 2

3. Analysis of the Kinetic Equations. The system of kinetic equations (5.1)-(5.10) describing the above model is given in the Appendix; this includes kinetic equations for the populations of the vibrational levels of the ozone molecule (Fig. 1) and for the rotational sublevels of the (000) and (001) states that participate in the pumping absorption, together with the equation describing the change in the gas temperature T. This system consists of fairly cumbersome nonlinear equations: thus analysis is difficult. Solutions have been obtained by numerical methods. However, for strong optical pumping ($W \gg 1/\tau_{RT}$) and short interaction time ($t \simeq 1/W \ll \tau_{RT}$) one can make some analytical estimates of the changes in T in relation to the system parameters (τ_{RT}, τ_{VV} and τ_{VV}') and the pumping wavelength (falling in the P, Q, or R branch of the (000-001) transition). Then we get the following from (5.10) for the function f describing dT/dt:

$$f(0)=f\big|_{t\simeq\frac{1}{W}}\sim\left[\frac{1}{\tau_{RT}}\sum_i\left(E_{j_1}^{(i)}-E_{j_0}^{(i)}\right)+\frac{2\Delta E_{VV_{(3)}}}{\tau_{VV}}\sum_i q_{j_0}^{(i)}+\left(\frac{\Delta E_{VV'_{(1)}}}{\tau_{VV'}^{(1)}}+\frac{\Delta E_{VV'_{(3)}}}{\tau_{VV'}^{(3)}}\right)\right]. \tag{3.1}$$

We see from Eq. (3.1) that the sign of f(0) is substantially dependent on the relationships between the characteristic energy-relaxation times τ and the energy defects in the relaxation processes ΔE. Substitution of the numerical values of Fig. 1 gives

$$f(0)\sim p\left(2.63\sum_i\left(E_{j_1}^{(i)}-E_{j_0}^{(i)}\right)/300\,^\circ\mathrm{K}+0.12\sum_i q_{j_0}^{(i)}-0.03\right), \tag{3.2}$$

where p is pressure.

If the laser radiation falls in the P branch of the (000—001) transition, we have the estimates $\sum_i q_{j_0}^{(i)}\simeq 10^{-2}-10^{-3}$ and $E_{j_1}^{(i)}-E_{j_0}^{(i)}\simeq -10\ \mathrm{cm}^{-1}$ [8] for the equilibrium proportion of ground-state molecules involved in the absorption and the energy differences of the rotational sublevels, which corresponds to $\sum_{i=1}^{r}\frac{E_{j_1}^{(i)}-E_{j_0}^{(i)}}{300\,^\circ\mathrm{K}}\simeq -0.05r$, where r is the number of rotational transitions involved in the absorption, and from Eq. (3.2) we get

$$f(0)\sim p(-0.13r-0.03)<0,$$

i.e., the gas is cooled by R—T and $V\text{—}V'_{(1)}$ processes. Other V—V' processes and the V—T process release heat, which restricts the kinetic-cooling time, and for $t > \tau_{VV'}^{(1)}$ the gas is heated. Figure 3 gives numerical results for pumping in the P branch, which confirm the qualitative analysis. The calculations were performed for the P(36) laser line (two rotational sublevels involved in the absorption), for an ozone pressure of 1333 Pa and a laser pulse of shape $I(t) = I_0 \exp(-t/300\ \mathrm{nsec})$. Curves 1-4 of Fig. 3 correspond to intensities of 10^6, 10^5, 10^4 and 10^2 W/cm². The maximum cooling is attained in a time $\sim(1.5-2)\,\tau_{VV'}^{(1)}$, while the cooling exists for a time $\sim 3\tau_{VV'}^{(1)}$. As the pumping intensity is reduced ($1/W \simeq \tau_{RT}$ and $1/W \gg \tau_{RT}$), the general behavior of T(t) remains the same, but the depth of the cooling is reduced. On increasing I_0 ($I_0 \gtrsim 1$ MW/cm²), the behavior of T(t) is almost unaltered, since the system goes to saturation in absorption during the pulse.

The following estimates are obtained from a similar analysis of Eq. (3.2) for pumping in the Q and R branches of the ν_3 mode:

$$f(0)\sim p(0.13r-0.03)>0 \quad \text{(R-branch)},$$

$$f(0)\sim p\left(0.12\sum_i q_{j_0}^{(i)}-0.03\right)\lesseqgtr 0 \quad \text{(Q-branch)}.$$

The sign of f(0) for the Q branch is substantially dependent on $q=\sum_i q_{j_0}^{(i)}$; a more precise analysis of the equations for pumping in the Q and R branches is given below. Figure 4 shows calculated T(t) curves for pumping in the P, Q, and R branches of ozone, which corresponds to laser lines produced on the P(36), P(26), and P(14) transitions. The pulse shape and the gas pressure are as in Fig. 3, I_0 = 1 MW/cm² ($1/W \ll \tau_{RT}$), and the system in all three cases is saturated in absorption. In accordance with (3.2) there is no kinetic cooling for the R branch, while the extents of the cooling for the Q branch are much less than those for the P branch.

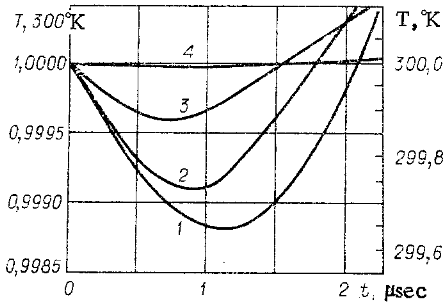

Fig. 3

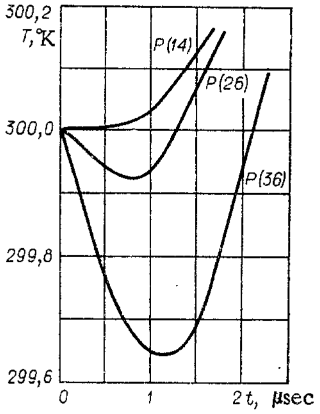

Fig. 4

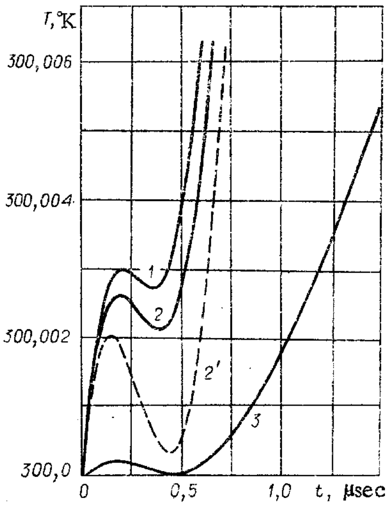

Fig. 5

We consider in more detail the case of pumping in the R branch. Here the R—T processes increase the energy in the translational degrees of freedom. Therefore, during the time of order τ_{RT} the gas is heated, and the V—V processes also increase the gas temperature. However, for times $\sim\tau_{VV'}^{(1)} \simeq 6\ \tau_{VV}$ $(\tau_{VV'}^{(1)} \gg \tau_{RT})$ there is competition with the V—V and R—T processes from the endothermic $V - V_{(1)}$ exchange, which in principle can produce if not general cooling in the gas then at least a dip in the T(t) characteristic within the characteristic time interval $\tau_{RT} \ll t \simeq \tau_{VV'}^{(1)}$. This type of T(t) relationship has been obtained by numerical solution of (5.1)-(5.10) for the R branch (Fig. 5). The P(14) transition was used in the calculations. The pulse shape and the gas pressure were as in Fig. 3. Curves 1-3 corresponding to intensities of 10^6, $5 \cdot 10^3$ and 50 W/cm². The dip occurs for any pumping intensity (from 50 W/cm² up to saturation at $I_{0s} \stackrel{\sim}{\sim} 1$ MW/cm²). The depth of the dip is very small $(\Delta T \lesssim 10^{-3}\,{}^{\circ}K)$, which means that there are severe difficulties in experimental observation. The dip is due to competition between the R—T and $V—V'_{(1)}$ processes, and the depth and duration are very much dependent on the V—V processes. This can be seen by comparing curve 2 in Fig. 5 with curve 2', which was obtained by numerical solutions of (5.1)-(5.6) and (5.9) with the data as used for Fig. 2, but neglecting the V—V processes and the $V—V'_{(2)}$ process (Fig. 1). It is clear that the V—V processes reduce the depth of the dip by a substantial factor and also shorten the duration, by bringing the turning points of T(t) together.

Therefore, pumping in the R branch produces a characteristic dip in the time dependence of the gas temperature on account of composition between the rotational—translational and vibrational—vibrational processes. A similar time dependence of the temperature can be observed in the Q branch, but there it is not due to competition between the rotational and vibrational processes but instead to composition between the various vibrational—vibrational

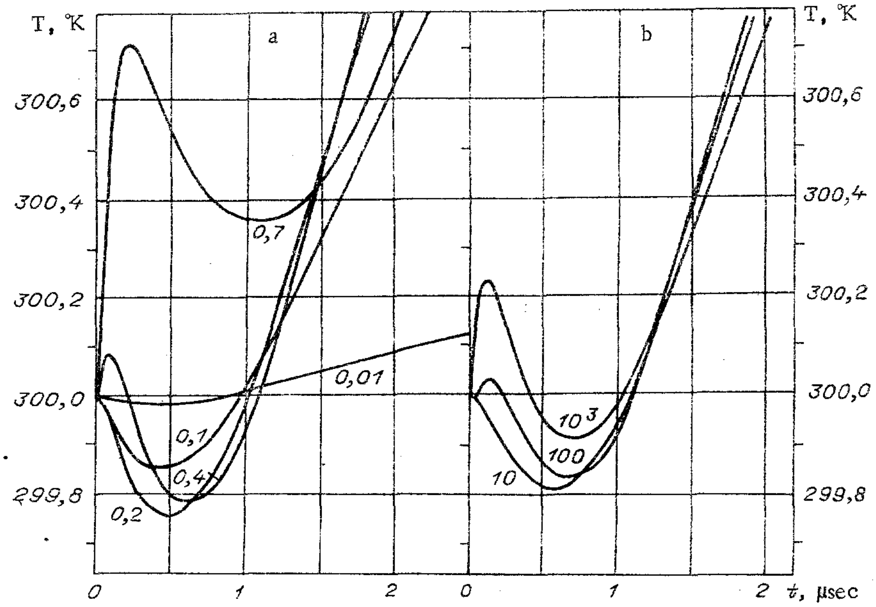

Fig. 6

transfers, which make contributions of different signs to the temperature change, namely V–V and V–V$'_{(1)}$ processes. Then (3.2) shows that the V–V process may compete with V–V$'_{(1)}$ at the start if the proportion of molecules involved in absorbing the laser radiation is fairly large, $q = \sum_i q_{j_0}^{(i)} \geqslant 0.25$. We now consider the numerical solution of the equations (Fig. 6).

When the laser radiation is absorbed in the Q branch, $E_{j_0}^{(i)} \simeq E_{j_1}^{(i)}$, and the rotational–translational processes make a small contribution to the temperature behavior. This enables us to neglect the contribution to the energy in the translational degrees of freedom for R–T relaxation. Therefore, we need not consider (5.1) and (5.2), and we replace the pumping terms in (5.3) and (5.6) by terms of the form

$$\pm W(N_{000} - QN_{001}), \tag{3.3}$$

where $Q = (1 - q/2)/(N_{001}(0)/N_{000}(0) + q/2)$; the factor Q in Eq. (3.3) incorporates the saturation in the absorbing transition when a proportion q of the ground-state molecules is involved in the absorption. Figure 6a, b shows the solutions to (5.3)-(5.9) and (3.3). The pulse shape and pressure were as in Fig. 3. Figure 6a shows the behavior of the gas temperature in saturation of the (000–001) transition at $I_0 = 1$ MW/cm^2. The numbers on the curves are the values of q. In accordance with the analytical estimate from (3.2) for $q < 0.25$, there is kinetic cooling at the start with a turning point near $t \simeq \tau_{VV'}^{(1)}$, which at $t \geqslant 2\tau_{VV'}^{(1)}$ is replaced by uniform heating. For $q \geqslant 0.25$, the gas is initially heated by V–V processes, but then follows the characteristic temperature dip due to V–V$'_{(1)}$ exchange, and then at $t > \tau_{VV'}^{(1)}$ we have heating again. As $q \to 1$, the times required to attain the maximum and minimum in T(t) increase: the maximum is attained for $t \to \tau_{VV'}^{(1)}$ (the V–V and V–V$'_{(1)}$ processes balance one another), while the minimum is attained for $t \simeq (2\text{-}3)\tau_{VV'}^{(1)}$. The length of the dip becomes much greater than $\tau_{VV'}^{(1)}$, and this is observed against a background of appreciable initial heating. If the intensity is less than the saturation value, the q dependence of T(t) is more complicated. For small I_0 ($I_0 \ll I_{0S}$), there is only cooling, whose depth increases with q. If I_0 is near saturation, the change in the T(t) curves as q increases is similar to that for saturation, but with the difference that the V–V process plays the main part not at the start but at $t \simeq \tau_{VV}$. Then if q is larger than some value q_0, the initial cooling is replaced at $t \simeq \tau_{VV}$ by heating, and then the V–V$'_{(1)}$ process results in cooling again in the range $\tau_{VV'}^{(1)} < t \leqslant 2\tau_{VV'}^{(1)}$, while for $t \geqslant 2\tau_{VV'}^{(1)}$ the gas is again heated. Therefore, the T(t) curve for t less than several times $\tau_{VV'}^{(1)}$ has two characteristic minima and one maximum. Figure 6b shows the different qualitative trends in T(t) as the pumping intensity varies for q = 0.5. The numbers on the curves give I_0 (in kW/cm^2). A maximum occurs on the

$T(t)$ curve at $t \approx \tau_{VV}$ as I_0 increases, which is due to V–V processes, and this moves to the start of the laser pulse and for $I_0 \geqslant I_{0s}$ determines the gas heating at the start of the pulse. Figure 6 shows that all the characteristic features of $T(t)$ can be observed only for large q, i.e., for sufficiently broad-band pumping in the Q branch of the ν_3 transition. This can be understood from the following simple considerations: the energy contributions from the V–V and $V\text{–}V'_{(1)}$ processes are similar in magnitude (but opposite in sign), while the rate of the V–V process is proportional to the square of the number of particles in the (001) level, while that of the $V\text{–}V'_{(1)}$ process is proportional to the first power. Therefore, the V–V process can complete successfully with $V\text{–}V'_{(1)}$ only if a large fraction of the particles is transferred from the (000) level to the (001) level, i.e., for large q.

4. Conclusions. This theoretical analysis shows that the thermalization in a resonant pumping of ozone by IR radiation is dependent in a complicated way on the parameters of the pumping radiation (intensity, pulse shape, line width, frequency). The turning points in $T(t)$ are related to the times of the R–T, V–V, V–V', and V–T relaxations in the ozone molecule. Therefore, experimental studies on the behavior of the temperature can provide considerable information on the contributions from the various transfer processes between the vibrational, rotational, and translational degrees of freedom as regards the gas temperature, and also on the relationship between the characteristic times of these processes.* The main experimental difficulties arise from the short time-scales of the processes and the relatively small temperature changes during these times, because in a laser instrument with a line width of $\sim 10^{-2}$ cm^{-1} only a small fraction of the ozone molecules ($\sim 10^{-3}$–10^{-2}) can participate in absorbing the pumping radiation.

The method used here for examining the gas temperature in a vibrationally excited gas on the basis of the various relaxation processes can be applied with advantage to other molecules. The behavior of the gas temperature here is of fairly general type, and it may be found also for other molecular gases resonantly excited by IR radiation in the lower vibrational levels.

5. Appendix. The following system of equations was used in analyzing the thermalization of vibrationally excited O_3:

$$\frac{dn_{j_0}^{(i)}}{dt} = -J_i + \frac{1}{\tau_{RT}^{(0)}}\left(N_{000}q_{j_0}^{(i)} - n_{j_0}^{(i)}\right); \qquad (5.1)$$

$$\frac{dn_{j_1}^{(i)}}{dt} = +J_i + \frac{1}{\tau_{RT}^{(1)}}\left(N_{001}q_{j_1}^{(i)} - n_{j_1}^{(i)}\right) \quad (i = 1, 2, \ldots); \qquad (5.2)$$

$$\frac{dN_{000}}{dt} = -\sum_i J_i + F_{VT}(N_{010}; N_{000}) + 2\sum_{k=1}^{3} F_{VV_{(k)}} + \qquad (5.3)$$

$$+ F_{VV'_{(2)}}(N_{001}, N_{100}; N_{000}, N_{101}) + \sum A_{klm}N_{klm};$$

$$\frac{dN_{100}}{dt} = -4F_{VV_{(1)}}(N_{100}, N_{100}; N_{000}, N_{200}) + \qquad (5.4)$$

$$+ F_{VV'_{(1)}}(N_{000}, N_{001}; N_{000}, N_{100}) - F_{VV'_{(2)}}(N_{001}, N_{100}; N_{000}, N_{101}) -$$

$$- F_{VV'_{(4)}}(N_{000}, N_{100}, N_{000}, N_{010}) - A_{100}N_{100} - N_{100}/\tau_d;$$

$$\frac{dN_{010}}{dt} = -4F_{VV_{(2)}}(N_{010}, N_{010}; N_{000}, N_{020}) + \qquad (5.5)$$

$$+ F_{VV'_{(3)}}(N_{000}, N_{001}; N_{000}, N_{010}) + F_{VV'_{(4)}}(N_{000}, N_{100}; N_{000}, N_{010}) -$$

$$- F_{VT}(N_{010}; N_{000}) - A_{010}N_{010} - N_{010}/\tau_d;$$

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*Variation of the relaxation constants (τ_{RT}, $\tau_{VV}^{(1)}$, etc.) by a factor 1.5–2 near the values used in the model calculations shows that the general behavior of the gas temperature is not critically dependent on the detailed values of the constants within these limits.

$$\frac{dN_{001}}{dt} = \sum_i J_i - 4F_{VV(3)}(N_{001}, N_{001}; N_{000}, N_{002}) - \tag{5.6}$$
$$- F_{VV'_{(1)}}(N_{000}, N_{001}; N_{000}, N_{100}) - F_{VV'_{(2)}}(N_{001}, N_{100}; N_{000}, N_{101}) -$$
$$- F_{VV'_{(3)}}(N_{000}, N_{001}; N_{000}, N_{010}) - A_{001}N_{001} - N_{001}/\tau_d;$$

$$\frac{dN_m}{dt} = 2F_{VV(m)} - N_m(\tau_d^{-1} + A_m), \tag{5.7}$$
$$m = (200), (020), (002);$$

$$\frac{dN_{101}}{dt} = F_{VV'_{(2)}}(N_{001}, N_{100}; N_{000}, N_{101}) - N_{101}(\tau_d^{-1} + A_{101}), \tag{5.8}$$

where N_{klm} is the population of the (klm) vibrational level, N is the total molecule concentration, $n_{j_0}^{(i)}$, $n_{j_1}^{(i)}$ are the populations of the $j_0^{(i)}$ and $j_1^{(i)}$ rotational sublevels of the (000) and (001) levels participating in the absorption. Terms of the form J_i describe the optical pumping on the basis of the saturation in the absorption transition: $J_i = W_i(n_{j_0}^{(i)} - (g_{j_0}^{(i)}/g_{j_1}^{(i)})$, where W is the optical pumping probability $\left(W = \sum_i W_i = \sum_i \frac{\sigma_{j_0 j_1}^{(i)} I}{h\omega_{j_0 j_1}^{(i)}}\right)$, i is the number of rotational sublevels of the ground state interacting with the radiation, σ and ω are the absorption cross section (in cm²) and frequency for each of the corresponding lines of the ν_3 vibration-rotation band, W_i is the probability of optical pumping in band i of ν_3 (proportional to the transition intensity, Fig. 2), $g_{j_0}^{(i)}$, $g_{j_1}^{(i)}$ are the statistical weights of the rotational sublevels, $q_{j_0}^{(i)}$, $q_{j_1}^{(i)} = g_j^{(i)} \exp(-E^{(i)}/T)/Q_{ro}(T)$ are the equilibrium proportions of the molecules in the rotational sublevels j (Q_{ro_0}, Q_{ro_1} are the rotational statistical sums), $E_{j_0}^{(i)}$, $E_{j_1}^{(i)}$, E_{klm} are respectively the edges of the rotational sublevels and the vibrational levels. By terms up to $F_{VV(k)}(\ldots)$, $F_{VV'(k)}(\ldots)$, and $F_{VT}(\ldots)$ we denote the rates of change in the populations of the corresponding vibrational levels due to V—V, V—V' and V—T processes, as shown by arrows in Fig. 1. For example, $F_{VV'_{(1)}}(N_{000}, N_{001}; N_{000}, N_{100}) = \frac{1}{N\tau_{VV'}^{(1)}}\left[N_{000}N_{001} - N_{000}N_{100}\exp\left(-\Delta E_{VV'_{(1)}}/T\right)\right]$ where τ_{VV}, $\tau_{VV'}$, and τ_{VT} are the characteristic times of the corresponding processes, $\Delta E_{VV, VV', VT}$ are the energy deficiencies of those processes, τ_{RT} is the R—T relaxation time, τ_d is the characteristic time for diffusion of vibrationally excited molecules from the region of interaction with the radiation, and A_{klm} are the probabilities of spontaneous radiated vibrational transitions. As τ_{RT} is much less than all the other characteristic relaxation times, we have neglected the collisional and spontaneous processes in (5.1) and (5.2). In the concentrations, in accordance with [11] we assume that $\tau_{VV}^{(1)} = \tau_{VV}^{(2)} = \tau_{VV}^{(3)} = \tau_{VV}$, $\tau_{VV'}^{(1)} = \tau_{VV'}^{(2)}$, $\tau_{VV'}^{(3)} = \tau_{VV'}^{(4)}$, and also that $\tau_{RT}^{(0)} = \tau_{RT}^{(1)} = \tau_{RT}$.

In analyzing (5.1)-(5.8) we have not considered the diffusion and spontaneous-radiative processes. The scope for neglecting diffusion is dependent on the transverse dimensions of the laser beam and cell. Our estimates show that for the usual parameters of a CO_2 laser beam ($S \geqslant 0.1$ cm²) and pressures used here ($p > 1$ GPa), the characteristic times for diffusion and heat transport transverse to the beam are of millisecond order, which are larger by 2-3 orders of magnitude than the times of the V—V and V—V' processes, and therefore diffusion cannot play an appreciable part for $t \leqslant \tau_{VV'}$. Incorporation of the spontaneous radiative processes does not influence the analysis of (5.1)-(5.8), since experimental data indicate that the probabilities A_{klm} of spontaneous radiative decay of the lower vibrational levels of ozone are very small ($A_{klm} \ll \tau_{VT}^{-1}$ at the pressures used): $A_{100} = 0.355$ sec⁻¹, $A_{010} = 0.25$ sec⁻¹, $A_{001} = 10.64$ sec⁻¹ [14]. With these assumptions, system (5.1)-(5.8) becomes closed (the total number of particles does not change).

The change in gas temperature T in the molecular gas is described by

$$\rho c_p \frac{dT}{dt} = f, \tag{5.9}$$

where f is the energy flux from the vibrational and rotational degrees of freedom into the translational degrees, which according to (5.1)-(5.8) takes the form

$$
\begin{aligned}
f = \sum_i \left[\frac{E_{j_0}^{(i)}}{\tau_{RT}^{(0)}} \left(n_{j_0}^{(i)} - N_{000} q_{j_0}^{(i)} \right) + \frac{E_{j_1}^{(i)}}{\tau_{RT}^{(1)}} \left(n_{j_1}^{(i)} - N_{001} q_{j_1}^{(i)} \right) \right] + \\
+ \Delta E_{VT} F_{VT} (N_{010}; N_{000}) + 2 \sum_{k=1}^{3} \Delta E_{VV_{(k)}} F_{VV_{(k)}} + \\
+ \Delta E_{VV'_{(1)}} F_{VV'_{(1)}} (N_{000}, N_{001}; N_{000}, N_{100}) + \\
+ \Delta E_{VV'_{(2)}} F_{VV'_{(2)}} (N_{001}, N_{100}; N_{000}, N_{101}) + \\
+ \Delta E_{VV'_{(3)}} F_{VV'_{(3)}} (N_{000}, N_{001}; N_{000}, N_{010}) + \\
+ \Delta E_{VV'_{(4)}} F_{VV'_{(4)}} (N_{000}, N_{100}; N_{000}, N_{010}).
\end{aligned}
\tag{5.10}
$$

In (5.9), only the translational and rotational degrees of freedom have been incorporated into c_p.

Analysis of (5.1)-(5.10) allows one to examine the thermalization of ozone in resonant vibrational excitation by IR radiation.

LITERATURE CITED

1. B. F. Gordiets, A. I. Osipov, and R. V. Khokhlov, "Gas cooling on the passage of high-power radiation from a CO_2 laser through the atmosphere," Zh. Tekh. Fiz., 44, 1063 (1974).
2. E. L. Breig, "Limitation on the atmospheric thermal effects for high-power CO_2 laser beams," J. Opt. Soc. Amer., 62, 518 (1972); H. Aung and M. Katayama, "Interferometric studies of transient cooling and heating of CO_2 induced by 10.6 μm laser pulse and vibration-translation relaxation," Jpn. J. Appl. Phys., 14, No. 1 (1975).
3. V. M. Gordienko, V. A. Gorshkov, et al., "Kinetic cooling of a CO_2–N_2 mixture by CO_2 laser radiation," Zh. Eksp. Teor. Fiz., 73, 874 (1977); S. A. Akhmanov, V. M. Gordienko, and V. Ya. Panchenko, "Thermalization of a molecular gas in resonant excitation by laser radiation," Izv. Vyssh. Uchebn. Zaved., Fizika, No. 11 (1977); V. N. Varakin, V. M. Gordienko, and V. Ya. Panchenko, "Temperature dependence of the kinetic-cooling effect," Kvant. Elektr., 6, No. 4 (1979); A. N. Vargin, V. V. Gogokhiya, et al., "A model for kinetic cooling of carbon dioxide," Kvant. Elektr., 5, No. 6 (1978); V. N. Varakin and V. Ya. Panchenko, "Theory of the kinetic cooling of a CO_2–N_2 mixture with a high carbon dioxide content," Zh. Prikl. Mat. Tekh. Fiz., No. 5 (1979).
4. S. A. Zhdanok, A. P. Napartovich, and A. N. Starostin, "Establishment of the distribution over vibrational levels for diatomic molecules," Zh. Eksp. Teor. Fiz., 76, No. 1 (1979).
5. B. F. Gordiets and V. Ya. Panchenko, "Cooling of a molecular gas stimulated by laser radiation," Pis'ma ZhTF, 4, No. 23 (1978).
6. V. M. Gordienko, A. V. Mikheenko, and V. Ya. Panchenko, "Cooling of selectively excited Cd_4 gas during vibrational–vibrational and rotational–translational relaxation," Pis'ma Zh. Tekh. Fiz., 5, No. 8 (1979).
7. A. Barbe, C. Secroun, and P. Jouve, "Infrared spectra of $^{16}O_3$ and $^{18}O_3$: Darling and Dennison resonance and anharmonic potential function of ozone," J. Mol. Spectr., 49, No. 2 (1974).
8. A. Barbe, C. Secroun, et al., "Infrared and microwave high-resolution spectrum of the ν_3 band of ozone," J. Mol. Spectr., 64, No. 3 (1977).
9. J. Shewchun, B. K. Garside, et al, "Pollution monitoring systems based on resonance absorption measurements of ozone with a 'tunable' CO_2 laser: some criteria," Appl. Opt., 15, No. 2 (1976).
10. R. R. Patty, G. M. Russwurn, W. A. McClenny, and D. R. Morgan, "CO_2 laser absorption coefficients for determining ambient levels of O_3, NH_3, and C_2H_2," Appl. Opt., 13, No. 12 (1974).
11. D. I. Rosen and T. A. Cool, "Vibrational deactivation of O_3 molecules in gas mixtures," J. Chem. Phys., 59, No. 11 (1973); J. Chem. Phys., 62, No. 2 (1975).
12. V. N. Kondrat'ev and E. E. Nikitin, Kinetics and Mechanisms of Gas-Phase Reactions [in Russian], Nauka, Moscow (1974).
13. M. S. Djidjoev, V. Ya. Panchenko, I. M. Sizova, and A. P. Sukhorukov, "Thermalization and dissociation dynamics of ozone excited by IR resonance radiation," in: Second International Conference on Multiphoton Processes, Budapest, April 1980. Abstracts.

14. C. W. von Rosenberg and D. W. Trainor, "Vibrational excitation of ozone formed by recombination," J. Chem. Phys., 61, No. 6 (1974).

LASER SONOLUMINESCENCE IN WATER UNDER INCREASED HYDROSTATIC PRESSURE

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The nature of the fairly recently discovered [1-3] pulsed luminescence accompanying the collapse of a single cavity initiated by laser breakdown in a liquid has still not been clarified, despite the importance of solving questions associated with the determination of the state variables of a substance in the vicinity of the special point during spherically symmetric collapse [4-6], which is manifested most distinctly, as was pointed out in [7], in the case of the laser method (as distinct from a high-voltage discharge or exploding wires) of initiation of inhomogeneities.

In [8] attention was concentrated on the purely recombinational mechanism of generation of the luminescence accompanying the collapse of a cavity initiated by laser breakdown in liquid nitrogen. We refer here to the recombination of active particles formed at the instant of spark breakdown. It is quite natural to postulate the role of processes of this type in sonoluminescent effects in water and aqueous solutions. The active particles contributing to laser sonoluminescence (LSL) in water could be, at least for several collapse regimes, H and OH radicals, which have been shown to play an appreciable role in the luminescence accompanying the pulsations of a microscopic cavity in an ultrasonic field of subcavitation intensity [9].

In the present investigation we availed ourselves of the opportunity to "control" the moment of collapse by using the hydrostatic pressure (due to the sharp dependence of the cavity pulsation period on the hydrostatic pressure: $T \sim 1/p^{5/6}$ [10]) and attempted an experimental and theoretical evaluation of the contribution of the luminescence component due to recombination of active particles (particularly H and OH radicals), initiated at different stages in the life of the cavity, including the moment of breakdown.

In addition, by conducting pressure experiments in water at temperatures close to the boiling point we could stimulate to some extent the thermodynamic situation in the induction of cavitation luminescence in liquid nitrogen and other cryogenic liquids (Ar, Xe, Ne).

<ins>1. Experimental Results and Their Brief Analysis.</ins> The apparatus used for the experiment was similar to that described in [11]. The working chamber, containing the water in which laser breakdown occurred ($E_L = 0.02$ J, $\tau \sim 10^{-8}$ sec), could withstand hydrostatic pressures up to $8 \cdot 10^6$ Pa. The luminous effects accompanying the breakdown of the liquid and the subsequent collapse of the cavity were detected by an FÉU-13 photomultiplier. The intensity of the shock-acoustic effects was determined by means of a hydrophone, based on the piezoceramic TsTS-19, with a resolving time of $\sim 3 \cdot 10^{-7}$ sec. The information obtained through the acoustic and light channels, i.e., from the FÉU and the hydrophone, was fed to an S8-2A two-beam storage oscillograph.

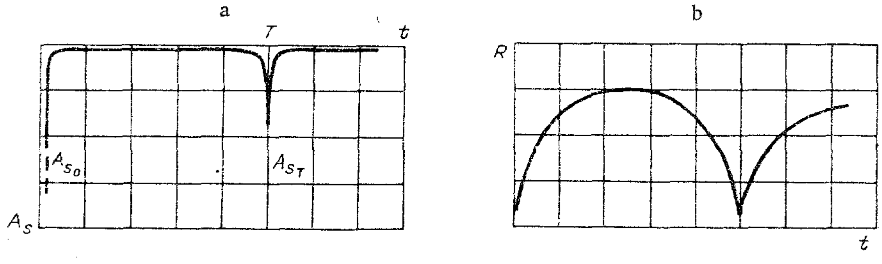

Fig. 1

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