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CREATION OF A POPULATION INVERSION IN POLYATOMIC MOLECULES THROUGH THE ENERGY OF CHEMICAL REACTIONS

M. S. DZHIDZHOEV, M. I. PIMENOV, V. G. PLATONENKO, Yu. V. FILIPPOV, and R. V. KHOKHLOV

Moscow State University

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It is suggested that polyatomic molecules can be employed in a chemical laser. A method for determining the vibrational temperatures of CO_2-type molecules produced or excited by a chemical reaction is proposed and realized. It is shown that population inversion of the energy levels of CO_2 occurs upon explosion of a mixture of hydrazoic acid and carbon dioxide.

1. AT the present time many attempts are being made to transform chemical energy into the energy of laser radiation. In all chemical lasers realized to date, diatomic molecules produced in a reaction are used to obtain population inversion. In this case vibrational or vibration-rotational inversion is created within a single vibrational degree of freedom.

In polyatomic molecules with several vibrational relaxation times, population inversion of vibrational levels of different degrees of freedom may be obtained in the post-reaction period, even if inversion does not occur as a result of the reaction. Let there be formed in a chemical reaction polyatomic molecules in which vibrational modes with maximum lifetime are excited rather strongly. During the reaction, or a short time after its completion, a Boltzmann distribution is established within each vibrational mode. The "temperatures" of the different vibrational degrees of freedom can remain different for a long time, since the degrees of freedom with the least lifetimes will cool faster. Then, generally speaking, it is possible to get population inversion among the levels of the different degrees of freedom, when their "temperatures" differ sufficiently strongly. The situation here is analogous to that which takes place in the electrical CO_2 laser.[1] It should be mentioned that there exists a possibility of regulating within certain limits the relaxation rates of the individual vibrational level systems by aiming for the optimum relation between them.

To obtain population inversion in polyatomic reaction products by the method described, it is necessary to fulfill a number of conditions: 1) a sufficiently fast rate of reaction compared to the rate of transfer of vibrational energy to other degrees of freedom; 2) the presence in the reaction products of a system of vibrational levels satisfactory for creating inversion (other molecular lasers have the same requirement[1]); 3) reaction products must be obtained in which an isolated vibrational mode with maximum lifetime is strongly excited. It is difficult to satisfy these requirements simultaneously. Moreover, the distribution of energy over the various degrees of freedom in polyatomic molecules is poorly known, so that promising systems can be found only by trial.

It would appear possible to combine the merits of diatomic and polyatomic molecules: having obtained in a chemical reaction strongly excited diatomic molecules with long vibrational relaxation times, use them for the resonant transfer of vibrational energy to an isolated vibrational mode of the polyatomic molecules with a system of levels convenient for creation of population inversion.

This method has the following advantages.

Since a diatomic molecule has only one vibrational degree of freedom, a significant portion of the reaction energy can be evolved in the form of vibrations of a single type. Since the energy is later transferred to an isolated vibrational mode of polyatomic molecules, and the density of the latter may be rather low, the free energy of the system diminishes only slightly during such a transfer. The vibrations of a polyatomic molecule isolated in this way can be excited much more strongly than the vibrations of other types. It is very important that in this case the distribution function of the reaction products over the vibrational levels does not play an essential role. It is only necessary that a significant portion of the energy be evolved in vibrational form. This circumstance greatly widens the class of reactions that can be used to realize chemical lasers.

The requirements imposed on the reaction are also strongly mitigated, since the vibrational relaxation time of many diatomic molecules is rather long. It should be noted that the maximum relaxation times are possessed by symmetric molecules, the direct utilization of which to obtain generation is impossible.

A disadvantage of the method is the necessity of choosing molecules between which there is a sufficiently effective exchange of vibrational energy. As will be seen below, in some cases this problem is already solved.

The molecules N_2, O_2, H_2, CO, and some others[2] have a long lifetime in the vibrationally excited state.

Of particular interest is the nitrogen molecule, which effectively exchanges vibrational energy with CO_2 and N_2O molecules and has been used successfully in electrical molecular lasers.[1)] The class of reactions in which N_2 appears as a source is rather broad. However, data on the distribution of energy among the different

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[1)] Basov and his co-workers [3] have also shown the possibility of obtaining population inversion in CO_2 by letting a mixture of N_2 and CO_2 escape into vacuum.

degrees of freedom of the products of these reactions are practically nonexistent. Hence, the question of which specific reactions hold promise needs special investigation.

2. In this paper we investigate the possibility of obtaining population inversion of the energy levels of CO_2 in an explosion of a mixture of hydrazoic acid HN_3 and CO_2.

Hydrazoic acid is easily synthesized and has high stability. The energy yielded by its decomposition into nitrogen and hydrogen is 71 kcal/mole. It may be assumed that most of this energy is transferred into the vibrational energy of the nitrogen molecules. According to Voronkov and Rozenberg,[4] the mechanism of the reaction is principally by the following processes:

$$HN_3^* \rightleftarrows NH + N_2 \; (-10\,\text{kcal}), \tag{1}$$

$$NH + HN_3 \rightleftarrows H_2 + N_2 + N_2^* \; (+152\,\text{kcal}), \tag{2}$$

$$N_2^* + \varkappa HN_3 \rightleftarrows \varkappa HN_3^* + N_2, \tag{3}$$

$$N_2^* + M \rightleftarrows N_2 + M^*, \tag{4}$$

$$M + HN_3^* \rightleftarrows M^* + HN_3. \tag{5}$$

Here HN_3^* and N_2^* are vibrationally excited molecules, M is a diluent molecule, and κ is the average number of HN_3 molecules activated by one N_2^* molecule, which appears as the result of elementary act (2).

This is a chain reaction with an energy chain. For $\kappa > 1$ the chain is branched. Process (3) has obviously a rather high probability, since the nitrogen 2330 cm^{-1} vibration frequency is close to one of the vibrational frequencies of HN_3, 2389 cm^{-1}.[5] Hence, it may be expected that the reaction proceeds rapidly (we do not know of any experimental data on the reaction rate). Processes (4) and, evidently, (5) also have a high probability when the role of particle M is played by the CO_2 molecule, since the vibrational frequencies of the colliding molecules are close. Hence, dilution of hydrazoic acid by carbon dioxide gas can lead to a considerable slowing down of the reaction. At the same time, these processes lead to excitation of the asymmetric vibrations and, in principle, to inversion of the populations of the vibrational levels with quantum numbers $v_1 + 1$, v_2, v_3, or v_1, $v_2 + 2$, v_3, and v_1, v_2, $v_3 + 1$.

The analysis below is based on the following assumptions.

1) Establishment of a Boltzmann distribution among the vibrational levels of one degree of freedom occurs quite rapidly, so that the population of the level $n(v_1, v_2, v_3)$ can be written in the form

$$n(v_1, v_2, v_3) \approx \frac{1}{Z_{\text{vib}}} \exp\left[-\frac{v_1 h\nu_1}{kT_1} - \frac{v_2 h\nu_2}{kT_2} - \frac{v_3 h\nu_3}{kT_3}\right](v_2 + 1), \tag{6}$$

where Z_{vib} is the vibrational statistical sum, and T_1, T_2, T_3 are the temperatures of the different vibrational degrees of freedom, unequal to each other in general. The factor $v_2 + 1$ is equal to the statistical weight of the level (splitting of levels with given v_2 is not important below).

2) As a consequence of strong coupling between deformational and symmetrical vibrations (Fermi resonance), the temperatures T_1 and T_2 are approximately equal.

The time for the establishment of the distribution (6) and the equality $T_1 = T_2$, according to estimates based on the results of [6], amounted to not more than 5 μsec under the conditions of the experiments described below.

3. The basic parameters that determine the populations of the vibrational levels are the temperatures T_2 and T_3. The method described below, which is based on investigations of the infrared spectrum of CO_2 emission, can be used to measure at least one of these temperatures as a function of time.

To determine T_2 and/or T_3 it is sufficient to obtain an analytical expression for the dependence of the intensity of emission on frequency $J(\nu)$, in which T_2 and/or T_3 is a parameter, and compare it with the dependence $J(\nu)$ obtained experimentally. The most convenient spectral region for the measurements in the case of CO_2 is the 4.3 μ region, which corresponds to the radiative transitions $v_1, v_2, v_3 + 1 \rightarrow v_1, v_2, v_3$. The zero of the corresponding band, according to [5], is at the frequency

$$\nu(v_1, v_2, v_3 + 1) \approx \nu_0 - x_{13}v_1 - x_{23}v_2 - 2x_{33}v_3, \tag{7}$$

where $\nu_0 = 2349.3\ cm^{-1}$, $x_{13} = 21.9\ cm^{-1}$, $x_{23} = 11\ cm^{-1}$, $x_{33} = 12.5\ cm^{-1}$. The contribution of the considered transition to the radiation intensity J at frequency ν is proportional to the population of the level $n(v_1, v_2, v_3 + 1)$, the transition probability $W_{v_1v_2v_3}^{v_1v_2v_3+1}$, and some frequency factor $I[\nu - \nu(v_1, v_2, v_3 + 1)]$ that depends on the difference $\nu - \nu(v_1, v_2, v_3 + 1)$ and on the distribution over the rotational levels:

$$J_{v_1v_2v_3+1}(\nu) \sim n(v_1, v_2, v_3)\, W_{v_1,\, v_2,\, v_3}^{v_1,\, v_2,\, v_3+1}\, I[\nu - \nu(v_1, v_2, v_3 + 1)]. \tag{8}$$

The distribution over the vibrational levels may be assumed to be in equilibrium with rotational temperature T_{rot}, equal to the ambient temperature T, since this distribution is established after a few molecular collisions. If the rotational structure of the band is not resolved, the frequency factor has the form[7]

$$I[\nu - \nu(v_1, v_2, v_3 + 1)] \approx \frac{|\nu - \nu(v_1, v_2, v_3 + 1)|}{2B} \times \exp\{-\alpha[\nu - \nu(v_1, v_2, v_3 + 1)]^2\}, \tag{9}$$

where B is the rotational constant of the molecule in cm^{-1}, and $\alpha = hc/4kTB$.

To find the total intensity J at frequency ν, we need to sum (8) over v_1, v_2, and v_3. Considering that $W_{v_1v_2v_3}^{v_1v_2v_3+1} \approx (v_3 + 1)W_{000}^{001}$, as well as Eqs. (6), (7), and (9), we obtain

$$J(\nu) \sim \sum_{v_1v_2v_3} (v_3 + 1)(v_2 + 1)\,|\nu_0 - \nu - x_{13}v_1 - x_{23}v_2 - 2x_{33}v_3| \times \exp[-\alpha(\nu_0 - \nu - x_{13}v_1 - x_{23}v_2 - 2x_{33}v_3)^2 - \alpha_1 v_1 - \alpha_2 v_2 - \alpha_3 v_3], \tag{10}$$

where

$$\alpha_i = hc\nu_i / kT_i; \quad i = 1, 2, 3.$$

Equation (10) may be used only in working with a wide monochromator slit (when the rotational structure of the band is not resolved). In this case it is valid to set $x_{13} = 2x_{23}$ (see Eq. (7)). In addition, when $T_1 \approx T_2$, we can assume that $\alpha_1 \approx 2\alpha_2$ (the difference $\alpha_1 - \alpha_2$ is large only at low temperatures T_2, i.e., large α_1 and α_2, when the terms with $v_1, v_2 \neq 0$ give an insignificant contribution to the sum in (10). Then (10) transforms to

$$J(\nu)\sim\sum_{v_3}\sum_{V}\sum_{v_2=0}^{V}(v_3+1)(v_2+1)\,|\nu_0-\nu-x_{23}V-2x_{33}v_3|$$
$$\times\exp[-\alpha(\nu_0-\nu-x_{23}V-2x_{33}v_3)^2-\alpha_2V-\alpha_3v_3]. \tag{11}$$

Summing over v_2 and replacing v_3 and v_2 by the differential operators $-\partial/\partial\alpha_3$ and $-\partial/\partial\alpha_2$, we obtain

$$J(\nu)\sim D\sum_{v_3}\sum_{V}|\nu_0-\nu-x_{23}v_2-2x_{33}v_3|$$
$$\times\exp[-\alpha(\nu_0-\nu-x_{23}v_2-2x_{33}v_3)^2-\alpha_2V-\alpha_3v_3], \tag{12}$$

where

$$D=-\Big(\frac{\partial}{\partial\alpha_2}-1\Big)\Big(\frac{\partial}{\partial\alpha_2}-2\Big)\Big(\frac{\partial}{\partial\alpha_3}-1\Big).$$

In order to be rid of the modulus signs, we represent (12) in the form

$$J(\nu)\sim D\Big\{\Big[\sum_{v_3=0}^{v_3^0}A(v_3,V)-\sum_{v_3=v_3^0+1}A(v_3,V)\Big]-2\sum_{v_3=0}\sum_{V=V^0}A(v_3,V)\Big\}, \tag{13}$$

where v_3^0 is the whole part of $(\nu_0-\nu)/2x_{33}$, and V, of $[(\nu_0-\nu)/x_{23}-2v_3x_{33}/x_{23}+1]$,

$$A(v_3,V)=(\nu-\nu_0+x_{23}V+2x_{33}v_3)\exp[-\alpha(\nu-\nu_0$$
$$+2x_{33}v_3+x_{23}V)^2-\alpha_2V-\alpha_3v_3].$$

At temperatures higher than room temperature we have $\alpha^{-1/2}>x_{23}$. Therefore, as V changes by unity, the terms in (13) vary rather smoothly, provided α_2 is not too large; the variation becomes abrupt for large values of $|\nu-\nu_0+2x_{33}v_3+x_{23}V|$; however, terms with such V and v_3 give a small contribution to the sum. Consequently, the sum over V may be replaced by an integral. As a result, small fluctuations of the function $J(\nu)$ will be averaged out, and a certain quantitative error will appear; however, the large-scale functional dependence of $J(\nu)$ should not be changed.

The expression for $A(v_3, V)$ is integrated by parts. As a result (13) is transformed to the form

$$J(\nu)\sim D\Big\{\exp\Big(-\frac{\nu_0-\nu}{2x_{33}}\alpha_2\Big)\Big[\sum_{v=-v_3^0}^{0}B(v,x)-\sum_{v=1}B(v,x)\Big]$$
$$-2\exp\Big(-\frac{\nu_0-\nu}{x_{23}}\alpha_2\Big)\sum_{v_3=0}^{v_3^0}\exp(-v_3\alpha_3')C(\alpha_2)\Big\}, \tag{14}$$

where

$$B(v,x)=\exp(-v\alpha_3)\{\exp[-\alpha(-x+2x_{33}v)^2$$
$$+\delta\exp(\delta^2/4)\Phi[\alpha^{1/2}(-x+\delta/2\alpha^{1/2}+2x_{33}v)]]\},$$
$$C(\alpha_2)=1+\delta\exp(\delta^2/4)\Phi(\delta/2),\quad \delta=\alpha_2/x_{23}\alpha^{1/2},$$
$$x=\nu_0-\nu-2x_{33}v_3^0,\qquad \alpha_3'=\alpha_3-2\alpha_2x_{33}/x_{23}.$$

When $\nu_0-\nu>2x_{33}$, the summation over v in the first of the sums in (14) can be carried out from $-\infty$. The expression in the square brackets then gives a periodicity with period $2x_{33}$ to the function $\nu_0-\nu$. Denoting this function by $F(\alpha_2, \nu_0-\nu)$, and carrying out the summation over v_3, we get

$$J(\nu)\sim D\{\exp(-\alpha_3v_3^0)\;F(\alpha_2,\nu_0-\nu)$$
$$-2\Big[\exp v_3^0-\exp\Big(-\frac{\nu_0-\nu}{x_{23}}\alpha_2\Big)\Big]$$
$$\times\Big[1-\exp\Big(-\alpha_3+\alpha_2\cdot2\frac{x_{33}}{x_{23}}\Big)\Big]^{-1}C(\alpha_2)\Big\}. \tag{15}$$

Substitution into (15) of the operator D from (12), differentiation, and averaging over ν in the segment $2x_{33}$ leads to an expression of the type

$$J_{\mathrm{cp}}(\nu)\sim(a_3+\nu_0-\nu)\exp\Big(-\frac{\nu_0-\nu}{2x_{33}}\alpha_3\Big)$$
$$+d[a_2+b_2(\nu_0-\nu)+(\nu_0-\nu)^2]\exp\Big(-\frac{\nu_0-\nu}{x_{23}}\alpha_2\Big). \tag{16}$$

The coefficients a_3, a_2, b_2 are easily found when

$$|\alpha_3-2\alpha_2x_{33}/x_{23}|\gg1, \tag{17}$$
$$a_3=2x_{33},\qquad a_2=2x_{23}^2,\qquad b_2=3x_{23}. \tag{17$'$}$$

From the physical meaning of these coefficients it follows that (17′) is valid even if (17) does not hold. The quantity $(a_3+\nu_0-\nu)/2x_{33}$ is connected by its origin to the coefficient of v_3+1 in (11), which is obtained rigorously, while $[a_2+b_2(\nu_0-\nu)+(\nu_0-\nu)^2]/x_{23}^2$ is connected to the coefficient of $(V+1)(V+2)$, which is represented in (12) by the operator $(\partial/\partial\alpha_2-1)(\partial/\partial\alpha_2-2)$. Calculation of the coefficient d is difficult.

From the form of the experimental curve of $J(\nu)$ it is easy to determine which of the exponentials in (16) decays more slowly. By approximating at large $\nu_0-\nu$ by means of the term containing this exponential, it is possible to find one of the temperatures T_2 and T_3. For example, when $\alpha_3>2\alpha_2x_{33}/x_{23}$ the principal role in (16) is played by the first term. Then α_3 and, consequently, T_3 are determined from the slope of $\ln[J(\nu)/(2x_{33}+\nu_0-\nu)]$ at large $\nu_0-\nu$. In principle, both temperatures T_2 and T_3 can be determined. However, in practice a high degree of experimental accuracy in the measurements is required for this.

4. Experimentally, we investigated the emission spectrum of reacting mixtures of $3HN_3+CO_2$ and $_3HN_3+CO_2+8Ar$ at a total pressure of 7 and 21 Torr, respectively. The measurements were carried out in the 4.3 and 2.6 μ regions.

The experimental arrangement is shown schematically in Fig. 1.

The mixture was let into a glass tube 50 cm long and 5 cm in diameter and ignited by a high-voltage electrical pulse. The length of the pulse was 1–2 μsec. The electrical energy fed into the reaction tube did not exceed 0.7 J, which is approximately 1% of the energy evolved in the decomposition of HN_3. The reaction tube had two symmetrical side windows and one end window of CaF_2. The radiation coming through one of the side windows was directed onto the slit of the monochromator MI from an IKS-12 spectrometer with a LiF prism and was registered at the output of the monochromator by a GeAu photodetector I cooled by liquid nitrogen. After preamplification, the signal was fed to the dual-beam oscilloscope S1-16. The other channel of the os-

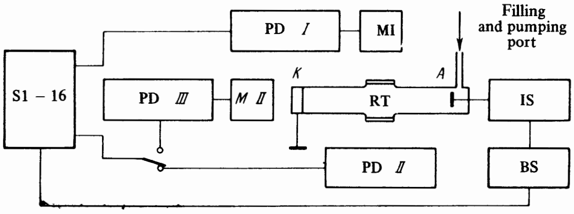

FIG. 1. Block diagram of experimental setup. RT – reaction tube; PD – photodetector and amplifier, M – monochromator; IS – ignition system; BS – block synchronization; C, A – electrodes.

cilloscope registered the signal from the monitoring photodetector II, which registered the radiation that came through the other side window, in the spectral interval 7–2 μ. The signal was photographed from the screen of the oscilloscope. The measurements were carried out with a spectral slit of 6 cm^{-1} in the region from 2400 to 2100 cm^{-1} every 14 cm^{-1}.

The second monochromator M II from an IKS-12 with a similar detection system was employed for the registration of radiation in the region 2.6 μ and for evaluating the influence of self-absorption in the 4.3-μ region.

The time resolution of the apparatus with the mixture $3HN_3 + CO_2$ was 15 μsec; with the mixture containing argon, the channel containing monochromator II had a time resolution of 100 μsec. In the region 2100 to 2360 cm^{-1}, the signal-to-noise ratio was not less than 10; in the region 2360 to 2400 cm^{-1} this ratio rapidly decreased with increasing ν (to 2, when the time resolution was 15 μsec).

Photographs of the reaction tube taken at the moment of discharge showed that in the mixture containing argon the discharge filled the volume uniformly. Control experiments demonstrated a high repeatability of the results (including those with a time resolution of 15 μsec.

In the mixture $3HN_3 + CO_2$ the discharge and reaction proceeded nonuniformly over the volume. The amplitude of the signal from detector I rapidly fluctuated with time relative to the envelope, and from ignition to ignition, within 30% limits. With decreasing energy of the igniting pulse the fast fluctuations disappeared; however, the character of the signal changed sharply to a succession of peaks of gradually diminishing amplitude (see Fig. 2). The separation between the peaks gradually increased.

To explain the appearance of these peaks, we carried out some additional investigations using a photomultiplier to register the radiation passing through the walls of the tube in different sections, as well as with monochromator M II with different diaphragms on the exit window of the tube. The measurements showed that the character of the radiation was the same in all transverse cross sections of the tube. The radiation and, consequently, the reaction began first near the tube walls and propagated to the axis. As a consequence of this, it is evident that strong acoustic waves arise, which distort the course of the reaction and of the processes that redistribute the energy. Spectral measurements were not made in the peak regime.

As the measurements showed, the total intensity of radiation in the 4.3-μ region was greater by an order of magnitude than the total intensity in the 2.6-μ region. Therefore, at vibrational temperatures greater than the Debye temperature the total intensity registered by the control detector II is approximately proportional to the temperature T_3. Thus, the function $T_3(t)$, to within a constant, coincides with the function $J_C(t)$, where J_C is the intensity registered by the control detector. This assertion is valid, however, only in the absence of density fluctuations. Such a regime occurred with the mixture $3HN_3 + CO_2 + 8Ar$. In the presence of fluctuations, the intensity J_C is proportional to some volume "average" temperature T_3 (the control detector was located insufficiently far from the reaction tube for the averaging to be strictly correct).

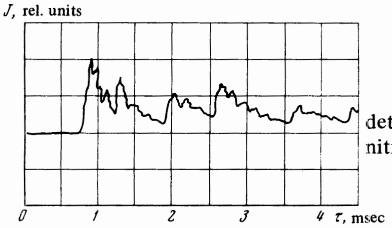

FIG. 2. Signal from the photodetector I during nonuniform ignition of the mixture $3HN_3 + CO_2$.

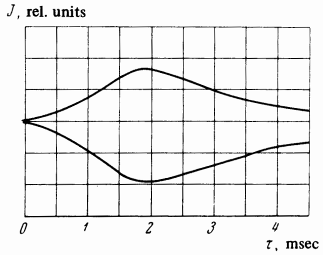

FIG. 3. Signal from the control photodetector II (lower curve) and from photodetector I (upper curve) during explosion of mixture $3HN_3 + CO_2 + 8Ar$.

5. Figure 3 shows an oscillogram of the signal from the control detector II for the case of the mixture $3HN_3 + CO_2 + 8Ar$. As was indicated above, the given dependence is approximately the same as the function $T_3(t)$.

In Fig. 4 is shown the function $J(\nu)$ in the region 2400 to 2100 cm^{-1} at different moments of time. As is seen from the curves, the curve $J(\nu)$ is not monotonic in the initial stages of the process. Maxima are resolved, which correspond to the transitions 0, 0, v + 1 → 0, 0, v. However, on the average this dependence is described by a function of the type $(a + x) \exp -\beta x$, from which it follows that $T_3 > T_2 x_{23}\nu_3/2x_{33}\nu_2 \approx 1.55 T_2$.

Later, with an increase in rotational temperature (and, obviously, of temperature T_2), the resolution became worse. At $\tau = 2$ msec the curve $J(\nu)$ to an accuracy of 10% (the experimental accuracy) is described by the function $(a + \nu_0 - \nu) \exp[-\beta(\nu_0 - \nu)]$, where $a = 25$ cm^{-1}, $\beta = 90$ cm. The value of the coefficient β and, consequently, of the temperature T_3 was determined from the slope of the line $\ln[J(\nu)/(25\ cm^{-1} + \nu_0 - \nu)]$. For the moment of time $\tau = 2$ msec, all experimental points lie on a straight line corresponding to $T_3 = 3.60\Theta \approx 12\,000°K$ to within an accuracy of 0.1 (Fig. 5). With decreasing τ the scatter increases.

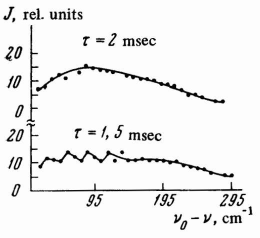

FIG. 4.

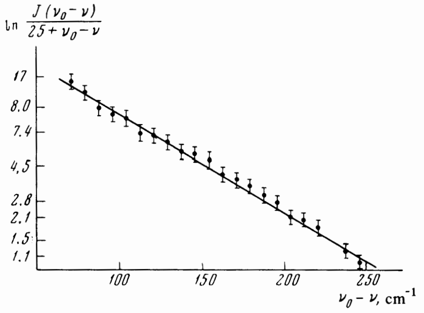

FIG. 5.

FIG. 4. Spectral dependence $J(\nu)$ of radiation of CO_2 during ignition of the mixture $3HN_3 + CO_2 + 8Ar$ for two moments of time.

FIG. 5. Plot of $\ln[J(\nu)/(25 + \nu_0 - \nu)]$ for $\tau = 2$ msec. Mixture: $3HN_3 + CO_2 + 8Ar$.

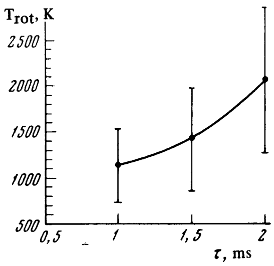

FIG. 6. Dependence of rotational temperature T_{rot} on time during ignition of the mixture $3HN_3 + CO_2 + 8Ar$.

Qualitatively, the curve $T_3(t)$ constructed from the points determined from the spectral function $J(\nu)$ agrees with the curve $J_c(t)$.

The rotational temperature was determined from the slope of the curve in the region 2400 to 2360 cm^{-1} corresponding to the R branch of the transition $001 \rightarrow 000$. The results are presented in Fig. 6. As noted above, in this region the signal-to-noise ratio was insufficiently high. Hence the accuracy of determination of T_{rot} is only 50%.

In the case of the mixture $3HN_3 + CO_2$, as we already mentioned, the radiation was irregular. Both the leading edge of the rise in intensity and its duration were found to be several times less than in the case of the mixture containing argon.

For a rough estimate of T_3 the fluctuations of intensity $J(\nu)$ with time were averaged, and the temperature T_3 was determined from the average values by the method described above. The maximum T_3 was 11 500°K. This value corresponds qualitatively to the total intensity of radiation $J_c(t)$ registered by the control detector.

The spectral dependence of radiation in the 2.6-μ region corresponding to the transitions $v_1, v_2, v_3 \rightarrow v_1 - 1, v_2, v_3 - 1$ or $v_1, v_2, v_3 \rightarrow v_1, v_2 - 2, v_3 - 1$ was not investigated in detail.

In preliminary experiments radiation was observed during ignition of hydrazoic acid HN_3 lasting about 100 μsec. However, its intensity was insufficient for spectral investigations. With the aid of different filters it was established that this radiation has a wavelength of 3 to 3.5 μ, which corresponds to vibrational transitions in HN_3.

The vibrational temperature T_2 was not determined directly in our work because of insufficient measurement accuracy. It is possible, however, to estimate the upper limit of this temperature from the energy yield of the reaction and the temperatures T_3 and T_{rot}. The estimates show that for $\tau = 2$ msec, $T_2 < 3000°K$. For these estimates it was assumed that the vibrational temperature of nitrogen and hydrogen equals T_3. Considering that the rate of relaxation of the deformational and symmetrical vibrations is high, it may be assumed that the temperature T_2 is close to the rotational temperature.

In any case, the ratio T_3/T_2 is sufficiently great that there must be a population inversion in the system among the levels $v_1 + 1, v_2, v_3$ and $v_1, v_2, v_3 + 1$. However, on account of the high temperatures T_{rot}, T_2, T_3 the gain coefficient of the medium is not high. Estimates show that, in the mixture $1.5H_2 + 4.5N_2 + CO_2 + 8Ar$ for $T_3 = 12\,000°K$, $T_{rot} = 1200°K$, $T_2 = 3000°K$ ($\tau = 1.25$ msec), the maximum gain coefficient is 1% per meter, and for $T_2 = T_{rot} = 1200°K$ and $T_3 = 12\,000°K$, of the order of 10% (Lorentzian line shape assumed; cross section of collision broadening assumed kinetic).

We should mention that we did not try to optimize the composition of the mixture. Obviously, a regime can be obtained in which the rotational temperature and the temperature T_2 will be much lower.

Thus, we propose the use of polyatomic molecules in chemical lasers. We have proposed and realized a method for determining the vibrational temperatures of CO_2-type molecules formed or excited as the result of a chemical reaction. We have shown that upon ignition of a mixture of hydrazoic acid and carbon dioxide, a population inversion of the CO_2 molecular levels is obtained.

In conclusion, the authors express their thanks to V. G. Samoĭlovich and B. V. Strakhov for helpful discussions and practical assistance.

Note added in proof (July 9, 1969).—We have recently obtained generation in the 10.6-μ region from a light-initiated explosion of a mixture of $5HN_3 + CO_2 + 6He$. A system of two coaxial quartz tubes 1 m long and 33 and 65 mm in diameter, respectively, was used. The working mixture was admitted into the inner tube, which was furnished with mirrors on its ends. The outer tube contained HN_3 at a pressure of 50 Tor. The reaction in the outer tube was ignited by a transverse electrical discharge. The radiation from the explosion initiated the reaction in the inner tube. With a pressure of the working mixture of 12 Tor, induced emission was observed 500 μsec after the discharge in the outer tube and had the form of a single pulse of about 200-μsec duration. The parameters of the system were not optimized for maximum radiated energy.

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