SOVIET PHYSICS JETP VOLUME 28, NUMBER 4 APRIL, 1969

OBTAINING INVERTED POPULATION ON VIBRATIONAL LEVELS OF POLYATOMIC MOLECULES

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Submitted May 8, 1968

Zh. Eksp. Teor. Fiz. 55, 1456–1469 (October, 1968)

A number of typical polyatomic molecules (N_2O, SO_2, CS_2, C_2N_2, HCN, H_2O) are investigated on the basis of the relaxation model proposed in[1,2] for the analysis of the operation of a CO_2 laser. The probabilities of the collision transitions that determine the relaxation of the vibrational energy and its pumping from the N_2 (or CO) molecule are calculated. The relaxation in electric discharges in various molecular gases are calculated. The possibilities of producing population inversion of the vibrational levels are investigated. Lasing in a large number of molecules is explained on the basis of the proposed approach. The estimates confirm the mechanism of generation on the $11^{1}0-04^{0}0$ transition of HCN. An explanation is proposed for the generation mechanism on several transitions in H_2O. The results make it possible to carry out a qualitative analysis and a fruitful search for other polyatomic gases suitable for lasing.

1. INTRODUCTION

INASMUCH as large generation powers were obtained in the vibrational transitions of the CO_2 molecule, increasing attention is being paid to an investigation of other polyatomic molecules. Thus, in recent times the generation of not fewer than 15 polyatomic molecules was obtained: CH_3CN, $(CH_3)_2SO_4$, H_2O, D_2O, ICN, ClNO, NO_2, COS, C_2N_2, CS_2, C_2H_2, C_2H_5CN, HCN, N_2O, and $(C_2H_5)_2O$. However, frequently it is impossible to determine not only the mechanism whereby the inverted population is produced or the transition to which the generation line belongs, but also the very substance responsible for the generation.

To explain the mechanism of population inversion in vibrational transitions and to design a CO_2 laser, a model of relaxation processes was proposed in[1,2]. According to this model, in each mode i there is established a Boltzmann distribution with vibrational temperature T_i, determined by the energy E_i stored in this mode. This is justified, if the energy exchange within the mode has a rate much higher than the rate of pumping and drawing the energy from the given mode. To calculate the relaxation processes it is necessary to solve the equation for the balance of the vibrational energies E_i simultaneously with the heat-conduction equation, since in molecular lasers the gas temperature plays an important and sometimes decisive role.

In the present paper we investigate a number of molecules (N_2O, SO_2, CS_2, COS, C_2N_2, HCN, H_2O), we calculate the probabilities of the collisional transitions, consider the relaxation processes, the pumping, and the possibility of obtaining inverted population. For comparison, we chose characteristic molecules with sufficient diversification of properties (linear and nonlinear, with three and four atoms, polar and dipole-less). On this basis we can explain the operation of a number of already existing molecular lasers, indicate ways for their optimization, and carry out a purposeful search for molecules suitable for generation, and choose a method of producing the inverted population.

2. PROBABILITIES OF COLLISIONAL TRANSITIONS. PHYSICAL PROCESSES

For an inverted population to exist, it is qualitatively necessary to have at least two relaxation times of the vibrational energy, for under this condition the vibrational temperatures T_i can be different. Two relaxation times were observed experimentally in a number of molecules. To find similar molecules, a rule was proposed in[3], according to which there should exist two close natural frequencies ν_1 and ν_2, satisfying the condition $2\nu_1 < \nu_2$, where the difference between the relaxation times increases with increasing difference $\nu_2 - 2\nu_1$. A number of molecules that are promising for lasing purposes (COS, C_2N_2, H_2Se) were proposed on this basis in[1].

However, for any detailed analysis of the relaxation properties it is necessary to know the cross sections of the collision transitions, which determine the relaxation. (The radiative processes can be significant only at small pressures $P \lesssim 0.1$ Torr). The probabilities of the collisional transitions then depend strongly on the molecular potential of interaction U(r). For nonpolar molecules, U(r) is usually chosen to be the Lennard-Jones potential

$$U(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right], \qquad (1)$$

and for polar ones, the Krieger potential

$$U(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6} - \delta^*\left(\frac{r_0}{r}\right)^{3}\right]. \qquad (2)$$

(Here ϵ, r_0, δ^* are constants, and the cubic term in the Krieger potential takes into account the dipole interaction.) To calculate the cross sections, a method was used[4-7], based on replacing the real potential (Lennard-Jones or Krieger) by an exponential one in the region of the effective interaction. In the absence of exact energy resonance, the probability that collision will cause two molecules a and b, initially in the vibrational states i_a and i_b of fundamental vibration modes with frequencies

ν_a and ν_b, to go over into the states k_a and k_b is given by the formula[5]:

$$P_{ik}(a,b)=11{,}2P_0(a)P_0(b)\left(1+1{,}1\frac{\varepsilon}{kT}\right)^{-1}\left(\frac{r_c}{r_0}\right)^2\left[\frac{\mu(v_0^*)^2}{2kT}\right]^{1/2}$$
$$\times V^2(a)V^2(b)\left[\frac{8\pi^3\mu(\Delta E)}{(\alpha^*)^2h^2}\right]^2\exp\left[-3\frac{\mu(v_0^*)^2}{2kT}+\frac{\Delta E}{2kT}+\frac{\varepsilon}{kT}\right]. \quad (3)$$

Here μ is the reduced mass of the collision, T the gas temperature, $\Delta E = h\nu_a(i_a - k_a) + h\nu_b(i_b - k_b)$ is the total change of the translational energy upon collision, and r_c is the coordinate of the point of closest approach of the molecules. The connection between the relative velocity v_0^*, which is most favorable for the transition, and the force constant α^* which enters in the exponential potential and is calculated for this velocity, is given by the relation

$$\frac{\mu(v_0^*)^2}{2kT}=\left[\frac{2\pi^4\mu(\Delta E)^2}{(\alpha^*)^2h^2kT}\right]^{1/3}. \quad (4)$$

By equating the real and exponential potentials at two points r_0 and r_c[6] we get the following expressions for α^*:

For a Lennard-Jones potential

$$\alpha^*=\frac{1}{r_0}\ln\left[\frac{\mu(v_0^*)^2}{2\varepsilon}+1\right]\left\{1-\left[\frac{1}{2}+\frac{1}{2}\sqrt{1+\frac{\mu(v_0^*)^2}{2\varepsilon}}\right]^{-1/6}\right\}^{-1}, \quad (5)$$

For a Krieger potential

$$\alpha^*=\frac{24\varepsilon}{r_0\mu(v_0^*)^2}\left(\frac{r_0}{r_c}\right)\left\{1+\frac{\mu(v_0^*)^2}{2\varepsilon}+3\delta^*\left(\frac{r_0}{r_c}\right)^3\right. \quad (6)$$
$$\left.+\sqrt{1+\frac{\mu(v_0^*)^2}{2\varepsilon}+4\delta^*\left(\frac{r_0}{r_c}\right)^3}\right\},$$
$$\frac{r_0}{r_c}=\left[\frac{1}{2}+\frac{1}{2}\sqrt{1+\frac{\mu(v_0^*)^2}{2\varepsilon}+4\delta^*\left(\frac{r_0}{r_c}\right)^3}\right]^{1/6}$$

The orientation factors $P_0(a)$ and $P_0(b)$ for the SO_2 molecule were assumed equal to 1/2, and for the remaining molecules 2/3. The vibrational matrix elements V(a) and V(b) for the 0—n transitions (n—number of vibrational quanta) were calculated from the formula[7]

$$V_{0n}^2(a)=\left\{24\left[\frac{1}{2}+\frac{1}{2}\sqrt{1+\frac{\mu(v_0^*)^2}{2\varepsilon}}\right]^{7/6}\frac{1-1/N}{r_0\sqrt{1+\mu(v_0^*)^2/2\varepsilon}}\right\}^{2n}$$
$$\times\left(\frac{\hbar}{4\pi\nu_aM_a}\right)^n\frac{1}{n!}. \quad (7)$$

Here ν_a and M_a are the frequency and reduced mass of the oscillator, and N is the number of atoms in the molecule for which the matrix element is sought.

In the presence of exact resonance, the calculations were performed in accordance with the formula[5]

$$P_{ik}(a,b)=P_0(a)P_0(b)V^2(a)V^2(b)\frac{64\pi^2\mu kT}{\alpha^2h^2}\exp\left(\frac{\varepsilon}{kT}\right), \quad (8)$$

and to calculate α we used the average relative energy of thermal motion of the molecules. In the calculation of the probabilities of transition as a result of collision of different molecules, we chose for the interaction constants r_0 and ϵ respectively, the arithmetic-mean and geometric-mean values of these quantities for the individual molecules that take part in the collision. The Lennard-Jones and Krieger constants were taken from[8].

The transition probability W_{ik} is determined by the ratio of the total number of collisions (in seconds) z_0 to the number of collisions z_{ik} which the molecule must experience in order for the given transition to take place

$$W_{ik}=z_0/z_{ik}=z_0P_{ik}(a,b)\varkappa, \quad (9)$$

where κ is the statistical weight of the transition, defined in accordance with[9].

Inasmuch as formulas (3) and (8) are not directly applicable for the case near resonance, z_{ik} was determined, as proposed in[5], by interpolation of these values calculated in a certain interval of the energy defect ΔE, including the case of total resonance ($\Delta E = 0$). Our estimates show that the error due to interpolation, which reaches several times 10%, is lower than that due to the use of the not quite accurate constants of the interaction potential. As seen from[8], different authors give rather greatly differing interaction constants. A 10—20% inaccuracy in the constants can lead to an error of 5—7 times in the final results. In the calculations we chose the values of those constants which were most reliable, in our opinion. However, further refinement of z_{ik} is determined primarily by the increased accuracy of the experiments in which the interaction constants are determined.

Let us discuss the possibility of obtaining population inversion of the vibrational levels of molecules with the aid of an electric discharge in a gas placed in a cylindrical tube.

The process of energy transfer from the electron gas to the translational degrees of freedom of the molecules can be divided into three stages: a) pumping of the energy by the electrons directly or with the aid of the pumping gas in one or several modes of oscillation of the given molecule, b) relaxation of the energy over the molecule levels, c) transfer of reaction to the translational degrees of freedom and heating of the gas. Chemical reactions are disregarded. This is justified both for a number of molecules that are relatively stable in a discharge, and for several special experimental conditions (flow-through systems with large flow rates, pulsed regime, separate excitation of the gases, etc.).

The balance equations for the vibrational energies E_i and the gas temperature T, are similar to those given in[2] and are distinct for each molecule. To solve them, the following simplifying assumptions are made: the radial distribution of the particles and temperatures are not taken into account. The pumping of the

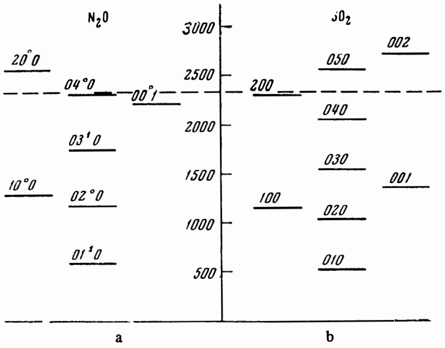


FIG. 1. Schemes of vibrational levels of N_2O and SO_2 molecules (the dashed line shows the vibrational level v = 1 of the N_2 molecule).

energy into the vibrational degrees of freedom of the molecules is effected only by collision with the vibrational-excitation degrees of freedom by electron impact by molecules N_2 or CO. The influence of the rotational transition on the relaxation of the vibrational energy is neglected. The diffusion of the excited molecules is taken into account approximately, and the calculation is made for a tube of two radii (2R = 25 and 50 mm). The probabilities of diffusion decay W_{dif} are determined in accordance with[2]. A stationary case prior to the generation regime is considered. The discharge parameters, the electron temperature T_e, the electron density N_e, and the average number α_{N_2} of the vibrational N_2 quanta excited by the electrons are also determined in accordance with[2]. The connection between E_i and the vibrational temperatures T_i is given by the formulas

$$E_i = h\nu_i N_0 x_i / (1 - x_i)^2$$

for nondegenerate oscillation,

$$E_i = 2h\nu_i N_0 x_i / (1 - x_i)^3$$

for doubly degenerate oscillations, where

$$x_i = \exp(-h\nu_i / kT_i),$$

and N_0 is the number of molecules in the vibrational ground state.

3. CALCULATION RESULTS. THE MOLECULES N_2O, SO_2, CS_2, COS, AND C_2N_2

In this section we consider a number of molecules, and present their characteristics and the level schemes, which show also the levels of the pumping gas (N_2 and CO). We present tables of z_{ik}, which determine the probability of the collisional transitions between the vibrational levels, and also z_{ik} for energy pumping from the N_2 (or CO) molecule in the electronic ground state with vibrational number v = 1. On this basis, we investigate the process of relaxation and analyze the possibility of producing inverted population in the discharge in the gas itself or in a mixture of the given gas with N_2.

1. **The N_2O molecule.** Linear, asymmetrical, weak-dipole molecule. Structural formula $N \equiv N = 0$; the constants of the Lennard-Jones potential are $\epsilon/k = 220.0°K$ and $r_0 = 3.879$ Å. The vibrational level scheme is shown in Fig. 1a. The values of z_{ik} for the collisional transitions are given in Table I.

Let us consider a mixture of N_2 and N_2O, where N_2 plays the role of the pumping gas. For simplicity we assume that the vibrational temperatures of the symmetrical and deformational modes are equal to the gas temperature. Then the system of balance equations for the energies E_{N_2} and $E_{00°v}$ is of the form

$$\begin{aligned} \frac{dE_{N_2}}{dt} = 0 = h\nu_{N_2}\Big(& \alpha_{N_2} W_{eN_2} N_e + W_{00°1,\,N_2} N_0 x_{00°1} \\ & - \alpha_{N_2} W_{eN_2} N_e \exp\left\{\frac{h\nu_{N_2}}{kT_e}\right\} x_{N_2} - W_{00°1,\,N_2} \exp\left\{-\frac{\Delta E_{00°1,\,N_2}}{kT}\right\} N_0 x_{N_2} \\ & - W_{\mathrm{dif}\ N_2} x_{N_2} - W_{N_2,\,1'0} N_0 x_{N_2}\Big) N_{0N_2}, \\ \frac{dE_{00°v}}{dt} = 0 = h\nu_{00°1}(& W_{N_2,\,00°1} N_{0N_2} x_{N_2} - W_{00°1,\,N_2} x_{00°1} N_{0N_2} \\ & - W_{00°1,\,\Sigma} x_{00°1} - W_{\mathrm{dif}\ N_20} x_{00°1}) N_0; \\ & W_{00°1,\,\Sigma} = W_{00°1,03^10} + W_{00°1,11^10}. \end{aligned} \tag{10}$$

The indices of the type 11^00, 03^10 ... number the vibrational levels of the polyatomic molecule, $W_{dif\,N_2}$ is the probability of diffusion decay, and the index pertains to the free electrons.

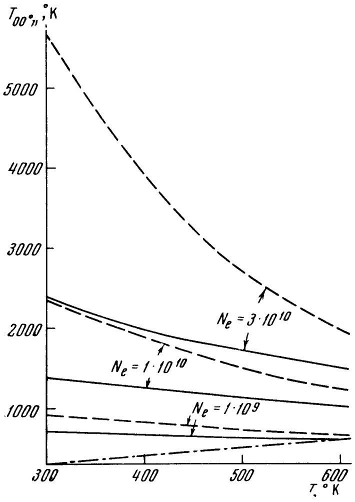


FIG. 2

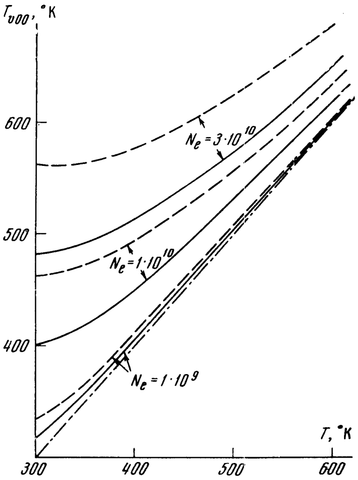


FIG. 3

FIG. 2. Vibrational temperature $T_{00°v}$ of the N_2O molecule versus the gas temperature T for different pump rates (N_e, cm^{-3}) and radii of the discharge tube (the solid curves pertain to a tube radius R = 12.5 mm, and the dashed ones to a tube with R = 25 mm).

FIG. 3. Vibrational temperature T_{v00} of the SO_2 molecule versus the gas temperature T at different pump rates (N_e, cm^{-3}) and discharge-tube radii (the solid curves pertain to a tube radius R = 12.5 mm, and the dashed ones to R = 25 mm).

Table I

Transition		T, °K 300	600	1000	ΔE, cm^{-1}
00°1	10°0	6.6^7 *	2.4^6	2.2^5	940
	11^10	1.8^5	3.0^4	8.0^3	350
	12°0	1.6^6	6.3^5	4.5^4	−230
	04°0	7.0^5	$3,5^5$	7.1^4	−115
	03^10	$9,0^6$	6.7^5	8.8^4	454
10°0	02°0	3.3^2	2.5^2	1.3^2	115
	01^10	1.7^5	1.9^4	2.3^3	696
01^10	00°0	2.5^3	3.0^2	7.6^1	589
N_2	20°0	2.3^5	3.2^4	1.3^4	−233
	12°0	2.2^6	3.5^5	1.3^5	−124
	04°0	1.8^6	4.6^5	1.6^5	25
	00°1	3.2^3	1.4^3	7.5^2	107
v = 1	11^10	2.9^6	3.0^5	6.0^4	457

*In this and all other tables, the symbol 6.6^7 denotes 6.6 x 10^7.

Figure 2 shows the dependence of the vibrational temperature $T_{00°v}$ of the asymmetrical mode on the gas temperature, obtained for $P_{N_2O} = P_{N_2}$ = 2 Torr at different electron densities N_e (i.e., different energy pumpings). The larger the energy pumping (the larger N_e) and the smaller the gas temperature, the higher the temperature of the asymmetrical mode and consequently the larger the difference between the different vibrational temperatures. The inverted population of the levels 00^01-10^00 in N_2O, according to this calculation, is approximately equal to the inverted population in a CO_2 laser prior to the lasing mode[2].

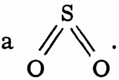
Patel[10] obtained generation at the transition 00^01-10^00 of the N_2O molecule. Although the transition agrees with theory, the output power was much lower

Table II

Transition		T,°K			ΔE, cm^{-1}
		300	600	1000	
200	100	1.1^{8}	1.4^{6}	1.0^{5}	1154
	021	6.3^{8}	3.3^{8}	1.5^{8}	—95
100	020	8.3^{3}	4.3^{3}	1.7^{3}	113
	001	5.5^{3}	$1,8^{3}$	5.9^{2}	—210
001	020	8.3^{5}	1.7^{5}	2.4^{4}	323
010	000	4.3^{3}	5.7^{2}	1.4^{2}	519
N_2	200	8.0^{4}	4.9^{4}	2.5^{4}	26
	120	3.6^{6}	1.4^{6}	—	40
	101	5.8^{6}	1.2^{6}	—	—182
$v = 1$	021	9.5^{6}	2.9^{6}	—	—70

than that of a CO_2 laser. In our opinion, this discrepancy is caused by three factors: a) larger instability of the N_2O molecule in the discharge as compared with CO_2, b) the experimentally obtained probability $W_{00^\circ1,\Sigma}$, which turned out to be several times larger than the calculated one (see[10]), c) difference in the radiative probabilities.

To optimize the operation of an N_2O laser it is apparently necessary to employ large flow rates.

2. **The SO_2 molecule.** Nonlinear polar molecule. Structural formula  . Krieger potential constants $\epsilon/k = 191.4°K$, $r_0 = 4.341$ Å, $\delta^* = 0.5995$. The vibrational-level scheme is shown in Fig. 1b. Table II gives the values of z_{ik} for the collisional transitions.

As seen from Table II, the modes v00 and 00v have a strong coupling and the relaxation of the vibrational energy is characterized by two relaxation times: for the levels v00 and 00v, and for the levels 0v0. These two relaxation times were also obtained experimentally[11]. The pumping from the N_2 molecule goes primarily through the 200 level, but by virtue of the fact that the energy changes by two quanta in resonant interaction of N_2 and SO_2, the transfer efficiency is low. The simplified balance equations for the vibrational energies E_{N_2} and E_{v00} in the stationary case are of the form

$$\frac{dE_{N_2}}{dt} = 0 = h\nu_{N_2}(\alpha_{N_2}W_{eN_2}N_eN_{0N_2} - \alpha_{N_2}W_{N_2e}N_eN_{0N_2}x_{N_2}$$

$$- N_0W_{N_2,200}N_{0N_2}x_{N_2} + W_{200,N_2}N_0x_{100}^2N_{0N_2} - W_{\mathrm{dif}\ N_2}N_{0N_2}x_{N_2}),$$

$$\frac{dE_{v00}}{dt} = 0 = h\nu_{100}(2W_{N_2,200}N_{0N_2}x_{N_2}N_0 - 2W_{200,N_2}N_0x_{100}^2N_{0N_2}$$

$$- W_{100,020}N_0x_{100} - W_{\mathrm{dif}\ SO_2}N_0x_{100} + W_{100,020}e^{-\Delta E/kT}N_0x_{010}^2). \quad (11)$$

The dependence of the vibrational temperature T_{v00} on the gas temperature at $P_{SO_2} = P_{N_2} = 2$ Torr at different N_e is shown in Fig. 3. T_{v00} increases with increasing N_e and decreases with increasing T. However, the difference in the vibrational temperatures is much smaller than for the N_2O molecule owing to the smaller probability of energy transfer from the N_2 and to the quite rapid energy relaxation of the v00 vibration. Population inversion on the vibrational levels of this molecule is therefore difficult and is possible only at large energy pumping and low gas temperature, something difficult to attain in general, since the gas temperature increases with increasing N_e.

3. **The CS_2 molecule.** Linear, symmetrical, dipoleless molecule. Structural formula S = C = S. The Lennard-Jones potential constants are $\epsilon/k = 488°K$ and $r_0 = 4.438$ Å. The vibrational level scheme is shown in Fig. 4, and the quantities z_{ik} for the determination of the collisional transition probabilities are given in Table III.

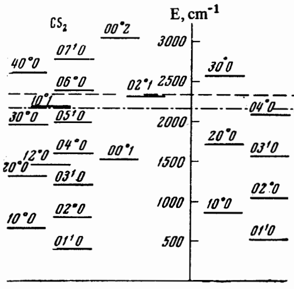


FIG. 4

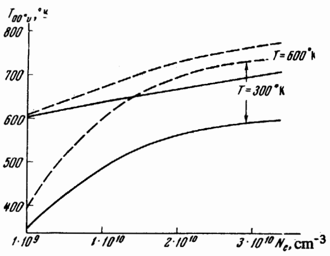


FIG. 5

FIG. 4. Vibrational level schemes of the molecules CS_2 and COS (the dashed line shows the vibrational level v = 1 of the molecule N_2, and the dash-dot line that of the molecule CO).

FIG. 5. Dependence of vibrational temperature $T_{00^\circ v}$ of the CS_2 molecule on the electron density at different gas temperatures T and different discharge-tube radii (the solid curves pertain to the tube radius R = 12.5 mm, and the dashed ones to a tube with R = 25 mm).

As seen from Table III, the pumping of the energy in CS_2 from the N_2 molecule is realized principally via the vibrational levels 10^01 and 02^01, with the energy proceeding directly to all three vibration modes. However, at the gas pressures under consideration ($P_{CS_2} = P_{N_2} \approx 2$ Torr), owing to the rapid relaxation, the vibrational temperatures $T_{v0^\circ0}$ and $T_{0v}l_0$ will be close to the gas temperature T. Under such an assumption, the simplified balance equations for the vibrational levels E_{N_2} and of the assmmetrical type of oscillation $E_{00^\circ v}$ of the CS_2 molecule are of the form

$$\frac{dE_{N_2}}{dt} = 0 = h\nu_{N_2}[\alpha_{N_2}W_{eN_2}N_eN_{0N_2} - \alpha_{N_2}W_{N_2e}N_eN_{0N_2}x_{N_2}$$

$$- (W_{N_2,10^\circ1} + W_{N_2,02^\circ1})N_{0N_2}x_{N_2}N_0 - W_{\mathrm{dif}\ N_2}N_{0N_2}x_{N_2}],$$

$$\frac{dE'_{00^\circ v}}{dt} = 0 = h\nu_{00^\circ1}\{[W_{N_2,10^\circ1} + W_{N_2,02^\circ1}]N_{0N_2}x_{N_2}N_0 - W_{\mathrm{dif}\ CS_2}N_0x_{00^\circ1}$$

$$- [W_{00^\circ1,200} + W_{00^\circ1,12^\circ0}]N_0x_{00^\circ1} + [W_{20^\circ0,00^\circ1}x_{10^\circ0}^2 + W_{12^\circ0,00^\circ1}x_{10^\circ0}x_{01^10}^2]N_0\}.$$

The dependence of the vibrational temperature $T_{00^\circ v}$ on the electron density at different gas temperatures T is shown in Fig. 5. The difference between $T_{00^\circ v}$ and $T_{v0^\circ0}$ or $T_{0v}l_0$ turns out to be small, although it does exceed the temperature difference in SO_2. If T is small it is possible to obtain in CS_2 population inversion of the levels 00°1—10°0 or 10°1—20°0. It is possible to

Table III

Transition		T,°K			ΔE, cm^{-1}
		300	600	1000	
00°1	20°0	5.0^{4}	3.0^{4}	5.6^{3}	213
	21¹0	3.5^{5}	2.0^{5}	5.0^{4}	—184
	12°0	1.0^{4}	$4,7^{3}$	1.6^{3}	72
	04°0	2.2^{5}	7.5^{4}	1.8^{4}	—80
	03¹0	4.0^{6}	5.0^{4}	3.3^{4}	323
20°0	03¹0	7.0^{5}	4.0^{5}	2.2^{5}	109
10°0	02°0	1.0^{3}	3.6^{2}	1.2^{2}	—140
	01¹0	4.0^{2}	1.6^{2}	5.3^{1}	258
01¹0	00°0	5.0^{2}	1.6^{2}	4.5^{1}	397
N_2	10°1	3.5^{5}	1.2^{5}	$4,1^{4}$	152
$v = 1$	02°1	1.7^{5}	7.4^{4}	$2,6^{4}$	12

Table IV

Transition		T,°K 300	600	1000	ΔE, cm⁻¹
CO $v = 1$	00°1	1.2^{3}	7.3^{2}	4.1^{2}	90
00°1	$21^{1}0$	1.10^{7}	3.3^{5}	6.6^{4}	—166
	20°0	2.00^{6}	3.3^{5}	6.6^{4}	361
	12°0	1.7^{5}	5.2^{4}	1.5^{4}	166
	04°0	2.1^{5}	8.2^{4}	2.5^{4}	—30
10°0	02°0	7.5^{3}	1.5^{3}	4.0^{2}	—195
	$01^{1}0$	2.0^{3}	3.8^{2}	$1{,}05^{2}$	332
$01^{1}0$	00°0	4.1^{3}	4.2^{2}	6.1^{1}	527

increase the difference in the vibrational temperatures and consequently to improve the conditions for obtaining population inversion by decreasing the partial pressure of the working gas (thereby decreasing the rates of energy relaxation). Generation of the CS_2 molecule was obtained experimentally in a flow-through system with pressures $P_{CS_2} \approx 0.1$ Torr and $P_{N_2} \approx 2$ Torr[12]; the transition responsible for the generation can be identified with the predictions of the calculation.

4. The COS molecule. Linear, weak-dipole, asymmetrical molecule. Structural formula O = C = S. The constants of the Lennard-Jones potential are $\epsilon/k = 335°K$ and $r_0 = 4.13$ Å. The vibrational-level scheme is shown in Fig. 4, and the values of z_{ik}, which determine the probabilities of the collisional transitions and the energy pumping from the CO molecule are given in Table IV.

For the COS molecule, the energy pumping is realized predominantly in an asymmetrical mode, just as in the N_2O molecule. The temperatures of the other modes, are close to the gas temperature owing to the rapid relaxation. The system of Eqs. (10) and its solution describe the relaxation also in the COS molecule, and give the value of the temperature of the asymmetrical mode in the case of pumping from CO. Owing to the larger rate of relaxation of the asymmetrical mode, compared with the N_2O molecule, the corresponding vibrational temperature and inverted population of the levels 10°0 and 00°1 are much smaller.

Lasing on the transition 00°1—10°0 at wavelengths 8.39 and 8.25 μ was obtained in[13], in agreement with the calculations. Inasmuch as COS decomposes under the influence of the current, the pumping in pure COS may be realized from the CO produced in the discharge.

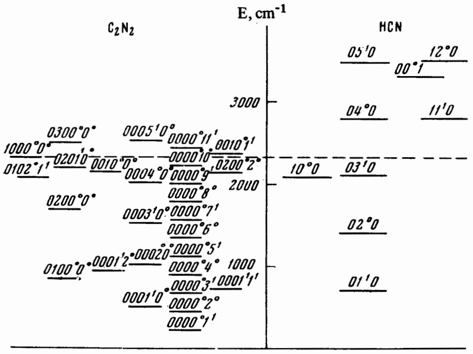


FIG. 6. Vibrational level schemes of C_2N_2 and HCN molecules (the dashed line shows the vibrational level v = 1 of the N_2 molecule).

Table V

Transition		T,°K 300	600	1000	ΔE, cm⁻¹
1000°0°	0010°0°	1.0^{3}	4.6^{2}	2.4^{2}	173
	0010°1	3.2^{2}	1.4^{2}	7.3^{1}	—53
0010°0°	$0201^{1}0°$	6.0^{3}	2.5^{3}	1.5^{3}	—47
	0200°2°	1.8^{3}	6.5^{2}	2.4^{2}	7
	0102°1	4.3^{3}	1.2^{3}	4.1^{2}	52
$0001^{1}0°$	0000°2°	1.6^{0}	1.0^{0}	1.0^{0}	54
$0000°1^{1}$	0000°0°	5.3^{0}	2.2^{0}	1.8^{0}	226
0200°0°	0100°0°	2.0^{5}	—	—	845
	$0002°3^{1}$	2.0^{4}	5.0^{3}	1.5^{3}	—14
0100°0°	$0001^{1}1^{1}$	3.0^{1}	1.0^{1}	4.6^{0}	113
	$0001^{1}2°$	1.1^{2}	2.0^{1}	5.6^{0}	—113
	$0000°3^{1}$	1.6^{2}	2.0^{1}	5.1^{0}	167
N_2 $v = 1$	1000°0°	4.9^{2}	3.5^{2}	2.4^{2}	8.5
	0010°0°	5.6^{3}	2.3^{3}	$1{,}1^{3}$	182
	$0010°1^{1}$	4.7^{3}	1.7^{3}	$7{,}6^{2}$	—44

5. The C_2N_2 molecule. Linear, dipole-less, symmetrical, four-atom molecule. Structural formula N ≡ C – C ≡ N. The Lennard-Jones potential constants are $\epsilon/k = 339°K$ and $r_0 = 4.38$ Å. The vibrational-level scheme is shown in Fig. 6, and the values of z_{ik}, which determine the probabilities of the collisional transitions and the pumping from the N_2 molecule are given in Table V.

The energy pumping is realized effectively in the modes v000°0° and 00v0°0°, which have close vibrational temperatures. The remaining modes have a temperature close to that of the gas. The system of relaxation equations is similar to (10), since essentially only two groups of types of oscillations are considered. However, the number of essential relaxation channels increases here, so that the difference between the vibrational temperatures and the population inversion turn out to be smaller than in N_2O.

For molecules with more than three atoms, the presence of many relaxation channels can greatly deteriorate the conditions for inversion. Lasing with the C_2N_2 molecule was obtained in[14], but the generation lines were not identified.

6. The HCN molecule. Linear dipole molecule. Structural formula H – C ≡ N. The level scheme is shown in Fig. 6. Inasmuch as the constants of the Krieger potential are now known with sufficient degree of accuracy, rough estimates of the cross sections and of the relaxation process were made for the HCN molecule. The results show that the vibration mode pumped with relative efficiency is v0°0, and that there is a noticeable difference between the vibrational temperatures of the modes v0°0 and $0v^{l}0$. However, the populations of the levels 10°0 and 02°0 are approximately the same. So far we have considered inversion between different modes, but inversion can arise also between combination levels.

The vibrational temperature $T_{v_1v_2v_3}$ of the system of combination levels that are multiples of $(v_1v_2v_3)$ can be determined from the relation

$$\exp\left(-\frac{h\nu_{v_1v_2v_3}}{kT_{v_1v_2v_3}}\right)=\exp\left(-\frac{v_1h\nu_{v_1}}{kT_{v_100}}\right)\exp\left(-\frac{v_2h\nu_{v_2}}{kT_{0v_20}}\right)\exp\left(-\frac{v_3h\nu_{v_3}}{kT_{00v_3}}\right)$$

$$\nu_{v_1v_2v_3}=v_1\nu_1+v_2\nu_2+v_3\nu_3. \tag{13}$$

By virtue of the different vibrational temperatures, population inversion is realized between the levels

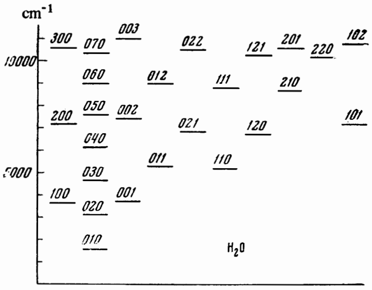


FIG. 7. Vibration level scheme of the H_2O molecule.

11^10—$04^\circ0$ (the combination 11^10 includes the level $10^\circ0$ which belongs to the $v0^\circ0$ mode with higher temperature).

The 335 μ laser transition of the "CN laser" was first interpreted as the vibrational-rotational transition 11^10—$04^\circ0$ by Lide and Maki[15].

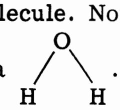
7. **The H_2O molecule.** Nonlinear, polar molecule. Structural formula . The constants of the Krieger potential are $\epsilon/k = 380°K$, $r_0 = 2.65$ Å, and $\delta^* = 1.7$. The vibrational level scheme is shown in Fig. 7, and the values of z_{ik}, which determine the probability of the collision transitions are given in Table VI.

Table VI

Transition		T,°K			ΔE, cm^{-1}
		300	600	1000	
001	100	1.0^0	1.8^0	6.4^0	104
100	020	2.6^0	4.2^1	1.7^2	500
010	000	3.1^0	2.2^1	2.2^1	1595

The water molecule is apparently well excited by electron impact. As shown by a calculation of the relaxation, the vibrational temperatures for the v00 and 00v modes are equal, and the temperature of the 0v0 mode is smaller, i.e., there are two relaxation times. Just as in HCN, it is possible to realize in water an inversion between combination levels. In particular, between the following levels: a) 012—060 (ΔE = 14.4 cm^{-1}), b) 300—022 (ΔE = 75.0 cm^{-1}), c) 201—022 (ΔE = 99.0 cm^{-1}), d) 131—080 (ΔE = 131 cm^{-1}), e) 202—122 (ΔE = 58.8 cm^{-1}).

In[16,17], continuous and pulsed generation at a number of frequencies was obtained. Continuous generation was obtained at the lines 27.9, 47.7, 55.0, 78.4, 118.7, and 220 μ. It should be noted that although so far the frequencies have not yet been identified, they fit within the framework of the present scheme. This interpretation is confirmed by experiment[17] in which the generation lines 47 and 118, 55 and 220 μ turned out to be connected with each other.

4. CHOICE OF MOLECULES; EXCITATION METHODS

The foregoing analysis of the number of characteristics of molecules can be used, by virtue of the generality and unity of the approach, also for the investigation of other molecules. Many conclusions based on the analysis of the calculated probabilities and the study of the relaxation of the vibrational energy are quite general in character. Thus, the most effective is the resonant transfer with change of energy by only one vibrational quantum. This is precisely why the energy pumping via the combination levels ($CS_2 + N_2$) or pumping with a change of energy by two vibrational quanta ($SO_2 + N_2$) is much more effective than for $CO_2 + N_2$ or $N_2O + N_2$. Another important fact is the presence of good resonance ($\Delta E \ll kT$). For the very same reasons, energy transfer from one mode to another proceeds predominantly via the lower levels of one mode to the nearest levels of the other modes (including combination levels). On the other hand, relaxation of the energy through the upper levels is insignificant, owing to the decrease of both the transition probabilities and the populations of these levels. Therefore a good approximation is the inclusion in the balance equation of the vibrational energies of the transitions through the lower levels only, as was done previously[1,2] and in the examples considered above.

In order for the energy pumping to be effective, it is necessary to use molecules that are well excited by direct electron impact. Large excitation cross sections were obtained experimentally for the molecules N_2, CO, N_2O, and COS[18]. A theoretical analysis is quite complicated and has been performed only for the N_2 molecule[19]. The total cross section for the collision between the electrons and the indicated molecules has a characteristic peak in the energy region at which the vibrational levels are well excited. A similar peak is found also in the total cross sections for the collision of electrons with the molecules CO_2, C_2H_2, and HCN, for which a large probability of excitation of the vibrational degrees of freedom can also be expected. To obtain different vibrational temperatures, the energy pumping should be predominantly into the mode with the larger relaxation time, compared with the remaining modes. If the pumping is distributed among several modes, then additional heating of the gas takes place. On the other hand, an increase of the gas temperature can greatly deteriorate the operation of the molecular laser, since it increases the relaxation probabilities and equalizes the vibrational temperatures. To decrease the gas temperature it is necessary to use effective external cooling, tubes with small diameter, and a buffer gas (helium) that increases the thermal conductivity[2]; in the pulsed mode it is also necessary to decrease the pulse repetition frequency.

From a qualitative analysis of the structure of the vibrational levels, from a calculation of the transition probabilities of the polyatomic molecules, and from the estimate of the pumping and the chemical stability, it can be concluded whether a molecule is suitable for population inversion in an electric discharge. In particular, population inversion is expected for the vibrational levels of the polyatomic molecules in the mixtures $H_2Se + N_2$ (ΔE = −19 cm^{-1}), $ClCN + N_2$ (ΔE = 130 cm^{-1}), and $BrCN + N_2$ (ΔE = 144 cm^{-1}) (the parentheses indicate the corresponding energy defects). Knowing the oscillation modes between which a difference in the vibrational temperature exists, it is possible to indicate concrete transitions in the near infrared with population inversion (to calculate the gain it is necessary to know the radiative transition probabilities). The example of the HCN and H_2O molecules shows that the foregoing approach also helps identify the generation lines in the far infrared and in the submillimeter regions of the spectrum.

The transition probabilities considered above can be useful also in the study of other different relaxation processes (in ultrasonic methods, shock waves, etc.). Of particular interest is the use of different polyatomic molecules with several relaxation times of the vibrational energy, in order to obtain population inversion of the vibrational levels by using different thermal and chemical methods of producing unbalance.

Basov et al.[20] have shown that population inversion can be produced in molecules by sufficiently rapid cooling of a gas previously heated to temperatures of 2,000°. Bosov et al.[20], and also Konyukhov and Prokhorov[21] proposed several methods of such a process (adiabatic cooling in rarefaction waves and shock tubes and in expansion of gas through a slit or a nozzle).

Dronov et al.[22] experimentally observed population inversion of the $00^\circ 1-10^\circ 0$ levels of the CO_2 molecule under adiabatic cooling of the gas in a rarefaction wave produced by interaction between a shock wave, reflected from the end of a tube, and a contact surface.

In principle, one can expect population inversion of the levels also by rapid heating of the gas behind the front of the shock wave. As a result of the rapid relaxation of the energy of the deformational and symmetrical modes, the vibrational temperatures in these modes rapidly increase and exceed the vibrational temperature of the asymmetrical mode. In this case, the levels of the asymmetrical mode will not be upper laser levels, as in the case of cooling, but the lower ones. Both in cooling and in rapid heating, it is desirable to have a large number of N_2 molecules, the vibrational levels of which constitute the energy reservoir, which either feeds this energy to the asymmetrical mode of CO_2 (on cooling), or draws energy from this mode (on heating). In all these cases, for a detailed analysis of the relaxation processes it is necessary to solve simultaneously the equations of gas dynamics and the equations of relaxation of the vibrational energies.

The authors thank N. N. Sobolev for useful discussions.

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Translated by J. G. Adashko
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