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CHEMICAL LASERS

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1. INTRODUCTION

A widespread search for methods for transforming chemical energy into laser radiation is being conducted at present. The interest in this subject derives from the possibility of concentrating large amounts of energy per unit volume in a chemical laser and, consequently, of developing - at least in principle - powerful coherent radiation sources. Moreover, chemical lasers may provide effective means for investigating elementary chemical processes, which would have advantages over traditional methods.

The idea of a chemical laser is fairly old,[1-6] and considerable success has already been achieved. Coherent radiation has been obtained from excited products of several reactions under pulsed[7-33] and continuous-wave (CW) conditions.[74-79] The maximum values of the coefficients of conversion of the chemical energy into the energy of coherent radiation reach a few percent, while the output power can be hundreds of watts under pulsed and CW conditions. The progress has been particularly rapid in the last few years.

The most promising reactions for laser systems are those of the branched chain type.[4,20,23,28-31,34,79] The maximum values of the energy conversion coefficient have been obtained precisely for these reactions.

Chemical compounds are, in principle, rich sources of energy. In many cases, it is possible to prepare a chemical mixture in a basically nonequilibrium state in which the concentrations of the initial reagents are considerably higher, and the concentrations of the final products considerably lower, than the equilibrium values. Such a nonequilibrium state may be retained indefinitely, i.e., the rate of reaction in an unperturbed mixture may be close to zero. In fact, such a mixture—considered as a whole—is in a metastable energy state.

As a rule, the free energy of such an unperturbed system cannot be used directly to carry out work in a radiation field. It is necessary to disturb the system artificially from its metastable state by initiating a chemical reaction by some external agency. This reaction may also take place without such a stimulus if the initial state of the system is not metastable.

In an irreversible reaction, the free energy of the system decreases. However, the distribution function of the energy levels of the reaction products is usually different from the equilibrium distribution either during the reaction or immediately after its completion. In some cases, the rate of formation of the reaction products in high-energy states may be faster than the corresponding rate resulting in low energy states. This situation is optimal from the point of view of obtaining coherent radiation but is not essential. Population inversion may occur also in the process of energy redistribution over various degrees of freedom of a molecular

system. An important requirement, which must be met by a reaction employed to produce population inversion, is that the substance obtained must be in a state greatly differing from its equilibrium. This requirement is satisfied by many reactions.

Relaxation processes exert a decisive influence on the distribution function. Some of these processes facilitate, at certain stages, population inversion, whereas others hinder such an inversion, but finally they all tend to establish an equilibrium distribution.

In most cases, the relaxation rates are considerably higher than the reaction rates and it is impossible to achieve population inversion. Therefore, one of the basic questions in the selection of a system suitable for a chemical laser is the question of the rates of the reactions and the various relaxation processes and of the optimal relationship between them.

As in other types of laser, the system of levels in the working molecule must satisfy the requirements necessary for the establishment of an inverted population. These requirements restrict considerably the number of systems that can be used in chemical lasers, and they also provide the criteria for the selection of the most promising systems. These points will be considered later in detail.

In principle, a chemical reaction can produce molecules with electronically and vibrationally excited states. We shall consider only the case of laser emission involving vibrational transitions. The problem of using a chemical reaction to produce a population inversion of electron levels has hardly been investigated although it has been considered in several papers.[3-5,35,36] It would be very interesting to use stimulated chemical reactions to generate coherent radiation in the way suggested recently by Pekar.[72] However, an analysis of the problem of developing lasers based on the use of chemically excited electron levels is outside the scope of the present review.

II. VIBRATIONAL AND VIBRATION-ROTATIONAL POPULATION INVERSION

The molecular systems used in chemical lasers are, in principle, multilevel systems. Their behavior during a reaction can be described conveniently by a function representing the distribution of their energy levels.

A vibration-rotational level of a molecule is specified by a set of vibrational $V(v_1, \ldots, v_n)$ and rotational J quantum numbers. Consequently, the level populations are described by the function $n(V, J)$. We shall consider mainly linear molecules: for these molecules, the set J consists of a single number j which gives the angular momentum of a molecule.

The energy $E(V, j)$ is described, in the first approximation, by

$$E(V, j) = E(V) + F_V(j), \quad E_V(j) = hcB_V j(j+1), \qquad (1)$$

where h is the Planck constant; c is the velocity of light; B_V is the rotational constant (in cm^{-1}) which, in general, depends on V.

An equilibrium distribution over the rotational levels is usually established in a time interval representing a few collisions of a molecule.[37,38] After this time interval, the population $n(V, j)$ can be represented in the form

$$n(V, j) = n(V) g_0(j)(2j+1) Z_{rot}^{-1} e^{-F_V(j)/kT},$$
$$Z_{rot} \approx kT/\sigma hcB; \qquad (2)$$

here, k is the Boltzmann constant; T is the kinetic temperature of the mixture being considered; the coefficients $g_0(j)$ and σ for molecules without an inversion center are equal to unity, whereas for centrosymmetric molecules $\sigma = 2$ and $g_0(j)$ depends on the symmetry of a level and lies between zero and unity. The kinetic temperature is understood to be the temperature of the rotational and translational degrees of freedom. In principle, the rotational and translational temperatures may be different but they usually become equal in a very short time, representing a few collisions (there are some exceptions to this rule).

In many nonequilibrium cases, the populations of the vibrational levels $n(V)$ can also be described by a Boltzmann distribution with different temperatures for the different types of vibration:[39]

$$n(V) = [g(V)/Z_{vib}] \exp\left[-\sum_l (v_l hc v_l/kT_l)\right],$$
$$Z_{vib} = \prod_l [1 - \exp(-hc v_l/kT_l)]^{-g_l}; \qquad (3)$$

here v_l are the quantum numbers belonging to the V set $(v_1, \ldots, v_n)$; v_l, g_l, T_l are, respectively, the frequency (in cm^{-1}), degree of degeneracy, and temperature of the l-th type of vibration; $g(V)$ is the statistical weight of the level V. After a time, equilibrium is established between the various degrees of freedom, and the temperatures corresponding to these degrees of freedom become equal.

The distribution given by Eq. (3) is established more rapidly than the equilibrium distribution over all the degrees of freedom. This is because a redistribution of the vibrational energy between the molecules within one degree of freedom takes place by resonance exchange of vibrational quanta in collisions. This exchange is very efficient.

However, the transfer of a vibrational quantum to a different degree of freedom (vibrational or kinetic) is, in general, a nonresonance process. The probability of nonresonance processes is considerably lower than that of resonance processes and, consequently, the rate of energy redistribution between different vibrational degrees of freedom or between vibrational and kinetic degrees is less than the rate of redistribution within the same degree of freedom.

For example, in carbon dioxide kept at a pressure of 2 mm Hg, a Boltzmann distribution over the levels of antisymmetrical vibrations is established in a time of the order of 10 μsec[40], whereas an equilibrium distribution of the energy over all the degrees of freedom is reached in over 1 msec.[41]

An inversion of the population of energy levels v V_1, j_1, and V_2, j_2 can be described qualitatively by

$$\Delta n = n(V_1, j_1) - n(V_2, j_2)[g(V_1, j_1)/g(V_2, j_2)]. \qquad (4)$$

It is meaningful to distinguish two types of inversion: vibrational or total, and vibration-rotational or partial.[23,24] In the total inversion case, we have the relationship

$$n(V_1) - [g(V_1)/g(V_2)] n(V_2) > 0 \qquad (5)$$

[it is assumed that $E(V_1) > E(V_2)$]. The total inversion can be realized quite simply between levels belonging to different degrees of freedom in a system of polyatomic molecules. Let us assume that the population $n(V)$ is described by the distribution (3). Then, in order to achieve a population inversion between the levels $V_1(\ldots, v_i + 1, \ldots, v_l, \ldots)$ and $V_2(\ldots, v_i, v_l + 1, \ldots)$, we must satisfy the condition

$$T_i/T_l > v_i/v_l \quad \text{for} \quad v_i > v_l. \qquad (6)$$

Equation (6) can be satisfied by relatively small values of T_i/T_l, because in cases of practical importance the ratio v_i/v_l is small.

However, radiative transitions between such levels are forbidden in the harmonic approximation and, therefore, their probability is low. Consequently, a relatively large absolute population inversion is required in order to achieve a relatively large gain. The partition functions Z_{rot} and Z_{vib} of complex polyatomic molecules are large and, therefore, the level populations are low. Thus, the laser effect is achieved more easily in molecules with few atoms and a small moment of inertia. The most favorable conditions for the laser effect are obtained in the case of linear triatomic molecules which have relatively few levels.

In the partial inversion case, the inequality of (5) has the opposite sign but[5,6]

$$n(V_1, j) - [g(V_1, j)/g(V_2, j+1)] n(V_2, j+1) > 0. \qquad (5')$$

Partial inversion is important in the case of diatomic molecules, for which total inversion can be achieved only for a brief interval because of the rapid establishment of an equilibrium distribution over the vibrational levels of one type. On the other hand, a state with $T_{vib} \gg T$ may be achieved and retained for a relatively long time in a system of diatomic molecules. The vibrations of such molecules are deactivated fairly slowly and the kinetic energy of the reaction products is redistributed very rapidly between all the molecules, including impurities. If the specific heat of the system is high (for example, if a mixture is diluted by a neutral gas of high specific heat), the kinetic temperature may be relatively low. In any case, this temperature is low at the beginning of a reaction.

If the distribution over the rotational levels is of the Boltzmann type, it follows from Eq. (2) that the population inversion between levels $v + 1$, j and v, j +1 of diatomic molecules can be achieved if

$$\frac{n(v+1)}{n(v)} \exp\left[-\frac{F_{n+1}(j)}{kT} + \frac{F_v(j-1)}{kT}\right] > 1. \qquad (7)$$

It is convenient to express the ratio $n(v+1)/n(v)$ in terms of the vibrational temperature T_{vib}. If the distribution $n(v)$ is not of the Boltzmann type, the temperature T_{vib} will be defined as the quantity $(hc v/k)\{\ln[n(v)/n(v+1)]\}^{-1}$. Using Eq. (1), we can rewrite the condition (7) in the form

$$T_{\text{vip}}/T > v/[2(j+1)B_v + \alpha j(j+1)] > 1, \tag{7'}$$

where $\alpha = B_v - B_{v+1}$ is the constant of the interaction between vibration and rotation.

Formally, we can show that there are always values of j which satisfy Eq. (7) provided $T_{\text{vib}} > T$. In fact, we may find that for such values of j the quantity $F(j)$ is greater than the dissociation energy, or that Eq. (2) is not satisfied. In practice, the most important restriction on the possibility of using partial inversion is imposed by the smallness of the relevant populations $n(j)$ if T_{vib}/T is not sufficiently high. In view of this, it is interesting to estimate the maximum value of the population inversion

$$\Delta n = n(v+1, j) - n(v, j+1)[g(j)/g(j+1)]$$

for given values of the temperatures T and T_{vib}. We shall write Δn in the form

$$\Delta n = \frac{(2j+1)}{Z_{\text{rot}}} n(v+1)\exp\left[-\frac{hcBj(j+1)}{kT}\right] \tag{8}$$
$$\times \left\{1 - \exp\left[\frac{hcv}{kT_{\text{vib}}} - \frac{2hcB(j+1)+\alpha hcj(j+1)}{kT}\right]\right\}.$$

Differentiating Eq. (8) with respect to j, we obtain the following condition for a maximum:

$$1 - \exp\left[\frac{hcv}{kT_{\text{vib}}} - \frac{2hcB(j+1)+\alpha hcj(j+1)}{kT}\right] \approx 2\frac{1+(\alpha/2B)(2j+1)}{2j+3-2[kT/hcB(2j+1)]}. \tag{9}$$

The argument of the exponential function in Eq. (9) is small. Expanding this argument in a series, we obtain the following expression for j_m, which corresponds to a maximum of the population inversion Δn:

$$j_m - j_0 \approx \frac{1}{2j_m+3}\frac{kT}{hcB}\frac{2j_0+1}{2j_m+1}, \tag{9'}$$

where j_0 is found by equating to zero the argument of the exponential function in Eq. (9):

$$j_0 + 1 \approx \frac{B}{\alpha}\left[\left(1+\frac{v\alpha}{B^2}\frac{T}{T_{\text{vib}}}\right)^{1/2}-1\right]. \tag{9''}$$

The most interesting case is the population inversion for moderately large values of T_{vib}/T and relatively large values of j_0. In such a case, j_m/j_0 is close to unity and we can replace $2j_m+3$ with $2(j_0+1)$ on the right-hand side of Eq. (9'). Then, it follows from Eqs. (8), (9), and (9') that

$$\Delta n \approx \frac{2n(v+1)}{Z_{\text{rot}}}\exp[-1-j_0(j_0+1)(hcB/kT)]. \tag{8'}$$

Equation (8') is suitable only for rough estimates. It may overestimate the value of Δn because j changes in discrete steps, whereas j_m is not necessarily an integer. Moreover, Eq. (8') is invalid if $2j_0+1$ is less than or close to $(2kT/hcB)^{1/2}$, i.e., when the value of T_{vib} is very high.

Table I lists the values of j_0 and of the argument of the exponential function in Eq. (8') for six molecules.

These values are calculated on the assumption that $T_{\text{vib}}/T = 10$, $T = 300°K$ or $500°K$ (the constants v, B, and α are taken from[42] and the estimates are given for $v = 0$). It is evident from Table I that, at these temperatures, a population inversion in the heavy molecules of CO and NO can be achieved only for very high rotational levels and the absolute value of the inversion is small.

In the case of the hydrogen compounds HF, HCl, etc., a partial inversion under the same conditions may ensure a fairly high gain because the $v+1 \to v$ transitions are allowed in the harmonic approximation and, therefore, they have a high probability. Moreover, the partition functions Z_{rot} of such molecules are small.

III. ENERGY DISTRIBUTION IN PRODUCTS OF CHEMICAL REACTIONS

In order to estimate the possibility of a population inversion as a result of chemical reaction, we must first know the distribution of the energy, liberated in elementary chemical processes, over the various energy levels or degrees of freedom of the reaction products. Many reactions are accompanied by the nonequilibrium emission of radiation in the visible and ultraviolet regions; they include, for example, the cold flames of hydrocarbons[43] and CS_2,[44] the combustion of carbon monoxide, the reactions $M + HgX \to MX + Hg$,[26] where M is a metal atom and X is a halogen, etc. In combustion reactions, a considerable fraction of the energy is usually liberated in the infrared part of the spectrum,[45] corresponding to the vibrational transitions, and the infrared radiation is frequently of the nonequilibrium type. However, a detailed distribution of reaction products over the energy levels has been investigated so far only for substitutional reactions of the type

$$A + BC \rightleftarrows AB + C. \tag{10}$$

These distributions were investigated by Polanyi and his colleagues (see[46-48] and investigations cited in those papers), as well as by others.[68,69]

A theoretical classical approach is used in[47] to discuss the problem of the energy distribution over the various degrees of freedom of the products of a reaction represented by Eq. (10). This approach is applied to arbitrary atoms A, B, and C, and to various types of interaction which can be described by a potential energy $V(r_{AB}, r_{BC})$. The results obtained obviously apply also to the case when C is a complex of atoms.

The process described by Eq. (10) can be divided schematically into three stages: 1) the approach of an atom A to a complex BC; 2) an intermediate stage when this approach continues but the bond B—C begins to stretch; 3) the separation of the reaction products AB and C. Let us assume that ϵ_1, ϵ_2, and ϵ_3 are the energies evolved during these three stages. We shall demonstrate later that the energy ϵ_1 is evolved mainly in the vibrational form and ϵ_3 mainly in the kinetic form. The fraction of ϵ_2 transformed into the vibrational energy of the molecules increases with the relative mass of atom A compared with atoms B and C.[47]

Thus, for example, in the case of the interaction $H + X_2$, the greater part of the energy is evolved in the

Table I

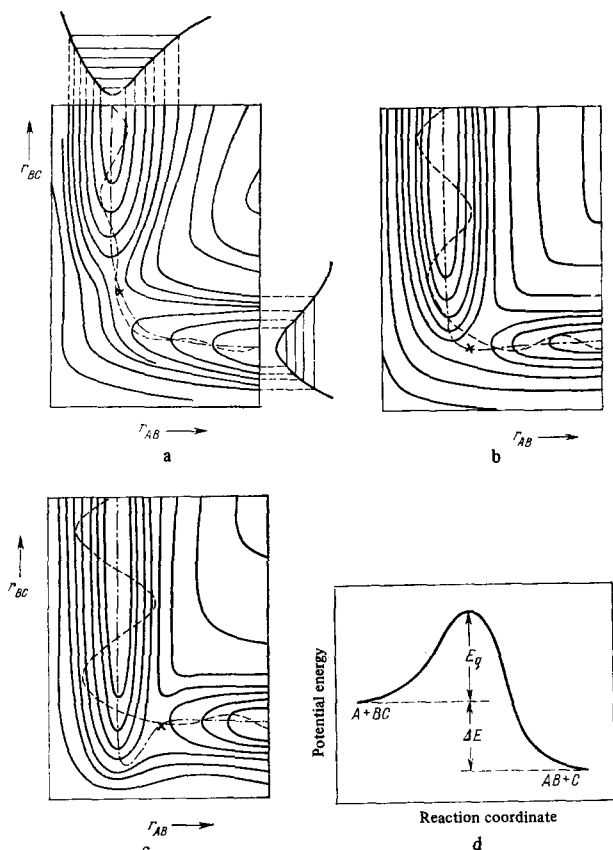| Molecule	v, cm⁻¹	B, cm⁻¹	a, cm⁻¹	j_0	$\exp[-1-j_0(j_0+1)(hcB/kT)]$	
					$T=300°$ K	$T=500°$ K
HF	3960	21	0.88	8	$3\cdot10^{-1}$	10^{-1}
HCl	2888	10.6	0.3	10.6	10^{-3}	$2\cdot10^{-2}$
HBr	2559	8.5	0.23	12.8	$3\cdot10^{-4}$	10^{-2}
CO	2142	1.93	0.017	45	$3\cdot10^{-8}$	$3\cdot10^{-5}$
NO	1877	1.7	0.018	45	$2\cdot10^{-7}$	10^{-4}
CN	2042	1.9	0.017	46.6	$1.5\cdot10^{-8}$	$1.5\cdot10^{-5}$

FIG 1

second and third stages.[46,47] High values of the ratio $\epsilon_{vib}/\epsilon_{kin}$ are obtained in similar reactions in which the hydrogen atom is replaced by a heavier atom, for example, by deuterium or a metal. Reactions which should have a high value of this ratio include $F + H_2$ (for other halogens this process is endothermic), $Cl + HI$, etc. The relative values of ϵ_1, ϵ_2, and ϵ_3 depend strongly on the nature of the potential energy $V(r_{AB}, r_{BC})$. We shall now consider the simplest case of collinear motion of particles when the potential energy depends only on two variables: $V(r_{AB}, r_{BC})$ = $V(r_{AB}, r_{BC})$. The potential surfaces of a system of atoms are shown in Figs. 1a-1c in terms of the coordinates r_{AB}, r_{BC}. The continuous curves in Fig. 1 represent the constant energy lines, the chain curves are the reaction coordinates (the potential energy increases on both sides of these coordinates), and the dashed curves show the possible trajectories of the motion of the system in the process described by Eq. (10). If the energy of the system exceeds only slightly the activation energy of the reaction, these trajectories pass close to the saddle point in the potential energy surface (shown by a cross in Fig. 1).

If the form of the function $V(r_{AB}, r_{BC})$ is that represented in Fig. 1c, the most probable trajectories are those in which energy is evolved during the approach stage between A and BC (when the system crosses a potential barrier, r_{AB} decreases but r_{BC} suffers little change). In the case in which $V(r_{AB}, r_{BC})$ corresponds to Fig. 1a, the value of r_{AB} changes little and r_{BC} increases after the crossing of the potential

barrier by the system, i.e., the energy is evolved during the final (third) stage.

In the intermediate case, represented by Fig. 1b, the nature of the most probable trajectories depends considerably on the relationship between the masses of the particles. (In the English-language literature the three types of potential energy represented by Figs. 1a, 1b, and 1c are called, respectively, repulsive, mixed, and attractive.)

In the majority of reactions of the Eq. (10) type the value of ϵ_1 is small. Therefore, the conclusions reached in[47] on the role of the mass of atom A are of general validity. They are particularly important because the vibration-rotational inversion, which is important in the case of diatomic molecules, can be achieved relatively easily only in the case of hydrogen-bearing molecules, which have a small moment of inertia.

We shall obtain a clearer idea of the influence of the masses m_A, m_B, and m_C of the interacting atoms on the nature of the energy distribution by a qualitative analysis of the process represented by Eq. (10), using a system of coordinates which is fixed relative to the center of mass of the particles A, B, and C. For the sake of simplicity, we shall assume that all the atoms are located on the same straight line and the approach of A to BC takes place along this line; we shall also assume that $r_{AD} < r_{AC}$ (Fig. 2a). There is then a moment in time t_0 when atom C and, consequently, the center of mass of atoms A and B are at rest. All the energy of the system at this moment t_0 consists of the potential energy of the interaction between the atoms and the kinetic energy representing the motion of the masses of atoms A and B relative to one another. This kinetic energy is similar in nature to the vibrational motion.

During the next period, the forces between atoms B and C are repulsive and they accelerate these atoms in the opposite directions. The interaction of atoms A and C should, at this stage, be weak because it depends strongly on the distance between the atoms; moreover, atom B screens the fields of atoms A and C. If the mass m_A is small, the acceleration of B is transferred to atom A without appreciable change in the potential energy of the A—B interaction. In the limiting case of $m_A \ll m_B$, all the repulsive energy evolved during the period $t > t_0$ is transformed into kinetic
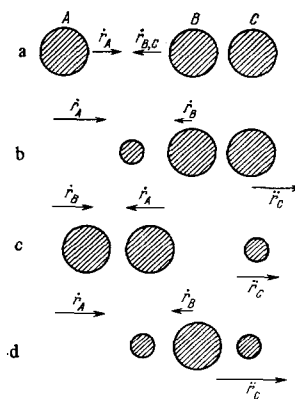

FIG 2

energy. If, moreover, $m_A \ll m_C$, the approach of A to BC is so rapid that at the moment t_0 the distance r_{BC} does not differ greatly from the equilibrium distance r_{BC}^0 in the molecule BC (Fig. 2b). Therefore, the potential energy of the interaction between atoms B and C, evolved as kinetic energy during the process of their separation, may represent a considerable proportion of the total reaction energy.

In the other limiting case m_A, $m_B \gg m_C$, during the separation stage atom B experiences practically no acceleration due to the forces separating the B—C particle because the action of these forces is very brief. Almost the whole energy of the interaction between the atoms B and C, evolved during the period $t > t_0$, is transformed into the kinetic energy of the mass m_C (Fig. 2c). Nevertheless, this energy need not be large. Since m_C is small, the distance r_{BC} during the approach of atoms A and B can vary as in an adiabatic process so that the potential energy of the repulsion between atoms B and C at the moment t_0 represents only a small fraction of the energy evolved in the reaction. Whether this is realized depends appreciably on the slope of the potential surface $V(r_{AB}, r_{BC})$.

The case m_A, $m_C \ll m_B$ is intermediate between the cases considered so far (Fig. 2d). The relationship m_A, $m_C \gg m_B$ is also inconvenient from the point of view of obtaining high values of $\epsilon_{vib}/\epsilon_{kin}$. When the last inequality is satisfied, the motion of A and C atoms can be almost adiabatic, i.e., vibrations of the particle AB are not strongly excited. Here again, the degree of adiabaticity depends very strongly on the slope of the potential surface $V(r_{AB}, r_{BC})$.

It is difficult to analyze the process represented by Eq. (10) for $m_A \gg m_B \approx m_C$, $m_A \approx m_B \ll m_C$, $m_A \approx m_B \approx m_C$, and one has to specify the actual form of the potential energy of the interaction.

According to the results of the numerical calculation reported in[47] the optimal situation is obtained when $m_A \approx m_B \gg m_C$. A very considerable decrease in $\epsilon_{vib}/\epsilon_{kin}$ compared with the optimal value occurs only if $m_A \ll m_B \approx m_C$ (the main part of the energy is evolved during the separation stage). Rankin and Light[68] have investigated the reaction

$$H + Cl_2 \rightarrow HCl + Cl$$
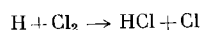
in the case of collinear motion of particles, using a quantum-mechanical approach. The results of Rankin and Light[68] confirm qualitatively the dependence, discovered in[47], of the ratio $\epsilon_{vib}/\epsilon_{kin}$ on the reaction stage (approach or separation) during which the major part of the energy is evolved. However, this ratio is greatly affected by the width of the potential barrier which a given system has to overcome (Fig. 1d). The narrower this barrier (its height is specified in advance), the less adiabatic is the process and the greater is the fraction of the energy transformed into vibrations.[68]

An important result of the investigation of Rankin and Light[68] is the discovery of the dependence of the ratio $\epsilon_{vib}/\epsilon_{kin}$ for an elementary $H + Cl_2 \rightarrow HCl + Cl$ event on the energy of the colliding particles and, consequently, the dependence of the reaction as a whole on the temperature. (The ratio $\epsilon_{vib}/\epsilon_{kin}$ decreases with

increasing energy of the interacting particles.) As far as we are aware, none of the published papers has taken note of this dependence.

The limits of validity of the classical approach were estimated by Russell and Light[69] by analyzing classically the same reaction for one of the types of the potential energy of interaction used in[68]. The classical and quantum-mechanical approach give close results if the sum of the kinetic energy of the system and the energy of the vibrations of Cl_2 greatly exceeds the activation energy of the reaction. However, if the excess energy of the system is only slightly greater or smaller than the activation energy, the influence of the quantum tunnel effect is considerable. Since the principal contribution to the reaction is made by the collisions of particles whose energies lie in the interval of the order of kT, a classical analysis is adequate only at high temperatures (at $T > 500°K$ for the particular reaction considered and the potential energy used by Russell and Light). At lower temperatures, the difference between the classical and quantum-mechanical values of the ratio $\epsilon_{vib}^0/\epsilon_{kin}$ is about 10—20%. The limits of validity of the classical analysis evidently depend on the nature of the potential energy of the system since the probability of the tunnel effect is governed not only by the height of the potential barrier but also by its width. The narrower the potential barrier, the wider is the range of temperatures in which the classical approach is inapplicable and the greater is the discrepancy between the classical and quantum-mechanical results in this temperature range.

The results reported in[47,68,69] are semiqualitative and cannot be used to obtain a numerical value of ϵ_{vib} for a particular reaction. An experimental investigation of the luminescence of reaction products[48] has yielded the relative populations $n(v)$ of the vibrational levels of the molecules formed in the following reactions: 1) $H + Cl_2$, 2) $H + Br_2$, 3) $Cl + HI$. The experimental arrangement used in this study made it possible to take into account the influence of relaxation processes resulting in a redistribution of the populations, or to eliminate such an influence (the reaction took place at low pressures in a gas stream, and the walls of the reaction chamber were cooled with liquid nitrogen so that the reaction products were deposited on the chamber walls without experiencing many collisions). Therefore, the measured values of $n(v)$ were close to the rates k_v of the various processes. The following values were obtained at 10^{-3} mm Hg for the ratio $n(1):n(2):n(3):n(4):n(5)$ under the experimental conditions employed: $0.371:1.38:1:(0.062):0$ for reaction 1 (0 denotes values below the sensitivity limit of the apparatus); $0:0.148:1:0.216$ for reaction 2; $0.3:0.6:1:0.7:0$ for reaction 3. Thus, in all the cases, there are levels v such that $n(v) < n(v+1)$ and, consequently, $k_v < k_{v+1}$, i.e., a total population inversion as a result of the reaction is possible. Reactions 1 and 3 can be used to generate coherent radiation by transitions in the P-branch,[48] i.e., by transitions in which the vibrational quantum number decreases and the rotational number increases.

It is interesting to note that, according to the results reported in[47], the relative amount of energy evolved in the Cl + HI reaction in the vibrational form is

greater than that in other cases (in any comparison of the results we must take into account that, according to the energy yields of reactions 1 and 2, we have v_{max} = 6, whereas v_{max} = 4 in reaction 3. The value of k_0 has been estimated in[48] for reaction 1: it is close to zero. Consequently, the vibrational energy evolved in this case represents about 45% of the total energy evolved. However, this estimate is not very reliable because the probability of deactivation of a vibrationally excited HCl molecule in collision with a hydrogen molecule is, in the relaxation model employed, two orders of magnitude higher than the experimental value reported in[32]. It should also be mentioned that according to the results of an earlier investigation[46] only 7% of the energy of this reaction is evolved in the vibrational form.

Polanyi and Tardy[73] recently employed the same method as in[48] to determine the relative rates k_v in the reaction H + F_2. It is reported in[73] that k_2/k_1 $\gtrsim$ 3.5, $k_3/k_2 \gtrsim$ 0.47. The fraction of energy evolved in the vibrational form is not less than 57%.[73]

We have considered so far only those elementary processes which produce, in general, some excited molecules. A chemical reaction may also include "undesirable" processes which result in the formation of molecules with lower vibrational levels. For example, in the chain reaction of hydrogen and chlorine

$$H + Cl_2 \rightleftarrows HCl + Cl, \qquad (11')$$

$$Cl + H_2 \rightleftarrows HCl + H, \qquad (11'')$$
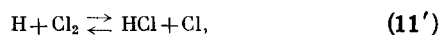
the second process is endothermic and, consequently, it should produce preferentially the molecules with v = 0 (if the reacting particles do not have sufficient excess kinetic or vibrational energy for the formation of molecules at high levels). In such cases, the ratio of the populations $n(v)/n(v + 1)$ may be considerably larger than k_v/k_{v+1} in the optimal elementary processes.

The distribution of the energy over various degrees of freedom has not yet been investigated in detail for the products of reactions different from those described in Eq. (10). We may assume that the relative proportion of the energy used to excite the vibrations of diatomic molecules is often large (see, for example,[29,49,71]). It is important to note that in the case of diatomic molecules the whole energy ϵ_{vib} is distributed over vibrational levels of one type, and, therefore, the temperature T_{vib} and the free energy of the system may be fairly high (see also Sec. V).

IV. KINETICS OF RELAXATION PROCESSES. ROTATIONAL RELAXATION

The distribution of molecules over their energy levels is governed not only by the reaction mechanism but also by the relaxation processes. The fastest of these is the establishment of a Boltzmann distribution over the rotational levels. This rotational relaxation is frequently useful because it may enrich the upper laser level and deplete the lower. In the case of heavy molecules, the rotational relaxation is completed within a few collisions.[37] This is because the differences between the energies of the rotational levels of heavy molecules are small compared with the average

energy of the kinetic motion. Moreover, transitions with arbitrary changes in the rotational quantum number can take place in a collision.

In a system of molecules with small moments of inertia the rotational relaxation is somewhat slower. For example, in the case of hydrogen, a time interval corresponding to 300 collisions is required.[37] The vibration-rotational inversion frequently occurs only in high rotational levels which are separated by large gaps (see Sec. I). If these gaps are comparable with or larger than kT, the probability of transitions between such levels decreases exponentially. At low pressures in a mixture, the relaxation may not be very effective.

A nonequilibrium distribution over the rotational states is reported in[48] for the products of the reaction Cl + HI. Laser emission involving transitions in the bands 3—2 and 2—1 of the P-branch is reported in[11] for HF molecules which are in excited vibrational states as a result of the preceding reaction. Convincing evidence shows that, at 4 mm Hg, the depletion of the upper laser level and the enrichment of the lower level is not fully compensated by the relaxation processes so that the distribution over the rotational levels is of the nonequilibrium type.

It should be mentioned that the rotational relaxation in a system of molecules with large dipole moments should be fast even if the moments of inertia of these molecules are small. Thus, in the case of HCl, the relaxation is completed in a time interval corresponding to seven collisions.[37] Evidently, collisions are effective in such a relaxation if both colliding molecules are polar. Bearing this in mind, we can explain the low rate of the rotational relaxation observed in[11] by the low partial pressure of the HF molecules under the experimental conditions.

The rate of the rotational relaxation may, in general, be increased by the addition of neutral impurities to a mixture. Practically any impurity can be used but their effects are diverse.

V. VIBRATION-VIBRATIONAL RELAXATION

As mentioned in Sec. II, the relaxation processes of the type

$$AB(v) + AB(v') \rightleftarrows AB(v+1) + AB(v'-1) \qquad (12)$$
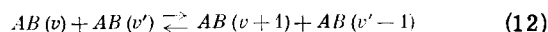
(diatomic molecules are considered for the sake of simplicity) are very fast. These processes establish a Boltzmann distribution over the vibrational levels but do not alter the average vibrational energy of the molecules. These processes are usually known as the vibration-vibrational relaxation.

We shall assume here that other relaxation processes are not important. We then find that the rate of redistribution of the populations $n(v)$ of molecules AB depends mainly on the partial pressure of these molecules in a mixture. In the initial stage of the reaction, when the pressure is low, the populations $n(v)$ are proportional to the values of k_v. Total or partial inversion is most likely during this period. Subsequently, the accumulation of AB molecules results in a rapid redistribution of the populations so that total inversion become practically impossible. This demonstrates the important disadvantage of diatomic molecules, i.e., the

absence of a relaxation process which would lead to a selective depletion of the lower levels without a change in the population of the upper levels. For these molecules the transitions $v + 1 \rightarrow v$ are usually faster than $v \rightarrow v - 1$.

In the limit, the populations of the vibration-rotational levels can be described by a quasi-Boltzmann distribution with two temperatures T_{vib} and T. The temperature T of the kinetic degrees of freedom increases during reaction whereas the vibrational temperature remains, at best, constant. Therefore, in the later stages of the reaction, the conditions for a partial inversion also become unfavorable. We shall now assume that k_v is the average (over all the elementary processes) value of the rate of formation of molecules AB in a vibrational state v, normalized to unity: $\Sigma k_v = 1$; $\overline{k}$ and $\overline{n}$ are collinear matrices with elements k_v, and $n_v = n(v)$, respectively; N_{AB} is the concentration of molecules AB. We then have

$$\frac{\partial \overline{n} N_{AB}}{\partial t} = \overline{k} \frac{\partial N_{AB}}{\partial t} - \widetilde{a} \overline{n} N_{AB}^2, \qquad (13)$$

where $\widetilde{a}$ is a matrix (reduced to unit concentration of the AB molecules) which determines the vibration-vibrational relaxation of the system in the absence of a chemical reaction, i.e., when $\partial N_{AB}/\partial t = 0$.

In the harmonic oscillator model, the elements of the matrix $\widetilde{a}$ are (see, for example,[37,50])

$$\left. \begin{array}{l} a_{v,\,v+1} = -(v+1)\,a_0, \\ a_{v+1,\,v} = e^{-hv/kT^\circ} a_{v,\,v+1}, \\ a_{vv} = [(v+1)\,e^{-hv/kT^\circ} + v]\,a_0, \\ a_{v,\,v'} = 0, \quad \text{if} \quad v' \ne v, \ v \pm 1, \\ a_{01} = [1 - e^{-hv/kT^\circ}]^{-1}/\tau_0; \end{array} \right\} \qquad (14)$$

Here, $1/\tau_0$ is the characteristic relaxation rate calculated per unit concentration N_{AB}; T° is the vibrational temperature corresponding to the average vibrational energy $E_{vib} = \sum\limits_{v} v h\nu n_v$.

In general, $1/\tau_0$ depends on the temperature but this dependence is relatively weak. Therefore, in considering the initial stage of the reaction, when the temperature changes only very slightly, we can assume that $1/\tau_0$ is a constant. We shall now

We shall now write an equation describing the rate of change in the difference $n_v - n_{v+1} = m_v$:

$$\frac{\partial m_v}{\partial t} = (v+2)\,a_0 m_{v+1} - \left\{ [v + (v+2)\,e^{-hv/kT^\circ}]\,a_0 + \frac{1}{N_{AB}} \frac{\partial N_{AB}}{\partial t} \right\} m_v \qquad (13')$$

$$+ v e^{-hv/kT^\circ} a_0 m_{v-1} + \frac{1}{N_{AB}} \frac{\partial N_{AB}}{\partial t} (k_v - k_{v+1}).$$

It follows from this equation that if m_{v+1}, m_v, and m_{v-1} have the same sign as $k_v - k_{v+1}$, the value of m_v cannot change its sign earlier than or simultaneously with m_{v-1} and m_{v+1}. Therefore, if k_v decreases monotonically with increasing v, a vibrational population inversion cannot be achieved. This follows from the observation that the relaxational transitions $v + 1 \rightarrow v$ are faster than $v \rightarrow v - 1$.

If, in a certain range defined by $v_1 \le v \le v_2$, the condition $k_v < k_{v+1}$ is satisfied, a population inversion which appears first in this range of levels may spread gradually to both sides $(v < v_1$ and $v > v_2)$ by cascade transitions $v \rightarrow v - 1 \rightarrow v - 2$, etc. The inversion between the levels in this interval disappears gradually, beginning at the limits of this interval.

If $\partial N_{AB}/\partial t$ is small, the distribution $\overline{n}$ tends eventually to approach a distribution $\overline{n}^\circ$ with a temperature $T_{vib} = T^\circ$, so that

$$\widetilde{a} \overline{n}^\circ \equiv 0, \qquad \sum v n_v^\circ = \sum v k_v. \qquad (15)$$

Conversely, if the role of the relaxation is not very important ($\widetilde{a} \approx 0$), it follows that $\overline{n} = \overline{k}$. We can use Eq. (13) to derive a condition for the distribution $\overline{n}$ to tend to a Boltzmann distribution:

$$N_{AB}^{-1} \int_0^t N_{AB}^2 \, dt' \cdot \frac{1}{\tau} \gg 1. \qquad (16)$$

The sufficient condition for the vibration-vibrational relaxation to have little effect on the distribution $\overline{k}$ near the level v is given by the inequality[70]

$$\frac{v}{\tau_0} N_{AB}^{-1} \int_0^t N_{AB}^2 \, dt' \ll 1. \qquad (17)$$

We can easily see that the concentration N_{AB} must increase at least hyperbolically $[N_{AB} \sim 1/(t_0 - t)]$ in order to satisfy the condition (17) throughout the whole process. Since such an increase is impossible, after a certain time interval the distribution $\overline{k}$ becomes considerably deformed by the vibration-vibrational relaxation. Formal integration of Eq. (13) or integration by the method of successive approximations gives $\overline{n}$:

$$\overline{n} = \frac{1}{N_{AB}} \int_{-\infty}^t \exp\left[-\int_{t'}^t N_{AB}(t'') \widetilde{a} \, dt'' \right] \frac{\partial N_{AB}}{\partial t'} dt' \overline{k}. \qquad (18)$$

The exponential function in Eq. (18) can be expanded in a series, as follows:

$$\overline{n} = \frac{1}{N_{AB}} \sum_{l=0}^{\infty} \frac{(-1)^l}{l} \widetilde{a}^l \int_{-\infty}^t \frac{\partial N_{AB}}{\partial t'} \left(\int_{t'}^t N(t'') \, dt'' \right)^l dt' \cdot \overline{k}. \qquad (18')$$

In the interesting special case of the exponential rise of the concentration $N_{AB} = N_0 e^{st}$, Eq. (18') can be easily transformed to

$$\overline{n} = \sum_{l=0}^{\omega} \frac{(-1)^l}{(l+1)!} \frac{N_{AB}^{l+1}}{s^l} \widetilde{a}^l \overline{k}. \qquad (18'')$$

This solution can be used conveniently when $N_{AB} a_0 s^{-1} < 1$ because, in this case, we need only a small number of terms. We note that the solution represented by Eqs. (18') and (18'') is valid irrespective of the nature of the matrix $\widetilde{a}$.

VI. VIBRATIONAL RELAXATION

In addition to the vibration-vibrational relaxation, the evolution of the distribution $\overline{n}$ is governed by the processes of deactivation of the vibrationally excited molecules by collisions and by luminescence. The term vibrational relaxation will be used for these processes. (The distribution $\overline{n}$ can be affected also by the deactivation of molecules in collisions with the walls of the reaction chamber. This influence is important only at low temperatures and we shall ignore it).

The vibrational relaxation can be taken into account by rewriting Eq. (13) in the form

$$\frac{\partial \overline{n} N_{AB}}{\partial t} + \widetilde{a} \overline{n} N_{AB}^2 + \widetilde{b} \overline{n} N_{AB} = \frac{\partial N_{AB}}{\partial t} \overline{k}. \qquad (13')$$

In the harmonic approximation, the elements $b_{vv'}$ are given by[37]

$$
\left.\begin{array}{l}
b_{v,\,v'} = 0 \text{ for } v' \neq v,\ v \pm 1, \\
b_{v,\,v+1} = (v+1)/\tau, \\
b_{v+1,\,v} = b_{v,\,v+1}\, e^{-h\nu/kT}, \\
b_{v,\,v} = [(v+1)\,e^{-h\nu/kT} + v]/\tau, \\
\dfrac{1}{\tau} = \dfrac{1}{\tau_{\text{rad}}} + \sum_n \dfrac{1}{\tau_n} N_N;
\end{array}\right\} \qquad (14')
$$

here, τ_{rad} is the characteristic time of a spontaneous radiative transition 1—0; N_n is the concentration of molecules of type n in a mixture; $1/\tau_n$ is a quantity representing the rate of relaxation per unit concentration N_n.

The efficiencies of various molecules in the deactivation of the vibrations of a molecule AB differ greatly. Moreover, these efficiencies usually depend very strongly on the kinetic temperature of the medium. Therefore, the quantity $1/\tau$ depends on time much more than does $1/\tau_0$.

We have so far assumed that the vibration-vibrational relaxation is faster than the vibrational relaxation. Before we specify the condition for this to be true, we shall represent the distribution $\bar{n}$ in the form $\bar{n} = \bar{k} + \bar{\Delta}$. We find from Eq. (13') that the correction Δ_v is small compared with k_v if

$$
\frac{v}{N} \int_{-\infty}^{t} \frac{N_{AB}^2}{\tau_0}\, dt' + \frac{v}{N} \int^{t} \frac{N_{AB}}{\tau}\, dt' \ll 1. \qquad (17')
$$

We may assume that the establishment of a Boltzmann distribution is governed solely by the vibration-vibrational relaxation if all the values of v which must be taken into account satisfy, for a certain value of t, the relationship

$$
\frac{v}{N} \int_{-\infty}^{t} \frac{N_{AB}}{\tau}\, dt' \ll \frac{v}{N} \int_{-\infty}^{t} \frac{N^2}{\tau_0}\, dt' \approx 1.
$$

(For subsequent time intervals, we must satisfy $N^2/\tau_0 \gg N/\tau$.)

We shall now consider the converse situation which, in general, is much less likely. We shall assume that the vibration-vibrational relaxation is unimportant (the condition for this will be given later). We then find from Eq. (13') that

$$
\bar{n} = \frac{1}{N_{AB}} \int_{-\infty}^{t} \exp\left(-\int_{t'}^{t} \frac{1}{\tau}\, dt''\cdot \bar{b}\right) \frac{\partial N_{AB}}{\partial t'}\, dt' \cdot \bar{k}. \qquad (19)
$$

We can show that the distribution represented by Eq. (19) is close to a Boltzmann distribution with a temperature $T_{\text{vib}} = T$ if[70]

$$
V(t) - N(t-\tau) \ll N(t). \qquad (16')
$$

For the sake of simplicity, we shall assume that τ is constant. If Eq. (16') is satisfied before Eq. (17) is violated, the vibration-vibrational relaxation may be ignored. These conditions are obtained only if $N_{AB}(t)$ increases less rapidly than an exponential function. In the case of exponential growth of the concentration $N_{AB} = N_0 e^{st}$, we find from Eq. (13') or Eq. (19) that

$$
\bar{n} = \frac{s}{s+\bar{b}}\, \bar{k}, \qquad (19')
$$

i.e., the distribution $\bar{n}$ does not vary with time. This distribution is close to $\bar{k}$ if $s \gg v/\tau$ in that range of v where k_v differs appreciably from zero.

Thus, in the case of an exponential or fast growth of the concentration N_{AB}, only a vibration-vibrational

relaxation can give rise to a Boltzmann distribution n_v. Therefore, this type of relaxation must be taken into account.

Any mechanism of variation of n_v may be encountered in the case of the slow growth of N_{AB}. In particular, at low values of v, the inequality (17') may be violated first because of the first term; at high values of v, which still have to be taken into account, this inequality may be violated because of the second term. In this case, an analysis of Eq. (13') is complex because this equation is nonlinear.

Having multiplied the equation for n_v by $vh\nu$ and having summed it with respect to v, we can obtain an equation for the average vibrational energy of a molecule $E_{\text{vib}} = \Sigma vh\nu n_v$:

$$
\frac{\partial E_{\text{vib}}}{\partial t} = -\frac{E_{\text{vib}} - E_0}{\tau} + E^0\, \frac{1}{N_{AB}}\, \frac{\partial N_{AB}}{\partial t}, \qquad (20)
$$

where E_0 is the average vibrational energy for $T_{\text{vib}} = T$, $E^2 = \Sigma vh\nu k_v$.

At high concentrations of N_{AB}, the value of $1/\tau$ depends, via the temperature, on the energy E_{vib}. Therefore, in general, Eq. (20) is nonlinear. In the case of such a dependence, Eq. (20) can be easily integrated:

$$
E_{\text{vib}} = \int_{-\infty}^{t} \exp\left(-\int_{t'}^{t} \frac{dt''}{\tau}\right)\left(\frac{E_0}{\tau} + E^0\, \frac{1}{N_{AB}}\, \frac{\partial N_{AB}}{\partial t'}\right) dt'. \qquad (20')
$$

We can easily see that E_{vib} remains close to E^0 if the concentration N_{AB} increases as $N_0 \exp[\int_0^t s(t')\, dt']$, where $s(t) \gg 1/\tau$.

It is shown in Sec. II that, even in the case of a Boltzmann distribution n_v, we can achieve laser emission as a result of partial inversion if T_{vib}/T is sufficiently large. The power and duration of such laser radiation can be estimated on the basis of the following considerations. We shall assume that the rotational and vibration-vibrational relaxations are so fast that the distributions n_v and $n(j)$ are close to the Boltzmann case. As a result of the laser effect, the vibrational temperature is maintained at such a level that the gain k in the medium is close to the threshold value k_0:

$$
k = \Delta n \cdot N_{AB}\varkappa \approx k_0, \qquad (21)
$$

where Δn is the maximum value of the population inversion given by Eq. (8'') with $v = 0$; $\varkappa$ is a coefficient which relates the absolute value of the population inversion to the laser gain.

Equations (8'), (9'), and (21) can be used to express the vibrational temperature $T_{\text{vib}}(t)$ in terms of the temperature of the kinetic degrees of freedom:

$$
v/T_{\text{vib}} \approx (\alpha k/Bhc)\ln AN_{AB} + 2\,[(kT/hcB)\ln AN_{AB}]^{1/2}, \qquad (22)
$$

where

$$
A = 2e^{-h\nu/kT}(1 - e^{-hc/kT_k})\, e^{-1}\varkappa/Z_{\text{rot}}k_0.
$$

Numerical estimates show that, at values of T above room temperature, the laser emission is possible if T_{vib} amounts to several thousands of degree, i.e., if it is of the order of the characteristic temperature $T = h\nu/k$.

Under these conditions, we can neglect the dependence of A on T_{vib} by assuming that $A \approx 0.5e^{-1}\varkappa(Z_{\text{rot}}k_0)^{-1}$. Equation (22) then gives the

explicit dependence $T_{vib}(T)$, and if $T(t)$ is known, we obtain also the dependence $T_{vib}(t)$.

The laser output power W_2 is found from the law of conservation of energy:

$$W_2 = \varepsilon^0 \frac{\partial N_{AB}}{\partial t} - N_{AB} \frac{\varepsilon_{vib}(T_{vib}) - \varepsilon_{vib}(T)}{\tau} - N_{AB} \frac{\partial \varepsilon_{vib}}{\partial T_{vib}} \frac{\partial T_{vib}}{\partial t} . \quad (22')$$

The first term on the right-hand side of Eq. (22') represents the vibrational energy evolved in a chemical reaction per unit time; the second term represents the losses due to deactivation; the third term gives the change in the vibrational energy of the system.

Strictly speaking, the right-hand side of Eq. (22') should be multiplied by $(T_{vib} - T)T_{vib}^{-1}$ but this quantity is close to unity.

The quantity described by Eq. (22') passes through zero twice: at the beginning and end of the laser emission period. Naturally, Eq. (22) is not satisfied in the region where Eq. (22') is negative.

VII. INFLUENCE OF THE ANHARMONICITY OF VIBRATIONS ON RELAXATION PROCESSES

The expressions in Eq. (14) for the elements of the matrix $\tilde{a}$ are valid only if we neglect the anharmonicity of the vibrations. They are derived on the assumption that the probability of the processes described by Eq. (12) is proportional to the product $v(v' + 1)P$, where P is independent of v and v'[37] If the anharmonicity is included, the energy defect in Eq. (12) is not equal to zero but is approximately proportional to the difference $v - v'$. It follows that the probability of the process (12) depends strongly on this difference. The elements of the matrix $\tilde{a}$ depend now on the distribution $n(v)$ and Eq. (13) becomes nonlinear and difficult to analyze.

In most cases, the principal relationship governing the operation of a chemical laser, associated with the relaxation processes described by Eq. (12), can be considered in the linear approximation. In fact, a change in the populations $n(v)$ affects the value of the population inversion much more than the elements of the matrix $\tilde{a}$. Let us assume, for example, that at a moment t_1 we have $n(v) = 0.3$, $n(v + 1) = 0.4$, and that at a moment t_1 we have $n(v) = 0.3$, $n(v + 1) = 0.4$, and that at a moment t_2 we have $n(v_0) = n(v_0 + 1) = 0.25$. The elements of the matrix $\tilde{a}$ do not change by more than 15% (it is assumed that changes in the populations of the other levels also do not exceed 15%). However, the change in the difference $n(v_0 + 1) - n(v_0)$ is very large.

Even more important is the circumstance that the rates of the relaxation processes (12) may slow down considerably because of the energy defect, i.e., because of the anharmonicity.

Since the anharmonicity of the vibrations is usually fairly weak, it follows that the energy defect for specific vibration-rotational transitions is small. We shall consider, for example, the following elementary event which is allowed in the case of a dipole interaction:

$$\text{HCl } (v = 0, j) + \text{HCl } (v_2 = 2, j') \rightleftarrows \text{HCl } (v = 1, j - 1) + \text{HCl } (v = 1, j' - 1).$$
$$(12')$$
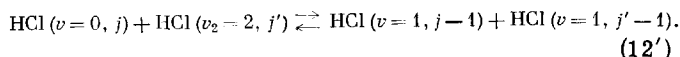
The vibrational energy of the molecules in the process described by Eq. (12') increases by about 100 cm^{-1} and the rotational energy decreases by about $2(j + j')10$

cm^{-1}. If $j + j' = 5$, the total energy defect in Eq. (12') is close to zero.

The strongest anharmonicity is exhibited by the vibrations of molecules containing hydrogen. The rotational constants of these molecules are also large. Consequently, the rotational levels j which correspond to a small energy defect in Eq. (12) and, therefore, make the principal contribution to the total probability of exchange of the vibrational quanta, are practically always low. The populations of these levels are not, generally speaking, low and they do not depend too strongly on the rotational temperature T_{rot}. Therefore, the rate of the relaxation processes (12) should also depend weakly on the temperature.

Finally, because of the anharmonicity of the vibrations the form of the matrix $\tilde{a}$ is generally different from that given by Eq. (14). An important property of the vibrational relaxation process, which this matrix represents, is that the rate of the $v + 1 \rightarrow v$, $v + 2$ transitions is always higher than the rate of the $v \rightarrow v + 1$, $v - 1$ transitions, i.e., the depletion of the upper level is always faster than the depletion of the lower level. This property is retained also in the presence of anharmonicity if the sum of the populations $\sum\limits_{v'=v+1}^{\infty} n(v')$ is not small compared with $\sum\limits_{v'=0}^{v-1} n(v')$. It is important to note that, in the presence of this anharmonicity, the probabilities of the forward and reverse processes in Eq. (2) are not generally equal. As shown in[80], the vibration-vibrational exchange produces a quasi-equilibrium distribution over the vibrational levels which differs considerably from a Boltzmann distribution. The difference grows with increasing vibrational energy of the molecules and with decreasing kinetic temperature T. The ratio $n(v + 1)/n(v)$ for such a distribution increases with increasing v and for high energy levels it may exceed unity.

The description of the matrix $\tilde{b}$ in the form given by Eq. (14') is, strictly speaking, correct only if we are dealing with a mixture AB consisting of monatomic gases. In other cases, the correctness of Eq. (14') must be tested specially. However, the cases when Eq. (14') is substantially wrong are exceptional. By way of example, we shall consider the system $H_2 + HF$, in which a vibrational energy exchange of the following type is possible:

$$\text{HF } (v) + \text{H}_2(0) \rightleftarrows \text{HF } (v - 1) + \text{H}_2(1) - \Delta E. \quad (12'')$$
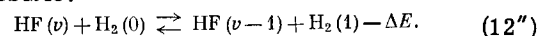
For $v = 1$, we find that $\Delta E = 200$ cm^{-1}. Because of the strong anharmonicity of the vibrations of HF, the value of ΔE increases rapidly with increasing v. We may expect the probability of the process (12'') to have its maximum value at $v = 1$ and to decrease rapidly with increasing v. Then, a vibrational population inversion may be achieved, in principle, even when $k_v > k_{v+1}$ for all the values of v. [The energy may be accumulated in the form of the vibrations of H_2 and, therefore, Eq. (13') is generally insufficient for the description of the process.]

Even when Eqs. (14) and (14') are violated, the majority of the qualitative results obtained so far remains valid because these results do not depend greatly on the actual form of the matrices $\tilde{a}$ and $\tilde{b}$.

The available theories give only very rough values of the probabilities of vibrational transitions in the collisions of molecules. Thus, the well-known Herzfeld-Schwartz-Slawsky method frequently gives values of τ_i which differ by several orders of magnitude from the experimental values. Obviously, the main deficiency in this method is that it ignores the change in the rotational states of molecules during collisions and their anisotropy. A considerable success has recently been achieved in the further development of the theory of vibrational transitions. For example, an allowance for the anisotropy of molecules has made it possible[51] to find some relaxation constants which are closer to the experimental values than those given by the Herzfeld-Schwartz-Slawsky method. The very good agreement between the theoretical probabilities of the vibrational transitions in CO_2-H_2, CO_2-N_2, and CO_2-D_2 collisions with the experimental values is reported in[52], where an allowance is made for the change in the rotational states of molecules in such collisions. Nevertheless, reliable values of the relaxation times can, in general, be obtained only by experimental methods.

The probabilities of the vibrational transitions in some molecular systems are listed in[37,38,43]. A great deal of experimental information has recently been obtained on the rates of such transitions by the use of laser techniques (see, for example,[40,41,32,33]).

VIII. CHEMICAL REACTION KINETICS. SIMPLE CHAIN REACTION

One of the most important factors which determines the possibility of using chemical energy in the generation of laser radiation is the chemical reaction rate. Usually, chemical reactions are relatively slow so that the inequality (17) may be satisfied only during the initial period of the process. The main cause of the slowness of chemical reactions is the finite activation energy required for the majority of chemical processes (Arrhenius's law). At low temperatures, only those few particles which have energies corresponding to the Maxwell distribution "tail" can take part in a reaction. The rate of reaction usually increases rapidly when the temperature is increased (the temperature may rise because of the evolution of the energy in the reaction if the specific heat of the system is not too large, i.e., if the mixture is not too dilute). In most cases, this increase in the reaction rate is greater than the corresponding increase in the relaxation rates. An increase in the temperature is useful only in the presence of a nonequilibrium distribution k_v of the reaction products. Otherwise, high temperatures degrade the conditions required for a partial inversion and, in all cases, high temperatures reduce the efficiency of the conversion of the vibrational energy into coherent radiation. The rate of reaction depends also on the pressure in a mixture (as well as on the relative concentrations of the components of the mixture, which will be assumed to have optimal values). In the important case of bimolecular reactions, the pressure dependence of the reaction rate is linear and, therefore, variation of the pressure does not alter the relative rates of the reaction and of the relaxation processes.

A high reaction rate may be induced by the genera-

tion of a large number of chemically active centers (for example, by electric discharge or photolysis). However, much energy is required in the forced acceleration of a chemical reaction. The most promising method is the use of branched chain reactions whose rates may be very high (these rates are not greatly influenced by the energy lost in the initiation of such reactions). Tal'roze[4] was the first to suggest and analyze theoretically the use of branched chain reactions in chemical lasers. This problem was investigated later by Oraevskiĭ[34] and by others.[20]

The general relationships governing the rate of chemical reactions can be found, for example, in monographs[43,53]. We shall consider briefly some specific reactions from the point of view of possible rates of rise of the concentrations of their products, and we shall see whether they satisfy the conditions set out in Eqs. (17) and (17'). We shall restrict our analysis to pulsed conditions.

We shall estimate the number of molecules AB which can be obtained when Eqs. (17) and (17') are satisfied. We shall do this by considering the simplest unbranched chain reaction described by Eqs. (11') and (11''). We shall show that the number of such molecules depends strongly on the rate of "nucleation" of chains, i.e., on the energy used in the initiation of the reaction. We shall assume that such initiation is photochemical in its nature:

$$Cl_2 + h\nu \rightarrow Cl + Cl. \tag{23}$$

For the sake of simplicity, we shall assume that the kinetic temperature T does not vary greatly during this reaction so that the cross sections of all the elementary processes remain constant (this assumption is valid during the initial period of the reaction when $N_{Cl} \ll N_{H_2} + N_{Cl_2}$).

The processes described by Eq. (11') are very fast[43] and the atom of hydrogen which appears in reaction (11'') interacts practically instantaneously (in the first collision with Cl_2) in accordance with Eq. (11'). Therefore, the rate of formation of HCl molecules can be expressed in the form

$$\frac{\partial N_{HCl}}{\partial t} = 2\sigma N_{Cl} N_{H_2}, \tag{24}$$

where σ is the rate constant of the reaction (11'), which depends on the temperature, in accordance with $\sigma = \sigma_0 \exp(-F_a/kT)$.

The processes (11')−(11'') do not affect the concentration of chlorine atoms [an atom of chlorine which interacts in accordance with (11'') is immediately replaced by another atom of chlorine as a result of (11')]. The concentration of chlorine atoms is governed by the number $w(p)$ of photochemical events [Eq. (23)] per unit time and by the rate of the annihilation processes in triple collisions. Numerical estimates show that the annihilation processes can be ignored during the time Eq. (17') is valid, so that $N_{Cl} \int_0^t w(t') dt'$. We shall assume that N_{Cl} is given in the form

$$N_{Cl} = At^n, \tag{25}$$

where $n \geq 0$ is not necessarily an integer. We shall assume also that N_{H_2} is sufficiently high and that

changes in this concentration can be neglected. We thus find from Eqs. (24) and (25) that

$$N_{HCl} = \frac{1}{n+1} \sigma N_{H_2} A t^{n+1}. \qquad (26)$$

Equations (17) and (26) yield the following expressions for the time t_0 during which the vibration-vibrational relaxation does not affect appreciably the distribution n_v and for the concentration $N_{HCl}(t_0)$:

$$t_0^{n+2} \ll (n+1)(2n+3) \tau_0/v\sigma N_{H_2} A, \qquad (27)$$

$$N_{HCl} \ll \left(\frac{2n+3}{v}\right)^{\frac{n+1}{n+2}} \left(\frac{\sigma N_{H_2} A \tau_0}{n+1}\right)^{\frac{1}{n+2}}, \quad N_{HCl}(t_0) < \left[\frac{2n+3}{n+1}\frac{\tau\sigma}{v} N_{H_2} N_{Cl}(t_0)\right]^{1/2}$$

Similarly, we can use Eqs. (17') and (26) to estimate the time t_0' during which the vibrational relaxation is of little importance, and to find the concentration $N_{HCl}(t_0')$. Usually, the experimental conditions are such that $1/\tau \approx N_{H_2}/\tau_{H_2}$. We then obtain

$$t_0' \ll \frac{n+2}{v}\tau_{H_2}/N_{H_2}, \quad N_{HCl}(t_0') \ll \frac{n+2}{n+1}\frac{\tau_{H_2}\sigma A}{v}\left(\frac{n+2}{v}\frac{\tau_{H_2}}{N_{H_2}}\right)^n,$$

$$N_{HCl}(t_0') < \frac{n+2}{n+1}\frac{\tau_{H_2}}{v}\sigma N_{Cl}(t_0'). \qquad (27')$$

We can easily see that, for a fixed value of N_{Cl}, the times t_0 and t_0' have minimal values and the concentrations $N_{HCl}(t_0)$ and $N_{HCl}(t_0')$ are maximal for $n = 0$, i.e., when the photoflash pulse is nearly a δ-like function. Usually, such a pulse is of long duration so that we need consider only its front which can be approximated by the dependence t^{n-1}, where $0 < n - 1 < 1$. Therefore, in Eqs. (25)–(27') we have $1 < n < 2$.

The right-hand sides of Eqs. (27)–(27') give the orders of magnitude of the times during which a population inversion is possible in the products of the reaction $H_2 + Cl_2$; they also give the corresponding concentrations N_{HCl}. The functional forms of these expressions are basically different, i.e., one or the other type of relaxation is the dominant process depending on the concentration N_{H_2}, the temperature, and the energy used in the initiation of the reaction.

It is interesting to note that if $n = 0$ the concentration $N_{HCl}(t_0')$ is independent of N_{H_2}. In this case, the maximum laser emission energy can be obtained by increasing the concentration N_{H_2} until the vibration-vibrational relaxation becomes negligible during a time interval of the order of t_0'.

The most likely situation in practice is that when $n \approx 2$ (laser emission observed during the rise time of a photoflash pulse). In this case, $N_{HCl}(t_0) \infty N_{H_2}^{1/4}$ and $N_{HCl}(t_0') \infty N_{H_2}^{-2}$. When the concentration of hydrogen is increased, the energy of the laser radiation should first increase slowly and this should be followed by a sharp fall. The dependence of this energy on the photoflash power (on the value of A), is monotonic.

We can easily show that at low photoflash powers the output energy is proportional to A, and at high powers it is proportional to $A^{1/(4+n)}$.

The temperature dependences of the quantities t_0, $N_{HCl}(t_0)$ and t_0', $N_{HCl}(t_0')$ are also quite different. The time interval t_0 always decreases and $N_{HCl}(t_0)$ increases with rising temperature: $t_0 \infty \sigma^{-1/(n+2)}$ $\infty \exp[Ea/(n+2)RT]$, $N_{Cl}(t_0) \infty \exp[-Ea/(n+2)RT]$. On the other hand, the values of t_0' and $N_{HCl}(t_0')$ depend on the temperature not only through $\sigma(T)$ but also

through $\tau_{H_2}(T)$ ($\tau_{H_2} \infty \exp[-\text{const}/T^{1/3}]$). Therefore, in different ranges of temperature and for different values of n, the temperature dependences of t_0' and $N_{HCl}(t_0')$ may be different.

We shall now estimate the values of t_0, $N_{HCl}(t_0)$, t_0', and $N_{HCl}(t_0')$ in the optimum case $n = 0$. According to[28], $\sigma = 10^{14} \exp[-5.5 \text{ kcal/RT}] \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$.

The values of τ_{H_2} and τ_0 at $T = 300°K$ are:[32,33] $\tau_{H_2} = 10^{-2}$ sec·torr and $\tau_0 = 10^{-5}$ sec·torr. For $v = 2$ (Sec. III) and $T = 300°K$, we obtain

$$t_0 \ll 4 \cdot 10^{-4} (N_{H_2}N_{Cl})^{-1/2}, \quad N_{HCl}(t_0) < 0.1 (N_{H_2}N_{Cl})^{1/2};$$

$$t_0' \ll 10^2 N_{H_2}^{-1}, \quad N_{HCl}(t_0') \ll 5N_{Cl}.$$

Thus, at $T = 300°K$, the number (n) of HCl molecules forming in a time interval during which the vibrational relaxation does not distort greatly the distribution k_c is found to be of the same order as the number of chlorine atoms generated by the photochemical processes of Eq. (23). When the temperature is increased, the value of $N_{HCl}(t_0')$ increases strongly because in this range of temperature, the exponential dependence $\sigma(T)$ in Eq. (27') is dominant in Eq. (27').

These estimates show that the concentration $N_{HCl}(t_0)$ is small compared with $N_{H_2} + N_{HCl}$ so that, in agreement with an assumption made earlier, the rise of temperature due to the energy evolved in the reaction is slight. Nevertheless, a change in the temperature during the reaction may be of considerable importance because the rate constant $\sigma(T)$ depends strongly on the temperature. Igoshin and Oraevskii[54] investigated the problem of achieving a vibrational inversion in the reaction $H_2 + Cl_2$ by numerical methods, taking into account the dependence $T(N_{HCl})$. Unfortunately, Igoshin and Oraevskii had to use unreliable values for the probabilities of the exchange of vibrational quanta in collisions of HCl molecules, which they calculated by the Herzfeld-Schwartz-Slawsky method.

Nevertheless, the results of Igoshin and Oraevskii[54] are valuable at least in offering a qualitative understanding of the kinetics of processes occurring in a pulsed chemical laser. According to their results, a population inversion between the 2-1 vibrational levels of the HCl molecule usually exists for a short time in the initial stage of the reaction (when about 1% of Cl_2 participates in the reaction). It is interesting to note that an inversion between the levels 3-2 is produced by cascade transitions of the $v \rightarrow v - 1$ type and that such inversion exists longer than that between the levels 2-1. This result depends strongly on the relationship between the probabilities of the exchange of vibrational quanta [Eq. (12')] corresponding to various values of v, v' which are used in the calculations. As expected, the time during which a population inversion exists decreases strongly and its peak value increases when the initial temperature is raised. Igoshin and Oraevskii report that the efficiency of a laser increases with rising temperature throughout most of the temperature range which can be used in practice (the possibility of using a partial inversion is ignored).

Igoshin and Oraevskii[54] ignore the deactivation of the vibrationally excited HCl molecules in collisions with hydrogen. Therefore, in the case of a slow rise of

the concentration N_{HCl} (low pumping energies) and a high concentration of N_{H_2}, the reliability of their results reported in[54] is low.

Concluding our analysis of the system $H_2 + Cl_2$, we shall compare the maximum value of the vibrational inversion Δn which can be achieved in the absence of relaxation processes (in the initial stage of the reaction) with the maximum value of the vibration-rotational inversion which may be achieved if a Boltzmann distribution n_v is established instantaneously and there is no deactivation. In these estimates we shall use the results reported in[48] for the distribution k_v (Sec. II) and we shall assume that $k_0 \ll k_1$. In the normalization of this distribution we must bear in mind that, in the processes described by Eq. (11'), almost all the molecules are formed in the unexcited state ($v = 0$). Then, in the case of a total inversion, we obtain

$$\Delta n_m \approx (k_2 - k_1)\max\{(2j + 1)\exp[-j(j+1)hcB/kT]\}Z_{rot}^{-1}, \quad (28)$$

$$\Delta n_m = \frac{(k_2 - k_1)e^{-1/2}}{Z_{rot}} = \frac{0.1}{Z_{rot}}. \quad (29)$$

The magnitude of a partial inversion can be estimated if the values of T_{vib} and T are known. The vibrational inversion in the absence of losses is governed by the distribution k_v and it is equivalent to 6000—7000°K. Estimates obtained from Eqs. (8') and (9") give, for $T_{vib} = 6000°K$ and $T = 500°K$, the value of Δn_m which is 10 times smaller than that predicted by Eq. (29); $\Delta n_m = 0.01 Z_{rot}^{-1}$.

A reduction in the inversion—and, consequently, in the gain—by a factor of 10, compared with the maximum value, is not unreasonable. The results of an experimental investigation of lasers based on the reaction $H_2 + Cl_2$ show that the laser effect is not observed in the presence of a Boltzmann distribution n_v (present section). This may mean that the vibrational relaxation is important in the investigated range of the concentrations N_{H_2}, N_{Cl}, and temperatures because the fraction of the energy evolved in the form of vibrations in the processes described by Eq. (11') is lower than the value assumed in our calculations. (We must also take into account the losses of the vibrational energy due to the laser effect. Although these losses are slight in relation to the currently obtainable efficiencies of chemical lasers, they should be eliminated in order to facilitate more rigorous investigations of the possibility of inducing the laser effect in the case of a Boltzmann distribution n_v. This may be achieved, for example, by the use of a Q-switched resonator).

If T_{vib} is estimated from the results reported in[46], according to which only 7% of the energy of the process (11') is evolved in the vibrational form, the temperature T_{vib} is found to be $\sim 2700°K$. Then, for $T = 500°K$, the inversion is negligibly weak:

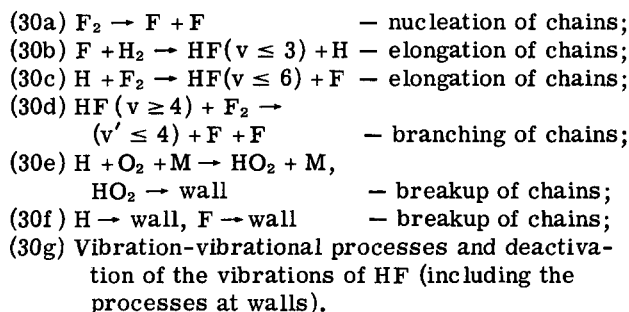$$\Delta n_m \approx 10^{-6}/Z_{rot}.$$

IX. BRANCHED CHAIN REACTIONS

As mentioned earlier, the fastest reactions are those of the branched chain type. Only few such reactions are known at present. They include the oxidation of H_2, PH_3, SiH_4, CS_2, CO, and phosphorus; the decomposition of NCl_3; some reactions involving molecular fluorine and, for example, H_2, CH_3, I, HI; and some

other reactions. The relationships governing branched chain reactions are usually considered by taking the well-known oxidation of hydrogen as the example.[34,54] We shall consider the reaction of hydrogen and fluorine because the results can be used later.

Semenov and Shilov[55] used the experimental results of Shilov et al.[56] to demonstrate that this reaction is of the branched chain type and that the branching affects the energy. This reaction proceeds as follows:

(30a) $F_2 \rightarrow F + F$ — nucleation of chains;
(30b) $F + H_2 \rightarrow HF(v \le 3) + H$ — elongation of chains;
(30c) $H + F_2 \rightarrow HF(v \le 6) + F$ — elongation of chains;
(30d) $HF(v \ge 4) + F_2 \rightarrow$
         $(v' \le 4) + F + F$ — branching of chains;
(30e) $H + O_2 + M \rightarrow HO_2 + M$,
         $HO_2 \rightarrow$ wall   — breakup of chains;
(30f) $H \rightarrow$ wall, $F \rightarrow$ wall   — breakup of chains;
(30g) Vibration-vibrational processes and deactivation of the vibrations of HF (including the processes at walls).

At low pressures, the collision frequencies and, therefore, the rates of the processes (30b), (30c), and (30d) are low and the probability of deactivation of the active H, F, and HF particles ($v \ge 4$) at the walls is high. Therefore, at low pressures, the reaction mixture is stable, i.e., it is not self-igniting. At high pressures, the probability of the loss of H atoms in triple collisions of the (30e) type (the HO_2 radicals are not very active and are deactivated at the walls) is high and, therefore, the mixture is again stable. At some intermediate range of pressures, the processes (30b), (30c), and (30d) may be dominant. In this case, the reaction gathers momentum, i.e., the mixture ignites spontaneously. This range of pressures depends on the temperature of the mixture. In a plane with the coordinates T and p, there is an "ignition peninsula" whose presence is typical of branched chain reactions (Fig. 3). The lower boundary of this peninsula is known as the first ignition limit, and the upper boundary is called the second limit. (V.L. Tal'roze shows that the $HO_2 + F_2 \rightarrow HF + O_2 + F$ processes give rise to a third ignition limit, shown dashed in Fig. 3.) The ignition limits depend naturally on the relative concentrations of the components of the mixture and the lower limit is affected strongly by the size and shape of the reaction chamber and by the material of its walls.

We note that the existence of this ignition peninsula is practically always a sure sign that the reaction is of
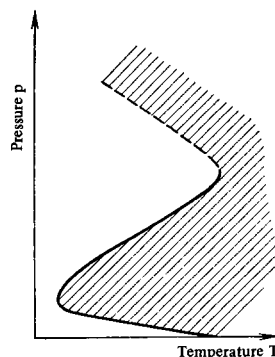

FIG 3

the branched chain type. (The opposite of this conclusion is not, generally, true.)

The presence of the upper (second and third) limits is typical of chain reactions but, in principle, they are not essential. For example, in the reaction considered here, the third limit is simply a result of the presence of oxygen in the mixture. Using Eqs. (30a)—(30g), we can derive equations which determine the rates of change of the concentrations N_H, N_F, $N_{HV(v)}$:

$$\frac{\partial N_H}{\partial t} = -(\omega_3 N_{F_2} + \omega_5 N_{O_2} N_M + \omega_8) N_H - \omega_2 N_{H_2} N_F, \quad (31a)$$

$$\frac{\partial N_F}{\partial t} = \omega_3 N_{F_2} N_H - (\omega_2 N_{H_2} + \omega_7) N_F + N_{F_2} \sum_{v \geqslant 4} \omega_{4,v} N_{HF(v)} + W(t), (31b)$$

$$\frac{\partial N_{HF(v)}}{\partial t} = \omega_3 k_v N_{F_2} N_H - \omega_{4,v} N_{F_2} N_{HF(v)} + \text{term representing} \quad (31c)$$
relaxation processes and deactivation at the walls.

Here, ω_2, ω_3, $\omega_{4,v}$, and ω_5 are the rate constants of the various processes ($\omega_{4,v>4} = 0$), $W(t)$ is the rate of nucleation of the chains [Eq. (30a)]; the meaning of the symbols ω_6 and ω_7 will be discussed later.

If the vibration-vibrational relaxation is ignored it is found that Eqs. (31a)—(31c) contain only the concentrations $N_{HF(v)}$ with $v = 4$, 5, and 6 [in practically all cases, $h\nu \gg kT$ and, consequently, $N_{HF}(7) = 0$, $\partial N_{HF}(v\geq4)/\partial t$ independent of $N_{HF}(v<4)$]. When the vibration-vibrational relaxation is included, the number of equations increases.

Under these conditions, the rates of loss of the particles H, F, and HF(v) are proportional to the gradients of their concentrations. Therefore, ω_6 and ω_7 contain the gradient operator and the expressions in Eq. (31) are equations with partial derivatives.

If we consider the initial stage of the reaction, we may assume that $N_{H_2} = N_{H_2}(t = 0)$, $N_{F_2} = N_{F_2}(t = 0)$, and $T = T(t = 0)$. If, moreover, the concentration N_{HF} is so low that the terms representing the vibration-vibrational relaxation can be omitted from Eq. (31c), we find that the expressions in Eq. (31) become linear.

These equations can be averaged out over the volume and then ω_6 and ω_7 are found to be some constants which depend on the size and shape of the reaction chamber and on the material of its walls. In this case, a system of simple differential equations (31) describes changes in the volume-average concentrations.

At high pressures (far from the lower ignition limit), the deactivation of the particles on the walls has little effect on the reaction over most of the reaction chamber volume and the terms proportional to ω_6 and ω_7 (as well as a similar term in the equation for $\partial N_{HF}(v)/\partial t$) can be omitted. Then the expressions in Eq. (31) are still simple but not linear.

We shall consider the initial period of the reaction, assuming that the rate of the nucleation of the chains $W(t)$ can be represented by a δ-function. Then, the solution of the linear system (31) is a sum of exponential functions. Retaining only the largest exponential function, we find that

$$N_{HF} = N_0 e^{st},$$

where s is the largest of the roots of the determinant of (31). An expression for s is obtained in[23,22] on the assumption that the rates of the processes 2 and 3 are considerably greater than the rates of all the other processes.

The limit of the ignition peninsula is found from the condition s = 0: within this peninsula s > 0, and outside it s < 0. The exponential growth of the concentration of the products or of the rate of reaction is typical of all the branched chain reactions. Naturally, this growth occurs only during the initial stage of the reaction when the concentrations of the reagents and the temperature are close to their initial values.

As demonstrated in the preceding section, the distribution n_v in the case of an exponential growth of the concentration and in the absence of the vibration-vibrational relaxation remains constant (for large values of st) and it is given by Eq. (19'). For given values of b and k_v, there is a minimum value s_{min} at which a population inversion is still retained by the vibrational level system. For example, let us assume that $k \approx 1$, $k_{v+1} \approx 0$, and that $\tilde{b}$ is given by Eq. (14'). For high values of st, we can then obtain from Eq. (23)

$$n_1/n_0 \approx st(1 - e^{-h\nu/kT})^{-1} = st.$$

Thus, the condition for the existence of a population inversion is, in this case,

$$st > 1.$$

In real situations, k_v and $\tilde{b}$ are different from those just used and they are not known exactly. However, the above condition for the existence of a population inversion remains basically sound. Knowing the dependences of s and τ on the pressure and temperature, we can, in principle, find the region in the T-p plane in which this condition is satisfied. Obviously, this region must lie within the ignition peninsula (Fig. 4). Such a region may be in the form of a peninsula (Fig. 4a), an island (Fig. 4b), or it may be altogether absent.[31]

Under experimental conditions, a mixture is prepared at temperatures and pressures outside the ignition region. Then, a brief stimulus (an electric discharge, photolysis, etc.) is used to transfer the mixture to the ignition region and, if the energy of such a stimulus is sufficient, to the region where a population inversion can be achieved (see[20]). However, if the energy of the stimulus is low, no population inversion is achieved during the stage of the reaction for which the expressions in Eq. (31) are linear and $t \gg 1/s$. The vibration-vibrational relaxation in the reaction of hydrogen with fluorine is basically ignored in the analysis represented by the linearized system of equations
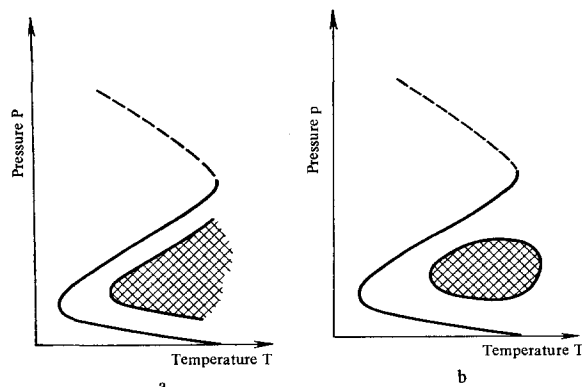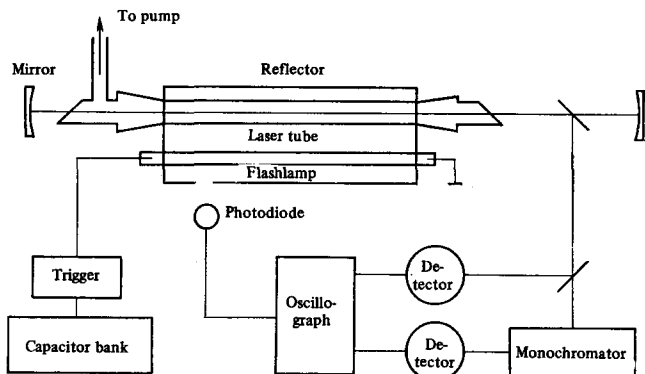

FIG 4

FIG 5

(31). We shall not consider here a system of equations with nonlinear terms.

We can make the following general comments on the influence of the vibration-vibrational relaxation on the reaction. If the processes represented by Eq. (30d) are very fast, this relaxation results in a weak population of the level v = 4 because of transitions from the third level. In this case, the rate of reaction may increase somewhat. However, if the processes represented by Eq. (30d) are slow, this type of relaxation produces a Boltzmann distribution n_v and the rate of reaction naturally decreases.

In the case of radical chains, the vibration-vibrational relaxation does not affect the course of the reaction and, therefore, its influence can be included within the framework of the linearized problem. This has been done, for example, in[20,34] for a two-level system. These papers also give estimates of possible efficiencies of lasers based on branched chain reactions.

X. CHEMICAL LASERS UTILIZING DIATOMIC MOLECULES

Laser action has been observed in several diatomic reaction products: HX, DX (X = F, Cl, Br), CO.[7-27] A typical experimental arrangement is shown in Fig. 5. A mixture, which is a potential source of such diatomic molecules, is admitted to a reaction tube with Brewster windows or internal mirrors (sometimes the mixture is pumped continuously through the tube[15,10,70,74-79]). In pulsed lasers, the reaction is initiated either by pulsed photolysis (photoflash energies from tens to thousands of joules are used) or by an electric discharge. The flash duration is tens of microseconds but the laser emission is usually shorter. The duration of an electric discharge may be less than 1 μsec and again the laser emission is shorter but it is of the order of 1 μsec) and it appears after a delay of a few microseconds.

The reactions used in CW lasers do not require an external stimulus and the working mixture is prepared immediately before its injection into the resonator.

The reported values of the total output energy do not exceed 2×10^{-2} J under pulsed conditions. The maximum output obtained under CW conditions is 11 W.[79] In most cases, a spectroscopic analysis of the laser radiation was carried out.

The first chemical laser was built by Kasper and Pimentel[7], who used HCl molecules formed in the

$H_2 + Cl_2$ reaction initiated by photolysis. The pressure in their mixture ranged from 3 to 16 mm Hg and the ratio of the partial pressures was $P_{Cl_2} : P_{H_2} \approx 1 : 12$

The laser emission was observed for several transitions, which were originally identified incorrectly with the 1-0 transitions. The laser emission for each of these transitions lasted less than 10 μsec and the beginning of emission at each of the transitions was practically coincident in time with the maximum of the preceding transition.

A partial inversion of the population of the levels v = 1 and v = 0 cannot be explained within the framework of our analysis of the values of k_v in the process described by Eqs. (11′) and (11″); it also cannot be explained by, for example, the results given in[48]. Corneil and Pimentel[14] later measured more accurately the frequency of the laser radiation and found that it corresponded to the 2-1 transitions of the P-branch. The gain maximum was observed for the transition $P_{2-1}(6)$ when the initial temperature of the mixture was $T_0 = 300°K$, and for the $P_{2-1}(8)$ transition when this temperature was $T_0 = 384°K$. This corresponded to the ratio n(2)/n(1) of 0.68 and 0.62, respectively. Cornell and Pimentel assumed that the distribution n(v) was distorted by processes described by Eq. (12″) so that the similarity with the results reported in[46] could be accidental. The cited values of the ratio n(2)/n(1) differed considerably from those reported in[48] for the reaction (11′).

The dependence of the output power on the initial temperature of the mixture T_0, reported in[14], was very interesting. The power increased with rising temperature right up to $T_0 = 530°K$ (at higher temperatures, the mixture used in[14] ignited spontaneously). The authors explained this effect by an acceleration of the rate of the reaction.

The laser effect was observed for the $D_2 + Cl_2$ mixture[14] only at temperatures $T_0 > 400°K$. At lower temperatures, the rate of this reaction was evidently insufficient for a population inversion.

Airey[8] reported laser emission for the P-transitions 1-0, 2-1, and 3-2 in the HCl molecules formed in the $Cl_2 + HI$ reaction. This reaction was also initiated by photolysis. Moore[9] achieved laser emission in the same mixture by exciting it with an electric discharge. In contrast to photolysis, a discharge produced not only chlorine atoms but also atomic hydrogen and iodine. Therefore, the processes represented by Eq. (11′), as well as the $Cl_2 + HI$ processes, played an important role in this reaction. The laser emission was obtained for the 3-2 and 2-1 P-transitions, starting from the 3-2 transition. No radiation was observed in the 1-0 band.

The total energy of the coherent radiation obtained in the electrical excitation case was 2×10^{-4} J, whereas photolysis of the same mixture (at a higher pressure) yielded 2×10^{-2} J.[9]

Although the reaction $Cl_2 + 2HI \rightarrow 2HCl + I_2$ is exothermic, it is fairly slow. An additional source of free chlorine atoms (generated by photolysis or discharge), i.e., an external energy source, is required before we can use the Cl + HI system in a chemical laser.

On the other hand, the elementary Cl + HI reaction

is extremely convenient from the point of view of obtaining high values of the ratio $\epsilon_{vib}/\epsilon_{kin}$ (Sec. II). Therefore, Cl_2 + HI lasers can be used to obtain higher output powers than those possible in other chemical lasers in which the HCl molecule is used in the laser emission. An important disadvantage of the Cl + HI system is the rapid exchange of the vibrational energy in processes of the type

$$HCl\,(v) + HJ\,(0) \rightarrow HCl\,(v-1) + HJ. \tag{32}$$
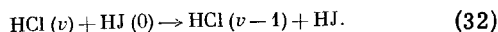
According to the results reported in[32,33], the rate of such exchange is $(5.1 \pm 0.4) \times 10^3\ sec^{-1} \cdot torr^{-1}$.

The analogous system HBr + Cl_2 was investigated by Airey,[25] who employed Q-switching. The working pressures in Airey's work[25] were: p_{HBr} + p_{Cl} ≈ 8.3 torr, $p_{HBr} : p_{Cl_2} \approx 1 : 3.44$. The reaction was initiated by photolysis and the output of the flash lamps was of the order of 800 J.

When no Q-switching was used, Airey[25] obtained laser emission pulses of 20 μsec duration, which were due to the P_1 transitions. In the Q-switched case, the duration of emission was governed by the rate of rotation of a prism or a mirror and was of the order of 1 μsec. The Q-switching did not alter the output power, i.e., an inversion population was established in a system in a time interval shorter than 1 μsec.
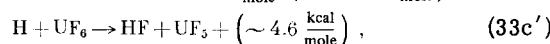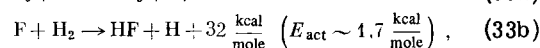
The main relaxation process in this reaction was HCl(v) + HBr(0) → HCl(v − 1) + HBr(1) + ΔF ≈ 300 cm^{-1}.

A reaction in mixtures of Cl_2 and NOCl with hydrogen, initiated electrically, also gave rise to the laser effect as a result of the 1-0 P-transitions in the HCl molecule.[10] In the H_2 + Cl_2 mixture, the laser emission began in the 3-2 transitions; then the 2-1 transition became active and finally the 1-0 stage was reached [$P_{1-0}(6)$ to $P_{1-0}(11)$]. Although the ratio $n(1)/n(0)$ should increase as a result of the cascade transitions 3-2 and 2-1, the observation of the laser emission due to the 1-0 transitions was unexpected. For example, in the case of a population inversion between the levels v = 1, j = 6, and v = 0, j = 7 [$P_{1-0}(6)$], the ratio $n(1)/n(0)$ should in accordance with Eq. (7′) correspond to a vibrational temperature $T_{vib} \sim 6000°K$ (T ≥ 300°K). Such a high population of n(1) contradicted the results reported in[46] but was in agreement with the results reported in[48] if it were assumed that $k_0 \leq k_1, \ldots$ for the reaction described by Eq. (10′).

We may assume that, under the conditions employed in[10], the vibrations of the H_2 molecule are excited quite effectively in an electric discharge. The vibrationally excited hydrogen should react easily in accordance with Eq. (11″) since the energy $h\nu_{H_2}$ of its vibrational quanta would be greater than the activation energy of this reaction. The HCl molecule can form any state with v > 0 [$h\nu_{H_2} > h\nu_{HCl}$ + energy defect in an elementary reaction represented by Eq. (11″) especially as the ratio of the atomic masses in Eq. (11″) is favorable for high values of the ratio $\epsilon_{vib}/\epsilon_{kin}$.

Several investigators[11,13] achieved laser emission from the HF and DF molecules which were formed in photolysis-initiated reactions in mixtures of uranium hexafluoride with hydrogen or with deuterated molecules: H_2, D_2, CH_4, CD_4, C_2H_8, CCl_3H. The mixtures of UF_6 with H_2 and D_2 were investigated in the greatest

detail.[11] The following processes were observed in the reaction UF_6 + H_2:[11]

$$UF_6 + h\nu \rightarrow UF_5 + F, \tag{33a}$$

$$F + H_2 \rightarrow HF + H + 32\ \tfrac{kcal}{mole}\ \left(E_{act} \sim 1.7\ \tfrac{kcal}{mole}\right), \tag{33b}$$

$$H + UF_6 \rightarrow HF + UF_5 + \left(\sim 4.6\ \tfrac{kcal}{mole}\right), \tag{33c'}$$

$$UF_5 + UF_5 \rightarrow UF_4 + UF_6, \tag{33c''}$$

$$H + UF_5 \rightarrow HF + UF_4. \tag{33d}$$

It was argued in[11] that the reactions (33c′) and (33d) were slow and did not affect appreciably the operation of a laser. Consequently, the principal process in which the excited HF molecules were formed in this reaction was that described by Eq. (33b). We should note that the number of such excited molecules was not larger than the number of quanta of light required to produce free fluorine atoms. Since, moreover, the energy required to break the U-F bond was greater than that evolved in the process (33b), the excited HF molecules were generated, in principle, at the expense of the light quanta.

At low pressures in the reacting mixture (a few mm Hg), the laser emission was observed for the $P_{2-1}(3)$-$P_{2-1}(8)$ transitions in the HF molecule and for the $P_{2-1}(3)$-$P_{2-1}(8)$ and $P_{3-2}(4)$-$P_{3-2}(9)$ transition in DF. The distribution over the rotational levels differed from the equilibrium case and, therefore, it was difficult to obtain information on the populations n_V.

When such a mixture was diluted with neutral gases, an equilibrium distribution over the rotational levels was achieved. In the case of HF, the laser emission was observed first for the $P_{2-1}(4)$ transitions and then for the $P_{2-1}(5)$ transitions, i.e., there was a competition between these transitions. Similar effects were observed for the DF molecule. The results obtained enabled the authors[11] to estimate the relative populations of the vibrational levels. Evidently, before the beginning of the laser emission, the value of n(v) was proportional to the rate k_V of the process (33b). It was estimated that $n(3)/n(2) \approx 0.83 - 1.11$ for DF and $n(2)/n(0) \geq 1$ for HF (the second estimate was less reliable than in the case of DF[14]).

Stimulated radiation corresponding to the 1-0 transitions was not observed in[11] and, therefore, it was not possible to estimate either the ratio $n(1)/n(0)$ or $\epsilon_{vib}/\epsilon_{kin}$ for the process (33b) which, according to the results reported in[47], could be quite effective in the sense of generation of vibrationally excited molecules.

The levels of the HF and DF molecules with v ≠ 0 could have been heavily depleted by processes of the type described by Eq. (4″) (in the DF-D_2 system the energy defect in this process was fairly small). The influence of such processes was not estimated in[11]. The actual values of k_{V+1}/k_V in Eq. (33b) were likely to be considerably higher than the values of the ratio $n(v + 1)/n(v)$ measured in[11].

Deutsch[15] observed laser emission from the HF and DF molecules which were obtained in discharge-initiated reactions in mixtures of hydrogen and deuterium with the Freons CF_4, $CBrF_3$ and CCl_2F_2; Deutsch also observed laser emission from the HCl, DCl, HBr, and DBr molecules using mixtures of H_2 or D_2 with Cl_2 or Br_2.

In the case of HF, the stimulated radiation was due to the $P_{1-0}(6)$-$P_{1-0}(15)$, $P_{2-1}(2)$-$P_{2-1}(15)$, $P_{3-2}(2)$-$P_{3-2}(8)$ transitions; in the case of DF, it was due to the $P_{1-0}(12)$-$P_{1-0}(16)$, $P_{2-1}(3)$-$P_{2-1}(17)$, $P_{3-2}(3)$-$P_{3-2}(4)$, and $P_{4-3}(5)$-$P_{4-3}(7)$ transitions. Obviously, in both cases the ratio $n(1)/n(0)$ was considerably smaller than the ratios $n(2)/n(1)$ and $n(3)/n(2)$. However, the data given in[15] were insufficient to obtain numerical values of these ratios.

The principal process responsible for the formation of excited molecules was again that described by Eq. (33b). As in the $H_2 + Cl_2$ reaction excited by an electric discharge,[9] the rate of this process and the distribution of its products could be affected considerably by the vibrational excitation of the hydrogen molecules.

When Freons or uranium hexafluoride are used as the sources of fluorine, a large amount of energy (electrical or optical) is necessary to start the reaction. Such reactions are of great interest from the point of view of the investigation of elementary chemical processes but they are not useful sources of energy.

Excited HF molecules were generated in[16] by the exothermic chain reaction $F_2O + H_2$, excited by flash photolysis. Although the energy of the stimulated radiation obtained from this reaction was low (less than 10^{-5} J), such reactions should be regarded as quite promising. The disadvantage of the particular reaction used ($F_2O + H_2$) was the formation of a large amount of water which deactivated the vibrations of the majority of the molecules, including, probably, those of hydrogen fluoride. Moreover, an undiluted mixture was used in[16] and, therefore, the specific heat of this mixture was relatively low and the kinetic degrees of freedom were rapidly excited. The efficiency of this system can be probably increased considerably by the use of high-specific-heat diluents such as SF_2, etc.

Laser emission due to the P transitions in HF was reported by the same authors in[26] for the $F_2O + H_2$ reaction excited by a shock wave.

As mentioned earlier, the most promising reactions for chemical lasers are those of the branched chain type. One such reaction, that of fluorine with hydrogen, was used in[20] for a chemical laser based on HF. The pressure and temperature of the mixture were selected near the lower ignition limit (Fig. 4). A weak electric discharge, whose energy was of the order of 1% of the energy evolved in the reaction, was used to increase the temperature and pressure in the mixture by an amount sufficient to move the coordinates of the point p, T within the ignition peninsula in Fig. 4 (in principle, the point p, T could be shifted to the ignition region by a change in the pressure or in the temperature of the mixture without the need to use electrical or optical energy for the ignition of the reaction). The laser emission was observed at several frequencies in the 3600—4200 cm^{-1} range; this indicated that a total vibrational inversion was achieved in the reaction products. The maximum ratio of the coherent radiation energy to the energy of the firing pulse (of the order of 2—10%) and the highest efficiency of pulsed chemical lasers (0.2%) were achieved in this reaction.[20]

The reaction reported in[20] was nonuniform over the cross section of the reaction tube and only a small part of the reaction volume, located near the tube axis, was active in the laser emission.

Obviously, the use of mixtures with the parameters p and T above the second ignition limit would make the reaction more uniform across the chamber volume and would make it possible to obtain higher output powers and efficiencies.

It is interesting to note that the laser emission reported in[20] was due to the P_{1-0} transitions of HF but that the output power was low.

The spectrum emitted by an $H_2 + F_2$ laser was investigated in detail in[22]. According to the results reported in[22], the greatest number of transitions was found in the 2-1 and 5-4 bands; the 0-1 transitions were not observed in[22,24].

The large number of transitions in the 5-4 band was probably due to the depletion of the $V = 4$ level by the process $HF(4) + F_2 \rightarrow HF(0) + F + F$, whose probability was evidently higher compared with the analogous processes in which molecules with $v \geq 4$ participated.

The high intensity of the 2-1 transitions could be due to a high population of the level 2 in the products of the reaction $H + F_2 \rightarrow HF + F$ and the reaction $F + H_2 \rightarrow HF + H$. Moreover, the level $v = 1$ was probably depleted at a higher rate because of the collisions with hydrogen. This conclusion was, to some extent, in conflict with the results reported in[20], where no laser emission was observed in the 1-0 transitions. Tal'roze suggested that the absence of the laser emission in the 1-0 transitions could be explained by the presence, before the reaction, of some HF(0) molecules in the mixture. This was quite likely because it was difficult to prepare a mixture of pure components.

Some interesting results were obtained by Dolgov-Savel'ev and his colleagues,[24] who investigated the laser emission of the HF molecules generated in the reactions $H_2 + F_2$, $H_2 + UF_6$, and $H_2 + MoF_6$.

An important disadvantage of all these reactions was the absence of any selective mechanism which would result in the preferential formation of molecules in one of the upper vibrational states. According to the results reported in[18], such a mechanism is active in the oxidation reaction $CS_2 + O_2$. One of the products of this reaction is in the form of vibrationally excited molecules of carbon monoxide. Pollack[17] reported laser emission for some of the P-transitions in carbon monoxide excited in this reaction by photolysis. A more detailed study of lasers based on this reaction was reported in[18]. This reaction was also initiated by the photolysis method. Laser emission was observed in various transitions of the $v \rightarrow v - 1$ type in the P branch ($v = 1$—16) and in the R branch ($v =9$—15). Thus, an almost total population inversion between the levels v and $v - 1$ ($9 \leq v \leq 15$) was observed for the CO molecule. (No laser emission in the R transitions was observed in any other laser but this did not mean that a total inversion was not achieved in other lasers; the absence of the R-transition emission could be a competition between transitions. It was reported in[18] that stimulated radiation for the R-branch transitions was observed only when a selective resonator was employed so that competition between the transitions was suppressed.)

As reported in[18], the laser emission by the CO molecules always started with the 13—12 vibrational transitions. This was explained as follows. The investigated reaction included the elementary processes:

$$S + O_2 \rightarrow SO_2 + 124 \text{ kcal/mole} \qquad (34a)$$

$$SO + O \rightarrow SO_2 + 123 \text{ kcal/mole} \qquad (34b)$$
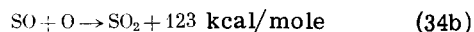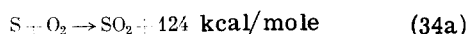
(the second of these processes had a much higher probability than the first). It was suggested in[18] that these processes produced electronically excited molecules of SO_2, which transferred their excitation energy to the CO molecules so that they were promoted from the ground state to the state with v = 13. This explanation was confirmed by the observation of a strong luminescence in the reaction with a maximum in the region of λ = 3640 Å, corresponding to an excitation energy of 78 kcal/mole, which was very close to the energy of the v = 13 vibrational level of CO. Such luminescence was observed also by Kondrat'eva and Kondrat'ev,[44] who noted its strongly nonequilibrium nature.

The laser emission due to the vibrational transitions v → v − 1 for v = 11—10 began earlier than for v = 12 or v ≤ 9. This was explained by the fact that in the elementary reaction

$$O + CS_2 \rightarrow CO + S_2 + 70 \text{ kcal/mole} \qquad (34c)$$
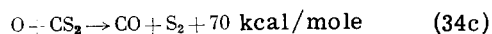
the rate of formation of the molecules with v = 10—11 was higher than that of the molecules in other states (the energy of the level v = 11 is 67.1 kcal/mole). However, strong selectivity was not observed. According to our analysis given in Sec. II, the process (34c) could be efficient from the point of view of vibrational excitation of the molecules.

Hancock and Smith[57] assumed that the principal processes responsible for the generation of the strongly excited CO molecules in this reaction were

$$S + O_2 \rightarrow SO + O, \qquad (34d)$$

$$O + CS \rightarrow CO + S. \qquad (34e)$$

The energy of the second process was not known exactly but Hancock and Smith estimated it to be 75 kcal/mole, which was sufficient for the generation of excited CO molecules (v = 13). A qualitative discussion[57] of the potential surface on which this reaction occurred has demonstrated that the reaction might be a very efficient source of strongly excited (in the vibrational sense) molecules of CO.

Arnold and Kimbell[70] reported laser emission for the P-branch transitions in CO molecules excited in the $CS_2 + O_2$ reaction initiated by an electric discharge in a flow-through system. Arnold and Kimbell discussed some mechanisms of the generation of excited CO molecules and concluded that the elementary reaction $CS + O_2 \rightarrow CO + SO$ was responsible for the excitation.

The reaction $CS_2 + O_2$ is, generally speaking, very complex and little is known about it. Therefore, it is difficult to judge whether it is promising from the point of view of its use in chemical lasers. An important disadvantage of this reaction is its relatively low rate. According to Kondrat'ev,[43] the activation energy of the elementary process which limits the rate of this reaction is 15.5 kcal/mole.

The use of a partial population inversion in a system of CO molecules cannot ensure a high value of the energy conversion coefficient. Because of the large moment of inertia of the carbon monoxide molecules, the partial inversion is weak when $n(v + 1)/n(v)$ is still close to unity. Therefore, a CO chemical laser can operate efficiently only in the presence of a strong influence of relaxation processes of the type given by Eq. (12″), i.e., at low partial pressures of carbon monoxide.

On the other hand, this reaction occurs at relatively low temperatures.

The combustion of carbon disulfide at T = 300°C without an external stimulus has been reported in[44]. Therefore, the free energy of the reaction products may be very high ($T_{vib} \gg T$). It is also known that this reaction is of the branched chain type. It is evident that this property of the reaction has not yet been utilized in full.

Some successes in obtaining CW emission in the reactions $F + HCl \rightarrow HF + Cl$[78] and $H_2 + F \rightarrow HF + H$[74] have been reported recently.

Airey et al.[78] achieved quasicontinuous radiation (pulses of the order of 1 msec duration) with an output power density of the order of 3 W/cm^2. Atomic fluorine was generated in[78] by thermal dissociation in a shock wave ($T \approx 1200°K$). Supersonic streams of partly dissociated fluorine and HCl were drawn into a vacuum chamber where they were mixed and where the reaction F + HCl = HF + Cl took place. The duration of the laser emission was determined by the time for which a high temperature was maintained in vacuum near the nozzle, and this duration exceeded considerably the vibration-vibrational relaxation time. Therefore, the generation of pulses of such duration could be regarded as continuous.

Prolonged continuous radiation (of the order of 30 sec) was reported in[74] when supersonic streams of fluorine atoms were injected into a hydrogen atmosphere. Fluorine atoms were generated by the dissociation of SF_6 in an $SF_6 + N_2$ mixture heated in an arc to 2000°C. The concentration of fluorine atoms was 4%. The heated and partly dissociated mixture flowed into a rectangular nozzle, of 0.375 × 7 in. in size. An optical resonator was placed across the gas stream at a distance of 3—5 in. from the nozzle exit.

The output power was 1 W. Control experiments showed that chemical processes were indeed responsible for the population inversion.[74]

Continuous emission of 500 W power in a similar system was reported in[81].

XI. CHEMICAL LASERS UTILIZING POLYATOMIC MOLECULES

The use of polyatomic molecules in chemical lasers can have important advantages over diatomic molecules. There are many suitable polyatomic molecules, each with several relaxation times.[43,58] In such molecules, a population inversion between the vibrational levels of different degrees of freedom can be achieved during the post-reaction period, even if an inversion is not possible during the reaction. Let us assume that a chemical reaction produces polyatomic molecules in

which a vibrational mode with the maximum lifetime is sufficiently strongly excited. A Boltzmann distribution within each vibrational mode is established during the reaction or soon after its completion. The temperatures of the different vibrational degrees of freedom may remain different for a long time since those degrees of freedom which have shorter lifetimes experience more rapid cooling. An inversion of the population may appear between levels of different degrees of freedom if their temperatures differ sufficiently strongly. For example, this may happen if the inequality (6) is satisfied. The situation is similar to that which obtains in the CO_2 laser.[59,60] The efficiency of such a system may be fairly high.

Since, within certain limits, one can control the rates of relaxation of different systems of vibrational levels, one can obtain an optimum relationship between them.

The most attractive are the reactions resulting in the formation of excited CO_2 molecules whose energy level system is very convenient for a population inversion. Unfortunately, because of the quantum forbiddenness, the oxidation of CO is very slow at moderate temperatures. Usually, CO oxidizes only in the presence of OH radicals and the mechanism is CO + OH $\rightleftarrows CO_2$ + H + 22 kcal/mole. The energy transferred to the vibrations of CO_2 does not exceed one-third of the total energy yield of the reaction CO + $\frac{1}{2}O_2$ = CO_2 + 65.4 kcal/mole. The presence of water in a mixture results in a very rapid deactivation of the vibrations of carbon monoxide and, therefore, a population inversion is difficult to achieve.[61] This explains the lack of success is achieving a population inversion in CO_2 by burning hydrocarbons in oxygen.[62-65]

Pimenov, Strakhov, and the present authors attempted to produce a population inversion in CO_2 formed by the oxidation reaction CO + O_3. At pressures of the order of several torr, the oxidation reaction was reasonably effective only in the presence of hydrogen (and, consequently, OH). No inversion was observed. However, this result should not be regarded as final.

Other oxidants have not been used to obtain a population inversion in CO_2 molecules.

In general, a population inversion in polyatomic reaction products can be achieved when the following conditions are satisfied: 1) the reaction rate should be sufficiently high compared with the rate of transformation of the vibrational energy into other degrees of freedom; 2) the reaction products must have levels convenient for a population inversion (they must satisfy the same requirements as other molecular lasers[58,59,60]); 3) the vibrational mode with the longest lifetime must be strongly excited in the reaction products.

It is quite difficult to satisfy all these requirements simultaneously. Moreover, it is not known precisely how the energy is distributed over the various degrees of freedom in polyatomic molecules. However, one can combine the advantages of diatomic and polyatomic molecules by producing (in a chemical reaction) strongly excited diatomic molecules with long vibrational relaxation times. These molecules can then be employed in the resonance transfer of the vibrational

energy to a particular vibrational mode in polyatomic molecules with a system of levels suitable for an inversion of the population.[29,58] This method would have the advantages described in the following paragraphs.

Since a diatomic molecule has only one vibrational degree of freedom, a considerable proportion of the reaction energy may be evolved in the form of vibrations of a given type. Next, the energy may be transferred to a particular vibration mode in polyatomic molecules and the concentration of such molecules may be sufficiently low so that the free energy of the system decreases only slightly in this transfer. Thus, the selected vibrations in polyatomic molecules may be excited much more strongly than other vibrations.

It is very important to note that, in this case, the nature of the distribution of the reaction products over the vibrational levels is not of great importance. All that is necessary is that a considerable fraction of the energy should be evolved in the vibrational form. This circumstance extends considerably the range of reactions which can be employed in chemical lasers.

The requirements governing the reaction rate are also less rigorous since the lifetimes of many diatomic molecules are fairly long and although the deactivation of the vibrations of polyatomic molecules may be fairly rapid, it cannot result in a rapid loss of vibrational energy by the whole system if the concentration of such molecules is low. It should be mentioned that the maximum relaxation times are exhibited by symmetrical molecules which cannot be used directly in lasers.

The disadvantage of the combination of diatomic and polyatomic molecules is the need to select those molecules between which the exchange of the vibrational energy is sufficiently efficient. We shall show later that this problem has been solved in some cases. Moreover, it is difficult to achieve a high gain in combined systems because radiative transitions between the vibrational levels of different degrees of freedom have a low probability and the concentration of polyatomic molecules should be low.

Long vibrational relaxation times are excited by the following molecules: N_2, O_2, H_2, CO, HCl_5, HF, DCl, DF, etc.

The nitrogen molecule, which has been used successfully in electrically excited lasers based on CO_2, is of special interest. Basov and his colleagues[66,67] demonstrated the possibility of a population inversion in CO molecules during the flow of an N_2 + CO_2 mixture into vacuum and they determined the numerical characteristics of such an inversion under various conditions.

A numerical calculation of the probabilities of the transfer of the vibrational energy in collisions between N_2 and some triatomic molecules is reported in[58]. The same paper also reports a determination of the conditions under which such transfer can give rise to a population inversion.

The class of reactions which can act as sources of N_2 molecules is fairly wide. However, there is little information on the distribution of the energy over various degrees of freedom of the products of such reactions. Therefore, special investigations are necessary of particular reactions in order to determine whether they are promising.

Measurements of the vibrational temperature of

molecules excited in collisions with products of the decomposition of hydrazoic acid HN_3, i.e., with nitrogen and hydrogen molecules, were reported in[28,29]. The reaction was carried out at partial pressures of HN_3 of 2—5 mm Hg and was initiated by an electric discharge whose energy was of the order of 1% of the energy evolved in the reaction.

When a mixture of $3HN_3 + 1CO_2 + 8Ar$ was used, the temperature of the antisymmetric vibrations of CO_2 reached 11 000°K, whereas other vibrations were "heated" to not more than 3000°K so that a population inversion was established between the levels

$$v_1 + 1, v_2, v_3 \quad \text{for} \quad v_1, v_2 + 2, v_3 \quad \text{or} \quad v_1, v_2, v_3 + 1.$$

The vibrational energy can be transferred from carbon monoxide, CO, to the same polyatomic molecules as in the case of nitrogen, and the best match of the levels with carbon monoxide is not given by CO_2 but by N_2O, COS, HCN, and C_2N_2. Unfortunately, the majority of the potential sources of CO molecules contains hydrogen and, consequently, the resultant reactions produce water, which rapidly deactivates the vibrations of all the molecules. In this sense, the reaction of oxidation of CS_2 is promising: it produces not only CO but also carbon oxysulfide, COS. In the presence of water, this reaction may also produce considerable amounts of CO_2. Moreover, it is possible that the transfer of energy of the electronic excitation of SO_2 to molecules of COS or CO_2 may be effective. Such a situation would be optimal from the point of view of the efficient use of this excitation energy.

In other cases, the criterion for the selection of molecules acting as acceptors of the vibrational energy may be the closeness of the vibrational frequencies of the diatomic and polyatomic molecules.

The vibrational frequency of DCl (2090 cm^{-1}) is close to the frequencies of COS (2050 cm^{-1}) and of HCN (2089 cm^{-1}). However, it may be very difficult to find a reaction whose product is DCl and not other molecules. This comment applies also to molecules of HF, DF, and HCl.

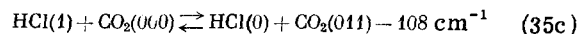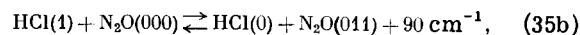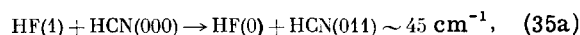The natural frequencies of the last two molecules (~ 2900 cm^{-1} and 2888 cm^{-1}) are close to the frequencies of other hydrogen-bearing molecules. for example, 2874 cm^{-1} of formaldehyde and 2914 cm^{-1} of methane. The system of levels of H_2CO and CH_4 are such that we can expect then to have several relaxation times and the maximum values of these times should be exhibited by the vibrations of the frequencies just cited. It is usual to assume that the vibrational relaxation of hydrogen-bearing molecules is very rapid. Nevertheless, experimental data on this point are available only for vibrations of the lowest frequencies. Therefore, it is difficult to determine a priori whether a population inversion is possible in systems of the $HCl-H_2CO$ type.

The molecules of H_2CO and CH_4 are satisfactory from the point of view of achieving a high gain in a laser. Although they have a large number of degrees of freedom, their natural frequencies are relatively high, and the distances between the levels of their rotational structure are relatively large so that the partition functions Z_{vib} and Z_{rot} may not be too large. Moreover, the vibrations of these molecules are fairly strongly anharmonic and, therefore, the probability of

transitions, forbidden in the harmonic approximation, may be quite reasonable.

There are no molecules with vibrational frequencies close to those of H_2 or HF. The closest to the vibrational level of 3960 cm^{-1} is the 3756 cm^{-1} level of H_2O. However, we cannot use water because of the fast relaxation although such a system would be satisfactory from the point of view of chemical compatibility.

The transfer of the vibrational energy may be also sufficiently effective in the elementary processes in which one vibrational quantum of a diatomic molecule with a high natural frequency is transformed into two vibrational quanta of a polyatomic molecule. For example,

$$HF(1) + HCN(000) \rightarrow HF(0) + HCN(011) \sim 45 \text{ cm}^{-1}, \quad (35a)$$

$$HCl(1) + N_2O(000) \rightleftarrows HCl(0) + N_2O(011) + 90 \text{ cm}^{-1}, \quad (35b)$$

$$HCl(1) + CO_2(000) \rightleftarrows HCl(0) + CO_2(011) - 108 \text{ cm}^{-1} \quad (35c)$$

and so on. Measurements of the rate of vibrational exchange in the $HCl + CO_2$ system are reported in[32,33]. Assuming that the main process in this exchange is

$$HCl(1) + CO_2(000) \rightarrow HCl(0) + CO_2(001) + \Delta E \approx 537 \text{ cm}^{-1}, \quad (35d)$$
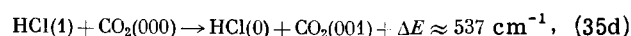
it is found in[32,33] that the rate of this process is $(p\tau)^{-1} = (9.4 \pm 0.8) \times 10^4 \text{ sec}^{-1} \cdot \text{torr}^{-1}$. The rate of the reverse process is, as expected, $\exp(\Delta E/kT)$ times smaller. The experimental arrangement used in[32,33] does not exclude the possibility that the measured rates apply to the forward and reverse processes described by Eq. (35c). (In this case, the rates of the forward and reverse processes are related by the same Boltzmann factor if the temperature of the deformation vibrations is equal to the kinetic temperature.)

Such very high rates of transfer of the vibrational energy from HCl to CO_2 have enabled the authors of[32,33] to construct a CO_2 laser in which the source of pumping energy is in the form of HCl molecules generated in the $HI + Cl_2$ reaction. This reaction was initiated by photolysis.

The duration and energy of the radiation emitted by such a CO_2 laser was several times higher than that of a laser based on HCl and using the same mixture without CO_2. (When CO_2 was added the output power of the HCl laser decreased and eventually the laser emission stopped; just before this happened, the emission by CO_2 began and it increased up to a certain saturation value.)

Similarly, Gross et al.[19] achieved laser emission ($\lambda = 10.6 \mu$) from CO_2 molecules by transferring the vibrational energy from DF to CO_2. The DF molecules were produced in the $D_2 + F_2O$ reaction initiated by photolysis. As in[32], laser emission by DF was observed in the absence of CO_2 from the mixture. When carbon dioxide was gradually added, this laser emission decreased in power. When the partial pressures of F_2O, D_2, and CO_2 became equal, laser emission was observed only in the $\lambda = 10.6 \mu$ region even when selective resonators were used to avoid competition between the different molecules. The output power was lower than for an $F_2O + D_2$ mixture but because the duration of laser emission was longer the total energy output was more than doubled.

Table II

Reaction	Rate of flow, 10^{-3} mole/sec				Pressure-torr	Output power, W
1) $Cl + HI \rightarrow HCl + I$	He 3.15	CO_2 0.88	HI 0.10	Cl_2 0.099	11.1	0.020
2) $F + D_2 \rightarrow DF + D$	He 3.15	CO_2 0.60	D_2 0.25	F_2 0.16	12.3	0.74
3) $D + F_2 \rightarrow DF + F$	He 21.8	CO_2 2.10	F_2 0.70	D_2 0.73	50	2 9
4) $F + DI \rightarrow DF + I$	He 2.91	CO_2 0.68	DI 0.046	F_2 0.064	9.6	0.084
5) $F + H_2 \rightarrow HF + H$	He 8.84	CO_2 1.27	H_2 0.20	F_2 0.28	23	0.079
6) $H + F_2 \rightarrow HF + F$	He 11.2	CO_2 1.79	F_2 0.26	H_2 0.16	26	0.050

The main process which resulted in the excitation of the antisymmetrical vibrations of CO_2 was

$$DF(1) + CO_2(000) \rightleftarrows DF(0) + CO_2(011) - \Delta E. \qquad (34e)$$
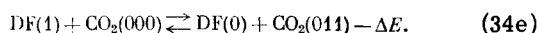
Laser emission at λ = 10.6 μ was also reported recently[28-31] for molecules excited by the exchange of the vibrational energy in the CO_2-N_2 system. Vibrationally excited nitrogen was generated by the decomposition of hydrazoic acid: $HN_3 \rightarrow \frac{1}{2}H_2 + \frac{3}{2}N_2$ + 71 kcal/mole.

Cool et al. carried out a series of investigations[75-77,79] on CW chemical lasers utilizing CO_2 molecules excited by the exchange of the vibrational energy with products of the reactions listed in Table II. Free atoms of chlorine, fluorine, deuterium, or hydrogen were generated in a high-frequency discharge in a mixture of helium and the appropriate gas (Fig. 6). The partly dissociated mixture was transferred into a Teflon reaction tube of 9 mm diameter, into which a mixture of CO_2 with the second component of the reaction (H_2, HI, D_2, DI, F_2) was injected simultaneously through a special nozzle which ensured rapid mixing.

The rate of flow of the gas in the Teflon tube was about 400 m/sec. The mixing and reaction took 100 – 200 μsec. The mixture which had reacted flowed into a Pyrex tube, 2.54 cm in diameter and 60 cm long. Cool et al.[76] concluded that the main contribution to the laser gain was made by the region inside the Teflon tube. Table II lists the partial velocities of the gases, the pressure at the entry to the Teflon tube (at the exit of this tube the pressure fell to 65% of its initial value, and at the Pyrex tube it fell to 9%), and the laser output power under optimal conditions. Reactions 2 and 3 as well as 5 and 6 in Table II were not independent but were branches of the same chain reaction because the primary mixture was only partly dissociated. Thus, this approach combined the advantages of the branched chain reactions and the resonance exchange of the vibrational energy between diatomic and polyatomic molecules.

Cool et al.[77] reported also the construction of a "purely chemical" laser without an external source of energy for the initiation of the reaction. They used a system similar to that described in the preceding paragraph but the source of atomic fluorine was not the reaction $NO + F_2 = NOF + F$, which took place in a side tube. Quite recently, Cool et al.[79] achieved CW laser emission at λ = 10.6 μ and the highest reported coefficient for the conversion of chemical energy into laser radiation, which was 4%. The output power was 11 W. They used a branched chain reaction, in a flow-through system without external initiation. Cool et al. expressed the opinion that it should be possible to increase the
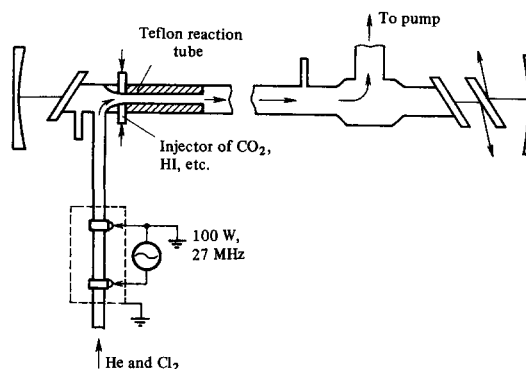

FIG 6

laser efficiency to 15% by the use of a transverse resonator.

XII. CONCLUSIONS

The direct conversion of chemical energy into coherent radiation is of very great importance in many branches of science and the national economy. About twenty types of chemical laser have already been constructed. The systems using vibration-rotational transitions in diatomic products of chemical reactions have been investigated in the greatest detail. Considerable difficulties are being encountered in achieving high efficiency in such systems. Greater promise is shown by lasers using a total vibrational inversion of population in polyatomic molecules (the first such lasers have already been constructed).

Further progress in chemical lasers depends on the success in the search for new fast reactions, particularly those with branched chains, which could serve as sources of excited molecules. It would be desirable also to investigate the possibility of operating at high pressures (of the order of the atmospheric pressure).

The work on chemical lasers is stimulating and enriching those branches of physical chemistry and chemical physics which deal with elementary chemical processes and with the mechanism and kinetics of reactions.

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