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VIBRATIONAL RELAXATION IN GASES AND MOLECULAR LASERS

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This article reviews the current status of the theory of vibrational relaxation in gases and its applications to the theory of molecular lasers. We discuss relaxation of the vibrational energy of diatomic and polyatomic molecules as represented by harmonic-oscillator models. The vibrational kinetics in a system of anharmonic oscillators is analyzed in detail. We treat quasi-steady-state population distributions of vibrational levels that arise under substantially non-equilibrium conditions, both in a single-component molecular system and in gas mixtures. We discuss relaxation that proceeds in the presence of sources of vibrationally-excited molecules: infrared resonance radiation, recombination, and dissociation; in particular, we analyze the process of non-equilibrium dissociation at low gas temperatures. We discuss from a unified standpoint based on vibrational kinetics the working mechanisms of lasers using vibrational-rotational transitions in diatomic and polyatomic molecules with various means of excitation (electrical, chemical, and gas-dynamic).

CONTENTS

1. INTRODUCTION

STUDY of vibrational relaxation in gases began about forty years ago. The first stage in the development of vibrational kinetics involved observing and explaining anomalous absorption and dispersion of ultrasonic waves in polyatomic gases. The studies of Herzfeld and Rice,[1] Knezer,[2] Rugers,[3] Landau and Teller,[4] Leontovich,[5] etc., have established the relaxational theory of sound propagation in gases. This theory was based on the hypothesis that absorption and dispersion of sound can arise not only from shear viscosity and heat conduction, but also from retarded energy exchange between the translational and intramolecular (vibrational) degrees of freedom. On a molecular scale whose natural unit is the time of free flight, the characteristic times for this exchange amount to tens or even hundreds of thousands.

The second stage in study of vibrational relaxation mainly involved study of shock waves. The first steps along this line were the studies of Bethe and Teller[6] and of Zel'dovich,[7] who studied spreading of shock waves caused by slow relaxation processes. Interest in studying shock waves was stimulated further by the development of rocketry in the forties and fifties, and it facilitated the appearance and refinement of the shock-tube method. Use of shock tubes made it possible to study vibrational relaxation over a broad temperature range: from thousands to tens of thousands of degrees. This was the stimulus for new theoretical studies. An entire series of results was obtained: calculation of transition probabilities in molecular collisions has been refined, processes of vibrational-translational and vibrational-vibrational energy exchange have been studied in pure gases and in mixtures, the role of excited-molecule sources has been examined, a relaxation theory of thermal dissociation has been devised, etc. The results of these studies are summarized in the reviews[8-10] and the monographs[11-16].

The third stage in studying vibrational kinetics was closely connected with molecular lasers. The sixties were marked by vigorous development of laser technology. Use of molecular gases as working media made possible great laser powers over a long spectral range from the near infrared to the submillimeter region. Molecular lasers based on vibrational-rotational transitions are currently the most powerful continuous-wave lasers. The development of lasers has elicited further development of vibrational kinetics, which has involved, in particular, detailed analysis of the population of vibrational levels, study of relaxation under substantially non-equilibrium conditions, both in diatomic and in polyatomic molecules, and taking account of the effect of various physical factors on the processes. Ideas of vibrational kinetics have made it possible to understand the working mechanisms of almost all lasers based on vibrational transitions. For a number of them, it has been possible to estimate the inverted populations and to construct the fundamental dependences on external parameters. Besides lasers, development of vibrational kinetics has also been stimulated by study of physical processes in gas dynamics, chemical kinetics, and atmospheric physics.

The aim of this article is to fill a gap involving the lack of a review literature on vibrational kinetics that might summarize the advances of recent years, includ-

ing application of the theory to molecular lasers. The treatment will be based on comparing the characteristic time of various energy-transfer processes in molecular systems. This approach makes it possible to study such complex systems as molecular gases. This permits us to distinguish the decisive processes from those that play a subsidiary role in a given phenomenon.

In terms of characteristic times, one can perform a general vibrational-relaxation analysis by using the definite hierarchy of the following kinetic processes: 1) V—T processes (energy exchange between vibrational and translational degrees of freedom); 2) V—V processes (vibrational exchange within a given type of vibrations); V—V′ processes (vibrational exchange between different types of vibrations and different molecules); 4) relaxation processes occurring in the presence of slowly-varying sources; 5) joint treatment of vibrational relaxation and other kinetic processes that have comparable characteristic times and which affect the behavior of real systems. Molecular lasers are an example of such systems.

A constituent part of the analysis of vibrational kinetics is to determine the probabilities of elementary processes. There are a number of reviews[17-21] and monographs[11,15,22] on the methods of calculating them. In this regard, we discuss briefly the problems concerning methods of calculation and selection of probabilities only in Chap. 2, and mainly only from the standpoint of direct application of the probabilities in vibrational kinetics. We treat a fundamental set of problems of vibrational kinetics in Chaps. 3—5. Relaxation processes in molecular lasers based on vibrational-rotational transitions are analyzed in Chap. 6.

2. VIBRATIONAL EXCITATION OF MOLECULES IN COLLISIONS

In concrete calculations of vibrational relaxation in gases, one must know the probabilities of the different elementary processes. We briefly treat below the methods of calculating probabilities of vibrational transitions in molecular collisions. Here we pay most attention to results directly bearing on problems of molecular kinetics. In analyzing vibrational excitation in molecular collisions (which belongs to the many-body type of problems), the region of interest is that of small energies of translational motion (below 10 eV). Here the condition of the adiabatic approximation is usually satisfied (with respect to electronic and translational motion). This condition can be written in the form

$$\tau_{coll} \gg \tau_{el} \sim \hbar/\Delta E_{el}. \tag{2.1}$$

Moreover, most molecules satisfy the adiabaticity condition with respect to electronic and vibrational motion:

$$\tau_{vib} \sim \hbar/\Delta E_{vib} \gg \tau_{el}. \tag{2.2}$$

In (2.1) and (2.2), $\tau_{coll} \sim a/v$ is the characteristic collision time, where a is the effective radius of action of the intermolecular forces, and v is the mean velocity of the molecules; τ_{el} and τ_{vib} are the characteristic times for electronic and vibrational motion; and ΔE_{el} and ΔE_{vib} are the energies of the electronic and vibrational transitions.

In the adiabatic approximation of (2.1) and (2.2), we

need not account in explicit form for electronic transitions and electronic motion (it is always taken into account implicitly in the interatomic and intermolecular interaction potentials). We need to treat only the translational, vibrational, and rotational degrees of freedom. Here molecular collisions are represented by models of collisions between rotating harmonic (or anharmonic) oscillators. They usually satisfy well the conditions:

$$\tau_{coll} \gg \tau_{vib}, \tag{2.3}$$

$$\tau_{coll} < \tau_{rot} \sim \hbar/\Delta E_{rot}; \tag{2.4}$$

Here τ_{rot} is the characteristic time for rotational motion with the transition energy ΔE_{rot}. Simultaneous fulfillment of these conditions implies that the probability of exciting rotational levels is considerably greater than the probability of vibrational excitation. Hence, we can assume in studying vibrational relaxation that equilibrium has already been established between the translational and rotational degrees of freedom.

The exceptions to rule (2.3) include the case of collision of a light with a heavy molecule (e.g., I_2—He, where ΔE_{vib} is small, but v is large) and the case of transition between upper vibrational levels, where ΔE_{vib} is small. Condition (2.4) is not satisfied by molecules of hydrogen and its heavy isotopes, and also by high rotational levels (ΔE_{rot} is large). The adiabaticity condition (2.2) may not be satisfied in collision of molecules in degenerate electronic states. Then energy can be exchanged between vibrational and translational degrees of freedom by electronic-vibrational resonance non-adiabatic transition. The theory of such transitions is only beginning to be developed. The results are reviewed in[19,21,22]; we should especially point out calculations of vibrational excitation probabilities of the molecules NO,[23] N_2 and O_2.[24]

With account taken of the stated restrictions, a method has been developed within the framework of the conditions (2.1)—(2.4) of calculating the probabilities of vibrational transitions in molecular collisions (see[11,15,17,18,20,22] and also[25-31]). In many cases, it gives qualitatively correctly the relation of the vibrational-excitation probabilities to the velocity of the particles. We only note that attraction effects due to long-range forces can play an important role in collisions of highly polar molecules, and also in resonance processes having small overall changes in vibrational energy ($\omega_{mn} \approx 0$). In many ways, then they determine the value of the transition probability and its temperature dependence.[20,32,34] Molecules with greatly differing nuclear masses also constitute a special case. For the latter, transformation of rotational into vibrational energy plays an important role, as well as that of translational into vibrational. Calculations of probabilities for such molecules must take account of this effect.[21,22,35-41]

We shall give the expressions that are currently used for practical calculations of vibrational-transition probabilities. For diatomic molecules, the probability P_{mn} of transition between the vibrational levels m and n (as calculated per collision) is:[11,15,22,42]

$$P_{mn} = \bar{V}_{mn}^2 Z_0^{-1} \frac{0.163 \mu T}{\alpha^2} f(\gamma_{mn}) \exp\left(\frac{\varepsilon}{T}\right) \exp\left(-\frac{\Delta E_{nm}}{2T}\right),$$

$$f(\gamma_{mn}) \approx \begin{cases} 8.2\gamma_{mn}^{7/3} \exp\left(-3\gamma_{mn}^{2/3}\right) \text{ when } \gamma_{mn} \gg 20, & (2.6a) \\ \frac{1}{2}\left[3-\exp\left(-\frac{2}{3}\gamma_{mn}\right)\right]\exp\left(-\frac{2}{3}\gamma_{mn}\right) \text{ if } \gamma_{mn} < 20, & (2.6b) \end{cases}$$

$$\gamma_{mn} = \left(\frac{0.32}{\alpha}\right)\left(\frac{\mu}{T}\right)^{1/2}|\Delta E_{nm}|; \qquad (2.7)$$

Here μ is the reduced mass of the colliding particles (in atomic units), α is the constant in the exponential intermolecular interaction potential $\sim e^{-\alpha r}$ (in Å^{-1}); ΔE_{nm} is the change in the vibrational energy in the transition (in °K), T is the temperature of the gas (in °K). The factor $\exp(-\Delta E_{nm}/2T)$ accounts for the change in relative velocity of the particles upon collision, and it fixes the Boltzmann factor $\exp(-\Delta E_{nm}/T)$ that relates the probabilities of forward and backward transitions between the states m and n. The factor $\exp(\epsilon/T)$ takes approximate account of attraction between the colliding molecules. Here ϵ (in °K) is the depth of the well in the intermolecular potential with account taken of this attraction. The function $f(\gamma_{mn})$ is called the <u>adiabatic factor</u>; when $\gamma_{mn} \gtrsim 20$ (large energy defects ΔE_{mn}, and relatively low temperatures), $f(\gamma_{mn}) \ll 1$, and the fundamental temperature-dependence of the probability is $\ln P_{mn} \sim T^{-1/3}$. In the other limiting case, $f(\gamma_{mn}) \approx 1$, and $P_{mn} \sim T$. Z_0 in (2.5) is an orientation factor. $Z_0 \sim 3$—30 for diatomic molecules. An expression for Z_0 for homonuclear molecules is given in[41]. The factor $\overline{V}_{mn}^2$ in (2.5) is the mean square value of the matrix element for the transition $m \to n$. When the molecule AB collides with the particle C, one must average over $\lambda_A = M_A/(M_A + M_B)$ and $\lambda_B = M_B/(M_A + M_B)$ (where M_A and M_B are the nuclear masses). This corresponds to taking account of the collisions AB—C and C—AB:

$$\overline{V}_{mn}^2 = (1/2)[V_{mn}^2(\lambda_A) + V_{mn}^2(\lambda_B)].$$

V_{mn}^{har} has been calculated in[27] for a repulsive potential $\sim e^{-\alpha r}$ and the wave functions of a harmonic oscillator.

For transitions $m \to m - k$ (a jump by k quanta), under the condition $\lambda\alpha/(E_1M)^{1/2} \ll 1$, which is usually satisfied,

$$\begin{aligned} (V_{m, m-k}^{har})^2 &\approx [m!/(m-k)!\, k!]\,(V_{k0}^{har})^2, \\ (V_{k0}^{har})^2 &= (k!)^{-1}\,(24.2\lambda^2\alpha^2/E_1M)^k; \end{aligned} \qquad (2.8)$$

Here E_1 and M are respectively the energy of a vibrational quantum of the oscillator (in °K) and its reduced mass (in atomic units). One can also use the wave functions of the anharmonic Morse oscillator in calculating the matrix elements of the transition (see[31]). Calculating V_{mn} from the wave functions of both harmonic and anharmonic oscillators gives approximately the same results for one-quantum transitions below lower levels. Hence, it is convenient to use Eq. (2.8) here owing to its simplicity. However, the difference between V_{mn}^{har} and V_{mn}^{Morse} can be considerable for many-quantum transitions, and also for transitions between upper levels. Sometimes people take approximate account of the effect of anharmonicity on the values of the matrix elements by using Eq. (2.8) for a harmonic oscillator, but with E_1 replaced by the value of a vibrational quantum for the upper levels in question.

Thus, according to (2.5) and (2.8), we have for one-quantum transitions in a harmonic oscillator:

$$P_{n+1, n} = (n + 1)P_{1,0}. \qquad (2.9)$$

For an anharmonic oscillator, the relation of the probabilities to the level number is more complex. Since the most substantial energy-dependence in (2.5) and (2.6) is given by the exponential factors, sometimes the only account that people take of anharmonic effects in making estimates is in calculating these factors. Then

$$P_{n+1,n} \approx (n + 1)P_{1,0} \exp(\delta n), \qquad (2.10)$$

where

$$\delta = \begin{cases} 4\gamma_0^{2/3}(\Delta E/E_1)-(\Delta E/T) \text{ when } \gamma_{n+1,\,n} \gg 20, \\ (4/3)(\Delta E/E_1)-(\Delta E/T) \text{ when } \gamma_{n+1,\,n} < 20, \end{cases} \qquad (2.11)$$

$$\gamma_0 = \left(\frac{0.32}{\alpha}\right)\left(\frac{\mu}{T}\right)^{1/2} E_1$$

When $\gamma_{n+1,n} \geq 20$ in (2.10), we must calculate $P_{1,0}$ by using (2.6a), but (2.6b) when $\gamma_{n+1,n} < 20$. The probabilities of the backward transitions are found by the principle of detailed balancing:

$$P_{n,\,n+1} = P_{n+1,\,n} \exp[-(E_1-2\Delta E_n)/T]. \qquad (2.12)$$

Probabilities of vibrational exchange, both within and between vibrational modes of diatomic or polyatomic molecules, can also be calculated by formulas like (2.5)—(2.8).[26,27,29] Now we must take the energy ΔE_{nm} in (2.5)—(2.8) to be the resultant change in the vibrational energy of the system upon transition from state m to n. Moreover, it is not the square of a single matrix element that will take part in (2.5), but the product of the squares of the matrix elements of the transitions between the initial and final states of the modes that take part in the exchange. For polyatomic molecules, we must take M in (2.8) to be the reduced mass of the oscillator corresponding to the given type of oscillation. The method of calculation and some values of M are given in[29]. The orientation factor Z_0 remains undefined for polyatomic molecules, and people usually use values 3/2—10 for it. The probabilities of one-quantum vibrational exchange for the transition $n + 1 \to n$, $m - 1 \to m$ within a mode depend on the level numbers n and m as follows:

$$Q_{n+1,\,n}^{m-1,\,m} = (n+1)\,mQ_{1\,\,0}^{0\,1} \quad \text{(harmonic oscillator)} \quad (2.13)$$

$$Q_{n+1,\,n}^{m-1,\,m} = (n+1)\,mQ_{1,0}^{01} \exp\left[(m-n-1)\frac{\Delta E}{T}-\frac{4}{3}\gamma_0\frac{\Delta E}{E_1}|m-n-1|\right]$$

$$\text{(anharmonic oscillator)} \quad (2.14)$$

We have derived Eq. (2.14) by using (2.6b), i.e., taking the case $\gamma_0(2\Delta E/E_1)\cdot|m-n-1| < 20$. The probabilities of the backward processes can be derived from the principle of detailed balancing:

$$Q_{n,\,n+1}^{m,\,m-1} = Q_{n+1,\,n}^{m-1,\,m} \exp[-(2\Delta E/T)(m-n-1)]. \qquad (2.15)$$

As we have stated, the method outlined above and Eqs. (2.5)—(2.8) are not applicable for calculating probabilities of vibrational excitation of molecules having atoms of widely varying masses and for the case in which the molecular collisions are not adiabatic (in terms of electronic-vibrational interaction). Probabilities for polyatomic molecules containing hydrogen or deuterium atoms have been calculated in[36], and for the hydrogen halide molecules in[38-41]. Here they used formulas like (2.5)—(2.8), but with the reduced mass μ in the latter replaced by some effective collision mass $\mu_{eff} < \mu$. In[40,41], where good agreement of theory with

experiment was obtained, the influence was also taken into account of molecular-orientation effects and long-range attractive forces. The probabilities of vibrational excitation in non-adiabatic NO—NO, N_2—O, and O_2—O collisions have been calculated in[23,24] and measured in[43,44].

The manner of determining the parameters of the intermolecular interaction potential $V(r)$ has a large effect on the accuracy of the results in calculating the transition probabilities. The various methods of determining the interaction potentials are discussed in the review[45].

We should note that this method of calculating the transition probabilities in molecules having no dipole moment is accurate only with respect to order of magnitude. It can be generally used for polar molecules only with great caution, since the details of accounting for the long-range forces can greatly change the results.[32,33,41] However, in problems of molecular kinetics, often it is not so much the absolute values of the probabilities that prove to be important as the order of magnitude of the ratios of probabilities of different processes. The existing methods of calculation permit us to calculate these ratios with a considerably higher accuracy.

3. EQUATIONS OF VIBRATIONAL KINETICS. RELAXATION OF MOLECULES AS REPRESENTED BY HARMONIC OSCILLATORS

a) The kinetic equations and methods of analyzing them. The pattern of relaxation processes in molecular systems is generally complex. We shall study below a purely vibrational kinetics. That is, we shall assume that we can separate the treatment of vibrational from electronic and rotational excitation. In any case, this is true when conditions (2.1)—(2.4) are satisfied. Vibrational kinetics includes analysis of relaxation processes in ensembles of diatomic molecules (one type of vibrations and tens of vibrational levels), of polyatomic molecules (several types of vibrations and a system of combination levels), and also in various molecular mixtures. In order to characterize the fundamental processes in vibrational systems, we shall write the kinetic equations describing a typical case, vibrational relaxation in a binary gas mixture of the diatomic molecules A and B:

$$\frac{dx_n}{dt} = Z_{AA} \sum_{m \neq n} [P_{mn}(AA) x_m - P_{nm}(AA) x_n]$$

$$+ Z_{AB} \sum_{m \neq n} [P_{mn}(AB) x_m - P_{nm}(AB) x_n]$$

$$+ \frac{Z_{AA}}{N_A} \sum_{i,j,\, m \neq n} [Q_{mn}^{ij}(AA) x_i x_m - Q_{nm}^{ji}(AA) x_j x_n] \qquad (3.1)$$

$$\frac{Z_{AB}}{N_B} \sum_{i,j,\, m \neq n} [Q_{mn}^{ij}(AB) y_i x_m - Q_{nm}^{ji}(AB) y_j x_n] +$$

$$+ \left(\sum_{m > n} A_{mn} x_m - \sum_{m < n} A_{nm} x_n \right) + \left(B_n + \sum_{m \neq n} C_m x_m - C_n x_n \right).$$

Analogously we can write down the system for the molecule B. Equations like (3.1) are balance equations for the populations of the vibrational levels of the molecules. In (3.1), x_n (y_n) is the population of the n-th vibrational level of the molecule A (B), e.g., per unit volume. Z_{AA} and Z_{BB} are the rates of collision of A

molecules with A and B molecules, respectively. N_A and N_B are the concentrations of A and B molecules, and A_{mn} is the probability of the spontaneous radiative transition m → n in molecule A. The first two square brackets in (3.1) describe vibrational-translational exchange (V—T processes) in which A molecules collide with A and B molecules with probabilities (per collision) of $P_{mn}(AA)$ and $P_{mn}(AB)$, respectively. The third bracket characterizes V—V processes, i.e., exchange of quanta between A molecules (with a probability per collision of $Q_{mn}^{ij}(AA)$, which corresponds to transition of the molecules from the levels m and i to the levels n and j). The fourth bracket describes vibrational exchange between different molecules (with a probability per collision) $Q_{mn}^{ij}(AB)$ as the A molecule goes from level m to n and B from level i to j). Finally, the last bracket in (3.1) takes account of positive sources (having a rate of formation B_n) and sinks (with a rate of annihilation C_n) of molecules in the level n, and also of transitions to the level n from other vibrational states of the molecule due to external agents (excitation of levels by electron impact, resonance optical radiation, etc.). Without stopping to justify the equations (see[46,47]), we shall treat the methods of analyzing them. Of course, it is practically impossible in most cases to solve directly kinetic equations like (3.1) without simplifying assumptions. The central point in all vibrational kinetics that permits one to simplify a system like (3.1) and successfully to solve numerous applied problems is to make use of the differences between the characteristic times of various vibrational processes. (In a number of cases in vibrational kinetics, more detailed results have been obtained than, e.g., in atomic kinetics.) Taking account of the "hierarchy" of characteristic times for various processes in simplifying the kinetic equations permits one to get results in treating relaxation that do not depend on refining the cross-section data.

In this chapter we analyze the harmonic-oscillator approximation with account taken of the relations between the times for V—T, V—V, and radiative processes (τ_{VT}, τ_{VV}, τ_r).

We must remember in practical applications of vibrational kinetics that the obtained relationships are not universal, but hold only under definite conditions. Thus, e.g., application of the harmonic oscillator is valid when the vibrational-energy pumping into the system is not excessive, for relatively small deviations from equilibrium, and whenever one is treating the populations of the lower vibrational levels. Since this approximation has been treated in the review literature,[8-16] we shall present below mainly the new results of recent years with a minimum of citation of the information given in[8-16].

b) Vibrational-translational relaxation. One can conveniently study the process of vibrational-translational energy exchange (V—T processes) with the example of vibrational relaxation of molecules that constitute a small admixture in an inert gas. Then we can neglect pure vibrational exchange in Eq. (3.1). Here vibrational relaxation of the diatomic molecules is represented by the model of a harmonic oscillator having a vibrational quantum energy E_1, and is described by the system of equations

$$dx_n/dt = Z\,(P_{n+1,\,n}\,x_{n+1} - P_{n,n+1}x_n + P_{n-1,n}x_{n-1} - P_{n,n-1}x_n),$$
(3.2)

Here we have accounted only for one-quantum transitions. According to (2.5)—(2.7) and (2.8), this is valid when the gas temperature T is not too high. Upon taking account of (2.9) and (2.12), one can derive from (3.2) an equation for the vibrational energy $E_{vib} = E_1 \sum_n nx_n(t)$:[4]

$$dE_{vib}/dt = -(\tau_{VT})^{-1}\,(E_{vib} - E^0_{vib});$$
(3.3)

Here $E^0_{vib} = \exp(-E_1/T)[1 - \exp(-E_1/T)]^{-1}E_1N$ is the equilibrium value of the vibrational energy, N is the number density of the molecules, and

$$\tau_{VT} = \{ZP_{1,0}\,[1 - \exp\,(-E_1/T)]\}^{-1}.$$
(3.4)

The relaxation time τ_{VT} is a quantity that in many cases can be measured directly by experiment (shock tubes, the spectrophone method, the ultraacoustic method, and recently lasers). There are now hundreds of experimental studies on the temperature-dependence of τ_{VT} (a detailed bibliography is given in[11,12,15,48-52]). An analysis of them shows that the temperature-dependence of the vibrational-relaxation time for the overwhelming majority of the studied gases is well described by the Landau-Teller formula

$$\ln\,(\tau_{VT}Z) \sim T^{-1/3}.$$
(3.5)

Based on this, a simple semiempirical relationship was proposed in[52] for the vibrational-relaxation time

$$\ln\,(\tau_{VT}p) = 1.16 \cdot 10^{-3}\mu^{1/2}E_1^{1/3}\,(T^{-1/3} - 0.015\mu^{1/4}) - 18.42;$$
(3.6)

Here τ_{VT} is expressed in seconds, p in atmospheres, T and E_1 in °K, and μ in atomic units. Equation (3.6) is useful for practical calculations of probabilities for non-polar and weakly-polar molecules. However, one should use it cautiously. As we have stated in Chap. 2, deviations from Eqs. (2.5)—(2.8), (this implies deviations also from (3.5) and (3.6)) can arise from a non-adiabatic type of collisions accompanied by electronic-vibrational interaction (NO—NO, N_2—O, O_2—O, and N_2—alkali metal atom collisions). They can also arise if vibrational-rotational transitions contribute substantially to relaxation (hydrogen halides and other molecules containing light nuclei), or if long-range attractive forces play an important role (polar molecules). Figure 1 illustrates the temperature-dependence for the hydrogen halides. Moreover, Eqs. (3.5) and (3.6) also do not describe vibrational relaxation in gases in a temperature range where the duration of collisions proves to be shorter than the period of molecular
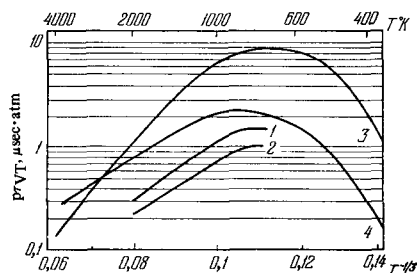

FIG. 1. Temperature-dependence of the vibrational-relaxation time for the collisions: HBr—HBr (1), HI—HI and HCl—HCl (2), DF—DF (3), and HF—HF (4) (from the data of [40,41,53]).

vibrations (non-adiabaticity with respect to vibrational-translational interaction). Typical examples of such gases are mixtures of I_2 and Br_2 with light inert gases. Experimental studies[53-55] have shown that the relaxation time first falls with decreasing temperature (in line with the Landau-Teller theory), it reaches a minimum when $\tau_{coll}/\tau_{vib} \sim 1$, and then it begins to increase. In particular,[55] the adiabaticity factor τ_{coll}/τ_{vib} varied over the range $0.5 \lesssim \tau_{coll}/\tau_{vib} \le 1.8$ in mixtures of Br_2 with He, Ne, Ar, and Xe.

In many cases one needs to know not only the relaxation laws of the total vibrational energy, but also the distribution function of the molecules over the vibrational levels and its time course. They found in[56] (see also[57,58]) a general solution of the system (3.2) (under isothermal conditions), and they established that the form of the Boltzmann distribution was conserved during the relaxation process. Here only the vibrational temperature varied. This property of the system (3.2) of kinetic equations is sometimes called canonical invariance.[59] We note that conservation of a Boltzmann distribution during vibrational relaxation is inherent only in a system of harmonic oscillators.

Many-quantum energy transitions during collisions can play an appreciable role as the gas temperature in the relaxing system increases. In this case, the vibrational-relaxation process is described by the system of equations

$$dx_n/dt = Z \sum_{m \ne n}\,(P_{mn}x_m - P_{nm}x_n),$$
(3.7)

which is usually solved numerically. There is a solution of this type for nitrogen in[60]. In the very interesting special case of high temperatures ($E_1/T \gg 1$) and low probability of vibrational excitation, we can simplify the system (3.7) by transforming from a quantum (discrete) to a classical (continuous) description and obtaining an analytical solution. Here the smallness of the transition probability, which in classical language implies smallness of the energy transferred from the translational to the vibrational degrees of freedom, permits us to transform from the integral-differential equation that replaces (3.7) to a Fokker-Planck type of differential equation:

$$\frac{\partial F(\varepsilon, t)}{\partial t} = \frac{\partial}{\partial \varepsilon}\left[B_\varepsilon\left(\frac{\partial F}{\partial \varepsilon} + \frac{F}{T}\right)\right].$$
(3.8)

$F(\varepsilon, t)$ is the density distribution of molecules in vibrational-energy space at the instant t of time (the distribution function $F(\varepsilon, t)$ is the classical analog of the quantum populations $x_n(t)$), and

$$B_\varepsilon = (1/2)\int\,(\Delta\varepsilon)^2\,W(\varepsilon, \Delta\varepsilon)\,d\,(\Delta\varepsilon),$$

where $W(\varepsilon, \Delta\varepsilon)$ is the number per unit time of those molecular collisions that transfer a molecule from the point ε to the neighborhood $d(\Delta\varepsilon)$ of the point $\varepsilon + \Delta\varepsilon$.

There is a direct derivation of Eqs. (3.8) from the Boltzmann gas-kinetic equation in[61,62] (see also[63]).

We note that Eq. (3.8) has the property of canonical invariance under the condition $B_\varepsilon = B\varepsilon$.[59] Then we can transform Eq. (3.8) to the form (3.3), where

$$\tau_{VT} = T/B.$$
(3.9)

Upon combining Eq. (3.9) with the expression for the

relaxation time (3.4) in the Landau-Teller theory, we can write[64]

$$\tau_{VT} = \exp(-E_1/T) \{Z \sum_{m=0}^{\infty} mP_{0m} [1 - \exp(-E_1/T)]\}^{-1}. \quad (3.10)$$

Comparison of the experimental values of τ_{VT} with the theoretical values calculated by Eqs. (3.4) and (3.10) permits one to determine the temperature range where many-quantum transitions begin to figure. For example, this region begins at 4000–5000° K for oxygen.[64]

c) **Vibrational relaxation in a one-component system of diatomic molecules.** In collisions of diatomic molecules, energy exchange between vibrational degrees of freedom can accompany the V—T processes. Vibrational relaxation in a one-component system is described by Eqs. (3.1) in which the first and third terms on the right-hand side, which account for both V—T and V—V processes, differ from zero. The equations are simplified in a system of harmonic oscillators, and upon taking account of the expressions (2.13) and (2.15) for the probabilities, we can write them in the form:

$$dx_n/dt = ZP_{1,0}\{(n+1)x_{n+1} - [(n+1)e^{-E_1/T} + n]x_n + ne^{-E_1/T}x_{n-1}\}$$
$$+ ZQ_{1,0}^{01}\{(n+1)(1+\bar{\epsilon})x_{n+1} - [(n+1)\bar{\epsilon} + n(1+\bar{\epsilon})]x_n + n\bar{\epsilon}x_{n-1}\},$$
$$(3.11)$$

Here $\bar{\epsilon} = N^{-1} \sum_{n=0}^{\infty} nx_n(t)$ is the mean number of vibrational quanta per molecule at the instant t of time. Since

$$Q_{1,0}^{01} \gg P_{1,0}, \quad (3.12)$$

for adiabatic collisions (the region of not very high temperatures), we can distinguish two stages in the process of vibrational relaxation: a fast stage that proceeds with a relaxation time $\tau_{VV} \sim 1/ZQ_{1,0}^{01}$, and a slow stage with the time $\tau_{VT} \sim 1/ZP_{1,0}$.[65-67] In the first fast stage, a quasi-steady-state Boltzmann distribution is established in the system in a time of the order of τ_{VV}. It has a temperature that is determined at each instant of time by the existing supply of vibrational quanta, and which does not depend on the other conditions. The fundamental elementary event that occurs in the collisions of the oscillators in this stage of the process is resonance exchange of vibrational quanta, with conservation of the total number $\bar{\epsilon}$ of vibrational quanta. (When $t \ll \tau_{VT}$, Eqs. (3.11) imply that $d(\bar{\epsilon}N)/dt = 0$, or $\bar{\epsilon}N$ = const.).

In the second, slow stage, which has the relaxation time τ_{VT}, we need not consider the fast process at all, but interest ourselves only in its result, the quasi-steady-state Boltzmann distribution. In the time interval $\tau_{VV} \ll t < \tau_{VT}$, V—T processes cause this distribution to evolve toward the equilibrium distribution corresponding to the gas temperature T. Creation of a quasi-steady-state Boltzmann distribution by the fast V—V processes makes it possible to simplify considerably the study of the kinetic laws, since we need only one variable (besides the total particle-number density) in order to describe the populations of the vibrational levels: the vibrational temperature. This latter circumstance has been widely applied in analyzing relaxation processes, e.g., behind a shock-wave front in gases[15] or in molecular lasers.[68-72]

One observes a sharp distinction between the discussed two stages in the process of vibrational relaxa-

tion only when $\tau_{VV} \ll \tau_{VT}$. As τ_{VV} and τ_{VT} approach one another, the V—V and V—T processes begin to overlap. That is, they proceed simultaneously. This overlap happens both with increasing temperature and upon diluting the molecular gas with a monatomic gas. A solution of the problem of vibrational relaxation of harmonic oscillators in this case has been found in[73]. We emphasize that the system of equations (3.11) has the property of canonical invariance, regardless of the size of the ratio τ_{VV}/τ_{VT}.

d) **Vibrational relaxation of a system of radiative oscillators.** In addition to the V—T and V—V processes arising from collisions of molecules, spontaneous radiative transitions can exert a considerable influence in a number of cases on the populations and the total supply of vibrational energy. Thus, it is important to take account of radiative effects in analyzing the operation of a number of lasers (e.g., lasers based on CO, HCl, and HF molecules) in which the pressures are relatively low (~ 1 Torr) and narrow tubes are used (diameters of the order of a centimeter). In these cases, reabsorption of the radiation can prove to be insubstantial, and the radiative probabilities can exceed the probabilities ZP_{mn} or $Z'Q_{mn}^{ij}$ of the collision processes. Radiative effects can also be substantial in vibrational relaxation in an expanding gas stream and in the wake of an object flying through the atmosphere. The effect of radiative processes on vibrational relaxation and on the intensity of infrared emission of the upper atmosphere is especially important[74] (at heights $\gtrsim 100$ km, NO molecules are one of the fundamental constituents that emit from vibrational-rotational transitions).

The populations of the levels for radiative oscillators are determined by Eqs. (3.11) with the following terms added to the right-hand sides:

$$(n+1)A_{1,0}x_{n+1} - nA_{1,0}x_n,$$

The latter terms describe radiative transitions (here we have taken into account the relationship $A_{n+1,n} = (n+1)A_{1,0}$, which holds for harmonic oscillators).

In the steady state ($dx_n/dt = 0$ for all n), which can occur under the condition T = const., the solution of this system is a Boltzmann distribution, whatever the relationship between the probabilities $Z'Q_{1,0}^{01}$, $ZP_{1,0}$, and $A_{1,0}$. It has the vibrational temperature[74]

$$T_{vib} = E_1 \{(E_1/T) + \ln[1 + (A_{1,0}/ZP_{1,0})]\}^{-1}. \quad (3.13)$$

Here the following equation holds for the vibrational energy E_{vib} instead of (3.3):

$$dE_{vib}/dt = 0 = -[(E_{vib} - E_{vib}^0)/\tau_{VT}] - A_{1,0}E_{vib}.$$

The non-steady-state problem for a system of radiative oscillators was solved in[75], where the distribution function was found under the condition $A_{1,0}Z'Q_{1,0}^{01} \gg ZP_{1,0}$. Its time evolution was found over the time interval $t \ll 1/ZP_{1,0}$ for arbitrary initial distributions. Given an initial Boltzmann distribution in the regions of small ($A_{1,0} \gg Z'Q_{1,0}^{01}$) and large ($A_{1,0} \ll Z'Q_{1,0}^{01}$) gas pressures, it was shown in[75] that the distribution function during the evolution process remains Boltzmann, with a temperature that varies in time. In the intermediate pressure range ($A_{1,0} \approx Z'Q_{1,0}^{01}$), the distribution is distorted, but the deviation from a quasi-

steady-state Boltzmann distribution is small.

e) Vibrational relaxation in a system of polyatomic molecules. One can also use the harmonic-oscillator approximation in analyzing relaxation in such a complex object as a system of polyatomic molecules. Here the treatment is considerably simplified by introducing for each type i of normal vibration a vibrational temperature T_i that characterizes the supply of vibrational energy in that mode.[68] For example, using this method has made possible an all-sided description of the kinetics of processes in lasers based on polyatomic molecules, including the well-known CO_2 laser.[68-72] The possibility of introducing the temperatures T_i arises from the fact that, just as for diatomic molecules, the exchange processes of vibrational quanta within each type of vibration occur in a time τ_{VV} much shorter than the times τ_{VT} for transfer of energy to the translational degrees of freedom or the times $\tau_{VV'}$ for exchange between different vibrational modes. Generally the temperatures T_i will differ from one another and from the gas temperature T, and they must be determined by a system of equations for the energies of the vibrational modes.

Let us examine the fundamental vibrational-relaxation equations in a system of polyatomic molecules, using the example of a binary mixture of the polyatomic gases A and B. Let the molecules A and B have L vibrational modes in all. Let us select in A some arbitrary mode ζ having a quantum energy $E_1(\zeta)$ and a vibrational temperature T_ζ. We shall be interested in the variation in the total supply $\bar{\epsilon}_\zeta$ of vibrational quanta of the given vibration (including, in particular, the combination levels as well). In this case

$$\bar{\epsilon}_\zeta = r_\zeta \exp\left[-\frac{E_1(\zeta)}{T_\zeta}\right] \left\{1 - \exp\left[-\frac{E_1(\zeta)}{T_\zeta}\right]\right\}^{-1},$$

where r_ζ is the degeneracy of the mode ζ.

The overall process that characterizes one of the possible channels of relaxation of $\bar{\epsilon}_\zeta$ upon collision of A and B can be written in the form

$$(A + B)_1 \to (A + B)_2 (+m_i, -m_j), \quad i = 1 \text{ to } p; \quad j = p + 1 \text{ to } L.$$

This notation implies that the molecules have transformed from some initial vibrational state 1 to the final state 2. Here the modes that are denoted by the index i (running from 1 to p) have undergone transitions to m_i levels below, and the remaining levels (denoted by j running from p + 1 to L) to m_j levels above. Modes belonging to the different molecules can exist within both the groups of modes i and j. For example, let a mode ζ of interest in molecule A belong to group i. That is, collision has caused a transition in it by m_ζ quanta downward. The equation describing the variation in $\bar{\epsilon}_\zeta$ in this relaxation channel has the form[78] 1)

$$\frac{d\bar{\epsilon}_\zeta}{dt} = Z_{AB} P(1 \to 2) m_\zeta \left\{ \prod_{i=1}^{p} [\bar{\epsilon}_i^0 + \rho_i(\bar{\epsilon}_i - \bar{\epsilon}_i^0)]^{m_i} \prod_{j=p+1}^{L} (\bar{\epsilon}_j/\rho_j)^{m_j} \right.$$
$$\left. - \prod_{i=1}^{p} (\bar{\epsilon}_i)^{m_i} \prod_{j=p+1}^{L} \left[\frac{\bar{\epsilon}_j^0}{\rho_j} + (\bar{\epsilon}_j - \bar{\epsilon}^0)\right]^{m_j} \right\};$$

$$(3.14)$$

_____

1)In [77] they also derived an expression like (3.14), but they treated incorrectly the case of degenerate oscillators.

Here $\rho_i = \exp(-E_1(i)/T)$, $\bar{\epsilon}_i^0$ is the equilibrium value of $\bar{\epsilon}_i$ at the gas temperature T, $P(1 \to 2)$ is the probability per collision of the process 1—2, as calculated without accounting for degeneracy; it corresponds to transition between the lowest levels of molecules A and B. That is, a transition occurs in the modes i from the levels m_i to the zero level, while it occurs in the modes j from the zero level to the levels m_j. In order to find the overall rate $(d\bar{\epsilon}_\zeta/dt)_{overall}$, we must deal with the other possible channels of relaxation, and sum expressions of the type of (3.14).

We note that in practice one can often restrict the treatment to a relatively small number of relaxation channels, and select for analysis only those whose corresponding transition probabilities are greatest. For example, for the CO_2 molecule, the energy of the asymmetric mode (0, 0, v₃) mainly relaxes by two channels:

$$(v_1, v_2, v_3) \to (v_1, v_2+3, v_3-1), \quad (3.15a)$$

$$(v_1, v_2, v_3) \to (v_1+1, v_2+1, v_3-1); \quad (3.15b)$$

Here v_i is the number of the vibrational level of the ith mode.

Equation (3.14) is the most general form of the relaxation equations for the vibrational energy in a mixture of harmonic oscillators. It describes relaxation upon collision of both different and identical molecules, as well as relaxation upon collision of polyatomic molecules with structureless particles. For collisions of identical molecules, we must multiply the probability $P(1 \to 2)$ in (3.14) by

$$\frac{1}{2} \sum_{i=1}^{p} m_i \sum_{j=p+1}^{L} m_j - 1$$

where L is the number of modes in the molecule. In the special case in which m_i, $m_j \leq 1$, Eq. (3.14) corresponds to relaxation involving one-quantum transitions.[78] When L = 1, (3.14) goes over into Eq. (3.3), which describes relaxation in diatomic molecules, and when L = 2, it becomes the relaxation equation for a binary mixture of diatomic molecules (see Sec. e in Chap. 4).

We note that in the general case, the equation (3.14) for the energy of a vibrational mode is non-linear, and it was derived only under the assumption that $\tau_{VV} \ll \tau_{VV_i}$ or τ_{VT} for all the modes, without concretizing the relations between $\tau_{VV'}$ and τ_{VT}. In the special case in which $\tau_{VV'} \gg \tau_{VT}$ and relaxation occurs only by one-quantum V—T processes, a system like (3.14) breaks down into the independent linear equations (3.3) that describe vibrational relaxation of each mode separately. The other limiting case $(\tau_{VV'} \ll \tau_{VT})$ will be analyzed in detail in Chap. 4.

4. NON-RESONANCE VIBRATIONAL EXCHANGE. THE ANHARMONIC OSCILLATOR. BINARY MIXTURES

a) Vibrational-translational relaxation in a system of anharmonic oscillators. It is especially important to take account of anharmonic vibrations (and consequently

also of processes of non-resonance vibrational ex-
change) in analyzing relaxation under substantially non-
equilibrium conditions in which the supply of vibrational
energy considerably exceeds the equilibrium value for
the gas temperature T. Such conditions are realized in
many experiments (electric discharges, chemical reac-
tions, outflow of gases from apertures and nozzles).
They are of practical interest in studying the working
mechanisms of certain molecular lasers (the CO laser
and chemical lasers based on hydrogen halides).

The variation in the overall supply of vibrational en-
ergy in a system of anharmonic oscillators is mainly
due to V—T processes. We can study these processes
with the example of vibrational relaxation of anharmonic
oscillators that constitute a small admixture in an inert
gas. Then Eqs. (3.2) hold for the one-quantum transi-
tions. However, the probabilities $P_{n+1,n}$ depend here in
a more complex way on n than in the harmonic-oscilla-
tor model (see (2.10)—(2.12)). Equation (3.2) has been
solved numerically in[79,80] with probabilities of the
type of (2.10) that take account of anharmonicity. It was
shown in[79] that if the mean vibrational energy per
molecule at the starting time is smaller than the
equilibrium value, then the distribution function deviates
from the Boltzmann distribution, exceeding it in the
upper levels (in the opposite case, the populations prove
to be less than the Boltzmann values[80]). This distinc-
tion is explained by the fact that the probability of the
transition n + 1 → n for an anharmonic oscillator is
larger than for a harmonic oscillator.

The deviations during relaxation of the true distribu-
tion from the Boltzmann distribution are small in the
lower levels (where the vibrational energy is mainly
concentrated). This fact permits a simplified estimate
of the effect of anharmonicity on the relaxation time of
the vibrational energy by taking account only of $P_{n+1,n}$
and $P_{n,n+1}$ in the expressions for the probabilities.
If we take these probabilities in the form of (2.10), then
we have the following equation for the rate of change of
the vibrational energy E_{vib}:

$$\frac{dE_{vib}}{dt} = -\frac{E_{vib}-E^0_{vib}}{\tau^{har}_{VT}}, \quad \tau^{anh}_{VT} = \tau^{har}_{VT}\left\{\frac{1-\exp[-(E_1/T_{vib})+\delta]}{1-\exp(-E_1/T_{vib})}\right\}^2, (4.1)$$

Here τ^{har}_{VT} is defined by Eq. (3.4). We see from (4.1)
that the difference between τ^{anh}_{VT} and τ^{har}_{VT} increases
with increasing T_{vib}. Here the effect of anharmonicity
will be stronger in deactivation processes in which T_{vib}
approaches T from above. However, Eq. (4.1) describes
best of all the process of excitation of vibrations behind
the front of not too strong a shock wave, where it has
been confirmed experimentally.[81] This formula also
gives the necessary correction that one must introduce
in calculating the probability $P_{1,0}$ from experimental
values of τ_{VT}.

b) Vibrational exchange in a system of anharmonic
oscillators. Under non-equilibrium conditions, non-
resonance processes in a system of anharmonic oscilla-
tors exert a substantial influence on shaping the popula-
tion distribution function and on the rate of relaxation of
the vibrational energy. In analyzing the vibrational re-
laxation described by a system of equations of the type
of (3.1), we must take into account here both the unequal
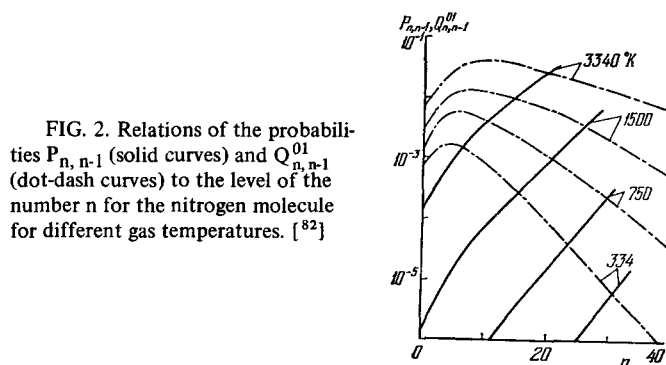spacing of the levels and the non-linear nature of the

FIG. 2. Relations of the probabili-
ties $P_{n,n-1}$ (solid curves) and $Q^{01}_{n,n-1}$
(dot-dash curves) to the level of the
number n for the nitrogen molecule
for different gas temperatures. [82]

relation of the probabilities $P_{n+1,n}$ and $Q^{m-1,m}_{n+1,n}$ to the
level number. For harmonic oscillators, the inequality
(3.12) and the relationships (2.9) and (2.13) imply that

$$Q^{m-1,m}_{n+1,n} \gg P_{n+1,n} \quad \text{for all } n \text{ and } m \qquad (4.2)$$

Owing to the non-equidistant spacing of the vibrational
levels for anharmonic oscillators, the probabilities
$P_{n+1,n}$ increase more rapidly than $(n+1)P_{1,0}$, while the
probabilities $Q^{m-1}_{n+1,n}$ increase more slowly than
$m(n+1)Q^{01}_{1,0}$. (For large $n > m + 1$, the probabilities
$Q^{m-1,m}_{n+1,n}$ even begin to fall with increasing n, owing to
increase in the resonance defect.) Hence, the upper
levels do not satisfy the inequality (4.2). Since the popu-
lations of the highly excited levels having numbers n + 1
are usually small in comparison with the populations of
the lower states, the exchange processes that occur with
probabilities $Q^{m-1,m}_{n+1,n}$ and $Q^{m,m-1}_{n,n+1}$ (with m ≪ n) play
the major role for the former. Hence, in elucidating the
roles of V—T and V—V processes for different levels,
it is of interest to compare the probabilities $P_{n+1,n}$ and
$Q^{01}_{n+1,n}$ (m = 1, or exchange with the lowest quantum
level). Figure 2 shows the dependence of these proba-
bilities on the level number n, as calculated for the N_2
molecule at different gas temperatures. We see that
$Q^{01}_{n+1,n} \gg P_{n+1,n}$ for the lower levels (for small n),
just as for harmonic oscillators. However, the opposite
situation holds for the upper levels. Thus, it seems
impossible to separate the V—T and V—V processes
completely (for all levels) for a one-component system
of anharmonic oscillators. However, one can make such
a separation for individual groups of levels. Thus, if we
select the group of lower levels for which vibrational-
exchange processes proceed considerably faster than
the V—T processes, we can substantially simplify the
relaxation analysis. We note that radiative transitions
can also exert an effect on the populations for radiating
molecules. However, even here, the lower levels will
obey the condition $ZQ^{01}_{n+1,n} \gg A_{n+1,n}$ when the pressure
is not too small. For these levels, we can represent the
system of equations describing the fast process of ex-
change of vibrational quanta, with (2.15) taken into ac-
count, in the form

$$\frac{dx_n}{dt} = \frac{Z}{N}\left\{\sum_m Q^{m,m+1}_{n+1,n}\left[x_m x_{n+1} - x_{m+1}x_n\exp\left(-\frac{E_m+E_{n+1}-E_{m+1}-E_n}{T}\right)\right]\right.$$
$$\left. - \sum_m Q^{m,m+1}_{n,n-1}\left[x_m x_n - x_{m+1}x_{n-1}\exp\left(-\frac{E_m+E_n-E_{m+1}-E_{n-1}}{T}\right)\right]\right\}.$$

$$(4.3)$$

The fast V—V process in the system of anharmonic oscillators establishes a quasi-steady-state distribution that makes the right-hand side of (4.3) vanish:

$$x_n = x_0 \exp(-\gamma n) \exp(-E_n/T). \qquad (4.4)$$

This distribution has been derived by Treanor et al.[82]

We note that (4.4) is directly implied by the principle of detailed balancing.[83] When the fluxes of particles that determine the population of any level are equal for the forward and backward transitions, the quantity within each curly bracket in (4.3) vanishes. Hence,

$$\ln\left(\frac{x_n}{x_{n+1}}\right) - \ln\left(\frac{x_m}{x_{m+1}}\right) = \frac{E_{n+1} - E_n}{T} - \frac{E_{m+1} - E_m}{T}.$$

Since this equation holds for any n and m, we get

$$\ln(x_n/x_{n+1}) = \gamma + [(E_{n+1} - E_n)/T],$$

from which (4.4) follows. The parameter γ does not depend on the level number, and we can express it, e.g., in terms of the effective vibrational temperature of the first level $T_1 = E_1/\ln(x_0/x_1)$. Here $\gamma = (E_1/T_1) - (E_1/T)$, and we can write the distribution of (4.4) in the form

$$x_n = x_0 \exp\left(-\frac{nE_1}{T_1} + \frac{nE_1 - E_n}{T}\right) = x_0 \exp\left\{-n\left[\frac{E_1}{T_1} - (n-1)\frac{\Delta E}{T}\right]\right\}. \qquad (4.5)$$

For harmonic oscillators, $\Delta E = 0$, and the distribution of (4.5) is reduced to a Boltzmann distribution with the vibrational temperature T_1. In a system of anharmonic oscillators, the quasi-steady-state distribution that is established by the fast V—V process will no longer be a Boltzmann distribution when $T_1 \neq T$. We can write the Treanor distribution (4.5) in the usual form $x_n = x_0 \exp(-E_n/\Theta_n)$, but with a "vibrational temperature" Θ_n that depends on the level number:

$$\Theta_{n+1} = (E_1 - \Delta En)[(E_1/T_1) - (\Delta E/T)n]^{-1}. \qquad (4.6)$$

Equation (4.5) implies that the greatest deviations from a Boltzmann distribution occurs in the upper levels at large values of T_1 (this amounts to a large supply of vibrational energy), with low temperatures of the translational degrees of freedom, and with molecules having a large anharmonicity ΔE. When $T_1/T > 1$, the upper levels are overpopulated with respect to the Boltzmann distribution.

In addition to the case $T < T_1$, which occurs, e.g., in gas lasers with energy pumped into the vibrational degrees of freedom, there is a large group of phenomena in which $T > T_1$. Thus, e.g., $T > T_1$ while equilibrium is being established behind a wave front in diatomic gases; the process of dissociation of molecules also as a rule occurs under conditions in which $T \geq T_1$. In this case, as we see from Eq. (4.6), the effective temperature Θ_n will decline with increasing level number, and this will deplete the upper levels.

We note that the quasi-steady-state non-Boltzmann distribution of (4.4) and (4.5) does not depend on the transition probabilities, and is rather general in nature. It can be derived from the principles of statistical physics without a knowledge of the concrete mechanism of the V—V processes. For example, it can be derived from the Boltzmann principle[82] or by using the grand canonical ensemble of Gibbs.[83] An important circumstance here is that the total number of vibrational quanta is conserved in V—V processes. In the case in which

V—V processes occur alone, the number of vibrational quanta is conserved for any form of the distribution function,[84] but the distribution will always acquire the form of (4.4) after the fast exchange stage has been completed.

c) **Joint treatment of processes of exchange with radiative and V—T processes.** If V—V processes are dominant in the lower levels of an anharmonic oscillator and the Treanor distribution of (4.4) holds, then the probabilities of V—T processes for the upper levels always exceed substantially the probabilities of exchange (see Fig. 2). Consequently, a distribution is established here whose vibrational temperature in terms of the relative populations of these levels is equal to the gas temperature. Both V—V and V—T processes are essential in the intermediate levels, as well as radiative processes in a number of cases. It is precisely the intermediate region that proves important for a number of lasers. The population distribution with V—V, V—T, and radiative processes taken into account is determined by the system of equations

$$dx_n/dt =$$
$$= (Z/N)\sum_m (Q_{n+1,n}^{m,m+1} x_m x_{n+1} - Q_{n,n+1}^{m+1,m} x_{m+1} x_n + Q_{n-1,n}^{m+1,m} x_{m+1} x_{n-1} - Q_{n,n-1}^{m,m+1} x_m x_n)$$
$$+ Z(P_{n+1,n} x_{n+1} - P_{n,n+1} x_n - P_{n,n-1} x_n + P_{n-1,n} x_{n-1}) +$$
$$+ A_{n+1,n} x_{n+1} - A_{n,n-1} x_n. \qquad (4.7)$$

One must use numerical methods to solve the system (4.7) exactly.[85,86] However, here also an analysis of the characteristic times of the different processes permits one to simplify the problem considerably and to find an approximate analytical solution.[87-90] The various characteristic times in (4.7) include the time τ_{vib}^*, which is determined by the "bottleneck" of the system where the probability that determines the flux of molecules from one level to another is smallest. For nonradiative molecules, the bottleneck corresponds to the level n* for which the total transition probability $\sim Q_{n^*,n^*-1}^{01} + P_{n^*,n^*-1}$ is a minimum. That is, $Q_{n^*,n^*-1}^{01} \approx P_{n^*,n^*-1}$. In this case the relaxation time is

$$\tau_{\text{vib}}^* \sim 1/ZP_{n^*,n^*-1}. \qquad (4.8)$$

The characteristic time $\tau_E \approx E_{\text{vib}} |dE_{\text{vib}}/dt|^{-1}$ for relaxation of the vibrational energy is usually determined by the probabilities of V—T transitions in the lower levels where this energy is mainly concentrated. $P_{n,n-1} \approx nP_{1,0}$ for these levels, and this means that[2]

$$\tau_E \sim 1/ZP_{1,0}.$$

Since $P_{1,0} \ll P_{n^*,n^*-1}$ for an anharmonic oscillator, $\tau_{\text{vib}}^* \ll \tau_E$. The characteristic time for variation of the gas temperature $\tau_T \approx T |dT/dt|^{-1}$ also usually obeys the inequality $\tau_{\text{vib}}^* \ll \tau_T$. After a time $\sim \tau_{\text{vib}}^*$ has elapsed, the system acquires a distribution of the molecules over the levels that is mainly determined by the relations between the probabilities $Q_{n+1,n}^{m,m+1}$, $P_{n+1,n}$, and $A_{n+1,n}$, as well as by the current values of the gas temperature and the vibrational energy. In the time interval τ_{vib}^*

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[2]For a harmonic oscillator τ_E coincides with τ_{VT} (see (3.4)).
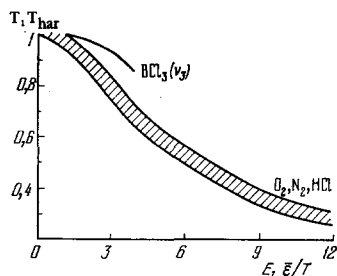
FIG. 3. Dependence of the ratio T_1/T_{har} to the parameter $E_1\bar{\epsilon}/T$ for various molecules ($E_1\bar{\epsilon}$ is expressed in °K; from the data of [89]).

$< t < \tau_E$, τ_T, we can get an approximate solution of the system (4.8) by expanding in a power series in (τ^*_{vib}/τ_E) and (τ^*_{vib}/τ_T):

$$x_n(N, T, E_{vib}, dT/dt, dE_{vib}/dt) \approx$$

$$\approx x^0_n(N, T, E_{vib}) + \delta x^1_n(N, T, E_{vib}, dT/dt, dE_{vib}/dt) + \dots,$$

or in a first approximation

$$x_n = x^0_n(1 + \chi_n). \qquad (4.9)$$

In the zero-order approximation, we get a system of algebraic equations for x^0_n. Further simplification of the system (4.7) involves linearizing it. This is made possible by the weak dependence of sums like $\sum_m Q^{m,m+1}_{n+1,n} x_m$ on the type of distribution. Since exchange with the lower quantum levels is most significant, terms with small m for which x^0_m is well described by the Treanor distribution (4.5) play the major role in these sums. In a number of cases, one can even use the Boltzmann distribution of a harmonic oscillator having the temperature T_{har} and the same supply of vibrational energy as the anharmonic model. We can find x^0_n from the linear system of algebraic equations found in this way:[87-89]

$$x^0_n = x^{Tr}_n \prod_{i=0}^{n} \varphi_i, \qquad (4.10)$$

where x^{Tr}_n is the Treanor distribution of (4.5). The functions φ_i account for the effect of radiative and V—T processes. We have for φ_i:

$$\varphi_{i+1} \approx \frac{\beta Q^{01}_{i+1, i} + P_{i+1, i} \exp[(E_1/T_1) - (E_1/T)]}{\beta Q^{01}_{i+1, i} + P_{i+1, i} + (A_{i+1, i}/Z)}, \qquad (4.11)$$

$$\beta = \left[1 - \exp\left(-\frac{E_1}{T_{har}}\right)\right] \left\{1 - \exp\left[-\frac{E_1}{T_{har}}\left(1 - \frac{\gamma_0 T_{har}}{3D}\right)\right]\right\}^{-2}, \qquad (4.12)$$

Here $D \approx E^2_1/4\Delta E$ is the dissociation energy of the molecule (in °K), and γ_0 is determined from (2.11). The coefficient β in (4.11) effectively accounts for the contribution that all the remaining excited levels besides the first make to the probability of the transition $i + 1 \to i$ occurring by vibrational exchange. We note that at low T ($\sim 300°$K) and with large supplies of vibrational energy (with $T_{har} \sim E_1$), the temperature T_{har} can differ substantially from T_1, owing to pumping of vibrational energy into the upper levels. (According to (4.5) and (4.6), the upper levels are overpopulated when $T_1 > T$.) Since the distributions (4.5) and (4.10) are very sensitive to T_1, this fact must be taken into account. Figure 3 shows the relation of T_1/T_{har} to the parameter $E_1\bar{\epsilon}/T$, as calculated for certain molecules.[89] We have the following equation instead of (4.6) for the vibrational temperature Θ_{n+1} in the case of (4.10):

$$\Theta_{n+1} = (E_1 - \Delta E \cdot n) \left(\frac{E_1}{T_1} - \frac{\Delta E}{T} n - \frac{1}{n+1} \sum_{i=0}^{n+1} \ln \varphi_i\right)^{-1}. \qquad (4.13)$$

We can represent Eqs. (4.10) and (4.11) approximately in a simple analytical form by dividing the whole system of levels into separate groups for which some given mechanism dominates the population. We can use concrete expressions like (2.5) here for the transition probabilities. Thus, for the lower levels in which $n < n^*$, $\varphi \approx 1$, and as we should expect, (4.10) transforms into the Treanor distribution (4.5). In the higher levels where $n > n^{**}$,

$$\varphi_{i+1} \approx \exp\left[\left(\frac{E_1}{T_1}\right) - \left(\frac{E_1}{T}\right)\right];$$

$$x^{(0)}_{n+1} \approx C \exp\left[n^{**}E_1\left(\frac{1}{T} - \frac{1}{T_1}\right)\right] \exp\left(-\frac{E_{n+1}}{T}\right). \qquad (4.14)$$

The distribution of (4.14) corresponds to a Boltzmann distribution with a certain effective number of particles. For a non-radiative oscillator,

$$C = (\beta A)^{n^{**}-n^*} \exp\left[-\left(\frac{4}{3}\right)\gamma_0\left(\frac{\Delta E}{E_1}\right)(n^{**} - n^*)(n^{**} + n^* + 1)\right],$$

$$A = \left(\frac{24.4\,\alpha^2}{ME_1}\right) \exp\left[\left(\frac{E_1}{2T}\right) - \left(\frac{2}{3}\right)\gamma_0\right]. \qquad (4.15)$$

The boundary levels n^* and n^{**} are determined by the relations between the probabilities. For non-radiative molecules in the frequently-encountered cases that satisfy the inequality

$$\gamma_0\left(\frac{2\Delta E}{E_1}\right)j < 20, \quad \gamma_0\left[1 - \left(\frac{2\Delta E}{E_1}\right)j\right] < 20 \text{ for } j = n^*, n^{**},$$

one can find analytical expressions for n^* and n^{**}:

$$n^* \approx \frac{3}{8}\frac{\ln(\beta A)}{\gamma_0}\frac{E_1}{\Delta E}, \quad n^{**} \approx n^* + \frac{D}{\gamma_0}\left(\frac{1}{T} - \frac{1}{T_1}\right). \qquad (4.16)$$

One can also get expressions for C, n^{**}, and the distribution over the intermediate levels under other conditions: when $T < T_1$ for a molecular gas partially diluted with an inert gas, and for systems of radiative oscillators.[89]

A concrete calculation of the distributions for an entire system of levels has been performed in[87-89] by Eqs. (4.10)—(4.12), and by direct solution on computers of a system like (4.7) in[85,86,91,95a]. Figure 4 shows some of the data from the calculations. In Fig. 4b and hereinafter in the text, T_{n+1} is the "vibrational tem-
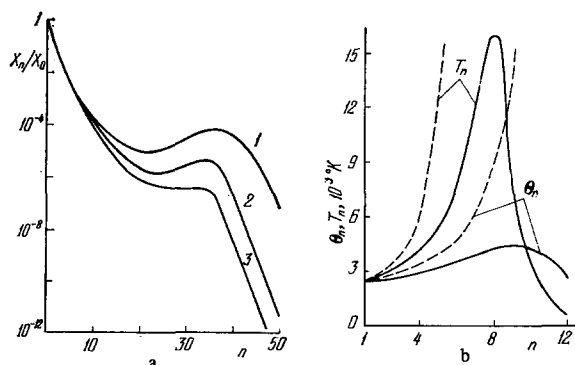

FIG. 4. a) Population distribution functions over the vibrational levels in a one-component N_2 gas under non-equilibrium conditions: T_1 = 3000°K, T = 800°(1), 900° (2), 1000°K (3); [85] b) relation of the effective temperatures Θ_n and T_n to the level number n for HI in a mixture 0.5 Torr HI + 5 Torr N_2 + 5 Torr He under non-equilibrium conditions (T_1 = 2400°K, T = 380°K; [87] the dotted curves are the temperature values for the distributions (4.5) and (4.6)).

perature'' of the levels n + 1 and n as determined by the relationship $T_{n+1} = (E_{n+1} - E_n) \ln^{-1} (x_n/x_{n+1})$.

The approximate analytical solution of the system (4.7) treated above for times $t > \tau^*_{vib}$ is based on introducing the quasi-equilibrium distribution $x^0_n(N, T_1, T)$. Apart from the overall density of molecules, the latter depends only on the two parameters T_1 and T. Solution of (4.7) in the next approximation makes it possible to account for the effect on the distribution of the rate dT/dt.[86,89] The numerical calculation of the system (4.7) performed in[86] under the above-stated physical assumptions (but without linearizing the equations) showed rapid convergence of the initial approximations to the exact solution.

A somewhat different approach to finding the distribution function x_n of the molecules over the vibrational levels in a one-component system of anharmonic oscillators was used in[95b]. There the problem was solved analytically in the classical approximation, i.e., under the assumption of a continuous energy spectrum of vibrations. The previous treatment was limited to accounting only for one-quantum energy transitions during exchange. For an anharmonic oscillator, the vibrational-energy difference $\Delta E_{n,n-1} = E_n - E_{n-1}$ declines with increasing level number. Hence, a level $n \approx E_1/4\Delta E$ will show the two-quantum resonance $\Delta E_{n+1,n} + \Delta E_{n,n-1} \approx E_1$. The level $n \approx E_1/3\Delta E$ will show the three-quantum resonance $\Delta E_{n+2,n+1} + \Delta E_{n+1,n} + \Delta E_{n,n-1} \approx E_1$. Naturally, the probabilities of two- and many-quantum transitions in exchange with a low quantum level can increase sharply here, and one must generally take them into account. The distribution function has been calculated under these conditions for the steady-state case for the CO molecule in[88]. It was shown there that if the probabilities of two-quantum exchange satisfy the inequality

$$Q^{01}_{n+1,n-1} \gg Q^{01}_{n+2,n} \exp[-(E_1 - 2\Delta E \cdot n)/T_{n+1}],$$

then the ''vibrational temperature'' Θ_{n+1} is determined by Eq. (4.13), but in contrast to (4.11), the functions φ_{n+1} have a more complex form:

$$\varphi_{n+1} = \frac{1}{2Q^\Sigma_{n+1}} \left\{ W_{n+1} + \left[W^2_{n+1} + 4Q^\Sigma_{n+1} Q^{01}_{n+1,n-1} \exp\left(\frac{E_1}{T_1} - \frac{E_1}{T}\right) \right]^{1/2} \right\}, \tag{4.17}$$

where

$$W_{n+1} = Q^{01}_{n+1,n} + P_{n+1,n} \exp[(E_1/T_1) - (E_1/T)], \tag{4.18}$$

$$Q^\Sigma_{n+1} = P_{n+1,n} + Q^{01}_{n+1,n} + Q^{01}_{n+1,n-1}. \tag{4.19}$$

As Eqs. (4.17)–(4.19) imply, whenever we must account for two-quantum exchange processes, the latter can substantially change the distribution function in the region of the level $n \sim E_1/4\Delta E$. However, we must note here the difficulties in reliable calculation of probabilities of two- and many-quantum processes. The results of calculation depend substantially both on the intermolecular interaction radius and on the chosen molecular model (e.g., on using the wave functions of either a Morse oscillator or a harmonic oscillator).

d) **The effect of exchange processes on relaxation of vibrational energy.** The quasi-steady-state distribution of (4.10) and (4.11) that is established in the system of anharmonic oscillators by the first fast stage in a time

$\sim \tau^*_{vib}$ then evolves through the V–T and radiative processes. While the slow process of relaxation of the vibrational energy maintains the form of the distribution of (4.10) and (4.11), the parameter T_1 in it varies, and it approaches a value that corresponds to a state of equilibrium or to some steady state, if we consider radiative processes and pumping. Here the rates of variation of the vibrational energy E_{vib} and the ''temperature'' T_1 can differ considerably from the values obtained for the harmonic-oscillator model.[82] Anharmonicity affects both the probabilities $P_{n+1,n}$ and the distribution function x_{n+1}. We discussed the role of the first of these two factors in Sec. a of this chapter, where we used a Boltzmann distribution. However, when $T_1 > T$, the distribution function can differ greatly from a Boltzmann distribution. Hence the vibrational relaxation is determined by processes in the upper levels where the probabilities of V–T processes are great enough and the populations are large.[82] When the amount of pumping is not too great, these levels lie below n^* (see (4.16)). Then the condition $\tau^*_{vib} \ll \tau_E$, which is necessary for the above-discussed variant of the analytical solution of the system (4.7), usually remains in force. The relaxation time τ^{anh}_E of the vibrational energy in a system of anharmonic oscillators has been calculated in[80,82,85,86,89]. Table I and Fig. 5 give values of $\tau^{har}_E/\tau^{anh}_E$ and the parameters

$$\psi = (dT_1/dt)_{anh}/(dT_1/dt)_{har}$$ for $T_1 = 3000°$K and various values of T for the one-component gases CO and N_2.[86]

We note that the time course of T_1 affects not only the variation of the vibrational energy, but also that of the gas temperature.[85,86] Thus, T_1 decreases when the gas temperature is decreased, owing to pumping of energy into the upper levels. We note that the vibrational energy in anharmonic oscillators can vary even when the supply of vibrational quanta is held invariant: $\bar{\epsilon}$ = const, if dT/dt $\neq$ 0. Just as when T_1 is varied, this is caused by redistribution of the quanta over the levels, and moreover, by their decreased energy for the upper states. According to the calculations of[86], the contribution of this mechanism to the overall rate of energy relaxation for the CO molecule proved to be inconsequential.

We see from Table I and Fig. 5 that the rate of relaxation increases considerably when $T_1/T \geq 3$. Such conditions are realized in expanding gas flows, when vibrations are excited by electron impact, and in chemically reacting mixtures in which the reacting products are vibrationally-excited molecules. Experiments on vibrational relaxation in expanding gas flows[96-99] are precisely where the measured relaxation rates were observed to deviate appreciably from the data obtained, e.g., with shock tubes, where one always has $T_1/T \lesssim 1$.

Table I

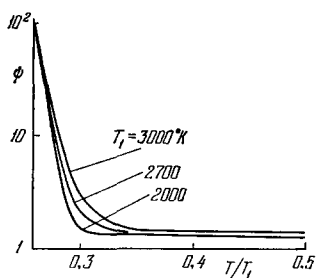| T, °K		800	1000	1500	2000
$\dfrac{\tau^{vib}_E}{\tau^{anh}_E}$	CO	80.8	2.06	1.59	1.45
	N_2	393	2.15	1.63	1.48
ψ	CO	45.1	1.57	1.37	1.32
	N_2	207	1.67	1.41	1.35

FIG. 5. The parameter $\psi = (dT_1/dt)_{\text{anh}} \cdot [dT_1/dt)_{\text{har}}]^{-1}$ for $dT/dt = 0$ as a function of the ratio T/T_1 for various T_1 values for a one-component gas of N_2 molecules as represented by anharmonic oscillators. [86]

One of the important reasons for this is precisely the effects of anharmonicity and non-resonance exchange. Another reason involves, in particular, the effect on relaxation of uncontrolled dissociating impurities.[99] The latter do not play such a role in shock-tube experiments, since vibrational relaxation here usually has ceased before the onset of dissociation of these impurities.

The effects of exchange and anharmonicity play a special role in molecular lasers, which use all three of the above-cited types of pumping, and where the ratio T_1/T can be considerably greater than three. Thus, $T_1/T \gtrsim 10$ in a continuous-wave electrically-pumped CO laser. In such cases, the harmonic-oscillator model can prove inapplicable, not only in analyzing the distribution function, but also in calculating the overall rate of relaxation of the vibrational energy.

e) **Vibrational relaxation in gas mixtures.** Study of vibrational kinetics in gas mixtures is very important in applications. However, owing to its complexity, only binary mixtures of diatomic molecules have been studied relatively well. The system of equations (3.1) with non-zero values of the first four terms on the right-hand side describes vibrational relaxation in a mixture of the molecules A and B. It contains the differing characteristic times: $\tau_{VV}(A)$, $\tau_{VV}(B)$, $\tau_{VT}(A)$, $\tau_{VT}(B)$, and $\tau_{VV'}$. Generally these times have different orders of magnitude, but two special cases are most widespread:

1) $\tau_{VV}(A),\ \tau_{VV}(B) \ll \tau_{VV'},\ \tau_{VT}(A),\ \tau_{VT}(B),$

2) $\tau_{VV}(A),\ \tau_{VV}(B),\ \tau_{VV'} \ll \tau_{VT}(A),\ \tau_{VT}(B).$

(4.20)

If we can neglect $V - V'$ processes, i.e., if $\tau_{VV'} \gg \tau_{VT}(A)$, $\tau_{VT}(B)$, then the system (3.1) breaks down into two independent systems of equations describing vibrational relaxation in each of the components A and B separately. Here the vibrational relaxation of each of the components occurs as though the molecules of the other component lacked internal degrees of freedom. Inclusion of the $V - V'$ processes mixes the vibrational energies of the individual components. However, the total number of vibrational quanta in the gas mixture will not vary as a result of one-quantum transitions. Then, if case 2) of (4.20) holds, the $V - V'$ process establishes a quasi-steady-state distribution in the mixture. It can be obtained by setting the fourth term on the right-hand side of (3.1) equal to zero. This may require existence of dynamic equilibrium for each of the two groups of molecules $y_m x_{n+1}$ and $y_{m+1} x_n$ involved in the $V - V'$ process. Then the equations for determining the quasi-steady-state distribution for a one-

quantum $V - V'$ process can be written in the form

$$Q_{n+1,\,n}^{m,\,m+1}(AB)\, y_m x_{n+1} - Q_{n,\,n+1}^{m+1,\,m}(AB)\, y_{m+1} x_n = 0. \quad (4.21)$$

In a mixture of harmonic oscillators having quanta of sizes E_1^A and E_1^B, the vibrational temperatures T_A and T_B with account taken only of $V - V$ processes are determined by the total supply of vibrational energy of each of the components, and they do not depend on one another. Inclusion of $V - V'$ processes relates T_A to T_B by the condition (4.21). Here one can derive the relationship[82,100]

$$(E_1^B/T_B) - (E_1^A/T_A) = (E_1^B - E_1^A)/T. \quad (4.22)$$

Equation (4.22) implies that when $E_1^B > E_1^A$ with $T_B > T$, then $T_A > T_B$. This means that a state can exist in which $V - V'$ processes overheat the vibrational degrees of freedom having the smaller vibrational quanta. The physical reason for the elevated temperature T_A is the same as that for the overpopulation of the upper levels in a system of anharmonic oscillators (see Sec. b). Experimentally, a separation between the vibrational temperatures T_A and T_B has been observed in a mixture of CO and N_2 upon non-equilibrium expansion in a supersonic nozzle.[101] However, if T_A, $T_B < T$ (conditions that are realized, e.g., behind a shock-wave front), then the $V - V'$ processes overheat the vibrational degrees of freedom of the harmonic oscillators having the larger vibrational quanta. This effect has not yet been studied experimentally.

The relationship (4.22) was derived under the assumption of one-quantum transitions. However, if $E_1^B - E_1^A \sim E_1^A$, then the one-quantum transitions can coexist with $V - V'$ processes in which two quanta of oscillator A are transformed into one quantum of oscillator B. This case has been analyzed in detail in[88,102].

A real molecule is always anharmonic. Let us briefly discuss $V - V$ and $V - V'$ processes in a mixture of two groups of anharmonic oscillators. The system of lower levels where the $V - V$ and $V - V'$ processes are separated in time from the $V - T$ processes will be limited to one-quantum exchange for the sake of simplicity. Then, if we consider only the $V - V$ processes, each of the groups A and B will have a Treanor distribution (4.4) with the constants γ_B and γ_A, which are determined by the total supply of vibrational energy of each of the components. Combined treatment of $V - V$ and $V - V'$ processes leads to formation of a quasi-steady-state distribution in which γ_A and γ_B are no longer independent. They are determined by the conditions that the Treanor functions for each of the oscillators will be a solution of (4.21). This requirement leads to the condition $\gamma_A = \gamma_B$,[82,103] or in terms of the vibrational temperature Θ_n (see (4.6)),

$$(E_n^B/\Theta_n^B) - (E_n^A/\Theta_n^A) = (E_n^B - E_n^A)/T.$$

This expression is a generalization of (4.22) to the case of a mixture of anharmonic oscillators.

Energy exchange between the vibrational and translational degrees of freedom in the binary mixture of diatomic molecules completes the evolution of the system, and it establishes full thermodynamic equilibrium. If $\tau_{VT} \gg \tau_{VV}$, $\tau_{VV'}$, then this process passes through

a continuous sequence of quasi-steady-state distributions (of the Boltzmann type for a mixture of harmonic oscillators or of the Treanor type for anharmonic oscillators) that are determined by the $V - V$ and $V - V'$ processes. Here the $V - V'$ processes can change the relaxation time substantially, as compared with a pure gas or a gas in an inert diluent.[88,104] Thus, when (4.20) is satisfied in a binary mixture of the diatomic gases A and B, the equation for the vibrational energy $E_{vib}(A)$ of one of the components (e.g., A) for the case $E_{vib}(A)/E_1^A N_A \ll 1$ has the following form[88,104] instead of (3.3):

$$\frac{dE_{vib}(A)}{dt} = - [E_{vib}(A) - E_{vib}^0(A)] \frac{1}{k\tau_{VT}(A)} -$$

$$- [E_{vib}(A) - E_{vib}^0(A)] \frac{N_B}{N_A} \frac{\exp[(E_1^A - E_1^B)/T]}{k\tau_{VT}(B)} - E_{vib}(A) \frac{k-1}{k} \frac{E_1^B - E_1^A}{T^2} \frac{dT}{dt},$$

$$k = 1 + \exp[(E_1^A - E_1^B)/T] N_B/N_A. \tag{4.23}$$

We see by comparing (3.3) and (4.23) that the effective relaxation time of the vibrational energy of the A molecules in a mixture of molecular gases will differ from that in a one-component system. The coefficient k in the first term on the right-hand side of Eq. (4.23) characterizes the change in the intrinsic vibrational relaxation time of the A molecules arising from the extra reservoir of vibrational energy in the form of excited B molecules. The second term involves the appearance of an extra channel of relaxation of the energy of A molecules via B molecules. Moreover, the effective relaxation time can vary when the gas temperature varies (the last term on the right-hand side of (4.23)). Here the rate of variation of T affects the relaxation only when the vibrational quanta of the molecules differ. This involves the fact that the $V - V'$ processes bring about a distribution of the type of (4.22), with energy pumped from one vibrational mode to another when the gas temperature T varies and differs from T_A and T_B. Increasing the effective energy-relaxation time in a gas mixture can prove to be very useful for optimizing the operation of a number of molecular lasers (in particular, in a $CO_2 - N_2$ mixture with an electric discharge). Moreover, a knowledge of the kinetic laws of non-resonance exchange opens up a number of possibilities for gas-dynamic lasers (using a variation in T).

Above we have treated non-resonance one-quantum exchange in a binary mixture. Expressions like (4.22) also figure in fast many-quantum exchange.[76,88,105] However, in this case establishment of quasiequilibrium requires that this exchange between different oscillators follows only one channel. For example, when n quanta of the harmonic oscillator A are exchanged for m quanta of the oscillator B, we get the following equation instead of (4.22):

$$(mE_1^B/T_B) - (nE_1^A/T_A) = (mE_1^B - nE_1^A)/T. \tag{4.24}$$

In fast non-resonance exchange, we can generalize Eq. (4.24) also to the case of a mixture of three or more oscillators.[76] The case is also of interest in which the $V - V'$ and $V - T$ processes have comparable rates. The distribution functions of the vibrational energy among the components that arise in these cases substantially differ from those discussed above in that they

depend on the relative concentrations of these components.[102]

5. VIBRATIONAL RELAXATION IN THE PRESENCE OF SOURCES OF MOLECULES

a) The harmonic approximation. Dissociation and recombination. In the previous sections we have treated processes establishing equilibrium in a system with arbitrary initial conditions, and in equations like (3.1), we have not considered terms describing sources of vibrationally-excited molecules. Here we have actually assumed that these sources acted over a time considerably shorter than the characteristic relaxation times. Below we shall study vibrational relaxation in systems having sources and sinks of vibrationally-excited molecules in the case in which the characteristic time τ_{source} of variation of the source is much longer than some of the characteristic relaxation times. For constant or slowly varying sources, we can refer to a process of establishment of a steady-state or quasi-steady-state distribution, and to the quasi-steady-state distribution itself. Such sources can include chemical reactions (e.g., dissociation and recombination) and various types of external agents that produce vibrationally-excited molecules (electric discharges and radiation). A number of the problems involved in slowly-varying sources have been studied in[9,14,15,106,107]. Thus, for example, a detailed analysis was made in[106,107] of the problem of distortion of the distribution function of the molecules over the levels by sources of vibrationally-excited particles in a system constituting a small admixture in a thermostatic inert gas.

Let us consider the effect of certain types of sources on the overall supply of vibrational energy and on the form of the distribution function over the levels in a system of identical molecules, i.e., in cases in which $V - V$ processes are essential. First, we shall elucidate the role of sources with the example of dissociation (a sink) and recombination (a source) of diatomic molecules as represented by a model of truncated harmonic oscillators.

By solving the gas-kinetic equations describing the populations of the vibrational levels, the process was analyzed in[108] of thermal dissociation (with characteristic time τ_D) of diatomic molecules at high temperatures, i.e., under the conditions $\tau_{VV} \ll \tau_{VT}, \tau_D$. It was shown that one can refer in the zero-order approximation to a Boltzmann distribution having the temperature T_{vib}. Owing to the appreciable loss of vibrational energy from the system due to dissociation, $T_{vib} < T$. This has a considerable effect on the rate of dissociation, $T_{vib} < T$. This has a considerable effect on the rate of dissociation. Moreover, dissociation distorts the Boltzmann distribution appreciably in the levels close to the dissociation boundary. One can also analyze approximately the T_{vib}/T relation and the variation of the dissociation rate constant $K^-(T_{vib})$ with respect to its equilibrium value $K^-(T)$ in a rapidly-heated dissociating gas by solving the system of equations for the total supply $\bar{\epsilon}$ of vibrational quanta and the degree of dissociation:[109,110]

$$\frac{d\bar{\epsilon}}{dt} = - \frac{\bar{\epsilon} - \bar{\epsilon}^0}{\tau_{VT}} + \left(\frac{D}{E_1} - \bar{\epsilon}\right) \frac{1}{\alpha} \frac{d\alpha}{dt},$$

$$d\alpha/dt = -\alpha K^-(T_{vib})(N+N_a)+4(1-\alpha)^2 K^+(N+N_a)[N+(N_a/2)];$$

(5.1)

Here α is the ratio of the total number of molecules to their number in the undissociated gas, K^+ is the rate constant for recombination, and N and N_a are the densities of molecules and atoms, respectively. The manner of writing (5.1) assumes that a Boltzmann distribution exists over the levels, and it takes no account of distortion of this distribution. The dependence of the ratio $K^-(T_{vib})/K^-(T)$ on T_{vib} and T has the form

$$\frac{K^-(T_{vib})}{K^-(T)} \approx \frac{T}{T_{vib}} \exp\left[D\left(\frac{1}{T}-\frac{1}{T_{vib}}\right)\right].$$

(5.2)

The relation of $K^-(T_{vib})/K^-(T)$ and T_{vib}/T to D/T was derived in[109] by using the expression for τ_{VT} and $K^-(T)$. This permitted estimating the deviations of $K^-(T_{vib})$ and T_{vib} from the equilibrium values in the dissociation of various molecules. Figure 6 gives the calculated data.[109] We see that an appreciable deviation from the equilibrium values sets in at $T \gtrsim D/20$.

By using the system of equations (5.1), we can also analyze the effect of recombination on the rate of vibrational relaxation when a heated gas flows from a nozzle.[111] When the instant of time t_{chem} of onset of chemical quenching (i.e., recombination ceases, owing to the decrease in density of the particles upon expansion) comes later than the instant t_{fr} of freezing of the vibrational temperature ($t_{chem} > t_{fr}$), the recombination process increases the effective vibrational relaxation time by a factor of approximately $1 + (D/T)^2[(1-\alpha)/\alpha]$. This quantity can be of the order of 10^2 and higher. Of course, in fast chemical quenching, when $t_{chem} < t_{fr}$, no energy will be pumped into the vibrational degree of freedom by recombination, and vibrational relaxation will not be retarded. The effect of retardation of vibrational relaxation when the condition $t_{chem} > t_{fr}$ is fulfilled can be used in gas-dynamic lasers.[112,113]

b) Action of infrared resonance radiation on molecules. Among the problems involving sources of molecules, the action of resonance laser radiation on some particular degree of freedom of a molecule has recently attracted especial attention. Here we should distinguish two sets of problems. The first of them is to analyze vibrational and rotational relaxation in systems that are used as optical filters in Q-modulated lasers having a passive shutter.[114,115]

The other set involves studying the possibility of control of chemical reactions by selective heating of a vibrational mode by resonance laser radiation.[89,116-119] The conditions for pumping of a large supply of vibrational energy upon absorption of radiation are analyzed in[116]. If we assume that the radiation frequency exactly coincides only with the frequency of the transition from the level $n = 0$, $j = j_0$ to the level $n = 1$, $j = j_1$ (where j_0 and j_1 are rotational quantum numbers), then the action of the radiation on the vibrational mode is described by adding to the right-hand side of (3.11) the following terms for the levels 0 and 1:

$$\pm (W_{01}x_0 - W_{1,0}x_1),$$

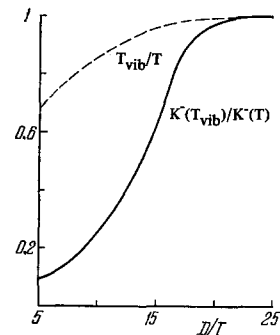(5.2a)

Here the plus sign is taken for the level 1, and the

minus sign for the level 0. Here W_{01} and $W_{1,0}$ are the corresponding transition probabilities, which are proportional to the radiation intensity J. The system of equations derived thus can be analyzed in two special cases.

The duration τ_{pulse} of the light pulse is considerably shorter than τ_{VV}. In this case, a Boltzmann distribution is established in the system in a time $t > \tau_{VV} \gg \tau_{pulse}$. The maximum temperature T_{vib}^{max} that can be attained is

$$T_{vib}^{max} \approx 0.9E_1.$$

The radiation intensity required to attain T_{vib}^{max} is very great. For example, according to the estimates of[116], it amounts to several tens of kilowatts per square centimeter at atmospheric pressure for CO_2 ($E_1 = 3380°K$) and N_2O ($E_1 = 3210°K$).

The duration of the light pulse considerably exceeds the characteristic time for the $V - T$ processes: $\tau_{pulse} \gg \tau_{VT} \sim 1/ZP_{10}$. In this case, the steady-state solution of (3.11) with the terms (5.2a) has the form

$$\begin{aligned} x_{n \ge 1} &= x_1 \exp[-(n-1)E_1/T_{vib}], \\ x_1 &\approx [\bar{\epsilon}+(W_{1,0}/ZQ_{1,0}^{01})][1+\bar{\epsilon}+(W_{1,0}/ZQ_{1,0}^{01})]^{-1}x_0, \\ \exp[-E_1/T_{vib}] &\approx \bar{\epsilon}(1+\bar{\epsilon})^{-1}; \end{aligned}$$

(5.3)

Here $\bar{\epsilon} = (x_1/N)[1 - \exp(-E_1/T_{vib})]^{-2}$. We see from (5.3) that, at any radiation intensity, the distribution in the levels above the first is a Boltzmann distribution with the vibrational temperature T_{vib}, as determined by the total supply $\bar{\epsilon}$ of vibrational quanta. However, at radiation intensities such that $W_{10}/ZQ_{1,0}^{01} \ll \bar{\epsilon}$, the distribution will be a Boltzmann distribution with the temperature T_{vib} in all levels including the levels 0 and 1. Then the relation between the radiation intensity and the obtained vibrational temperature T_{vib} can be determined directly from the equation for the vibrational energy. For low enough gas temperatures ($e^{-E_1/T} \ll 1$), we have

$$W_{1,0} \approx ZP_{1,0}\exp(-E_1/T_{vib})[1 - \exp(-E_1/T_{vib})]^{-3}.$$

When $W_{1,0} \approx ZP_{1,0}$, $T_{vib} \approx 0.8 E_1$. According to the estimates of[116], relatively small radiation densities ($\sim 3 \times 10^{-2}$ watt·cm^{-2} Torr^{-2} for the ν_3 vibration of the CO_2 and N_2O molecules, and $\sim 2 \times 10^{-4}$ watt·cm^{-2} Torr^{-2} for CO) are required to attain such a vibrational temperature. Such intensities can easily be attained now, and there are a number of recent experiments[120-125] in which various chemical reactions have been carried out by the action of laser radiation on molecular systems.

While in a number of cases the harmonic-oscillator model can be used successfully for determining the supply of vibrational energy of the molecules, we must note that one should apply the harmonic model cautiously in calculating the rate of a reaction that involves highly-excited molecules. Thus, the model of truncated harmonic oscillators is not suitable for estimating the rate of dissociation under highly non-equilibrium conditions when $T_1/T > 1$ (see below and[89]). In this case, the anharmonicity of the vibrations plays an essential role in the population of the upper levels. It is also important to take account of anharmonicity in calculating the non-equilibrium supply of vibrational energy whenever this supply depends substantially on the reaction rate itself.

c) **The anharmonic approximation. Non-equilibrium dissociation of diatomic molecules.** The rate of dissociation in a one-component diatomic gas represented by the model of a system of anharmonic oscillators has been calculated in[83] for the non-equilibrium case in which $T_1/T < 1$. The analysis was based on treating the system (5.1), with the harmonic-oscillator model (see (3.4)) used for calculating the relaxation time τ_{VT}, but with anharmonicity taken into account only in calculating the constant $K^-(T_1)$ for the non-equilibrium rate of dissociation. In finding $K^-(T_1)$, a quasiequilibrium distribution of the molecules over the levels was used. It was a Treanor distribution for the levels of numbers $n < n^*$ (see (4.16)) and a Boltzmann distribution for $n > n^*$. The distorting effect of dissociation on the form of the distribution was not taken into account. The found values of the ratios $K^-(T_1)/K^-(T)$ and T_1/T as functions of the parameter D/T proved to be close to the data for the truncated harmonic-oscillator model (see Fig. 6). This is explained by the fact that anharmonicity is not very important in the population of the highly-excited states from which dissociation occurs when $T_1/T \lesssim 1$ for relatively large gas temperatures, as we see from (4.5) and (4.10). However, the situation differs at low gas temperatures and when $T_1/T > 1$.

Let us consider a dissociation process in a one-component system of anharmonic oscillators for the arbitrary non-equilibrium case $T_1/T \neq 1$.[89] The variation in the number N of molecules per unit volume is determined by the relationship

$$dN/dt = -v + (dN/dt)^*,$$
$$v = ZP_{kd}x_k - ZP_{dk}N_a^2, \quad (dN/dt)^* = \sum_i (B_i - C_i x_i); \quad (5.4)$$

Here v is the rate of dissociation of the molecules, and B_i and $C_i x_i$ are, respectively, the rates of formation and loss of molecules in the level i owing to extraneous sources. We assume that dissociation occurs because of transition of molecules (with probability P_{kd}) to the continuous spectrum from some boundary level k that lies near the dissociation limit (at a distance of the order of T from D). The term $ZP_{kd}N_a^2$ describes the rate of recombination to the level k by triple collisions (N_a is the number density of atoms arising from decomposition of molecules). In order to find v, we must calculate the population x_k in terms of the probabilities, the molecular density, and the vibrational energy E_{vib} by solving a system of the type of (4.7) (with the sources accounted for as well.) Just as in Sec. c of Chap. 4, we can find an approximate analytical solution here by as-

suming that the relaxation time of the populations of the vibrational levels τ^*_{vib} (see (4.8)) is much shorter than the dissociation time τ_D and the characteristic times for variation of the gas temperature τ_T, of the vibrational energy τ_E, and for variation in the number of molecules owing to extraneous sources τ_{ex}. The instants of time $t > \tau^*_{vib}$ are essential in determining the rate of dissociation. Hence we can seek a solution in the form of (4.9), taking into account in a first approximation the additional dependence of x_n on the rate v and on $(dN/dt)^*$. In the zero-order approximation, the solution of the system is the function (4.10), which can differ substantially from a Boltzmann distribution when $T_1 \neq T$. In the next, or first-order, approximation, which takes account of the distorting effect of dissociation and of extraneous sources, the approximate solution has the form[89]

$$\chi_n \approx \frac{1}{Z} \sum_{m=0}^{n-1} \frac{1}{W_m} \left\{ \frac{1}{N} \left[-v + \left(\frac{dN}{dt} \right)^* \right] \sum_{i=0}^{m} x_i^0 - \sum_{i=0}^{m} (B_i - C_i x_i^0) \right\}, \quad (5.5)$$

$$\chi_0 = 0, \quad W_m = x_{m+1}^0 [\beta Q_{m+1, m}^{01} + P_{m+1, m} + (A_{m+1, m}/Z)]; \quad (5.6)$$

and x_i^0 is the function (4.10) of the zero-order approximation. The quantities χ_n can easily be found, even when $\chi_0 \neq 0$. Then χ_0 must be determined from the normalization conditions.

In their structure, Eqs. (5.5) and (5.6) resemble the expressions derived in[9,14,15,106-108]. However, it is important to emphasize that the quasi-equilibrium populations entering into (5.5) and (5.6) are essentially not Boltzmann distributions, in contrast to [9,14,15,106-108]. We can easily find from (5.4)—(5.6) a general expression for v or for the dissociation rate constant $K^-(T_1)$ under non-equilibrium conditions (cf. (5.2)):

$$K^-(T_1) \approx C \exp\left[n^{**} E_1 \left(\frac{1}{T} - \frac{1}{T_1} \right) \right] \frac{Q(T)}{Q(T_1)} K^-(T); \quad (5.7)$$

Here $Q(T)$ and $Q(T_1)$ are the partition functions of the oscillator at the temperatures T and T_1. The level n^{**} is defined by a relationship like (4.16), while the constant C (cf. (4.15)) differs appreciably from unity. For the group of intermediate levels $n^* < n < n^{**}$, it characterizes the deviation, both from the Treanor distribution (4.5) and from the Boltzmann distribution.

When $T_1 > T$, the coefficient of $K^-(T)$ in (5.7) can substantially increase the rate of dissociation. Nevertheless, it is difficult to get appreciable dissociation rates of diatomic molecules under non-equilibrium conditions at low temperatures (of the order of room temperature) and with large stores of vibrational energy, owing to the very small value of $K^-(T)$. Physically this is because the relative population of the upper levels is determined mainly by the gas temperature through the V − T processes, which predominate for these levels in anharmonic oscillators, in spite of the large supply of energy. Hence, their relative population declines sharply with increasing level number at low T. We emphasize that application of the harmonic model in such cases can lead to a considerable overestimation of the calculated rate of non-equilibrium dissociation (by many orders of magnitude).

d) **Non-equilibrium dissociation of polyatomic molecules.** The treatment given above for the rate of non-equilibrium dissociation pertained to diatomic

molecules. Evidently, when the vibrational modes interact weakly, all of the above discussion can be applied also to polyatomic molecules in treating the individual type of vibration that has the minimum dissociation energy limit D_{min}. However, when one uses a polyatomic molecule and pumps a large supply of vibrational energy into a type of vibration that has a dissociation energy limit D larger than D_{min}, the situation changes substantially. In this case, the molecule can decompose by predissociation, i.e., transition of the molecule to the continuum from a vibrational level lying above the minimum dissociation energy. Owing to interaction of different vibrations of the molecule in the upper levels, the rate of such a transition is usually high.[3][128] Under these conditions, the rate of dissociation will be determined by the probability of supply of molecules to the level k + 1 and by the population of the level k, whose level number is determined by the condition $E_k \leq D_{min} \leq E_{k+1}$. If the level k lies near the level n* (see (4.16)), or even if k < n*, then V − T processes or radiative decay of this level can affect its population weakly. With large enough supplies of vibrational energy, its population can be considerable and this can bring about a high dissociation rate. As usual, one can obtain the non-equilibrium energy supply here by various methods: by optical, thermal, chemical, and electrical pumping, or by vibrational exchange with another molecular system that has a non-equilibrium energy supply.

In the case k < n*, with $dT_1/dt = dT/dt = 0$ and $C_n = B_n = 0$, we have for large n[86]

$$K^-(T_1) \approx Z \frac{\beta}{Q(T_1)} k Q_{0i}^{1,0} \exp\left(-\frac{D_{min}}{T}\right) \exp\left[kE_1\left(\frac{1}{T}-\frac{1}{T_1}-\frac{\gamma_0}{3D}\right)\right](1+J_k)^{-1}$$

$$J_k = Q(T_1)\left(\frac{\pi T}{4\Delta E}\right)^{1/2} \exp\left[\frac{D}{T}\left(\frac{T}{T_1}+\frac{\gamma_0 T}{3D}-\frac{E_1}{2D}k\right)^2\right]$$
$$\times \left\{1-\Phi\left[\left(\frac{D}{T}\right)^{1/2}\left(\frac{T}{T_1}+\frac{\gamma_0 T}{3D}-\frac{E_1}{2D}k\right)\right]\right\}^{-1}.$$

(5.8)

One can also easily derive a formula for $K^-(T_1)$ like (5.8) for the case k > n*. The expression (5.8) has two essential differences from the analogous expression (5.7) for the non-equilibrium rate of dissociation of diatomic molecules. The first feature is that the rate of non-equilibrium dissociation of polyatomic molecules can be large, even at low gas temperatures T (of the order of room temperature), in contrast to diatomic molecules. As we can easily see from (5.8), this can be attained at relatively small $T_1 > T$. In this regard, we should note[120], where they found an appreciable rate of dissociation at room temperature when energy was pumped by CO_2-laser radiation into one of the types of vibration of the BCl_3 molecule (see also[122-125,127]).

The second important distinction consists in a possible anomalous temperature-dependence of the dissociation rate of a polyatomic molecule under non-equilibrium conditions in which $T \neq T_1$. As we see from (5.8), when there is a constant supply of vibrational energy (at constant T_1) and $T < T_1$, $K^-(T_1)$ does not increase with T, but falls, in contrast to the usual Arrhenius relation. The strong dependence of $K^-(T_1)$ on T and T_1 permits one to control dissociation by varying both the supply of vibrational energy and the gas temperature. We must emphasize that the generation of high concentrations of

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[3] In addition to predissociation among the vibrations, one can also consider predissociation due to crossing with another electronic term.

free atoms by non-equilibrium dissociation at low gas temperatures has led to a marked increase in the power of chemical lasers (see Sec. c of Chap. 6).

Dissociation and recombination are special cases of chemical reactions. The non-equilibrium nature of most chemical reactions in the gas phase[128] opens up a number of possibilities of influencing their kinetics, including the stage of branching of energy chains. Here, in addition to laser radiation acting on molecules, one can in principle control chemical reactions with non-equilibrium streams of the reacting gases.[89]

6. VIBRATIONAL RELAXATION AND MOLECULAR LASERS

a) On the combined treatment of vibrational relaxation with other processes. The process of vibrational relaxation in molecular gases depends on such parameters as the gas temperature, the concentrations of the components, and the power and duration of action of sources, etc. In general, the characteristic times for variation of these parameters (which are determined by the external conditions) can be comparable with one of the vibrational-relaxation times. In such cases, one can no longer treat the vibrational system in isolation (e.g., with equations like (3.1)) in making a valid description of the relaxation. It becomes necessary to analyze the vibrational relaxation jointly with the processes that change the external conditions and disturb the equilibrium between the vibrational and translational degrees of freedom of the molecules. One must also perform such an analysis in order to concretize the quantities B_i and C_i (see (3.1)). The latter are the parameters for sources and sinks of vibrationally-excited molecules, and they only formally characterize the effect of external agents on the vibrational relaxation. The concrete features of solving such problems involve the locations of the characteristic times for variation of the parameters on the scale of relaxation times (τ_{VV}, τ_{vib}^*, $\tau_{VV'}$, τ_E, τ_{VT}, etc.) Thus, in the absence of sources, there is a very simple case of relaxation in which the density and temperature of the gas change rapidly within a time shorter than τ_{VV}, and they remain constant thereafter. This case is described by equations like (3.1) with $B_i = C_i = 0$ and with the given initial conditions. For times greater than τ_{VV} (τ_{vib}^*), one can often use the vibrational temperatures T_{vib} or distributions like (4.10) or (5.5) in solving the system of equations.

An approach based on analyzing the vibrational-relaxation times with account taken of the characteristic times for the external parameters permits one to reject inessential aspects of the phenomena and to construct adequate models of the physical processes in various molecular systems. A typical example of such systems is molecular optical lasers based on vibrational-rotational transitions. Study of the processes in these lasers belongs to the class of relaxation problems that are characterized by treating vibrational relaxation jointly with chemical reactions, electronic or optical excitation of vibrations, and processes of variation of the gas temperature and density.

We shall discuss in this section the operating mechanisms of lasers based on polyatomic and diatomic

molecules. There are currently very many studies on this topic (see, e.g., the reviews and monographs[129,141]). However, the purpose of the treatment below is not to review in detail these largely experimental studies, but to discuss the models of the physical processes in lasers that have been constructed on the basis of vibrational kinetics. For simplicity, we shall not analyze the operation of lasers in an oscillation mode, but we shall study the mechanisms of creation of an inverted population of levels. The treatment begins with optical lasers based on polyatomic molecules, since one can conduct the theoretical analysis here mainly within the framework of the harmonic-oscillator model.

b) **Lasers based on polyatomic molecules.** In most lasers based on vibrational-rotational transitions in polyatomic molecules, laser action occurs between low-lying levels belonging to different vibrational modes. We can characterize the populations of these levels by using the harmonic-oscillator model and introducing the vibrational temperatures T_i of the different modes (Sec. e of Chap. 3). In order to obtain an absolute inverted population in the states having the vibrational numbers $(v_1, ..., v_i, ..., v_L)$ and $(w_1, ..., w_i, ..., w_L)$ (L is the number of modes in the molecule), the following relationship must be satisfied:

$$\exp\left(-\sum_{i=1}^{L} \frac{v_i E_1(i)}{T_i}\right) > \exp\left(-\sum_{i=1}^{L} \frac{w_i E_1(i)}{T_i}\right), \text{ i.e., } \sum_{i=1}^{L} \frac{(v_i - w_i) E_1(i)}{T_i} < 0, \quad (6.1)$$

according to which the T_i must differ. Divergence among the T_i can occur only if there is a non-equilibrium supply of the total vibrational energy of the molecule, and it can be produced by various mechanisms of pumping: excitation of vibrations of electron impact, by resonance infrared radiation, by chemical means (in which vibrationally-excited molecules are formed by a reaction), by thermal means (with abrupt heating or cooling of a gas), by energy transfer from other molecules that have been excited in some way, etc.

In order to create a divergence between the T_i, it is convenient to use molecules having different relaxation times for different modes.[70,72] However, under non-equilibrium conditions one can get laser action even with molecules having a single relaxation time. Owing to fast $V - V'$ processes, the temperatures of the modes will be connected here by relationships like (4.22) and (4.24). Then we can easily find from (4.24) and (6.1) the divergence of T_B from T needed for inversion between the level v of mode A and level w of mode B:

$$\frac{T_B}{T} > E_B\left[v\frac{m}{n}(E_1^B - E_1^A)\left(v\frac{m}{n} - w\right)\right]^{-1}.$$

Thus it is easier to get an inverted population at low gas temperatures and with upper levels. However, the absolute populations decline on the upper levels. Hence, in concrete treatment of the possibilities of laser action, we must also know the density of the molecules and the probabilities of radiative transitions in addition to T_i. At present, laser action has been obtained experimentally, both in the infrared and in the submillimeter regions of the spectrum by using various molecules including: N_2O,[142-144] SO_2,[145] CS_2,[146,147] COS,[148] C_2H_2,[149] HCN,[150] ICN,[151] H_2O,[131,152] BCl_3,[115] CH_3F, and CH_3OH[153] (see also the re-

views[131,134]). Here thermal[144] and optical[115,153] pumping have been used in a number of cases, in addition to the electric discharge that is usually applied to excite molecules.

Analysis of the processes and choice of best conditions for laser action has much in common for different lasers based on polyatomic molecules, and in essence, it is one of the problems of vibrational kinetics.[4][70] Hence, we can conveniently study the fundamental qualitative features of these lasers with a concrete example. Below we shall mainly analyze the CO_2 laser. Optical lasers based on the CO_2 molecule (wavelength 10.6 μm, $00^0 1 \rightarrow 10^0 0$ transition) are currently very widely used. They are characterized by record-breaking power in the continuous-wave mode and by application of various pumping mechanisms. A simplified system of equations that describes vibrational relaxation, e.g., in a CO_2-N_2 mixture, has the form:

$$d\bar{\varepsilon}_4/dt = W_{43} N_{CO_2} (\bar{\varepsilon}_3 - \bar{\varepsilon}_4),$$

$$\frac{d\bar{\varepsilon}_3}{dt} \approx W_{43} N_{N_2} (\bar{\varepsilon}_4 - \bar{\varepsilon}_3) - \frac{1}{8} W_{3\Sigma} N [\bar{\varepsilon}_3 (2 + \bar{\varepsilon}_2)^3 - e^{-500/T} \bar{\varepsilon}_2^3 (1 + \bar{\varepsilon}_3)], \quad (6.2)$$

$$\frac{d(\bar{\varepsilon}_2 + 2\bar{\varepsilon}_1)}{dt} \approx \frac{3}{8} W_{3\Sigma} N [\bar{\varepsilon}_3 (2 + \bar{\varepsilon}_2)^3 - e^{-500/T} \bar{\varepsilon}_2^3 (1 + \bar{\varepsilon}_3)] - W_{20} N (\bar{\varepsilon}_2 - \bar{\varepsilon}_2^0).$$

Here we have used the same notation as in Sec. e of Chap. 3, with the subscript 4 referring to the N_2 molecule, and 1, 2, and 3, respectively, to the symmetric, bending, and asymmetric types of vibrations of CO_2. The equations (6.2) are derived from the overall expression (3.14) with the simplifying assumptions: $\exp[-(E_1(2)/T_2)] \ll 1$, $E_1(1) = 2E_1(2)$, $E_1(3) = E_1(4)$. We shall consider the two channels (3.15a) and (3.15b) of relaxation of ε_3 and ε_4 having the overall probability $W_{3\Sigma}$, W_{20} and W_{43} are, respectively, the probabilities of vibrational-translational relaxation for the bending mode of CO_2 and of vibrational exchange between N_2 and the asymmetric mode of CO_2. Very complete data for these probabilities are given as graphic material in the review.[51] Table II gives analytical formulas for the probabilities (in cm^3/sec) for vibrational relaxation in CO_2 upon collision with various molecules (the temperature interval T in °K is given in brackets) as obtained by reduction of the data of[51,154]. In the presence of external agents (e.g., excitation of vibrations by electron impact), we must add terms to the right-hand sides of (6.2) that describe the change in the vibrational energy of the mode arising from this agent. We shall briefly analyze the different ways of forming an inverted population of the $00^0 1-10^0 0$ levels in the CO_2 laser.

1) The electrical continuous-wave CO_2 laser. The experimental studies on electrically-pumped CO_2 lasers are reviewed in[129,130,137-139]. The mechanism of formation of an inverted population has been well studied.[68,69,154-157] In an electric discharge in a CO_2-N_2-He mixture, vibrations of the molecules N_2, CO (which is formed by dissociation of CO_2 in the discharge), and CO_2 are excited by electron impact. Vibrational energy is transferred from N_2 and CO by resonance transfer to the $00^0 v$ levels of the CO_2 molecule, and then by molecular collisions along the channels (3.15) to the bending and symmetric modes. A

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[4]In a number of cases, one must also consider rotational relaxation, whose rate for dipole molecules can prove to be comparable with the rate of vibrational relaxation.

Table II

Probabili-ties	Molecules				
	CO_2	N_2	He	H_2	H_2O
$W_{3\Sigma}$	$1.31\cdot10^{-10}\times$ $\times\exp\left(-\dfrac{62.75}{T^{1/3}}\right)$ $(300-2000)$	$2.97\cdot10^{-10}\times$ $\times\exp\left(-\dfrac{75.46}{T^{1/3}}\right)$ $(300-2000)$	$1.1\cdot10^{-12}\,T^{1/2}\times$ $\times\exp\left(-\dfrac{58.82}{T^{1/3}}\right)$ $(300-1000)$	$1.8\cdot10^{-13}\,T^{1/2}\times$ $\times\exp\left(-\dfrac{22.22}{T^{1/3}}\right)$ $(300-1000)$	$4\cdot10^{-15}\,T$ $(300-600)$
$W_{2,0}$	$1.6\cdot10^{-11}\times$ $\times\exp\left(-\dfrac{72}{T^{1/3}}\right)$ $(300-3000)$	$4.7\cdot10^{-11}\times$ $\times\exp\left(-\dfrac{72}{T^{1/3}}\right)$ $(300-3000)$	$4.8\cdot10^{-11}\times$ $\times\exp\left(-\dfrac{40.63}{T^{1/3}}\right)$ $300-1000)$	$5.3\cdot10^{-11}\,T^{-1/2}$ $(300-1000)$	$3.9\cdot10^{-9}\,T^{-1}$ $(300-1000)$
W_{34} ($CO_2 \rightarrow N_2$) = $4.2\cdot10^{-14}\,T^{1/2}\exp\,[10^{-3}\,T\,(8.84\cdot10^{-4}\,T - 2.07)]$					

quasi-equilibrium distribution is established in the latter by fast vibrational exchange. The vibrational energy is dissipated into the translational degrees of freedom by V — T processes, mainly involving the bending type of vibrations. At low pressures (~ 1 Torr), diffusion of excited molecules out of the volume with deactivation on the walls of the discharge tube is also important.

Vibrational relaxation in a discharge in a CO_2—N_2—He mixture in a through-flowing system (in which we can neglect the decomposition of CO_2) is described by the system (6.2) with terms added to the right-hand side that take account of pumping of vibrational energy by electron impact, and also of decomposition of excited molecules that have diffused to the vessel wall. However, the system (6.2) still does not adequately describe the processes in the CO_2 laser, since the characteristic time for cooling of the gas by heat conduction is comparable with the times of the V — T processes, and consequently it becomes heated. Since the gas temperature determines the probabilities of the processes and the populations of the levels, it becomes necessary to solve simultaneously the equations of (6.2) and the heat-conduction equation (see[69,156-159]).

For sealed systems and for relatively low rates of through-pumping of gas, we must supplement this system with an equation for vibrational relaxation of CO molecules. The latter are formed by decomposition of CO_2 in the discharge, and since they have a large cross-section for excitation of vibrations by electron impact, they can act as an additional channel for pumping of energy by vibrational exchange with the asymmetric mode of CO_2.[155-157] Simultaneous solution of this system of equations, which describes the physical processes in the electrical CO_2 laser, gives the values of the vibrational and gas temperatures, the inverted population, and the amplification coefficient as functions of the relative concentrations of CO_2, N_2, and He, of the overall pressure, of the density of free electrons, and of the radius and temperature of the walls of the discharge tube.[69,156,157,159] These functions are not monotonic, a fact that involves competition of various factors that increase or decrease the inversion. Thus, for example, adding helium to the working mixture lowers the temperature by increasing the heat conductivity. This implies a decrease in the rate of dissipation of the energy $E_{vib}(3)$ of the asymmetric mode. This increases the inversion. A density of helium 5-7 times greater than that of the CO_2 molecules proves to be optimal. Figure 7 shows a typical example of the relation of the inverted population ΔN to the pressure.[157] The
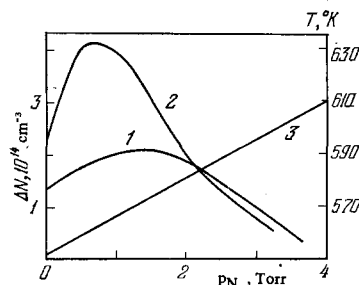

FIG. 7. Relation of the inverted population ΔN (1, 2) and the gas temperature T (3) to the nitrogen pressure in a mixture of 2 Torr CO_2 + p Torr N_2. Current 30 mA; curve 1—experiment, 2—theory (from the data of [157]).

rate of pumping of energy into the asymmetric mode increases with the partial pressure of nitrogen. This facilitates the growth of inversion, but the gas temperature also rises, and this decreases ΔN. In the last analysis, the increase in gas temperature is precisely the main factor limiting the gain in power of the continuous-wave electrical CO_2 laser. (This conclusion also holds for most other types of molecular lasers.) We note in addition a series of studies that have treated the thermal pattern and properties of the electric discharge in CO_2.[160-165] The most effective way to lessen the overheating of the gas in molecular lasers has been to use high velocities of through-flow of gas and to use a transverse discharge. The characteristic time for heat removal by through-flow must here be shorter than the corresponding time for heat consuction. The heat pattern for cylindrical systems with an arbitrary rate of through-flow has been analyzed in[160], and the relation of various characteristics of the laser (including the inverted population) to the rate of through-flow, the total pressure, and the partial pressure of CO_2 has been calculated in[166a] for a system with transverse flow. The processes in lasers having a transverse discharge and an ultrasonic rate of through-flow were studied in[166b]. Simple formulas that permit one to estimate the energy parameters of through-flow (and also pulsed) lasers are given in[167]. In order to analyze the processes in a laser with transverse flow, one can actually use the model of a pulsed laser (see below), but with the time t replaced with l/v (v is the flow rate, and l is the distance from the beginning of the discharge zone), and the pulse duration τ_{pulse} by l^*/v (l^* is the length of the electrodes). Currently, lasers with fast transverse gas flow and discharge are the most powerful continuous-wave lasers, and they operate at pressures close to atmospheric (see, e.g., the review[139]).

2) The pulsed CO_2 laser with electrical pumping. In

analyzing the operation of the pulsed CO_2 laser, we shall restrict our treatment to the case in which the pulse duration $\tau_{pulse} > \tau_{VV}$. Hence, we can speak of partial vibrational temperatures T_i. In order to find the T_i, we must solve simultaneously a system like (6.2) for the non-steady-state case ($d\epsilon_i/dt \neq 0$, $dT/dt \neq 0$) with an external agent that is a function of the time.

The physical processes in the pulsed laser have been analyzed theoretically in[112,168-170]. When τ_{pulse} $\tau_{E(3)}$, τ_T, the results are analogous to a steady-state system. Here the gas temperature can rise appreciably and restrict the population inversion. However, if one uses relatively short pulses with $\tau_{pulse} < \tau_{E(3)}$, the situation changes substantially. Then the maximum population of the 00^01 level, and hence also the maximum inversion, does not depend on the relaxation time $\tau_{E(3)}$, but is determined by the total supply of vibrational energy $E_{vib}(3)$ obtained from the electrons. If we keep the current in the pulse constant, this supply will increase approximately linearly with the pressure. Hence, the use of high pressures and $\tau_{pulse} \lesssim \tau_{E(3)}$ can substantially increase the inverted population and the laser energy per pulse. Moreover, temperature effects play a smaller role here, and some decline in inversion with increasing temperature can occur only because of increase in the equilibrium population of the lower level laser 10^00. In pulsed electron excitation, the characteristic parameter that determines the pulse energy, the supply of vibrational energy acquired by the molecules, the maximum inversion ΔN_{max}, the gas temperature, and the degree of dissociation is the product $N_e\tau_{pulse}$.

Figure 8 shows the relation of ΔN_{max} to τ_{pulse} for constant values of $N_e \tau_{pulse}$ equal to 10^7 and 3×10^7 sec/cm^3, and for varying partial pressures $p_{CO_2} = 1$ and 10 Torr.[112] We see that when τ_{pulse} is small enough, the inversion does not depend on τ_{pulse}, but is determined by the quantity $N_e \tau_{pulse}$. When $\tau_{pulse} > \tau_{E(3)}$, ΔN_{max} begins to fall with increasing current pulse duration, owing to loss of molecules from the upper laser level by relaxation processes during the time of action of the current. The increase in this case of the relaxation rate with increasing pressure gives rise to an optimum CO_2 pressure. However, this effect can be compensated by a corresponding decrease in τ_{pulse}.

Thus, by working with pulses shorter than the relaxation time of the energy of the asymmetric mode of CO_2, and by using high pressures $p_{CO_2} \sim 10^2$ Torr and high currents ($N_e \sim 10^{12}-10^{13}$ cm^{-3}), one can get considerable ($\sim 10^{-2}$ J/cm^3) specific laser energies per pulse. Here the laser power can amount to $\sim 10^3$ watt/cm^3. One can increase this power by 2-3 orders of magnitude further by shortening the pulse duration by working on a Q-switched mode, since the lines are considerably broadened at high pressures by an impact mechanism ($\gtrsim 10^8$ sec^{-1} at 1 atm). Laser instruments have already been built that operate at pressures of the order of atmospheric and higher. Here one uses transverse discharges with a short distance between electrodes in order to cause breakdown of the
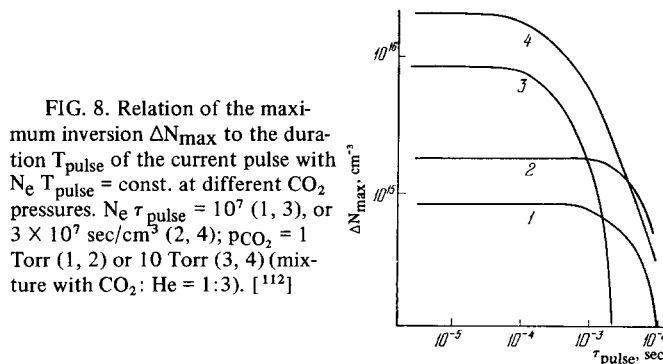

FIG. 8. Relation of the maximum inversion ΔN_{max} to the duration T_{pulse} of the current pulse with $N_e T_{pulse}$ = const. at different CO_2 pressures. $N_e \tau_{pulse} = 10^7$ (1, 3), or 3×10^7 sec/cm^3 (2, 4); $p_{CO_2} = 1$ Torr (1, 2) or 10 Torr (3, 4) (mixture with CO_2: He = 1:3). [112]
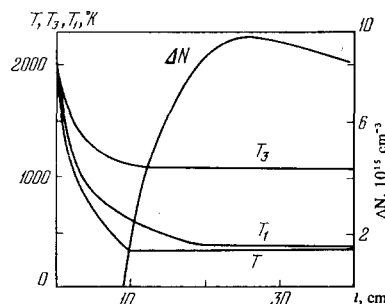

FIG. 9. Typical values of the inversion ΔN, the temperatures T_3 and T_1 for CO_2, and the gas temperature T at a distance l from the critical cross-section in flow of gases from a nozzle (the mixture is 10% CO_2, 89% N_2, 1% H_2O, $P_0 = 15$ atm, $T_0 = 2000°K$). [181]

gas and other special devices (see the reviews[137,138] and also[167,171]).

People have also used organic additives (xylene, benzene, toluene, etc.) in order to get a uniform high-pressure discharge.[172]

3) The gas-dynamic laser. In addition to the electric discharge, one can also bring about a separation between the vibrational temperatures T_i and create an inverted population by thermal pumping.[173,174] The possibility of getting an inverted population of the 00^01-10^00 levels of CO_2 molecules in a CO_2-N_2 mixture by cooling the gas by flow from a nozzle was first examined in[175]. (Using gas-dynamic expansion to attain an inverted population in electronic levels was proposed in[176,177].) Relaxation of an inverted population in a supersonic flow of gas from a nozzle has been analyzed in detail in[71,178-181], and for free gas-dynamic expansion in[112,182]. Chemical and vibrational relaxation in supersonic CO_2 flows has also been studied in[183].

The main point in analyzing vibrational relaxation in a rapidly-expanding molecular gas is the fact that the characteristic times for change in the density and temperature of the gas, τ_ρ and τ_T, are comparable with the relaxation times $\tau_{E(i)}$ of the vibrational energies. Here one must solve simultaneously vibrational-relaxation equations like (6.2) and the gas-dynamic equations. Figure 9 gives typical time-dependences of the temperatures T, T_3, and T_1 and of the inversion ΔN, as obtained by such a simultaneous solution.[181] The condition (6.1) for inverted population is realized when the following inequalities are satisfied:

$$\tau_{E(3)} > \tau_T, \tau_{E(1,2)};$$

At a distance ~ 9 cm from the critical cross-section, the rate of cooling and the density are such as to satisfy these inequalities, and a deviation of the temperature T_3 from T and T_1 sets in that suffices to produce an inversion. People usually use a CO_2-N_2 mixture in order to increase $\tau_{E(3)}$. Here the nitrogen serves as an additional reservoir of vibrational energy, and it effectively retards the relaxation of $E_{vib}(3)$ (see (4.23)) by vibrational exchange with the asymmetric mode of CO_2. One uses He and small admixtures ($\sim 3\%$ of the total concentration) of water vapor to decrease $\tau_{E(1,2)}$. It has also been suggested to use sputtered microparticles for this purpose.[184a] We note that laser action has recently been obtained[184b] in a mixture having a large amount of water vapor (up to 20%). This substantially simplifies the practical use of lasers of this type. Just like the electrical laser, the gas-dynamic laser has optimal parameters (composition of mixture, stagnation pressure and temperature, and characteristic dimensions of the nozzle or orifice) that give maximum values of the inverted population and laser power. Thus, for example, when the gas flows through a slit according to a free-expansion model, the optimum composition of the mixture is $CO_2:N_2 \approx 1:3$, the initial gas temperature is $\sim 1200-2000°$ K, and the initial partial pressure of $CO_2 \sim 4-12$ atm, and the dimension of the slit is ~ 2 mm.[112] Similar values of the optimal parameters have also been obtained in supersonic flow from a nozzle.[71] In a pure mixture of CO_2 and N_2 in the absence of such impurities as H_2O and H_2, which sharply increase the rate of relaxation of the vibrational energy of N_2 and of the asymmetric mode of CO_2, we note that the pressure optimum can shift into the region of higher pressures, up to 10^4 atm, owing to a decrease in the relative concentration of CO_2.[184c] This possibility involves the decrease in the rate of relaxation of the system N_2 + asymmetric mode of CO_2 with decrease in the relative concentration of CO_2, since these two types of vibrations relax mainly by way of CO_2. Just as in the electrically-pumped laser, the existence of optima is due to competition of opposing factors. Thus, for example, as the initial gas temperature increases, on the one hand, the number of vibrationally-excited molecules and the initial rate of cooling increase, but on the other hand, the relaxation time $\tau_{E(3)}$ decreases.

The maximum value of the population inversion of the levels $00°1-10°0$ of CO_2 can be greater than $\sim 10^{16}$ cm^{-3}. Here the total concentration of CO_2 molecules amounts to $\sim 10^{18}$ cm^{-3}. It is hard to get a higher density of active molecules when using an ordinary system of adiabatic cooling of a preheated mixture of the gases CO_2 and N_2, since the actually attainable rates of cooling of the gas are such that the inequality $\tau_{E(3)} > \tau_T$ holds only when $N_{CO_2} \lesssim 10^{18}$ cm^{-3}. Nevertheless, in spite of the relatively low efficiency $\sim 1\%$ (as compared with the electrical CO_2 laser),[71] the laser power per unit volume can be considerable (~ 3 watts/cm^3).[185] An advantage of gas-dynamic lasers is also the relatively easy way of creating large volumes containing active molecules.

Experimentally, laser action in CO_2 has been obtained upon efflux of a gas mixture from a nozzle[144,185-190] and from a slit.[191-193a] The powers

that can be collected are at present record-breaking for continuous-wave action (according to[187], this power amounts to ~ 60 kilowatts).

4) Chemical and chemico-gas-dynamic lasers. In addition to electrical and thermal pumping, one can also use chemical reactions to create an inverted population in polyatomic molecules.[72,135] Here the separation between the vibrational and gas temperatures can arise either from direct chemical pumping, in which the reaction products are vibrationally-excited polyatomic molecules, or from processes of non-resonance exchange with highly-excited diatomic molecules obtained in a chemical reaction. If the $V - V'$ process is fast and the vibrational quantum of the diatomic molecule is larger than that of the chosen mode of the polyatomic molecule, then one can get a high vibrational temperature in the stated mode (cf. (4.22), (4.23)) by energy redistribution. An example is a laser based on a $CO_2 + DF$ mixture in which the DF is produced by a chemical reaction, while laser action arises from the $00°1-10°0$ levels of CO_2 (a $CO_2 + HF$ mixture is less effective because of slow pumping of energy into the asymmetric mode of CO_2 due to a large difference between the vibrational quanta).

Without taking up the concrete features of lasers based on pumping from exothermic bimolecular replacement reactions, which have been treated in detailed reviews,[135,136] we shall briefly discuss the possibility of using a recombination reaction that occurs in triple collisions[11] for laser pumping:

$$A+B+M \rightarrow AB^*+M.$$
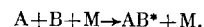
The rate of such a reaction strongly depends on the gas density. It can proceed efficiently at low gas temperatures, and usually almost all the energy of the reaction, which is equal to the dissociation energy, is liberated as vibrational energy. If the initial concentration $[A]_0 \gg [B]_0$, so that $[A] \approx$ const. $= [A]_0$ as the reaction proceeds, then the variation in the concentrations $[AB]$ and $[B]$ is described by the equation

$$d[AB]/dt = -d[B]/dt = K^+[A]_0[M][B] \equiv (\tau_{chem})^{-1}[B]. \quad (6.3)$$

We must solve (6.3) simultaneously with the heat-conduction equation and an equation like (5.1) for vibrational relaxation, with account taken for pumping of energy into the vibrational degree of freedom by recombination. The vibrational energy $E_{vib}(i)$ calculated from this model, which determines the absolute inverted population and the laser power, is a non-monotonic function of the time. Its maximum value for $T =$ const. is

$$E_{vib}^{max}(i) = D[B]_0(\varkappa-1)^{-1}[\varkappa^{1/(1-\varkappa)} - \varkappa^{\varkappa/(1-\varkappa)}]; \quad (6.4)$$

Here D is the dissociation energy, and $\varkappa = \tau_{chem}/\tau_{E(i)}$ is the ratio of the time for the chemical recombination reaction to the vibrational-relaxation time. If we increase the total concentration of particles, i.e., decrease τ_{chem} and $\varkappa$, we can in principle get large values of $E_{vib}^{max}(i)$, and hence, get large specific laser powers (there is a limitation here that involves increased requirements on the rate of preparation of the initial mixture). A calculation was performed in[113] for recombination of CO to give CO_2 under the assumption of

equal efficiencies of recombination in the different vibrational modes of CO_2. It showed that one can get a considerable inversion ($\sim 10^{17}$ cm^{-3}) without very rigid conditions of preparation of the recombining mixture of gases (one can make such a mixture by combining streams of cold CO gas with a lesser amount of hot, dissociated oxygen in the absence of water vapor).

There is another mechanism in three-particle recombination that gives rise to a population ratio x_{n+1}/x_n for a series of vibrational levels that is close to unity, or even to an absolute population inversion. This is the effect of recombination as a source of highly-excited particles (see Sec. c of Chap. 5). Such a source, combined with the downward flow of molecules through the vibrational levels among the group of highly-excited states belonging to a particular type of vibration, creates conditions favorable for laser action, even with a small supply of vibrational energy. Such a type of recombination laser based on vibrational transitions has been treated in[193b], where it was shown that the amplification coefficient suffices for laser action, given typical molecular parameters, a pressure $p \gtrsim 50$ Torr, and a non-equilibrium degree of dissociation $\alpha \gtrsim 0.01$. A virtue of this system is that one can get a considerable specific power and a relatively high efficiency (owing to amplification of the radiation simultaneously by many transitions). Here the laser-action power increases in proportion to the cube of the pressure, while the amplification coefficient is proportional to either the square (when $p \lesssim 10$ Torr) or the first power of the pressure (when $p \lesssim 10$ Torr). One can get the degree of dissociation of the gas exceeding the equilibrium value that is required for laser action in various ways: photodissociation, dissociation of molecules in collisions with electrons or heavy particles (atoms, ions, or neutrons), and by rapid cooling of a very hot, partly dissociated gas. Recombination molecular lasers of the two types have not yet been built experimentally.

It is also of considerable interest to combine the chemical and gas-dynamic methods for laser pumping: chemico-gas-dynamic lasers.[112,113] Thus, for example, according to[111], in the expansion of the molecules of a dissociated gas, recombination under certain conditions can substantially hinder vibrational relaxation and bring about a separation between the vibrational temperature and the gas temperature and formation of an inversion. Such a situation can also happen in bimolecular reactions. Gas-dynamic effects can also play a role in continuous-wave chemical lasers of the DF* + CO_2 type that operate with mixing of gas streams. In such cases, the model describing the physical processes must include a relaxation equation, a gas-dynamic equation, and a chemical kinetic equation. The currently most efficient lasers are those based on CO_2 that operate by expansion of a mixture of gases obtained by burning a fuel.[186,187] The chemical reaction of combustion is characterized by a high energy yield, and it can provide considerable pumping into the vibrational degrees of freedom. However, the role of the chemical processes in the expansion stage in these lasers has not yet been elucidated. Besides burning coal[194] to create an inversion, one can burn petroleum

products[180,189] or natural gas, or detonate a solid[193a], etc.

c) **Lasers based on diatomic molecules.** Formation of an inverted population of the vibrational-rotational levels of a given mode is based on creating a separation between the temperature T_{rot} of the rotational degrees of freedom and the effective vibrational temperature T_{n+1} of the vibrational levels n + 1 and n being treated.[195a] For the transition (n + 1, j_1) $\rightarrow$ (n, j_2) (n is the vibrational and j is the rotational quantum number), this condition has the form[135,136]:

$$(E_{n+1} - E_n)/T_{n+1} < [B_{n j_2}(j_2 + 1) - B_{n+1 j_1}(j_1 + 1)]/T_{rot}; \quad (6.5)$$

here B_{n+1} and B_n are the rotational constants of levels n + 1 and n. Equation (6.5) implies that when $T_{n+1} < 0$ (i.e., when there is an absolute population inversion of the vibrational levels), amplification is possible in the P, Q, and R branches of the vibrational-rotational transition. However, when $T_{n+1} > 0$, it can occur only when $j_2 = j_1 + 1$, i.e., only in the P branch. In order that (6.5) be satisfied for relatively low vibrational levels where the populations might still suffice for getting an appreciable coefficient, T_{n+1} must considerably exceed T_{rot}. Since usually T_{rot} coincides with the gas temperature, (6.5) can be satisfied only when the supply of vibrational energy exceeds the equilibrium value. Just as with polyatomic molecules, one can get such a supply by using various pumping mechanisms. The most widespread of these have been chemical and electrical pumping with molecules of the hydrogen halides and CO as the active media.

1) <u>Hydrogen halide lasers.</u> Lasers with working transitions between vibrational-rotational levels of hydrogen halide molecules are currently the main type of chemical lasers (see the reviews[135,136]). Use of exothermic replacement reactions that form hydrogen halides for chemical pumping is based on the fact that vibrationally-excited molecules constitute an appreciable fraction of the products of these reactions. One must analyze the kinetics and the conditions for formation of an inverted population in these lasers by simultaneous solution of the vibrational-relaxation equations and the equation for the gas temperature and the chemical-kinetic equation. For times shorter than τ_{VV}, the populations of the levels are determined by the rates of formation of molecules in the individual vibrational states. Here one can get an absolute population inversion (the rigid time requirements are a defect).

In many cases, the relative rates of formation of molecules in different vibrational levels in a reaction process can be determined from the relationships found in[195b]. The processes in the HCl chemical laser have been analyzed in[87,135,136,196,197]. Figure 10 shows a typical time course for this laser of the effective vibrational temperatures T_n and the amplification coefficient. After a time of the order of τ_{VV} has elapsed since the beginning of the reaction, a quasi-steady-state distribution of the type of (4.5), (4.10) and (5.5) is established over the vibrational levels. If here the reaction imparts an appreciable energy into the vibrational degree of freedom of the molecules, then amplification of radiation can occur in the P-branch (see Fig. 10) that does not depend on the relative rates of the reac-
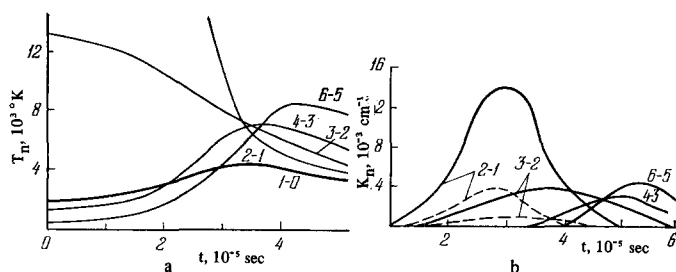
FIG. 10. A Typical time course of the effective vibrational temperatures T_n (a) and of the amplification coefficient k_n for the transition $n \to n-1$ (b) for HCl during a chemical reaction. Original mixture: 1 Torr Cl_2 + 1 Torr H_2 + 10 Torr He. The solid and dotted curves in Fig. b) are for models in which respectively ~40% or ~10% of the chemical energy is converted to vibrational energy. [87]

FIG. 11. Populations of vibrational levels in the CO molecule at various gas temperatures T under typical conditions of laser operation (the mixture is 0.2 Torr CO + 6 Torr He, N_e = 2.5 × 10^9 cm^{-3}, T_e = 20,000 °K). [91]

tions in the different excited states, but is determined by the gas temperature and the total non-equilibrium supply of vibrational energy. One can roughly estimate this energy for a reaction that occurs with an excess of one of the original components by using Eqs. (6.3) and (6.4) and taking τ_{chem} as the characteristic time of the chemical reaction, and D as the reaction energy that is imparted into the vibrational degree of freedom. When the τ_E are relatively large, one can get a considerable density of excited molecules, and hence also considerable laser power. (Often people have obtained laser action from the levels of CO_2 in mixtures of HCl, DF, and HCl with CO_2, rather than from the hydrogen halide molecules.) We emphasize that in the system being studied it is essential to take account of anharmonicity of the vibrations of the molecules, since anharmonic-oscillator processes increase the effective temperatures T_n for the upper levels when $T_1 > T$, (see (4.5) and (4.10)). This also makes it easier for these levels to satisfy the condition (6.5) for forming an inverted population.

A qualitative jump occurred in 1969 in the development of chemical lasers. It involved invention of methods of obtaining considerable concentrations of free atoms,[198-203] and this led to a marked increase in laser power. We can expect a further refinement of chemical lasers along the line of influencing individual steps of chemical reactions and by using high pressures of the reacting gases.[204]

One can also use other ways besides chemical pumping for exciting vibrations in the hydrogen halides. The possibility of getting laser action in HCl and HF from a three-particle recombination reaction has been discussed in[193b] (see also Sec. 4 of Part b). The possibility of getting laser action under steady-state and quasi-steady-state conditions in mixtures like HCl—N_2—He and HI—N_2—He in an electric discharge has been analyzed in[87]. Electrically-excited hydrogen halide lasers can show a number of advantages involving the large size of the rotational quanta (this makes it easier to satisfy (6.5)) and the large anharmonicity of the molecular vibrations (this makes it possible to attain large temperatures T_n). A defect of these systems (as compared with the CO laser) is the high rate of relaxation of the vibrational energy, and apparently, chemical instability in the discharge.
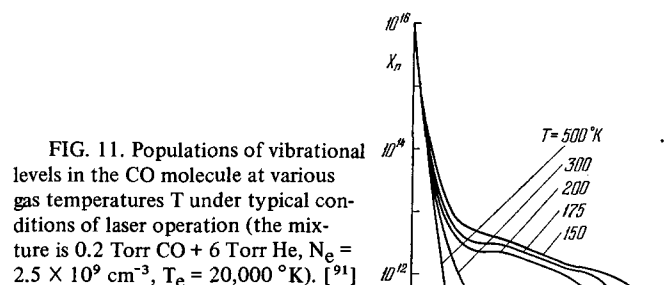
2) The CO laser. The electrical laser based on the

CO molecule is one of the most powerful continuous-wave lasers. Laser action in it occurs in the P-branch and from several vibrational transitions $n \to n-1$, where n usually lies in the range 6—15.[205-209a] One can also get laser action from higher levels up to n = 37 in the Q-modulated pulsed mode.[209a] The studies on the CO laser are reviewed in the publications[141b]. Since the CO laser is a system in which the supply of vibration energy substantially exceeds the equilibrium value, and laser action occurs on the upper levels, one must use an anharmonic molecular model to describe correctly the kinetics of the processes, according to Secs. b—d of Chap. 4. The probabilities of the V − V and V − T transitions between the vibrationally-excited states of CO molecules have been calculated in[209b], and the probabilities were found experimentally in[209C]. The processes in the steady-state CO laser have been analyzed by treating a system of anharmonic Morse oscillators for a CO_2—N_2 mixture in[92], and for a CO_2—He mixture in[91,94,95a]. In[91], the distribution function over the vibrational levels (of the type of (4.10) and (5.5)) and the amplification coefficient for various $n \to n-1$ transitions were obtained as functions of the discharge parameters (the temperature and density of the electrons, the gas temperature T, and the partial pressure of helium) by numerical solution of a non-linear system of 80 equations like (4.7) (with addition of sources that describe excitation of levels by electron impact). Figure 11 shows the distribution function for various values of T. We see that the effective temperature T_n is large for the levels $8 \le n \le 40$, and the conditions are most favorable for appearance of a partial inversion with a sufficient amplification coefficient. On the whole, the analysis based on the anharmonic model gives satisfactory agreement with experiment. We note that, at low gas temperatures and in the absence of helium, which increases the rate of V − T processes, two-quantum exchange (which was ignored in[91-95a]) may prove to be essential. The latter increases the effective temperature on a group of levels above the 40th (see Sec. c of Chap. 4). Therefore, a second band of levels can exist here in which laser action is possible.[88] In order to get an appreciable population on these levels and to attain the necessary amplification coefficient, one apparently needs relatively high pressures ($\gtrsim$ 20 Torr), intense cooling (T ~ 150° K), and a powerful pulsed discharge ($N_e \gtrsim 10^{12}$ cm^{-3}).

One can also get laser action from vibrational-rotational transitions of CO molecules with other pumping mechanisms: chemical[210-213] and thermal.[214] In a chemical laser based on the reaction CS + O → CO* + S, the role of vibrational-exchange processes that form an inverted population has not yet been elucidated. Laser action is observed here in transitions from the 7th up to the 13th level. Here, since amplification can also occur in the R branch (which requires an inverted population in the vibrational levels), it is assumed that CO molecules in highly-excited states are formed by the reaction, with the relative yield increasing with the level number up to n = 13. The rates of the reaction O + CS → S + CO + 75 kcal/mole to produce CO molecules in individual vibrational levels have been measured in[213].

Recently laser action has been obtained from CO transitions by rapid expansion of the gas mixture N_2—CO—Ar.[214] The relaxation processes in the gas-dynamic CO laser have been analyzed in[93] by simultaneous numerical solution of the system of equations for the level populations and gas-dynamic equations. They showed that addition of argon, which hardly affects the rates of the V − T processes, permits a lower gas temperature. As usual, nitrogen serves as an extra reservoir of vibrational energy. Here, since the lowest quantum of N_2 is larger than the quantum of CO, the temperature T_1 for CO does not decline during the cooling process, but it even rises, owing to non-resonance vibrational exchange with N_2 (see (4.23)), and this facilitates creation of an inverted population. Amplification coefficients $\sim 10^{-3}$ cm^{-1} are obtained for transitions on levels 4—16, i.e., sufficient for laser action.

7. CONCLUSION

Analysis of the processes in molecular lasers is only one of the examples of practical application of vibrational kinetics. In general, one must encounter vibrational-relaxation processes in all cases in which the parameters of a molecular gas are altered. These include both the field of gas-dynamic flow accompanied by fast compression or expansion (shock waves, flow through nozzles, etc.), and phenomena involved in the behavior of a gas when acted on by constant or variable generalized forces (temperature and pressure gradients, pumping, etc.). It is also important to take account of vibrational non-equilibrium in chemical kinetic problems. As we know, chemical reactions mainly involve active molecules. Vibrational excitation is one of the forms of activation of molecules. Hence, the stage of vibrational excitation or deactivation can be decisive for an entire series of chemical processes. Within certain limits, a controlled influence on this stage makes it possible to regulate the rate of the overall chemical process. Currently, the field of application of vibrational kinetics is continually expanding, and here we can expect to obtain new and interesting results.

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