VIBRATIONAL-KINETICS METHODS AND THEIR APPLICATIONS TO MOLECULAR LASERS AND LASER CHEMISTRY*

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The vibrational kinetics of molecules simulated by anharmonic oscillators is developed under essentially nonequilibrium conditions. Analytic expressions are obtained for the vibrational distribution function, the relaxation time, and the dependence of the vibrational energy on the pump power; the limiting capacity of the energy reservoir of the anharmonic molecules is estimated. Vibrational kinetics is investigated in mixtures and a redistribution of the vibrational energy among the modes is observed as a function of the component concentration. The singularities of vibrational relaxation in liquids and molecular crystals, due to collective interactions, are studied. A number of concrete applications are considered: the rate of nonequilibrium dissociation is calculated, an analytic model is developed for the CO laser, isotope separation in chemical reactions of vibrationally excited molecules is investigated, and a new type of lasers based on intramolecular transitions in liquids and molecular crystals is proposed.

INTRODUCTION

The last decade has seen a very rapid development of vibrational kinetics, which is the basis of a large number of practical applications, including questions of chemical kinetics and the physics of the atmosphere, gasdynamics and rocket technology, molecular lasers and laser chemistry. By the early 1970s it was recognized that the model of harmonic oscillators and the concept of vibrational kinetics have limitations. For a number of processes, the functional role of the anharmonic molecules was clarified, since it is precisely the system of anharmonic oscillators, which simulates a set of different molecules (diatomic and monatomic), that describes correctly the behavior of real gases in a wide range of nonequilibrium conditions. After the discovery of the new type of population distribution of the vibrational levels (the Treanor distribution), which depends not only on the reserve of vibrational energy but also on the gas temperature and is due to the anharmonicity of the molecules, other quasiequilibrium population distributions were also obtained, valid for nonequilibrium conditions in definite time intervals or for definite level groups. The use of these distributions has made it possible to replace the system of balance equations for many dozens of levels by equations for two or three parameters, made it possible to understand the generation mechanisms of a number of molecular lasers, and to investigate certain aspects of the action of laser radiation on matter. In particular, it made it possible to analyze, for certain regimes, the processes of stimulating a nonequilibrium dissociation chemical reaction with IR radiation.

At the same time, practical needs have raised new important problems of vibrational kinetics, connected with the recently noted three basic trends in the development of the physics of molecular lasers and in the investigation of the interaction of resonant IR laser radiation with molecules:

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First, the use of intense mechanisms for pumping energy into the vibrational degrees of freedom; this use calls for analysis of the vibrational kinetics under conditions of strong deviation from equilibrium, when the temperature of the medium is low, and the nonequilibrium reserve of vibrational energy substantially exceeds the equilibrium volume.

Second, the use of mixtures of molecular gases and gases of polyatomic molecules in the experiments; this requires a theoretical investigation of vibrational relaxation in such systems.

Third, the use of high working gas pressures in pulsed lasers on vibrational—rotational transitions, which raises the question of the possibility of using liquids and molecular crystals as active laser media. It becomes necessary then to study the vibrational relaxation in these media.

The present paper is devoted to the development of these most vital trends of vibrational kinetics. Their analysis yields important information on the electrical, optical, thermal, and other types of action on the molecular systems, and on the use of such systems for laser generation in chemical reactions.

Much attention is being paid in the article to applications of the developed theory of vibrational relaxation to the analysis of concrete physical and physicochemical problems. These problems deal with stimulation of the dissociation reaction, investigation of processes in a CO molecular laser, and the study of the question of isotope separation in chemical reactions of vibrationally excited molecules. The general premises obtained in the paper have made it possible to consider not only the qualitative but also the quantitative aspects of these phenomena.

In Chap. I is developed the theory of vibrational relaxation in a single-component mixture of anharmonic oscillators at strong deviations from equilibrium. The vibrational distribution is considered, the relaxation time of anharmonic oscillators is calculated, and the dependence of the vibrational energy and of the temperature on the pumping probability is investigated.

In Chap. II questions of vibrational kinetics in gas mixtures are considered. The distribution of the vibrational energy among the modes and the vibrational distribution functions inside the modes are obtained for different ratios of the vibrational-process times; the relaxation rates in the presence of two relaxation channels and the rate of energy exchange in the binary mixture of anharmonic oscillators are calculated; the influence of the concentrations of individual components on the distribution of the vibrational energy in the mixture is investigated.

Chapter III considers various applications of the developed theory of vibrational relaxation to concrete physical problems, namely, the analysis of nonequilibrium dissociation of diatomic molecules and the dissociation in a mixture, calculation of the coefficient of isotope separation in chemical reactions, and investigation of physical processes in an electric-discharge CO laser.

In Chap. IV the probabilities of the vibrational processes in liquids and molecular crystals are calculated; the possibility of developing lasers based on intramolecular vibrational transitions in these media, when pumped with a high-power electron beam, is investigated. Also considered is the possibility of stimulating laser-chemical reactions in the liquid phase.

SURVEY OF THE LITERATURE ON VIBRATIONAL KINETICS AND ITS APPLICATIONS

The main stages in the development of vibrational kinetics up to the early 1970s were considered in [1]. In this review the role of various vibrational processes is analyzed (VV — vibrational exchange within a given oscillator, VV' — vibrational exchange between different oscillators, VT — vibrational—transitional exchange). The harmonic approximation and the role of anharmonicity are also discussed in detail. An analysis is presented of the mechanisms of population inversion and lasing on vibrational—rotational transitions of molecules. We mentioned below only the published data dealing with the new trends in the development of vibrational kinetics, and only directly related to the results of the present paper.

The importance of a consistent allowance for the anharmonicity of molecules in vibrational kinetics has already been noted in the Introduction. We consider first papers dealing with the relaxation of a single-component mixture of anharmonic oscillators. As shown in the basic paper of Treanor, Rich, and Rem [2], under nonequilibrium conditions, in contrast to the harmonic model, the distribution of the populations of the vibrational levels in a system of anharmonic oscillators (even if the distorting action of the sources is neglected) differs substantially from a Boltzmann distribution. In the cited paper they solved the kinetic equations for the populations of the vibrational levels under the assumption that the VV processes play the dominant role, and obtained the following expression for the vibrational distribution function f(n) in a single-component system of anharmonic oscillators:

$$f(n) = f(0)\exp\left\{-n\left[\frac{E_1}{T_1} - (n-1)\frac{\Delta E}{T}\right]\right\}. \tag{0.1}$$

Here n is the number of the vibrational level; E_1 and ΔE, values of the lower vibrational quantum and the anharmonicity of the oscillator (°K); T, gas temperature; and T_1, "vibrational temperature" of the first level:

$$T_1 = E_1/\ln[f(0)/f(1)]. \tag{0.2}$$

Distribution (0.1), later called the Treanor distribution, is characterized already not by one but by two parameters (T_1 and T), and its difference from a Boltzmann distribution is larger the greater the difference between T and T_1 and the larger ΔE. At $T_1 > T$, repopulation of the upper vibrational levels takes place, and starting with the level

$$n^* = \frac{E_1}{2\Delta E}\frac{T}{T_1} + 0.5, \tag{0.3}$$

absolute calculation inversion between the vibrational levels is realized.

Kuznetsov [3] derived distribution (0.1) from the detailed balancing principle and from the grand canonical distribution of a system of anharmonic oscillators in energy and in particle number, and calculated the rate of the quasistationary thermal dissociation. For real molecular systems, the Treanor distribution, obtained without allowance for the VT and radiation processes, and positive and negative molecule sources, is valid only for sufficiently low vibrational levels. To take into account these processes, a number of numerical calculations were made to determine the quasistationary [4-13] or nonstationary [14] distribution functions for individual molecules under concrete conditions.

Vibrational relaxation in molecules (anharmonic oscillators) that constitute a small admixture in a gas of structureless particles (i.e., in the case when there are no VV processes) was theoretically investigated in [15-18]. Frequently, however, great practical interest is attached to molecular systems in which the dominant role is played by VV processes, at least for the group of lower vibrational levels. For such systems, in the particular case of weak deviation from equilibrium, the problem of finding the vibrational distribution function for the entire vibrational spectrum was analytically solved in the papers of Gordiets, Osipov, and Shelepin [19-21], and also in the papers of Savva [22]. The lucid solutions they obtained for the kinetic equations show that when account is taken of the vibrational—translational processes, the distribution on the intermediate vibrational levels is neither Boltzmann nor Treanor. Using the analytic form of the vibrational distribution function, the authors of [21] estimated the rate of nonequilibrium dissociation that takes place at low gas temperature.

The influence of two-quantum VV transitions (i.e., transitions in which one quantum of one oscillator is exchanged for two quanta of another oscillator) and the vibrational distribution function were investigated in [19]. This function is determined on different sections of the vibrational spectrum by the competition between the probabilities of the single-quantum and two-quantum exchanges and of the VT process. In each of these sections, an analytic expression was obtained for the populations.

The investigations reported in [19-21] are valid for weak deviations from equilibrium. In the case of strong deviations, when the margin of the vibrational energy greatly exceeds the equilibrium value, the upper vibrational levels are noticeably populated. In addition, besides the other processes, a significant role is assumed by resonant exchange of vibrational quanta, i.e., as a result of the strong dependence of the exchange probability on the

transition-energy deficit, an important role is assumed in the kinetic equations by the terms that describe exchange with neighboring levels of colliding molecules. For these conditions, Brau [23] obtained in a classical approximation a kinetic equation for the distribution function and found its solution for a bounded region of the spectrum. This equation, however, is unsuitable for the case of practical importance, that of low gas temperatures $T \ll E_1$.

Besides the analysis of the distribution function of the populations for a one-component system of anharmonic oscillators, some studies [2, 4, 5, 24] investigated the characteristic times τ_{VT} of the VT processes in anharmonic oscillators. The strong dependence of the probabilities on the transition energy leads in such oscillators to a deviation of the time τ_{VT} from the classical Landau–Teller expression $\tau_{VT} \approx P_{10}^{-1}$, where P_{10} is the probability of deactivation of the first vibrational level. This difference is illustrated in the papers of Treanor et al. [2] and Bray [4, 5]. We note that the calculation was carried out in these papers by numerical methods for certain concrete cases. For this reason, it is difficult to analyze the calculation and to draw generalizing conclusions.

Losev, Shatalov, and Yalovik [24] obtained an analytic expression for τ_{VT}^{anh}, taking into account the exponential dependence of the probabilities of the VT process on the number of the level. However, owing to the proposed Boltzmann type of distribution function of the populations, the result (which agrees qualitatively with experiments in shock waves) is only approximate at low T.

A number of studies [25-33] were made of the dependence of the reserve of vibrational energy ε (or T_1) on the pump power ("external" positive source). Artamonova, Platonenko, and Khokhlov [25] obtained such a dependence in the harmonic model also for the case where the pump acts on the 0–1 transition. The maximum value of T_1/E_1 was determined in this case by the expression $\sqrt{Q_{10}/P_{10}}$ where Q_{10} and P_{10} are the probabilities of VV and VT processes for the lower levels. The nonequilibrium kinetics of molecules in resonant radiation (of any multiplicity) and in a cascade mechanism was considered in general for a harmonic model in [26-30], and for an anharmonic model, assuming the VV processes to play the dominant role, in [33].

It is thus seen from the brief survey of the works on single-component systems of anharmonic oscillators that whereas the case of weak deviation from equilibrium has been investigated quite satisfactorily, the case of strong deviation from equilibrium has hardly been developed, although the practical need for it is great. The analysis of the vibrational distributions, the investigation of characteristic times, and the questions dealing with the pumping are therefore most vital problems for this regime.

Vibrational relaxation in gas mixtures, connected with the analysis of multicomponent oscillator systems, has a more complicated character and was much less investigated than relaxation in single-component systems. Principal attention was paid here to the study of the distribution of the energy among the modes as a result of VV' processes of vibrational nonresonant exchange. The quasiresonant distribution among two modes in single-quantum nonresonant VV' exchange was first determined by Osipov [34]. It was shown in [2] for this case that the vibrational temperatures T_A and T_B of two harmonic oscillators A and B are connected by the relations

$$E_A/T_A = E_B/T_B - (E_B - E_A)/T. \tag{0.4}$$

Here E_A and E_B are the values of the vibrational quanta for the oscillators A and B, respectively. It is seen that at T_A, $T_B > T$ a redistribution of the vibrational levels of the oscillator with the smaller quantum takes place. This result was qualitatively confirmed in experiment [35]. Expression (0.4) was subsequently generalized to include the case of one-quantum exchange with participation of arbitrary vibrational modes [36], two-quantum exchange with participation of two oscillators [19], and multiquantum exchange between oscillators [37]. Biryukov and Gordiets [38] obtained in the harmonic approximation the most general kinetic equations for a multicomponent mixture, and generalized expression (0.4) to include multiquantum VV' exchange with participation of an arbitrary number of modes. The distribution functions and the dependence of the vibrational energy of the modes on the probability of the excitation of the vibration were obtained in [30] for a two-component system of harmonic oscillators with different rates of the VT processes in both modes.

The distribution function in a two-component system of anharmonic oscillators was investigated only in particular cases: in VV' exchange [39], and with allowance for VT processes with weak deviation from equilibrium [21].

We note that expression (0.4) describes a rigid connection between the temperatures of the individual vibrational modes and is valid if the following relation holds between the characteristic times of the VV, VV', and VT processes:

$$\tau_{VV},\ \tau_{VV'} \ll \tau_{VT}. \tag{0.5}$$

It is thus seen from the foregoing discussion that the investigation of vibrational kinetics in gas mixtures is far from complete. For many practical applications it is important to lift restriction (0.5) and to investigate the case $\tau_{VV'} \sim \tau_{VT}$, and to determine $\tau_{VV'}$ with account taken of the anharmonicity. It is also very important to analyze the distribution functions of multicomponent systems of anharmonic oscillators in the case of strong deviation from equilibrium.

Vibrational relaxation in dense gases and liquids can differ strongly from the relaxation in gases of moderate density. We note here that the vibrational kinetics of liquids is in any case in the initial stage of development at present. The reason is that besides binary collisions, which determine in practice the vibrational processes in gases, it is necessary to take into account in liquids the collective actions of neighboring molecules. (For superdense gases it is necessary to take into account multiple collisions [40-42].)

Various model assumptions were made in [43, 44] to estimate the probabilities of vibrational—translational transitions of molecules in liquids. The probability of VT processes under conditions when the action of neighboring molecules is simulated by the effect of an external periodic force on a selected molecule was estimated by Ismailov [44], but he did not specify the connection of the amplitude and frequency of this force with the parameters of the liquid. Herzfeld [43] simulated the nearest environment by a sphere whose action on a molecule situated at its center is given by a Lennard-Jones potential. He also calculated the relaxation time due to collective interaction of neighboring molecules for a particular case (see also [41]) and showed that it is several dozen times larger than the experimental values. It was therefore concluded in [41, 54] that the mechanism of vibrational relaxation in nonassociated and weakly associated liquids is due principally to binary collisions. It was shown in [45, 46] that there exist a number of liquids for which explanation of the experimental data calls for the assumption that two or more relaxation times are present.

The question of vibrational relaxation in molecular crystals have been studied even less. Notice should be taken here of the work of Ovchinnikov and Zel'dovich [47, 48]. In [47] estimates are made of the times of VV exchange of a highly excited quantum of an anharmonic oscillator with the lowest quantum, and it is shown that these times can be quite long as a result of the large energy defect. Vibrational kinetics in molecular crystals, which were simulated by anharmonic oscillators, was investigated in [48], where a distribution function was found similar to the distribution function in gases at weak deviation from equilibrium [21]. On the whole, the general situation for liquids in molecular crystals in this region is such that, in contrast to gases, it is necessary above all to analyze the foundations of the vibrational relaxation, i.e., to estimate the characteristic times of the vibrational processes.

Various aspects of the application of vibrational kinetics, particularly to dissociation, molecular lasers, and chemical kinetics, were considered in [1, 49-61]. A new recent trend is the focusing of attention on the important problem of the action of infrared (IR) radiation on matter.

Artamonov, Platonenko, and Khokhlov [25] were the first to consider the possibility of controlling a chemical reaction by acting on a selected vibrational mode of the molecule with coherent IR radiation. The estimated laser power turned out to be quite sufficient for an effective "heating" of the vibrations. Chemical reactions induced by IR laser radiation were experimentally investigated in [62-64].

Theoretical investigations of the chemical reactions induced by resonant IR lasers are the subject of [21, 26, 27, 65-72]. In [21] the dissociation rate constant is calculated, and in [65] the dissociation rate and the energy reserve in a one-component system of

harmonic oscillators is calculated, under the assumption that the energy dissociates via a dissociation channel. In [69], similar calculations were carried out for anharmonic oscillators. The dissociation rate in the case of cascaded multiphoton excitation of oscillations by laser radiation with participation of VV and VT processes, for the harmonic and anharmonic models of truncated oscillators, was calculated in [26, 27, 66]. In [67, 70] the problem of dissociation of truncated harmonic oscillators in the case when high-power laser radiation "chases" the molecules to the dissociation limit was considered. Quasistationary adiabatic dissociation is considered in [71], where it is shown that the gas can be cooled as a result of an endothermic dissociation reaction.

We note, however, that dissociation in the most intensive regime of strong deviation from equilibrium and in molecule mixtures has hardly been considered. Since monatomic gases and molecular mixtures are used in the experiments, and a very large amount of energy is fed to the vibrational degrees of freedom when laser radiation acts on the substance, while the temperature of the gas of the medium usually remains low, an analysis of this problem under the indicated conditions is becoming vital.

A new field of application of vibrational kinetics is isotope separation in chemical reactions of highly excited molecules. This possibility was first pointed out in [73], where the isotope-separation coefficient was calculated under the assumption that each component of the isotopic molecules has a Boltzmann distribution. Soon afterwards, Basov et al. [74, 75] obtained an experimental confirmation of this phenomenon. On the other hand, a quantitative study of this problem is possible only on the basis of the development of the theory of vibrational kinetics in mixtures.

As emphasized in [1], one of the most important applications of vibrational relaxation is the investigation of the operation of molecular lasers. A detailed analysis of the vibrational kinetics of anharmonic oscillators has demonstrated the need for taking into account the influence of the anharmonicity of the molecule on the physical processes that take place in the laser medium. In the case of lasers based on vibrational—rotational transitions of diatomic molecules (e.g., CO lasers), it turned out to be even impossible to explain the lasing mechanism without invoking the anharmonicity of the working-gas molecules. The theoretical investigations, however, were made in this case on the basis of a numerical solution of a large number (from 20 to 80) population-balance equations [6-11, 52-54]. It is obvious that while this approach is indeed capable, in principle, of providing the necessary accuracy, its practical use is restricted.

The applied problems considered above are, in our opinion, the most vital. Therefore, besides developing methods of vibrational kinetics on their basis, we have also carried out a quantitative and qualitative analysis of the indicated applied problems.

CHAPTER I

VIBRATIONAL KINETICS OF A SINGLE-COMPONENT SYSTEM OF ANHARMONIC OSCILLATORS

A theory of vibrational relaxation is developed for a single-component system of anharmonic oscillators. An approximation based on a stong deviation from equilibrium is proposed and obtained. Analytic expressions are derived for the distribution functions of the populations and for the relaxation rates of the vibrational energy. The dependence of the reserve of the vibrational energy and of the "vibrational temperature" on the pump is investigated. The results of this chapter are based on [76-80].

1. Vibrational Distribution Function

A single-component system of anharmonic oscillators that simulate the gas of diatomic molecules can have, under nonequilibrium conditions, a vibrational-level population distribution that differs substantially from a Boltzmann distribution. For the group of lower levels there is realized the Treanor distribution (0.1), obtained under the assumption that the only process in this system is VV exchange. In real systems, however, an important role is played for the highly excited states by the VT processes, by radiative transitions (for radiating molecules), and by chemical reactions (e.g., dissociation). In the general case, therefore, the vibrational distribution function should be obtained by solving a nonlinear system containing a large number of population-balance equations (up to several dozen). On

the other hand, the known analytic distribution functions [19-23] describe only cases of relatively small deviations of the vibrational energy from the equilibrium, when the principal role among the VV processes is played by nonresonant vibrational—vibrational exchange of highly excited states with the lower quanta. The only exception is [23], but the kinetic equations obtained there are not suitable for the case of greatest interest, that of low gas temperatures, and the distribution function was obtained for a limited number of vibrational levels.

To find the population distribution of the vibrational levels under nonequilibrium conditions we shall use, following [22, 23], the diffusion approximation and assume a smooth variation of the populations on going from level to level. In the derivation of the equation for the corresponding vibrational distribution function, however, we shall start from the usual system of balance equations for the populations N_n of the vibrational levels n:

$$\frac{dN_n}{dt} = \frac{1}{N}\sum_m (Q^{m,m+1}_{n+1,n} N_m N_{n+1} - Q^{m+1,m}_{n,n+1} N_{m+1} N_n) - \frac{1}{N}\left(\sum_m Q^{m,m+1}_{n,n-1} N_m N_n - Q^{m+1,m}_{n-1,n} N_{m+1} N_{n-1}\right) + \\ + (P_{n+1,n} N_{n+1} - P_{n,n+1} N_n) - (P_{n,n-1} N_n - P_{n-1,n} N_{n-1}) + \\ + A_{n+1,n} N_{n+1} - A_{n,n-1} N_n + F_n, \quad n = 0, 1, 2, \ldots, k. \tag{1.1}$$

Here N is the density of the molecules; $Q^{p,q}_{i,j}$, probability (in sec^{-1}) of the vibrational exchange when a transition to the levels q and j takes place as a result of collision of molecules located on the levels p and i; P_{ij} and A_{ij}, probabilities (in sec^{-1}) of the collisional and spontaneous radiative transitions $i \to j$; F_n, a term describing the change of the population of the n-th level on account of external actions (its form will be specified later for electric and optical pumping); and k, total number of vibrational levels of the molecule. Equation (1.1) takes into account only single-quantum transitions, which play the principal role in the population of the levels.

Transferring F_n in (1.1) to the left-hand side and summing over n from 0 to i, we obtain

$$\sum_{n=0}^{i}\left(\frac{dN_n}{dt} - F_n\right) = \frac{1}{N}\sum_m (Q^{m,m+1}_{i+1,i} N_m N_{i+1} - Q^{m+1,m}_{i,i+1} N_{m+1} N_i) + P_{i+1,i} N_{i+1} - P_{i,i+1} N_i + A_{i+1,i} N_{i+1}. \tag{1.2}$$

The physical meaning of (1.2) is quite simple: in energy space this is the total flux of molecules through an arbitrary cross section between the energy levels i + 1 and i. The probabilities of direct and inverse transitions in (1.1) and (1.2) are connected by the usual relations:

$$Q^{m+1,m}_{i,i+1} = Q^{m,m+1}_{i+1,i} \exp[-2\Delta E(m-i)/T], \tag{1.3}$$

$$P_{i,i+1} = P_{i+1,i} \exp[-(E_1 - 2\Delta E i)/T]. \tag{1.4}$$

Here T is the gas temperature (in °K) and E_1 and ΔE are, respectively, the values of the lower vibrational quantum of the molecule and its anharmonicity (in °K).

We shall assume hereafter that the gas temperature is substantially lower than the characteristic value (i.e., $T \ll E_1$), and shall be interested in the populations of the levels i such that

$$E_1 - 2\Delta E i \gg T. \tag{1.5}$$

In addition, we shall assume that exchange of vibrational quanta can influence the level populations only when the resonance defect $2\Delta E(m - i)$ is such that

$$2\Delta E\,|m - i| \ll T. \tag{1.6}$$

If the populations vary slowly with changing number of the level, then the term $P_{i,i+1}N_i$ in (1.2) can be neglected if (1.5) is satisfied. We note also that condition (1.6) is not stringent and is usually satisfied in a wide range of temperatures.

It is now convenient to change from (1.2) to the diffusion approximation. Considering, for simplicity, a quasistationary regime and assuming that the external perturbations take place only for the very lowest levels, we can set the left-hand side of (1.2) equal to zero. We introduce a continuous vibrational distribution function f(i) such that

$$N_i = Nf(i), \qquad N_{i+1} = Nf(i)\left[1 + \frac{d\ln f(i)}{di}\right]. \tag{1.7}$$

Form (1.7) presupposes a smooth variation of the populations on going from level to level, i.e., satisfaction of the relation

$$d\ln f(i)/di \ll 1. \tag{1.8}$$

Expanding the exponential in (1.3) in a series of substituting (1.3) and (1.7) in (1.2), we obtain, after replacing the summation by integration,

$$\int Q_{i+1,i}^{m,m+1} f(m)\left[\frac{d\ln f(i)}{di} - \frac{d\ln f(m)}{dm} + \frac{2\Delta E}{T}(m-i)\right]dm + P_{i+1,i} + A_{i+1,i} = 0. \tag{1.9}$$

Relation (1.9) is an integrodifferential equation for the vibrational distribution function f(i) in the quasistationary regime, and is valid if the relations (1.5), (1.6), (1.8) are satisfied, i.e., under the conditions of interest to us. The main difference between (1.9) and the analogous equations of [22, 23] lies in the expression for the term that describes the vibrational–translational relaxation, inasmuch as it was included in (1.9) with relations (1.4), (1.5), and (1.8) taken into account. If we put $P_{i+1,i} = 0$ in (1.9), then its solution is, as expected, the Treanor distribution function [2]

$$f_{\mathrm{Tp}}(i) = f(0)\exp\left\{-i\left[\frac{E_1}{T_1} - \frac{\Delta E}{T}(i-1)\right]\right\}, \tag{1.10}$$

where $T_1 = E_1/\ln[f(0)/f(1)]$ is the "vibrational temperature" of the first level, determined from the overall nonequilibrium reserve of the vibrational energy of the system.

To solve (1.9) we must know the dependence of the probabilities on the number of the vibrational levels. We shall henceforth use, for simplicity, mainly probabilities, where the anharmonic effects are taken into account only in calculations of the exponential factors that give the most significant dependence on the energy, and consequently also on the anharmonicity ΔE. If in this case, when determining the exchange probabilities, we take into account only the short-range interaction forces of the colliding molecules, we get [1, 81, 82]:

$$\begin{gathered} Q_{i+1,i}^{m,m+1} \approx (m+1)(i+1)Q_{10}\exp(-\delta_{VV}|i-m|)\left[\frac{3}{2} - \frac{1}{2}\exp(-\delta_{VV}|i-m|)\right], \\ P_{i+1,i} \approx (i+1)P_{10}\exp(\delta_{VT}i), \qquad A_{i+1,i} \approx (i+1)A_{10}. \end{gathered} \tag{1.11}$$

Here $\delta_{VV} \approx 0.427\sqrt{\mu/T}\Delta E/\alpha$, μ is the reduced mass of the colliding particles (in a.u.), α is the constant in the exponential potential of the intermolecular interaction (in A). The expression for δ_{VT} is similar, but μ and α can be different if the VT processes are determined by collisions with the impurity gas.

An analytic solution of (1.9) with allowance for the last two terms can be obtained only under certain approximations. Let us examine these approximations, transforming (1.9) to differential form.

We discuss first the case of "weak" deviation from equilibrium. By this term we designate a regime in which the principal processes for highly excited molecules are collisions with molecules in low vibrational states (this regime is analogous to that considered in [19-21] in the discrete approximation). The main contribution to the integral in (1.9) is then made by terms with small m. Substituting, therefore, function (1.10) in place of f(m) as a first approximation, and integrating approximately, we obtain for f(i) the differential equation

$$\frac{1}{f}\frac{df}{di} \approx -\left(\frac{E_1}{T_1} - \frac{2\Delta E i}{T} + \frac{\Delta E}{T}\right) - \frac{2}{3f(0)}\left(\frac{E_1}{T_1} - \delta_{VV}\right)^2\left\{\frac{P_{10}}{Q_{10}}\exp[(\delta_{VV} + \delta_{VT})i] + \frac{A_{10}}{Q_{10}}\exp(\delta_{VV}i)\right\}. \tag{1.12}$$

This equation has a simple solution

$$\begin{gathered} f(i) = f(0)\exp\left\{-i\left[\frac{E_1}{T_1} - \frac{\Delta E}{T}(i-1)\right] - \frac{2}{3}\left(\frac{E_1}{T_1} - \delta_{VV}\right)^2 \right. \\ \left. \left[\frac{P_{10}\{\exp[(\delta_{VV} + \delta_{VT})i] - 1\}}{Q_{10}f(0)(\delta_{VV} + \delta_{VT})} + \frac{A_{10}[\exp(\delta_{VV}i) - 1]}{Q_{10}f(0)\delta_{VV}}\right]\right\}. \end{gathered} \tag{1.13}$$

It can be shown that under conditions when (1.12) and (1.13) are applicable $f(0) \approx E_1/T_1$. On the lower levels, owing to the low values of P_{10}/Q_{10} and A_{10}/Q_{10}, expression (1.13) is close to (1.10), as expected. We note that in distribution (1.13), at certain values

of the parameters T, T_1, P_{10}, Q_{10}, and A_{10}, absolute inversion of the population of the vibrational levels is possible. This inversion can exist only for states above the level corresponding to the minimum of function (1.10). The number n* of this level is

$$n^* = \frac{E_1}{2\Delta E}\frac{T}{T_1} + \frac{1}{2}. \tag{1.14}$$

It is necessary to bear in mind, however, that if i > n*, the terms containing P_{10} and A_{10} in (1.13) remain considerably smaller than the first term in the argument of exponential, then Eq. (1.13) cannot be used to calculate the distribution function. Indeed, in this case, owing to the appreciable absolute inversion, the populations of the levels i > n* will be comparable with the populations of the lower states, and the principal role among the VV processes will be played not by exchange with the lower vibrational quanta (this was assumed in the derivation of (1.13)), but by collisions of two highly excited molecules with a small resonance defect in the quantum exchange. This situation takes place usually at the strongest deviations of the vibrational energy from the equilibrium value, i.e., at low gas temperatures and high values of T_1. This will hereafter be called the regime of "strong" deviation from equilibrium.

For the indicated case, Eq. (1.12) is not valid, and (1.9) can be transformed to differential form in a different manner, by recognizing that at low gas temperatures the parameter δ_{VV} (see (1.11)) is such that the exchange probability $Q^{m,m+1}_{i+1,i}$ has a sharp maximum at m = i. This means that the main contribution to the integral in (1.9) is made by the vicinity of the point i, where function f(m) can be expressed in terms of f(i) by expansion in powers of (m − i) [23]:

$$f(m) \approx f(i) + \frac{df(i)}{di}(m-i) + \frac{1}{2}\frac{d^2 f(i)}{di^2}(m-i)^2 + \ldots \tag{1.15}$$

Substituting (1.11) and (1.15) in (1.9) and integrating with respect to m, we obtain one more form of the differential equation for the vibrational distribution function f(i):

$$\frac{3Q_{10}}{\delta^3_{VV}}\frac{d}{di}\left[(i+1)^2 f^2\left(\frac{2\Delta E}{T} - \frac{d^2 \ln f}{di^2}\right)\right] + P_{10}(i+1)e^{\delta_{VT} i} f + A_{10}(i+1) f = 0. \tag{1.16}$$

Thus, the system with a large number of equations, of the type (1.1), is replaced by a single nonlinear differential equation of the third order. Even this circumstance alone greatly simplifies the problem of finding the distribution function. Unfortunately, Eq. (1.16) does not have a clear analytic solution. It is possible, however, to obtain an approximate analytic solution for the levels i > n*, by recognizing that for a wide range of the parameters T, T_1, Q_{10}, P_{10}, A_{10} in the region $i \gtrsim n^*$†

$$d^2 \ln f/di^2 \ll 2\Delta E/T. \tag{1.17}$$

Under condition (1.17), the solution of (1.16) takes the form

$$f(i) = \frac{C}{i+1} - \frac{P_{10}}{Q_{10}}\frac{T\delta^3_{VV}}{12\Delta E\delta_{VT}}\frac{e^{\delta_{VT} i}}{i+1} - \frac{A_{10}}{Q_{10}}\frac{T\delta^3_{VV}}{12\Delta E}, \qquad i \geqslant n^*. \tag{1.18}$$

Following [23], we determine the integration constant C from the boundary condition at the point i = n*:

$$f(n^*) = e^{-0.5} f(0)\exp\left\{-n^*\left[\frac{E_1}{T_1} - (n^*-1)\frac{\Delta E}{T}\right]\right\} = f(0)\exp\left[-\frac{\Delta E}{T}(n^*)^2 - 0.5\right]. \tag{1.19}$$

In this case it can be assumed with good accuracy that on the levels i < n* the distribution function takes the form (1.10). Only in a small vicinity of the point n* at i < n* will the exact solution of (1.16) differ from the Treanor solution (1.10) and go over smoothly into (1.18).

One frequently uses in the calculations, besides (1.11), also probabilities in which the anharmonic effects are taken into account approximately also when the preexponential factors are calculated. In this case the probabilities $Q^{m,m+1}_{i+1,i}$, $P_{i+1,i}$ and $A_{i+1,i}$ in (1.11) must be multiplied, respectively, by the factors

†When solving (1.16) it was assumed in [76, 77] that $d^2 \ln f/di^2 = -4\Delta E/T$. A correction factor must be introduced in the corresponding formulas of [76, 77] if the more accurate condition (1.17) is used.

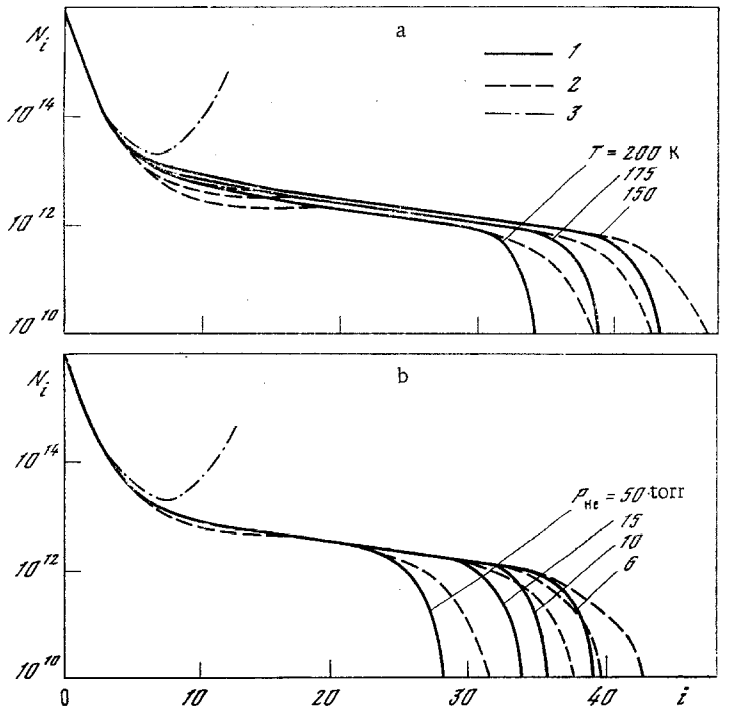

Fig. 1. Dependence of the populations of the CO vibrational levels, on the number i of the level, in a mixture 0.2 torr CO + 6 torr He at various gas temperatures (a) and in mixtures 0.2 torr CO + p torr He (b) at an exciting-electron density $2.5 \cdot 10^9$ cm^{-3}. 1) Present results, 2) numerical calculation by Rich [6], 3) the Treanor distribution [2] at T_1 = 1950 K, T = 150 K (a) and T_2 = 2050 K, T = 175 K (b).

$$\left(1-\frac{\Delta E}{E_1}i\right)^{-1}\left(1-\frac{\Delta E}{E_1}m\right)^{-1},\quad \left(1-\frac{\Delta E}{E_1}i\right)^{-1},$$
$$\left(1-\frac{\Delta E}{E_1}i\right)^{-1}\left(1-\frac{2\Delta E}{E_1}i\right)^{3}.$$

Equations (1.12) and (1.16) are also correspondingly modified, and the solution that takes the place of (1.18) has the form

$$f(i)=\left[C-\frac{P_{10}}{Q_{10}}\frac{T\delta_{VV}^3}{12\Delta E\delta_{VT}}e^{\delta_{VT}i}+\frac{A_{10}}{Q_{10}}\frac{T\delta_{VV}^3}{12\Delta E}\frac{E_1}{8\Delta E}\left(1-\frac{2\Delta E}{E_1}i\right)^4\right]\frac{1-\Delta Ei/E_1}{i+1},\quad i\geqslant n^*. \tag{1.20}$$

From the form of solutions (1.18) and (1.20) it is clear that they have no physical meaning for the group of levels where f(i) < 0. This restriction on the domain of the solution is due to the use of relation (1.17) in the derivation of (1.18) and (1.20), and also to the fact that Eq. (1.16) itself is valid only for levels where (1.5) is satisfied. We note, however, that the level populations for which (1.18) and (1.20) yield negative f(i) are quite small and make no contribution to the overall reserve of the nonequilibrium vibrational energy.

Figure 1 shows a comparison of the distribution function calculated from formulas (1.10), (1.19), (1.20) with exact calculations made in [6] by numerically solving 80 nonlinear balance equations. It is seen that the agreement is good for a large group of levels. For levels i < n* the distribution is of the Treanor type (1.10), and at i > n* no inversion of the vibrational levels is produced and the distribution takes the form of a gently sloping plateau, this being due to the predominant role of the first terms in (1.18) and (1.20). With increasing i, an ever-increasing role is assumed by the second terms of (1.18) and (1.20), causing in the final analysis an abrupt decrease of the populations. The number n** of the level corresponding to this sharp inflection in the distribution func-

tion can be approximately determined from the condition $f(n^{**}) = 0$. For nonradiating oscillators we have

$$e^{\delta_{VT} n^{**}} = C\,\frac{Q_{10}\cdot 12\Delta E\delta_{VT}}{P_{10}T\delta_{VV}^3} = e^{\delta_{VT} n^*} + (n^*+1)\,\frac{Q_{10}}{P_{10}}\,\frac{12\Delta E\delta_{VT}}{T\delta_{VV}^3}\,f(0)\exp\left[-\frac{\Delta E}{T}(n^*)^2 - 0.5\right]. \qquad (1.21)$$

Knowledge of the inflection point n^{**} is important for the determination of the relaxation rate of the vibrational energy under strong nonequilibrium conditions. Thus, when the conditions (1.5), (1.6), (1.8) are satisfied, the functions (1.10), (1.13), (1.18) and (1.20) are the vibrational distribution functions, respectively, for the conditions of "weak" and "strong" deviation from equilibrium. It is clear that with increasing reserve of vibrational energy and with decreasing gas temperature, function (1.13) should be gradually transformed into (1.10), (1.18), and (1.20). The values of T_1 and T corresponding to this change of regimes can be approximately determined from the condition that for functions (1.10), (1.18), and (1.20) the particle flux through the level n^* due to the nonresonant vibrational exchange with the lower quanta is equal to the flux due to the quasiresonant collisions with the molecules on the levels $n \geqslant n^*$:

$$\sum_{m=1}^{n^*-1} Q_{n^*,\,n^*+1}^{m,\,m-1} f(m) f(n^*) = \sum_{m=n^*}^{n^{**}} Q_{n^*,\,n^*+1}^{m,\,m-1} f(m) f(n^*). \qquad (1.22)$$

Substituting in the left-hand side of (1.22) the function (1.10), and in the right-hand side the expression

$$f(m) \approx \frac{C}{m+1} = f(0)\,\frac{n^*+1}{m+1}\exp\left[-\frac{\Delta E}{T}(n^*)^2 - 0.5\right],$$

we obtain after approximate summation

$$\exp\left(-\frac{E_1}{T_1} - \delta_{VV} n^*\right)\left[1 - \exp\left(-\frac{E_1}{T_1} + \delta_{VV}\right)\right]^{-2} = \frac{n^*+1}{\delta_{VV}}\exp\left[-\frac{\Delta E}{T}(n^*)^2 - 0.5\right]. \qquad (1.23)$$

The dependences of T_1/E_1 on $\Delta E/T$, satisfying the condition (1.23) at various δ_{VV}, are shown in Fig. 2. The obtained curves divide the plane of the points (T_1/E_1, $\Delta E/T$) into two regions corresponding to the regimes of "strong" and "weak" deviations from equilibrium. The upper region, where the right-hand side of (1.23) becomes larger than the left-hand side, corresponds to the "strong" deviation from equilibrium, and the vibrational distribution function is determined in this case by expressions (1.10), (1.18), and (1.20). For the points (T_1/E_1, $\Delta E/T$) from the lower region, the inequality is reversed, meaning a weak deviation from equilibrium and a distribution function either in the form (1.13) (for $T_1/E_1 > 1$) or in the form obtained in [19, 21] (at arbitrary T_1/E_1).

The entire preceding analysis of the distribution functions is based on the assumption that the exchange probabilities $Q_{i+1,i}^{m,m+1}$ are determined only by the short-range interaction forces of the colliding molecules. However, for molecules having a nonzero dipole moment, in collisional exchange of quanta with a small resonance defect, an important contribution to the exchange probability can be made by a long-range interaction force [14, 82-84]. In this case, the quantity $Q_{i+1,i}^{m,m+1}$ is equal to the sum of the probabilities calculated with account taken of short-range and long-range forces. If the anharmonicity is taken into account here only in the calculation of the exponential factors, then we can write in place of (1.11) [14]

$$Q_{i+1,\,i}^{m,\,m+1} = (m+1)(i+1)\left\{Q_{10}^{S}\exp(-\delta_{VV}|i-m|)\right.$$
$$\left.\left[\frac{3}{2} - \frac{1}{2}\exp(-\delta_{VV}|i-m|)\right] + Q_{10}^{L}\exp[-\Delta_{VV}(i-m)^2]\right\}, \qquad (1.24)$$

where Q_{10}^{S} and Q_{10}^{L} are the probabilities of resonant exchange for the lowest levels 0 and 1, calculated with account taken respectively of only the short-range and long-range forces, and Δ_{VV} is a parameter determined by the temperature of the gas, by the masses of the colliding particles, and by the character of the long-range forces.

When (1.24) is used in place of (1.11), analytic expressions can be obtained also for the vibrational distribution function at "strong" deviation from equilibrium. In this case, the calculation is perfectly analogous to that considered above and reduces in final analysis to replacement in (1.16) and in Eqs. (1.18), (1.20), and (1.21) of the quantity Q_{10} by $\varkappa Q_{10}^{S}$, where the factor $\varkappa$ is calculated from the equation

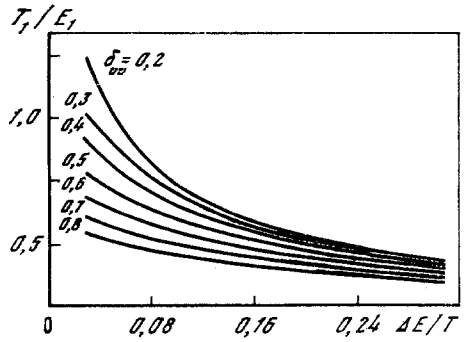

Fig. 2. Values of T_1/E_1 as functions of $\Delta E/T$ at different δ_{VV}.

$$\varkappa = 1 + \frac{\delta_{VV}^3}{12\Delta_{VV}} \sqrt{\frac{\pi}{\Delta_{VV}}} \frac{Q_{10}^L}{Q_{10}^S}. \tag{1.25}$$

2. Vibrational-Energy Relaxation Time

The concrete form of the distribution function obtained in the preceding section is determined by the deviation of the vibrational energy of the molecules from the equilibrium value. In a system of harmonic oscillators, the relaxation time of this energy does not depend on its magnitude, and in accordance with the well-known Landau–Teller expression, is determined only by the probability P_{10} of deactivation of the first vibrational level. On the other hand, for anharmonic oscillators under nonequilibrium conditions, owing to the repopulation of the upper levels, where the deactivation probabilities are large, the relaxation time can be substantially decreased and, furthermore, depends on the reserve of vibrational energy. An exact calculation of this time, just as in the case of the distribution function, can be made only numerically, is very cumbersome, and has so far been performed only for individual cases [2, 4, 5]. On the other hand, the analytic expressions obtained in [24] are mainly purely qualitative in character and can be used in practice only for a "weak" deviation from equilibrium.

We turn now to finding an analytic expression for the relaxation time of the vibrational energy in a system of anharmonic oscillators at an arbitrary deviation of this energy from equilibrium. We carry out the analysis for a single-component system, or else for a diatomic molecular gas partially diluted by a gas of structureless particles. Multiplying (1.1) by n/N and summing over all n, we obtain an equation for the rate of change of the average reserve of quanta $\varepsilon = \left(\sum_{n=0}^{k} nN_n\right)/N$ per molecule:

$$\frac{d\varepsilon}{dt} = -\frac{1}{N}\sum_{n=0}^{k} P_{n+1,\,n}N_{n+1} + \frac{1}{N}\sum_{n=0}^{k} P_{n,\,n+1}N_n - \frac{1}{N}\sum_{n=0}^{k} A_{n+1,\,n}N_{n+1} + \frac{1}{N}\sum_{n=0}^{k} nF_n. \tag{1.26}$$

In this section we are not interested in the last term of (1.26), which describes the energy pumped into the vibrational degree of freedom from external sources, and consider only the change of the reserve of quanta on account of vibrational–translational energy exchange (the first two terms) and spontaneous radiative transitions (third term).

For a harmonic oscillator, relation (1.26) assumes after summation the known Landau–Teller form. For low gas temperatures $T \ll E_1$ and for large deviations from equilibrium, we have in this case

$$d\varepsilon/dt = -\varepsilon/\tau_{VT}^{\text{har}} - A_{10}\varepsilon, \quad \tau_{VT}^{\text{har}} = P_{10}^{-1}. \tag{1.27}$$

For an anharmonic oscillator, if the probabilities are chosen in form (1.11), the radiative relaxation ε, as can be easily seen from (1.26), does not depend on the form of the distribution function and, just as in the case of the harmonic model, is described by the second term in (1.27). However, the rate of vibrational–translational energy exchange can depend substantially on the form of the vibrational distribution function and, as will be shown below, exceeds (by up to several orders of magnitude) the rate given by (1.27). To

find this relaxation rate, we start from the distribution functions (1.10) and (1.18). Changing in (1.26) from summation to integration, and taking (1.5) and (1.21) into account, we obtain for nonradiative oscillators

$$\frac{d\varepsilon}{dt} \approx -P_{10}\int_0^k ie^{\delta_{VT}i} f(i)\,di \approx -P_{10}\left[\int_0^{n^*} ie^{\delta_{VT}i} f_{Tr}(i)\,di - P_{10}\frac{Q_{10}\cdot 6\Delta E}{P_{10}T\delta_{VV}^3}(n^*+1)^2 f^2(n^*)\right., \tag{1.28}$$

where $f_{Tr}(i)$, n^*, $f(n^*)$ are defined by (1.10), (1.14), and (1.19). It was taken into account in (1.28) that the populations of the levels $i > n^{**}$ are low and do not influence the relaxation rate.

To represent the relaxation rate $d\varepsilon/dt$ in form (1.27), we calculate also the value of ε:

$$\varepsilon = \frac{1}{N}\sum_{n=0}^{k} nN_n \approx \int_0^{n^{**}} if(i)\,di \approx \int_0^{n^*} if_{Tr}(i)\,di + (n^*+1)f(n^*)(n^{**}-n^*-\delta_{VT}^{-1}). \tag{1.29}$$

Further transformations connected with the calculation of the integrals in Eqs. (1.28) and (1.29) are more conveniently carried out for different values of the parameters $\sqrt{\Delta E/T}\,|n^* - 1 + \delta_{VT}T/2\Delta E|$. Usually this parameter exceed unity. In this case $f(0) \approx E_1/T_1$, and approximate integration in (1.29) yields

$$\varepsilon \approx f(0)\frac{T_1^2}{E_1^2} + f(n^*)(n^*+1)(n^{**}-n^*-\delta_{VT}^{-1}). \tag{1.30}$$

Calculating now the integral in (1.28) and using (1.30), we obtain a general expression for the VT relaxation time

$$\frac{1}{\tau_{VT}} = P_{10}\left\{\left(\frac{E_1}{T_1}-\delta_{VT}\right)^{-2} + f(n^*)\left[\frac{T}{2\Delta E}(1+\delta_{VT}n^*)\exp(\delta_{VT}n^*+0.5) + \right.\right.$$
$$\left.\left. + \frac{Q_{10}}{P_{10}}\frac{6\Delta E}{T\delta_{VV}^3}(n^*+1)^2 f^2(n^*)\right]\right\}\Big/\left[\frac{T_1^2}{E_1^2} + (n^*+1)f(n^*)(n^{**}-n^*-\delta_{VT}^{-1})\right]. \tag{1.31}$$

The calculation $(\tau_{VT}P_{10})^{-1}$ in accordance with Eq. (1.31) for pure CO gas in the mixture 3.2% CO + 96.8% He at different parameter T_1 and T is shown in Fig. 3. It is seen that, with increasing T/T_1, the relaxation rate for the anharmonic model begins, starting with a certain instant of time, to exceed substantially the corresponding value for the harmonic model.

Expression (1.31) can be substantially simplified by considering various relations between the reserve of vibrational quanta on the levels $i \leqslant n^*$ and $n^* \leqslant i \leqslant n^{**}$. If T_1 and T are such that the entire energy is concentrated mainly on the levels $n^* \leqslant i \leqslant n^{**}$ (case of large deviation from equilibrium), then the first term in (1.30) and in the factors in (1.31) can be neglected, and we have for τ_{VT}

$$\frac{1}{\tau_{VT}} = Q_{10}\frac{6\Delta E(n^*+1)}{T\delta_{VV}^3} f(n^*)/(n^{**}-n^*-\delta_{VT}^{-1}), \tag{1.32}$$

or, taking (1.19) into account, we get

$$\frac{1}{\tau_{VT}} = Q_{10}\frac{6\Delta E}{T\delta_{VV}^3}\frac{E_1}{T_1}\frac{n^*+1}{n^{**}-n^*-\delta_{VT}^{-1}}\exp\left[-\frac{\Delta E}{T}(n^*)^2 - 0.5\right]. \tag{1.33}$$

Equations (1.32) and (1.33) clearly illustrate the fact that in the case of strong deviation from equilibrium the vibrational—translational energy exchange in a system of anharmonic oscillators is produced mainly via levels that are close to the level n^{**}, where the populations are still relatively high, and the probabilities considerably exceed (by a factor $\exp(\delta_{VT}n^{**}$ for the level n^{**}) the corresponding values for the harmonic model.

It is also seen from (1.33) that, in the limit, the relaxation rate can be determined not by the value of P_{10} but by the probability of the vibrational exchange Q_{10}. Physically this is explained by the fact that in the case of rapid deactivation on the levels in the vicinity of n^{**} the role of the "bottleneck" for the transition of the vibrational energy to the translational degrees of freedom is assumed by the rate, governed by the vibrational exchange, of supply of molecules to these levels. It is of interest to note that in this

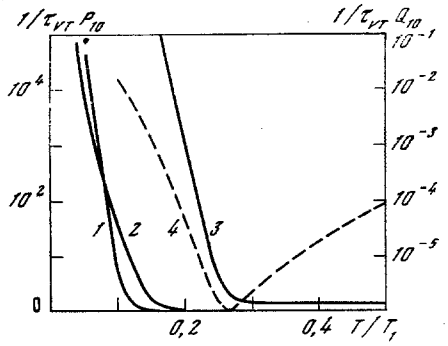

Fig. 3

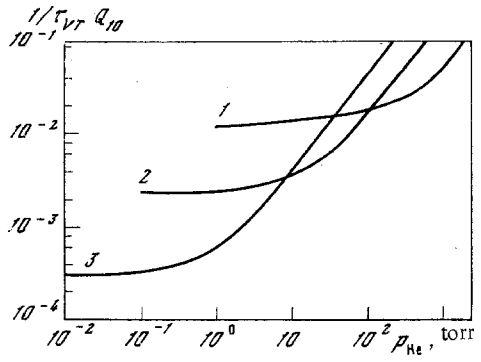

Fig. 4

Fig. 3. Dependence of the quantities $1/\tau_{VT}P_{10}$ (curves 1-3) and $1/\tau_{VT}Q_{10}$ (curve 4) on T/T_1 for the mixture 3.2% CO + 96.8% He (curves 1 and 2) and for pure CO gas (curves 3 and 4) (1 — T_1 = 1850 K, 2-4 — T_1 = 3000 K).

Fig. 4. Dependence of $1/\tau_{VT}Q_{10}$ on the He pressure in the mixture 0.2 torr CO + p torr He at T_1 = 3000 K and at a temperature T equal to 300 (curve 1), 400 (curve 2), and 500°K (curve 3).

case the dependence of τ_{VT} on the gas temperature T can differ greatly from the usual law $\tau \sim \exp(A/T^{1/3})$ and has a nonmonotonic character. The dependence on the gas pressure can also be unusual. Thus, in a gas mixture, when the probability P_{10} in the investigated gas is determined by collisions with the impurity gas (e.g., in typical laser mixtures CO + He), the time τ_{VT} may nonetheless not be inversely proportional to the concentration of this impurity, and can change only very little (see (1.33)). The dependences of τ_{VT} on the temperature and on the pressure of the impurity gas under strong nonequilibrium conditions are illustrated by curve 4 of Fig. 3 and by Fig. 4, respectively.

Expression (1.31) becomes simpler also when the vibrational energy is concentrated in the lower levels $i \leqslant n^*$. If at the same time the principal role in (1.28) is played by the second term in the right-hand side, then we obtain for τ_{VT}

$$\frac{1}{\tau_{VT}} = Q_{10} \frac{6\Delta E E_1^2}{T\delta_{VV}^3 T_1^2} (n^* + 1)^2 \exp\left[-\frac{2\Delta E}{T}(n^*)^2 - 1\right]. \tag{1.34}$$

Finally, in the case when the vibrational—translational energy exchange takes place on the levels $i \leqslant n^*$, we have

$$\frac{1}{\tau_{VT}} = P_{10}\left\{\left(1 - \delta_{VV}\frac{T_1}{E_1}\right)^{-2} + \frac{2\Delta E}{T}(n^* - 0.5)^2 \exp\left[-\frac{\Delta E}{T}(n^*)^2 + \delta_{VT} n^*\right](1 + \delta_{VT} n^*)\right\}. \tag{1.35}$$

In many practical cases, the second term of (1.35) can be neglected; this indicates that the integral $\int_0^{n^*} i \exp(\delta_{VT} i) f_{Tr}(i)\, di$ is insensitive to the upper integration limit. Then (1.35) coincides with the expression obtained in [24]. The relation (1.35) can be used to calculate the relaxation rate of ε also in the case when the distribution function is of the form (1.13).

We note that the value $f(0) \approx E_1/T_1$ and expressions (1.30) and (1.35) were obtained under the assumption that for the level group $0 \leqslant i \leqslant n^*$ the sums of the type $\sum_{i=0}^{n^*} f(i)$, $\sum_{i=0}^{n^*} i \exp(\delta_{VT} i) f(i)$, and $\sum_{i=0}^{n^*} i f(i)$ can be replaced by integrals. Such a replacement is possible if $E_1/T_1 \ll 1$. However, the fact that the integrals turned out to be insensitive to the upper limit of integration makes possible a direct approximate summation of the indicated expressions, and hence a generalization of the results to the case of low temperatures $E_1/T_1 > 1$. Indeed, when the vibrational temperature T_1 is decreased to values at which $E_1/T_1 > 1$, the population of the level n^* decreases and consequently the sums, just as the

integrals become insensitive to the upper summation limit. This means that the energy for the level group $0 \leqslant i \leqslant n^*$ is concentrated mainly in the very lowest states $i \ll n^*$. Since the anharmonicity is still not strongly manifested here, it follows that, by using in the summation in the region $0 \leqslant i \leqslant n^*$ a Boltzmann distribution with the temperature T_1, we obtain for f(0), ε and τ_{VT} in place of (1.30) and (1.31)

$$f(0) = 1 - \exp(-E_1/T_1),$$
$$\varepsilon = \frac{\exp(-E_1/T_1)}{1-\exp(-E_1/T_1)} + f(n^*)(n^*+1)(n^{**}-n^*-\delta_{VT}^{-1}),$$
$$\frac{\varepsilon}{\tau_{VT}} = P_{10} f(0) \frac{\exp(-E_1/T_1)}{[1-\exp(-E_1/T_1+\delta_{VT})]^2} + Q_{10}\frac{6\Delta E}{T\delta_{VV}^3}[(n^*+1)f(n^*)]^2. \tag{1.36}$$

Thus, expressions (1.36) together with (1.19), (1.14), and (1.21), which determine the values of f(n*), n* and n**, yield for the anharmonic-oscillator model analytic dependences of f(0), of the reserve of vibrational quanta ε, and of the relaxation time τ_{VT} on the vibrational temperature in a large interval of values of T_1. They clearly illustrate the difference between the anharmonic and harmonic models. This difference is largest in the case of "strong" deviation from equilibrium. In the case of "weak" deviation equilibrium, from $n^{**} \approx n^*$, the expression for the quantum reserve ε is the same for both models, and τ_{VT} coincides in this case with the value given in [24].

Equations (1.30)-(1.36) were obtained under the assumption that the parameter $\sqrt{\Delta E/T}\,|n^* - 1 + \delta_{VT}T/2\Delta E| > 1$. It can be shown that if the inverse inequality holds, practically the entire vibrational energy is concentrated on the levels $i > n^*$. To calculate the relaxation rate in this case, we can therefore use Eqs. (1.30) and (1.33), but we must remember that f(0) is no longer equal to $1 - \exp(-E_1/T_1)$ but, as can be easily shown, is determined from the relation

$$f(0) \approx [n^* e^{-0.5} \ln(n^{**}/n^*)]^{-1}. \tag{1.37}$$

We note, however, that this case is very rarely realized in practice.

To conclude this section, we present at the value of the parameter $\sqrt{\Delta E/T}\,|n^* - 1 + \delta_{VT}T/2\Delta E| > 1$ equations for f(0), ε, τ_{VT} and for the time τ_R of the radiative relaxation of ε, obtained on the basis of the distribution function (1.20) as well as allowance for the anharmonic effects in the preexponential factors for the probabilities of the processes:

$$f(0) = 1 - \exp(-E_1/T_1), \tag{1.38}$$
$$\varepsilon = \frac{\exp(-E_1/T_1)}{1-\exp(-E_1/T_1)} + C(n^{**}-n^*) - \frac{P_0}{\delta_{VT}}[\exp(\delta_{VT}n^{**}) - \exp(\delta_{VT}n^*)] + A_0\frac{k}{5}[\eta^5(n^*) - \eta^5(n^{**})], \tag{1.39}$$
$$\frac{\varepsilon}{\tau_{VT}} = P_{10}\left\{\frac{f(0)\exp(-E_1/T_1)}{[1-\exp(-E_1/T_1+\delta_{VT})]^2} + \frac{C}{\delta_{VT}}[\exp(\delta_{VT}n^{**}) - \exp(\delta_{VT}n^*)] - \frac{P_0}{2\delta_{VT}}[\exp(2\delta_{VT}n^{**}) - \exp(2\delta_{VT}n^*)] + \frac{A_0}{\delta_{VT}}[\xi_1(n^{**})\exp(\delta_{VT}n^{**}) - \xi_1(n^*)\exp(\delta_{VT}n^*)]\right\}, \tag{1.40}$$
$$\frac{\varepsilon}{\tau_R} = A_{10}\left\{\frac{\exp(-E_1/T_1)}{1-\exp(-E_1/T_1)} + C\frac{k}{4}[\eta^4(n^*) - \eta^4(n^{**})] - \frac{P_0}{2\delta_{VT}}[\xi_2(n^{**})\exp(\delta_{VT}n^{**}) - \xi_2(n^*)\exp(\delta_{VT}n^*)] + \frac{A_0}{8}k[\eta^8(n^*) - \eta^8(n^{**})]\right\}. \tag{1.41}$$

We have introduced here the notation

$$C = \frac{n^*+1}{1-n^*/2k} f(0)\exp\left[-\frac{\Delta E}{T}(n^*)^2 - 0.5\right] - A_0\eta^4(n^*) + P_0\exp(\delta_{VT}n^*),$$
$$P_0 = \frac{P_{10}}{Q_{10}}\frac{T\delta_{VV}^3}{12\Delta E\delta_{VT}}, \qquad A_0 = \frac{A_{10}}{Q_{10}}\frac{T\delta_{VV}^3}{12\Delta E}\frac{k}{4}, \qquad \eta(n) = 1 - n/k,$$
$$\xi_1(n) = \eta^4(n) + \frac{4}{k\delta_{VT}}\eta^3(n) + \frac{12}{(k\delta_{VT})^2}\eta^2(n) + \frac{24}{(k\delta_{VT})^3}\eta(n) + \frac{24}{(k\delta_{VT})^4},$$
$$\xi_2(n) = \eta^3(n) + \frac{3}{k\delta_{VT}}\eta^2(n) + \frac{6}{(k\delta_{VT})^2}\eta(n) + \frac{6}{(k\delta_{VT})^3}. \tag{1.42}$$

The quantity k is the total number of vibrational levels of the oscillator, and their values n* and n** are determined from (1.14) and from the condition that the function (1.20) vanish:

$$P_0 \exp(\delta_{VT} n^{**}) = C + A_0 \eta^4 (n^{**}). \tag{1.43}$$

The first terms in the right-hand sides of (1.39)-(1.41) yield ε, ε/τ_{VT}, and ε/τ_R for "weak" deviation from equilibrium. The presence of terms containing P_0 and A_0 is due to allowance, in the course of the calculation of the quantum reserve and of the relaxation times, for the second and the third terms in the right-hand side of expression (1.20) for the distribution function. In many cases these terms can be neglected. Expressions (1.39) and (1.40) then become close to (1.36), thus indicating that the quantities ε and ε/τ_{VT} are insensitive to anharmonic effects in the preexponential factors for the probabilities. Only the radiative relaxation time τ_R becomes a weak function of T_1, if the probabilities are chosen in the form $A_{n+1,n} = (n+1) A_{10} \left(1 - \frac{2\Delta E}{E_1} n\right)^3 \Big/ \left(1 - \frac{\Delta E}{E_1} n\right)$, and differs from $\tau_R \approx A_{10}^{-1}$.

3. Dependence of the Vibrational Energy and of the "Temperature" T_1 on the Excitation Probability

One of the important aspects in the study of selective "heating" of oscillations is an analysis of the nonequilibrium reserve of vibrational energy (or of the parameter T_1) on the pumping probability. By determining these dependences we ascertain the external-source power necessary to obtain one degree of "heating" or another, and what the limiting "heating" can be at all, i.e., the energy capacity of the investigated vibrational degree of freedom in the saturation regime.

This question has been recently considered in a number of papers [25-32, 66], using for the analysis either the harmonic model [25-32] or the model of truncated anharmonic oscillators with the assumption of a weak deviation from equilibrium [66]. However, as will be shown in the present section, for real molecular systems, in many cases at low gas temperatures the dependence of the vibrational energy on the pump and its limiting values can differ substantially from those obtained in [25-32, 66].

To solve this problem it is necessary at first to obtain the definite form of the terms F_n (see (1.1), (1.2), (1.26)) that describe the pump. For simplicity, we assume hereafter that the pump does not change total number of particles and acts only on the vibrational levels 0 and 1.* In this case the last term of (1.26) takes the simple form

$$(W_{10} N_1 - W_{01} N_0)/N, \tag{1.44}$$

where W_{01} and W_{10} are the probabilities (in $\sec^{-1}$) of excitation and deactivation of the first vibrational level under the influence of the external action. In the experiments this action is usually either electron impact (e.g., in an electric-discharge CO-molecule laser) or absorption of infrared laser radiation (e.g., in experiments on initiation of chemical reactions by laser radiation). In excitation by electron impact

$$W_{01} = \langle \sigma_{01} v \rangle n_e, \tag{1.45}$$

where σ_{01} is the cross section for the excitation of the first vibrational levels by the electrons, and n_e and v are the density and velocity of the electrons, respectively; the averaging is over the electron distribution function. In the case of a Maxwellian distribution with temperature T_e, the values of W_{01} and W_{10} are connected by the usual relation

$$W_{01} = W_{10} \exp(-E_1/T_e).$$

In optical excitation, the probability W_{01} is proportional to the intensity J of the absorbed laser radiation, and is given by

$$W_{01},\ \sec^{-1} = \frac{6 \cdot 10^{21} q A_{10}}{\Delta\nu E_1^3} J. \tag{1.46}$$

Here $\Delta\nu$ is the width of the absorption line (in $\sec^{-1}$); q, fraction of the radiation-absorbing molecules on the vibrational level: J, expressed in W/cm^2; A_{10}, $\sec^{-1}$; and E_1, °K. It can frequently be assumed with good accuracy that $W_{10} = W_{01}$.

We turn now to a determination of the dependence of ε and of T_1 on W_{10}. For the stationary case, with allowance for (1.44) and for the relation between W_{10} and W_{01}, Eq. (1.26) can be written in the form

*The generalization to other cases is not a fundamental problem and can be easily realized.

$$\varepsilon/\tau_{VT} + \varepsilon/\tau_R = W_{10} f(0)\,[\exp(-E_1/T_e) - f(1)/f(0)]. \tag{1.47}$$

In the case of optical pumping we must put $T_e = \infty$ in (1.47). In a regime far from saturation, $f(1)/f(0) = \exp(-E_1/T_1)$. However, in order for the balance equation (1.47) to describe also the saturation regime, it is necessary to take into account also the possible distortion of the distribution function (i.e., of the value of f(1)) by the pump. For this purpose, taking the pump into account, as well as the fact that A_{10}, $P_{10} \ll Q_{10}$, will obtain the ratio f(1)/f(0) from Eq. (1.1) written out for n = 0. Substituting its value in (1.47), we obtain

$$\frac{\varepsilon}{\tau_{VT}} + \frac{\varepsilon}{\tau_R} = W_{10} f(0)\,\frac{\exp(-E_1/T_e)\sum\limits_{m=0}^{k} Q_{10}^{m,\,m+1} f(m) - \sum\limits_{m=0}^{k} Q_{01}^{m+1,\,m} f(m+1)}{W_{10} + \sum\limits_{m=0}^{k} Q_{10}^{m,\,m+1} f(m)}. \tag{1.48}$$

Owing to the decrease of $Q_{10}^{m,m+1}$ and f(m) with increasing m, the main contribution to the sum in (1.48) is made by terms with small m, for which the distribution is still close to the Boltzmann distribution. Taking this into account, we obtain after approximate summation

$$\sum_{m=0}^{k} Q_{10}^{m,\,m+1} f(m) = Q_{10}\varphi,$$
$$\varphi \equiv [1 - \exp(-E_1/T_1)]/[1 - \exp(-E_1/T_1 - \delta_{VV})]^2. \tag{1.49}$$

Substituting now (1.49) in (1.48), we obtain a final expression, which jointly with (1.36) (or (1.38)-(1.43)) determines the dependence of T_1 and of ε on W_{10} in a wide range of values of W_{10}*:

$$\frac{W_{10}}{Q_{10}} = \frac{(\varepsilon/\tau_{VT} + \varepsilon/\tau_R)\,\varphi}{Q_{10} f(0)\,[\exp(-E_1/T_e) - \exp(-E_1/T_1)]\,\varphi - \varepsilon/\tau_{VT} - \varepsilon/\tau_R}. \tag{1.50}$$

By way of illustration, the $T_1(W_{10})$ and $\varepsilon(w_{10})$ dependences were obtained by a numerical method from (1.50) and (1-38)-(1.43) at various temperatures and pressures of the gas, for the pure gases CO and HCl, as well as for the mixture CO + He. The results of the calculation are shown in Fig. 5. For comparison, this figure shows the analogous dependences for the harmonic as well as for the anharmonic model, but considering only "weak" deviation from equilibrium (this corresponds to inclusion of only the first terms in expressions (1.39)-(1.41)). It is seen from the figure that at relatively low pump probabilities, when $T_1/E_1 \lesssim 0.4$-0.7, $\varepsilon \lesssim (1\text{-}3)\cdot 10^{-1}$, the harmonic and anharmonic models give identical results. But further increase of W_{10}/Q_{10}, however, for the harmonic model and consideration of only the "weak" deviation from equilibrium yield for ε, and particularly for T_1, substantially overestimated (by several orders of magnitude) values. Thus, the energy capacity of a reservoir of real anharmonic molecules-oscillators under strong nonequilibrium conditions turns out to be considerably smaller than predicted on the basis of the simplest molecular models. The physical reason is that in a system of anharmonic oscillators, in selective "heating" of the oscillations, the regime changes from "weak" to "strong" deviation from equilibrium. As a result, owing to the repopulation of the highly excited states, the relaxation rate of the vibrational energy increases, and this leads to a sharp decrease in the growth rates of ε and T_1 with increasing pump.

From a comparison of curves 4 and 4' in Fig. 5c it follows that whereas for radiating molecules at low pressure and with "weak" deviation from equilibrium the values of ε and T_1 are determined by the radiative decay of the levels (initial section of curve 4'), in the regime of "strong" deviation from equilibrium the vibrational relaxation has a purely collisional character (curve 4 and 4' merge into one). Physically, this is due to the fact that in this case the dissipation of the vibrational energy proceeds via the upper levels, where even at low pressures the collisional probabilities for the VT processes exceed the radiative probabilities.

*We note that in the saturation regime $f(1)/f(0) \approx \exp(-E_1/T_e)$. Therefore, in the case of saturation the quantity T_1 contained in (1.36), (1.38), (1.43), (1.48), (1.49) should be taken to mean the vibrational temperature for the levels 1 and 2, i.e., $T_1 = E_1/\ln[f(1)/f(2)]$.

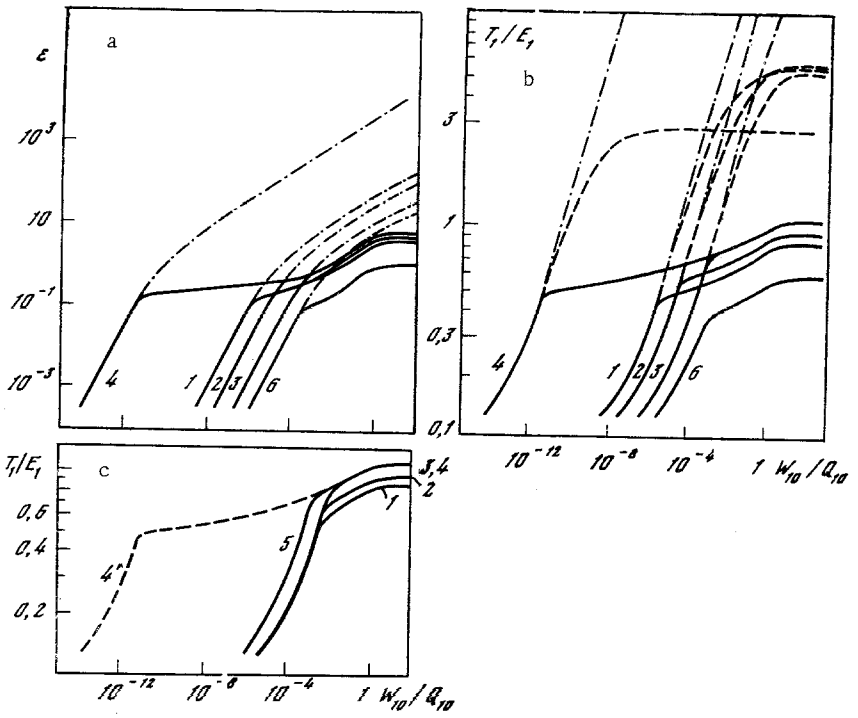

Fig. 5. Dependence of the reserve of vibrational quanta ε (a) and T_1/E_1 (b, c) on the pump power W_{10}/Q_{10} without allowance (a, b) and with allowance (c) for the radiative transitions for the different molecules. Curves 1-3) CO in a mixture 0.2 torr CO + 6 torr He; 4, 5) pure CO (pressure 0.2 and 1 torr, respectively); 6) pure HCl at various gas temperatures (curve 1 — 150, 2 — 200, 3-6 — 300 K). a) Continuous lines — anharmonic model, dash—dot lines — harmonic, b) dashed lines — calculation for anharmonic model in the approximation of only "weak" deviation from equilibrium, c) curve 4' — calculation for pure CO and T = 300°K without allowance for radiative transitions.

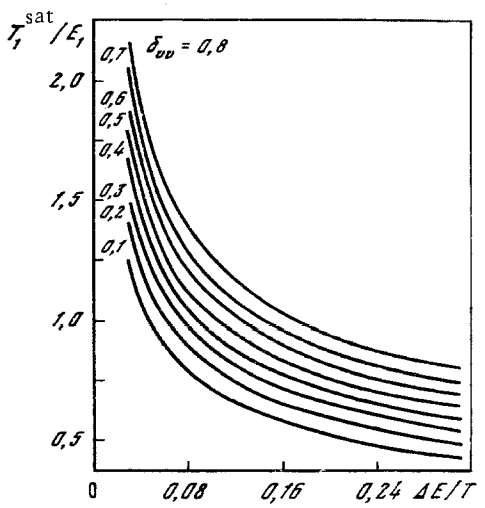

Fig. 6. Dependence of the vibrational saturation temperature T_1^{sat}/E_1 on $\Delta E/T$ for different parameters δ_{VV}.

When He gas is added to CO as an admixture, owing to the strong increase in the rates of VT processes, the values of T_1 (curves 1-3 on Fig. 5b) and ε (curves 1-3 on Fig. 5a) decrease substantially in the regime of "weak" deviation from equilibrium. In the case of "strong" deviation, however, the temperature T_1 is insensitive and ε is little sensitive to the pressure of the admixture gas. The reason is that the time τ_{VT} is determined in this regime mainly by the rate of supply of molecules to the upper vibrational levels, i.e., by the probability Q_{10} (see the preceding section).

It is seen from Fig. 5 that at $W_{10}/Q_{10} \gtrsim 1$ the values of ε and T_1 saturate. The saturation regime follows directly from expression (1.50) if its denominator is equated to zero. Physically, however, the presence of this regime is due to the fact that the energy input to the system is limited by the rate of its spreading over the entire vibrational spectrum, i.e., by the exchange probability Q_{10} [26, 27].

An analytic expression can be obtained for T_1^{sat} in the saturation regime in the case of "strong" deviation from equilibrium. Neglecting in (1.50) the terms that describe the radiative relaxation, and equating the denominator to zero, we obtain for optical pumping at saturation

$$\varepsilon^{sat}/\tau_{VT} = f^2(0)\,\varphi Q_{10}. \tag{1.51}$$

If we use for ε and τ_{VT} in (1.51) the simplified expressions (1.36) with "strong" deviation from equilibrium, we obtain for T_1^{sat}

$$\frac{T_1^{sat}}{E_1} \approx \left\{\sqrt{\frac{2\Delta E}{T}\ln\left[2.2\,\frac{\Delta E\,(n^*)^2}{T\delta_{VV}^3\varphi}\right]} - \frac{\Delta E}{T}\right\}^{-1}, \tag{1.52}$$

with the factor $(n^*)^2/\varphi$ in (1.52) a function of T_1^{sat}. Since, however, T_1^{sat} depends weakly on $(n^*)^2/\varphi$, we can put $(n^*)^2/\varphi \approx T^2/(2\Delta E)^2$ in the practical calculations; this corresponds to a value $T_1 \approx E_1$.

Thus, as follows from (1.52), in the saturation regime T_1^{sat} does not depend on the probabilities of the processes and is determined only by the parameters δ_{VV} and $\Delta E/T$. This conclusion differs qualitatively from the results obtained in the analysis of the harmonic model, where $T_1^{sat}/E_1 \approx \sqrt{Q_{10}/P_{10}}$ [25-27]. The independence of T_1^{sat} of the probabilities for the anharmonic model is explained by the fact that in the saturation regime, at a "strong" deviation from equilibrium, both the rate of energy input into the system and the rate of energy dissipation are determined by the same probability Q_{10}. The dependence of T_1^{sat}/E_1 on $\Delta E/T$ at different values of δ_{VV} is shown in Fig. 6.

Equation (1.50) makes it possible to obtain the analytic $T_1(W_{10})$ dependence even ahead of the saturation regime. At low pump probabilities, when the harmonic and anharmonic models yield identical results at $T_1/E_1 < 1$, we have [26, 27]

$$\frac{T_1}{E_1} = 1\Big/\ln\left(\frac{P_{10}+A_{10}}{W_{10}}\right). \tag{1.53}$$

For "strong" deviation from equilibrium, using (1.36), we obtain

$$\frac{T_1}{E_1} = \left\{\sqrt{\frac{2\Delta E}{T}\ln\left[2.2\,\frac{Q_{10}}{W_{10}}\,\frac{\Delta E\,(n^*)^2}{T\delta_{VV}^3}\right]} - \frac{\Delta E}{T}\right\}^{-1}. \tag{1.54}$$

It is seen from a comparison of (1.52) and (1.54) that the saturation regime is reached at $W_{10}/Q_{10} = \varphi\,(T_1^{sat})$.

On the whole, the results obtained in this chapter indicate that the vibrational relaxation in the case of "strong" deviation from equilibrium differs qualitatively from the relaxation at low pump intensities. These data can serve as a basis for the analysis of high-power lasers operating on vibrational—rotational molecule transitions and for the investigation of the action of laser radiation on matter.

CHAPTER II

VIBRATIONAL RELAXATION IN MOLECULAR MIXTURES

Vibrational relaxation is investigated in binary and ternary gas mixtures. The distributions of the vibrational energy among the components, the relaxation channels of this

energy, the rate of vibrational exchange, and the vibrational distribution functions in each of the components are studied. The results of this chapter are based on [76, 80, 85-87].

1. Quasistationary Distribution in the Presence of Two VV' Channels

In contrast to a single-component oscillator system, the vibrational relaxation in a mixture has not yet been sufficiently fully studied even within the framework of the model of harmonic oscillators. It is therefore useful to study some interesting features of the vibrational kinetics of molecular gas mixtures on the basis of the simpler harmonic model in the present section and in the next two. The analysis for the anharmonic model will be carried out later on.

We shall show that in contrast to the previously considered cases [2, 20, 34, 36, 37] in which a nonstationary distribution existed with one channel for the exchanges of quanta between different modes, such a distribution can occur also in the presence of two and more relaxation channels for processes of this type.

We consider a binary mixture of gases of diatomic molecules A and B, simulated by harmonic oscillators, with molecule densities N_A and N_B and with vibrational-quantum energies E_A and E_B. Let $E_A > E_B$, and let single-quantum and two-quantum exchange be possible between the oscillators A and B. In two-quantum exchange, two quanta of the oscillator B go over into a single quantum of oscillator A (the generalization to the case of exchange of a larger number of quanta is obvious). Assuming a fast VV' process which leads to establishment of Boltzmann distributions with temperatures T_A and T_B between the modes A and B, the relaxation equations for the average number of vibrational quanta ε_A and ε_B per molecule can be written in the form

$$\frac{d\varepsilon_A}{dt} = N_B Q_{01}^{10}\left[\varepsilon_B(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_B)\exp\left(\frac{E_A-E_B}{T}\right)\right] + N_B Q_{01}^{20}\left[\varepsilon_B^2(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_B)^2\exp\left(\frac{E_A-2E_B}{T}\right)\right] + $$
$$+ (N_A P_{10}^{AA} + N_B P_{10}^{AB})\left[1-\exp\left(-\frac{E_A}{T}\right)\right](\varepsilon_A^0 - \varepsilon_A) + \frac{1}{N_A}\sum_{n=0}^{\infty} nJ_n^A, \tag{2.1a}$$

$$\frac{d\varepsilon_B}{dt} = -N_A Q_{01}^{10}\left[\varepsilon_B^2(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_B)\exp\left(\frac{E_A-E_B}{T}\right)\right] - 2N_A Q_{01}^{20}\left[\varepsilon_B^2(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_B)^2\exp\left(\frac{E_A-2E_B}{T}\right)\right] + $$
$$+ (N_A P_{10}^{BA} + N_B P_{10}^{BB})\left[1-\exp\left(-\frac{E_B}{T}\right)\right](\varepsilon_B^0 - \varepsilon_B) + \frac{1}{N_B}\sum_{n=0}^{\infty} nJ_n^B, \tag{2.1b}$$

where $\varepsilon_A = [\exp(E_A/T_A) - 1]^{-1}$, $\varepsilon_B = [\exp(E_B/T_B) - 1]^{-1}$, ε_A^0 and ε_B^0 are the equilibrium (at the gas temperature T) values of ε_A and ε_B. The first two brackets in each of the equations of (2.1) describe, respectively, single- and two-quantum exchange with probabilities Q_{01}^{10}, Q_{01}^{20} (per molecule), and P_{10}^{AA}, P_{10}^{AB} and P_{10}^{BA}, P_{10}^{BB} are the probabilities (per molecule) of the VT processes for the deactivation of the first vibrational level of molecules A and B when they collide with molecules A and B. The last terms in (2.1) describe the pumping processes, with J_n^A and J_n^B the rates of formation of the molecules A and B on the n-th vibrational level.

Since $E_A > E_B$, we shall assume hereafter for simplicity that the vibrational—translational relaxation is effected only through molecules B (i.e., we put $P_{10}^{AA} = P_{10}^{AB} = 0$).

We consider first the case of energy pumping into the vibrational degrees of the molecules by means of short pulses of duration $\tau_{pul} \ll \tau_{VT}, \tau_{VV'}$. The vibrational relaxation process in such a system is described by system (2.1) without sources, but with nonequilibrium initial conditions. Let $\tau_{VV'} \ll \tau_{VT}$, then for instants of time t such that $\tau_{VV'} < t \ll \tau_{VT}$, the solution of (2.1) in the zeroth approximation can be obtained by putting $P_{10}^{BA} = P_{10}^{BB} = 0$. As seen from (2.1), in this case a stationary solution at T_A, $T_B \neq T$ (meaning the existence of a quasistationary distribution) is possible only when there is only one channel for the VV' processes with exchange, e.g., of m quanta of oscillator A for n quanta of oscillator B. (In the considered example m = 1 and n = 1 or else n = 2.) The quantity

$$n\varepsilon_A N_A + m\varepsilon_B N_B = \text{const} \tag{2.2}$$

is conserved, and the temperatures T_A, T_B, T are connected by the relation

$$mE_A/T_A - nE_B/T_B = (mE_A - nE_B)/T. \quad (2.3)$$

This relation was obtained in a different manner in [37] and is a generalization of Eq. (0.4) to the case of multiquantum exchange of two oscillators.

In the presence of several channels for the VV' processes, there is no stationary solution (2.1) with T_A, $T_B \neq T$ at $P_{10}^{BA} = P_{10}^{BB} = 0$. Even here, however, one can speak in a number of cases of a definite relation between the densities N_A and N_B of a quasistationary distribution. Let, e.g., the probabilities Q_{01}^{10} and Q_{01}^{20} in (2.1) be of the same order, and let $N_B \gg N_A$. Then, considering times $t > \tau_A \sim (N_B Q_{01}^{10})^{-1}$, $(N_B Q_{01}^{20})^{-1}$, we can assume with good accuracy that in Eq. (2.1a) we have ε_B = const, and the connection between T_A, T_B, and T can be obtained from the condition

$$d\varepsilon_A/dt = 0. \quad (2.4)$$

Of course, in this case $d\varepsilon_B/dt \neq 0$, but the time variation of ε_B in (2.1a) can be neglected if the increment of the vibrational energy in B within a time on the order of τ_A is small compared with the energy itself, i.e.,

$$|d\varepsilon_B/dt|\,\tau_A \ll \varepsilon_B. \quad (2.5)$$

This equation, with allowance for (2.1b), can be written at $\tau_A \sim (N_B Q_{01}^{20})^{-1}$ in the form

$$\frac{N_B}{N_A} \gg \left|\varepsilon_B(1+\varepsilon_A) - \frac{\varepsilon_A}{\varepsilon_B}(1+\varepsilon_B)^2 \exp\left(\frac{E_A - 2E_B}{T}\right)\right|. \quad (2.6)$$

Inequality (2.6) yields the necessary relation between the densities, at which a quasistationary distribution of the vibrational energies of the components is possible as a result of the VV' processes that take place simultaneously through two channels (single- and two-quantum exchanges). The time τ_A is the characteristic time for the establishment of this distribution. An expression connecting in this case the temperature T_A with T_B and T was obtained in [20]. The result is of interest primarily because the distribution of the energy between the different modes in VV' processes that proceed effectively through two and more channels, in contrast to the case of a single channel, turn out to depend on the relative densities of the components.

At a constant pump ($\tau_{pul} \gg \tau_{VT}$, $\tau_{VV'}$) a stationary solution of (2.1) with T_A, $T_B \neq T$ always exists. In the general case, T_A and T_B are connected not only through the gas temperature T, but also through the concentrations of the components and the source power. Let, e.g., the excitation of the molecular vibrations be effected by collision with the electrons of molecules located at the zeroth vibrational level (0→n transitions). In this case

$$\frac{1}{N_A}\sum_{n=0}^{\infty} {}^{A}_{n} = \left[1 - \exp\left(-\frac{E_A}{T_A}\right)\right]\sum_{n=0}\left[W_{0n} - W_{n0}\exp\left(-\frac{nE_A}{T_A}\right)\right]n_e. \quad (2.7)$$

Here $n_e W_{0n}$ and $n_e W_{n0}$ are the probabilities (in sec^{-1}) of the excitation and deactivation of the n-th vibrational level of the molecule A, and n_e is the electron density. A similar expression holds also for the molecule B.

It follows from (2.1) and (2.7) that T_A and T_B are determined by the relation between N_A, N_B, and n_e. At large values of N_B the pump in (2.1a) can be neglected, and the remaining parts of (2.1a) are connected only with T_A, T_B, and T. This connection, with the VT processes neglected, is given by expressions cited in [20].

2. Relaxation of Vibrational Energy in VV' Processes

As seen from (2.1), in a mixture of molecular gases, in the presence of several channels for the exchange of vibrational quanta between different species of molecules in the absence of sources and of VT processes, the only stationary solution of a system of type (2.1) is a solution corresponding to the equilibrium state for which $T_A = T_B = T$. This means that in such a system, at an initial nonequilibrium value of the total vibrational energy, relaxation will take place to an equilibrium energy even in the absence of the usual vibrational–translational exchange. In the considered case of a binary mixture of gases A and B ($E_A > E_B$), the mechanism of establishment of complete statistical equilibrium via only VV' processes includes exchange of energies between the vibrational and transla-

tional degrees of freedom, which takes place, e.g., when two quanta of molecule B go over into one quantum of molecule A, followed by a transition of a quantum of molecule A into a quantum of molecule B (i.e., in accordance with the scheme $2E_B \to E_A \to E_B$). In this process the number of quanta ε_A and ε_B (or a certain combination of them of the type (2.2)) is not conserved, and the difference of the vibrational energy between the initial and final states is compensated by the change of the translational energy.

Let us ascertain under which conditions and in which molecular mixtures can the rate of relaxation of energy via the VV' process exceed the corresponding rate for the ordinary VT processes. For a binary mixture with close molecular masses and concentrations N, the characteristic time τ_{VV} of the energy relaxation on account of the VV' processes is on the order of

$$\tau_{VV'} \sim 1/[N \min (Q_{01}^{10}, Q_{01}^{20})],$$

therefore the highest rate of relaxation via the indicated channel takes place in a molecular gas mixture for which

$$Q_{01}^{10} \approx Q_{01}^{20}. \tag{2.8}$$

To estimate the probabilities, we shall use Herzfeld's expressions [41], and take into account in them only the most significant exponential dependence on the energy:

$$\begin{aligned} P_{10} &\approx C_1 V_B^2 \exp(-3a^{2/3}E_B^{2/3} + E_B/2T), \\ Q_{01}^{10} &\approx C_2 V_A^2 V_B^2 \exp[-3a^{2/3}(E_A - E_B)^{2/3} + (E_A - E_B)/2T], \\ Q_{01}^{20} &\approx C_3 V_A^2 V_B^2 \exp[-3a^{2/3}(2E_B - E_A)^{2/3} + (2E_B - E_A)/2T]. \end{aligned} \tag{2.9}$$

Here $a = 0.32\sqrt{\mu/T}/\alpha$, α is a parameter in the exponential potential of the intermolecular interaction $\exp(-\alpha r)$ (in Å^{-1}), μ is the reduced collision mass (in a.u.); T, E_A, E_B are expressed in °K. The squares of the matrix elements V_A^2, V_B^2 and the factors C_1, C_2, C_3 depend relatively weakly on the quantum energy, so that we can assume that $C_1 \approx C_2 \approx C_3$, $V_A^2 \approx V_B^2$.

Practical interest attaches to the variant

$$E_A = (1.5 + \eta) E_B, \tag{2.10}$$

where $\eta \ll 1$, inasmuch as only in this case can we expect satisfaction of (2.8), meaning also of the condition $P_{10} \ll Q_{01}^{10}$, Q_{01}^{20}. Substituting (2.10) in (2.9), expanding the arguments of the exponential in powers of η and retaining only first-order terms in η, we obtain

$$\eta \approx (\ln V_B^2)/(E_B/T - 5.04a^{2/3}E_B^{2/3}). \tag{2.11}$$

At this value of η, the ratio

$$Q_{01}^{10}/P_{10} \sim \tau_{VT}/\tau_{VV'}$$

is maximal:

$$(Q_{01}^{10}/P_{10})_{\max} \approx V_B^2 \exp(1.11a^{2/3}E_B^{2/3} - E_B/4T). \tag{2.12}$$

Expressions (2.11) and (2.12) were obtained for the case when aE_B, $a(E_A - E_B)$, $a(2E_B - E_A) > 20$. When the inverse inequality is satisfied, we can use in place of (2.9) a simpler (linear in the argument of the exponential) dependence of the probabilities on the energy defect [21, 81]. In this case we obtain in place of (2.11) and (2.12)

$$\eta \approx (\ln V_B^2) \Big/ \left(\frac{E_B}{T} - \frac{4}{3} aE_B\right), \qquad \left(\frac{Q_{01}^{10}}{P_{10}}\right)_{\max} \approx V_B^2 \exp\left(\frac{aE_B}{2} - \frac{E_B}{4T}\right). \tag{2.13}$$

It follows from (2.12) and (2.13) that at typical values of V_B, E_B, μ, and α the condition $\tau_{VT} \gg \tau_{VV'}$, which corresponds to predominant relaxation of the energy via the VV' processes, is as a rule not satisfied for a binary mixture. It can take place only at low gas temperatures $T \leqslant 300$°K and for molecules with large values of the vibrational quanta $E_B \gtrsim 3000$°K (it is necessary here, of course, to choose mixtures for which the condition (2.8) would be satisfied).

The situation can change significantly, however, in the presence of three and more vibrational modes with quantum energies E_i satisfying, e.g., the condition

$$E_1 < E_2 < E_3 < \ldots < E_k < 2E_1. \tag{2.14}$$

Condition (2.14) is quite typical of vibrational modes of a polyatomic molecule. In this case, owing to the relatively small energy defects $2E_1 - E_k$, $E_k - E_{k-1}$, ..., $E_2 - E_1$ the rate of the summary VV' process, which follows the scheme

$$2E_1 \to E_k \to E_{k-1} \to \ldots \to E_1, \tag{2.15}$$

can be high enough. Confining ourselves to the case $a\Delta\mathscr{E} < 20$ ($\Delta\mathscr{E}$ is the maximum defect of the vibrational energy in collisions in accordance with the scheme (2.15)), and assuming that $Q_{01}^{20}(2E_1 \to E_k) \approx Q_{01}^{10}(E_k \to E_{k-1}) \approx \ldots \approx Q_{01}^{10}(E_2 \to E_1)$, we obtain for a mixture of k vibrational modes

$$\left(\frac{\tau_{VT}}{\tau_{VV'}}\right)_{\max} \sim V_1^{2(k+1)/k} \exp\left[E_1\left(a - \frac{1}{2T}\right)\frac{k-1}{k}\right]. \tag{2.16}$$

It is seen from a comparison of (2.13) and (2.16) that the condition $\tau_{VT} \gg \tau_{VV'}$ in a multicomponent mixture of oscillators can be satisfied for a much larger class than in binary mixtures.

Thus, the process of establishment of complete statistical equilibrium on account of VV' processes alone, in accordance with the scheme of (2.15), may turn out to be decisive in polyatomic systems in a number of cases. Naturally, such a mechanism can play in this case a role in the relaxation of systems where the vibrational temperatures $T_i \gtrsim T$. In the opposite case, the equilibrium will always be established as a result of VT processes.

3. Energy Distribution in Gas Mixtures at $\tau_{VV'} \sim \tau_{VT}$. Role of Concentrations

We consider a three-component mixture of diatomic gases A, B, and C. The vibrational relaxation in such a system, simulated by a mixture of harmonic oscillators with vibrational-quantum energies E_A, E_B, E_C, is described in the single-quantum transition approximation by the equations

$$\begin{aligned}
\frac{d\varepsilon_A}{dt} &= (P_{10}^{AA}N_A + P_{10}^{AB}N_B + P_{10}^{AC}N_C)\left[1 - \exp\left(-\frac{E_A}{T}\right)\right](\varepsilon_A^0 - \varepsilon_A) + \\
&+ Q_{01}^{10}(AB)N_B\left[\varepsilon_B(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_B)\exp\left(\frac{E_A - E_B}{T}\right)\right] + \\
&+ Q_{01}^{10}(AC)N_C\left[\varepsilon_C(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_C)\exp\left(\frac{E_A - E_C}{T}\right)\right] + \frac{1}{N_A}\sum_{n=0}^{\infty} nJ_n^A, \\
\frac{d\varepsilon_B}{dt} &= (P_{10}^{BA}N_A + P_{10}^{BB}N_B + P_{10}^{BC}N_C)\left[1 - \exp\left(-\frac{E_B}{T}\right)\right](\varepsilon_B^0 - \varepsilon_B) - \\
&- Q_{01}^{10}(AB)N_A\left[\varepsilon_B(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_B)\exp\left(\frac{E_A - E_B}{T}\right)\right] + Q_{01}^{10}(BC)N_C\left[\varepsilon_C(1+\varepsilon_B) - \varepsilon_B(1+\varepsilon_C)\exp\left(\frac{E_B - E_C}{T}\right)\right], \\
\frac{d\varepsilon_C}{dt} &= (P_{10}^{CA}N_A + P_{10}^{CB}N_B + P_{10}^{CC}N_C)\left[1 - \exp\left(-\frac{E_C}{T}\right)\right](\varepsilon_C^0 - \varepsilon_C) - \\
&- Q_{01}^{10}(AC)N_A\left[\varepsilon_C(1+\varepsilon_A) - \varepsilon_A(1+\varepsilon_C)\exp\left(\frac{E_A - E_C}{T}\right)\right] - Q_{01}^{10}(BC)N_B\left[\varepsilon_C(1+\varepsilon_B) - \varepsilon_B(1+\varepsilon_C)\exp\left(\frac{E_B - E_C}{T}\right)\right].
\end{aligned} \tag{2.17}$$

The notation here is similar to that in (2.1), and the pump is included for simplicity only in the equation for ε_A. The stationary (but not equilibrium) distribution of the vibrational energy in all three components A, B, and C is determined from the solution of system (2.17) at

$$d\varepsilon_A/dt = d\varepsilon_B/dt = d\varepsilon_C/dt = 0.$$

Just as before, it is necessary to assume that T is constant, i.e., that the energy flux due to pumping into the translational degrees of freedom should be offset by the outflow of heat from the system.

Equations (2.17) contain the concentrations of the components, so that in the general case the relation between the vibrational temperatures T_A, T_B, T_C will change with changing N_A, N_B, N_C. Only in the particular cases $\tau_{VV} \leqslant \tau_{VT} \ll \tau_{VV'}$ and τ_{VV}, $\tau_{VV'} \ll \tau_{VT}$ will there be no such dependence. If $\tau_{VV} \ll \tau_{VT} \ll \tau_{VV'}$, we always have $T_B = T_C = T$, and if τ_{VV}, $\tau_{VV'} \ll \tau_{VT}$ the connection between T_A, T_B, and T_C is determined by the Treanor relations [2], i.e., by formula (2.3) with m = n = 1. The purpose of the present section is to study

the dependences of the vibrational temperatures on the concentrations for the case $\tau_{VV'} \sim \tau_{VT}$.

We consider the specific three-component system N_2–O_2–NO and its particular case, the binary mixture N_2–O_2 (E_{N_2} = 3357 K, E_{O_2} = 2240 K, E_{NO} = 2700 K). We assume that the pumping is by electron collisions. Since the excitation cross section for collisions of an electron with N_2 greatly exceeds the corresponding cross sections for O_2 and NO, we take into account the pump only in N_2 (therefore the index A in (2.17) pertains only to N_2, B pertains to O_2, and C to NO).

The probabilities used in the calculations are given in [85]. They were taken from the experimental papers (see the review [88]) or were calculated from the semiempirical formula of Milliken and White [89]. We note that in accordance with the results of the preceding chapter, the energy relaxation rates can increase as a result of the VT processes considerably at T_A, T_B, T_C > T because of the actually existing anharmonicity. Here, however, the calculation will be carried out only for the case of a relatively high temperature T = 800 K. In this case the deviation from equilibrium is "weak" and the change of the time τ_{VT} can be taken into account in accordance with Sec. 2 of Chap. I by multiplying the probability P_{10} by the factor $[1 - \exp(-E_{O_2}/T_{O_2})]^2[1 - \exp(-E_{O_2}/T_{O_2} + \delta_{VT})]^{-2}$. For the term in (2.17), which describes the pumping by electron impact in N_2, we used the expression

$$\frac{1}{N_{N_2}}\sum_{n=0}^{\infty} nJ_n^A \approx 5\cdot 10^{-9} n_e\left[1-\exp\left(-\frac{E_{N_2}}{T_{N_2}}\right)\right]\left[1-1.1\exp\left(-\frac{E_{N_2}}{T_{N_2}}\right)\right]. \tag{2.18}$$

The system of equations (2.17) for the stationary case $d\varepsilon_{N_2}/dt = d\varepsilon_{O_2}/dt = d\varepsilon_{NO}/dt = 0$ were solved with a computer for T_{N_2}, T_{O_2}, T_{NO} at $n_e = 10^9$ cm^{-3}, at different N_{N_2}, N_{O_2}, N_{NO} concentrations, and at a gas temperature T = 800 K.

Binary Mixture. The dependence of the vibrational temperatures T_{N_2} and T_{O_2} on the nitrogen concentration N_{N_2} at different values of N_{O_2} is illustrated in Fig. 7. This dependence can be understood from a qualitative analysis of system (2.17). At low concentrations N_{N_2} the probability of transfer of vibrational quanta from N_2 to O_2 is much less than the probability for the VT processes in O_2:

$$N_{N_2}Q_{01}^{10}(N_2 \to O_2) < P_{10}^{O_2-O_2}N_{O_2} + N_{N_2}P_{10}^{O_2-N_2}. \tag{2.19}$$

Since there is no pumping by electron impact for O_2 ($J_n^B = 0$), $T_{O_2} \approx T$, and the vibrational temperature in N_2 is constant and is determined by the ratio of the rate of electronic pumping (meaning also n_e) and the deactivation energy. The latter is determined at $N_{N_2}/N_{O_2} \leqslant$ 0.1–1 by the VV' process, inasmuch as in this case

$$N_{O_2}Q_{01}^{10}(N_2 - O_2) > P_{10}^{N_2-N_2}N_{N_2} + P_{10}^{N_2-O_2}N_{O_2}. \tag{2.20}$$

From the ratio of the pumping rates and deactivation rates it follows that at low N_{N_2} the constant value of T_{N_2} is determined by the ratio n_e/N_{O_2}. With increasing relative concentration N_{N_2}/N_{O_2}, the flux of the quanta in O_2 on account of the VV' process increases, inequality (2.9) no longer holds, and the vibrational temperature T_{O_2} increases. However, with further increase of N_{N_2}, the VT processes on account of the collision of N_2 and O_2 with N_2 and O_2 become predominant, and both vibrational temperatures begin to decrease.

Thus, allowance for the VT processes in the case of $\tau_{VV'} \sim \tau_{VT}$ causes the simple relation (2.3) between the vibrational temperatures of the components to be replaced by a more complicated expression that depends on the concrete relations between the pumping rate, the rate of the VT processes, and the rates of the VV' processes in the forward and backward directions, which are determined in turn both by the gas temperature and by the concentrations of the components.

The Three-Component Mixture N_2–O_2–NO. Role of Impurities. The substantial dependence of the vibrational temperatures on the component concentrations, which was demonstrated with the binary mixture N_2–O_2 as an example, is due primarily to the low rate of the VV' processes. One can expect an increase of this rate, effected in some manner, to lead to a redistribution of the energies amongthe vibrational modes, so that the relation between the vibrational temperatures will approach (2.3). For a binary mixture of molecules with vibrational quanta $E_A > E_B$, $E_A < 2E_B$ and one-quantum exchange between the different types of oscillators, an increase in the rate of the VV' process between A and B can be realized by introducing into the gas impurity molecules with vibrational quantum E_C such that $E_A > E_C >$

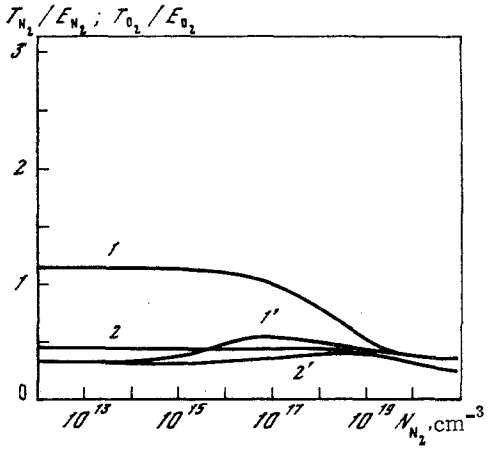

Fig. 7

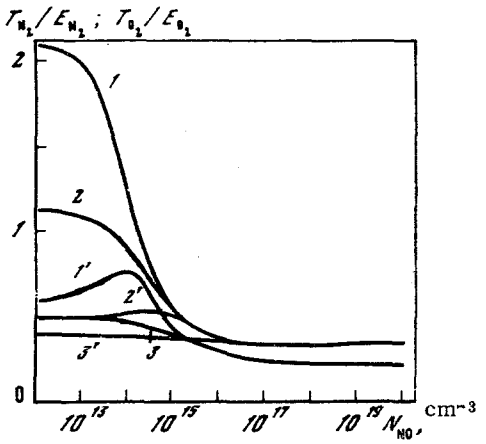

Fig. 8

Fig. 7. Dependence of the vibrational temperatures of nitrogen T_{N_2} (curves 1 and 2) and of oxygen T_{O_2} (1', 2') on the concentration N_{N_2} at different concentrations of O_2. 1, 1') $N_{O_2} = 10^{16}$ cm^{-3}; 2, 2') $N_{O_2} = 10^{17}$ cm^{-3}. T = 800 K, $n_e = 10^9$ cm^{-3}.

Fig. 8. Dependence of T_{N_2} (curves 1-3) and of T_{O_2} (curves 1'-3') on N_{NO} at different values of N_{N_2} and N_{O_2}. 1, 1') $N_{N_2} = N_{O_2} = 10^{15}$ cm^{-3}; 2, 2') $N_{N_2} = N_{O_2} = 10^{16}$ cm^{-3}; 3, 3') $N_{N_2} = N_{O_2} = 10^{17}$ cm^{-3}. T = 800 K, $n_e = 10^9$ cm^{-3}.

E_B. In this case the exchange $E_A \rightleftarrows E_B$ can proceed via impurity molecules, $E_A \rightleftarrows E_C \rightleftarrows E_B$, and since the exchange probability satisfies usually in this case the relation $Q_{01}^{10}(AB) < Q_{01}^{10}(AC)$, $Q_{11}^{10}(CB)$, the total rate of the VV' process for A and B can increase substantially.

An illustration of the foregoing is the mixture N_2–O_2–NO ($E_{N_2} > E_{NO} > E_{O_2}$). Figure 8 shows the dependence of T_{N_2}, T_{O_2} on the concentration, calculated for different values of N_{O_2}, N_{N_2} and $N_{O_2}/N_{N_2} = 1$. It is seen from the figure that when NO is added, increase in the rate of exchange between the O_2 and N_2 causes the vibrational temperature of the oxygen first to increase. The appearance of a maximum and the subsequent decrease of T_{O_2} as well as of T_{N_2} with further increase of the NO concentration are due to the increase in the rate of the VT processes in the collisions.

It is important to note that a noticeable change of T_{O_2}, as follows from Fig. 8, takes place when small amounts of the impurity are added (on the order of several percent of the total concentration). In the case of arbitrary mixtures, the sensitivity of the nonequilibrium distributions of the vibrational energy to the impurity additions, which change the ratio of the vibrational temperatures of the modes, making it closer to (2.3), will be larger the greater the increase in the rate of the VV' processes upon addition of the impurities.

Thus, by changing the concentrations of the individual components in the molecular-gas mixture and by introducing different impurities with corresponding choice of energies of the vibrational quanta, it is possible, under equilibrium conditions, to alter judiciously the distribution of the vibrational energy among the components. This is a very important circumstance since it uncovers a possibility of controlling various physicochemical processes that depend substantially on the nonequilibrium energies of the vibrational modes, e.g., chemical reactions with participation of vibrationally excited molecules. Nor is it excluded that catalytic and inhibiting properties of impurities in a number of chemical reactions are due precisely to the action of these impurities on the relative reserves of the vibrational energies of the molecules that participate in the reaction.

Another region where a practical application of the "controlling" action of the impurities is possible is chemical lasers, particularly lasers based on the mixture DF–CO_2 or HF–CO_2. In these lasers, exothermic chemical reactions produce vibrationally excited DF or HF molecules. As a result of the VV' processes the vibrational energy from these molecules is transferred into the asymmetrical mode of CO_2. This produces in CO_2 a gap between the

vibrational temperatures of the asymmetrical and symmetrical modes, and the gap is sufficient to produce inverted population and lasing on the $00^{\circ}1 \to 10^{\circ}0$ transition.

Rough estimates, however, show that owing to the large energy defect in the nonresident vibrational exchange $DF-CO_2(\nu_3)$, $HF-CO_2(\nu_3)$ the rate of this exchange is comparable with the rate of the VT processes, and this limits the favorable possibility of raising the temperature of the asymmetrical mode ν_3 in CO_2 and the lasing power. Addition of $DF-CO_2$ of C molecules with quantum energy $E_{CO_2} < E_C < E_{DF}$ (e.g., HBr molecules) to the binary mixture should apparently increase the rate of the VV' process and improve the operation of the laser. At the present time, however, owing to the absence of reliable values of the probabilities for a number of processes, a detailed analysis of the distribution of the vibrational energy in a system of the $DF-CO_2-HBr$ type is impossible, and the performance of an appropriate experiment is most useful here.

The high sensitivity of the partial vibrational temperatures to the concentration of the impurities makes it also possible to raise the question of diagnostics of the decisive stages of various chemical or physical processes, but this group of questions calls for additional research.

4. Vibrational Distribution Function of Anharmonic Oscillators in a Mixture with a Rapidly Relaxing Molecular Component

Besides the distribution of the total reserve of vibrational energy among the various modes, which was analyzed in Secs. 1-3 of the present chapter for molecular mixtures, great interest is attached also to the distribution functions of the populations within each of the modes. For the model of harmonic oscillators in a quasistationary regime, these are Boltzmann distribution functions [30]. For the anharmonic model the situation, of course, is different but the distribution within the modes was analyzed only for two particular cases: when the role of the VV' predominates [39] (the distribution function in this case is of the Treanor type (0.1)) and with account taken of the VT processes, but for a regime with a slight deviation from equilibrium [19]. The purpose of this and following sections is to investigate the distribution functions in a binary mixture of gases of diatomic molecules A and B under substantially nonequilibrium conditions.

To find these functions we add to the right-hand sides of the kinetic equations (1.1) for the oscillator A terms that describe the quantum exchange between A and B

$$\sum_k (\tilde{Q}^{k,\,k+1}_{n+1,\,n} N^{B}_{k} N^{A}_{n+1} - \tilde{Q}^{k+1,\,k}_{n,\,n+1} N^{B}_{k+1} N^{A}_{n}) + \sum_k (\tilde{Q}^{k+1,\,k}_{n-1,\,n} N^{B}_{k+1} N^{A}_{n-1} - Q^{k,\,k+1}_{n,\,n-1} N^{B}_{k} N^{A}_{n}), \tag{2.21}$$

where $\tilde{Q}^{p,j}_{i,q}$ is the probability (in $cm^3 \cdot sec^{-1}$) of quantum exchange between molecules A and B; $N^{A,B}_{p}$ are the population densities of the p-th level of the oscillators A and B; N_A and N_B are the total densities of oscillators A and B.

Equations (1.1), which take into account terms of the type (2.21), must be supplemented by a system of equations for the level populations of the oscillator B. In the general case, it is difficult to solve such a system analytically. For a "strong" deviation from equilibrium in both oscillators, this system can be reduced in principle to two coupled nonlinear equations of third order (see the next section). Here, however, we consider the case when the impurity oscillators B are rapidly relaxing, so that the populations in them are at equilibrium and are described by a Boltzmann distribution with a gas temperature T. This case is of practical interest when a study is made of relaxation in molecular mixtures containing a gas of polar (and consequently rapidly relaxing) molecules.

Since we are considering only low temperatures $T \ll E_A, E_B$ (E_A and E_B are the characteristic temperatures for the lower quanta of the oscillators A and B), we can confine ourselves, owing to the rapid decrease of the populations on the upper levels of the oscillators B, to allowance for the vibrational exchange between A and B with participation of only the lowest quantum of the oscillator B, and can neglect the transfer of energy from B to A. After summing (2.21) from 0 to i we then obtain $N^{B}_{0}\tilde{Q}^{01}_{i+1,\,i,}\ N^{A}_{i+1}$.

We note that the influence of the gas B on the vibrational relaxation in the oscillators A depends on the relation between E_A and E_B. Thus, if $E_B < E_A$, the probability

$\tilde{Q}^{01}_{i+1}$, decreases because of the increase of the resonance defect with increasing i. It follows therefore that the VV' processes influence in this case mainly the vibrational temperature T_A of the oscillators A, without changing the form of the distribution in A.

If $E_A > E_B$ the situation can be different. In this case the probabilities $\tilde{Q}^{01}_{i+1,i}$ are maximal at exact resonance, i.e., for m_0 determined from the expression

$$E_B = E_A - 2\Delta E_A m_0. \tag{2.22}$$

The determination of the distribution function in the oscillators A is similar to this case to that considered in Sec. 1 of Chap. I. It is then convenient to specify the exchange probabilities $\tilde{Q}^{01}_{i+1,i}$ in the simplest form, analogous to (1.11):

$$\tilde{Q}^{01}_{i+1,i} = \tilde{Q}_{10}(i+1)\exp[\delta_{AB}m_0 - |\delta_{AB}(m_0 - i)|], \tag{2.23}$$

where $\tilde{Q}_{10}$ is the probability (in $cm^3 \cdot sec^{-1}$) of the transfer of a quantum from A to B between the very lowest levels, $\delta_{AB} = 0.427\sqrt{\mu_{AB}/T}\Delta E_A/\alpha$, and m_0 is given by (2.22). Taking (2.21) and (2.23) into account, it is necessary to add in the right-hand side of (1.16) the term

$$N_0^B \tilde{Q}_{10}\exp(m_0\delta_{AB} - \delta_{AB}|m_0 - i|)(i+1)f(i). \tag{2.24}$$

Under the condition $m_0 > n^*$ the solution of such an equation $i > n^*$ for nonradiative oscillators is of the form

$$f(i) = \frac{C}{i+1} - \frac{P_{10}}{Q_{10}}\frac{T\delta^3_{VV}}{12\Delta E}\frac{\exp(\delta_{VT}i)}{\delta_{VT}(i+1)} - N_0^B\frac{\tilde{Q}_{10}\exp(\delta_{AB}m_0)\delta^3_{VV}T}{Q_{10}\cdot 12\Delta E\delta_{AB}(i+1)}\exp(\delta_{AB}|m_0 - i|)\,\mathrm{sign}(m_0 - i). \tag{2.25}$$

The integration constant C, as before, is determined by joining together the Treanor functions (1.10) and (2.25) at the point $i = n^*$.

The last term in (2.25) describes in fact the influence of the rapidly relaxing impurity on the distribution function for the oscillators A in the case of a "strong" deviation from equilibrium in A and under the condition $m_0 = n^*$. As seen from (2.25), the influence can be very substantial in a number of cases.

5. Distribution Functions in a Mixture under Essentially Nonequilibrium Conditions

We turn now to an analysis of the vibrational distribution functions in a binary mixture of molecular gases A and B for strong deviation from equilibrium. We obtain first for this regime differential equations analogous to (1.16). If we add to Eq. (1.1) the term (2.21) which describes the VV' process, then, summing (1.1) over n from 0 to i, going over to a continuous distribution function of the type (1.8), and replacing the summation by integration, we obtain in place of (1.9) an integrodifferential equation for the distribution functions f(i) in the oscillator A. This equation differs from (1.9) by the presence of additional terms

$$\frac{N_B}{N_A}P^{AB}_{i+1,i} + \frac{N_B}{N_A}\int \tilde{Q}^{m,m+1}_{i+1,i}f_B(m)\left[\frac{d\ln f_A(i)}{di} - \frac{d\ln f_B(m)}{dm} + \frac{E_A - E_B - 2\Delta E_A i + 2\Delta E_B m}{T}\right]dm. \tag{2.26}$$

An equation for $f_B(i)$ can be written out also in analogy with (1.9) and (2.26). The system of such simultaneous integrodifferential equations is very complicated to analyze. But if it is recognized that at low temperatures of the gas the probabilities $\tilde{Q}^{m,m+1}_{i+1,i}(AB)$ have a sharp maximum at resonant VV and VV' energy exchange, then these equations can be rewritten in a differential form similar to (1.16). For this purpose, specifying the probabilities $Q^{m,m+1}_{i+1,i}$ (AA) and $\tilde{Q}^{m,m+1}_{i+1,i}$ (AB) in the form (1.11) and (2.23) and expanding $f_A(m)$ in a series in the vicinity of the point $m = i$, and $f_B(m)$ in the vicinity of the point $m = m_i \equiv m_0 + (\delta_{AB}/\delta_{BA})_i$ we obtain after integrating in (1.9) with respect to m with account taken of (2.26)

$$\frac{3Q_{10}N_A}{\delta^3_{VV}}\frac{d}{di}\left\{(i+1)^2 f_A^2(i)\left[\frac{2\Delta E}{T} - \frac{d^2\ln f_A(i)}{di^2}\right]\right\} + N_A P^{AA}_{i+1,i}f_A(i) + N_B P^{AB}_{i+1,i}f_A(i) + A^A_{i+1,i}f_A(i) +$$
$$+ \frac{2\tilde{Q}_{10}N_B}{\delta_{AB}}e^{\delta_{AB}m_0}(i+1)f_A(i)(m_i+1)f_B(m_i)\left[\frac{d\ln f_A(i)}{di} - \frac{d\ln f_B(m_i)}{dm_i}\right] = 0. \tag{2.27}$$

A second equation that connects f_A and f_B can be obtained in similar fashion.

A system of such two nonlinear coupled differential equations has a lucid approximate analytic solution if the concentration of one of the components greatly exceeds the concentration of the other. This case is also of practical interest, since it makes it possible to estimate the coefficient of separation of the isotopes in chemical reaction of vibrationally excited isotopic molecules with a considerable excess of a definite isotope in the initial mixture of molecules (see Chap. III).

Let, e.g., $N_B \gg N_A$. Then the system of equations of type (2.27) breaks up into two independent equations. The distribution function $f_B(i)$ is formed in B–B collisions, and the equations for it, as well as the approximate analytic solution, coincides with (1.16) and (1.10), (1.18). On the other hand, a simplified equation for f_A is obtained if one neglects in (2.27) the terms that contain N_A. The solution of such an equation with account taken of (1.10) and (1.18) is

$$f_A(i) = C_2\left\{f_B\left(m_0 + \frac{\Delta E_A}{\Delta E_B} i\right) \exp\left[-\frac{P_{10}^{AB}}{\tilde{Q}_{10}} \frac{\delta_{BA}}{2} \int \frac{\exp(\delta_{BA} m_i)\, dm_i}{(m_i+1) f_B(m_i)}\right]\right\}^{\Delta E_B/\Delta E_A}. \tag{2.28}$$

The integration constant C_2 is determined from the normalization condition $\sum_i f_A(i) = 1$. If the exponential factor in (2.28) is approximately equal to unity and $\Delta E_B/\Delta E_A \approx 1$, then it is seen that f_A "duplicates" the function f_B with a shift amounting to several levels. Physically this is explained by the fact that $f_A(i)$ is formed in resonant processes of quantum exchange between A and B.

6. Rate of Energy Exchange in a Binary Mixture of Anharmonic Oscillators

It is clear that anharmonicity of the oscillations can exert an influence not only on the distribution function, but also on the rate of exchange of vibrational quanta between different modes. In the case of harmonic oscillators, the term responsible for the single-quantum VV' processes in the relaxation equation (2.1) for the reserve of vibrational quanta is the first term. To obtain an expression that replaces this term for the anharmonic model, it is necessary, after specifying the probabilities of the processes, to calculate the distribution functions $f_A(n)$ and $f_B(k)$, by multiplying Eq. (1.1) with allowance for the added terms (2.21) by n, and sum over all the n. Since, however, in the general case it is difficult to obtain analytic expressions for $f_A(n)$ and $f_B(k)$ in a gas mixture, we confine ourselves below to weak deviation from equilibrium for both oscillators and to the case when the impurity gas is rapidly relaxing. In the first case, as indicated above (see Chap. I, Sec. 2, as well as [24]), it is possible to use Boltzmann distribution functions in the summation and take the anharmonicity into account only in the expressions for the probabilities.

We obtain, after specifying the probabilities of the VV' processes in the form (2.23), the rate of energy exchange between anharmonic oscillators with $E_A > E_B$. If it is assumed that m_0 is relatively large, then upon summation in (1.1) the expression (2.23) for the exchange probability can be additionally simplified by leaving out the absolute-value sign. We than obtain

$$(d\varepsilon_A/dt)_{VV'} = -\tilde{Q}_{10} N_B \varphi(E_A/T_A, -\delta_{AB})\, \varphi(E_B/T_B, \delta_{BA})\, \{\exp(-E_A/T_A) - \exp[-E_B/T_B - (E_A - E_B)/T]\}. \tag{2.29}$$

The function $\varphi(x, y)$ in (2.29) is defined in analogy with (1.49):

$$\varphi(x, y) = (1 - e^{-x})/(1 - e^{-x-y})^2. \tag{2.30}$$

It is seen from (2.29) that the presence of anharmonicity increases the rate of energy exchange in oscillator A and decreases it in oscillator B. Physically, the reason is that at $E_A > E_B$ the exchange of the upper quanta in A with the lower quanta in B becomes more effective in anharmonic oscillators on account of the improvement of the resonance conditions. At the same time, in exchange of the upper quanta in B with the lower quanta in A, owing to the increase of the resonance defect, the rate of exchanges decreases.

Expression (2.29) can be generalized also to the case of multiquantum exchange, if m quanta of oscillator A are exchanged with n quanta of oscillator B when the molecules A and B collide. In this case we obtain

$$\left(\frac{d\varepsilon_A}{dt}\right)_{VV'} = N_B \widetilde{Q}_{m0}^{0n} \frac{1-\exp(-E_A/T_A)}{[1-\exp(-E_A/T_A+m\delta_{AB})]^{m+1}} \frac{1-\exp(-E_B/T_B)}{[1-\exp(-E_B/T_B-n\delta_{BA})]^{n+1}} \times$$
$$\times \left[\exp(-mE_A/T_A) - \exp\left(-n\frac{E_B}{T_B} - \frac{mE_A - nE_B}{T}\right)\right]. \tag{2.31}$$

It is easy to show that if $E_A < E_B$ then the expression for $(d\varepsilon_A/dt)_{VV'}$ takes the form (2.29) or (2.31), but δ_{AB} and δ_{BA} have opposite signs.

In the case when the impurity gas B is rapidly relaxing, we can obtain an expression for the rate of transfer of vibrational energy from A to B even without assuming a "weak" deviation from equilibrium in A. If at the same time we use for the distribution function A expressions (1.10) and (2.25) (without taking the second and third terms in the right-hand side of (2.25) into account), then after summation and integration in (2.21), we obtain in the same manner as in Sec 2 of Chap. I

$$\left(\frac{d\varepsilon_A}{dt}\right)_{VV'} \approx -N_B \widetilde{Q}_{10}\varphi\left(\frac{E_A}{T_A}, -\delta_{AB}\right)\exp\left(-\frac{E_A}{T_A}\right) + \frac{C}{\delta_{AB}}[\exp(\delta_{AB}n^{**}) - \exp(\delta_{AB}n^{*})] \text{ for } E_A > E_B, \tag{2.32a}$$

$$(d\varepsilon_A/dt)_{VV'} \approx -N_B \tilde{Q}_{10}\varphi(E_A/T_A, \delta_{AB})\exp(-E_A/T_A) \text{ for } E_A < E_B. \tag{2.32b}$$

The constant C in (2.32) is the same as in expression (2.25), while n* and n** are determined from (1.14) and from the condition that the right-hand side of (2.25) vanish.

To conclude this chapter, we note that the foregoing analysis of the vibrational relaxation in gas mixtures is to some degree fragmentary. However, although the equations of vibrational kinetics for the mixture of anharmonic molecules cannot be solved in general form, an analysis of concrete particular cases demonstrates the need for taking into account the real anharmonicity in practical problems. At the same time, these results give grounds for an analysis of the energy distributions that exert a substantial influence on the course of the physical-chemical processes (e.g., on the rate of a chemical reaction) and on the operation of various physical devices (e.g., chemical lasers), as well as for an analysis of the possibilities of a judicious action on this distribution.

CHAPTER III

APPLICATIONS OF VIBRATIONAL GENETICS

We consider the applications of the analyzed vibrational-relaxation theory questions to concrete problems such as the calculation of the rate of nonequilibrium dissociation in a gas of diatomic molecules and in a mixture of molecular gases, the calculation of the isotope separation coefficient in chemical reactions in which vibrationally excited molecules particulate, as well as an investigation of processes in a carbon dioxide electric-discharge laser.

1. Dissociation of Diatomic Anharmonic Molecules in Selective "Heating" of the Oscillations

One of the most vital problems whose analysis is connected with the use of the results of Chaps. I and II is the action of monochromatic radiation on matter and the possibilities of stimulating and controlling chemical reactions in which infrared laser radiation is absorbed by a gas.

The simplest chemical reaction whose rate can be calculated as a function of the power absorbed in the vibrational transitions is the dissociation reaction. In this section we investigate the dissociation of diatomic molecules in selective "heating" of the oscillations. (We note that selective "heating" can be produced not only by optical methods but also, e.g., by electric pumping.) We consider here the case, not analyzed so far, of "strong" deviation from equilibrium, which leads to the largest reaction rate and is consequently of greatest interest for the problem of initiation of chemical reactions by laser radiation.

We shall regard dissociation as motion of molecules upward in energy space over the vibrational levels, followed by a transition of the levels from the boundary level k to the continuous spectrum.

For a Morse oscillator, the value of k is connected with the energy E_1 of the vibrational quantum, the anharmonicity ΔE, and the dissociation energy D by the relation

$$k = 2D/E_1 \approx E_1/2\Delta E. \tag{3.1}$$

The dissociation rate is proportional to the population of this level, and its calculation calls for knowledge of the distribution function (up to the level k). Unfortunately, at so "strong" a deviation from equilibrium it is difficult to obtain exact analytic expressions for f(i) in the entire vibrational spectrum range, and the function f(i) obtained in Sec. 1 of Chap. I is suitable only when $i < n^{**}$, where n^{**} is determined from expressions of the type (1.21). The situation, however, is facilitated by the fact that at $i > n^{**}$ the principal role is assumed in the formation of f(i) by VT processes and by dissociation. Therefore the distribution here should be close to a Boltzmann distribution with the gas temperature T and is distorted by the dissociation process. Assuming that this distortion is the same as in the case of equilibrium dissociation, we can write for the rate constant $K_D(T_1)$ of nonequilibrium dissociation

$$K_D(T_1)/K_D(T) \approx f(i)/f(i,T) \quad \text{for} \quad i \geqslant n^{**}, \tag{3.2}$$

where $K_D(T)$ and f(i, T) are the rate constant of the dissociation and the distribution function at equilibrium with temperature T. The value of $K_D(T)$ for the anharmonic-oscillator model can be calculated by following [90]. If at the same time the probabilities of the processes can be chosen in the form (1.11), then we obtain

$$K_D(T) \approx P_{10} k f(0,T) \sqrt{4\Delta E/\pi T} \exp(-D/T + k\delta_{VT}) [1 + \Phi(x)]^{-1}, \tag{3.3}$$

where $x = \delta_{VT}\sqrt{T/4\Delta E}$, $\Phi(x)$ is the error function. Since we are interested in the case $T \ll E_1$, we have then $f(0, T) \approx 1$. The nonequilibrium function f(i) at the point $i = n^{**}$, for the case of "strong" deviation from equilibrium, can be approximately estimated by using expression (1.18) and neglecting in it the terms that describe the influence of the radiative and VT processes. Taking this into account and using a Boltzmann function for f(i, T), we obtain from (3.2) and (3.3) the value of $K_D(T_1)$:

$$\begin{aligned} K_D(T_1) &\approx K_D(T) \frac{n^*+1}{n^{**}+1}\left[1 - \exp\left(-\frac{E_1}{T_1}\right)\right] \exp\left[\frac{E_1 - \Delta E n^{**}}{T} n^{**} - \frac{\Delta E}{T}(n^*)^2 - 0.5\right] \approx \\ &\approx P_{10} k (n^*+1) \sqrt{\frac{4\Delta E}{\pi T}}\left[1 - \exp\left(-\frac{E_1}{T_1}\right)\right] \{(n^*+1)[1+\Phi(x)]\}^{-1} \times \\ &\times \exp\left[-\frac{D}{T} + k\delta_{VT} + \frac{E_1 - \Delta E n^{**}}{T} n^{**} - \frac{\Delta E}{T}(n^*)^2 - 0.5\right], \end{aligned} \tag{3.4}$$

where n^* and n^{**} are calculated from relations (1.14) and (1.21).

We note that expression (3.4) differs from the analogous formulas for $K_D(T_1)$, obtained earlier in [3, 21]. This difference is due to the substantial difference between the vibrational function of the type (1.18) and the functions obtained in [3, 21] for the case of "weak" deviation from equilibrium.

The dependence of the rate constant K_D on the pumping probability W_{10} and its value at saturation can be easily obtained by using (3.4) and expressions (1.54) and (1.52) for $T_1(W_{10})$ and T_1^{sat}. It is clear, of course, that the result is valid if the dissociation process itself does not influence the reserve of vibrational energy, since Eqs. (1.52) and (1.54) were obtained for such a case.

In the more general case, the quantities $T_1(W_{10})$ and T_1^{sat} must be calculated by adding to the left-hand sides of (1.47) and (1.48) the term $K_D(T_1)D/E_1$, which describes the dissipation of the vibrational energy by dissociation. However, since the time τ_{VT} of the energy relaxation on account of the VT processes decreases considerably with increasing T_1, the existence of such a regime becomes difficult and is possible only at a definite relation between the molecular parameters Q_{10}/P_{10}, $\Delta E/T$, δ_{VV}, δ_{VT}, and k. Let us obtain this relation, assuming that to overcome the energy dissipation due to dissociation it is necessary to satisfy the condition

$$K_D(T_1)D/E_1 \geqslant \varepsilon/\tau_{VT}. \tag{3.5}$$

Substituting here the expressions (3.4) and (1.36) for $K_D(T_1)$ and ε/τ_{VT}, we obtain the condition imposed on T_1 and necessary to satisfy (3.5):

$$\frac{T_1}{E_1} \geqslant \frac{T_1^*}{E_1} = \left\{\left[\frac{4\Delta E}{T}\left(\ln B_1 - \delta_{VT}\left(k - \frac{\delta_{VT}T}{2\Delta E} - \sqrt{\frac{T}{\Delta E}\ln B_2}\right)\right)\right]^{1/2} - \frac{\Delta E}{T}\right\}^{-1}, \tag{3.6}$$

where

$$B_1 = \frac{Q_{10}}{P_{10}} \frac{12\Delta E}{T\delta_{VV}^3} (n^* + 1)\left[1 - \exp\left(-\frac{E_1}{T_1}\right)\right] e^{-0.5},$$

$$B_2 = \frac{2k^2\delta_{VT}\sqrt{\Delta E/\pi T}}{n^{**}[1 + \Phi(x)]}.$$

We note that condition (3.6) is quite stringent and it can be far from always satisfied, since the temperature T_1, which can be obtained by increasing the pump, cannot exceed the value of T_1^{sat} given by Eq. (1.52). Thus, the regime in which the energy dissipation is effected by dissociation is possible only if $T_1^{sat} \geqslant T_1^*$. Substituting for these temperatures their values (1.52) and (3.6), and assuming that $k/n^{**} \approx 1$, $[1 - \exp(-E_1/T_1)]^3/[1 - \exp(-E_1/T_1 - \delta_{VV}]^2 \approx 1$, we obtain a relation between the parameters Q_{10}/P_{10}, $\Delta E/T$, δ_{VV}, δ_{VT}, and k at which the indicated regime is satisfied. For a pure gas, when $\delta_{VT} = \delta_{VV}$, we obtain

$$\frac{Q_{10}}{P_{10}}\sqrt{\frac{24\Delta E}{T\delta_{VV}^3}} \geqslant \exp\left\{\delta_{VV}\left[k - \frac{\delta_{VV}T}{2\Delta E} - \sqrt{\frac{T}{\Delta E}\ln\left(\frac{2k\delta_{VV}}{1+\Phi(x)}\sqrt{\frac{\Delta E}{T}}\right)}\right]\right\}. \quad (3.7)$$

Figure 9 shows, on the plane of the points (k, Q_{10}/P_{10}) at different δ_{VV} and $\Delta E/T$, the "demarcation" lines obtained from (3.7) with the equality sign; they divide the plane into two regions of values of k and Q_{10}/P_{10}. The inequality (3.7) is satisfied, and consequently the dissipation of the energy from the system proceeds mainly via dissociation at values of k and Q_{10}/P_{10} that lie in the lower right-hand region. Estimates carried out for the HCl molecule at 300 K ($k = 25$, $\Delta E/T = 0.25$, $Q_{10}/P_{10} = 1.6 \cdot 10^2$ [91, 92], $\delta_{VV} = 0.43$ [93]) show that the nonequilibrium dissociation of this molecule is slow and does not influence the energy balance. On the other hand, for the CO molecule at T = 300 K the point (k, Q_{10}/P_{10}) of Fig. 9 will lie in a region where dissociation can exert an overwhelming influence on the relaxation of the energy only if the long-range forces of molecule interaction are taken into account in the calculation of Q_{10} (this leads to an increase of Q_{10}).

The degree of selective action by laser radiation on the rate of a preferred chemical reaction is determined also by the conditions for the maintenance of a low gas temperature in the course of the reaction. It is clear that the transition of vibrational energy from the vibrational mode "heated" by the radiation to the translational degrees of freedom leads to a lowering of the selectivity. The most favorable regime must therefore be taken to be the one in which the investigated chemical reaction takes place within a time shorter than τ_{VT}.

Figure 10 shows for pure molecular gases CO and HCl the dependences of the parameter $K_D(T_1)\tau_{VT}$, which determines the ratio of the rates of two competing processes (dissociation and vibrational—translational relaxation) on the pumping probability. It is seen that even in the saturation regime (at $W_{10}/Q_{10} \geqslant 1$) it is impossible to produce dissociation within times shorter than τ_{VT}. In the general case, on the other hand, the requirements imposed on the parameters Q_{10}/P_{10}, $\Delta E/T$, δ_{VV}, δ_{VT}, k and needed for such a rapid dissociation are also stringent, since it is clear that it is even more difficult to satisfy the condition $K_D(T_1) \geqslant \tau_{VT}^{-1}$ than relation (3.5).

The obtained conclusions pertain, of course, only to the dissociation reaction. It is obvious that for other reactions, with account taken of vibrationally excited diatomic molecules, large rate constants under nonequilibrium conditions are possible provided the steric factor of the reaction is large enough, and the activation energy of the reaction is such that in the saturation regime we have $\mathscr{E}_{act} \leqslant n^{**}[E_1 - \Delta E(n^{**} - 1)]$.

2. Nonequilibrium Dissociation in a Mixture

As shown above, it is difficult to effect rapidly (within a time of the order of τ_{VT}) nonequilibrium dissociation in a single-component system of diatomic molecules. This circumstance decreases considerably the possibility of controlling the dissociation process by "heating" the oscillations by laser radiation, inasmuch as the radiation energy goes over in this case to the translational degrees of freedom. More promising therefore is the use of polyatomic molecules with selective heating of some preferred vibrational mode as the chemically active components. Rapid dissociation becomes possible in this case if it is due to predissociation of the molecules from such vibrational levels of this mode, for which

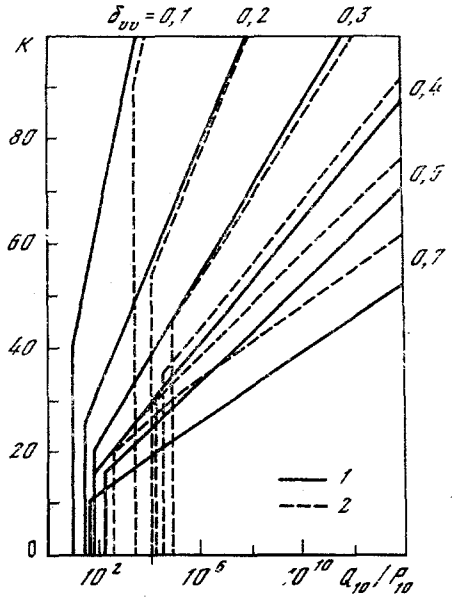

Fig. 9

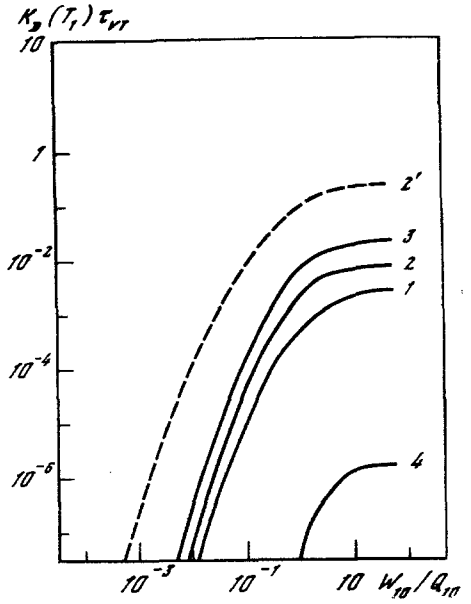

Fig. 10

Fig. 9. Demarcation lines that separate the values of the molecular parameters (k, Q_{10}/P_{10}) at different δ_{VV} and $\Delta E(T$ into regions into which dissipation of vibrational energy via the dissociation channel is possible (region to the right of the curves) and impossible (to the left of the curves). The dissociating molecular gas is assumed to be diatomic and single-component ($\delta_{VT} = \delta_{VV}$). 1) $\Delta E/T = 0.25$, 2) $\Delta E/T = 0.0625$.

Fig. 10. Dependence of the parameter $K_D(T_1)\tau_{VT}$ on the pump power W_{10}/Q_{10} for the molecules CO (curves 1-3) and HCl (curve 4) at different gas temperatures (1 — 500, 2, 2', 4 — 300, 3 — 200 K). Curve 2' — calculation with allowance for the influence of the long-range forces on the probability Q_{10}.

the VT processes do not yet influence the formation of the distribution function. This conclusion is confirmed both by experiments [62, 63] and by theoretical analysis [21, 66].

In a number of cases, however, it may turn out that for one reason or another (e.g., for lack of a laser of the necessary wavelength) it is difficult to obtain a direct selective "heating" of a preferred vibrational mode. Interest is attached in this connection in an investigation of dissociation with indirect "heating" of the vibrations in a mixture of molecular gases, when the external source (e.g., laser radiation) excites one vibrational mode, and the "heating" and dissociation by a second mode are decreased by nonresonant vibrational exchange between the modes (VV' processes). One should note here one more important feature of chemically active molecular mixtures, which was indicated in Sec. 3 of Chap. II. It consists in the fact that for a mixture, by varying the relative concentrations of the molecular components, it is possible, by selective "heating" of the oscillations, to vary judiciously the distribution of the vibration energy among the modes, and consequently to control chemical processes.

We investigate below nonequilibrium dissociation in a binary mixture of a diatomic gas and a monatomic gas, when an external source pumps energy into the vibrations of the diatomic molecule, and the dissociation is produced as a result of predissociation from the vibrational levels of one of the oscillation modes of the monatomic molecule.

In the analysis, following Sec. 1 of the present chapter, we shall neglect for the diatomic molecules the dissipation channel of vibrational energy by dissociation. For the investigated vibrational mode B of the polyatomic molecule, we choose the truncated anharmonic Morse oscillator model with m vibrational levels such that the VT processes in B still do not influence the form of the distribution function, and can become important only for the determination of the reserve of vibrational energy in B. For the oscillators A we shall

consider an arbitrary degree of deviation from equilibrium, while for B we confine ourselves to the assumption that only a "weak" deviation takes place. Then, using for the expression ($d\varepsilon_A/dt_{VV'}$) of the single-quantum vibrational exchange between A and B the formula (2.29), with optical pumping acting on the levels 0 and 1 of the oscillators A, we easily obtain a system of equations for the reserves of the vibrational quanta ε_A and ε_B in A and B. If we disregard here the spontaneous radiative decay of the levels and neglect small equilibrium values of ε_A and ε_B, then we have

$$\frac{d\varepsilon_A}{dt} = -\frac{\varepsilon_A}{\tau_{VT}^A} - N_B Q_{10}'\varphi\left(\frac{E_A}{T_A}, -\delta_A\right)\varphi\left(\frac{E_B}{T_B}, \delta_B\right)\left[\exp\left(-\frac{E_A}{T_A}\right) - \exp\left(-\frac{E_B}{T_B} - \frac{E_A - E_B}{T}\right)\right] +$$
$$+ W_{10} f_A(0)\left\{Q_{10}^A f_A(0)\varphi\left(\frac{E_A}{T_A}, \delta_{VV}^A\right) + N_B\tilde{Q}_{10}\varphi\left(\frac{E_B}{T_B}, \delta_B\right)\times\right.$$
$$\left.\times\left[1 - \exp\left(-\frac{E_B}{T_B} - \frac{E_A - E_B}{T}\right)\right]\right\}\left[W_{10} + Q_{10}^A\varphi\left(\frac{E_A}{T_A}, \delta_{VV}^A\right) + N_B\tilde{Q}_{10}\varphi\left(\frac{E_B}{T_B}, \delta_B\right)\right]^{-1}, \tag{3.8}$$
$$\frac{d\varepsilon_B}{dt} = -\frac{\varepsilon_B}{\tau_{VT}^B} - K_D^B(m - \varepsilon_B) + N_A\tilde{Q}_{10}\varphi\left(\frac{E_A}{T_A}, -\delta_A\right)\varphi\left(\frac{E_B}{T_B}, \delta_B\right)\left[\exp\left(-\frac{E_A}{T_A}\right) - \exp\left(-\frac{E_B}{T_B} - \frac{E_A - E_B}{T}\right)\right].$$

Here ε_A, τ_{VT}^A, and $f_A(0)$ are determined by relation (1.36), and the function $\varphi(x, y)$ by Eq. (2.30), while for ε_B and τ_{VT}^B we use the expressions that describe the "weak" deviation from equilibrium (i.e., the first terms in Eqs. (1.36)). The second term in the right-hand side of the second equation of (3.8) takes into account the dissipation of the vibrational energy of the oscillators B as a result of their dissociation. The expression for the dissociation rate constant K_D in a single-component system of truncated anharmonic oscillators was investigated in [21, 66]. It can be easily generalized to include the case of a binary mixture, and for single-quantum vibrational exchange between the oscillators it takes the form

$$K_D^B = f_B(0)\,Q_{10}^B\varphi\left(\frac{E_B}{T_B}, \delta_{VV}^B\right)\left\{\sum_{i=1}^{m}\frac{1}{i}\exp\left[i\left(\frac{E_B}{T_B} - (i-1)\frac{\Delta E_B}{T} + \delta_{VV}^B\right)\right]\right\}^{-1} +$$
$$+ f_B(0)\,\tilde{Q}_{10}N_A\exp\left(-\frac{E_A}{T_A}\right)\varphi\left(\frac{E_B}{T_B}, \delta_B\right)\left\{\sum_{i=1}^{m-1}\frac{1}{i}\exp\left[i\left(\frac{E_B}{T_B} - (i-1)\frac{\Delta E_B}{T} + \delta_B\right)\right]\right\}^{-1}. \tag{3.9}$$

Thus, the system (3.8) jointly with (3.9) determines the dependence of T_A, T_B, and K_D^B on the pump probability W_{10} and on the relative concentrations N_A/N_B for a binary mixture of anharmonic oscillators, one of which is truncated. In the quasistationary regime we can assume in the analysis of (3.8) that $d\varepsilon_A/dt = d\varepsilon_B/dt = 0$.

By way of illustration, Eqs. (3.8) under the conditions $d\varepsilon_A/dt = 0$, $d\varepsilon_B/dt = 0$ were solved for the specific mixtures N_2–N_2O and CO–N_2O at T = 300 K (in the case of N_2–N_2O we assumed not optical but electric pumping of N_2). The calculation results are given in Figs. 11 and 12, which show plots against W_{10}/Q_{10}^A and N_A/N_B of the values of T_A/E_A, T_B/E_B, K_D^B/Q_{10}^B and of the parameter $S = mK_D^B(\varepsilon^A/\tau_{VT}^A + \varepsilon^B/\tau_{VT}^B)^{-1}$. This parameter, which is the ratio of the energy fluxes going into dissociation and into the translational degrees of freedom, just as the parameter $K_D\tau_{VT}$ (see Sec. 1 of the present chapter), characterizes the selectivity of the action of the absorbed radiation on the dissociation reaction. It is seen from the figures that the vibrational temperatures T_A and T_B can depend strongly both on W_{10} and on the relative concentrations of the components, and the connection between them is not determined by the known Treaner relation [2], when $E_B/T_B = E_A/T_A - (E_A - E_B)/T$ (see curves 2 and 2'). The reason is that the VV' processes are not dominant for the considered mixtures, and consequently the quasiequilibrium between the oscillator, which is assumed in the Treanor relation, is not present.

A change of T_B/E_B leads, naturally, to substantial changes of K_D^B and of the "selectivity" coefficients S. It should be noted that in certain regimes one can obtain S > 1 and this, naturally, should lower the degree of heating of the gas. In a saturation region, when $W_{10}/Q_{10} \gg 1$, high dissociation rates can be reached at large relative densities $N_A/N_B \gg 1$, but the value of S decreases in this case, owing to the increased role of the VT processes for the oscillators A.

On the whole, however, the results of the calculation of the nonequilibrium dissociation in a mixture of molecular gases make it possible to conclude that the use of mixtures for a purposeful action on the rates of chemical reactions of laser radiation is promising, for this extends the class of investigated substances and offers an additional possibility of controlling the reactions by changing the relative concentrations of the molecular components.

3. Isotope Separation in Chemical Reactions of Vibrationally Excited Molecules

One of the most important recent applied problems is isotope separation in chemical reactions that take place at a low translational temperature with participation of molecules in vibrationally excited states. This possibility of isotope separation by this method and its high efficiency were pointed out in [73] and demonstrated experimentally in [74, 75]. A theoretical analysis of this problem and, in particular, an estimate of the isotope separation coefficient and of the absolute concentrations of the isotopes, obtained after the separation, calls for a calculation of the vibrational distribution functions in a mixture of molecular gases.

The purpose of the present section is to estimate, using the results of Chap. II, for the case of low gas temperatures and large reserves of vibrational energy, which is of greatest interest for applications, the isotope separation coefficient in the reactions that take place in a mixture of vibrationally excited isotopic molecules A and B with a considerable excess initial concentration of one of the isotopes.

We shall assume in the analysis, for simplicity, that the reaction takes place only between molecules A and B that land on levels higher than the respective levels k_A and k_B whose energy is equal to or larger than the activation energy $\mathscr{E}_{act}$. Since the anharmonicities of the isotopic molecules are close, and the quantum energies E_A and E_B differ insignificantly (with the exception of hydrogen isotopes), it follows that $k_A \approx k_B = k$. During the initial stage, when a small relative fraction of the molecules takes part in the reaction, the separation coefficient is determined by the rate constants γ_A and γ_B of the reactions with participation of A and B [73]: $\beta = \gamma_A/\gamma_B - 1$. Since $\gamma_{A(B)} \sim Z_{A(B)} f_{A(B)}(k)$, ($Z_A$, Z_B are the steric factors of the reactions) we have

$$\beta = \frac{Z_A}{Z_B}\frac{f_A(k)}{f_B(k)} - 1. \tag{3.10}$$

At relatively small Z_A and Z_B, the reactions do not distort the form of the distribution function. In this case at a concentration $N_B \gg N_A$, in accordance with Sec. 5 of Chap. II, we can use for $f_B(k)$ expressions (1.18), and for $f_B(i)$ Eq. (2.28). A particularly lucid form of $f_A(i)$ is obtained if one neglects in (2.28) the terms containing P_{10}^{AB}, P_{10}^{BB}, A_{10}^{B} (this can be done in many practical cases). We then obtain

$$f_A(i) = \begin{cases} f_A(0)\exp\left[-\frac{E_A}{T_A}i + \frac{\Delta E_A}{T}i(i-1)\right], & 0 \leqslant i \leqslant n^* - m_0, \quad (3.11a) \\ C_2\left[f_B\left(m_0 + \frac{\Delta E_A}{\Delta E_B}i\right)\right]^{\Delta E_B/\Delta E_A}, & i \gtrsim n^* - m_0. \quad (3.11b) \end{cases}$$

For the separation coefficient β we have in this case

$$\beta = \begin{cases} \frac{Z_A}{Z_B}\exp\left(\frac{E_B - E_A}{E_B}\frac{E_B k}{T}\right) - 1, & n^* \geqslant k + m_0, \quad (3.12) \\ \frac{Z_A}{Z_B}\exp\left[\frac{E_B - E_A}{E_B}\frac{E_B(n^* - m_0/2)}{T}\right] - 1, & n^* \leqslant k. \quad (3.13) \end{cases}$$

Expression (3.12) was obtained in [73] for a system of harmonic oscillators, and was later generalized in [74] to include also Morse oscillators. Under substantially nonequilibrium conditions, however, Eq. (3.12) is valid only if $f_A(i)$ and $f_B(i)$ are Treanor distribution functions up to the level k corresponding to $\mathscr{E}_{act}$. When T is lowered or the nonequilibrium reserve of the vibrational energy is increased, the level n^* can become lower than k, the functions f_A and f_B on the upper levels take the form (1.18) and (3.11b), and the separation coefficient β should be calculated from (3.13). Notice should be taken of new qualitative distinguishing features of β, which follows from (3.13). In contrast to

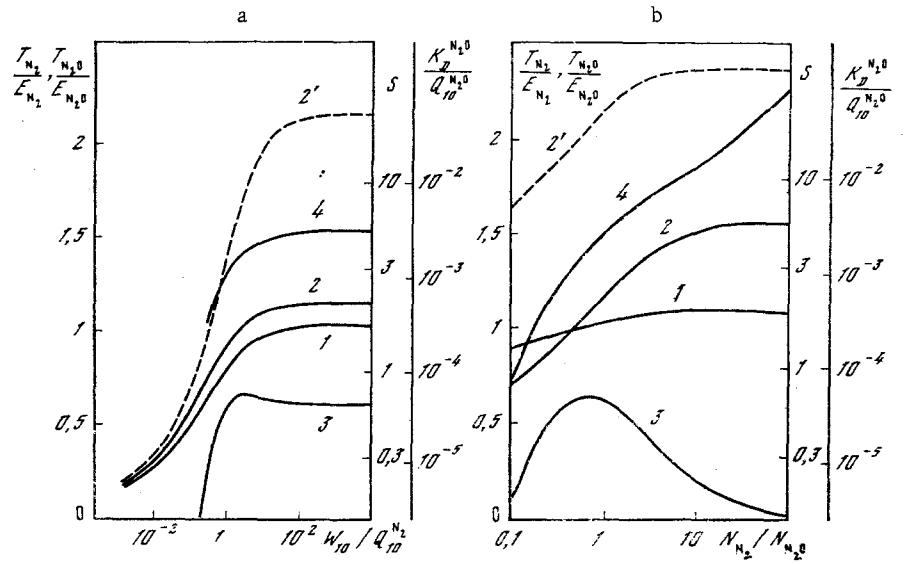

Fig. 11. Plots, for the gas mixture N_2–N_2O, of the vibrational temperatures T_{N_2}/E_{N_2} (curves 1), T_{N_2O}/E_{N_2O} (curves 2), the parameter S (curve 3), and the dissociation-rate constant of N_2O $K_D^{N_2O}/Q_{10}^{N_2O}$ (curve 4) on the pump power in N_2 $W_{10}/Q_{10}^{N_2}$ (a) and on the relative concentration N_{N_2}/N_{N_2O} (b) at T = 300°K. a) $N_{N_2}:N_{N_2O}$ = 1:1, b) $W_{10}/Q_{10}^{N_2} = 10^2$. Curves 2' correspond to the value of the vibrational temperature in N_2O at quasiequilibrium of the vibrational energy in N_2 and N_2O.

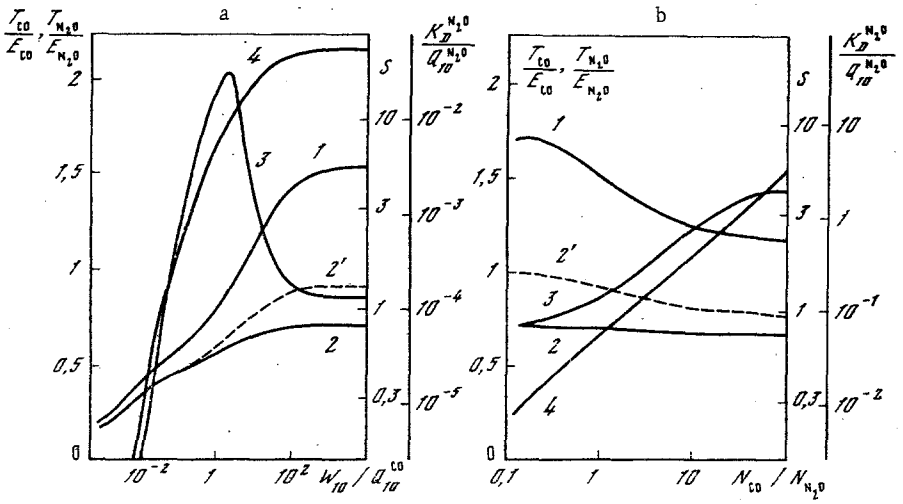

Fig. 12. Plots, for the gas mixture CO–N_2O, of the vibrational temperatures T_{CO}/E_{CO} (curve 1), T_{N_2O}/E_{N_2O} (curves 2), the parameter S (curves 3), and the NO_2 dissociation-rate constant $K_D^{N_2O}/Q_{10}^{N_2O}$ (curves 4) on the pump power in CO W_{10}/Q_{10}^{CO} (a) and on the relative density N_{CO}/N_{N_2O} (b) at T = 300°K. a) N_{CO}: N_{N_2O} = 1:1, b) $W_{10}/Q_{10}^{CO} = 10^3$. Curves 2' correspond to the value of T_{N_2O}/E_{N_2O} at quasiequilibrium of the vibrational energy of CO and N_2O.

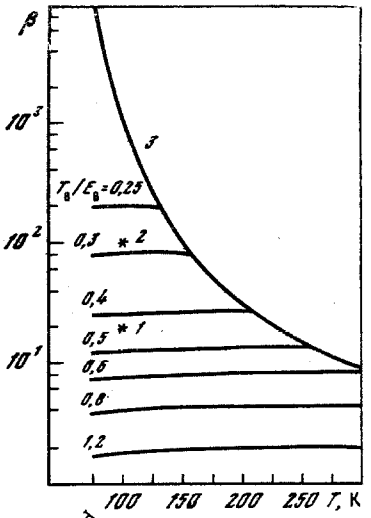

Fig. 13. Dependence of the separation coefficient β of the isotopes $N^{15}O$ and $N^{14}O$ in the chemical reaction $O + N_2 \rightarrow NO + N$ on the gas temperature T at different values of the vibrational temperature T_B of the nitrogen molecules. Curve 3 was plotted in accordance with Eq. (3.12).

(3.12), the separation coefficient under essentially nonequilibrium conditions becomes dependent on the nonequilibrium reserve of the vibrational energy (i.e., T_B) and is practically independent of T. Indeed, if account is taken of the explicit dependence of n* on T_B and T (Eq. (1.14)), then (3.13) takes the form

$$\beta = \exp\left[\frac{E_B - E_A}{T_B}\,\frac{E_B}{2\Delta E}\left(1 - \frac{T_B}{E_B}\,\frac{E_B - E_A - 2\Delta E}{2T}\right)\right]. \tag{3.14}$$

By way of illustration, Fig. 13 shows the dependence of β on T at different values of T_B calculated from Eqs. (3.12) and (3.13) for the case of separation of nitrogen isotopes N^{14} and N^{15} in the reaction $O + N_2 \rightarrow NO + N$, which proceeds with a nonequilibrium reserve of vibrational energy in N_2, and which has an activation energy $\mathscr{E}_{act}$ = 38,300 °K (3.3 eV). The value $Z_A/Z_B = 1$ was used in the calculations. It is seen that with decreasing gas temperature and with increasing T_{N_2} the separation coefficient can differ considerably (by up to several orders of magnitude) from the value obtained from (3.12). The same figure (points 1 and 2) shows the experimental values of β measured in [74, 75], respectively, in which the reaction of formation of $N^{14}O$ and $N^{15}O$ in air was stimulated by exciting vibrations of N_2. The initial temperature of the gas mixture was equal to the liquid nitrogen temperature but, unfortunately, no measurements of T and T_{N_2} are carried out in the course of the reaction. Since, however, the reaction constants are proportional to the populations of the level k, which according to (1.10), (1.18), and (3.11) increase under nonequilibrium conditions with decreasing T, one can expect the experimentally measured relative concentrations of $N^{14}O$ and $N^{15}O$ to correspond to the initial reaction temperatures. The experimental values of β in the figure correspond, therefore, to the temperature T ≈ 100°K. It is seen that in this case a good agreement with experiment can be obtained only by calculation in accordance with Eq. (3.13) or (3.14).

We note that when the component concentrations in the mixture are of the same order the analysis is different from the case when the chemical reactions distort the distribution functions. It is to be expected, however, from physical considerations and from a comparison of the results obtained here with calculations in the approximation of "weak" deviation from equilibrium [20, 74, 77], that the main conclusions of this section remain unchanged.

4. Analytic Model of Gas-Discharge CO Laser

The high efficiency and the large radiation power in the stationary regime distinguish the gas-discharge CO laser, in analogy with the CO_2 laser, from among the remaining gas lasers operating in the IR band. Many studies have by now been devoted to both the experimental and the theoretical study of the properties of this laser (see, e.g., the reviews [31, 52-55]). The important role played in the formation of the inverted population and in the lasing mechanism by the anharmonicity of the vibrations of the CO molecule has been elucidated [2, 94]. For a correct theoretical description of the kinetic processes in an active laser medium with allowance for this anharmonicity, an analysis of the populations of more vibrational levels is necessary. Such an analysis was carried out by now on the basis of the numerical solution of a system of a considerable number (from 20 to 80) of nonlinear population-balance equations. Despite the high accuracy, this approach has also significant shortcomings: it is very cumbersome and lacks physical clarity. It is precisely for these reasons that a number of features of the operation of CO lasers (dealing, e.g., with the thermal regime) have not yet been made clear, no quantitative interpretation was proposed for the experimental results, and the question of optimizing the laser parameters has not been investigated.

In the present section we theoretically investigate, on the basis of the analytic theory developed in Chap. I, the vibrational relaxation of anharmonic oscillators. We study also the phsyical processes that occur in a stationary electric-discharge laser based on a CO—He mixture, and solve the self-consistent problem of determining the properties that are important for lasing (the gain, the vibrational and translational temperatures, the populations of the vibrational levels) as functions of the discharge parameters (current density, electric field intensity, radius and temperature of the discharge tube, total and partial pressures of the gases). It is the examination of just this problem which makes it possible in principle to solve the problem of optimizing the laser parameter.

In a theoretical analysis of the processes in a CO laser, the results of Chap. I on the determination of the distribution function and the relaxation rate of the vibrational energy in a system of harmonic oscillator should be modified and account must be taken of the possible influence, under real operating conditions, of the diffusion of the excited molecules towards the walls of the discharge tube and the reabsorption of the radiation. Let us consider in succession the roles of these factors.

Influence of Diffusion on the Vibrational Distribution Function. A rigorous account of this influence is extremely difficult and calls for solving the diffusion equation with boundary conditions that characterize the vibrational relaxation on the walls of the discharge tube [58]. However, since (as will be shown by subsequent analysis) the diffusion plays a negligible role in the regime of greatest interest for practice, we shall take its role into account approximately, by adding to the kinetic-population-balance equations a term that describes the loss of the vibrationally excited molecules (with a single-quantum transition of these molecules to a lower vibrational level), with a diffusion probability V_d $D(2.4/R)^2$, where D is the diffusion coefficient and R is the radius of the discharge tube. In the investigated CO—He mixture, taking into account the dependence of D on the gas temperature T and on the partial pressures of the helium and carbon monoxide p_{He}, p_{CO} [95, 96], we obtain

$$V_d,\ \mathrm{sec}^{-1} \approx \frac{8.4\cdot 10^{-3} T^2 (2.4/R)^2}{7p_{CO} + p_{He}}. \tag{3.15}$$

Here and below T is expressed in K, the partial and total pressures in torr, and R in cm.

If the influence of the diffusion is taken into account by the indicated method, analytic expressions can be obtained for the distribution function f(i) of the CO molecules over the vibrational levels i. For a weak deviation from equilibrium, when the vibrational—vibrational exchange process that makes the largest contribution to the population is the exchange with the lower vibrational quantum of CO, we obtain for f(i), following the calculations of [19],

$$f(i) \approx f(0) \exp\left[-i\frac{E_1}{T_1} + i(i-1)\frac{\Delta E}{\Gamma}\right] \prod_{j=0}^{i-1} \Psi_{j+1}, \tag{3.16}$$

where the factors Ψ_{j+1} take into account the influence of the vibrational-translational energy exchange and of the single-quantum spontaneous radiative transitions and of diffusion:

$$\Psi_{j+1} = \frac{Q^{01}_{j+1,j} + P_{j+1,j}\exp(E_1/T_1 - E_1/T)}{Q^{01}_{j+1} + P_{j+1,j} + A_{j+1,j} + \Gamma_d}. \tag{3.17}$$

For a strong deviation from equilibrium, when the most substantial of the VV processes are the resonant ones, we obtain for the distribution function with allowance for diffusion, by the same procedure as in Sec. 1 of Chap. I,

$$f(i) = \begin{cases} f(0)\exp\left[-\frac{E_1}{T_1}i + \frac{\Delta E}{T}i(i-1) - \frac{1}{2}\left(\frac{i}{n^*}\right)^2\right], & i \leqslant n^*, \quad (3.18a) \\ \left[C - \frac{P_{10}}{Q_{10}}\frac{T\delta^3_{VV}}{12\Delta E\delta_{VT}}e^{\delta_{VT}i} + A_0\eta^4(i) - V^0_d\ln(i+1)\times\right. \\ \left.\times\left(1 - \frac{\Delta E}{E_1}i\right)\right]\frac{1-\Delta Ei/E_1}{i+1}, & n^* < i \leqslant n^{**}. \quad (3.18b) \end{cases}$$

We have introduced here the notation $V^0_d = V_d T\delta^3_{VV}/12Q_{10}\Delta E$. In contrast to (1.10), in (3.18a) we took additionally into account the factor $\exp\{-(i/n^*)^2/2\}$. By writing down (3.18a) with this factor, we eliminate the discontinuity of function f(i) and of its derivative df/di from (1.10) and (1.20), and ensure a better agreement between (3.18) and the exact numerical calculations. The factor C in (3.18b), just as before, is determined in this case from the condition that (3.18a) and (3.18b) be equal at the point n^*.

Allowance for Reabsorption of the Radiation. Simple estimates show that for practically all the realizable CO-laser operating regimes, the reabsorption of the radiation due to the vibrational—rotational transitions between the upper ($i \geqslant 5$) levels is absent. For this reason, we can use Eqs. (3.16)-(3.18) to calculate the distribution function over these levels with allowance for the radiative transitions under these conditions. It follows from the estimates, however, that at a tube radius and a partial carbon monoxide pressure such that $p_{CO}R \geqslant 1$ torr·cm, reabsorption of the radiation can take place for transitions between lower states, and can influence (at least in the case of weak deviations from equilibrium) the relaxation rate of the vibrational energy of the system. We shall take this reabsorption into account by using the method of Holstein and Biberman [97, 98], which was developed for the calculation of the degree of reabsorption of radiation of an individual line.

In the presence of many spectral lines of the vibrational—rotational transitions $(i, j)\to(i-1, j\pm 1)$, $j = 1, 2, 3, \ldots$, the radiative decay of the level i can be determined by summing, with allowance for reabsorption, the radiation fluxes from the individual rotational sublevels of the vibrational state:

$$\sum_j (F^{i,j}_{i-1,j+1}A^{i,j}_{i-1,j+1} + F^{i,j}_{i-1,j-1}A^{i,j}_{i-1,j-1})n_{i,j} \equiv F_{i,i-1}A_{i,i-1}N_i. \tag{3.19}$$

Here n_{ij} are the populations of the individual rotational states j of the vibrational level i; N_i, total population of this level; $A^{i,j}_{i-1,j\pm1}$, probabilities of the spontaneous radiative transitions $(i, j)\to(i-1, j\pm 1)$; $A_{i,i-1}$, total probability of the spontaneous radiative vibrational transition $i\to i-1$, multipliers $F^{i,j}_{i-1,j\pm1}$, dragging factors and describe thee degree of reabsorption of an individual vibrational—rotational line; and $F_{i,i-1}$, analogous factor for the entire vibrational band $i\to i-1$. In the absence of reabsorption we have $F^{i,j}_{i-1,j\pm1} = F_{i,i-1} = 1$, and the presence of reabsorption $F^{i,j}_{i-1,j\pm1} < 1$.

We calculate now the dragging factor $F_{i,i-1}$, which is needed for the analysis of the vibrational relaxation, assuming Doppler broadening and the absence of overlap of individual vibrational—rotational lines. For this case and for a cylindrical geometry, the factors $F^{i,j}_{i-1,j\pm1}$ are given by [97-99]

$$F^{i,j}_{i-1,j-1} = \begin{cases} 1 & \text{at} \quad R\alpha^{i,j}_{i-1,j+1} \leqslant 2, \\ 1.6/[R\alpha^{i,j}_{i-1,j-1}\sqrt{\pi\ln(R\alpha^{ij}_{i-1,j+1})}] & \text{at} \quad R\alpha^{i,j}_{i-1,j+1} > 2. \end{cases} \tag{3.20}$$

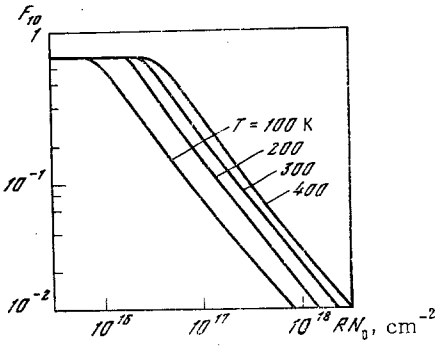

Fig. 14. Dependence of the dragging factor F_{10} on the parameter RN_0 at different gas temperatures T.

Here $\alpha^{i,j}_{i-1,j-1}$ is the absorption coefficient in the center of the line on the transition $(i, j)\to(i-1, j-1)$. If $N_i \ll N_{i-1}$, then

$$\alpha^{i,j}_{i-1,j-1} = j\exp\left[-\frac{B_i}{T}j(j-1)\right]\alpha_{i-1,i}, \qquad \alpha_{i-1,i} = \frac{\lambda^2}{8\pi}\frac{B_i}{T}\frac{A_{i,i-1}}{\Delta\nu}N_{i-1}, \tag{3.21}$$

where λ is the radiation wavelength (in cm); B_i, rotational constant (in °K); $\Delta\nu$, absorption line width (in cm^{-1}). The dragging factors and the absorption coefficients for the P branch lines are written in analogy with (3.20) and (3.21). To carry out the summation in (3.19), we neglect the weak dependence of the logarithmic factor in (3.20) on j, and use for it the value $j \approx \sqrt{T/2B_i}$ corresponding to the maximum absorption coefficient. Next, summing (3.19) approximately with allowance for (3.20) and (3.21), we obtain

$$F_{i,i-1} \approx 1 - \exp\left[-\frac{B_i}{T}j_{R1}(j_{R1}+1)\right] - \exp\left[-\frac{B_i}{T}j_{R2}(j_{R2}+1)\right] + \frac{0.8}{R\alpha_{i-1,i}}[\pi\ln(R\alpha_{i-1,i}\sqrt{T/2B_i}) - 0.5]^{1/2}\times$$
$$\times\left\{\exp\left[\frac{2B_i}{T}(j_{P2}+1)\right] - \exp\left[\frac{2B_i}{T}(j_{P1}+1)\right] + \exp\left(-\frac{2B_i}{T}j_{R1}\right) - \exp\left(-\frac{2B_i}{T}j_{R2}\right)\right\}, \tag{3.22}$$

where j_{R1}, j_{R2} and j_{P1}, j_{P2} are the solutions of the equations

$$R\alpha_{i-1,i}(j+1)\exp\left[-\frac{B_i}{T}j(j+1)\right] = 2 \text{ and } R\alpha_{i-1,i}j\exp\left[-\frac{B_i}{T}j(j-1)\right] = 2. \tag{3.23}$$

On the other hand, if the product $\alpha_{i,i-1}R$ is such that (3.23) has no solution, then we must put in (3.23) $j_{R1} = j_{R2}$, $j_{P1} = j_{P2}$ and $F_{i,i-1} = 1$, i.e., there is no reabsorption in this case. For a Lorentz line shape, the summation in (3.19) must be carried out numerically [99].

The values of the factor F_{10} calculated from (3.19)-(3.23) as functions of the discharge-tube radius R and of the population N_0 of the ground vibrational level of the CO molecules, for different gas particles, are shown in Fig. 14. It is seen that at $N_0R \gtrsim 10^{17}$ cm^{-2} and $T \leqslant 100$°K the reabsorption of the radiation can be appreciable and in some cases can influence the relaxation of vibrational energy of the system.

Effect of Diffusion and Reabsorption of the Radiation on the Vibrational-Energy Relaxation Rate. The change of the distribution function on account of diffusion and reabsorption leads in turn to a change in the relaxation rate of the vibrational energy of anharmonic oscillators. In analogy with Sec. 2 of Chap. I, we calculate f(0), the vibrational energy margin ε per molecule, and the relaxation rates due to the VT processes, to diffusion, and to radiative decay. Retaining in (1.26) after summation (in the case of weak deviation from equilibrium) or integration (in the case of strong deviation from equilibrium) the most essential terms that contribute to their relaxation, we get in place of (1.38)-(1.41)

$$f(0) = 1 - \exp(-E_1/T_1), \tag{3.24}$$

$$\varepsilon = (\varepsilon)_0 - V_d^0[n^{**}\ln n^{**} - n^*\ln n^* - n^{**} + n^* + \delta_{VT}^{-1}], \tag{3.25}$$

$$\frac{\varepsilon}{\tau_{VT}} = \left(\frac{\varepsilon}{\tau_{VT}}\right)_0 - P_{10}V_d^0\frac{1}{2\delta_{VT}}\ln\frac{n^{**}}{n^*}[\exp(\delta_{VT}n^{**}) - \exp(\delta_{VT}n^*)], \tag{3.26}$$

$$\frac{\varepsilon}{\tau_R} = \left(\frac{\varepsilon}{\tau_R}\right)_0 - A_{10}V_d^0\left[n^{**}\left(1-\frac{n^{**}}{2k}\right)\ln n^{**} - n^*\left(1-\frac{n^*}{2k}\right)\ln n^* - n^{**}(1-n^{**}/k) + n^*(1-n^*/k)\right], \quad (3.27)$$

$$\varepsilon/\tau_d \approx V_d \exp(-E_1/T_1), \quad k \equiv E_1/2\Delta E. \quad (3.28)$$

Here $(\varepsilon)_0$, $(\varepsilon/\tau_{VT})_0$, and $(\varepsilon/\tau_R)_0$ are the values of these quantities in accordance with Eqs. (1.38)-(1.41), but with C determined by matching together (3.18a) and (3.18b).

We note that allowance for the diffusion and for the radiative transitions does not reduce merely to consideration of the terms ε/τ_R and ε/τ_d. Spontaneous decay of the levels and diffusion can change the value of n** and, as follows from (3.26), affect the rate of the VT processes. The value of n** is determined from the condition that (3.18b) vanish:

$$\exp(\delta_{VT}n^{**}) = \exp(\delta_{VT}n^*) + \frac{Q_{10}\cdot 12\Delta E\delta_{VT}}{P_{10}T\delta_{VV}^3(1-n^*/2k)}(n^*+1)f(n^*) -$$

$$-\frac{kA_{10}}{4P_{10}}\delta_{VT}[\eta^4(n^*) - \eta^4(n^{**})] + (V_d\delta_{VT}/P_{10})\left[\left(1-\frac{n^*}{2k}\right)\ln n^* - \left(1-\frac{n^{**}}{2k}\right)\ln n^{**}\right]. \quad (3.29)$$

It can be seen from (3.28) and (3.29), however, that in the case of a strong deviation from equilibrium, which usually takes place in the operating regimes of the CO laser, the diffusion and the radiative decay of the levels, and consequently also the reabsorption, exert no influence on the margin of the vibrational energy.

Energy Balance and Gas Heating. One of the main problems in the theoretical analysis of the processes that take place in the active medium of a CO laser is to find the vibrational distribution function and the gas temperature. To calculate f(i) from Eqs. (3.16) or (3.18), it is necessary to determine first of all the vibrational temperature T_1 from the balance equation for the reserve of the vibrational quanta ε. This equation is connected with T_1 by formula (3.25). In the stationary case this equation takes the form

$$\Phi = \varepsilon/\tau_{VT} + \varepsilon/\tau_R + \varepsilon/\tau_d, \quad (3.30)$$

where Φ is the quantum flux (per molecule) into the vibrational system on account of the excitation of the CO vibrations by the electrons. To calculate this flux we must know, besides the excitation cross section, also the free-electron velocity distribution functions, the electron density, and the connection of this density with the current density. Since these factors are not known sufficiently accurately, a more reliable method is, in our opinion, to find Φ from the total energy input into the discharge. Calculations [100] show that in typical CO–He laser mixtures, the electron-energy loss in the discharge, due mainly to excitation of the CO vibrations, amounts to 70-90% of the total loss. For this reason it can be assumed with good accuracy that on the discharge-tube axis

$$\Phi = 0.8\frac{\mathscr{E}J}{10^{-7}kE_1N_{CO}}\cdot 2.3 = 4.3\cdot 10^{19}\frac{p}{p_{CO}}\frac{\mathscr{E}}{N}J, \quad (3.31)$$

where $\mathscr{E}$ is the field intensity of the discharge (in V/cm); J, average current density (in A/cm²); and N, total particle density (in cm⁻³).

An extremely important parameter that determines the operation of the CO laser is the gas temperature T. To calculate it we must add to (3.30) also the heat-conducting equation. For a heat-source Bessel distribution function and for a linear dependence of the thermal conductivity coefficient $\lambda = \lambda_0 + \lambda_1 T$ on T, this equation was solved in [101], and we can write for the temperature at the center of the tube

$$T = \left\{\left[(\lambda_0+\lambda_1T_0)^2 + 0.14\lambda_1R^2\frac{p_{CO}}{T}\frac{\varepsilon}{\tau_{VT}}\right]^{1/2} - \lambda_0\right\}\Big/\lambda_1 \quad (3.32)$$

(T_0 is the tube-wall temperature).

It is assumed in (3.32) that the gas heating is due to vibrational–translational exchange. For the thermal conductivity we can use the following values:

$$\lambda, \text{W/cm}\cdot\text{deg} = \begin{cases} 2.6\cdot 10^{-4} + 3.5\cdot 10^{-6}T & \text{at} \quad p_{H_2}/p_{CO} \approx 10, \\ 3.4\cdot 10^{-4} + 3.8\cdot 10^{-6}T & \text{at} \quad p_{He}/p_{CO} \approx 30. \end{cases} \quad (3.33)$$

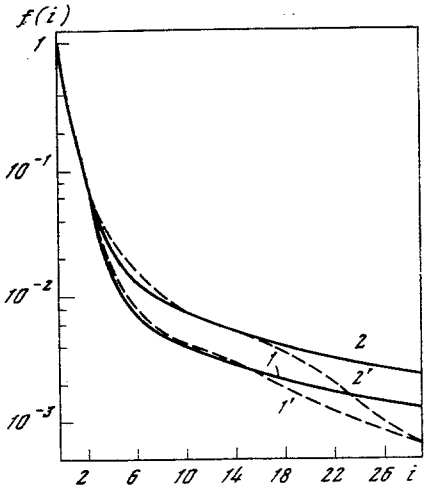

Fig. 15

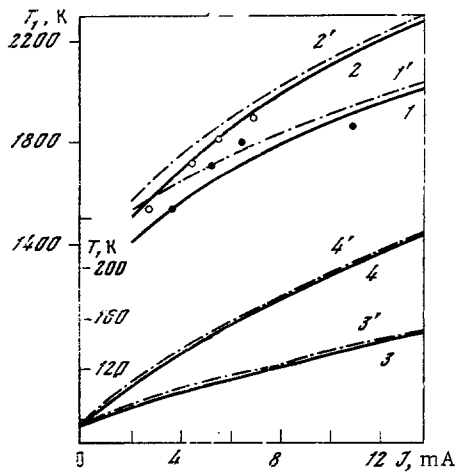

Fig. 16

Fig. 15. Vibrational distribution of function f(i) of CO in the CO + He mixture at a total pressure p = 3 torr. 1, 1') p_{He}/p_{CO} = 11.5; 2, 2') p_{He}/p_{CO} = 30.8, dashed — experiment [102], solid curves — calculation of the present paper.

Fig. 16. Dependence of the vibrational (T_1) and gas (T) temperature on the discharge current J in the mixture CO—He—O_2 (1:10:0.07). 1, 1', 3, 3' — total pressure p = 4 torr; 2, 2', 4, 4' — 10 torr; light circles — experiment at p = 10 torr, dark — p = 4 torr [104].

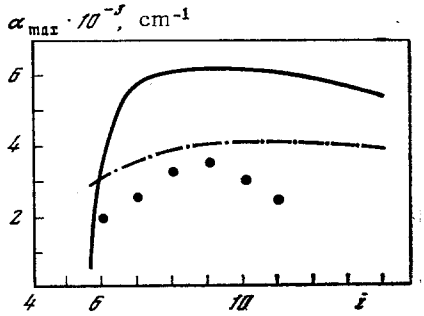

Fig. 17. Maximum gain for different vibrational levels in the mixture CO—He—O_2 (1:30:0.07) at a total pressure p = 4 torr, at a tube voltage 7 kV, and at a discharge current J = 15 mA. Circles — experiment [103], solid line — present calculation.

Calculation and Comparison with Experimental Data. To find T_1 and T at different values of the pump and of the pressure, Eqs. (3.30) and (3.32) with account taken of (3.24)-(3.28), (3.31), and (3.33), were solved simultaneously. The following values were used in the calculation for the probabilities and the parameters δ_{VV} and δ_{VT}:

$$Q_{10}, \text{sec}^{-1} = 230\sqrt{T}\,\varkappa p_{CO}, \qquad \delta_{VV} = 5.58/\sqrt{T}, \qquad \delta_{VT} = 2.08/\sqrt{T},$$
$$P_0^{1\,CO-He}, \text{sec}^{-1} = 350\sqrt{T}\exp\left(-\sqrt{3.09\cdot 10^4/T}\right)p_{He}. \tag{3.34}$$

The quantity $\varkappa$ in (3.34) takes into account the contribution of the long-range forces to the exchange probability (see Chap. I). From an analysis of the experimental and calculated probabilities [83], we found that in the temperature interval T = 100-700 K the value of $\varkappa$ can be determined from the formula

$$\varkappa = 1 + 2.6\cdot 10^7\,(1.16 + 1.6\cdot 10^{-2}\,T)^3/T^{3.5}. \tag{3.35}$$

TABLE 1

	T_1, K	T, K	$\alpha^{5,9}_{4,10}$, cm^{-1}	$\alpha^{12,9}_{11,10}$, cm^{-1}	System
Expt. [102]	2400	149	$-1{,}475\cdot10^{-2}$	$7{,}82\cdot10^{-3}$	CO — He, $p=3$ torr, $p_{He}/p_{CO}=11{,}5$, $\mathscr{E}/N=2{,}7\cdot10^{-16}$ V·cm^2, $R=1{,}5$ cm, $J=29$ mA
Theory	2350	181	$-1{,}26\cdot10^{-2}$	$3{,}07\cdot10^{-3}$	

	T_1, K	T, K	$\alpha^{11,9}_{10,10}$, cm^{-1}	$\alpha^{28,9}_{27,10}$, cm^{-1}	System
Expt. [102]	2450	132	$7{,}37\cdot10^{-3}$	$1{,}06\cdot10^{-3}$	CO — He, $p=3$ torr, $p_{He}/p_{CO}=30{,}8$, $\mathscr{E}/N=1{,}4\cdot10^{-6}$ V·cm^2, $R=1{,}5$ cm, $J=29$ mA
Theory	2397	147	$4{,}08\cdot10^{-3}$	$1{,}6\cdot10^{-3}$	

	T, K	α_{max}, cm^{-1}	System	T, K	α_{max}, cm^{-1}	System
Expt. [103]	140	$2{,}2\cdot10^{-3}$	CO : He : O_2 (1 : 10 : 0,07) $U=7$ kV, $J=7$ mA, $p=4$ torr, $R=1$ cm, $L=85$ cm	150	$3{,}5\cdot10^{-3}$	CO : He : O_2 (1 : 30: :0,07) $p=6$ torr, $R=1$ cm, $U=6$ kV, $J=15$ mA, $L=83$ cm
Theory	140	$5{,}9\cdot10^{-3}$		150	$6{,}1\cdot10^{-3}$	

Note. U is the voltage on the discharge tube and L is the length of the tube.

The results of the simultaneous solution of Eqs. (3.30) and (3.32) are shown in Figs. 15-17 and in Table 1, which show also the experimental values of the measured quantities. As seen from Fig. 15, the calculated distribution function agrees well with the experimental curve in a large range of vibrational levels. The calculated vibrational and gas temperatures, as well as the gain for individual lines, also agree with experiment (see Table 1). Unfortunately, the current—voltage characteristic was not published in [104]. When account is taken of the dependence of $\mathscr{E}/N$ on the current density, one can expect an even better agreement between the calculated plot of the temperature T_1 in Fig. 16 and the experimental data.

Figure 17 shows the calculated gain α for different vibrational levels and its experimental value [103] for the mixture CO—He—O_2 (1:30:0.07).

We note that the solution of (3.30) and (3.32) can be simplified and represented in simple analytic form, by considering the most interesting case of a strong deviation from equilibrium. As already indicated, estimates show that in this regime we can neglect in (3.30) the quantities ε/τ_R and ε/τ_d. Substituting in (3.30) the explicit value of ε/τ_{VT} (see (1.34)) and solving it with respect to T_1 with account taken of (3.31) and (3.34), we obtain

$$\frac{T_1}{E_1}\approx\left\{\frac{37}{T}\ln\left[9\cdot10^{-22}T^3\varkappa p_{CO}^2/(pJ\mathscr{E}/N)\right]-\frac{18.6}{T}\right\}^{-1}. \tag{3.36}$$

In the regime of strong deviation from equilibrium, the gain α is largest for the levels $i \geqslant n^*$, for it is precisely here that the effective vibrational temperature of the neighboring levels becomes large. Recognizing that for the indicated group of equations their populations are determined by the first term in (3.18b), we can obtain for $\alpha^{i,j-1}_{i-1,j}$ the simple expression

$$\alpha^{i,j-1}_{i-1,j},\ \text{cm}^{-1}\approx6.2\cdot10^{13}\sqrt{\frac{\mathscr{E}}{N}pJ\Big/\varkappa}\,\frac{B_i j}{T^3}\left(1-\frac{i}{k}\right)^3\left[\frac{i}{i+1}-\exp\left(-\frac{2B_i}{T}j\right)\right]\exp\left[-\frac{B_i}{T}j(j-1)\right]. \tag{3.37}$$

The dash—dot lines in Figs. 16 and 17 show T, T_1, and α_{max}, calculated from Eqs. (3.32), (3.36), and (3.37) under the condition that 85% of the energy goes over from the vibrational to the translational degree of freedom. In this case j_{opt}, which gives the maximum gain at a specified vibrational temperature, was calculated from the equation [52]

$$j_{\text{opt}} \approx \frac{T}{B_i}\left(\frac{1}{4i} + \sqrt{\frac{1}{16i^2} - \frac{3B_i}{T}}\right). \tag{3.38}$$

We note in conclusion that for a comprehensive theoretical analysis of the VT processes in a CO laser it is necessary to know the densities of the various impurities produced in the discharge (O atoms, CN molecules, etc.) as well as the probabilities of the vibrational transitions induced in CO by these impurities [105, 106]. In a number of cases the influence of these impurities can be quite substantial. However, if the presence of the impurity leads only to an increase of the probability $P_{i,\ i-1}$ for the VT processes, then, as follows from Chap. 1 and from Eqs. (1.38)-(1.41), their influence on the operation of the CO laser can be insignificant and reduces mainly to a possible change of the parameter $\mathscr{E}/N$ and to a shortening of the gently sloping plateau of the distribution function f(i) in the region i > n* (i.e., to a decrease of n**). In all other respects the vibrational relaxation does not change and is determined by the probability Q_{10}. It is precisely for this reason that the results obtained here agree well with experiment.

CHAPTER IV

VIBRATIONAL RELAXATION AND LASERS OPERATING ON INTRAMOLECULAR VIBRATIONAL TRANSITIONS IN LIQUIDS AND IN MOLECULAR CRYSTALS

The principles of vibrational relaxation in liquids and molecular crystals are considered, the influence of collective interactions on the intramolecular vibrational transitions is analyzed. The possibilities are investigated of using liquids and molecular crystals as active media for lasers operating on vibrational transitions, as well as the possibility of stimulating laser-chemical reactions in the liquid phase. The results of this chapter are based on [107-110].

1. Calculation of the Probabilities of Intramolecular Vibrational Transitions Induced by Collective Interaction of Molecules

To assess the possibilities of using liquids in laser chemistry, as well as liquids in molecular crystals for the development of IR lasers based on vibrational transitions of the molecules, it is necessary to analyze the vibrational kinetics in these media and primarily to estimate the characteristic times for the vibrational—translational and vibrational—vibrational energy exchange. The difficulties encountered here are due to the need of taking into account the collective interactions. Owing to the important role of these interactions, vibrational relaxation in liquids, and especially in molecular crystals, can differ substantially from relaxation in a gas. We turn, therefore, to a quantitative estimate of the contribution of the collective interactions to the probabilities of the vibrational processes.

For a clear description of the collective effects we shall consider, following [41, 43], the interactions of a molecule with a number $\tilde{N}$ of partner molecules disposed on the surface of a spherical cell with radius a. The action on a molecule located at the center of the cell will be described by a sum of Lennard-Jones potentials. If the molecule is deflected by a distance $R \ll a$, then after expanding the total potential of the interaction V in powers of R/a we have

$$V = \sum A_i (R/a)^i, \quad i = 0, 2, 4, \ldots, \tag{4.1}$$

where the expansion coefficient A_i is given by

$$A_i = \frac{\varepsilon\tilde{N}}{\beta^2}\,\frac{2}{5}\,\frac{(i+10)!}{9!\,(i+1)!}\left[1 - \frac{5\cdot 9!\,(i+4)!}{2\cdot 3!\,(i+10)!}\,\beta\right], \tag{4.2}$$
$$\beta = (a/r_0)^6, \quad a^3 = M\tilde{N}/4\pi\rho.$$

Here ε and r_0 are the constants in the Lennard-Jones potential for a substance with an individual-molecule mass M and a density ρ. From now on, following [43], we shall assume that $\tilde{N} = 12$.

In (4.1), the term with i = 0 determines the binding energy. The terms of the first (i = 2) and next (i $\geqslant$ 4) approximations describe the intermolecular vibrations and their interaction with the intramolecular ones. Let us calculate for this interaction, in general form, the probabilities of the intramolecular vibrational transitions in a polyatomic molecule. First, however, for the sake of clarity, we solve in a purely classical approximation the problem of finding the probability of vibrational—translational energy exchange.

We represent the quantity R in (4.1) in the form $R = R_c + bx$, where R_c is the coordinate of the mass center of the molecule, while x and b are the intramolecular coordinate of the oscillator and the direction cosine. The equations of motion for the mass center and for the intramolecular oscillator, with allowance for (4.1) and for the fact that $R_c \gg x$, are of the form

$$M\ddot{R}_c = -\frac{\partial V(R_c, x)}{\partial R_c} \approx -\sum_n (i+1)\frac{A_{n+1}}{a}\left(\frac{R_c}{a}\right)^n, \tag{4.3}$$

$$M_1\ddot{x} + M_1(2\pi\nu)^2 x = F(t) = -\frac{\partial V(R_c, x)}{\partial x} \approx \tag{4.4}$$

$$\approx -\sum_n b(n+1)\frac{A_{n+1}}{a}\left(\frac{R_c}{a}\right)^n, \quad n = 1, 3, 5, \ldots$$

Here M_1 and ν are, respectively, the reduced mass of the intramolecular oscillator and frequency, and F(t) is the force due to the collective effects and acting on this oscillator.

It follows from (4.3) that in the first-order approximation (n = 1) the molecule executes harmonic oscillations about the center of the cell with a frequency $\nu_{ph}^0 = (1/2\pi)\cdot\sqrt{2A_2/a^2M}$. We note, however, that this result is to a certain degree illustrative in character, for actually the spectrum of the frequencies of the intermolecular vibrations is continuous and lies in the range $0 \leqslant \nu_{ph} \leqslant \nu_D$, where ν_D is the Debye frequency, equal, according to [43], to the quantity

$$\nu_D, \text{sec}^{-1} = \sqrt{2}\,\nu_{ph}^0 = \frac{10.4}{a\beta}\sqrt{\frac{\varepsilon}{M}\left(1 - \frac{5}{22}\beta\right)}. \tag{4.5}$$

The expressions (4.1), (4.3), and (4.4) are also illustrative, since they do not take into account the deviations from the equilibrium positions of all the molecules. If these deviations are taken into account, then in accordance with the theory of crystal-lattice vibrations and the theory of phonon interactions [111] we should have in place of the expansion (4.1) and the expressions in the right-hand sides of (4.3) and (4.4) an expansion in the product $R_{c1}R_{c2}\ldots R_{cn}$ of the independent deviations from equilibrium.

Despite the foregoing limitations, however, the considered approach to the solution of the problem of calculating the intramolecular vibrational transitions is quite useful, since it provides a clear physical picture of the phenomenon, and makes it possible to estimate quantitatively the intermolecular potential, the expansion coefficients A_i, the force F(t) acting on the intramolecular oscillator, and in final analysis, when account is taken of the indicated singularities of the ν_{ph} spectrum and of the expansion of the potential, it makes it possible to calculate the transition probability.

To find this probability, we shall assume that at the initial instant of time the intramolecular oscillator is at rest: $x|_{t=0} = 0$, $\dot{x}|_{t=0} = 0$. Next, an external periodic force F(t) begins to act on the oscillator so that after a time t the oscillator acquires an energy

$$\Delta\mathscr{E} = (M_1/2)[\dot{x}^2 + (2\pi\nu)^2 x^2].$$

The change $\Delta\mathscr{E}/t$ of the vibrational energy per unit time as a function of F(t) can be calculated by integrating Eq. (4.4) with the indicated initial conditions [59]:

$$\frac{\Delta\mathscr{E}}{t} = \frac{1}{2M_1 t}\left|\int_0^t F(\xi)\exp(-2\pi i\nu\xi)\,d\xi\right|^2. \tag{4.6}$$

An explicit $F(\xi)$ dependence should be obtained in this case by substituting in (4.4) the values $R_{ci}(t)$ obtained from the solutions (4.3). For the sake of clarity we confine

ourselves in the expansion (4.1) to the first three terms. This is equivalent to retaining the first two terms in the right-hand sides of (4.4).*

In this case the periodic force F(t), that acts on the intramolecular oscillator and causes the change of its energy, takes the form

$$F(t) = -\frac{2bA_2}{a^2} R^0_{c1} \sin(2\pi\nu_{ph1}t) - \frac{4bA_4}{a^4} R^0_{c1} R^0_{c2} R^0_{c3} \sin(2\pi\nu_{ph}t) \sin(2\pi\nu_{ph2}t) \sin(2\pi\nu_{ph3}t). \tag{4.7}$$

The amplitudes R^0_{ci} of the intermolecular oscillations can be easily determined from energy considerations and from the assumption that the energy of these oscillations is at equilibrium and corresponds to a temperature of the medium T:

$$R^0_{ci} = \sqrt{kT/(2\pi^2\nu^2_{phi}M)}. \tag{4.8}$$

If the product of the three sine functions in (4.7) is represented in the form of a sum of sine functions $^1/_4\{\sin[2\pi(\nu_{ph1} + \nu_{ph2} - \nu_{ph3})t] + \sin[2\pi(\nu_{ph2} + \nu_{ph3} - \nu_{ph1})t] + \sin[2\pi(\nu_{ph3} + \nu_{ph1} + \nu_{ph2})t] - \sin[2\pi(\nu_{ph1} + \nu_{ph2} + \nu_{ph3})t]\}$, then after substituting (4.7) in (4.6), we easily see that as $t\to\infty$ and under the condition $\nu > \nu_D \gg \nu_{phi}$ a nonzero value of $\Delta\mathscr{E}$ can be due only to harmonics of the force F(t) with frequencies $(\nu_{ph1} + \nu_{ph2} - \nu_{ph3})$, $(\nu_{ph2} + \nu_{ph3} - \nu_{ph1})$, $(\nu_{ph3} + \nu_{ph1} - \nu_{ph2})$, $(\nu_{ph1} + \nu_{ph2} + \nu_{ph3})$. Standard integration in (4.6) and the condition $t\to\infty$ yield in this case a delta function in the differences between these frequencies and the intramolecular frequency ν. Taking this into account, as well as relation (4.8), we obtain for the probability p_{01} of the excitation (and to the deactivation probability p_{10}, which is equal to it in the classical case) of the vibrational level 1 of the intramolecular oscillator per unit

$$p_{01} \approx p_{10} = \frac{\Delta\mathscr{E}}{th\nu}\bigg|_{t\to\infty} = \left(\frac{8b\pi A_4}{h}\right)^2 \left(\frac{h}{8\pi^2 M_1 \nu a^2}\right) \prod_{i=1}^{3} \left(\frac{kT}{8\pi^2 M \nu^2_{phi} a^2}\right) \delta[\nu - (\pm\nu_{ph1} \pm \nu_{ph2} \pm \nu_{ph3})], \tag{4.9}$$

where $\delta[\ldots]$ is a delta function.

To obtain the total probability P_{10} it is necessary to integrate (4.9) over the spectrum of the frequencies of the intermolecular oscillations $0 \leqslant \nu_{phi} \leqslant \nu_D$ with spectral density $D(\nu_{phi})$:

$$P_{10} = \int_0^{\nu_D} D(\nu_{ph1})\, d\nu_{ph1} \int_0^{\nu_D} D(\nu_{ph2})\, d\nu_{ph2} \int_0^{\nu_D} D(\nu_{ph3})\, p_{10}(\nu_{ph1}, \nu_{ph2}, \nu_{ph3})\, d\nu_{ph3}.$$

The integration operation can be easily carried out by assuming that the oscillations have a Debye spectrum $D(\nu_{phi}) = 3\nu^2_{phi}/\nu^3_D$. In this case averaging over the spectrum reduces to a calculation of the integral

$$\int_0^{\nu_D} d\nu_{ph1} \int_0^{\nu_D} d\nu_{ph2} \int_0^{\nu_D} \delta[\nu - (\pm\nu_{ph1} \pm \nu_{ph2} \pm \nu_{ph3})]\, d\nu_{ph3} = \frac{1}{2}(3\nu_D - \nu)^2. \tag{4.10}$$

Taking (4.9) and (4.10) into account, we obtain ultimately for the probability P_{10}

$$P_{10} = \left(\frac{8\pi b A_4}{h}\right)^2 \left(\frac{h}{8\pi^2 M_1 \nu a^2}\right) \left(\frac{3kT}{8\pi^2 M \nu^2_D a^2}\right)^3 \frac{(3\nu_D - \nu)^2}{2\nu^3_D}. \tag{4.11}$$

A probability P_{10} analogous to (4.11) was calculated quantum-mechanically in [43], but an incorrect dependence of P_{10} on ν and ν_D was obtained because of an inaccurate integration over the phonon spectrum.

In the integration in (4.10) it was assumed that $3\nu_D > \nu$. If this condition is not satisfied, then we obtain for the probability $P_{10} = 0$. This situation can be easily explained physically from energy considerations and means that at $3\nu_D < \nu$ a vibrational transi-

*Strictly speaking, it is necessary to retain in the right-hand side of (4.3) also the term with n = 3. However, neglect of terms of order higher than n = 1 (i.e., the assumption that there is no interaction between the different molecular oscillations) does not lead to a substantial error in the calculation of the transition probability, since it means that after substituting $R_{ci}(t)$ in the right-hand side of (4.4) we neglect in it terms of the same order of magnitude. This circumstance, while substantially simplifying the analysis, does not change the order of magnitude of the calculated probability.

tion induced by a periodic force with maximum harmonic frequency $3\nu_D < \nu$ is impossible, since this frequency is lower than the frequency of the intramolecular oscillations. In this case, to obtain a nonzero probability P_{10} it is necessary to retain in the sum of the right-hand side of (4.4) terms of higher order of smallness with a value of n such that the condition $n\nu_D > \nu$.

Thus, expression (4.11) determines for the particular case $3\nu_2 < \nu$ the probability of deactivation (or excitation) of intramolecular oscillations with participation of three phonons.

We turn now to a quantum-mechanical calculation, in general form, of the probabilities inside the molecular vibrational transitions in a polyatomic molecule, induced by collective interaction of the type (4.1). We consider the transition of one vibrational-mode quantum with frequency ν_1 into m quanta of another mode of frequency ν_2 with participation of n phonons.

Recognizing that $R = R_c + b_1x_1 + b_2x_2$, where R_c is the coordinate of the mass center of the molecule, x_1, x_2 and b_1, b_2 are the intramolecular coordinates and the direction cosines, we represent (4.1) in the form of a series in powers of R_c, x_1, x_2. For simplicity we use in the calculation of the matrix elements the wave functions of harmonic oscillators (for both the intermolecular and the intramolecular oscillations).* In this case, from among the anharmonic terms in (4.1), the one responsible for the considered transition will be $\frac{(n+m+1)!}{n!\,m!\,a^{n+m+1}} A_{n+m+1} R_c^n b_1 x_1 (b_2x_2)^m$. However, as already indicated, this expression is symbolic in character, since it does not reflect the actual deviation of all the molecules from the equilibrium positions.

In the general theory of phonon interaction, R_c^n is replaced by a product of n displacements $R_{c1}R_{c2}\ldots R_{cn}$ [111]. Taking this into account and using ordinary perturbation theory, we have

$$q_{10}^{0m}(v_1 \to v_1 \pm 1; v_2 \to v_2 \pm 1; \ldots; v_n \to v_n \pm 1) = \frac{4\pi^2}{h^2}\left[\frac{(n+m+1)!\,b_1 b_2^m A_{n+m+1}}{n!\,m!\,a^{n+m+1}}\right]^2 \times \tag{4.12}$$
$$\times |\langle 1|x_1|0\rangle|^2 |\langle 0|x_2^m|1\rangle|^2 |\langle v_1|R_{c1}|v_1 \pm 1\rangle|^2 \ldots \times |\langle v_n|R_{cn}|v_n \pm 1\rangle|^2 \delta\left[m\nu_2 - \nu_1 + \sum_{j=1}^{n} \nu_{\mathrm{ph}\,i}(v_j \pm (1-v_j))\right].$$

Expression (4.12) is the probability in the intramolecular modes ν_1 and ν_2 in the molecule that there will take place the transition $1 \to 0$ and $0 \to m$, and the transitions $v_j \to v_j \pm 1$ will take place between n phonons. To obtain the overall probability Q_{10}^{0m} of an intramolecular transition with participation of n phonons it is necessary to sum (4.12) over all possible $\nu_j \to \nu_j \pm 1$ transitions with account taken of the Boltzmann distribution of the phonons over the vibrational levels (with a temperature equal to the temperature T of the medium). Recognizing that

$$|\langle v|R_{ci}|v-1\rangle|^2 = v|\langle 1|R_{ci}|0\rangle|^2 = v|\langle 0|R_{ci}|1\rangle|^2,$$

we have for the deactivation of the phonons

$$\sum_{v=1}^{\infty} |\langle v|R_{ci}|v-1\rangle|^2 [1-\exp(-h\nu_{\mathrm{ph}\,i}/kT)]\exp(-vh\nu_{\mathrm{ph}\,i}/kT) = |\langle 1|R_{ci}|0\rangle|^2 [1-\exp(-h\nu_{\mathrm{ph}\,i}/kT)]^{-1}\exp(-h\nu_{\mathrm{ph}\,i}/kT), \tag{4.13a}$$

and for the excitation of the phonons

$$\sum_{v=0}^{\infty} |\langle v|R_{ci}|v+1\rangle|^2 [1-\exp(-h\nu_{\mathrm{ph}i}/kT)]\exp(-vh\nu_{\mathrm{ph}\,i}/kT) = |\langle 0|R_{ci}|1\rangle|^2 [1-\exp(-h\nu_{\mathrm{ph}\,i}/kT)]^{-1}. \tag{4.13b}$$

The right-hand sides of (4.13a) and (4.13b) simplify at high temperatures $kT > h\nu_D \geqslant h\nu_{\mathrm{ph}i}$ and become equal. If account is taken here of the explicit form of the matrix element for the transition $1 \to 0$ (or $0 \to 1$), then we obtain in the right-hand sides of (4.13a) and (4.13b) the value

*This approximation is analogous to the assumption used above in the classical problem, that the intermolecular oscillations are independent and harmonic. As indicated in the preceding footnote, this approximation does not change the order of magnitude of the calculated probability.

$$|\langle 1|R_{ci}|0\rangle|^2 \frac{kT}{h\nu_{phi}} = |\langle 0|R_{ci}|1\rangle|^2 \frac{kT}{h\nu_{phi}} = \frac{kT}{8\pi^2 M\nu_{ph}^2}. \tag{4.14}$$

If we integrate, with account taken of (4.14), the expression (4.12) over the spectrum of the phonon frequencies with the Debye distribution function $D(\nu_{phi}) = 3\nu_{phi}^2/\nu_D^3$ $(0 \leqslant \nu_{phi} \leqslant \nu_D)$, then we obtain ultimately for the probability Q_{10}^{0m} of the process that proceeds in the exothermal direction $(\nu_1 - m\nu_2 > 0)$

$$Q_{10}^{0m},\ \text{sec}^{-1} = \left[\frac{(n+m+1)!\,A_{n+m+1}}{n!m!h\nu_D}\right]^2 \frac{h\bar{b}_1^2}{2M_1\nu_1 a^2}\left(\frac{h\bar{b}_2^2}{8\pi^2 M_2\nu_2 a^2}\right)^m \left(\frac{3kT}{8\pi^2 M\nu_D^2 a^2}\right)^n \left(n - \frac{\nu_1 - m\nu_2}{\nu_D}\right)^{n-1} \frac{\nu_D}{(n-1)!\,m!}. \tag{4.15}$$

Here M_1 and M_2 are the masses of the oscillators for the normal vibrations ν_1 and ν_2. The number n of phonons participating in the vibrational transition is an integer in the interval

$$\frac{\nu_1 - m\nu_2}{\nu_D} \leqslant n \leqslant \frac{\nu_1 - m\nu_2}{\nu_D} + 2 \tag{4.16}$$

and satisfies the condition $n + m + 1 = i$ (i is an even number). The probability Q_{01}^{m0} of the inverse process is determined from the detailed balancing principle: $Q_{01}^{m0} = Q_{10}^{0m} \cdot \exp[-(h\nu_1 - mh\nu_2)/kT]$.

Expression (4.15) is quite general and, besides the VV' process, it can describe also other relaxation channels. Thus, at $m = 1$, $\nu_1 = \nu_2$, $M_1 = M_2$ and $\bar{b}_1^2 = \bar{b}_2^2 = 1/3$ we obtain from (4.15), taking (4.2) and (4.16) into account, an expression for the probability of the resonant VV process

$$Q_{10}^{10},\ \text{sec}^{-} = 2.1\cdot 10^{-4}\left[\frac{M\nu_D}{M_1\nu_1}\right]^2 \left[\frac{kT}{\varepsilon}\right] \frac{(1-\beta/14.3)^2\beta^4}{(1-\beta/4.4)}\,\nu_D. \tag{4.17}$$

In analogy with (4.17), it is also easy to write down expressions for the probabilities of single-quantum exchange (both resonant and nonresonant) between highly excited states. These probabilities were calculated for an anharmonic oscillator by a somewhat different method in [47]. At $m = 0$, expression (4.15) is the probability P_{10} of the VT transition $1\to 0$ with participation of n phonons:

$$P_{10},\ \text{sec}^{-1} = \frac{(n+1)^2}{(n-1)!}\left[\frac{A_{n+1}}{h\nu_D}\right]^2 \frac{h}{6M_1\nu_1 a^2}\left[\frac{3kT}{8\pi^2 M\nu_D^2 a^2}\right]^n \left(n - \frac{\nu_1}{\nu_D}\right)^{n-1}\nu_D. \tag{4.18}$$

In the particular case $n = 3$, Eq. (4.18) coincides with expression (4.11) calculated in the classical approximation.

Inasmuch as in a liquid the particles have besides collective motion also a disordered motion, an important influence can be exerted on the vibrational relaxation also by ordinary binary collisions which cause this random motion. To assess the contribution of the binary collisions to the probability of the vibrational transitions, we can use the usual Hertz–Schwarz–Slawsky procedure to estimate these probabilities.

Table 2 lists for certain liquids the probabilities P_{10} and Q_{10} calculated from expressions (4.17), (4.18) (P_{10}^{coll}, Q_{10}^{coll}) and from the usual Herzfeld–Schwarz–Slawsky formulas (P_{10}^{bin}, Q_{10}^{bin}). The calculation was performed for a normal oscillation with the lowest frequency for the given molecule, for it is precisely this normal oscillation which determines on the whole the character of the VT processes. The table also lists the experimental values of P_{10}^{exp}, taken from [41, 45]. It is seen that at room temperatures the experimental probabilities agree better with the theoretical ones, calculated under the assumption of binary collisions. The conclusion that the binary collisions play a predominant role for the VT processes in weakly associated liquids was drawn earlier in [41, 45]. It is clear, however, that owing to the different dependences of P_{10}^{coll} and P_{10}^{bin} on the frequency ν_1 of the intramolecular oscillations and on the temperature T, it cannot be generalized to a wide range of temperatures and to all liquids. With decreasing T and at low frequencies $\nu_1 < 3\nu_D$ the principal role for the VT process can be played by collective effects, when the intramolecular oscillation decays into only three phonons.

An important conclusion of the calculations of the times of the vibrational relaxation is also the fact that in liquids, just as in single-component molecular gases, the VT and VV processes have different times, with $\tau_{VV} \sim 1/Q_{10} \leqslant \tau_{VT} \sim 1/P_{10}$. This makes it possible to apply certain results of vibrational kinetics in a gas to a liquid and, in particular,

TABLE 2

Molecule	T, K	$\nu_1 \cdot 10^{-12}$, sec^{-1}	$\nu_p \cdot 10^{-12}$, sec^{-1}	n	P_{10}^{coll}, sec^{-1}	P_{10}^{bin}, sec^{-1}	$P_{10}^{exp} \cdot 10^{-9}$, sec^{-1}	$Q_{10}^{bin} \cdot 10^{-10}$, sec^{-1}	$Q_{10}^{coll} \cdot 10^{-9}$, sec^{-1}	$Z^{bin} \cdot 10^{-12}$, sec^{-1}
C_6H_6	303	12	4,10	3	$1,9 \cdot 10^6$	$1,2 \cdot 10^9$	3,7	8	1,3	1,4
CS_2	298	11,9	3,71	5	$1,3 \cdot 10^4$	$2,4 \cdot 10^9$	3,53	12	2,8	2
CCl_4	293	6,51	2,90	3	$2,2 \cdot 10^8$	$4,9 \cdot 10^9$	7,95	89	1,3	0,9
C_4H_4O	276	16,5	4,94	5	$4,94 \cdot 10^2$	$7,6 \cdot 10^7$	0,72	5,5	0,79	1,7
$CHCl_3$	300	3,3	3,15	3	$5,3 \cdot 10^9$	$4,5 \cdot 10^{11}$	6,6	63	11	1,2
CH_2Cl_2	300	8,55	5,60	3	$5,2 \cdot 10^8$	$1,5 \cdot 10^{10}$	1,5	19	2,3	1,8
C_5H_5N	303	11,2	2,21	7		$8,5 \cdot 10^8$	—	7	2,4	1,2
C_4H_4NH	303	16,95	5,63	5	$7,30 \cdot 10^2$	$9,9 \cdot 10^7$	—	6,5	0,84	1,9

Note. N is the number of phonons participating in the VT process; in the calculation of P_{10}^{bin}, Q_{10}^{bin} the parameter of the potential of the intermolecular interaction $\sim\exp(-\alpha r)$ was assumed to be $\alpha = 5$ Å^{-1}; the frequencies of the binary collisions Z^{bin} were calculated by linear extrapolation of the values of these frequencies for gases into the region of larger (corresponding to a liquid) particle densities.

to describe the degree of excitation of various types of intramolecular oscillations in a liquid by means of vibrational temperature, so owing to the smallness of τ_{VV} there will be established within each vibrational mode a quasistationary distribution (a Boltzmann distribution for the harmonic model).

Besides the VT and VV processes, an important role for the vibrational modes of the polyatomic molecule can be played also by VV' processes, i.e., by energy exchange between the different modes. In many cases (this is confirmed by a calculation with account taken already of only binary collisions and by experiment [112]) the times of these processes for liquids are shorter than the time of the vibrational—translational relaxation mode with the lowest oscillation frequency, and the relaxation of the vibrational energy of the molecules is characterized by only one time of this VT process, which is usually measured for a liquid by an acoustic method [45]. However, to use liquids as the active media for lasers operating on vibrational transitions, a more favorable (although not essential) situation is one in which the energy relaxation from some vibrational mode (or group of modes) proceeds more slowly than from the other modes, and consequently on the whole the relaxation of the vibrational energy is characterized not by one but by several times. The presence of several vibrational-relaxation times in a number of liquids is indicated by experiments performed by the acoustic method [45, 46].

All the presented results, and particularly Eqs. (4.1)-(4.18), concerning the influence of collective interaction on the vibrational relaxation in liquids, are fully applicable to molecular crystals. The decisive role in the vibrational relaxation for crystals is played by collective interactions, while the binary interactions are inessential.

By way of illustration, we present below the probabilities of certain vibrational processes, calculated from Eqs. (4.2)-(4.18) at T = 170°K for the molecular crystal CO_2:

	T, K	$Q_{10}^{(1)}$ *	$Q_{10}^{(2)}$	$Q_{10}^{(3)}$	$P_{10}^{(2)}$	$Q'(3\to1,2)$	$Q'(1\to2)$
Molecular-crystal	170	$2.8 \cdot 10^8$	$1.1 \cdot 10^9$	$9.6 \cdot 10^7$	12	$1.1 \cdot 10^3$	$2.0 \cdot 10^7$
Gas ($p = 1$ atm)	300	—	—	—	$8.5 \cdot 10^4$	$2.9 \cdot 10^5$	—

*Values are given in units of sec^{-1}.

Here $Q_{10}^{(1)}$, $Q_{10}^{(2)}$, $Q_{10}^{(3)}$, $P_{10}^{(2)}$ are the probabilities of the VV and VT processes in the symmetric, deformation, and asymmetric modes, respectively, $Q'(3\to1, 2)$ is the probability of the VV' transition of a lower quantum of the asymmetric mode into lower quanta of the symmetric and deformation modes, $Q'(1\to2)$ is the probability of a VV' transition of a lower quantum of the symmetric mode into two lower quanta of the deformation mode.

An important conclusion that follows from the analysis of (4.15), (4.18), and the concrete calculations is that the VT processes in molecular crystals can be much slower than in

liquids and compressed gases, especially in cases when the crystal temperature is low and the lowest of the frequencies of the intramolecular oscillations greatly exceeds the Debye frequency ν_D, so that the VT relaxation takes place with participation of a large number of phonons.

2. Lasers Based in Intramolecular Vibrational Transitions in Liquids and in Molecular Crystals, Pumped by an Intense Electron Beam

We consider now the possibilities of using liquids and molecular crystals as active media for lasers based on vibrational transitions. Recently much attention has been paid to the development of high-power gas lasers on vibrational—rotational transitions of molecules with high (1-20 atm) pressure of the working gas [57, 113]. An important advantage of such systems is the possibility, in principle, of obtaining, by simultaneous increase of the gas pressure and of the pump intensity, large concentrations of active molecules. It is clear that from this point of view it is tempting to use liquids and molecular crystals as the active laser media.

Compared with gases of moderate density ($\sim$20 atm at 300°K), liquids and molecular crystals have a number of obvious advantages: they have a much higher density (by approximately two orders of magnitude) and at the same time require no special means of containment. In addition, the widths of the vibrational bands coincide in essence with those of gases of moderate density ($\Delta\nu \sim 5$-20 cm^{-1}), a fact of no little importance when it comes to amplifying the radiation. A significant advantage of molecular crystals over superdense gases and liquids is also (see Sec. 1 of the present chapter) the slower rate of the vibrational-translation relaxation, which facilitates considerably the obtaining of the necessary values of the inverted population and of the gain. Highly important for condensed media is the choice of a pumping method that would make it possible to excite oscillations in a relatively large volume of matter and obtain the gain needed for the lasing. We shall show that these conditions can be realized when modern high-power electron beams are used.

The depth of penetration δ (in cm) of an electron beam into a substance can be estimated from Feather's known formula [114]

$$\delta = (0.546E_e - 0.16)/\rho, \tag{4.19}$$

where E_e is the energy of the electron in the beam (in MeV), ρ is the density of the liquid in g/cm³. At $E_e \approx 2$ MeV, $\rho \approx 0.9$ g/cm³ we have $\delta \approx 1$ cm and consequently, when beams with cross sections 1 × 10 cm are used, their energy can be pumped into a considerable volume of liquid.

It is known that the beam energy is lost primarily to ionization. One ionization act consumes usually an energy $E_i \approx 30$ eV. Nonetheless, it is possible to excite effectively also molecule vibrations. Indeed, for a liquid there are at least two channels of energy pumping into vibrational degrees of freedom: 1) direct excitation of the oscillations by secondary ionization electrons with initial energy $E_i/2 \approx 15$ eV; 2) pumping via recombination processes. The effectiveness of the first pumping channel is determined by the ratio of the cross sections for the excitation of the oscillations by the electrons to the cross sections for the remaining processes at secondary-electron energies from 15 eV down. The second pumping mechanism is produced in the following manner. After a certain cooling of the secondary electrons, dissociative electron recombination sets in. The resultant neutral particles then recombine to form molecules on high excited levels, ensuring by the same token energy pumping into the vibrational degrees of freedom. The use of a chemical atom-recombination reaction to produce lasers based on vibrational transitions in molecular gases is discussed in [115, 116].

We shall consider the possibility of using high-power electron beams to pump a liquid laser operating on vibrational transitions, using as a concrete example a beam with the following parameters: current density $j = 500$ A/cm²; electron energy in the beam $E_e \approx 2$ MeV; beam pulse duration $\tau_{beam} \approx 5\cdot10^{-8}$ sec. These parameters are perfectly attainable [117] and correspond to a beam power 10^9 W/cm² and to an approximate energy 55 J/cm². The liquid chosen is carbon oxysulfite COS at a temperature 150°K (density $\rho = 1.24$ g/cm³, molecular weight M = 60 a.u., specific heat c = 0.2878 cal/(g·deg), molecule concentration $N_{liq} = 1.24\cdot10^{22}$ cm^{-3}). Calculation based on binary collisions yields for the liquid, for

the modes with $\nu_1 = 862\ cm^{-1}$ and $\nu_2 = 516\ cm^{-1}$, a relaxation time $\tau \approx 2\cdot10^{-8}$ sec, and for the mode $\nu_3 = 2050\ cm^{-1}$, a time $\tau \approx 2\cdot10^{-7}$ sec [118].

We estimate now the vibrational-level inverted population which can be expected when the oscillations are pumped with an electron beam. We consider first the recombination pumping mechanism. The cooling time τ_{cool} of the secondary electrons from an energy $E_i/2 \approx 15$ eV to thermal energies is short and at a typical cross section for inelastic scattering by the molecules $\sigma_i \approx 10^{-17}\ cm^2$ we have $\tau_{cool} \approx (\langle\sigma v\rangle N_{liq})^{-1} \ll \tau_{beam}$. The change of the volume concentration N_e of these cooled electrons with time is described approximately by the equation $dN_e/dt = J - k_r N_e^2$, the solution of which is

$$N_e(t) = \sqrt{J/k_r}\,\frac{1-\exp(-2\sqrt{Jk_r}t)}{1+\exp(-2\sqrt{Jk_r}t)}, \tag{4.20}$$

where k_r is the rate constant of the dissociative recombination, J is the bulk ionization rate by an electron beam,

$$J = \frac{E_e}{E_i}\frac{j}{e\delta}, \tag{4.21}$$

and e is the electron charge. For the electron-beam and liquid parameters indicated above, we have $\delta \approx 1$ cm and $J \approx 2.6\cdot10^{26}\ cm^{-3}\cdot sec^{-1}$. At these ionization rates and at the typical value $k_r \approx 10^{-7}\ cm^3/sec$, the quasistationary value is $N_e = \sqrt{J/k_r} = 5\cdot10^{16}\ cm^{-3}$, and the time of establishment of the quasistationary regime is $\tau_{est} \approx 1/2\sqrt{Jk_r} \approx 10^{-10}$ sec.

Inasmuch as $\tau_{est} \ll \tau_{beam}$ for the considered example, we can assume that during the entire time that the liquid is bombarded with fast beam electrons the recombination flux $k_r N_e^2$, which ensures in final analysis the energy pumping into the vibrational degrees of freedom, is equal to the bulk ionization rate J. The total recombination energy flux is consequently $E_iJ/2$, but it is clear that only a fraction η of this flux goes into the vibrational degrees of freedom. If the molecules are produced in the course of the recombination on vibration levels that are close to the dissociation limit with energy D_e, then $\eta_{max} \approx 2D_e/E_i$ can be of the order of unity. In the estimates that follow we shall use the value $\eta = 0.2$, assuming thus that only 20% of the recombination energy flux (or 10% of the total flux E_iJ) goes into the vibrational degrees of freedom.

When the oscillations are directly excited by secondary electrons in a quasistationary regime, it can be assumed that the rate of energy pumping into the oscillations is $\eta E_iJ/2$, where η is determined by the ratio of the cross section for the excitation of the oscillations by the electrons to the total cross section for their inelastic scattering, and by the average value of the energy that goes over into the vibrational energy in one excitation act.

To determine the populations of the individual vibrational levels it is necessary to know, besides the total energy flux into the oscillations of the polyatomic molecules, also how the various oscillation modes are excited. The most favorable for the production of inverted populations is a situation in which the modes predominantly excited are those having a long relaxation time (this is precisely the case realized in an electrically pumped CO_2 gas laser). Since, however, the relative energy pumping rates into different oscillation modes are unknown for most molecular systems, we shall hereafter assume them all to be equal. Assuming now that in a liquid of polyatomic molecules with a number of normal intramolecular oscillations there are two groups of modes n and k (n + k = m), which relax with different characteristic times $\tau(n) < \tau(k)$, we obtain for the nonequilibrium reserve of energy $E_{vib}(n)$ and $E_{vib}(k)$ in each of the groups of modes in the quasistationary relaxation regime*

$$E_{vib}(n) = \frac{n}{m}\eta\frac{E_i}{2}J\tau(n) + E_{vib}^0(n), \quad E_{vib}(k) = \frac{k}{m}\eta\frac{E_i}{2}\tau_{beam} + E_{vib}^0(k), \tag{4.22}$$

where E_{vib}^0 is the equilibrium value (at the temperature T) of E_{vib}.

Estimating E_{vib} and recognizing that in each of the groups of modes n and k, owing to the rapid energy exchange between the modes, a quasiequilibrium Treanor relation is estab-

*In the considered example, for the group n of modes we have $\tau(n) < \tau_{beam}$, i.e., a quasistationary relaxation regime sets in. On the other hand, for the group k of modes we have $\tau(k) > \tau_{beam}$, therefore in (4.22) the expressions for $E_{vib}(n)$ and $E_{vib}(k)$ contain, respectively, the times $\tau(n)$ and τ_{beam}.

lished [2], it is easy to determine the populations of the different levels. Thus, for the considered COS example n = 2, k = 1, and the populations of the lowest levels $N_1(n)$ and $N_1(k)$ of the modes with the smallest quanta $\nu_2 = 516\ cm^{-1}$ and $\nu_3 = 2050\ cm^{-1}$ from the groups n and k will be, respectively, equal to $2\cdot10^{20}$ and $5\cdot10^{19}\ cm^{-3}$. The inverted population is produced then between the levels 001 and the level 100 from the group n = 2 of the rapidly relaxing modes ν_1 and ν_2, and amounts to $\approx 4.5\cdot10^{19}\ cm^{-3}$. We note that it is precisely at this transition (wavelength $\lambda = 8.4\ \mu m$) that inverted population and lasing was obtained for COS in the gas phase with electric pumping [119, 120].

Assuming for the line width and for the probability of a spontaneous radiative transition the typical values $10\ cm^{-1}$ and $1\ sec^{-1}$, we find that for the indicated transition the gain is $\alpha \approx 4.5\cdot10^{-2}\ cm^{-1}$, i.e., quite sufficient for lasing. We note also that at these values the time of development of lasing $\tau_{gen} \approx 40(\alpha c)^{-1} \approx 3.3\cdot10^{-8}$ sec [121] (c is the speed of light) remains less than the duration τ_{beam} of the pump pulse.

An important factor that influences the operation of a liquid laser (as, incidentally, also that of an electron-beam-controlled gas laser) is the heating of the medium. In a liquid, however, owing to the substantially larger capacity per unit volume, this heating may be small even at considerable energy inputs. Thus, in the case considered here the maximum heating of the liquid upon absorption of the energy of one pulse of the electron beam ($\approx 75\ J/cm^3$) is only about 50°.

From the particle flux to the upper laser vibration level with energy $h\nu_{min}(k)$ we can also roughly estimate the expended power W_{rad} and energy E_{rad} in one radiation pulse

$$W_{\text{rad}} \lesssim \frac{\nu_{\text{rad}}}{\nu_{\min}(k)} \frac{k}{m} \eta \frac{E_i}{2} J, \qquad E_{\text{rad}} \lesssim W_{\text{rad}} \tau_{\text{beam}}.$$

For the considered example $W_{rad} \lesssim 2\cdot10^7\ W/cm^3$ and $E_{rad} \lesssim 1\ J/cm^3$. These estimates show that if liquid lasers based on vibrational transitions are eventually developed, they can successfully compete with respect to their energy characteristics with modern electroionization lasers [57, 113]. To be sure, when the pumping is by an electron beam, owing to the predominant loss of beam energy to ionization, the efficiency of such liquid lasers is small compared with electroionization gas lasers. However, to increase this efficiency and by the same token improve additionally the energy characteristics of the laser, it is possible apparently by using an excitation that combines an electron beam with an external electric field that heats the secondary electrons. Thus, simple estimates show that at a cross section for excitation of oscillations by electrons of the order of $10^{-18}\ cm^2$ in the region of superthermal energies 1-3 eV, the concentration of the secondary electrons N_e (in our example, about $5\cdot10^{16}\ cm^{-3}$) is sufficient to obtain a concentration of vibrationally excited molecules of $\approx 5\cdot10^{21}\ cm^{-3}$. Analogous calculations yield for liquid CS_2 at 195°K an inverted population on the order of $6\cdot10^{20}\ cm^{-3}$, while for furan C_4H_4O it yields a value on the order of $10^{19}\ cm^{-3}$.

It is clear that with decreasing temperature, owing to the growth of the time of vibrational relaxation, the efficiency of liquid lasers will increase. From this point of view it is of interest to use molecular crystals as active laser media. In molecular crystals, unlike in liquids, all the collective interactions are significant. As seen from the estimates presented for the probabilities, the rates of the VT processes in collective interactions are usually lower than in binary processes. Particularly small values of P_{10}^{coll} take place for molecular crystals with $\nu_{min}/\nu_D > 3$, and consequently the intramolecular vibrational excitations decay into five or more Debye quanta. For these cases, a resonant or near-resonant collective VV process, which calls for participation of only two Debye quanta (see (4.17)), proceeds much more rapidly, i.e., the relation $\tau_{VV} \ll \tau_{VT}$ between the characteristic times of the VV and VT processes remains satisfied. In such molecular crystals, just as in one-component gases and liquids, a quasistationary distribution will be established within the modes.

The indicated circumstance was used in [48] to find the distribution in a system of anharmonic oscillators. The energy exchange between the different modes (the VV' process) in molecular crystals can proceed at different rates, but it is clear that for multiquantum exchange with a considerable energy defect, which calls for several Debye modes to participate in the process, these rates can be relatively low, so that on the whole the vibrational relaxation will be characterized by several relaxation times. Thus, the use of molecular

crystals as the active media for lasers based on vibrational transitions between levels of different intramolecular modes is promising and will make it possible in principle to obtain large inverted populations and gains.

It is quite interesting to use for this purpose solid carbon monoxide, since the spectroscopic parameters and the cross sections for excitation of oscillations by electron impact are well known for CO_2. Pumping, just as for liquids, can be effected by powerful electron beams. Estimates made for a beam with the parameters given above and using the probabilities cited on p. 48, have shown that at the end of the action of the pump pulse the inversion on the vibrational transition 00^01-10^00 amounts to $2\cdot10^{19}$ cm^{-3}, corresponding to a stored energy 0.4 J/cm^3.

3. Laser-Chemical Reactions in the Liquid Phase

In addition to the problem of producing liquid lasers, it is undoubtedly of interest to stimulate, in liquids, chemical reactions by using IR laser radiation for selective heating of the oscillations. So far, the investigations were limited to the gas phase [21, 25, 27, 63, 67]. We discuss here briefly the question of stimulating chemical reactions in the liquid phase. It is known [25, 27, 67] that when energy is dissipated from a mode as a result of a VT or a VV' process with probability P_{10}, it is necessary to provide by laser radiation an optical-pumping probability $W_{10} \approx P_{10}$ to obtain a mode vibrational temperature equal to the characteristic temperature of this vibration. In this case, taking into account the connection between the pumping density J and the probability W_{10}, we have

$$J \approx 1.5\cdot10^{-11}\nu^3_{rad}\,\Delta\nu P_{10}/qA_{10},$$

where J is in W/cm^2; ν_{rad} and $\Delta\nu$ are the frequency of the absorbed radiation and the width of the absorption line (in cm^{-1}), respectively; q is the fraction of molecules participating in the absorption, and the radiative and collisional probabilities A_{10} and P_{10} are expressed in sec^{-1}.

At typical values $P_{10} = 10^9$ sec^{-1}, $A_{10} \approx 10$ sec^{-1}, $q \approx 0.15$, $\Delta\nu \approx 10$ cm^{-1}, $\nu_{rad} \approx 10^3$ cm^{-1} (the emission frequency of a CO_2 laser), we obtain $J \approx 10^8$ W/cm^2, and the vibrational temperature of the mode is $\approx$1400°K. On the other hand, to obtain a vibrational temperature smaller by a factor 2.3 ($\approx$610°K) the power needed is on the order 10^7 W/cm^2. These powers, while appreciably higher than in the case of stimulation of laser-chemical reactions in gases of low (1-100 torr) pressures, are nonetheless easily attainable for modern pulse IR lasers. An important feature of laser-chemical reactions in the liquid phase is also their local character, due to the high concentration of the radiation-absorbing molecules. Thus, in the indicated example, the cross section for the absorption of radiation amounts to $\approx2\cdot10^{19}$ cm^2, which at a liquid-molecule density on the order of 10^{22} cm^{-3} corresponds to a radiation penetration depth $\delta \sim 5\cdot10^{-4}$ cm. Using radiation with a frequency that is a multiple of the oscillation frequency, for which the absorption cross section is considerably smaller (by an approximate factor 10^2 and more) than for the resonant frequency, the volume in which the reaction takes place can be substantially increased. We note a recently published and interesting communication [64] concerning the first experiments on the realization of biochemical reactions in the liquid phase under the action of IR laser radiation. To be sure, the employed radiation powers were low, but they apparently offer evidence either of anomalously low probabilities of deactivation of the excitation energy, or of a thermal character of the biochemical processes in this experiment.

On the whole, the results obtained in the present chapter point to the possibility of effecting laser-chemical reactions in liquids and to the promise offered by using liquids and molecular crystals as active media for lasers based on intramolecular vibrational transitions.

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