NONEQUILIBRIUM DISSOCIATION PROCESSES AND MOLECULAR LASERS

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The dissociation of diatomic and polyatomic molecules described by anharmonic oscillators is considered under nonequilibrium conditions when the vibrational energy does not correspond to the gas temperature. Quasiequilibrium energy distributions over the molecular levels are studied, taking into account dissociation, nonresonant exchange, $V - T$ relaxation, and pumping. The dissociation rates are found and the factors affecting them are discussed. Conditions for the effective dissociation of molecules at low gas temperatures are established for the case of polyatomic molecules. The control of chemical reactions is briefly reviewed and possible applications of the theory to chemical lasers are discussed.

1. INTRODUCTION

THE analysis of elementary processes in excited molecules, which lead to energy relaxation and vibrational exchange, plays an important role in gas dynamics, the theory of molecular lasers, and chemical kinetics. Although gas dynamics initially attracted most of the attention as far as applications were concerned,[1,2] there has been increasing interest in recent years in methods of producing inverted populations using vibrational levels of molecules. When chemical methods of excitation and high-energy pumping rates are considered, it is no longer possible to restrict one's attention to the partial Boltzmann energy distribution over the vibrational degrees of freedom, which was quite satisfactory for CO_2 lasers.[3] Modern chemical and gas lasers require a more detailed analysis of molecular kinetics, including nonresonant vibrational exchange[4-6] and the effect of dissociative-recombinational processes in the case of the upper levels. Moreover, dissociation and recombination are simple chemical reactions which may be used as examples to illustrate the effect of molecular relaxation on the kinetics of chemical processes. It will be shown below that nonequilibrium conditions can provide a situation under which it will be possible to control chemical reactions, and this is of particular importance for chemical lasers.

There are various theories of dissociation[1,2,7-11] which, in many cases, can be used to calculate the rate of this reaction. However, for molecules described by the anharmonic Morse oscillator in the most general and interesting case when the vibrational energy E_{vib} differs from the equilibrium value E_{vib}^0, which corresponds to the gas temperature, a systematic analysis of dissociation has not been carried out. This analysis is performed in the present paper, using the solution of the kinetic equations for the vibrational-level populations. Radiating and nonradiating diatomic molecules as well as polyatomic molecules are discussed. Particular attention is paid to the case when $E_{vib} \gg E_{vib}^0$. This particular case is especially important for both chemical reactions leading to the appearance of vibrationally excited molecules and for the possibility of controlling such reactions. It is also important for the analysis of

processes in molecular chemical lasers and gas lasers, and for dissociation in sealed-off CO_2 and CO lasers with electrical pumping.

2. FUNDAMENTALS OF DISSOCIATION THEORY. QUASIEQUILIBRIUM POPULATIONS OF VIBRATIONAL LEVELS

We shall use the kinetic approach developed in[1,7-9] for the analysis of the nonequilibrium dissociation of diatomic molecules. In this method the process is looked upon as the upward motion of molecules in energy space toward the dissociation limit, followed by their transition to the continuous spectrum from some limiting level k at a distance $\sim T$ from the dissociation limit. The molecular dissociation rate is determined by the level population and the decay probability P_{kv} for molecules occupying this level. To find the population of the level k we must solve the complete set of kinetic equations for the populations N_n of all the low-lying vibrational levels n of the molecule. The rates of level population are determined by the probabilities of one photon $(Q_{n+1, n}^{i, i+1})$ and two-photon $(Q_{n+2, n}^{i, i+1})$ exchange, by one-photon probabilities of vibrational-translational relaxation $(P_{n+1, n})$, and the probability of radiative decay $(A_{n+1, n})$. The multiphoton vibrational-translational relaxation will not be considered because, according to[7], it usually occurs in a region of the order of T near the dissociation limit, and this is unimportant.

The expressions for dN_n/dt (n $<$ k) in the system of kinetic equations are of the form analogous to Eq. (16) in[6], and will not be reproduced here. It is only in the presence of extraneous sources of molecules that these expressions acquire the additional terms $B_n - C_nN_n$ which describe the appearance (at the rate B_n) and disappearance (with probability C_n) of molecules occupying the level n due to these sources. In addition, the expressions for dN_k/dt must be augmented by the terms $-zP_{kd}N_k + zP_{dk}N_d^2$ which describe the dissociation of molecules from level k (with the probability P_{kd} per collision) and recombination to the level k (with the probability $P_{dk}N_d$ per collision). In these expressions z is the number of molecular collisions per unit time and N_d is the density of atoms produced during the decay

of the molecules. Hence, the change in the total number N of molecules per unit volume is given by

$$\frac{dN}{dt} = -v + \left(\frac{dN}{dt}\right)^{\cdot}, \quad v = zP_{hd}N_k - zP_{dh}N_d^2, \quad (1)$$

$$\left(\frac{dN}{dt}\right)^{\cdot} = \sum_i (B_i - C_i N_i).$$

Here, v is the molecular dissociation rate. To find v we must calculate the population N_k in terms of known probabilities, the density N of the molecules, and the vibrational energy E_{vib} which is determined by the rate of vibrational-translational relaxation (V—T processes) and the pumping mechanism (i.e., the quantities B_i and C_i).

In the course of the solution of the kinetic equations we shall assume that the relaxation time τ_v^* for the populations of the vibrational levels is much less than the dissociation time τ_d and the characteristic times τ_T, τ_E, and τ_{ex} for changes in the gas temperature, vibrational energy, and number of molecules due to extraneous sources, respectively. The time τ_v^* is determined by the smallest of the probabilities of population or deactivation of any level $n \leq k$.

During the time $t - \tau_v^*$ the distribution of the molecules over the levels, which is determined by the gas temperature, the vibrational energy E_{vib}, the total number of molecules N, and the ratio of the various process probabilities, is established. When $\tau_v^* < t < \tau_d$; τ_T; τ_E; τ_{ex}, the solution of the system may be sought in the form

$$N_n\left(N, T, E_{vib}, v, \left(\frac{dN}{dt}\right)^{\cdot}, \frac{dT}{dt}, \frac{dE_{vib}}{dt}\right) = N_n^{\circ}(N, T, E_{vib})$$

$$+ \delta N_n^{1}\left(N, T, E_{vib}, v, \left(\frac{dN}{dt}\right)^{\cdot}, \frac{dT}{dt}, \frac{dE_{vib}}{dt}\right) \equiv N_n^{\circ}(1 + \chi_n), \quad (2)$$

where $\delta \sim \tau_v^*/\tau_d$, τ_v^*/τ_T, τ_v^*/τ_E, τ_v^*/τ_{ex} is a small parameter. Substituting Eq. (2) into the set of differential equations to be solved, we obtain a set of algebraic equations for N_n^0 in the zero-order approximation (since the values of

$$\left|\frac{dN_n^{\circ}}{dt}\right| \equiv \left|\frac{dN_n^{\circ}}{dN}\frac{dN}{dt} + \frac{dN_n^{\circ}}{dT}\frac{dT}{dt} + \frac{dN_n^{\circ}}{dE_{vib}}\frac{dE_{vib}}{dt}\right|$$

are of the next order of small quantities). This system and its solution for anharmonic oscillators, is given in[5], taking into account one-phonon vibrational exchange and V—T relaxation, and in[6] for two-photon exchange. It is important to note that, in the case of the nonequilibrium value of the vibrational energy E_{vib}, the resulting distribution of the molecules over the vibrational levels (we shall call it the quasiequilibrium distribution) is essentially different from the Boltzmann distribution even in the zero-order approximation, which does not take into account the rate of change of N, T, and E_{vib}.

When the two-photon exchange is unimportant this distribution is[5]

$$N_{n+1}^{\circ} = N_{n+1}^{Tr} \prod_{i=0}^{n} \varphi_{i+1}, \quad (3)$$

where

$$N_n^{Tr} = \frac{N}{Q} \exp\left\{-n\left[\frac{E_1}{T_1} - (n-1)\frac{\Delta E}{T}\right]\right\} \equiv \frac{N}{Q} X_n^{Tp} \quad (4)$$

is the Treanor distribution[4] found for the anharmonic oscillator for one-photon exchange alone. In these expressions Q is the partition function for the oscillator, E_1 and ΔE are, respectively, the energy of the lowest oscillator quantum and its anharmonicity (in °K), T_1 is the effective vibrational temperature for the 1—0 levels, and in the absence of equilibrium $T_1 \neq T$. The functions φ_i represent the effect of radiative and V—T processes which are important for the upper levels. The expression for φ_i in terms of the probabilities $P_{i+1, i}$, $A_{i+1, i}$, and the sum $\sum Q_{i+1, i}^{m-1, m} X Tr_{m-1}$ are given in[5] [Eq. (7)]. If we evaluate the above sum approximately[11], and substitute it into the formula for φ_i, we obtain

$$\varphi_{i+1} \approx \frac{\beta Q_{i+1, i}^{01} + P_{i+1, i} \exp(E_1/T_1 - E_1/T)}{\beta Q_{i+1, i}^{01} + P_{i+1, i} + A_{i+1, i}/z}. \quad (5)$$

The factor β, in effect, takes into account not only the first but also the contribution of all the remaining excited levels to the probability of the $i + 1 \rightarrow i$ transition due to the vibrational exchange

$$\beta = \left[1 - \exp\left(-\frac{E_1}{T_{har}}\right)\right]\left\{1 - \exp\left[-\frac{E_1}{T_{rap}}\left(1 - \frac{\gamma_0}{3}\frac{T_{har}}{D}\right)\right]\right\}^{-2}, \quad (6)$$

$$\gamma_0 = 0.32\alpha^{-1}\gamma\overline{\mu} / TE_1. \quad (7)$$

In Eqs. (6) and (7) $D \approx E_1^2/4\Delta E$ is the molecular dissociation energy (in °K), α is a characteristic parameter in the exponential potential $e^{-\alpha r_0}$ for the intermolecular interaction (expressed in $\overset{\circ}{A}^{-1}$), μ is the reduced mass (in atomic units), T and E_1 are expressed in °K, and T_{har} is the vibrational temperature of the molecules in the harmonic-oscillator model with the same store of energy as in the case of the Morse oscillator. At low gas temperatures (of the order of room temperature), and when $T_{har} \gtrsim E_1$, the difference between T_1 and T_{har} can be quite substantial. Figure 1 shows the calculated ratio T_1/T_{har} as a function of $E_1\epsilon/T$, where ϵ is the store of vibrational quanta per molecule, i.e., the vibrational energy in dimensionless units. Since, as will be seen below, the dissociation rate is very sensitive to the value of T_1, it is essential to take the difference between T_1 and T_{har} into account.

The above values of the quasiequilibrium distribution of $N_n^Q = NX_n^0/Q$ and the functions φ_i are essential both
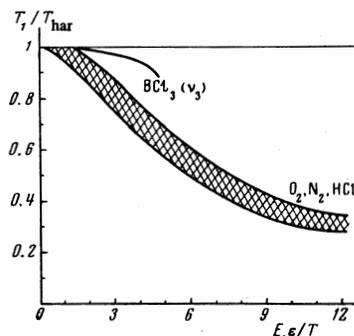
FIG. 1. Ratio T_1/T_{har} as a function of $E_1\epsilon/T$ for different molecules. The calculation was carried out for gas temperatures in the range $T = 200\text{-}5000°K$.

for the calculation of the dissociation rate and the analysis of the properties of the molecular gas under nonequilibrium conditions. In cases which are of importance in practice, it turns out to be possible to find a relatively simple form for these distributions. This is achieved by splitting the entire level system into individual groups whose populations are predominantly governed by one or another mechanism. The limiting level numbers n^*, n^{**}, r, etc. for these groups are determined by the equality of the individual terms in the numerator and denominator of Eq. (5).

This problem is analyzed in detail in[12]. Let us consider the values of X_n^0 which are important for the determination of the dissociation rate, i.e., for the uppermost levels. In all cases, the quasiequilibrium function for these levels is of the form

$$X_{n+1} = CX_{r+1}^{\mathrm{Tr}} \exp\left\{-(n-r)\left[\frac{E_1}{T} - (n+r+1)\frac{\Delta E}{T}\right]\right\} \qquad (8)$$

$$\approx C \exp\left(-\frac{E_{n+1}}{T}\right)\exp\left[rE_1\left(\frac{1}{T}-\frac{1}{T_1}\right)\right], \qquad n > r,$$

and $E_{n+1} = (n+1)[E_1 - n\Delta E]$ is the energy of the level $n+1$. The constant C and the limiting level r are determined by the specific probability ratios for the various processes and the temperatures T_1 and T. Thus, when $\beta Q_{i+1,i}^{01} + P_{i+1,i} \gg A_{i+1,i}/z$ we have for all $i = 0, 1, 2, \ldots$ (nonradiating oscillator) and $T_1 > T$

$$C = (\beta A)^{r-n^*}\exp\left[-\frac{4}{3}\gamma_0\frac{\Delta E}{E_1}(r-n^*)(r+n^*+1)\right], \qquad (9)$$

where

$$A = \frac{24,4\alpha^2}{Z_0 M_0 E_1}\exp\left(-\frac{E_1}{2T}+\frac{2}{3}\gamma_0\right). \qquad (10)$$

In these expressions Z_0 is the orientation factor, M_0 is the reduced mass of the oscillator in atomic units, E_1 is expressed in $^\circ$K, and α in Å^{-1}. For temperatures T for which $\gamma < 20$, the factor A is the probability ratio Q_{10}^{01}/P_{10}. For the limiting levels n^* and r we have

$$n^* = \frac{3}{8}\frac{\ln(\beta A)}{\gamma_0}\frac{E_1}{\Delta E}, \qquad r = n^* + \frac{D}{\gamma_0}\left(\frac{1}{T}-\frac{1}{T_1}\right). \qquad (11)$$

When for the lower levels $A_{i+1,i}/z > P_{i+1,i}$ (radiating oscillator) and

$$C = \left(\frac{z\beta Q_{10}^{01}}{A_{10}}\right)^{i^{**}-i^*}(\beta A)^{r-i^{**}}\exp\left[-\left(\frac{E_1}{2T}+\frac{2}{3}\gamma_0\right)\frac{\Delta E}{E_1}(i^{**}-i^*)\right. \qquad (12)$$

$$\times (i^{**}+i^*+1)\Bigg]\exp\left[-\frac{4}{3}\gamma_0\frac{\Delta E}{E_1}(r-i^{**})(r+i^{**}+1)\right].$$

This value of C is given for conditions (determined by the temperature and pressure of the gas) when $i^* < i^{**} < r$. In this case, r is found from Eq. (11), and

$$i^* = \ln\left(\frac{z\beta Q_{10}^{01}}{A_{10}}\right)\left(\frac{2}{3}\gamma_0 + \frac{E_1}{2T}\right)^{-1}\frac{E_1}{2\Delta E},$$

$$i^{**} = \left[1-\left(\frac{2}{3}\gamma_0-\frac{E_1}{2T}\right)^{-1}\ln\left(\frac{zQ_{10}^{01}}{A_{10}}\frac{M_0 E_1 Z_0}{24,4\alpha^2}\right)\right]\frac{E_1}{2\Delta E}. \qquad (13)$$

We note that the analytic expressions given by Eqs. (11) and (13) are valid for a gas consisting of identical molecules when

$$\gamma_0\frac{2\Delta E}{E_1}j \leqslant 20, \qquad \gamma_0\left(1-\frac{2\Delta E}{E_1}j\right)\leqslant 20, \qquad j = n^*, i^*, i^{**}, r. \qquad (14)$$

When these conditions are not satisfied the corresponding limiting levels have to be determined from transcendental equations. Formulas similar to those given by Eqs. (9)–(13) can also be obtained for a gas mixture when $T_1 < T$ and $r = i^{**}$ (for further details see[12]).

Let us find a simplified expression for the quasi-equilibrium distribution function when two-photon exchange processes are important (see[6]). We shall assume that, beginning with some level m^* (which is approximately determined from the condition $\beta Q_{m^*+1,m^*}^{01} = Q_{m^*+1,m^*-1}^{01}$), the dominant role in the population of the vibrational levels is played by two-photon exchange, whereas vibrational-translational relaxation becomes important only for the uppermost levels $n > m^{**}$, where m^{**} is determined from the condition $Q_{mm^{**}+1,m^{**}-1}^{01} = P_{m^{**}+1,m^{**}}$).[1] In that case, we can readily show that for $n > m^{**}$

$$X_{n+1}^0 = X_{m^*+1}^{\mathrm{Tr}}\exp\left\{-\frac{m^{**}-m^*}{2}\left[\frac{E_1}{T_1}+\frac{E_1-2(m^{**}+m^*+1)}{T}\Delta E\right]\right. $$
$$\left.+ (n-m^{**})\left[\frac{E_1}{T}+(n+m^{**}+1)\frac{\Delta E}{T}\right]\right\} \qquad (15)$$
$$\approx \exp\left(-\frac{E_{n+1}}{T}\right)\exp\left[\frac{m^*+m^{**}}{2}E_1\left(\frac{1}{T}-\frac{1}{T_1}\right)\right].$$

There is another possible case when the two-photon exchange is important for the population of only a small group of upper levels with $n \approx E_1/4\Delta E$. It is precisely for these levels that $E_{n+1} - E_{n-1} \approx E_1$, i.e., we have resonance for the two-quantum exchange with the lowest quantum, and the corresponding exchange probability $Q_{n+1,n-1}^{01}$ is a maximum. Since for these levels $\beta Q_{n+1,n} \ll P_{n+1,n}$ the two-quantum exchange may play a role in the population of the levels but only for $Q_{n+1,n-1}^{01} \approx P_{n+1,n}$ when $n \approx E_1/4\Delta E$.

The probabilities are estimated in[6] using the Herzfeld method[13] and the harmonic oscillator wave functions. These estimates have shown that, for example, for the CO molecule at $T = 300^\circ$ we have $Q_{n+1,n-1}^{01} \gg P_{n+1,n}$ for $n \sim E_1/4\Delta E$. It is important to note,
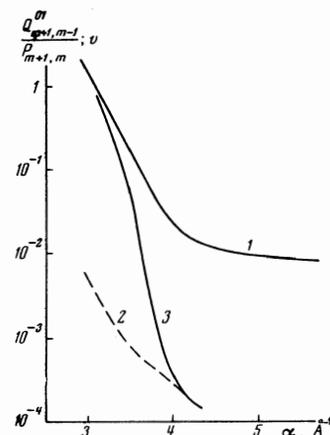
FIG. 2. The probability ratio $Q_{m+1,m-1}^{01}/P_{m+1,m}$ (curve 1) and the dissociation rate v (curves 2 and 3, relative units) as functions of the force constant α. The dissociation rate v was calculated with and without allowance for two-photon exchange (curves 3 and 2, respectively). Data refer to O_2–O_2 collisions, $T_{har} = 2000^\circ$, $T = 500^\circ$, $m \approx E_1/4\Delta E \approx 33$.

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[1] This situation can take place only at low temperatures $T \lesssim 300^\circ$ and only for some molecules with $E_1 \gtrsim 3000^\circ$.

however, that when the wave functions for the anhar-monic Morse oscillator are employed,[14] the probabili-ties may be quite different. We have carried out the corresponding calculations for various molecules (O_2, N_2, HCl, BCl_3, Cl_2) at different temperatures and for different values of the force constant α. These have shown that the probabilities of multiphoton exchange are very dependent on α and rapidly increase as α decrea-ses. This leads to a change in the relationship between $Q_{n+1,n-1}^{01}$ and $P_{n+1,n}$ in the region where $n \approx E_1/4\Delta E$.

Curve 1 in Fig. 2 illustrates the dependence of $Q_{n+1,n-1}/P_{n+1,n}$ on α for $T = 500°$ and $n \approx E_1/4\Delta E \approx 33$ in the case of oxygen molecules. It is clear that as α is reduced from 5.6 down to 3 $\mathring{A}^{-1}$, this ratio increa-ses by two orders of magnitude and reaches unity.

Therefore, the choice of α is important for calculat-ing the probabilities $P_{n+1,n}$, $Q_{n+1,n-1}^{01}$, the ratio of which governs the form of the distributions for the quasiequilibrium populations of the upper vibrational levels. Knowledge of the populations of these levels is, in turn, important for the determination of the dissocia-tion rate in the system of anharmonic oscillators.

3. RATE OF DISSOCIATION OF DIATOMIC MOLECULES

To find the rate of nonequilibrium dissociation we must solve the set of differential equations for the popu-lations of the vibrational levels in the next, i.e., first, approximation which takes into account the effect of dissociation on the populations. Substituting Eq. (2) in these equations, we can readily obtain the set of alge-braic equations for the first approximation N_n^1, i.e., for the functions χ_n. After certain simplifications, and if we solve this system by the double-sum method by analogy with[5,6,9,10], we find that

$$\chi_n = \frac{i}{z}\sum_{n=1}^{n-1}\frac{1}{W_m}\left\{\frac{1}{N}\left[-v+\left(\frac{dN}{dt}\right)^{\cdot}\right]\sum_{i=1}^{m}X_i^0 + \frac{dT_1}{dt}\frac{E_1}{T_1^2}\sum_{i=0}^{m}iX_i^0\right.$$
$$\left.-\frac{dT}{dt}\frac{\Delta E}{T^2}\sum_{i=0}^{m}i(i-1)X_i^0 - \frac{1}{Q}\frac{dQ}{dt}\sum_{i=0}^{m}X_i^0 - \frac{Q}{N}\sum_{i=0}^{m}B_i + \sum_{i=0}^{m}C_iX_i^0\right\}, \quad (16a)$$

$$W_m = X_{m+1}^0\left[\frac{1}{Q}\left(Q_{m+2,m}^{01}\frac{X_{m+2}}{X_{m+1}^0}+Q_{m+1,m-1}^{01}\right)\right.$$
$$\left.+\beta Q_{m+1,m}^{01}+P_{m+1,m}+\frac{A_{m+1,m}}{z}\right]. \quad (16b)$$

Substituting N_k in Eq. (1), using Eq. (16), we obtain the relation from which we can determine the required dis-sociation rate v. This expression and the formula given by Eq. (16a) are similar in their structure to the expressions obtained in[1,7-9] for the truncated harmonic oscillator and the anharmonic oscillator in the case of dissociation in an inert gas, i.e., when $E_{vib} = E_{vib}^0$. It is important to emphasize, however, that the quasi-equilibrium populations X_v^0 in Eq. (16) and in the ex-pression for v are very different from the Boltzmann distribution, in contrast to[1,7-9].

Numerical calculations for various molecules in a broad range of vibrational energies and gas tempera-tures have shown that the rapid reduction in the popula-tions of the higher levels ensures that there is a reduc-tion in W_m for these levels [see Eq. (16b)], and for

small $T \lesssim E_1$ there is a particularly rapid fall in W_m beginning with a level r [see Eq. (11)], where the main role begins to be played by V–T processes, and the relative populations are determined by the gas tempera-ture T. The outer sum in Eq. (16a) can then begin with m = r, and for $m > r$

$$W_m \approx P_{m+1,m}X_{m+1}^0 \approx P_{m+1,m}C\exp\left(-\frac{E_{m+1}}{T}\right)\exp\left[rE_1\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]$$

$$\sum_{i=0}^{m}X_i^0 \approx Q, \quad \varepsilon = \exp\{-E_1/T_{har}\}[1-\exp\{-E_1/T_{har}\}]^{-1}. \quad (17)$$

We note that although the expression for W_m in Eq. (17) does not involve the exchange probabilities and the radiative probability $A_{m+1,m}$, they do play an impor-tant role in generating the quasiequilibrium distribution X_{m+1}^0 for the upper levels. If we substitute Eq. (17) in Eq. (16a), replace summation by integration, and take the mean value $\overline{P}_{m+1,m}$[2] from under the integral sign, we obtain

$$I_n = X_n^0\sum_{m=r}^{n-1}\frac{1}{W_m} \approx X_n^0\frac{1}{\overline{P}_{m+1,m}}\int^{n-1}\frac{am}{X_{i+1}^0}$$

$$\approx \frac{1}{\overline{P}_m}\sqrt{\pi\frac{T}{4\Delta E}}\exp\left(\frac{D-E_n}{T}\right)[\Phi(R_r)-\Phi(R_n)], \quad (18)$$

where $R_m = \sqrt{(D-E_m)/T}$, and $\Phi(R_m)$ is the error func-tion. The parameter I_n governs the deviation from quasiequilibrium and may be substantially greater than unity at the dissociation limit (for $n \approx k$), which leads to a reduction in the dissociation rate (see[12] for fur-ther details). Substituting Eqs. (17) and (18) in Eq. (16a), and using Eq. (1), we finally obtain the following form-ula for the dissociation rate[3]

$$v = Nz\overline{P}_{m+1,m}\frac{1}{Q}\sqrt{\frac{E_1^2}{\pi DT}}\exp\left(-\frac{D}{T}\right)[\Phi(R_r)-\Phi(R_k)]^{-1}\cdot$$
$$\times C\exp\left[rE_1\left(\frac{1}{T}-\frac{1}{T_1}\right)\right] - N_d^2z\frac{P_{dk}}{P_{hd}}\overline{P}_{m+1,m} \quad (19)$$
$$\times\sqrt{\frac{E_1^2}{\pi DT}}\exp\left(-\frac{D-E_k}{T}\right)[\Phi(R_r)-\Phi(R_k)]^{-1}.$$

Let us consider the above expression for v in greater detail. Suppose that recombination, which is described by the last term in Eq. (19), is absent. In that case, for r such that $R_r \gg 1$ we have

$$v = v_T C\exp\left[rE_1\left(\frac{1}{T}-\frac{1}{T_1}\right)\right], \quad (20)$$

where

$$v_T = Nz\frac{1}{Q}\overline{P}_{m+1,m}\sqrt{\frac{E_1^2}{\pi DT}}\exp\left(-\frac{D}{T}\right)[1-\Phi(R_k)]^{-1} \quad (21)$$

is the rate of molecular dissociation in an inert gas at temperature T.[9] We note that Eqs. (20) and (21) in-clude as a special case the result given in[11] (in the case of nonradiating molecules at relatively high tem-

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[2]This can be done since for large m the probability $P_{m+1,m}$ is not very dependent on m.

[3]In the absence of sources and when $n > r$, terms with $(dN/dt)^*$, $\sum_{i=0}^{m}C_iX_i^0$, $\sum_{i=0}^{m}B_i$, will not be present in Eq. (19) because, by definition,
$$\left(\frac{dN}{dt}\right)^{\cdot} = -\sum_{i=0}^{k}C_iN_i + \sum_{i=0}^{k}B_i.$$

peratures when $\frac{3}{2}\ln(\beta A) \gg E_1|T^{-1} - T_1^{-1}|$ and $C = 1$).

In conclusion, we reproduce the formula for the dissociation rate in the case when two-photon exchange plays an important role in the level population. Using Eq. (15) and proceeding by analogy with the steps leading to Eqs. (17)−(19), we obtain, neglecting recombination,

$$v \approx Nz\bar{P}_{m+1,m}\frac{1}{Q}\sqrt{\frac{E_1^2}{\pi DT}}\exp\left(-\frac{D}{T}\right)\frac{\exp[\frac{1}{2}E_1(m^* + m^{**})(T^{-1} - T_1^{-1})]}{\Phi(R_{m^{**}}) - \Phi(R_k)} \quad (22)$$

When $R_{m^{**}} = \sqrt{(D - E_{m^{**}})/T} \gg 1$, we have

$$v = v_T \exp\left[\frac{1}{2}(m^* + m^{**})E_1(T^{-1} - T_1^{-1})\right]. \quad (23)$$

Comparison of Eqs. (22) and (23) with Eqs. (20) and (21) will show that since $(m^* + m^{**})/2 \geq r$, allowance for two-photon exchange, when it is important for the population of vibrational levels, may lead to a substantial increase in the molecular dissociation rate.

It follows from Eqs. (20)−(23) that the uncertainties in the calculated level numbers r, m^*, m^{**} and may have an important effect on calculations of the nonequilibrium dissociation rate. The uncertainty in the quantities r, $i^*(i^{**})$, m^*, m^{**}, on the other hand, is determined by the adopted physical model and the specification of the computational formulas such as Eqs. (11) and (13), as well as by the uncertainty in the molecular interaction constant α. We have used a computer to calculate the dissociation rates for different molecules and different values of the vibrational energy, the temperature T, and the parameter α. Figure 2 shows the dissociation rate v in relative units (curves 2 and 3) as a function of α for the oxygen molecule. When two-photon exchange is ignored the dependence on α can be explained by the change in the level number n^* with varying α.

Curve 2 of Fig. 2 thus illustrates the sensitivity of v to the choice of α and the uncertainty in n^* and r. Curve 3 in Fig. 2 shows v as a function of α when two-photon processes are taken into account. For $\alpha \lesssim 4$ Å^{-1} when $Q^{01}_{n+1,n-1}/P_{n+1,n} > 2 \times 10^{-2}$, the dissociation rate v may be substantially greater than the corresponding value obtained without the exchange process (curve 2). We note also that in a precise calculation of the dissociation rate we must take into account the contribution of the vibrational levels and other electronic states to the total dissociation rate. These effects are represented by additional factors in the formula for v, but the determination of these factors is similar to the procedure for equilibrium conditions ($T = T_1$) and will not be considered here (see[1,7,8]).

4. NONEQUILIBRIUM DISSOCIATION OF POLYATOMIC MOLECULES

The above expressions for the distribution over the vibrational levels and the nonequilibrium dissociation rates are valid for diatomic molecules.

It is clear that, when the interaction between the vibrational modes is weak, all the above formulas will apply to polyatomic molecules as well, if we consider a given type of vibration with minimum energy at the dissociation limit. The condition that the interaction between given and other types of vibration is small means

that the reaction probability $P_{m,m-1} + \beta Q^{01}_{m,m-1}$ for a given type of vibration and given level m corresponding to this vibration should be greater than the exchange probability $\widetilde{\beta}\widetilde{Q}^{ij}_{m,m-1}$ with other vibrational modes. It is important to note that it is clear from Eqs. (20) and (21) that it will be difficult to use diatomic molecules to obtain high dissociation rates under equilibrium conditions at low gas temperatures (of the order of room temperature) and high vibrational energies. This is also the case for polyatomic molecules for vibrations with minimum energy at the dissociation limit (as compared with other types of vibration). This is connected with the fact that, in spite of the high store of energy, the V−T processes which are important for the upper levels ensure that the relative population of these levels is determined by the gas temperature and, consequently, falls rapidly with increasing level number. In chemical kinetics, on the other hand, it is often important to have high dissociation rates under nonequilibrium conditions. Thus, when one is concerned with the development of high-power chemical lasers which operate continuously, one of the current important problems is to obtain relatively high concentrations of free atoms or radicals at low gas temperatures (for example, in the HF* + CO$_2$ laser), and it is essential to produce F atoms which participate in the reaction leading to the appearance of the vibrationally excited HF* molecule. High concentrations of these molecules, on the other hand, can be obtained at high dissociation rates of the molecules which contain these particles.

One way of obtaining high dissociation rates at low gas temperatures may be to use a polyatomic molecule which is pumped with a high store of vibrational energy into a type of vibration which has a dissociation limit D that is higher than the minimum dissociation energy D_{min} of the molecule.

In this case, the decay of the molecule may occur through predissociation, i.e., the transition of the molecule to the continuous spectrum from a vibrational level lying above the minimum dissociation energy. The rate of this transition is usually high because of the interaction between the different molecular vibrations.[15] [4] Hence, the dissociation rate is determined by the probability with which the molecules reach the level $k + 1$, and the population of the level k whose number is determined by the condition

$$E_k = k[E_1 - (k-1)\Delta E] \leqslant D_{min} \leqslant E_{k+1}$$
$$= (k+1)[E_1 - k\Delta E].$$

If the level k lies near $n^*(i^*)$ [see Eqs. (11a) and (13a)] or even $k < n^*(i^*)$, then V−T processes or radiative decay of this level has little effect on its population, and for sufficiently high stores of vibrational energy it can be substantial, ensuring a high dissociation rate. The nonequilibrium energy store can then, as usual, be obtained by various pumping methods, for example, optical, thermal, chemical, and electrical, and by vibrational exchange with another molecule with its own nonequilibrium energy.

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[4] In addition to predissociation during vibrations, one may also consider predissociation due to intersection with another electronic term.

Let us now find the dissociation rate for a polyatomic molecule, assuming that $k < n^*(i^*)$. In this case, we have [see Eq. (16b)]

$$W_m = X_{m+1}^0 \beta Q_{m+1, m}^{01}; \qquad I_k' = X_k^0 \beta Q_{k, k+1}^{10} \sum_{m=0}^{k-1} \frac{1}{W_m}$$

$$\approx X_k^0 Q_{k, k+1}^{10} \int_0^{k-1} \frac{dm}{X_{m+1}^0 Q_{m+1, m}^{01}} \approx \frac{k+1}{(m+1)} \sqrt{\frac{\pi T}{4 \Delta E}} \exp(y^2) [1 - \Phi(y)];$$

$$y = \sqrt{\frac{D}{T}} \left(\frac{T}{T_1} + \frac{\gamma_0}{3} \frac{T}{D} - \frac{E_1}{2D} (k-1) \right). \qquad (24)$$

Substituting Eqs. (16) and (24) into Eq. (1), we obtain

$$v = zN \frac{1}{Q} X_k^0 \beta Q_{k, k+1}^{10} (1 + I_k')^{-1} \approx zN \frac{1}{Q} (k+1) \beta Q_{01}^{10} \exp \left(-\frac{D_{min}}{T} \right)$$

$$\times \exp \left[k E_1 \left(\frac{1}{T} - \frac{1}{T_1} - \frac{\gamma_0}{3D} \right) \right] (1 + I_k')^{-1}. \qquad (25)$$

We note that a formula similar to Eq. (25) can readily be obtained for the case $k > n^*(i^*)$.

Equation (25) differs in two important respects from the nonequilibrium dissociation rate of diatomic molecules [Eqs. (19)–(21)]. The first difference is that, even at low gas temperatures T (of the order of room temperature), the rate of nonequilibrium dissociation of the polyatomic molecule may be quite high, in contrast to the diatomic case. It is readily seen from Eq. (25) that this can be reached for relatively high $T_1 > T$. In this connection, we note the results of[16], where the pumping of CO_2 laser radiation into one of the vibrational modes of the BCl_3 molecules made it possible to achieve an appreciable dissociation rate in the BCl_3 at room temperature.

It is interesting that, for this type of molecular vibration at $T \sim 300°$, our estimates show that $k < n^*$, and we can use Eq. (25) to calculate the dissociation rate.

The second important difference is the possible anomalous dependence of the dissociation rate of polyatomic molecules under nonequilibrium conditions with $T \neq T_1$. It is clear from Eq. (25) that for a constant store of vibrational energy (or constant T_1) the dissociation rate v for $T < T_1$ will fall with increasing T, in contrast to the usual Arrhenius law under which it is expected to increase.[5] Figure 3 shows the dissociation probability v/zN for the BCl_3 molecule as a function of gas temperature, calculated from Eq. (25) for ν_3 vibrations, assuming constant T_1.

This variation of v with T, and its strong dependence on T_1, enable us to control the dissociation process by varying the gas temperature and the vibrational energy store.

5. CHEMICAL KINETICS AND CHEMICAL LASERS

The above analysis of nonequilibrium processes which accompany the dissociation reaction enables us to draw certain conclusions with regard to chemical kinetics and the operation of chemical lasers. The nonequilibrium nature of most chemical reactions reveals new possibilities for influencing their kinetics.
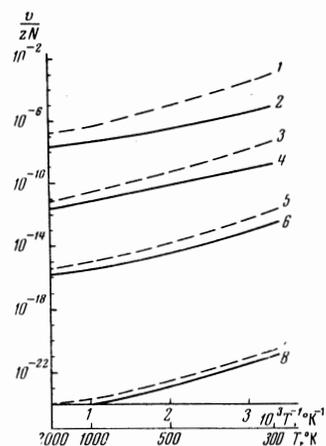
FIG. 3. Dissociation probability v/zN for the BCl_3 molecule (ν_3 vibration) as a function of temperature; BCl_3-BCl_3 collisions. $T_1 = 3000°$ (curves 1 and 2), 2000° (curves 3 and 4), 1500° (curves 5 and 6), and 1000°K (curves 7 and 8). The calculation was performed with (curves 2, 4, 6, 8) and without (curves 1, 3, 5, 7) taking into account the effect of dissociation on upper-level populations.

The possibility of controlling the simple chemical reaction of nonequilibrium dissociation, mentioned in Sec. 4, is a special case of this.

Let us illustrate this, taking chain reactions as an example. Excited molecules are formed in the course of the reaction, and there is the unavoidable violation of the equilibrium energy distribution over the degrees of freedom. Molecules having excess energy may become active reaction centers. Semenov[17] has considered the reaction $H_2 + Cl_2 \rightarrow HCl$ and has noted the possibility of branching in accordance with the scheme $HCl^* + Cl_2 \rightarrow HCl + Cl + Cl$. However, under ordinary conditions, the HCl^* molecules formed in the reaction $H + Cl_2 \rightarrow HCl^* + Cl$ have a vibrational energy store which was insufficient for branching.[18] By increasing this store in HCl it is probably possible to realize the above scheme. This increase in vibrational energy can be introduced in various ways and, in particular, through nonresonant vibrational exchange and by electrical or optical pumping.

We may thus conclude that it is possible, at least in principle, to control the reactions both at the initial and at the branching stages. In practice, the reaction control can be carried out by means of nonequilibrium streams of the reacting gases. This involves producing a stream containing free radicals (atoms) which are necessary for the initiation of the reaction (at low temperatures they can be obtained by nonequilibrium dissociation of polyatomic molecules in accordance with Sec. 4), a gas stream necessary to produce the reacting mixture, and a control stream used for the purposes of branching. By introducing the necessary impurities into the reacting mixture with the aid of this stream one can change the vibrational energy store of the molecules participating in the chemical reaction through nonresonant exchange[6], and hence one can affect the reaction rate. The influence of these impurities is particularly important when the number of molecules is still small. The resultant stream formed after the mixing of the initial streams should exhibit a discontinuity in the gas and vibrational temperatures; gas-dynamic methods can be used to produce it or enhance it.

We note that, in addition to the possible control of chemical processes under specially produced nonequilibrium conditions, impurities may also affect the course

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[5]The increase of v with increasing T for T_1 = const may begin when the condition $k < n^*(i^*)$ is not satisfied, or the usual thermal dissociation becomes important.

of the reaction through the nonequilibrium properties of the reaction itself. Thus, the phenomenon of catalysis in the gaseous medium at high temperature may be directly associated with vibrational exchange resulting in the formation of active centers.

We emphasize that in the case of control of chemical reactions, including optical pumping by laser radiation[19,20], it is important to take into account vibrational exchange since in a complicated system the energy pumped into particular levels may be drastically redistributed. However, the above approach is particularly important for chemical lasers (see[21]). It is interesting to note that an appreciable increase in the output of chemical lasers which has recently been achieved is connected with the possibility of producing high concentrations of free atoms.[20-24] Thus, the gas-dynamic spreading of a mixture produced by separate streams of SF_6 and N_2 heated to 2000° was used in[23]. It is reasonable to expect that the formation of free fluorine atoms through the dissociation of SF_6 takes place as a result of the predissociation of SF_6 because of the nonresonant vibrational exchange with excited N_2 (see Sec. 4). However, quantitative comparisons of dissociation processes in chemical lasers[22-24] with the theoretical predictions will require more detailed experimental data. Further studies of the effect of the vibrational kinetics on the various stages of chemical processes is very important, both for the optimization of existing lasers and for the development of new ones.

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