

DISSOCIATION OF ANHARMONIC MOLECULES  
BY MEANS OF HIGH-POWER INFRARED EMISSION

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The kinetics of nonequilibrium molecular dissociation when vibrations are excited by high-power infrared emission is investigated for a model of anharmonic oscillators. The case when exchange of vibrational quanta during collision with molecules in the lower states plays a fundamental role in the formation of the vibratory distributionfunction at the upper level is analyzed. Dependences of the "vibration temperature" and the rate constant for nonequilibrium dissociation, as a function of the optical pumping probability are obtained for different pumping conditions. The results are compared with similar calculations for a harmonic model.

1. Exposure of a molecule to laser emission is one of the most promising physical methods for stimulating chemical processes. The possibility of such exposure can be demonstrated by one of the simplest reactions, namely the dissociation reaction of diatomic or multiatomic molecules. A number of interesting experimental and theoretical [1-11] results have been obtained in this field. In all cases (except for [2]) a molecular model of a blocking harmonic oscillator was considered in theoretically analyzing the kinetics of nonequilibrium dissociation of molecules exposed to infrared laser emission. The rates of nonequilibrium dissociation of diatomic and multiatomic molecules under selective vibration "run-up" condition, i.e., at low gas temperature and high vibratory energy margin, were calculated previously [2] for an anharmonic model of Morse oscillators. However, questions directly connected to optical energy pumping at vibrational degrees of freedom were not dealt with in [2], and neither was the dependence of dissociation rate on the power of the emission absorbed by the molecules investigated.

While preparing this article for printing an article [11] appeared which analyzed dissociation occurring when diatomic anharmonic molecules were exposed to laser emission to a diffusion approximation. The particular case when energy loss from the system is determined only by dissociation processes was examined in this article.

The purpose of the current work was to analyze the behavior of the nonequilibrium distribution function of vibrational energy during dissociation and to find the dissociation rate under cascaded and multi-quantum pumping of molecular vibrations by laser emission. Unlike our preceding studies [7, 8] we will consider there an anharmonic molecular model and clarify the role of anharmonicity in the dissociation process of molecules excited by emission.

To describe the kinetics of nonequilibrium dissociation, we take the following model:

1) The molecules are represented in the form of anharmonic Morse oscillators;

2) There can exist either vibrational transitions  $i-1 \rightleftharpoons i$  with probability  $W_{i-1,i} = W_{i,i-1} = iW_{10}$ ,  $i = 1, 2, \dots, k$  (cascaded pumping of vibrations to level  $k$ ) or the transition  $i = 0 \rightleftharpoons i = k$  with probability  $W_{0k} = W_{k0}$  (multistage pumping) in absorption of laser emission. Here,  $i$  is the vibrational quantum number and the value of  $k$  is determined by the pumping conditions and the ratios between the laser emission frequency and the vibration frequency of the oscillator;

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3) The gas temperature  $T$  is assumed constant during dissociation. This assumption is justified since we will consider below the possibility of carrying out nonequilibrium dissociation in less time when that taken by energy transition from vibrational to translational degrees of freedom, i.e., during which the gas is not heated;

4) Rotational relaxation is assumed to have been completed and is not treated;

5) Vibrational relaxation in the system is caused by single quantum vibrational-vibrational exchange ( $v-v$  processes) with probability  $Q_{i+1,i}^{i,i+1}$  and by single-quantum vibrational-translational energy exchange ( $v-t$  processes) with probability  $P_{i+1,i}$ ;

6) The molecular gas under investigation is assumed to be weakly diluted with other gases, so that  $\beta Q_{i+1,i}^{01} > P_{i+1,i}$  always for the level  $i < i^*$ . The level  $i^*$  is determined from the condition  $\beta Q_{i^*,i^*-1}^{01} \approx P_{i^*,i^*-1}$  where the factor  $\beta$  approximately takes into account the contribution of the level  $j > 1$  in the probability of the transition  $i \rightarrow i-1$  in vibrational exchange [cf. [2] and Eq. (2.3)];

7) Molecular dissociation begins at some level  $m > k$ .

This model is similar to a previous model [7, 8], differing from it in taking into account the anharmonicity of the molecular vibrations. In the general case, anharmonicity substantially complicates the physical picture of vibrational relaxation and nonequilibrium dissociation. Therefore, we take below the additional condition  $m < i^*$  in order to obtain results in a graphically analytic form. Since, in accordance with 6),  $\beta Q_{i+1,i}^{01} > P_{i+1,i}$ , always when  $i < i^*$ , the condition  $m < i^*$  means that  $v-t$  processes do not exert any influence throughout the region  $i < m$  on the form of the vibrational distribution function and can only determine the total vibrational energy margin in the system.

This model of nonequilibrium dissociation for a system of blocking anharmonic oscillators narrows the class of systems to be treated and is not suitable for analyzing collisional dissociation of diatomic molecules with high boundary levels, since in this case  $P_{i,i-1} \gg \beta Q_{i,i-1}^{01}$ , always at the dissociation boundary due to the low magnitude of the vibrational quanta. However, for the case of practical importance that shall be analyzed below and which is typical of low (on the order of room) gas temperatures, such dissociation is often not of interest since it proceeds at a low rate. Physically speaking, this is because this population in spite of the possibility of selective oscillation run-up due to  $v-t$  processes, which are substantial at the upper levels, will be primarily determined by the gas temperature, so that at low  $T$  it will sharply fall upon transition to the boundary level. In the model we will take for blocking anharmonic oscillators with the boundary level  $m < i^*$ , the population of the upper states when running up the vibrations by means of emission can be sufficiently great, which ensures a high dissociation rate.

Our model can describe dissociation of multiatomic molecules if their dissociation occurs from a comparatively low level due to predissociation, as well as dissociation of diatomic and multiatomic molecules when their transition in the continuous spectrum from a level  $m < i^*$  occurs by an particular method (for example, by photodissociation).

To determine the dependence of the nonequilibrium dissociation rate on the power of absorbed emission it is necessary to solve a system of gasokinetic equations for the population  $x_i$  of the vibrational levels  $i$ . Under assumptions 1, 2, 4-7 it can be written in the form

$$\frac{1}{N} \frac{dx_i}{dt} = P_{i+1,i} y_{i+1} - (P_{i,i+1} + P_{i,i-1}) y_i + P_{i-1,i} y_{i-1} + G_i - P_{md} x_m \delta_{im} + \left( \sum_j Q_{i+1,i}^{j,j+1} y_j \right) y_{i+1} - \sum_j (Q_{i,i+1}^{j+1,j} y_{j+1} + Q_{i,i-1}^{j+1,j} y_j) y_i + \left( \sum_j Q_{i-1,i}^{j+1,j} y_{j+1} \right) y_{i-1}, \quad i = 0, 1, 2, \dots, m \quad (1.1)$$

Here,  $y_i = x_i/N$  is the relative population of the  $i$ -th vibrational level of the gas molecules with total concentration  $N$ ,  $P_{md}$  is the transition probability of the molecules in the continuous spectrum from the level  $m$ ,  $\delta_{im}$  is the Kroneker symbol,  $G_i$  describes the change in population exposed to absorbed emission in cascaded 1) and multiquantum 2) pumping, which respectively take the form

$$G_i = \begin{cases} [(1 - \delta_{ik})(i+1)y_{i+1} - (1 - \delta_{ik})y_i - iy_i + iy_{j-1}] W_{10} \\ [(y_k - y_0)\delta_{i0} - (y_k - y_0)\delta_{ik}] W_{k0} \end{cases} \quad (1.2)$$

To solve Eqs. (1.1) it is necessary to know the dependence of the probabilities  $Q_{sd}^{pq}$  and  $P_{st}$  on the number of the vibrational level. Anharmonicity is usually taken into account to find this dependence only in calculating the exponential factors, which yield the most important dependence on the transition energy. In this case we have

$$Q_{i+1,i}^{j,j+1} = Q_{10}^{01} (i+1)(j+1) e^{\delta_{vt} (i-j)}, \quad P_{i+1,i} = P_{10} (i+1) e^{\delta_{vt} i} \quad (1.3)$$

Here,  $\delta_{VV} = 0.427 l_{VV} (\mu_{VV}/T)^{1/2} \Delta E - \Delta E/T$ ;  $\mu$  is the reduced mass of the colliding molecules in atomic units;  $l$  is the characteristic constant in the exponential in intermolecular interaction in Å; and  $\Delta E$  is molecular anharmonicity expressed in degrees ( $\Delta E = \omega_e \chi_e$ , where  $\omega_e$  and  $\chi_e$  are the spectroscopic constants of the molecule). The expression for  $\delta_{vt}$  is similar, however  $\mu$  and  $l$  may be different if v-t processes are determined by collision with an impure gas. The probabilities of opposite transitions are determined from the detailed-balance principle.

Multiplying Eq. (1.1) by  $i$  and adding over all  $i$ , we obtain an equation for the vibrational quantum margin  $\alpha$  taken over one molecule, that is

$$d\alpha / dt = \alpha - \alpha_T / \tau_{vt}^a - (m - \alpha) K_d + F \quad (1.4)$$

Here  $\alpha_T$  is the equilibrium quantum margin at temperature  $T$ ,  $K_d = T_{md} y_m$  is the rate constant of nonequilibrium dissociation,  $\tau_{vt}^a$  is the relaxation time of vibrational energy due to v-t processes for the anharmonic model, and  $F$  is the quantum pumping rate due to absorption of emission in multiquantum 1) and cascaded 2) pumping given, respectively, by

$$F = \begin{cases} kW_{k0}(y_0 - y_k) \\ W_{10} \left( -ky_k + \sum_{i=0}^{k-1} y_i \right) \end{cases} \quad (1.5)$$

The variable  $\tau_{vt}^a$  depends in the general case on  $\alpha$  and can substantially differ from the corresponding relaxation time for the harmonic model. The value of  $\tau_{vt}^a$  has been previously calculated [12] for an arbitrary nonequilibrium margin  $\alpha$ . It has the form for a comparatively small deviation from equilibrium [12, 13]

$$\tau_{vt}^a = \tau_{vt}^h [1 - \alpha (e^{\delta_{vt} i} - 1)]^2 \quad (1.6)$$

Below, we will use Eq. (1.6) everywhere as the definition of  $\tau_{vt}^a$ . It was obtained for small deviations from equilibrium assuming a Boltzmann [13] or Trnavorovskii [12] form of the vibrational distribution function. In the latter case,

$$y_i^T = y_0 \exp \left\{ - \left[ \frac{E_1}{T_1} - \frac{\Delta E}{T} (i-1) \right] i \right\} \quad (1.7)$$

where  $T_1 = E_1 / \ln(y_0/y_1)$  is the "vibrational temperature" of the first level, which can be determined by the total nonequilibrium vibrational energy margin of the system. This function has a minimum depending on  $i$  which taken over one level is given by

$$i_{\min} = \frac{T}{T_1} \frac{E_1}{2\Delta E} + \frac{1}{2} \quad (1.8)$$

Under actual condition, the distribution function when highly deviating from equilibrium at levels  $i > i_{\min}$  takes the form due to the effect of v-t processes of a flat plateau, whose presence can substantially increase the energy relaxation rate and falsify Eq. (1.6) [12]. This plateau will be absent in the model being analyzed here only if

$$i_{\min} \gtrsim m \quad (1.9)$$

Thus inequality (1.9) determines the maximum value of  $T_1$  at a given boundary level  $m$  and, consequently, the maximum  $\alpha$  at which Eq. (1.6) is still true. Moreover, condition (1.9) allows us to obtain a simple dependence of the quantum margin  $\alpha$  and the value of  $y_0$  on the vibrational temperature  $T_1$  for many pumping conditions (under weak optical pumping when  $W_{10}$  and  $W_{k0} \ll Q_{10}$ , and for strong pumping when  $W_{10}$  and  $W_{k0} \gg Q_{10}$  and  $kE_1/T_1 \ll 1$ ). This dependence can be highly accurate, represented by formulas that coincide with similar expressions for the model of a harmonic oscillator;

$$\alpha = \exp \left( - \frac{E_1}{T_1} \right) / \left[ 1 - \exp \left( - \frac{E_1}{T_1} \right) \right], \quad y_0 = \left[ 1 - \exp \left( - \frac{E_1}{T_1} \right) \right]^{-1} \quad (1.10)$$

An examination of the case of a weak deviation from equilibrium [condition (1.9)] makes it possible to obtain analytic expressions for the vibrational distribution function and the dissociation rate.

2. Let us consider a rectangular emission pulse of len  $\tau_i > \tau_d = 1/K_d$ . We assume, as in [7,8] that

$$\tau_\alpha \ll \tau_d \quad (2.1)$$

for the characteristic time  $\tau_\alpha \approx \alpha / |d\alpha/dt|$  of the relaxation of the quantum margin  $\alpha$ .

Since, in accordance with Eq. (1.4),  $\tau_\alpha \sim \min[\tau_{vt}^\alpha; (\alpha/m) 1/K_d]$ , and, moreover,  $\alpha \gg m$  usually, Eq. (2.1) holds for many cases of practical interest. The exception is only high-power (with probabilities  $W_{10}, W_{k0} \gg Q_{10}^{01}$ ) pumping to the level  $k \sim m$  and the case of small  $m$ . Under these conditions  $\alpha/m \approx 1$  and it may turn out that  $\tau_d \sim \tau_\alpha$ .

If Eq. (2.1) holds for an interval of time  $\tau_\alpha \ll \Delta t \ll \tau_d$ , we may assume  $d\alpha/dt = 0$ , and the population  $x_i(t)$  is found in the form (cf. [7, 8])

$$x_i(t) = N(t) y_i, \quad \sum_{i=0}^m y_i = 1 \quad (2.2)$$

Exchange in collision with molecules at lower levels where the distribution (1.7) is valid plays the greatest role for molecules at the  $i$ -th pumping level for a small deviation from equilibrium in  $v-t$  processes. Therefore, using Eq. (1.7) as the zero approximation, it is possible to linearize the nonlinear part of Eqs. (1.1) that describe the variation in the particle number at the  $i$ -th level due to  $v-t$  processes. An approximation of the sums in this case yields [2]

$$\sum_{j=0}^m Q_{i+1,i}^{j,j+1} y_j \approx \beta Q_{i+1,i}^{01}, \quad \beta = \frac{1 - \exp(-E_1/T_1)}{[1 - \exp(\delta_{vv} - E_1/T_1)]^2} \quad (2.3)$$

The system of balanced equations thus linearized for the populations, which takes into account Eq. (2) can be solved by the double-summation method [2, 7, 8]. As a result, we obtain for the vibrational distribution function the following expressions:

For multiquantum pumping

$$\begin{aligned} y_n &= (-K_d - W_{k0} y_k + W_{0k} y_0) y_n^T f_n (\beta Q_{10})^{-1} + y_n^T \quad (0 \leq n \leq k) \\ y_n &= -K_d y_n^T (f_n - f_k) \beta Q_{10}^{-1} + (y_k / y_k^T) y_n^T \quad (k+1 \leq n \leq m) \end{aligned} \quad (2.4)$$

For cascaded pumping

$$\begin{aligned} y_n &= -K_d y_n^T \varphi_n \sum_{i=1}^n [i y_i^T \varphi_i (\beta Q_{10} e^{-(i-1)\delta} + W_{10})]^{-1} + y_n^T \varphi_n \quad (0 \leq n \leq k) \\ y_n &= -K_d y_n^T (f_n - f_k) (\beta Q_{10})^{-1} + (y_k / y_k^T) y_n^T \quad (k+1 \leq n \leq m) \\ f_n &= \sum_{i=1}^n [i e^{-(i-1)\delta_{vv}} y_i^T]^{-1} \\ \varphi_i &= \prod_{j=1}^i \left[ \beta Q_{10} \exp(-j\delta_{vv}) + W_{10} \exp\left(\frac{E_1}{T_1} - j \frac{2\Delta E}{T}\right) \right] [\beta Q_{10} \exp(-j\delta_{vv}) + W_{10}]^{-1} \end{aligned} \quad (2.5)$$

As is evident from Eqs. (2.4) and (2.5) the vibrational distribution function in a gas dissociating due to emission, differs from the Trnavoroskii equation (1.7). Using Eqs. (2.4) and (2.5) and taking into account the fact that  $K_d = T_{md} y_m$ , it is possible to find the dissociation rate constant  $K_d$ . We have for the most frequently encountered case  $P_{md} \gg Q_{m,m-1}^{01}$  for multiquantum and cascaded pumping respectively,

$$\begin{aligned} K_d &= \beta Q_{10} \left( 1 + \frac{W_{0k}}{\beta Q_{10}} f_k \right) \left[ \left( 1 + \frac{W_{k0}}{\beta Q_{10}} y_k^T f_k \right) f_m \right]^{-1} \\ K_d &= \beta Q_{10} \varphi_k \left[ f_m - f_k + \varphi_k \sum_{i=1}^k i y_i^T \varphi_i \left( e^{-(i-1)\delta_{vv}} + \frac{W_{10}}{\beta Q_{10}} \right) \right] \end{aligned} \quad (2.6)$$

Equations (2.4)–(2.6) are close in form to the corresponding expressions for the harmonic-oscillator model [7, 8]. However, the function (1.7) occurs as the undistorted optical pumping and dissociation distribution function in place of the Boltzmann equation, and, moreover, the influence of anharmonicity on the vibrational exchange probability is taken into account by factors of the type  $\exp[-(i-1)\delta_{vv}]$ . Equations (2.6) together with Eqs. (1.4) and (1.5), (1.6) and (2.3) determine the dependence of the constant  $K_d$  and temperature  $T_1$  on the probability of optical molecular pumping. Dependences of  $T_1$  and  $K_d$  on the probability  $W_{10}$  at  $k=1$  and on different values of the parameters  $Q_{10}/T_{10} m$ ,  $\Delta E/T$ , and  $\delta_{vv} \approx \delta_{vt}$  were calculated by these equations, assuming that  $\alpha_T \ll \alpha$  (i.e., the gas temperature  $T < T_1$ ).

Results on the dependence of vibrational temperature  $T_1/E_1$  on the dimensionless probability of optical pumping  $W_{10}/T_{10}$  are depicted in Figs. 1 and 2, which also present data of similar calculations for the harmonic-oscillator model [7, 8] for comparison. Curves 1, 1', and 1'' (Fig. 1a) characterize the

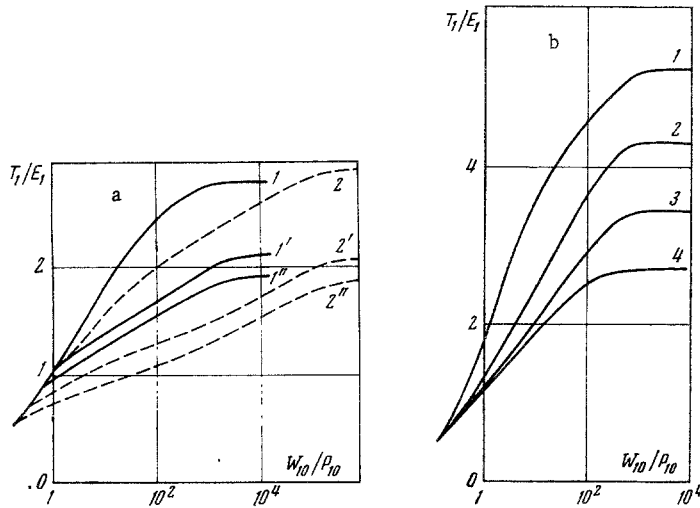


Fig. 1

following values:  $k = 1$ ,  $m = 15$ , and  $Q_{10}/P_{10} = 10^2$ , while curves 2, 2', and 2'' characterize a value for  $Q_{10}/P_{10}$  of  $10^4$ . The value of  $\Delta E/T$  is  $3 \cdot 10^{-2}$  for curves 1' and 2' and  $4 \cdot 10^{-2}$  for curves 1'' and 2''. We also have  $\delta_{VV} \approx \delta_{VT} = 2.7 \cdot 10^{-1}$  for 1' and 2' and  $2.6 \cdot 10^{-1}$  for 1'' and 2''. Curve 1 and 2 correspond to the harmonic model. The values of the parameters for the curves in Fig. 1b are as follows  $k = 1$ ,  $m = 40$ ,  $Q_{10}/P_{10} = 10^2$ , and  $\Delta E/T = (4, 5, 7) \cdot 10^{-3}$  for curves 2, 3, and 4, respectively, curve 1 corresponds to a harmonic model. The number of the curves in Fig. 2ab correspond to the same values of the parameters as in Fig. 1a,b.

As is evident from these figures, the values of  $T_1/E_1$  and, in particular,  $K_d/P_{10}$  for anharmonic oscillators can significantly differ in a given range of probabilities of optical pumping from the corresponding values for a harmonic model. For example,  $W_{10}/P_{10} \approx 10^2$  (when  $Q_{10}/P_{10} \approx 10^4$ ), and  $2 \cdot 10^2$  (when  $Q_{10}/P_{10} \approx 10^2$ ) are required for reaching the regime  $K_d/P_{10} \approx 1$  for  $BCl_3$  molecules ( $k = 1$ ,  $m \approx 40$ ,  $E_1 \sim 1440^\circ K$ ,  $\Delta E/T \approx 7 \cdot 10^{-3}$ , and  $\delta_{VV} \approx \delta_{VT} \approx 6.3 \cdot 10^{-2}$ ), which amounts to respectively  $\approx 0.7 \cdot 10^2 \text{ W/cm}^2 \cdot (\text{mm Hg})^2$  upon conversion to the emission intensity  $I$  of a  $CO_2$  laser [8] at pressures  $p \gtrsim 10 \text{ mm Hg}$ .

In the harmonic model  $I \approx 4 \text{ W/cm}^2 \cdot (\text{mm Hg})^2 \cdot p^2$  for the first case and when  $Q_{10}/P_{10} = 10^2$  this regime is impossible. To obtain an explicit dependence of  $T_1$  and  $K_d$  on  $W_{k0}$  (or  $W_{10}$ ) and the parameters  $Q_{10}/P_{10}$ ,  $m$ ,  $\Delta E/T$ ,  $\delta_{VV}$ , and  $\delta_{VT}$  we simplify Eqs. (1.4)–(1.6), (2.3), and (2.6), considering the different regimes of weak ( $W_{10}, W_{k0} \ll Q_{10}$ ) and strong ( $W_{10}, W_{k0} \gg Q_{10}$ ) pumping.

3. Let us consider dissociation under weak optical pumping ( $W_{10}, W_{k0} \gg Q_{10}$ ). In this case, Eqs. (2.6), which determined the dependence of  $K_d$  on  $T_1$ ,  $Q_{10}$ ,  $m$ , and  $\Delta E/T$  under multiquantum and cascaded pumping take the form

$$K_d = \beta Q_{10} f_m^{-1} \quad (3.1)$$

The relationship between  $T_1$  and  $W_{k0}$  ( $W_{10}$ ) is determined by Eqs. (1.2)–(1.4) and (1.8), taking into account the fact that  $\alpha \ll m$  and  $d\alpha/dt = 0$ . A further simplification of Eqs. (1.2)–(1.4) becomes and the derivation of dependence of  $K_d$  and  $T_1$  on  $W_{10}$  ( $W_{k0}$ ) become possible if, following [7, 8], we examine the case of high and low  $T_1$ . Thus, for small  $T_1/E_1 < 1$ , by considering the quantum margin as independent of the dissociation rate [i.e., ignoring the second term in the right side of Eq. (1.2)], we find

$$K_d \approx Q_{10} m \left( \frac{A_k}{P_{10}} \right)^m \exp(\eta_m), \quad \frac{E_1}{T_1} \approx \ln \left( \frac{P_{10}}{A_k} \right) \quad (3.2)$$

Here  $r_m = (\Delta E/T)m^2 - m\delta_{VV}$ , and  $A_k = kW_{k0}$  for multiquantum pumping and  $A_k = W_{10}$  for cascaded pumping. As is evident from Eq. (3.2) the temperature  $T_1$  and dissociation rate constant  $K_d$  rapidly increase with increasing pumping power. Beginning at some  $W_{k0}$  (or  $W_{10}$ ) the value of  $K_d$  can be such that the loss of vibrational energy from the system will be basically caused by dissociation, i.e., by the second term in the right side of Eq. (1.2). In this case, we have from Eqs. (1.2)–(1.4) and (3.1),

$$K_d \approx \frac{1}{m} A_k, \quad E_1/T_1 \approx \frac{1}{m} \ln \left( m^2 \frac{Q_{10}}{A_k} \right) + \frac{\eta_m}{m} \quad (3.3)$$

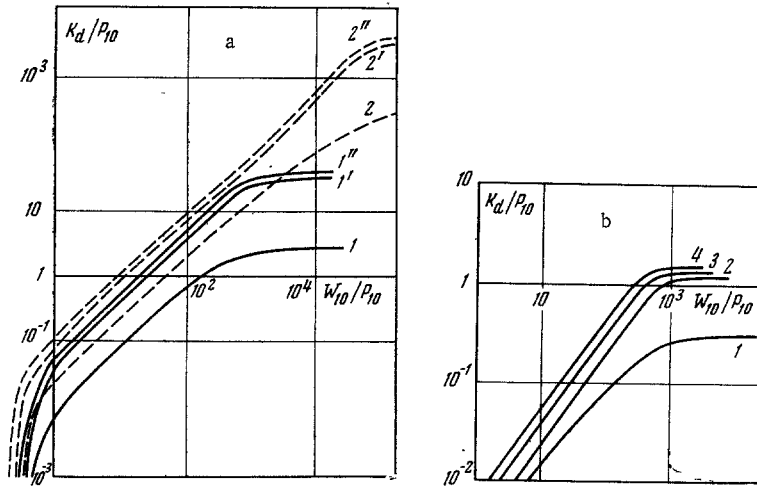


Fig. 2.

The values of  $W_{k0}^*$  (or  $W_{10}^*$ ) and of  $T_1^*$  at which the regime (3.2) changes into (3.3) can be found by using Eq. (3.1) and assuming that the first and second terms of the right side of Eq. (1.2) are the same, that is

$$\frac{E_1}{T_1^*} = \frac{1}{m+1} \left[ \eta_m + \ln \left( \frac{Q_{10}}{P_{10}} m^2 \right) \right], \quad A_{k0}^* = P_{10} \exp \left[ \eta_m + \frac{E_1}{T_1^*} (1-m) \right] \quad (3.4)$$

Equations (3.2) and (3.3) at  $\eta_m = 0$  change into the corresponding expressions for the harmonic model [7, 8]. Since  $|\eta_m| \gg 1$  often for anharmonic oscillators, the temperature  $T_1$  in the case (3.3) and the dissociation rate in the case (3.2) can significantly differ from the expressions assumed for the harmonic model (cf. also Figs. 1 and 2). Here and below, blocking anharmonic and harmonic oscillators with identical  $E_1$  and  $m$  are compared. Consequently, the dissociation energy in an anharmonic oscillator is always less than that of the harmonic oscillator being compared.

Physically, the variation in  $\exp(\eta_m)$  and of the dissociation rate constants in Eq. (3.2) due to anharmonicity is related to the variation in particle flow from level  $m-1$  to the boundary level  $m$ , which is caused by an increase in the population of level  $m-1$  by a factor  $\exp(m^2 \Delta E/T)$  and by the decrease in the transition probability  $Q_{m-1, m}^{01}$  by a factor  $\exp(-\delta_{vV} m)$ . The gas temperature can affect the size of  $\exp(\eta_m)$  and, consequently, the dissociation rate in the case (3.2). For example, we have  $\exp(\eta_m) = 40 \cdot 10^3$  and  $4 \cdot 10^3$ , respectively, for BCl molecules used in experiments into molecular dissociation in the emission field of a CO<sub>2</sub> laser at  $T = 500$  and  $300^\circ\text{K}$ . As has been previously noted [2], it thus becomes possible additionally to regulate the nonequilibrium dissociation rate by varying the gas temperature. The dependence of  $K_D$  on  $\Delta E/T$  when  $W_{10}/P_{10}$  is held constant at 10 is illustrated in Fig. 3. The values of the parameters in Fig. 3 are as follows:  $Q_{10}/P_{10} = 10^2$ ,  $\delta_{vV} \approx \delta_{0k} = 10^{-1}$  and  $m = 5, 15,$  and  $40$  for curves 1, 2, and 2', and 3 and 3', respectively. The straight lines correspond to the harmonic model.

As  $W_{k0} \gg W_{k0}^*$  ( $W_{10} \gg W_{10}^*$ ), which is the case when Eq. (3.3) holds, anharmonicity does not vary  $K_D$  and leads to values for  $T_1$  that somewhat differ from the vibration temperature of harmonic oscillators (cr. Eq. (3.3) and Figs. 1a and 2a). This is because the dissociation rate is determined by the energy pumping rate at a vibrational degree of freedom, and, consequently, is proportional to  $W_{k0}$  ( $W_{10}$ ) and independent of the form of the vibrational distribution function.

At a high vibrational temperature  $T_1 > E_1$  an explicit dependence of  $K_D$  on  $W_{k0}$  (or  $W_{10}$ ) cannot be found. If in this case the dissipation of vibrational energy from the system is determined only by  $v-t$  processes, it is suitable to use Eq. (3.1) for  $K_D$  and the dependence of  $T_1$  on  $W_{k0}$  (or  $W_{10}$ ) is found from the relationships

$$B_k \approx P_{10} (E_1/T_1 - \delta_{vi})^{-2} \left[ E_1/T_1 - (k-1) \frac{\Delta E}{T} \right]^{-1}, \quad k \frac{E_1}{T_1} \ll 1 \quad (3.5)$$

where  $B_k = k^2 W_{k0}$  for multiquantum pumping and  $B_k = k(k+1)W_{10}/2$  for cascaded pumping.

Whenever  $v-t$  processes are ignored and it is assumed that energy lost from the system is caused solely by dissociation,

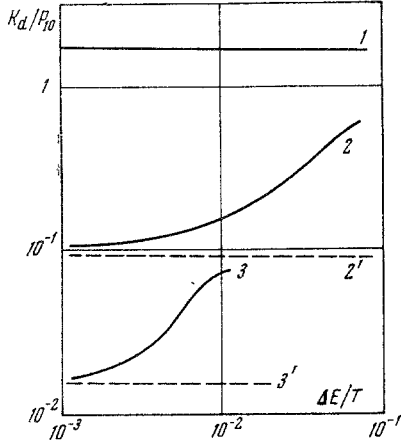


Fig. 3

$$K_d \approx \frac{1}{m} B_k \frac{E_1}{T_1} \left[ \frac{E_1}{T_1} - (k-1) \frac{\Delta E}{T} \right] \quad (3.6)$$

$$B_k \approx Q_{10} m \frac{E_1}{T_1} \left( \frac{E_1}{T_1} - \delta_{vv} \right)^{-2} \left[ \frac{E_1}{T_1} - (k-1) \frac{\Delta E}{T} \right]^{-1} f_m^{-1}$$

When  $k(E_1/T_1) < 1$  the function  $f_m$  occurring in Eqs. (3.1) and (3.6) has the form

$$f_m^{-1} \approx y_0 m \sqrt{\frac{4\Delta E}{\pi T}} \exp\left(\delta_{vt} - z^2 \frac{T}{\Delta E}\right) \times \left[ \Phi\left(m \sqrt{\frac{\Delta E}{T}} - z \sqrt{\frac{T}{\Delta E}}\right) - \Phi\left(\sqrt{\frac{\Delta E}{T}} - \sqrt{\frac{T}{\Delta E}} z\right) \right]^{-1} \quad (3.7)$$

where  $\Phi$  is the error function and  $z = 1/2(\delta_{vv} + E_1/T_1)$ .

Proceeding on the basis of Eqs. (3.5)–(3.7) it is possible to clarify the nature of the behavior of  $K_d$  as a function of  $W_{10}$  in Fig. 2 within the region  $T_1/E_1 < 1$ . For example, if for a regime (3.3), (3.6)

within the region  $T_1/E_1 < 1$  harmonic and anharmonic models yield identical values for  $K_d$  as a function of  $W_{10}$  [cf. Eq. (3.3)], when  $T_1/E_1 > 1$ , these values will begin to differ. This is caused by the appearance in the expression for  $K_d$  of factors containing the parameter  $E_1/T_1$  and by the difference in  $T_1$  for the two models.

4. We now consider dissociation of molecules at high optical pumping ( $W_{10}, W_{k0} \gg Q_{10}$ ). In this case, a saturation regime is attained, and the values of  $K_d$  and  $T_1$  become independent of optical pumping intensity. Physically, this is due to the presence of a "narrow site" for energy input to a vibrational degree of freedom. The maximum energy input rate is determined by its concentration rate at all vibrational levels, i.e., by exchange probability. In the saturation regime, the limiting values  $K_d^{\max}$  and  $T_1^{\max}$  for this anharmonic model and the most often encountered case  $T_1^{\max} > E_1$  can be found using the method similar to a previous method [7, 8]. We present some final results. If dissociation does not affect the limiting margin of the vibrational quanta,  $K_d^{\max}$  will be determined from Eq. (3.1) and  $T_1^{\max}$  from the relationship

$$\frac{T_1^{\max}}{E_1} = \left( C_k \frac{Q_{10}}{P_{10}} \right)^{1/2} \left[ \frac{E_1/T_1^{\max} - \delta_{vt}}{E_1/T_1^{\max} - \delta_{vv}} \right] \quad (4.1)$$

where  $C_k = k^2 \sum_{i=1}^k i^{-1}$  for multiquantum pumping and  $C_k = k(k+1)/2$  for cascaded pumping. In the other limiting case, namely when vibrational energy lost from the system is caused by dissociation, we have

$$K_d^{\max} \approx Q_{10} \frac{C_k}{m} \frac{(E_1/T_1^{\max})^3}{(E_1/T_1^{\max} - \delta_{vv})^2}, \quad \frac{T_1^{\max}}{E_1} \approx \left( \frac{C_k}{m} f_m \right)^{1/2} \quad (4.2)$$

It is of interest to analyze, besides the dissociation kinetics treated above for the model of blocking anharmonic oscillators possessing a small deviation from equilibrium (condition (1.9)), the case of a strong deviation from equilibrium, as well as to investigate nonequilibrium dissociation of diatomic molecules when their transition in the continuous spectrum occurs from the boundary levels, i.e., from levels whose population is substantially affected by  $v$ - $t$  processes. In the latter case, the distribution function and the dissociation rate can be found by the technique we have considered. If vibrational energy dissipation is caused by dissociation, the constant  $K_d$  can be estimated to within a factor on the order of 2–3 from the equations [including Eqs. (3.3), (3.6), and (4.2)] for any deviation from equilibrium and for any model when  $k = 1$ . In the case of weak ( $W_{10} \ll Q_{10}$ ) and strong ( $W_{10} \gg Q_{10}$ ) optical pumping, we find, respectively

$$K_d \approx \begin{cases} \frac{h\nu}{D} W_{10} \\ \frac{h\nu}{D} Q_{10} \end{cases}$$

Here,  $D$  is the dissociation energy of a molecule and  $\nu$  is the frequency of the emission absorbed. Such a form for  $K_d$  is due to the fact that it weakly depends on the form of the vibrational distribution function and, in actual practice, can be estimated by equating the energy flows, namely, the translational flow as a function of emission and the dissociation flow [cf. Eq. (1.4)], under the indicated regime of the vibrational energy balance. Such a regime of nonequilibrium dissociation of diatomic anharmonic molecules has been previously analyzed [11].

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