Kinetics of nonequilibrium dissociation of molecules in cascade excitation of oscillations by laser radiation

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The possibility of a controlled action of laser raidation on the rate of chemical reactions is studied in the particular case of molecular dissociation. Heating of a fixed vibrational mode in a molecular gas by laser radiation is theoretically investigated for a harmonic oscillator with allowance for vibrational-vibrational and vibrational-translational energy exchange, and also by taking into account the dissociation reaction. The rate of nonequilibrium dissociation as a function for power is calculated in a broad range of laser pumping power. The dissociation kinetics in the presence of two laser sources is also studied (radiation from the first laser transfers the molecule from the ground state to a vibrationally excited state, and radiation of the second laser transfers the molecule from a discrete vibrational state to a continuum).

The development of laser technology has opened up new possibilities in the control of chemical reactions. The most promising approach is to activate the molecules by selectively increasing the energy of some of the vibrational degrees of freedom through the absorption of laser radiation. A number of interesting experimental results have now been obtained in this field.[1-6] Theoretical analyses of resonance processes in the effect of electromagnetic radiation on molecular vibration and molecular dissociation under nonequilibrium conditions were reported in[7-11]. Nevertheless, a systematic analysis of such processes, which would take into account the combined effect of various factors, has not as yet been reported.

The aim of the present work was to provide a detailed analysis of the vibrational kinetics and nonequilibrium dissociation of molecules exposed to one or two laser beams. Since our aim has also been to elucidate the basic effect of different factors affecting the above processes, we have used the truncated harmonic oscillator model in our calculations. This model can provide quantitative results when the molecular dissociation proceeds from vibrational levels which are not too high so that the anharmonicity is still small.

1. BASIC EQUATIONS

We shall use the following model to describe the nonequilibrium dissociation of molecules in the presence of laser radiation:

(a) The molecules can be represented by truncated harmonic oscillators.

(b) The absorption of monochromatic radiation of frequency ν is accompanied by the cascade transitions $i - 1 \rightleftarrows i$, $i = 1, 2, \ldots, k$, where i is the vibrational quantum number.

(c) Vibrational relaxation in the system is due to single-quantum vibrational-vibrational exchange (v-v processes) and single-quantum vibrational-translational exchange of energy (v-t processes).

(d) Rotational relaxation is not considered and it is assumed that it has ended, i.e., we analyze the behavior of the molecular system within time intervals longer than the characteristic times for rotational relaxation, τ_{rot}/q, where q is the fraction of molecules occupying the rotational state.

(e) Molecular dissociation during collisions with the gas particles occurs from the limiting vibrational level m (the collisional dissociation channel).

(f) Absorption of radiation of frequency ν_1 may transfer the molecule from the vibrational level $l > k$ to the continuum (photodissociation channel).

To find the rate of nonequilibrium dissociation as a function of the various parameters of the adopted model, we must, in general, solve simultaneously the equations describing vibrational kinetics and the population of the vibrational levels, as well as the heat transfer equation that describes the gas temperature. However, in the ensuing analysis we shall be largely interested in the possibility of producing nonequilibrium dissociation over a time interval shorter than the time necessary for the transfer of energy from vibrational to translational degrees of freedom. In this case the gas is not heated, and its temperature can be looked upon as an independent and time-invariant parameter governing the probability of collisional transitions in the gas-kinetic equations for the populations of the vibrational states. Subject to assumptions (b)—(f), the system of equations can be written in the form

$$\begin{aligned}\frac{dx_i}{dt} &= (1-\delta_{ik})W_{i+1,i}x_{i+1} - [(1-\delta_{ik})W_{i,i+1} + W_{i,i-1}]x_i \\ &\quad + W_{i-1,i}x_{i-1} + T(x_i) + V(x_i), \qquad i = 0, 1, \ldots, k; \qquad (1.1) \\ \frac{dx_i}{dt} &= T(x_i) + V(x_i) - \mathscr{V}\delta_{im} - W_{ld}\delta_{il}x_i, \qquad i = k+1, \quad k+2, \ldots, m.\end{aligned}$$

In these expressions x_i is the density of molecules occupying the vibrational level i, $W_{i,i\pm 1}$ is the probability of the $i \rightarrow i \pm 1$ transition initiated by the laser beam of frequency ν, W_{ld} is the probability of dissociation of a molecule from the level l by radiation of frequency ν_1, and δ_{pq} is the Kronecker symbol. The quantity $\mathscr{V}$ is the rate of decay of molecules due to collisions with the gas particles:

$$\mathscr{V} = NK_d - P_{dm}x_d^2, \qquad (1.2)$$

where $K_d = P_{md}x_m/N$ is the rate constant for collisional dissociation, P_{md} and P_{dm} are the probabilities of transition from the limiting level m to the continuum and vice versa during double and triple collisions, respectively, per unit time, x_d is the density of atoms forming during the decay of the molecules, and N is the density of the molecules.

The operators $T(x_i)$ and $V(x_i)$ in Eq. (1.1) describe the change in the populations x_i due to v-t and v-v processes and assume the following form in the truncated harmonic oscillator model:[12]

$$T(x_i) = P_{10}\{(i+1)x_{i+1} - [(i+1)\exp(-\Theta_T) + i]x_i + ix_{i-1}\exp(-\Theta_T)\},$$
$$V(x_i) = Q_{10}^{01}\{(i+1)(1+\alpha)x_{i+1} - [(i+1)\alpha + i(1+\alpha)]x_i + i\alpha x_{i-1}\}. \tag{1.3}$$

In these expressions P_{10} and Q_{10}^{01} are the probabilities per unit time of transitions between vibrational levels due to vibrational-translational and vibrational-vibrational energy exchange, α is the number of quanta per molecule, i.e.,

$$\alpha = \frac{1}{N}\sum_{i=0}^{m} ix_i, \quad N = \sum_{i=0}^{m} x_i; \quad \Theta_T = \frac{h\nu}{kT},$$

ν is the frequency of the oscillator, and T is the gas temperature.

Multiplying Eq. (1.1) by i and summing over all i on the assumption that $W_{i,i-1} = iW_{10}$, $W_{10} = W_{01}$, we obtain

$$\frac{d\alpha}{dt} = -\frac{\alpha - \alpha_T}{\tau_{vt}} - (m-\alpha)K_d - (l-\alpha)K_{pd} + \frac{W_{10}}{N}\left(-kx_k + \sum_{i=0}^{k-1} x_i\right), \tag{1.4}$$

where $K_{pd} = W_{ld}x_l/N$ is the photodissociation rate constant, $\alpha_T = \exp(-\Theta_T)/[1 - \exp(-\Theta_T)]$, and $\tau_{vt} = [P_{10}(1 - \exp(-\Theta_T)]^{-1}$.

In final analysis, the aim of this work is to use Eqs. (1.1) and (1.4) to determine the rate of dissociation as a function of the laser beam intensity (or the probabilities W_{10} and W_{ld}). In the ensuing analysis the laser pulses will be assumed to be rectangular with lengths much greater than the collision and photodissociation times $\tau_d \sim 1/K_d$ and $\tau_{pd} \sim N/W_{ld}x_l$. This means that those terms in Eqs. (1.1) and (1.6) which describe transitions between levels under the action of the laser radiation are not zero in the time interval in which we are interested.

To obtain the analytic solution of Eqs. (1.1) and (1.4), we consider the case where the characteristic time $\tau_\alpha \approx \alpha/|d\alpha/dt|$ is such that

$$\tau_\alpha \ll \tau_d, \tau_{pd}. \tag{1.5}$$

Since it follows from Eq. (1.4) that

$$\tau_\alpha \sim \min\left[\tau_{vt}; \ \frac{\alpha}{m}\frac{1}{K_d}; \ \frac{\alpha}{l}\frac{1}{K_{pd}}\right],$$

and, moreover, we usually have $\alpha \ll m$ and $\alpha \ll l$, the inequality (1.5) is, in fact, satisfied in many cases that are of interest in practice. The only exception is fast photodissociation from the lowest vibrational levels (when l is small) and strong (with probability $W_{10} \gg Q_{10}, P_{10}$) stepwise optical excitation to high vibrational levels $k \sim m$. Under these conditions α/m or α/l will be approximately equal to unity, and it may turn out that $\tau_\alpha \sim \tau_d, \tau_{pd}$.

2. GENERAL EXPRESSIONS FOR THE RATE OF DISSOCIATION

When Eq. (1.5) is satisfied in the most interesting time interval Δt for the analysis of the dissociation process, i.e., $\tau_\alpha \ll \Delta t \ll \tau_d, \tau_{pd}$, the solution of Eqs. (1.1) and (1.4) can be sought in the form

$$x_i(t) = N(t)y_i(\alpha), \quad \sum_{i=0}^{m} y_i = 1. \tag{2.1}$$

The validity of this equation can be justified physically as follows. It follows from Eqs. (1.4) and (1.5) that after a time $t \gtrsim \tau_\alpha$ following the introduction of the laser beam the vibrational levels follow the distribution $x_i(t)$ which is determined by the instantaneous pumping rate (i.e., W_{10}), the instantaneous rate of vibrational relaxation (i.e., Q_{10} or P_{10}) and the rate of dissociation (i.e., K_d or K_{pd}). If these rates vary sufficiently slowly [in accordance with Eq. (1.5)], we have a quasi-stationary but nonequilibrium distribution $x_i(t)$ with a constant stock α of vibrational quanta, whose time dependence is determined only by the change in the total number of molecules. In other words, Eq. (2.1) can be regarded as the zero-order approximation in the expansion of $x_i(t)$ into a series in terms of the parameter $\tau_\alpha/\tau_d(\tau_\alpha/\tau_{pd})$.

Substituting Eq. (2.1) in Eq. (1.1), neglecting recombinations, and remembering that

$$\frac{dx_i}{dt} = \frac{dN}{dt}y_i, \quad \frac{dN}{dt} = -(K_d + K_{pd})N,$$

we have, after summing Eq. (1.1) between i = 0 and i = j, the relations between y_{j+1} and y_j which contain the sums

$$\sum_{i=0}^{j} y_i.$$

Assuming that $\sum_{i=0}^{j} y_i \approx 1$ [which, according to Eq. (2.1), is well satisfied at least for large j], and summing these relations between j = 0 and j = n − 1, we obtain

$$y_n = F^n y_0 - \frac{(K_d + K_{pd})}{B + W_{10}}\sum_{j=1}^{n}\frac{F^{n-j}}{j}, \quad 1 \leqslant n \leqslant k,$$
$$y_n = \exp\{-(n-k)\Theta_v\}\,y_k - \frac{(K_d + K_{pd})}{B}\sum_{j=k+1}^{n}\frac{\exp\{-(n-j)\Theta_v\}}{j}, \quad k+1 \leqslant n \leqslant l, \tag{2.2}$$
$$y_n = \exp\{-(n-l)\Theta_v\}\,y_l - \frac{K_d}{B}\sum_{j=l+1}^{n}\frac{\exp[-(n-j)\Theta_v]}{j}, \quad l+1 \leqslant n \leqslant m.$$

Here and henceforth we have

$$B = P_{10} + (1+\alpha)Q_{10},$$
$$F = \frac{P_{10}\exp(-\Theta_T) + \alpha Q_{10} + W_{10}}{P_{10} + (1+\alpha)Q_{10} + W_{10}}, \quad \exp(-\Theta_v) = \frac{P_{10}\exp(-\Theta_T) + \alpha Q_{10}}{P_{10} + (1+\alpha)Q_{10}} \tag{2.3}$$

The quantity y_0 in Eq. (2.2) is given by the normalization condition in Eq. (2.1).

Equation (2.2), subject to the assumptions given by Eqs. (1.5) and (2.1), is the most general expression for the distribution over vibrational states in the dissociating gas with stepwise optical excitation. If we ignore the effect of dissociation on the distribution function Eq. (2.2) becomes identical with the expression reported in[7] in the special case k = 1.

We note that, even in the absence of dissociation, the distribution given by Eq. (2.2) is not, in general, of the Boltzmann type (when $W_{10}/Q_{10} \geq 1$, P_{10}/Q_{a0}). It follows from Eq. (2.2) that when $K_d + K_{pd} = 0$, $W_{10} > Q_{10}$, P_{10}, and $F \neq \exp(-\Theta_v)$ we have a Boltzmann distribution with a vibrational temperature $h\nu/k\Theta_v$ only for n > k. Physically, this means that, in this case, the v-v and v-t processes do not succeed in transforming the distribution function into the Boltzmann form, and optical excitation has a substantial effect on this function even for the low-lying levels which provide the main contribution to the vibrational energy.

We must now determine the constants K_d and K_{pd} which represent the rate of dissociation. If we determine y_l and y_m from Eq. (2.2), and recall that $K_d = P_{md}y_m$ and $K_{pd} = W_{ld}y_l$, we have

$$K_d = P_{md}y_0\, e^{-m\Theta_v}\left\{F^k e^{k\Theta_v} - \frac{K_{pd}}{y_0 B}\left[\frac{B}{B+W_{10}} e^{k\Theta_v}\sum_{i=1}^{k}\frac{F^{k-i}}{i} + \sum_{i=k+1}^{l}\frac{e^{i\Theta_v}}{i}\right]\right\}$$

$$\times\left\{1 + e^{-m\Theta_v}\frac{P_{md}}{B}\left[\frac{Be^{k\Theta_v}}{B+W_{10}}\sum_{i=1}^{k}\frac{F^{k-i}}{i} + \sum_{i=k+1}^{m}\frac{e^{i\Theta_v}}{i}\right]\right\}^{-1}, \quad (2.4)$$

$$K_{pd} = W_{ld}y_0\, e^{-l\Theta_v}\left\{F^k e^{k\Theta_v} - \frac{K_d}{y_0 B}\left[\frac{Be^{k\Theta_v}}{B+W_{10}}\sum_{i=1}^{k}\frac{F^{k-i}}{i} + \sum_{i=k+1}^{l}\frac{e^{i\Theta_v}}{i}\right]\right\}$$

$$\times\left\{1 + e^{-l\Theta_v}\frac{W_{ld}}{B}\left[\frac{Be^{k\Theta_v}}{B+W_{10}}\sum_{i=1}^{k}\frac{F^{k-i}}{i} + \sum_{i=k+1}^{l}\frac{e^{i\Theta_v}}{i}\right]\right\}^{-1}. \quad (2.5)$$

Equations (2.4) and (2.5) together with Eq. (1.4) (for $d\alpha/dt = 0$) and Eq. (2.2) completely determine the rate of dissociation and the vibrational temperature $T_{vib} = h\nu/k\Theta_v$ (or the quantity α which is uniquely determined by it) as functions of the probabilities of stepwise optical excitation W_{10} and photodissociation W_{ld}, respectively. The terms in denominators in Eqs. (2.4) and (2.5) determine the reduction in the corresponding rate of dissociation due to the distortion of the distribution function by the dissociation process, and the second term in the numerators describes the distortion due to dissociation along the other channel. When $K_{pd} = 0$ and $W_{10} = 0$, Eq. (2.4) becomes identical with the expression obtained earlier in[13].

We shall now use the above general expressions to consider a number of special cases.

3. COLLISIONAL DISSOCIATION OF MOLECULES. NUMERICAL CALCULATIONS

Let us now analyze the rate of collisional dissociation K_d as a function of the optical pumping probability W_{10} when there is no photodissociation, i.e., $K_{pd} = 0$ in Eqs. (1.4) and (2.4). Since, in practically all cases,

$$P_{md} \gg B = P_{10} + (1+\alpha)Q_{10},$$

we can neglect the unity in the denominator of Eq. (2.4). Subject to the above simplifications, and assuming that $\exp(-\Theta_T) \ll 1$, the simultaneous numerical solution of Eqs. (1.4), (2.2), (2.4) yields K_d and T_{vib} as a function of the pumping probability W_{10}.

The characteristic dimensionless parameters that determine the nonequilibrium state of the dissociating gas are K_d/P_{10}, $\Theta_v = h\nu/kT_{vib}$, W_{10}/P_{10}, Q_{10}/P_{10}, m and k, which is clear from Eqs. (1.4), (2.2)–(2.5). The results of calculations of T_{vib} and K_d/P_{10} as functions of the dimensionless probability of optical excitation W_{10}/P_{10} when k = 1 are shown in Figs. 1 and 2 for different values of Q_{10}/P_{10} and m. It is clear from these figures that the vibrational temperature T_{vib} and the dissociation rate constant K_d increase monotonically with increasing pump intensity up to certain limiting values $T_{vib}^{(max)}$ and $K_d^{(max)}$. This type of saturation was mentioned in[7,8].

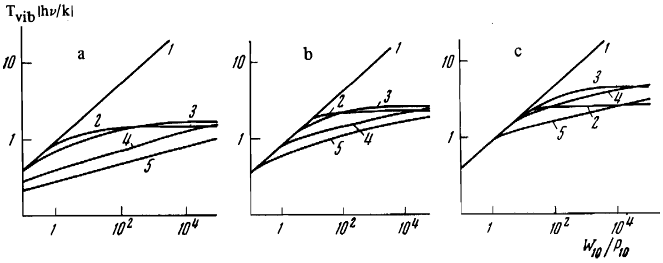

FIG. 1. Vibration temperature T_{vib} as a function of the dimensionless optical pumping probability W_{10}/P_{10}. Curve 1—taken from [7]; curves 2, 3, 4, 5 correspond to Q_{10}/P_{10} = 10, 10^2, 10^4, 10^6. The values of m in Figs 1a, 1b, and 1c are 5, 15, and 40, respectively.

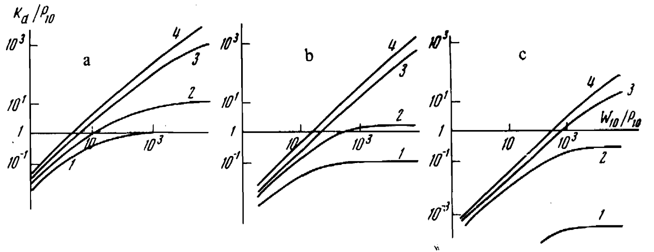

FIG. 2. Dimensionless dissociation rate K_d/P_{10} as a function of the dimensionless optical pumping probability W_{10}/P_{10}. Curves 1, 2, 3, and 4 correspond to Q_{10}/P_{10} = 10, 10^2, 10^4, and 10^6. The values of m in Figs. 1a, 1b, and 1c are 5, 15, and 40, respectively.

It is clear from Fig. 1 that the vibrational temperatures under saturation conditions are usually much higher than the characteristic values, and the probabilities W_{10} of optical excitation necessary for reaching this state are $\sim(1+\alpha)Q_{10}$ and can be very high. The corresponding laser intensities are also very high. For example, when $\alpha \approx 3$ and the molecular parameters assume typical values ($Q_{10} \approx 10^5\ \text{sec}^{-1}\cdot\text{Torr}^{-1}$, absorption linewidth $\Delta\nu \approx 5\times10^6\ \text{sec}^{-1}\cdot\text{Torr}^{-1}$, spontaneous radiative transition probability $A_{10} \approx 1\ \text{sec}^{-1}$, fraction of molecules in the vibrational level participating in absorption $q \approx 10^{-2}$), the CO_2 laser intensity ($\nu = 10^3\ \text{cm}^{-1}$) which is necessary for saturation is about $300\ p^2\ \text{W/cm}^2\cdot\text{Torr}^2$, where p is the gas pressure in Torr [see Eq. (4.7) below].

The most interesting practical case from the standpoint of laser control led dissociation is the state when dissociation occurs in a time $\sim\tau_{vt} \approx 1/P_{10}$, since the activation of molecules is then produced only by the selective increase in the energy of vibrational degrees of freedom which absorbs the radiation.1) On the other hand there will be no nonselective activation due to the heating of the gas. It follows from Fig. 2 that when $Q_{10}/P_{10} \gtrsim 10^2$ it is possible to reach $K_d/P_{10} \approx \tau_{vt}/\tau_d \approx 1$ without reaching saturation. This, of course, substantially reduces the requirements imposed on W_{10} and, consequently, on the intensity of the exciting laser. Thus, for the above molecular parameters and absorption of CO_2 laser radiation with k = 1, m = 5, 15, 40, the value of $K_d/P_{10} \approx 1$ is reached for intensities $3\times10^{-4}p^2$, $2\times10^{-3}p^2$, $2\times10^{-2}p^2$ (when $Q_{10}/P_{10} = 10^6$), and $3.5\times10^{-2}p^2$, $4\times10^{-1}p^2$, $4p^2\ \text{W/cm}^2\cdot\text{Torr}^2$ (when $Q_{10}/P_{10} = 10^4$), respectively. We note that k = m, m = 40 correspond to the BCl_3 molecule. If, however, $Q_{10}/P_{10} < 10^2$, it follows from Fig. 2 that $K_d/P_{10} \lesssim 1$ even in the case of saturation. This means that the selective increase in the vibrational energy is impeded.

A simple analytic dependence of the rate of dissociation and vibrational temperature on the probability of optical pumping can be obtained by considering weak ($W_{10} \ll Q_{10} + P_{10}$) and strong ($W_{10} \gg Q_{10} + P_{10}$) pumping. Let us consider these cases in detail.

4. DISSOCIATION FOR WEAK OPTICAL PUMPING ($W_{10} \leqslant Q_{10} + P_{10}$)

Here, $F = \exp(-\Theta_V)$, $y_0 = 1 - \exp(-\Theta_V)$, and from Eq. (2.4) we have the simple expression

$$K_d = [Q_{10} + P_{10}(1 - \exp(-\Theta_T))]f^{-1}(m), \tag{4.1}$$

where

$$f(m) = \sum_{i=1}^{m} \frac{\exp(i\Theta_v)}{i}.$$

The relation which gives Θ_V as a function of W_{10} is obtained by substituting Eqs. (2.2), (4.1), and (2.3) in Eq. (1.4).

It follows from Eq. (2.3) that, when the molecular gas under investigation is a small impurity, i.e., when $Q_{10} \ll P_{10} \exp(-\Theta_T)$, we find that Θ_V breaks away from Θ_T, i.e., the selective increase in the energy of the vibrational mode is not possible. We shall therefore consider henceforth that the impurity gas which absorbs the laser radiation is not very diluted, so that $Q_{10} \gg P_{10}$. Assuming in addition that

$$e^{-\Theta_T} \ll 1, \quad e^{-\Theta_T} \ll e^{-\Theta_v}, \quad e^{-m\Theta_v} \ll 1,$$

we find from Eqs. (1.4), (2.2), (2.3), and (4.1) that the relation between Θ_V and W_{10} is

$$\frac{W_{10}}{P_{10}}[1 - (k+1)\exp\{-k\Theta_v\} + k\exp\{-(k+1)\Theta_v\}] \approx \frac{\exp\{-\Theta_v\} + m(1 - \exp\{-\Theta_v\})Q_{10}f^{-1}(m)/P_{10}}{1 - \exp\{-\Theta_v\}}. \tag{4.2}$$

If we neglect the second term in the numerator on the right-hand side of Eq. (4.2) for k = 1, this expression becomes identical with that given in[7] which determines the vibrational temperature in the case when the dissipation of vibrational energy is due to v-t processes alone. The second term on the right-hand side of Eq. (4.2), on the other hand, additionally takes into account the change in the vibrational energy due to the dissociation of highly excited molecules. In many cases, this mechanism of energy dissipation may be substantial and may appreciably reduce the vibrational temperature, thus slowing down the increase in the rate of dissociation with increasing rate of pumping.

For low and high vibrational temperatures, Eqs. (4.1) and (4.2) can be further simplified and yield an explicit expression for K_d as a function of W_{10}. Thus, for small vibrational temperatures ($\exp\{-\Theta_V\} \ll 1$), when the dissociation does not affect the vibrational temperature, we have

$$K_d = Q_{10}m\left(\frac{W_{10}}{m}\right)^m, \quad \Theta_v = \ln\left(\frac{P_{10}}{W_{10}}\right) \gg 1. \tag{4.3}$$

If we can neglect v-t processes and assume that the loss of vibrational energy from the system is due to dissociation alone, we obtain

$$K_d = \frac{W_{10}}{m}, \quad \Theta_v = \frac{1}{m}\ln\left(\frac{m^2 Q_{10}}{W_{10}}\right) \gg 1. \tag{4.4}$$

We note that Eqs. (4.3) and (4.4) do not include k. Physically, this means that when $\Theta_V \gg 1$ the low populations of the excited states ensure that the only transition which participates effectively in optical pumping is 0 → 1.

The situation is different at high vibrational temperatures, when $\Theta_V \ll 1$, The value of Θ_V and, consequently, of K_d will then, in general, depend on k. A simple relationship between K_d and W_{10} can be obtained here for the case when k is relatively small (so that $k\Theta_V \ll 1$) and when k is large ($k\Theta_V \gg 1$). Thus, if the relaxation of vibrational energy is determined exclusively by v-t processes, then for $\Theta_V \ll 1$ we can replace Eq. (4.3) by

$$K_d = mQ_{10}\left[\frac{2P_{10}}{k(k+1)W_{10}}\right]^{1/3} \exp\left[-m\left(\frac{2P_{10}}{k(k+1)W_{10}}\right)^{1/3}\right],$$
$$\Theta_v = \left(\frac{2P_{10}}{k(k+1)W_{10}}\right)^{1/3} \ll 1, \quad k\Theta_v \ll 1, \tag{4.5a}$$

$$K_d = mQ_{10}\frac{P_{10}}{W_{10}}\exp\left(-m\frac{P_{10}}{W_{10}}\right), \quad \Theta_v = \frac{P_{10}}{W_{10}} \ll 1, \quad k\Theta_v \gg 1. \tag{4.5b}$$

If, on the other hand, the dissipation of vibrational energy is determined exclusively by dissociation, then

$$K_d = \frac{k(k+1)}{2m}\Theta_v^2 W_{10}, \quad \frac{1}{\Theta_v}e^{-m\Theta_v} = \frac{k(k+1)}{2m^2}\frac{W_{10}}{Q_{10}}, \quad k\Theta_v \ll 1, \tag{4.6a}$$

$$K_d = \frac{W_{10}}{m}, \quad \Theta_v \exp\{-m\Theta_v\} = \frac{1}{m^2}\frac{W_{10}}{Q_{10}}, \quad \Theta_v \ll 1, \quad k\Theta_v \gg 1. \tag{4.6b}$$

It follows from Eqs. (4.3)–(4.6) that the dependence of the rate of nonequilibrium dissociation on the probability of optical excitation (and, consequently, on the intensity of the exciting radiation) has a different character under different conditions. A particularly strong nonlinear dependence occurs when the dissipation of the vibrational energy is determined exclusively by the v-t processes [Eqs. (4.3) and (4.5)]. It is also clear from Eq. (4.5) that, at high vibrational temperatures, optical cascade transitions between excited states (k > 1) may substantially increase the rate of dissociation. We note that in the case of stepwise excitation to high levels $k\Theta_V \gg 1$, the quantities Θ_V and K_d no longer depend on k [Eqs. (4.5b) and (4.6b)]. However, this method of excitation is difficult to realize in practice because the anharmonicity of the molecules ensures that there is a difference between the laser radiation frequency and the vibrational frequency of the molecules which increases with increasing level number and eventually leads to a reduction in the absorption cross section and hence in the probabilities $W_{n,n\pm1}$.

Equations (1.4) and (4.2)–(4.6) were obtained on the assumption that $W_{n,n-1} = nW_{10}$. This is satisfied by the harmonic oscillator when there is no saturation over the vibrational states and the rotational distribution function is of the Boltzmann form. The probability W_{10} is then proportional to the intensity I of the absorbed laser radiation and is given by

$$W_{10}\left[\frac{1}{\text{sec}}\right] = \frac{1}{h\nu}\sigma_{10}I \equiv \frac{qI}{1.4 \cdot 10^{-21}\Delta\nu A_{10}\nu^3}. \tag{4.7}$$

In this expression σ_{10} is the absorption cross section for the 0 → 1 transition, A_{10} is the spontaneous radiative probability of the vibrational transition 1 → 0 in sec^{-1}, $\Delta\nu$ is the absorption linewidth in sec^{-1}, q is the fraction of molecules occupying the vibrational level which absorbs the radiation, ν is in cm^{-1}, and I in W/cm^2.

Thus, in the absence of saturation over the vibrational levels, we can obtain the rate of dissociation and vibrational temperature as functions of I in the case of low rate of pumping by substituting Eq. (4.7) in Eqs. (4.2)–(4.6).

However, Letokhov and Makarov[11] have shown that, in the general case,

$$W_{10}=\frac{\sigma_{10}}{h\nu}I\Big/\left(\frac{2\sigma_{10}I}{h\nu qW_{\mathrm{rot}}}+1\right), \tag{4.8}$$

where W_{rot} is the probability of rotational relaxation. It follows from Eq. (4.8) that in the case of saturation over the vibrational levels which is reached when $\sigma_{10}I/h\nu > \frac{1}{2}qW_{\mathrm{rot}}$, the probability W_{10} becomes independent of J and reaches its maximum value $W_{10}^{\max} = \frac{1}{2}qW_{\mathrm{rot}}$. A similar situation occurs for vibrational-rotational transitions between the upper vibrational levels. Since W_{rot} is practically independent of the number of the vibrational level, we have, in this case, $W_{n,n-1} = W_{10}^{\max}$. Hence, to explain the role of cascade excitation in the case of saturation over the vibrational levels, we must modify the formulas given by Eqs. (1.4) and (4.2)–(4.6).

It is readily seen that the last term on the right-hand side of Eq. (1.4) is then of the form $\frac{1}{2}qW_{\mathrm{rot}}(y_0 - y_k)$, and W_{10} and the factor in square brackets on the left-hand side of Eq. (4.2) are, respectively, replaced by $\frac{1}{2}qW_{\mathrm{rot}}$ and $(1 - \exp\{-\Theta_v\})(1 - \exp\{-k\Theta_v\})$. If, at the same time, $\Theta_v \gg 1$, the formulas for K_d and Θ_v are again given by Eqs. (4.3) and (4.4) with W_{10} replaced by $\frac{1}{2}qW_{\mathrm{rot}}$. If, on the other hand, the vibrational temperatures are high, then instead of Eqs. (4.5) and (4.6) we have

$$\Theta_v=\left(\frac{2P_{10}}{kqW_{\mathrm{rot}}}\right)^{1/3}\ll 1,\qquad k\Theta_v\ll 1, \tag{4.9a}$$

$$\Theta_v=\left(\frac{2P_{10}}{qW_{\mathrm{rot}}}\right)^{1/2}\ll 1,\qquad k\Theta_v\gg 1, \tag{4.9b}$$

$$\frac{1}{\Theta_v}e^{-m\Theta_v}=\frac{kqW_{\mathrm{rot}}}{2m^2Q_{10}},\qquad \Theta_v\ll 1,\quad k\Theta_v\ll 1, \tag{4.10a}$$

$$\Theta_v=\frac{1}{m}\ln\left(\frac{2m^2P_{10}}{qW_{\mathrm{rot}}}\right)\ll 1,\qquad k\Theta_v\gg 1. \tag{4.10b}$$

At the same time, the dissociation rate is given by the following formula which is obtained from Eq. (4.1):

$$K_d\simeq mQ_{10}\Theta_v\exp\{-m\Theta_v\}. \tag{4.11}$$

5. DISSOCIATION IN THE CASE OF STRONG OPTICAL PUMPING ($W_{10} \gg Q_{10} + P_{10}$)

Here, K_d and Θ_v are independent of W_{10}, i.e., saturation is reached.[8,9,14] Substituting $W_{10} \gg Q_{10} + P_{10}$ in Eqs. (2.2) and (2.3), and assuming that $k \ll m$, we obtain the following formulas from Eqs. (1.4) and (2.4) which determine K_d and Θ_v under these conditions:

$$\begin{gathered}
K_d^{max}\approx y_0(1+\alpha)Q_{10}e^{k\Theta_v}\left(\sum_{i=k+1}^{m}\frac{e^{i\Theta_v}}{i}\right)^{-1},\\
\frac{k(k+1)}{2}Q_{10}y_0=\frac{\alpha-\alpha_T}{\tau_{vt}}+(m-\alpha)K_d^{max},\\
y_0\approx[1-\exp(-\Theta_v)]\,/\,\{k[1-\exp(-\Theta_v)]+1\},\\
\alpha\approx y_0\left[\frac{k(k+1)}{2}+\frac{(k+1)\exp\{-(k+1)\Theta_v\}}{1-\exp(-\Theta_v)}+\frac{\exp\{-(k+2)\Theta_v\}}{(1-\exp\{-\Theta_v\})^2}\right].
\end{gathered} \tag{5.1}$$

It follows from Fig. 1 that, usually, $\Theta_v \ll 1$ under saturation conditions and Eq. (5.1) can be simplified further. If dissociation does not influence the store of vibrational quanta, then

$$K_d^{\max}\approx\frac{m}{k}(P_{10}Q_{10})^{1/2}\exp\left\{-\frac{m}{k}\left(\frac{P_{10}}{Q_{10}}\right)^{1/2}\right\}\quad \Theta_v^{\min}\approx\left(\frac{P_{10}}{Q_{10}}\frac{2}{k(k+1)}\right)^{1/2}. \tag{5.2}$$

When $k = 1$ the expression for $\Theta_v^{\min}$ in Eq. (5.2) is identical with that reported in[7]. We note that since $P_{10} \ll Q_{10}$ we have, in this case, $k\Theta_v \ll 1$. If, on the other hand, the loss of energy by the vibrational degrees of freedom is governed largely by dissociation, then

$$\begin{gathered}
K_d^{max}\approx\frac{k(k+1)}{2m^2}Q_{10}\ln\left[\frac{2m^2}{k(k+1)}\right],\\
\Theta_v^{min}\approx\frac{1}{m}\ln\left[\frac{2m^2}{k(k+1)}\right],\qquad k\Theta_v\ll 1,\\
K_d^{max}\approx\frac{k}{m}Q_{10},\quad \Theta_v^{min}\approx\frac{1}{m}\ln\left[\frac{m^2\Theta_v(3+k)}{k(k+1)}\right],\qquad k\Theta_v\gg 1.
\end{gathered} \tag{5.3}$$

Comparison of Eqs. (5.2) and (5.3) (for $k\Theta_v \ll 1$) shows that the v-t processes begin to have an important influence on the limiting rate of dissociation when

$$\frac{P_{10}}{Q_{10}}\gtrsim\frac{k(k+1)}{2m^2}\ln^2\frac{2m^2}{k(k+1)}. \tag{5.4}$$

When this condition is satisfied, $K_d^{\max}/P_{10} \lesssim 1/\Theta_v m < 1$ and, consequently, the gas may become heated in the course of dissociation due to v-t processes. For a typical value $m \approx 30$, $k = 1$, the left-hand side of Eq. (5.4) amounts to about 20.

We note that when $k\Theta_v \ll 1$, the expression given by Eqs. (5.2) and (5.3) can be obtained from Eqs. (4.5) and (4.6) for a low rate of pumping by replacing W_{10} with Q_{10}/Θ_v in the last two equations. This can be interpreted physically as the addition of energy to the vibrational degree of freedom through a "small window" which is determined by the rate of distribution of the energy pumped in over the entire vibrational spectrum, i.e., by the exchange probability Q_{10}. It is readily shown that when $k\Theta_v \ll 1$ and the rate of pumping is arbitrary, the left-hand sides of Eqs. (4.2) and (5.1), which determine the energy flux into the vibrational degree of freedom can be written in the form

$$\frac{k(k+1)}{2}\Theta_v^2\frac{W_{10}}{1+\Theta_vW_{10}/Q_{10}}.$$

The dependence of K_d on Θ_v, on the other hand, is always given by Eq. (4.11).

6. PHOTODISSOCIATION OF VIBRATIONALLY EXCITED MOLECULES

We must now analyze the case when the excitation of molecular vibrations is produced by a laser beam with a single wavelength, while dissociation from the vibrationally excited levels is produced by a light source with a different wavelength. For the sake of simplicity, we shall suppose that photodissociation is the leading process resulting in decay of the molecules. This is typical for the nonequilibrium dissociation of diatomic molecules since, in this case, the rate of collisional dissociation from the limiting level is always low at low gas temperatures. This is connected with the fact that, for a large store of vibrational energy, the anharmonicity of the upper levels ensures that the v-t processes predominate and the relative populations are determined by the gas temperature T, so that at relatively low T they will fall rapidly as one approaches the limiting level m from which collisional dissociation is possible.[10] Therefore, to achieve effective dissociation of such molecules, these molecules must be taken into the continuum directly from relatively low-lying levels, where a high population can be produced at low gas temperatures. The transition of the molecules from the excited state to the continuum, on the other hand, can be produced by an optical method. Ambartsumyan and Letokhov[6] have investigated experimentally the dissociation of HCl molecules under the action of two optical sources, while the laser power necessary for this has been estimated by Karlov, Konev, and Prokhorov.[9]

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The rate of dissociation as a function of the intensities of the two sources can be determined from Eqs. (1.4) and (2.5) by substituting $K_d = 0$. When the unity in the numerator of Eq. (2.5) can be neglected, the expressions for K_{pd} will be identical with the formulas for the rate of collisional dissociation given by Eqs. (4.1)–(4.6), (4.9)–(4.11), and (5.1)–(5.4) (with m replaced by l). The rate of photodissociation then turns out to be independent of W_{ld}. Physically, this means that the saturation state is due to the fact that at high intensities of the source of dissociation, the rapid departure of molecules from the level l to the continuum ensures that the population of this level is much less than the equilibrium value, and the overall rate of photodissociation K_{pd} is determined not by the rate of loss of molecules into the continuum from the level l under the action of the radiation, but the rate of increase in the number of such molecules due to v-v processes. The intensity at which the above saturation state is reached is given by

$$\frac{W_{ld}\exp\{-l\Theta_v\}}{(1+\alpha)Q_{10}}f(l)\approx\frac{W_{ld}}{lQ_{10}}\gtrsim 1.$$

If, on the other hand, $W_{ld} < lQ_{10}$, the rate of photodissociation is a linear function of W_{ld}. The relation between the intensities of the two sources for which effective photodissociation can be produced without an appreciable increase in the translational energy can be obtained from Eq. (2.5) with $K_{pd}/P_{10} \approx 1$.

Figure 3 shows an example of such a calculation for $l = 5$. The axes $W_{ld}/Q_{10} \approx l$ and $W_{10}/Q_{10} \approx 1 + \alpha$ define the range of intensities of the optical sources for which saturation sets in, i.e., the rate of photodissociation is independent of the source intensity. The curves which depend on the parameter Q_{10}/P_{10} correspond to intensities for which $K_{pd}/P_{10} \approx 1$ (curves 1, 2, 3, and 4 in Fig. 3 correspond to $Q_{10}/P_{10} = 10^3$, 10^4, 10^5, and 10^6). The regions bounded by these curves and the two axes will therefore give the probabilities W_{ld} and W_{10} and hence the intensities for which effective photodissociation with $K_{pd}/P_{10} > 1$ can be produced, and this rate can be controlled by the source intensity.

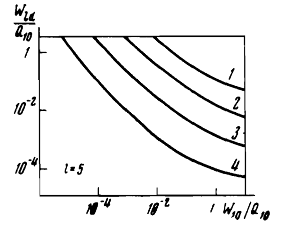

FIG. 3

We note in conclusion that the nonequilibrium dissociation during the absorption of radiation at a frequency which is a multiple of the oscillator frequency ($0 \rightleftarrows k$ transitions) is discussed in detail elsewhere.[14] Dissociation at high pumping rates, on the other hand, cascade excitation up to the limiting level m, and dissociation in the anharmonic oscillator model require separate analysis.

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[1] In the case of optical excitation of an individual vibrational mode of a polyatomic molecule, the quantity τ_{vt} must be interpreted as the characteristic relaxation time for the vibrational energy of this mode either through the v-t processes, or through vibrational exchange with other unexcited types of vibration (v-v′ processes).

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