Double Step-Ladder Model of Activation in the Processes of High-Temperature Dissociation of Polyatomic Molecules

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Abstract—A unified mechanism of the interaction of vibrational relaxation and dissociation of polyatomic molecules working in a wide temperature range (from 2000 to 10 000 K) is proposed, which is described by a double step-ladder model. Relaxation due to collisions with the transfer of small and large portions of energy is taken into account. The transfer efficiency of the portions of thermal energy in the high-temperature decomposition upon the collisions of CO_2 molecules with atomic and molecular partners is determined. The reaction rate constant of high-temperature dissociation of carbon dioxide is calculated. The data presented in the article suggest a new method for elucidating the mechanism of energy exchange in the absence of vibrational and translational equilibrium and at ultrahigh temperatures when the dissociation takes place during the time of several collisions.

INTRODUCTION

One of the most rapidly developing branches of chemical physics is the kinetics of high-temperature chemical reactions. Progress in this field is due to the development of new technologies, as well as to the interest in the processes in the planet atmospheres nearest to the Earth and relaxation processes in strong shock waves. However, energy exchange and chemical reactions at temperatures above ~10 000 K, which take place under nonequilibrium conditions, are poorly studied.

The main problem of the kinetics of high-temperature processes is the description of dissociation under the conditions of a strong difference between vibrational and translational temperatures, as well as determination of the activation mechanism under these conditions.

Experimental values of dissociation rate constants k_d at temperatures higher than $(1/17–1/20)D$ (where D is dissociation energy[1]) are lower than the values calculated according to equilibrium theories, such as the RRKM theory [2]. This discrepancy is due to the relation between vibrational relaxation and molecule dissociation. A number of two-temperature models are available for calculating the rate constants of the dissociation of diatomic molecules under vibrationally nonequilibrium conditions. Sergievskaya, Kovach, and Losev described these models most completely in their monograph [3]. However, this approach is not always suitable because it does not consider the mechanism of

vibrational relaxation and thus prevents experiment-independent determination of vibrational temperatures.

Zuev *et al.* [4] analyzed the mechanism of dissociation and reasons for a decrease in the rate of k_d growth at high temperatures and pointed to a change in the rate-determining step of vibrational relaxation. At a high temperature, k_d becomes dependent on vibrational relaxation at low levels. Kondrat'ev and Nikitin [5] suggested that, to calculate k_d adequately, it is necessary to take into account the contribution from multi-quantum transitions to the rate of vibrational relaxation at high temperatures. Thus, the mechanism for the interaction of vibrational relaxation with dissociation at a high temperature remains debatable.

It has been experimentally found that the values of rate constants of relaxation processes and, therefore, the values of rate constants of the dissociation of polyatomic molecules are very sensitive to a diluent gas [6, 7]. The efficiency of different buffer gases is characterized by an average portion of energy $\overline{\Delta E}$ that transfers to an active molecule in a collision with a diluent gas molecule:

$$\overline{\Delta E} = \int_0^\infty \Delta E p(E', E)\mathrm{d}E' / \int_0^\infty p(E', E)\mathrm{d}E, \qquad (1)$$

where $p(E, E')$ is the probability of the collisional transition of a molecule from the state with energy E to the state with energy $E' = E + \Delta E$, where ΔE has a dimension of temperature [1].

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[1] Henceforth, the value of D is expressed in kelvins as in Kuznetsov's monograph [1].

Many researchers analyzed the effective value of $\overline{\Delta E}$ in various systems and came to a conclusion that relatively weak collisions with $\overline{\Delta E} \leq \theta_{min}$ (where θ_{min} is a characteristic temperature of the minimal quantum of dissociating molecules) make the principal contribution to the activation of polyatomic molecules [6]. We refer to these collisions with the transfer of small portions of energy as small-step (SS) transitions. Moreover, until recently, it was common to assume that the solution to the master kinetic equation (MKE) is independent of the type of the function that describes the dependence of the transition probability $p(E, E')$ on energy [8]. This idea changed after the discovery of so-called supercollisions during which large portions of energy ($>5\overline{\Delta E}$) transfer. Supercollisions were found experimentally [9, 10] and in trajectory calculations [11]. Bernshtein et al. [12] showed that supercollisions may substantially affect the rates of chemical reactions. We suppose that the role of these collisions becomes more significant at a high temperature when kinetic energies of interacting particles (expressed in kelvins) are much higher than the vibrational temperatures of activated molecules.

Bernshtein et al. developed a new approach to the analysis of bimodal distributions of collisional transition probabilities [12]. Partial contributions from weak collisions and supercollisions are taken into account as follows:

$$p(E', E) = [a_1 \exp(-\Delta E/\alpha_1) + a_2 \exp(-\Delta E/\alpha_2)]/C(E), \quad (2)$$

where $C(E)$ is a normalizing constant; a_1 and a_2 are the contributions from weak and supercollisions, respectively; and α_1 and α_2 are the parameters of their energy dependencies. Parameters a_1, a_2, α_1, and α_2 are approximated by the linear functions of energy E. Independent variables are obtained from trajectory calculations by a trial method and then used for solving MKE.

However, the calculation of rate constants and MKE solution, taking into account the probabilities of transitions, are difficult due to uncertainty in the probability normalization. This leads to uncertainty in the calculated contribution of supercollisions to the total characteristics of the processes. In addition, the definition of supercollisions given in [12] only enable the consideration of processes with the transfer of very large portions of energy $\Delta E > 5\overline{\Delta E}$. However, collision processes with lower energy should also be considered. For example, the results of [13] confirm that relatively large portions of energy ($\Delta E \sim T$) efficiently transfer during collisions of polyatomic molecules at $T \sim \theta$ (θ is a characteristic vibrational temperature of molecules). Adamovich et al. [14] emphasized the importance of bi- and multiquantum transitions. In this work, we analyze transitions resulting from the transfer energy portion comparable to the thermal energy and to several

vibrational quanta of molecules. In contrast to supercollisions, we refer to them as large-step (LS) transitions.

In this work, we describe collision processes in terms of reaction rates, rather than probabilities of transitions. This description simplifies the approach and removes the problem of uncertainties in normalizing transition probabilities. In addition, the analysis of activation mechanisms is carried out over a wide temperature range. That is, the translational energy of molecules at the highest temperature in the range is several times higher than their energy at the lowest temperature in the range and higher than the characteristic vibrational temperature (θ) of molecules. Therefore, we consider in this work the collisions with the transfer of the portion of energy $\Delta E \sim T$ at $T \geq \theta$. Indeed, these collisions can be considered as collisions with rather large-step transitions.

Thus, the goal of this work is to determine the relation between the rates of vibrational relaxation and dissociation and the distribution of vibrational energy of polyatomic molecules at high temperatures ($T > \theta$), as well as to determine the role of large-step transitions in high-temperature decomposition. With this goal in mind, the MKE describing the activation and dissociation of polyatomic molecules was solved within step-ladder approximation [15, 16]. The contribution from small and large-step mechanisms was taken into account. Carbon dioxide molecules were considered as an example.

KINETIC MODEL

The adequate description of microscopic and macroscopic parameters and the rates of energy exchange processes in polyatomic molecules is achieved by solving MKE for which a step-ladder model [15–17] was developed. On the basis of this approach, the mechanisms of the population of highly excited (including over-threshold) states of CO_2 and SO_2 in the processes of dissociation and recombination, as well as energy exchange and dissociation in vibrationally nonequilibrium mixtures of $CO_2 + N_2$, were studied. The dissociation of CO_2 was studied at 2300–4000 K; the dissociation of SO_2 was studied at $T \leq 5000$ K [15–17]. In our work, these studies were extended to a high-temperature range.

According to the basic principle of the step-ladder model, MKE for a polyatomic molecule with a finite number of macroscopic states A_i can be written as a set of equations

$$\frac{dA_i}{dt} = W_+ + W_- + W_d(i) + W_{bm}(i) + W_{el}(i), \quad (3)$$

which takes into account collisional vibrational relaxation in each electronic state of a molecule at a rate $W_+ + W_-$, transitions between different electronic terms W_{el}, spontaneous decay of over-threshold states W_d, and bimolecular reactions W_{bm}. Symbols W_+ and W_- denote

the rates of collisional activation and deactivation of a level i, respectively

$$W_+ = \Sigma_j(k_a(i)MA_{i-j} + k_d(i+j)MA_{i+j}),$$

$$W_- = -\Sigma_j(k_d(i)MA_i + k_a(i+j)MA_i),$$

where k_a and k_d are the respective rate constants and M is the total concentration of particles in the system.

Let us analyze the characteristics of the dissociation of polyatomic molecules at 10 000 K using as an example the mechanisms of high-temperature decomposition of carbon dioxide. The step-ladder model developed earlier was extended in accord with the conclusions of a review paper [18]. The extended model directly accounts for the contribution of two types of collisions with the transfer of small and large portions of energy. Therefore, in this work, we give the main part of our attention to the description of two mechanisms of vibrational relaxation. The rate constant of deactivation $k_d(i)$ of a level i was written as equation

$$k_d(i) = a_1(T)k_{d, ss}(i) + a_2(T)k_{d, ls}(i), \qquad (4)$$

where terms $k_{d, ss}$ and $k_{d, ls}$ describe two mechanisms of relaxation. The first term describes weak SS transitions between vibrational levels with the steps of the first step-ladder, $\Delta E_1 = \theta_2 = 2000$ K. This step is equal to the vibrational quantum of the symmetric mode of the CO_2 molecule. The second term describes LS transitions determined by the step of the second step-ladder, $\Delta E_2 = T$. $a_1(T)$ and $a_2(T)$ are temperature dependent variable coefficients, which determine the efficiency of the corresponding processes. These coefficients characterize the partial contributions from each channel. As before [15, 16], the constants of activation and deactivation of every type in this case are related by detailed balance. Therefore, the essence of our approach is the description of the mechanism using the double activation step-ladder with steps equal to ΔE_1 and ΔE_2, respectively.

Eremin et al. [16] showed that the dissociation of CO_2 takes place from the highly excited state (HES) of an asymmetric mode, while vibrational energy transfers to this mode through the double symmetric mode. A difference in the temperatures of population of HES for symmetric and asymmetric modes is possible if the rate constant k_{23} of exchange between modes is not high enough. In this case, the exchange between modes limits the rate of CO_2 dissociation. Figure 1 presents an extrapolation of the rate constants of the dissociation and of the vibrational relaxation of CO_2 to high temperatures. These extrapolations were carried out using formulas recommended in [19–21]. Figure 1 shows that the dissociation, for example, in shock waves at temperature lower than ~4000 K takes place under the conditions of vibrational equilibrium between modes, because the rate constant of the intermode V–V-exchange of CO_2 (k_{23}) is higher than the rate constant of the collisional deactivation of a symmetric mode k_{20}, and these constants are much higher than the rate constant of dissociation k_d. In this case, the rate of CO_2 dissociation is

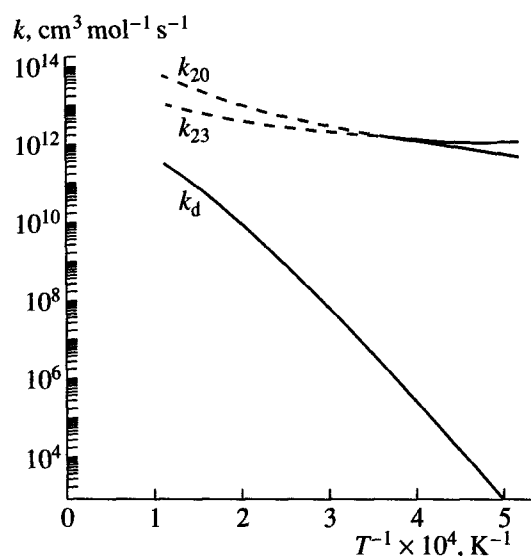k, $cm^3 mol^{-1} s^{-1}$

Fig. 1. The extrapolation of the rate constants of CO_2 dissociation to 10000 K (k_d) [20], V–T-relaxation of the symmetric mode of CO_2 (k_{20}) [19], and V–V-exchange of CO_2 (k_{23}) [21].

limited only by the relaxation of the symmetric mode, which limits the rate of the acquisition of complete vibrational energy by the CO_2 molecule. At higher temperatures, an increase in k_{20} is slower, which limits an increase in k_d with an increase in temperature. The depletion of the dissociating HES of the asymmetric mode compared with the isoenergetic states of the symmetric mode is also possible. This is due to a decrease in k_{23} as compared to k_{20}. A similar effect of a decrease in the rate of CO_2 dissociation by 30–100 times was observed in [16] even at low temperatures (2500–3000 K) because of the conditions for vibrational relaxation in the mixtures with nitrogen.

In the model suggested here, SS transitions are introduced in a manner which means that these transitions determine the rate of vibrational relaxation under the conditions of vibrational exchange between modes, that is, at the lowest temperatures under consideration. The rate for the acquisition of the complete vibrational energy by a molecule is limited by the rate of relaxation of the softest vibrational mode. Therefore, it is assumed that $k_{d, ss}(1) = k_{20}$ and the constant k_{20} from [19] is related to the experimentally measured deactivation time τ_{20} of the symmetric mode of CO_2 by a known formula

$$P\tau_{20} = [k_{20}(1 - \exp(-\theta_2/T))]^{-1}, \qquad (5)$$

where $\theta_2 = 960$ K is the characteristic temperature of the deformation mode coupled with the symmetric mode, P is the pressure in atmospheres. The energy dependence of $k_{d, ss}$, as a function of the number of step-ladder level is determined using the model of a harmonic oscillator [28] and written taking into account

the real number of the corresponding physical level of symmetric mode n:

$$k_{d, ss}(n) = nk_{20}. \tag{6}$$

Another mechanism for vibrational relaxation is introduced to take into account the dependence of the probability of collisional transition on temperature (that is, on the average energy of collisions) using the value of step of the second activation step-ladder $\Delta E_2 = T$. Already at $T > 3000$ K, ΔE_2 becomes higher than the value of the largest quantum of CO_2. Therefore, the order of magnitude of the probability of such a transition on low vibrational levels is close to the probability of multiquantum transitions on the low levels, which is negligible as compared to the probability of single-quantum transitions. Thus, it is assumed that $k_{d, ls}(1) = 0$. However, for the levels higher than the threshold level n^* of the quasi-continuum of CO_2 vibrational states with an energy E^* of 35 000 K [23], the probability of collisions with the transfer of the portion of energy $\Delta E_2 = T$ independent of the lattice structure of molecular levels is determined by the efficiency of mixing of different types of vibrations. Because of this, the mechanism of the LS transitions of collisions is based on the assumption that the rate of HES population of the decaying mode can be limited by the rate of exchange between modes; that is, the rate constant of this process is described by the following expression

$$k_{d, ls}(n > n^*) = k_{23}^*(n)\exp(-\Delta E_2/T) \sim k_{23}^*(n), \tag{7}$$

where $k_{23}^*(n) = \beta n k_{23}$ is the rate constant of V–V-exchange of HES of the v_2 and v_3 modes of a CO_2 molecule in a certain buffer gas [16]; β is a parameter varying between 1 at $\beta|_{E = E^*}$ and 6 at $\beta|_{E = E_0}$. The latter value was evaluated in [16]. $E_0 = 5.45$ eV is the energy of the low dissociation threshold. This means that the probability of LS transition is proportional to the probability of vibrational exchange between modes with a certain energy. This energy determines its dependence on the energy of the vibrational level and on the composition of the buffer gas. The value of $k_{d, ls}(n)$ for levels with $1 < n \leq n^*$ was calculated using the exponential interpolation between $k_{d, ls}(1) = 0$ and $k_{d, ls}(n) = n^*$.

The physical sense of two activation step-ladders thus introduced is that they describe two alternative activation mechanisms. The first is the single-quantum SS mechanism of usual vibrational relaxation (with constant k_{ss}), determined by the internal structure of the molecule. The second is the LS mechanism of transitions with the transfer of large energy portions (with the constant k_{ls}), determined by the energy of collisions of the molecules under study with the buffer gas, as well as by the properties of buffer gas.

The solution to this system of stiff kinetic equations was carried out by inspecting the corresponding analytical solution at each integration step with a maximal error of 1% according to the method described in [17].

DISCUSSION

In the suggested double step-ladder model, the choice of variable coefficients $a_1(T)$ and $a_2(T)$ in equation (4) at the rate constants of SS and LS collisional transitions was performed using the data on temperature dependence of the relaxation time of the total vibrational energy of CO_2 [19] and the rate constant for the dissociation of CO_2 [20]. The description of these processes enabled the determination of temperature dependences of the efficiency coefficients for the alternative mechanisms of vibrational relaxation $a_1(T)$ and $a_2(T)$:

T, K	2000	4000	6000	8000	10000
a_1	1.0	0.5	0.25	0.2	0.18
a_2	0.085	0.11	0.98	0.99	1.0

The analysis of the interaction of vibrational relaxation with dissociation in the framework of the model suggested in this work led to the following conclusions. At 2000–4000 K, the population of low levels is determined by the efficiency of SS transitions. This agrees with the results reported in [16], where it was shown that the main mechanism, which determines the population of the low vibrational levels of CO_2, is the relaxation of the symmetric mode with the transfer of a portion of energy equal to the quantum $\theta_1 = 2000$ K. However, the calculation shows that the population of HES also depends on the intensity of LS transitions. The efficiency of the latter increases with an increase in the temperature. Figure 2 compares the pseudostationary vibrational distribution of the term $(^3B_2)$ for the CO_2 molecule calculated without taking into account LS transitions to the distribution calculated using the complete mechanism with account for these collisions under the same conditions. We see that, at $T = 2500$ K, the account of strong collisions does not lead to any distinguishable modification of the distribution shape.

At temperatures higher than 4000 K, CO_2 dissociates under nonequilibrium conditions even in the inert gas. This means that rather low vibrational levels are depleted and this results in a distinguishable difference between the vibrational temperature mainly characterizing the population of low levels and the translational temperature. The rate of vibrational relaxation on low levels starts to limit the dissociation rate. Figure 3 compares the pseudostationary vibrational distributions of the ground state of $CO_2(X^1\Sigma)$ (a) and its excited state $CO_2(^3B_2)$ (b), calculated without taking into account LS transitions and with the application of the complete mechanism at $T = 6000$ K, $P = 1$ atm, and $t = 1$ μs. Comparison of Figs. 2 and 3 shows that an increase in the temperature leads to: (1) stronger depletion of highly excited and over-threshold states, (2) noticeable depletion of vibrational distribution even on low energetic levels, and (3) a considerable increase in the role of LS transitions in the formation of the function of distribution of HES.
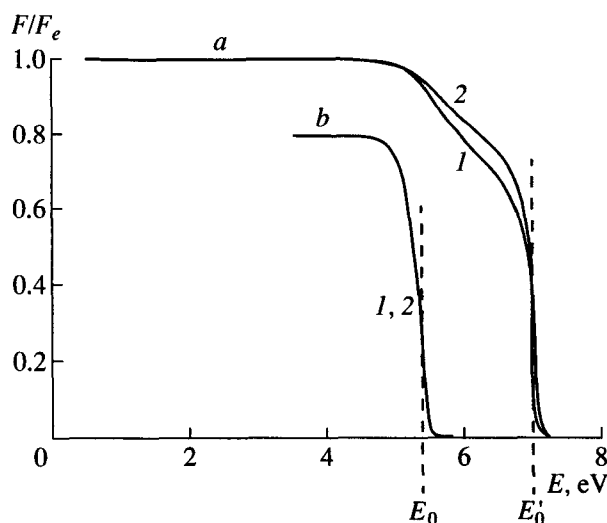
Fig. 2. Pseudostationary vibrational distributions of (a) the ground ($X^1\Sigma$) and (b) excited ($^3B_2$) states of CO_2 calculated (1) without taking into account KC transitions and (2) according to the complete mechanism at $T = 2500$ K, $P = 1$ atm, and $E_0 = 5.45$ eV.
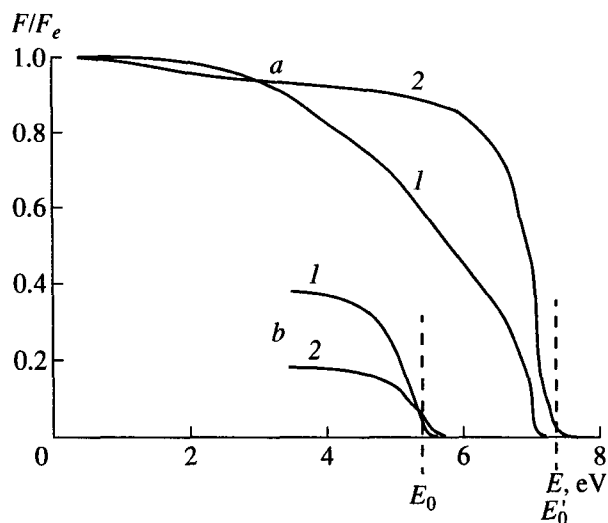

Fig. 3. Pseudostationary vibrational distributions of (a) the ground ($X^1\Sigma$) and (b) excited ($^3B_2$) states of CO_2 calculated (1) without taking into account KC transitions and (2) according to the complete mechanism at $T = 6000$ K, $P = 1$ atm, $t = 1$ μs, and $E'_0 = 7.42$ eV.

An important application of the mechanistic model of vibrational relaxation is the description of the deviation of the rate constant of CO_2 dissociation from the values calculated using the RRKM theory [20]. The RRKM theory overestimates these constants as compared with experimental values at high temperatures. The practical significance of this approach consists in the possibility for calculating k_d for CO_2 at ~10 000 K, because it is rather complicated to obtain reliable experimental data in this temperature range. Figure 4 presents the rate constant of CO_2 dissociation in argon as a function of the temperature. The curve 1 corresponds to the high-temperature approximation performed using the RRKM theory, curve 2 corresponds to the calculation performed with the application of the double step-ladder model without taking into account LS transitions of collisions, and curve 3 corresponds to the calculation performed using the mechanism of vibrational relaxation suggested in this work. The last curve agrees well with the results of approximation (marked by "+" signs), which were recommended in [20] for temperatures up to 11000 K.

Eremin *et al.* [16] studied the influence of the value of step-ladder parameter ΔE on the slope of the temperature dependence of the experimental rate constant for CO_2 dissociation. They showed that an increase in the average portion of energy transferred in collisions leads to a decrease in the effective activation energy of the process. This explains the fact that the contribution of LS transitions with a large value of ΔE leads to a decrease in the effective activation energy of dissociation.

The data presented below characterize the relative contribution of the particle flows to the dissociation limit via the channels of SS and LS transitions (W_{ss} and W_{ls},

respectively) and via the low (spin-prohibited) channel to the total flow of dissociating particles:

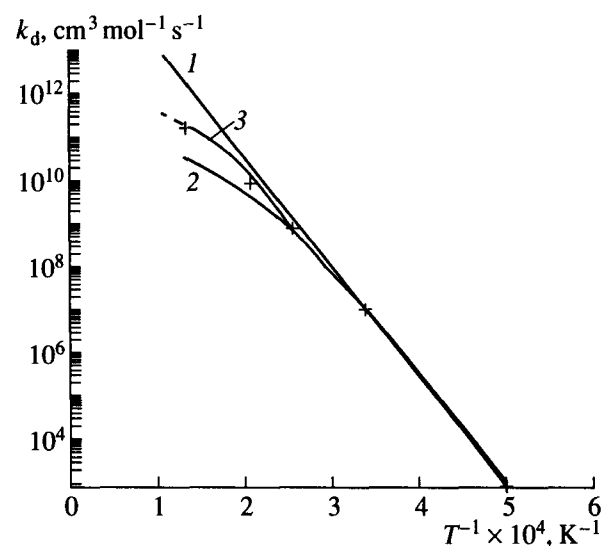| T, K	2000	4000	6000	10000
W_{ss}, %	76	32	3	1
W_{ls}, %	24	68	97	99

Fig. 4. Rate constant of CO_2 dissociation in argon as a function of temperature: (1) high-temperature approximation of calculation using the RRKM theory, (2) calculation with the step-ladder model without taking into account KC transitions, and (3) calculation using the complete mechanism of vibrational relaxation suggested in this work. The "+" sign denotes the results of the approximation of experimental data obtained in [20].
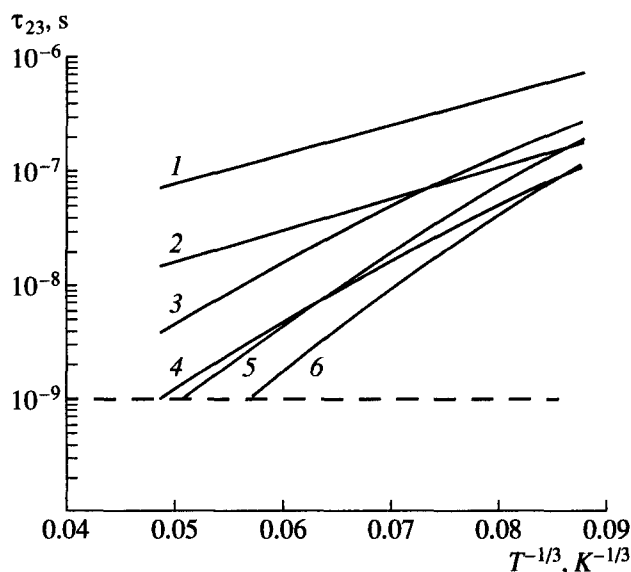
Fig. 5. Extrapolation of temperature dependencies of the V–V-relaxation time of CO_2 in various gases: (1) Ar, (2) NO [23], (3) CO, (4) CO_2 [19], (5) N_2, and (6) O_2.

The values of W_{ss} and W_{ls} were calculated using the equations

$$W_{ls} = \sum_{E_0 - \Delta E_2 \leq E_i \leq E_0} k_{a,ls}(i)A_i, \qquad (8)$$

$$W_{ss} = k_{a,ss}(j)A_j, \qquad E_j = E_0 - \Delta E_1. \qquad (9)$$

An increase in the temperature leads to an increase in the contribution of LS transitions to the flow of dissociating particles.

Thus, LS transitions have a key effect on the rates of high-temperature decomposition of polyatomic molecules. Therefore, comparison of the rate constants for CO_2 dissociation in various diluent gases at high temperatures enables, in our opinion, the evaluation of the relative efficiencies of strong collisions of CO_2 molecules with different partners. Unfortunately, as mentioned above, reliable experimental data on the rates of CO_2 dissociation in different gases are practically unavailable. Therefore, these estimates require the use of theory. The analysis of the results presented in [16, 20] makes it possible to draw the following conclusions.

Relative efficiencies of collisions of CO_2 with diatomic molecules M

T, K	N_2	CO_2	CO	NO	O_2
1500	3.8	6.8	2.7	4.1	6.3
2000	6.5	9.4	3.4	4.3	11.4
4000	23.0	24.0	7.0	4.6*	56.7
8000	80.0	63.0	17.0	4.9*	

* The value can be underestimated because it is obtained by extrapolating the results of low-temperature measurements at lower temperatures [24].

Eremin *et al.* [16] showed that the decomposition of CO_2 takes place from the HES of the asymmetric mode. These HESs are populated in the inert gas by intramolecular energy transfer from the isoenergetic states of rapidly relaxing symmetric modes. Many molecular gases are more favorable for efficient intramolecular energy transfer in CO_2. Quasi-resonant vibrational exchange between dissociating states of CO_2 and the excited states of buffer molecules plays an important role in these mixtures. Specifically, this effect explains the triplicate acceleration of the dissociation rate of CO_2 in vibrationally equilibrium nitrogen and acceleration by ~2.5 times in CO_2 as compared to the rate of this reaction in argon at ~2000 K [20]. In the framework of the model suggested in this work, this means that the efficiency of LS transitions during CO_2 collisions with vibrationally equilibrium N_2 (or CO_2) molecules is higher by a factor of ~6 than at collisions with Ar atoms, and this ratio increases at high temperatures.

The results of this work enable us to determine to what degree the efficiency of LS transitions in the collisions of CO_2 with diatomic molecules (O_2, CO, NO, etc.) is higher than in the collisions with Ar atoms. The characteristic time of the V–V-exchange of v_3 with these partners qualitatively corresponds to the absolute value of this effect. Temperature dependences of the V–V-relaxation time for CO_2 in different gases (including the data of [19] and [24]) are presented in Fig. 5. On the basis of these results, the table was compiled presenting the data on the relative efficiency of LS transitions in the collisions of CO_2 molecules with the molecules M as compared to Ar atoms ($\gamma(M) = a_2(M)/a_2(Ar)$) at 2000–10000 K. LS transitions at high temperatures determine the rate of dissociation; therefore, the data of the table can be used to estimate the ratio of k_d for CO_2 in the gas M to k_d for CO_2 in argon.

CONCLUSION

In this work, the mechanism of the relation between vibrational relaxation with the dissociation of a polyatomic molecule in the framework of the unified model was solved for a wide temperature range. The double step-ladder model describing the relation of relaxation with dissociation at 2000–10000 K was developed using CO_2 as an example. In this model, collisional activation due to the transfer of small and large portions of energy is considered, taking into account stepwise transitions. The efficiency and the role of collisions accompanied by the transfer of thermal portions of energy was analyzed for the high-temperature decomposition of CO_2 in atomic and molecular buffer gases. The rate constant of carbon dioxide dissociation was calculated.

The results of this work provide a new method for the elucidation of the mechanism of energy exchange processes at vibrationally and translationally nonequilibrium conditions of different types (in molecular beams, in the front and relaxation zone of a shock

wave) and at ultrahigh temperatures (>20 000 K), when dissociation is completed for several collisions.

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