

Application of the Monte Carlo Method to Modeling of Kinetic Processes with the Participation of Polyatomic Molecules and Clusters: 1. Kinetics of Energy Transfer during Collisions of Polyatomic Molecules

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Abstract—The Monte Carlo method was used to model the collisional energy transfer for polyatomic molecules within the framework of the statistical theory of reactions. A model describing energy transfer through the formation of a statistical collisional complex was suggested. It was assumed that the total energy of the complex was randomized in the course of collisions and statistically distributed among the internal and translational degrees of freedom. The method was verified by comparing the equilibrium distribution functions for the vibrational, rotational, and total energies of the molecule. The mean energy portion and the root-mean-square energy portion transferred per collision, as functions of the total molecular energy, were determined. The relaxation parameters of the population distribution over energy after a sharp increase in the bath-gas temperature were calculated.

INTRODUCTION

The Monte Carlo method is widely used in statistical physics [1]. The history of its applications in chemical kinetics is much shorter (see, e.g., [2–10]). We consider only relaxation and reactions of highly excited states (HESs) of polyatomic molecules and emphasize that the main problem along this line is in solving microkinetic equations with the aim of calculating the population distribution of HESs, kinetic rate coefficients, and radiative characteristics (see, e.g., [9] and references therein).

Stochastic methods can also be used to solve the same problems. The Monte Carlo method was first applied to molecular kinetics in [2–4] and further developed in [5]. Gillespie [2] suggested a mechanism of complete randomization of molecular vibrations, in accordance with which a molecule completely forgets its previous history, and the probability of further events depends only on its overall molecular energy. Gillespie [2] used two random numbers r_1 and $r_2 \in [0, 1]$ to determine (a) the probability that the molecule that is in state n at time t will change its state during the period τ as described by the equation $\int_0^\tau A_n(\tau')d\tau' = \ln\left(\frac{1}{r_1}\right)$ and (b) the probability that this is a transfer to a new state m determined by $\sum_{j=1}^{m-1} A_{jn}(\tau) < r_2 A_n(\tau) \leq$

$\sum_{j=1}^m A_{jn}(\tau)$, where $A_{mn}(\tau)$ is the probability of the molecular transfer from state n to state m and $A_n(\tau) \equiv \sum A_{mn}(\tau)$ is the overall probability density for the molecule to react in state n . The sampling of the random numbers r_3 and r_4 generated collisional transitions. The exponential model of collisional transitions was used. Gillespie considered the case of the constant probability $A_{mn}(\tau) = \text{const}$ and the exponential dependence $A_{mn}(\tau) = a_n \exp(-k\tau)$ for a situation corresponding to the excitation by an exponentially decaying laser pulse [2].

Anderson and co-workers reported direct Monte Carlo modeling of chemical reactions [10, 11]. These works were based on the Bird method, which was formerly applied to gas dynamic processes [12]. According to this method, the reaction volume is divided into cells with a size commensurate with the mean free path of molecular motion, and the concentration of molecules is selected so that the number of molecules in a cell is about 30. To maintain dynamic self-similarity, the cross-section was increased in the corresponding proportion. Then, about $\sim 10^5$ molecules are introduced into the reaction volume, and their velocity components $v_{xi} = r_2(2kT/M_i)^{1/2} \text{erf}(r_1)$ are assigned using two random numbers $r_1 \in [0, 1]$ and $r_2 = \pm 1$. It is assumed that the molecules move during time τ without collisions (which corresponds to ~ 0.1 of the cell size); after this

period, the collisions between molecules are allowed to occur in the cell between randomly selected pairs of molecules. The number of random collisions corresponds to the number of collisions in real time during time interval τ . The velocities of the molecules change because of collisions; if the energy of a collision is higher than a certain threshold value E^* , the reaction may take place with a certain probability. After this event, the molecules move during time interval τ with new velocity components. Simple bimolecular $A + B \rightarrow C + D$ [10] and unimolecular reactions $AB + M \rightleftharpoons A + B + M$ [11] were considered. It was assumed that only collisions provide the energy required to overcome the reaction barrier: the internal energy was not taken into account.

The treatment of the kinetic behavior of molecules within the framework of the theory of unimolecular reactions together with the Monte Carlo method was described in [7, 8]. These works reported the studies of metal clusters formation during the nucleation of supersaturated metal vapors behind incident shock waves and metal cluster decomposition after their secondary heating behind the reflected shock wave (where the clusters emit free metal atoms, electrons, and light photons). The clusters were considered as large molecules for which all internal degrees of freedom were assumed to be at equilibrium. It was assumed that the distribution of the clusters over the internal energy was formed as a result of energy transfer in collisions of the clusters with atoms of the bath-gas, as well as the emissions of atoms, electrons, and light photons. The specific rate coefficients $k_n(E_i)$ for each of these processes were determined. In accordance with the calculation procedure, the probability of each process is proportional to its specific rate coefficient. The probabilities of these processes were calculated for each elementary event, after which the resultant energy of the cluster was fixed. Based on these data, the distribution of the cluster over the internal energy (DCE) was determined. The apparent rate coefficients for the thermal decomposition $k_d(T)$, thermal ionization $k_e(T)$, and light emission were calculated as functions of the wavelength using the specific rate coefficients and the calculated nonequilibrium distribution function. This approach allowed the authors to adequately describe their experimental data. These examples show that the Monte Carlo method is applicable to a large number of molecular kinetic problems. In this work, the Monte Carlo method was used to model energy transfer and reactions in the framework of the statistical theory of unimolecular reactions of polyatomic molecules (STUR). This paper considers only energy transfer processes.

DESCRIPTION OF ENERGY TRANSFER BY THE MONTE CARLO METHOD

The energy exchange between reacting molecules A and inert species M is treated in the subsequent development below using the model of activation via a colli-

sional complex (AM) [13–18]. In accordance with this model, the overall energy of the complex consists of the internal energy of the molecule A and the kinetic energy of the collision, which is statistically redistributed within the internal degrees of freedom of the complex AM. After the decomposition of the complex, this energy is redistributed between the internal degrees of freedom of the molecules A and M and their translational motion. The energy distribution occurs according to the statistical weights of its modes of motion.

To obtain the function of distribution of the internal molecular energy, the Monte Carlo method was used. This method imitates the random walks of molecules A in the energy space under the action of collisions with bath-gas molecules. The consideration is based on the ergodic hypothesis, which postulates that a statistical result obtained from a long monitoring of a selected species from an ensemble of reacting molecules and that obtained by averaging the states of a representative sample of the ensemble at a given moment are equivalent.

Let us consider a collision between a molecule A and a bath-gas molecule M. The total internal energy of A is $E_0 = E_{v0} + E_{r0}$, where E_{v0} and E_{r0} are the vibrational and rotational energies, respectively. We assumed that the bath gas is monatomic and the translational motion obeys the Boltzmann distribution. The translational motion of colliding species can be generally described by four degrees of freedom, one of which corresponds to the motion of the center of gravity of the colliding species, and, therefore, its energy does not participate in the energy exchange. In this case, the distribution collisions over the energy is given by

$$f_t(E) = \rho_t(E) \exp(-E/RT), \quad (1)$$

where $\rho_t(E) = A_t E^{1/2}$ is the density of energy states associated with relative motion of the colliding molecules and A_t is a normalization factor. The energy E_t of a collision was determined by sampling random numbers within $\xi_1 \in [0, 1]$ from the equation

$$\xi_1 = \frac{\int_0^{E_t} f_t(E) dE}{\int_0^{\infty} f_t(E) dE}. \quad (2)$$

Equation (2) was solved numerically; the appropriate solution was presented in the polynomial form $X_t(\xi_1) =$

$RT \sum_{n=0}^{n_{\max}} a_n \varphi^n(\xi_1)$, where $\varphi(\xi_1)$ is written as

$$\varphi(\xi_1) = \begin{cases} \xi_1^{2/3} & 0 \leq \xi_1 \leq 0.26 \\ \xi_1 & 0.26 < \xi_1 \leq 0.8 \\ \ln(1 - \xi_1) & 0.8 < \xi_1 < 1. \end{cases}$$

The polynomials were adjusted so that the relative uncertainty of E_t was less than 10^{-4} . The n_{\max} value in each interval was less than 5.

The total collisional energy of the complex AM is $E_{\text{AM}} = E_0 + E_t$, and it consists of the kinetic energy of the departing partners and the total energy of the molecule A after collision (which in turn consists of the vibrational and rotational components). It was assumed that all of the rotational degrees of freedom are active in the energy exchange process; in other words, there are no restrictions on the energy exchange between the rotational and other degrees of freedom; that is, the conservation of rotational momentum is not fulfilled. The probability of particular energy distribution is proportional to the density of energy states corresponding to this distribution. To estimate the density of vibrational states, we used

$$\rho_v(E) = A_v(E + E_z)^{v-1}. \quad (3)$$

The density of rotational states was described by the classical expression

$$\rho_r(E) = A_r E^{r/2-1}, \quad (4)$$

where r and v are the numbers of rotational and vibrational degrees of freedom, respectively; E_z is the zero-point vibrational energy; and A_r and A_v are normalization factors.

The optimal calculation procedure is to find the energy distribution among the vibrational degrees of freedom of the molecule A and the other degrees of freedom and then to find the distribution between the rotational and translational degrees of freedom. The energy distribution between various types of motion during the decomposition of the collisional complex can be performed in several ways. The ultimate result is independent of the sequence of calculations. The density of energy states for the rotational-vibrational subsystem of the energy spectrum of the collisional complex is

$$\rho_{rv}(E) = \int_0^E \rho_r(\epsilon) \rho_v(E - \epsilon) d\epsilon = A_{rv} E^{r/2+1/2}. \quad (5)$$

The energy distribution among the vibrational degrees of freedom of the molecule A and the other degrees of freedom after a collision reads as follows:

$$\xi_2 = \frac{\int_0^{E_{\text{AM}}} (E_{\text{AM}} - \epsilon + E_z)^{v-1} \epsilon^{r/2+1/2} d\epsilon}{\int_0^{E_{\text{AM}}} (E_{\text{AM}} - \epsilon + E_z)^{v-1} \epsilon^{r/2+1/2} d\epsilon} = \frac{B_{X_n}(v, r/2 + 3/2)}{B_{X_{\text{AM}}}(v, r/2 + 3/2)}, \quad (6)$$

where $\xi_2 \in [0, 1]$ is a random number, $X = E/(E_{\text{AM}} + E_z)$, and $B_X(a, b)$ is the incomplete β -function. The denominator of (6) can be readily calculated to obtain

$$B_{X_n}(v, r/2 + 3/2) = \xi_2 B_{X_{\text{AM}}}(v, r/2 + 3/2) = \xi_2^*.$$

The solution to this equation, as in the case of equation (2), was presented in the polynomial form: $X_n(\xi_2^*) = \sum_{n=0}^{n_{\max}} a_n \times \varphi^n(\xi_2^*)$. The vibrational energy of the molecule A after a collision is equal to $E_{v1} = E_{\text{AM}} - E_n$. The energy distribution between the rotational and translational degrees of freedom was found from

$$\xi_3 = \frac{\int_0^{E_{\text{rl}}} \epsilon^{r/2-1} (E_{\text{rl}} - \epsilon)^{1/2} d\epsilon}{\int_0^{E_{\text{rl}}} \epsilon^{r/2-1} (E_{\text{rl}} - \epsilon)^{1/2} d\epsilon}. \quad (7)$$

This equation was solved numerically similarly to equation (6).

By solving equations (2), (6), and (7), we obtain the new values of the total energy of the molecule A and its vibrational and rotational components. Using this procedure many times and fixing each time a new state of the molecule A, we obtained the distributions for the total, vibrational, and rotational energies. The calculation procedure consisted of two steps. First, we solved equations (2), (6), and (7) and determined the polynomial coefficients satisfying these equations. Note that equation (2) is universal in the sense that it should be solved only once, whereas equations (6) and (7) should be solved for each type of molecules. Since normally $r = 3$, the solution to (7) is also universal. For linear molecules ($r = 2$), the solution can be simplified to $E_{\text{rl}} = E_{\text{rl}}[1 - (1 - \xi_3)^{2/3}]$. At the second step, the procedure of collision sampling is performed. The generation of $N \approx 10^5$ collisions takes about 1 min of computation using a PC based on a 486 processor.

To simulate DFE at energies $E \gg RT$, a large number of collisions should be generated ($N > 10^9$). Since it is impossible using even the most powerful modern computers, we employed the method of gradual approach to the high-energy range. First, a set of N tests is used to

find a total internal molecular energy E_1 for which the fraction of detected collisions is $\beta \approx 10\%$. At the second step, a series of N tests was prepared in which collisions occurred at energies $E > E_1$. The statistical weight of each collision which occurred during the second step of the tests is higher than that for the first step by a factor of $1/\beta$. If the molecule penetrated in the range of lower energies, it was forcibly returned. For this purpose, we preliminary determined the mean energy $E_{1,up}$ in the range $E < E_1$ corresponding to molecular transitions into the range $E > E_1$. The initial value of molecular energy was set at $E_{1,up}$, and the kinetic energy was sampled at random in the range $E_t > E_{1,up}$, with the sampling intervals of the random numbers ξ_2 and ξ_3 adjusted so that the final total energy would be higher than E_1 . If after the second step it was necessary to move further into the range of high energies, we determined for each further step the energy range where more than 90% of the results of the previous step is located and then randomly generated collisions at higher energies.

CALCULATION RESULTS

Based on the above treatment, we developed several computer programs for solving various problems of molecular kinetics. Let us consider several examples. The calculations were performed for a five-atom molecule A with the following parameters: $v = 9$, $r = 3$, and $E_z = 32.5$ kcal/mol (these parameters are typical of the CH_3Cl molecule).

Calculation of the equilibrium distribution function. The solution to this problem makes it possible to test the reliability of the method. In the absence of external factors (e.g., chemical reactions) which may influence the HES population, DFE calculated by the proposed method should be at equilibrium. Equilibrium DFE were calculated by

$$E_r(E) = \frac{2\sqrt{E} \exp(-E/RT)}{\sqrt{\pi}(RT)^{3/2}}, \quad (8)$$

$$E_v(E) = \frac{(E + E_z)^{v-1} \exp[-(E + E_z)/RT]}{\Gamma(v, E_z/RT)(RT)^{v-1}},$$

where $\Gamma(v, E_z/RT)$ is the incomplete γ -function. The distribution function of the population of the total internal energy (the sum of the vibrational and rotational energies) is given by

$$F_s(E) = \int_0^E F_r(\varepsilon) F_v(E - \varepsilon) d\varepsilon. \quad (9)$$

Figure 1a presents DFEs obtained using the Monte Carlo method and in comparison with equilibrium DFE calculated by equations (8) and (9) at $T = 2000$ K. In Fig. 1b, the same DFEs are shown along with equilibrium DFE. As can be seen, with variations in DFEs

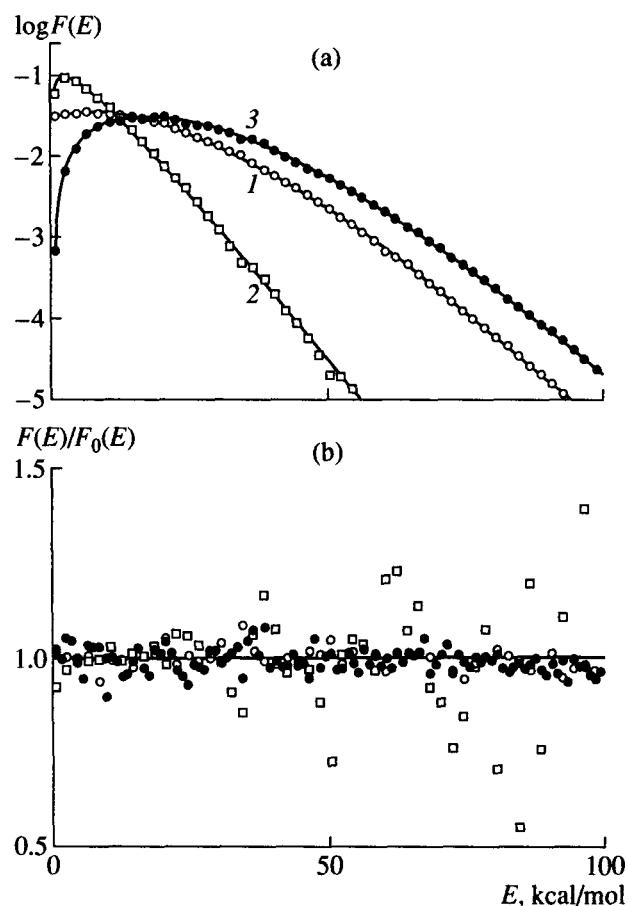


Fig. 1. DFE for (1) vibrational, (2) rotational, and (3) total energies obtained by the Monte Carlo method: (a) the absolute values of DFE calculated by equations (8) and (9); (b) DFE calculated by the Monte Carlo method.

within 4–5 orders of magnitude, the difference between the equilibrium distribution functions calculated analytically and by the Monte Carlo method is less than 10%. Thus, the Monte Carlo method is reliable in the calculations of DFEs.

Parameters of energy transfer during collisions.

The mean portion energy $\bar{\Delta E}$ transferred per collision and root-mean-square energy portion transferred per collision $\bar{\Delta E}^2$ are important parameters characterizing intermolecular energy transfer. The proposed Monte-Carlo-based approach makes it possible to calculate these parameters as functions of the total molecular energy. With this aim, we generated the random sequence of collisions for the molecule in the state with the complete energy E_0 as described in detail in the previous section. As a preliminary step, a random energy distribution of the overall energy E_0 among the vibrational and rotational degrees of freedom was generated; in other words, the random values of E_{v0} and E_{r0} ($E_{v0} + E_{r0} = E_0$) were determined. With this aim, a random

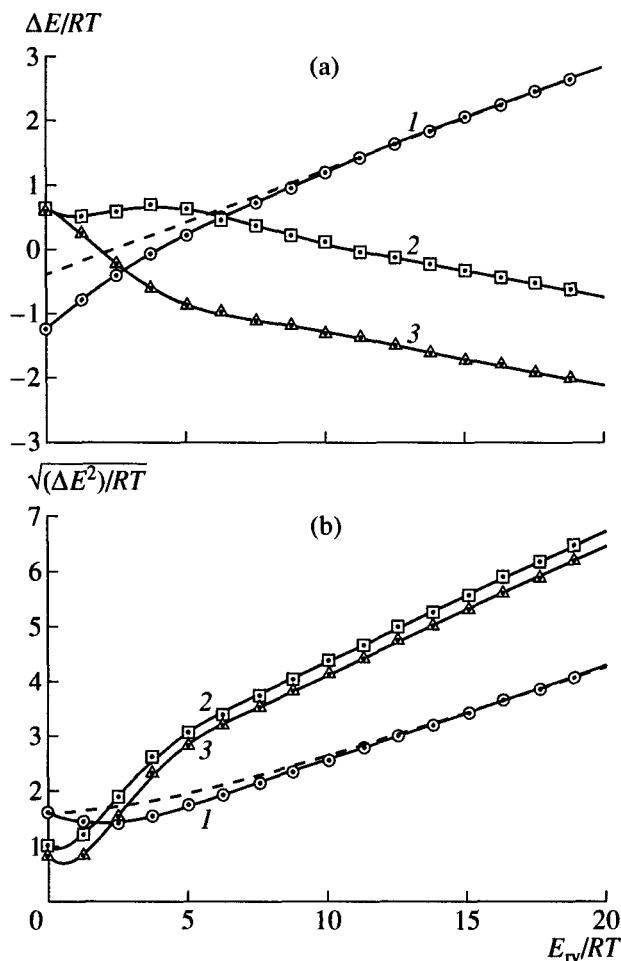


Fig. 2. (a) Mean energy portion and (b) the root-mean-square energy portion transferred during one collision as a function of the total molecular energy before the collision at a temperature of the bath-gas of 2000 K: (1) overall energy, (2) vibrational energy, and (3) rotational energy. The dashed line corresponds to the values calculated by equation (11).

number ξ_4 was generated, and the following equation was solved

$$\xi_4 = \frac{\int_{E_0}^{E_r} (E_0 - \varepsilon + E_z)^{v-1} \varepsilon^{r/2-1} d\varepsilon}{\int_0^{E_0} (E_0 - \varepsilon + E_z)^{v-1} \varepsilon^{r/2-1} d\varepsilon} \quad (10)$$

in the same manner as equation (6). For each step, the changes in the vibrational and rotational energies caused by collisions were calculated. Repeating this procedure at different energies E_0 , the dependence of $\overline{\Delta E}$ and $\overline{\Delta E^2}$ on the total molecular energy was obtained. As a rule, to find $\overline{\Delta E}$ and $\overline{\Delta E^2}$ at a given

value of E_0 , about $\sim 10^4$ collisions were randomly generated. Figure 2 shows the calculated values of $\overline{\Delta E}$ and $\overline{\Delta E^2}$ at a bath-gas temperature of 2000 K. The activation of molecules via the formation of collisional complexes was theoretically studied in [16], where expressions for $\overline{\Delta E}$ and $\overline{\Delta E^2}$ were obtained in the classical approximation. Similar expressions with due regard to zero-point vibrations read

$$\begin{aligned} \frac{\overline{\Delta E}}{RT} &\approx \frac{f - (E_0 + E_z)/RT}{f/2 + 1}, \\ \frac{\overline{\Delta E^2}}{(RT)^2} &\approx \frac{6}{(f+2)(f+3)} \\ &\times \left[\left(\frac{E_0 + E_z}{RT} \right)^2 - \frac{4}{3} f \frac{E_0 + E_z}{RT} + f(f+1) \right], \end{aligned} \quad (11)$$

where f is the total number of internal degrees of freedom. In Fig. 2, the dependences of $\overline{\Delta E}$ and $\overline{\Delta E^2}$ calculated by (11) are shown by a dashed line. The appreciable differences between the dependences calculated analytically and by the Monte Carlo method are due to the fact that the highest error in $\overline{\Delta E}$ and $\overline{\Delta E^2}$ calculated by (11) occurs at $E \leq E_z$.

Kinetics of DFE relaxation. An important application of the Monte Carlo algorithms to studies of energy transfer in polyatomic molecules is the modeling of the transformation of the vibrational energy distribution during the approach of the system to its equilibrium state. Let us consider typical shock-tube experiments, when the temperature of the gas mixture drastically increases from the initial value T_0 to T_g . To model this situation, we distributed about T_g molecules A according to DFE at T_0 . First, a collision was generated and new distributions of the populations over the total, vibrational, and rotational energies were obtained. Then this new distribution was used as the initial state, and so on. Figure 3 shows DFE obtained by this procedure at $N \approx 10^5$ molecules, an initial molecular temperature of 300 K, and a bath-gas temperature of 2500 K. After 15–20 collisions, DFE approaches a stationary shape corresponding to equilibrium DFE at the bath-gas temperature. For each intermediate state, the effective temperature T_{eff} that yields the best approximation for the DFE was obtained by the trial-and-error method. This procedure was applied to DFEs for the vibrational and rotational degrees of freedom; in all cases, the vibrational and rotational temperatures were found equal. Figure 4a shows the dependence of T_{eff} on the number of collisions. This dependence is closely approximated by the equation (see Fig. 4b)

$$\frac{dT_{\text{eff}}}{dt} = k v (T_g - T_{\text{eff}}),$$

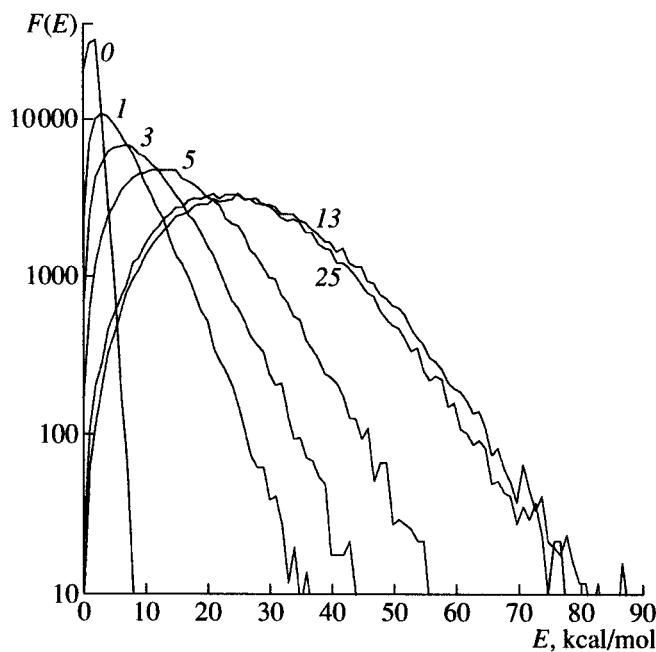


Fig. 3. Transformations of the population distribution of the total molecular energy under the action of collisions. The numbers near the curves indicate the number of collisions. Initial DFE was calculated at $T = 300$ K, the temperature of the environment was 2500 K, and the total number of molecules, 10^5 .

where v is the collisional frequency and $\tau = 1/kv$ is the characteristic time of temperature relaxation ($k = 0.213$ collisions $^{-1}$).

DISCUSSION

The examples presented above illustrate the efficiency of the Monte Carlo method applied to collisional energy exchange. The first two examples were used to test the agreement between the energy exchange parameters calculated by Monte Carlo and accurate analytical methods. Surprisingly, the Monte Carlo

method makes it possible to determine $\overline{\Delta E}$ and $\overline{\Delta E^2}$ in the quasi-classical approximation with an accuracy higher than that obtained using analytical expressions involving some simplifications. Analytical expressions for vibrational and rotational states are still more difficult to obtain.

Let us consider the results on the modeling of vibrational relaxation kinetics in more detail. Figure 4 shows that the equilibrium over the vibrational degree of freedom is attained after a few collisions. The effective molecular temperature attains its threshold value after about 10 collisions. In most cases, the relaxation requires from 10 to 1000 collisions. A significant increase in the vibrational relaxation time may be due to a small probability of transitions between low-lying discrete molecular levels. However, as a rule, the transitions between low-lying levels do not limit the pro-

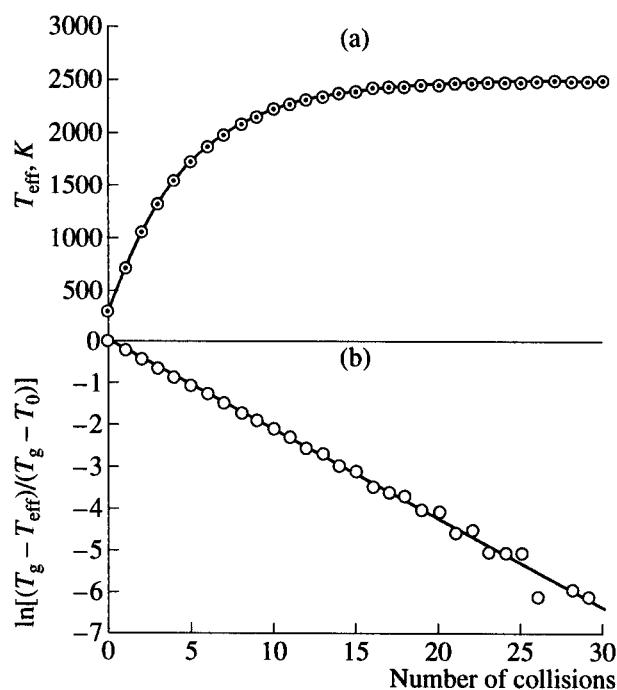


Fig. 4. Effective temperature as a function of the number of collisions; see the text for details. The conditions are the same as for data in Fig. 3.

cess of activation at $T > 1000$ K. In addition, for most cases, the assumption that a complete randomization of the internal energy of the collisional complex occurs during each collision is oversimplification. We are planning to develop the proposed approach on the basis of the model of locally statistical collisional activation [17]. This model postulates that the statistical equilibrium during collisions is attainable only for certain groups of vibrations and rotations of the collisional complex AM with a further redistribution of energy among the other degrees of freedom, which occurs during the intervals between collisions.

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