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## A STOCHASTIC MODEL OF DECOMPOSITION OF SELECTIVELY EXCITED POLYATOMIC MOLECULES

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In the model proposed it is assumed that intramolecular processes (fluctuation of energy) corresponding to the Poisson process on the time scale occur in excited polyatomic molecules. On the scale of number of events (reorganizations, fluctuations), the probability of decomposition depends on the distance from the termination of the excitation process. This model enables the basic features of the lifetime distribution of selectively excited molecules to be derived.

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In connection with the application of techniques for the selective activation of polyatomic molecules (IR multiphoton excitations, single-photon overtone vibrational excitations), models of decomposition in which instantaneous randomization of the excitation energy into all the representative oscillators is not a priori assumed have been gaining in importance. Model molecules with limited exchange (redistribution, reorganization) of vibrational energy are referred to as non-RRK molecules and the corresponding unimolecular kinetic behaviour of such molecules, as non-RRK behaviour<sup>1</sup>. An observable consequence of the limited intramolecular energy redistribution in the collisionless region is a nonexponential time decrease in the number of nondecomposed molecules<sup>2,3</sup> and, in the case of a two-channel decomposition, nonexponential kinetics of formation of the decomposition fragments and their nonstatistical proportions during the reaction<sup>4,5</sup>. The importance of these models has also increased with the progress of femtochemistry techniques<sup>6,7</sup>. As it seems, in a near future it will become possible, at a rather sharply defined moment to create an assembly of molecules with a well-defined excitation energy stored at a site (bond) of the molecule, and to subsequently monitor their decomposition on a time scale of hundreds or even tens of femtoseconds. A question then arises as to how long the molecule keeps information on the initial localization of the excitation energy (on what time scale the molecular memory extinguishes)<sup>8</sup>.

A stochastic model enabling us to describe the kinetics of decomposition of molecules possessing memory, excited selectively at a site which may be either rather distant from the reaction coordinate or rather near to it, is suggested and discussed in this paper.

*The Stochastic Model of Decomposition*

As a result of anharmonic interactions, an excited molecule with a total vibrational energy  $\varepsilon$  undergoes energy reorganizations (fluctuations) into the various representative oscillators; these processes play a crucial role in the decomposition<sup>9</sup>. The molecule decomposes if a random fluctuation brings about accumulation of energy exceeding the threshold decomposition energy  $\varepsilon_0$ . In the simple model of intramolecular processes of the collision type suggested previously<sup>3,10</sup>, these fluctuations are represented by a time series of random events of the Poisson type. The reorganizations themselves are virtually instantaneous, and the time between them is distributed with an exponential density.

Let  $p_n$  be the probability that during the  $n$ -th reorganization, energy higher than  $\varepsilon_0$  accumulates in the reaction coordinate ( $0 < p_n < 1$ ). The probability that the molecule will decompose just during this reorganization is  $\prod_{i=1}^{n-1} (1 - p_i) p_n$ . The lifetime of this molecule on the scale of number of events<sup>3</sup> is  $n$ . If the reorganizations proceed as Poisson processes<sup>11</sup>, then the probability that  $n$  reorganizations will take place in the molecule within the time interval  $(0, t)$  is  $(\nu t)^n \exp(-\nu t)/n!$ , where  $\nu$  is the mean frequency of reorganizations; the probability that reorganization will take place within the interval  $(t, t + \Delta t)$ ,  $\Delta t \rightarrow 0$ , is  $\nu \Delta t$ . Thus, the probability that the lifetime  $\tau$  of the molecule on the laboratory time scale is from  $t$  to  $t + \Delta t$  (the time origin  $t = 0$  is identified with the moment of excitation) is

$$\begin{aligned} \text{Prob} \{t < \tau < t + \Delta t\} &= f(t) \Delta t = \\ &= \sum_{n=0}^{\infty} (\nu t)^n \exp(-\nu t) \prod_{i=0}^n (1 - p_i) \nu p_{n+1} \Delta t/n!, \end{aligned} \quad (1)$$

where  $f(t)$  is the lifetime probability density and  $p_0$  is zero by definition (reaction products are not immediately formed by the excitation process).

The statistical RRK model ( $\nu \rightarrow \infty$ )<sup>12,13</sup> of unimolecular decomposition and its more recent modification ( $0 < \nu < \infty$ )<sup>10,14,15</sup> are equivalent to the assumption that  $p_n = p$  where  $p$  is the stationary (microcanonical) probability of microstates corresponding to energy in the critical oscillator higher than  $\varepsilon_0$ . In the classical approximation<sup>12</sup>,  $p = (\varepsilon - \varepsilon_0)^{s-1}/\varepsilon^{s-1}$ , where  $s$  is the number of representative oscillators. The dependence of  $p_n$  on  $n$  expresses a gradual delocalization of energy, which is an effect that is considered plausible<sup>16,17</sup>. As  $n$  increases,  $p_n$  approaches monotonically the stationary value  $p$  (the relaxation mechanism of energy flow, rather than the oscillation mechanism, is assumed)<sup>18</sup>. If, immediately after the excitation, the energy is localized in the reaction coordinate or in its vicinity, then  $p_n$  decreases with increasing  $n$ , whereas if the energy is localized at a site distant from the reaction coordinate, then  $p_n$  increases with increasing  $n$ . A simple model of this

type is defined by the probabilities

$$p_n = q_1 \quad (0 < n \leq N) \quad (2a)$$

$$p_n = q_2 \quad (n > N), \quad (2b)$$

where  $N$  is an integer parameter characterizing the relaxation time of extinction of the memory of the molecule. With regard to the assumed relaxation mechanism of energy flow, we can put  $q_2 = p$ . For this model the molecule lifetime density can be derived from Eq. (1) in the form

$$f(t) = \sum_{n=0}^{N-1} (vt)^n \exp(-vt) (1 - q_1)^n vq_1/n! + \\ + [(1 - q_1)/(1 - q_2)]^N \sum_{n=N}^{\infty} (vt)^n \exp(-vt) (1 - q_2)^n vq_2/n!. \quad (3)$$

The Laplace transform of this density is

$$\mathcal{L}\{f(t)\} = (1 - q_1)^N / (1 + z/v)^N (1 + z/vq_2) + \\ + 1 / (1 + z/vq_1) - (1 - q_1)^N / (1 + z/v)^N (1 + z/vq_1), \quad (4)$$

where  $z$  is the transformation variable. The distribution moments can be readily derived from this transform. The mean lifetime of the molecule is

$$\bar{\tau} = 1/vq_1 + (1 - q_1)^N (1/vq_2 - 1/vq_1) \quad (5)$$

with the limiting values of  $N/v + 1/vq_2$  for  $q_1 \rightarrow 0$ ,  $1/vq_1$  for  $N \rightarrow \infty$  and  $1/vq_2$  for  $N = 0$ .

The dependence of  $p_n$  on  $n$  according to Eq. (2) represents, on the scale of number of events, a jump change in the probability of decomposition. Actually, the model might be improved by introducing some more complex dependence of  $p_n$  on  $n$ , such as  $p_n = q_1 \exp(-\lambda_1 n) + q_2(1 - \exp(-\lambda_2 n))$ ,  $\lambda_1, \lambda_2 > 0$ , or  $p_n = (q_1 + n\lambda_3 q_2) / (n\lambda_3 + 1)$ ,  $\lambda_3 > 0$ , but the experimental data would hardly make it possible to distinguish such dependences from the dependence (2).

## DISCUSSION

The density (3) is exponential for  $q_1 = q_2 (= p)$ , which corresponds to the statistical RRK model with a decomposition rate constant  $k(\varepsilon) = vp$ . Adopting this interpretation of the microcanonical rate constant  $k(\varepsilon)$  (which reminds us of the controversial<sup>19</sup> Slater's interpretation<sup>20</sup>), we obtain values of  $v \approx 10^{13} - 10^{14} \text{ s}^{-1}$  from experimental data of the rates of unimolecular reactions<sup>21,22</sup>. For  $q_1 \ll q_2$  (excita-

tion at a site distant from the reaction coordinate), the density  $f(t)$  exhibits a pronounced maximum (for the particular case of  $q_1 = 0$  see ref.<sup>3</sup>); for  $q_1 \gg q_2$  (excitation in the vicinity of the reaction coordinate) the density  $f(t)$  is inclined with respect to the exponential density and, to a crude approximation, corresponds to a superposition of the exponential functions  $vq_1 \exp(-vq_1 t)$  and  $vq_2(1 - q_1)^N \exp. [-vq_2(t - N/v)]$  (Fig. 1).

The nonexponential lifetime distribution is indicative of the occurrence of a temporary memory in the molecule; the shape of the distribution (position of the maximum, changes in skewness) enables the relaxation time of memory extinction to be estimated (in this model it is approximately  $N/v$ ). Experimental data of the rate of decomposition of chemically or photon activated excited polyatomic molecules indicate<sup>8,23-25</sup> that the information about the site of location of the excitation energy is lost in several picoseconds, so that the expected  $N$  values are on the order of  $10^2$  (the energy flow velocity  $\omega$  introduced previously<sup>10,13</sup> corresponds to the quantity  $v/N$  in this model). The process of gradual loss of information, however, has not yet been disclosed by a direct experiment (suitable systems making such observation possible have been devised recently by Reinhardt and Dunczky<sup>17</sup>).

The density  $f(t)$  cannot be determined from the experimental data directly. Let us consider a dissociation reaction  $A \rightarrow P + Q$  and assume that the excitation process produces, at time  $t = 0$ , an assembly of  $N_A(0)$  molecules A with excitation energy  $\varepsilon \pm \Delta\varepsilon$  where  $\Delta\varepsilon$  is small. At a time  $t > 0$  the system will contain  $N_A(t)$  undissociated molecules A and  $N_P(t) = N_Q(t) = N_A(0) - N_A(t)$  molecules P (or Q) (single-channel decomposition and a negligible rate of deexcitation are assumed, so that  $N_A(0) = N_P(\infty) = N_Q(\infty)$ ). The experimentally accessible concentration of A (or P) and the density  $f(t)$  are interrelated through

$$N_P(t) = N_A(0) - N_A(t) = N_A(0) \int_0^t f(t) dt. \quad (6)$$

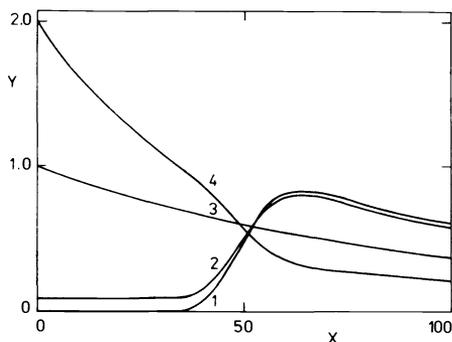


FIG. 1  
Molecular lifetime distribution according to Eq. (3).  $X = vt$ ,  $Y = f(t)/vq_2$ ;  $N = 50$ ,  $q_2 = 10^{-2}$ ,  $q_1$ : 1 0, 2  $10^{-3}$ , 3  $10^{-2}$ , 4  $2 \cdot 10^{-2}$

The density  $f(t)$  can be derived from the variation of concentration of one of the decomposition products with time:

$$f(t) = dN_p(t)/N_A(0) dt . \quad (7)$$

Implicit assumptions for this way of determination of  $f(t)$  are a sufficiently short excitation process, enabling the time origin to be well-defined, and a sufficiently narrowly defined excitation energy width. These conditions could be satisfied by the laser femtosecond technology<sup>6,7</sup>.

The density  $f(t)$  is interrelated with the decomposition rate constant  $k(\varepsilon)$  through

$$k(\varepsilon) = -dN_A(t)/N_A(t) dt = f(t)/\int_t^\infty f(t) dt . \quad (8)$$

The probability that an excited molecule undecomposed at time  $t$  will decompose in the interval  $(t, t + dt)$  (the so-called infinitesimal transition probability) is  $k(\varepsilon) dt$ . The constant  $k(\varepsilon)$  is time independent if and only if  $f(t)$  is exponential density, the molecule behaves like a chaotic memoryless system, and the dissociation process obeys the exponential decomposition law. For  $q_1 \neq q_2$  the dependence of  $k(\varepsilon)$  on  $t$  has a sigmoid shape with the limits  $vq_1$  for  $t \rightarrow 0$  and  $vq_2$  for  $t \rightarrow \infty$  and with the inflection point at  $t \approx N/v$ .

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