

# EXPONENTIAL LIFETIMES DISTRIBUTION AND INTERNAL DYNAMICS OF ENERGIZED POLYATOMIC MOLECULES

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It is shown that the assumption of an exponential distribution of the lifetimes of energized molecules involved in the RRKM theory of unimolecular decomposition is fulfilled if the reacting molecule represents a dynamic system with the property of mixing in the phase space. If the rate of mixing is large in comparison with the decomposition proper, then the ensemble of molecules with energies from  $\varepsilon$  to  $\varepsilon + \delta\varepsilon$  is represented in the course of the decomposition by a microcanonical ensemble. The mean lifetime of the molecules is then independent of the choice of the origin of the time scale and is equal to the reciprocal value of the specific decomposition rate.

The assumption of an exponential distribution of lifetimes of isolated energized molecules (*i.e.*, molecules with internal energy greater than the critical energy of decomposition) is one of the postulates of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular reactions<sup>1–3</sup>. The question is whether this postulate can be interpreted with the aid of more general concepts about the internal dynamics of the energized molecule and on a statistical-mechanical basis. An attempt in this sense was made in a recent study<sup>4</sup> on the properties of the lifetimes distribution and in the present work the original concept is further developed. The energized molecule is considered as a dynamic system obeying the laws of classical mechanics; its instantaneous state is characterized by a point in the phase space of internal coordinates  $q_i$  and conjugated momenta  $p_i$ .

## *Definition of Lifetimes Distribution Function*

We shall consider a polyatomic molecule A characterized by internal coordinates  $q_1, \dots, q_n$  and momenta  $p_1, \dots, p_n$ . The phase space  $(q_1, \dots, p_n)$  is divided by a  $(2n-1)$ -dimensional hypersurface  $\eta(q_1, \dots, p_n) = 0$  into a part corresponding to the original molecule A ( $\eta < 0$ ) and a part corresponding to its decomposition products ( $\eta > 0$ ) (by decomposition we mean dissociation or isomerization of the molecule). The equation  $H(q_1, \dots, p_n) = \varepsilon = \text{const.}$ , where  $H(q_1, \dots, p_n)$  is the internal Hamiltonian of the molecule, defines a  $(2n-1)$ -dimensional hypersurface of constant

energy  $\varepsilon$ . The decomposition of the molecule A with energy  $\varepsilon > \varepsilon_D$  ( $\varepsilon_D$  denotes dissociation or isomerization energy) corresponds to a transition of a representative point moving on the hypersurface of constant energy  $\varepsilon$  through the boundary  $\eta = 0$  towards increasing values of  $\eta$ . In the part of the phase space corresponding to the original molecule A with energy  $\varepsilon > \varepsilon_D$  we can assign to every point a positive quantity  $\tau(q_1, \dots, p_n)$  equal to the time interval between realization of the state  $q_1, \dots, p_n$  and the first transition of the isolated molecule through the boundary  $\eta = 0$  (the lifetime of the isolated molecule with respect to the decomposition). All states with energy  $\varepsilon < \varepsilon_D$  are stable with respect to the decomposition; it cannot be excluded that stable states exist even for  $\varepsilon > \varepsilon_D$  (the inequality  $\varepsilon > \varepsilon_D$  is only a necessary condition for the decomposition).

Let  $\delta V(\varepsilon)$  be a part of the phase space enclosed by the hypersurfaces of energies  $\varepsilon$  and  $\varepsilon + \delta\varepsilon$ ,  $\varepsilon > \varepsilon_D$ . The part  $\delta V(\varepsilon)$  corresponding to the undecomposed molecule A ( $\eta < 0$ ) will be denoted as  $\delta V_A(\varepsilon)$ , that corresponding to the decomposition products ( $\eta > 0$ ) as  $\delta V_B(\varepsilon)$ . The activation process realizing at time  $t = 0$  the states in  $\delta V_A(\varepsilon)$  is described by the density of states in  $\delta V_A(\varepsilon)$  at time  $t = 0$ ,  $\varrho_\varepsilon(q_1, \dots, p_n; 0)$  i.e., the probability that the activation process realizes the state whose representative point lies in the infinitesimal volume  $dq_1 \dots dp_n$  surrounding the point  $q_1, \dots, p_n$  in  $\delta V_A(\varepsilon)$  is proportional to the product  $\varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1 \dots dp_n$ .

In the volume  $\delta V_A(\varepsilon)$  we introduce a function of a nonnegative parameter  $s$ ,

$$F_\varepsilon(s)_0 = \int \dots \int h(s - \tau(q_1, \dots, p_n)) \varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1 \dots dp_n / \int \dots \int \varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1 \dots dp_n. \quad (1)$$

Here  $h(s - \tau(q_1, \dots, p_n))$  denotes Heaviside step function and  $\int \dots \int \dots dq_1 \dots dp_n$   $2n$ -fold integral over the volume  $\delta V_A(\varepsilon)$ . If the molecule A represents a dynamic system which is ergodic<sup>5</sup> in  $\delta V(\varepsilon)$ , there does not exist another constant of motion than  $\varepsilon$  and a trajectory starting at any point in  $\delta V_A(\varepsilon)$  passes finally through the boundary  $\eta = 0$ . The inequality  $\varepsilon > \varepsilon_D$  is then also a sufficient condition for the decomposition. In this case we have

$$\lim_{s \rightarrow \infty} (1 - F_\varepsilon(s)_0) = \lim_{s \rightarrow \infty} \int \dots \int h(\tau(q_1, \dots, p_n) - s) \varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1, \dots, dp_n / \int \dots \int \varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1 \dots dp_n = 0. \quad (2)$$

The function  $F_\varepsilon(s)_0$  can be interpreted as a distribution function of the random

variable  $\tau(\varepsilon)$  – the lifetime of molecules A with energy from  $\varepsilon$  to  $\varepsilon + \delta\varepsilon$ : the probability that a molecule A chosen randomly from the ensemble of molecules in  $\delta V_A(\varepsilon)$  characterized at time  $t = 0$  by a phase density  $\varrho_\varepsilon(q_1, \dots, p_n; 0)$  will have a lifetime smaller than  $s$  is  $\text{Prob}\{\tau(\varepsilon) < s\} = F_\varepsilon(s)_0$ . (The introduction of a distribution function of lifetimes also for molecules representing a nonergodic system was discussed earlier<sup>4</sup>.)

The probability density of lifetimes of molecules A in  $\delta V_A(\varepsilon)$  is defined as

$$f_\varepsilon(s)_0 = dF_\varepsilon(s)_0/ds \quad (3)$$

and the mean lifetime of molecules A in  $\delta V_A(\varepsilon)$  is

$$\begin{aligned} \overline{\tau(\varepsilon)}_0 &= \int_0^\infty s f_\varepsilon(s)_0 ds = \langle \tau(q_1, \dots, p_n) \rangle_0 = \int \dots \int \tau(q_1, \dots, p_n) \\ &\varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1 \dots dp_n / \int \dots \int \varrho_\varepsilon(q_1, \dots, p_n; 0) dq_1 \dots dp_n \end{aligned} \quad (4)$$

on the assumption that these integrals converge.

#### *The Property of Mixing in Phase Space*

We assume that at a time  $t = 0$  an ensemble of mutually noninteracting molecules A with a phase space density  $\varrho_\varepsilon(q_1, \dots, p_n; 0)$  in  $\delta V_A(\varepsilon)$  is prepared by some activation process. At a time  $t > 0$  this ensemble will be characterized by a phase space density  $\varrho(q_1, \dots, p_n; t)$  which will generally differ from the initial density. A change in the density occurs owing both to the internal dynamics of the original molecules A and to the transition of some molecules A from  $\delta V_A(\varepsilon)$  to  $\delta V_B(\varepsilon)$ . The ensemble of molecules at time  $t$  formed from the original one can be considered as a new starting ensemble and we can define for it a distribution function  $F_\varepsilon(s)_t$ , density  $f_\varepsilon(s)_t$ , and mean value  $\overline{\tau(\varepsilon)}_t$  of lifetimes of molecules A with respect to the origin of the time scale at time  $t$ . We have obviously

$$F_\varepsilon(s)_t = (F_\varepsilon(t+s)_0 - F_\varepsilon(t)_0) / (1 - F_\varepsilon(t)_0), \quad (5)$$

$$f_\varepsilon(s)_t = f_\varepsilon(t+s)_0 / (1 - F_\varepsilon(t)_0), \quad (6)$$

$$\overline{\tau(\varepsilon)}_t = \int_t^\infty (1 - F_\varepsilon(\xi)_0) d\xi / (1 - F_\varepsilon(t)_0). \quad (7)$$

The ensemble mean value of the quantity  $X(q_1, \dots, p_n)$  at time  $t$  is

$$\langle X(q_1, \dots, p_n) \rangle_t = \int \dots \int X(q_1, \dots, p_n) \varrho_\varepsilon(q_1, \dots, p_n; t) dq_1 \dots dp_n / \int \dots \int \varrho_\varepsilon(q_1, \dots, p_n; t) dq_1 \dots dp_n \quad (8)$$

The dynamic system with the property of mixing<sup>6</sup> obeys the limit law

$$\lim_{t \rightarrow \infty} \langle X(q_1, \dots, p_n) \rangle_t = \int \dots \int X(q_1, \dots, p_n) dq_1 \dots dp_n / \int \dots \int dq_1 \dots dp_n, \quad (9)$$

*i.e.*, the ensemble mean value of the dynamic function approaches the equilibrium microcanonical value of this quantity.

We now shall assume that the molecule A fulfils the mixing property in  $\delta V_A(\varepsilon)$  and the decomposition rate of molecules A (*i.e.*, their transition from  $\delta V_A(\varepsilon)$  to  $\delta V_B(\varepsilon)$ ) is much slower than the rate at which  $\langle X(q_1, \dots, q_n) \rangle_t$  attains its microcanonical mean value (the mixing rate in the phase space is large as compared with the rate of loss of the molecules from  $\delta V_A(\varepsilon)$ ). Let the system at time  $t = 0$  be represented by a microcanonical ensemble. On the assumption of rapid mixing, this will be true also during the decomposition (this corresponds to the quasiequilibrium hypothesis of the RRKM theory), and the ensemble mean value of an arbitrary function of coordinates and conjugated momenta will be independent of the time. Then

$$F_\varepsilon(s)_0 = \langle h(s - \tau(q_1, \dots, p_n)) \rangle_0 = \langle h(s - \tau(q_1, \dots, p_n)) \rangle_t = F_\varepsilon(s)_t \quad (10)$$

Hence it follows that  $F_\varepsilon(t + s)_0 = F_\varepsilon(t + s)_t$  and  $F_\varepsilon(t)_0 = F_\varepsilon(t)_t$ ; if we introduce these expressions into (5), we obtain after rearrangement

$$(1 - F_\varepsilon(s)_t)(1 - F_\varepsilon(t)_t) = 1 - F_\varepsilon(t + s)_t; \quad t, s > 0. \quad (11)$$

By solving this functional equation<sup>7</sup> we obtain

$$1 - F_\varepsilon(s)_t = \exp(-\lambda_\varepsilon s), \quad \lambda_\varepsilon > 0, \quad (12)$$

where  $\lambda_\varepsilon$  is a parameter independent of  $t$  and  $s$ . Hence,  $F_\varepsilon(s)_0 = F_\varepsilon(s)_t = 1 - \exp(-\lambda_\varepsilon s)$  and  $f_\varepsilon(s)_0 = f_\varepsilon(s)_t = \lambda_\varepsilon \exp(-\lambda_\varepsilon s)$ , which is the exponential probability density corresponding to the decomposition rate of molecules A in the considered ensemble according to a kinetic first-order equation. The mean lifetime is  $\overline{\tau(\varepsilon)}_0 = \overline{\tau(\varepsilon)}_t = 1/\lambda_\varepsilon$ .

The form of the lifetimes distribution of molecules for the system with the property

of rapid mixing can be derived also in an alternative manner: If the ensemble mean value of an arbitrary function of the coordinates and momenta is independent of the time, then also according to Eq. (7)

$$\overline{\tau(\varepsilon)}_t = \int_t^\infty (1 - F_\varepsilon(\xi)_0) d\xi / (1 - F_\varepsilon(t)_0) = 1/\lambda_\varepsilon = \text{const.}, \quad (13)$$

and after differentiation  $f_\varepsilon(t)_0 / (1 - F_\varepsilon(t)_0) = \lambda_\varepsilon$  (the random quantity  $\tau(\varepsilon)$  is memoryless). Solution of this equation gives  $1 - F_\varepsilon(t)_0 = \exp(-\lambda_\varepsilon t)$  and  $f_\varepsilon(t)_0 = \lambda_\varepsilon \exp(-\lambda_\varepsilon t)$ , which on introducing into Eq. (6) gives the exponential density  $f_\varepsilon(s)_t = \lambda_\varepsilon \exp(-\lambda_\varepsilon s)$ .

The obtained result suggests that the property of rapid mixing is a sufficient condition for the distribution of molecules lifetimes to be exponential. The decomposition of the molecules in the ensemble is then characterized by a single constant – specific rate of the decomposition<sup>4</sup>

$$\kappa_\varepsilon(s)_t = \kappa_\varepsilon(s + t)_0 = f_\varepsilon(s)_t / (1 - F_\varepsilon(s)_t) = \lambda_\varepsilon, \quad (14)$$

which does not depend on the time and is a function only of the total internal energy  $\varepsilon$ .

If the property of rapid mixing in the phase space is fulfilled, then it can be expected that the lifetimes distribution will be in general exponential (except for values of  $t$  close to zero) even when the starting density  $\rho_\varepsilon(q_1, \dots, p_n; 0)$  is not uniform, since in a short time interval after activation the ensemble becomes an equilibrium microcanonical ensemble. The way of the activation is then unessential for the kinetics of the decomposition (we note that the property of rapid mixing in the phase space represents a more general formulation of the concept of rapid intramolecular energy redistribution introduced in model theories of unimolecular reactions<sup>8</sup>). The mixing property can be expected with systems of anharmonic oscillators with strong mutual interactions<sup>6</sup>. Studies of the trajectories in the phase space show indeed that the distribution of lifetime of molecules modelled by anharmonic oscillators does not depend on the type of activation and is nearly exponential after a time of about 15 vibration cycles (about  $10^{-13}$  s) elapsed from the activation<sup>9</sup>. It was also proved<sup>4</sup> that the introduction of a rapid intramolecular redistribution of energy among the representative oscillators into Slater's harmonic (nonergodic) model of the unimolecular decomposition<sup>10</sup> leads to lifetime densities close to the exponential density.

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