Classical dynamics of a coupled double well oscillator in condensed media. II

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Classical dynamics of a coupled double well oscillator in condensed media. II[a]

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The influence exerted on reaction processes by the coupling between the reaction coordinate x and transverse nonreactive modes is discussed. Attention is mainly focused on the synergism of inertia and multiplicative fluctuation, which enhances the reaction rate throughout a wide domain, ranging from the high to the low-friction region. The high-friction region is explored by applying the adiabatic elimination procedure (AEP) described in the first paper of this series: When the relaxation time of x is larger than that of the nonreactive mode, a new term occurs. This term is shown to be responsible for making the "noise-induced phase transition effects" discussed in the first paper more pronounced. The low-friction region is explored with a first-passage time procedure by using energy as the slow variable. The synergism of inertia and multiplicative noise is then shown to produce finite reaction rates even in conditions where Kramers theory predicts them to be vanishingly small.

I. INTRODUCTION

In an earlier paper,[1] henceforward called paper I, we used the framework of the classical (stochastic) dynamics to study the influence of nonreactive normal modes on a chemical reaction. When the irrelevant dynamics, i.e., that of the nonreactive normal modes, is much faster than the reactant dynamics, we can replace the actual reaction potential with an effective one obtained via a suitable averaging over the equilibrium distribution of the nonreactive normal modes. This effective potential makes more energy available for motion along the reaction coordinate thereby speeding up the chemical reaction. This is the classical counterpart of the quantum-mechanical effect found by Christoffel and Bowman.[2] We refer to this as a *standard* adiabatic effect. In paper I we focused our attention on *nonstandard* adiabatic effects, i.e., significant contributions to the increase of the reaction rate coming from the interaction between reactive and nonreactive modes, which cannot be interpreted using a modified potential.

To stress the elements of novelty of the present paper, it is worthwhile to review the basic approximations underlying the analytical results of paper I. Let x be the reaction coordinate with a potential $\Phi(x)$, a friction γ, and a stochastic force $f(t)$; this coordinate is coupled to a harmonic transverse mode y which has a friction λ and a stochastic force $f'(t)$:

$$\dot{x} = v,$$
$$\dot{v} = -\Phi'(x) - \gamma v - \Psi'(x)y^2 + f(t),$$
$$\dot{y} = w, \qquad\qquad (1.1)$$
$$\dot{w} = -\lambda w - 2y\Psi(x) - y\omega_0^2 + f'(t).$$

$f(t)$ and $f'(t)$ are independent white Gaussian noises defined by

$$\langle f(0)f(t)\rangle = 2D\delta(t),$$
$$\langle f'(0)f'(t)\rangle = 2D'\delta(t). \qquad (1.2)$$

Variables x and y interact with one another via the coupling potential $\Psi(x)y^2$, where we assume

$$\Psi(x) = -\frac{\omega_0^2}{2}\lambda_{\text{int}}\,e^{-x^2/r^2}. \qquad (1.3)$$

The reaction potential is

$$\Phi(x) = \frac{V_0}{a^4}(x^2 - a^2)^2. \qquad (1.4)$$

Both $\Psi(x)$ and $\Phi(x)$ are the same as those used in paper I. ω_0 is the frequency of the nonreactive normal mode.

Throughout the present paper we shall assume for simplicity that the nonreactive mode is overdamped, i.e., $\lambda \gg 2\omega_0$. This will allow us to replace Eqs. (1.1) by

$$\dot{x} = v,$$
$$\dot{v} = -\Phi'(x) - \gamma v - \Psi'(x)y^2 + f(t),$$
$$\dot{y} = -\frac{2}{\lambda}y\Psi(x) - \frac{y}{\lambda}\omega_0^2 + \frac{f'(t)}{\lambda}. \qquad (1.5)$$

To clarify the role of nonstandard adiabatic effects, the situation where the reactive mode is also overdamped (i.e., $\gamma \gg 4\sqrt{V_0}/a$) was discussed in paper I; Eqs. (1.5) then take the form

$$\dot{x} = -\frac{1}{\gamma}\Phi'(x) - \frac{1}{\gamma}\Psi'(x)y^2 + \frac{f(t)}{\gamma}, \qquad (1.6)$$
$$\dot{y} = -\frac{2}{\lambda}y\psi(x) - \frac{y}{\lambda}\omega_0^2 + \frac{f'(t)}{\lambda} \quad \text{(scheme A)}.$$

The relaxation dynamics of y has to be assumed faster,

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though not infinitely faster, than the reaction dynamics. This is a basic prerequisite for the application of the adiabatic elimination procedure (AEP) of paper I, implying that

$$\Gamma_x \equiv \frac{\omega_0'^2}{\gamma} < \Gamma_y \equiv \frac{\omega_0^2}{\lambda}, \tag{1.7}$$

where Γ_x^{-1} and Γ_y^{-1} denote x and y time scales, respectively. [$\omega_0' = \sqrt{4V_0/a^2}$ is the imaginary frequency of $\Phi(x)$ at the origin, $x = 0$.]

A major aim of the present paper is to discuss the role played by the inertia of coordinate x, which is completely disregarded when using the scheme of calculation from Eqs. (1.6). It is convenient to express the relaxation time of the irrelevant variable v, $1/\gamma$, in units of the relaxation time of the other irrelevant variable y, i.e., via the ratio of $1/\gamma$ to $1/\Gamma_y$,

$$R = \Gamma_y/\gamma = \omega_0^2/(\lambda\gamma). \tag{1.8}$$

Scheme A applies when $R \ll 1$. In the present paper we shall show that a novel *nonstandard* adiabatic effect comes into existence when exploring the region $R \sim 1$, while still assuming both Γ_y and γ very large. To this end we apply the AEP to Eqs. (1.5), while regarding both v and y as fast variables. This will be referred to as the scheme B of calculation.

To shed further light into the role of inertia, we shall consider also the case when both x and v are slow variables (scheme C below).

The formalisms of the three schemes of calculation just mentioned are presented in Sec. II and results obtained in each of these schemes by a continued fraction numerical procedure are compared. To explore further into the inertial region, we introduce in Sec. III a first-passage time procedure with the energy as the slow variable.

This research has been stimulated by the theoretical remarks of Graham and Schenzle[3] on the role of inertia in a system belonging to the same family as that of Eqs. (1.5).

II. THE ROLE OF INERTIA IN THE HIGH-FRICTION REGIME

Within scheme A, the AEP described in Sec. II of paper I leads to

$$\frac{\partial}{\partial t}\rho(x,t) = \left\{ \frac{\langle y^2\rangle}{\gamma}\frac{\partial}{\partial x}\Psi'(x) + \frac{1}{\gamma}\frac{\partial}{\partial x}\Phi'(x) \right. $$
$$+ \frac{\langle v^2\rangle}{\gamma}\frac{\partial^2}{\partial x^2}\bigg\}\rho(x,t) + \frac{\lambda}{\omega_0^2}\frac{\langle y^2\rangle}{\gamma}\frac{\partial}{\partial x}\Psi'(x)$$
$$\left\{ \frac{\langle y^2\rangle}{\gamma}\frac{\partial}{\partial x}\Psi'(x) - \frac{2}{\lambda}\Psi(x) \right\}\rho(x,t). \tag{2.1}$$

The term

$$\frac{\langle y^2\rangle}{\gamma}\frac{\partial}{\partial x}\Psi'(x) \tag{2.2}$$

is responsible for the adiabatic effects of *standard* type. The last term on the right-hand side of Eq. (2.1) can be written

$$\frac{\lambda}{\omega_0^2}\frac{\langle y^2\rangle^2}{\gamma^2}\frac{\partial^2}{\partial x^2}[\Psi'(x)]^2 - \frac{\lambda}{\omega_0^2}\frac{\langle y^2\rangle^2}{\gamma^2}\frac{\partial}{\partial x}\Psi'(x)\Psi''(x)$$
$$- \frac{2}{\omega_0^2}\frac{\langle y^2\rangle}{\gamma}\frac{\partial}{\partial x}\Psi'(x)\Psi(x). \tag{2.3}$$

When a large amount of energy is pumped into the transverse mode, the third term of Eq. (2.3) can be neglected. According to the discussion given in detail, e.g., in Ref. 4, the interplay between the remaining two terms is proven to be responsible for "noise-induced phase transition" phenomena. As shown in paper I, the same analytical form as that discussed in Ref. 4 can be recovered when $r \gg a$ and the additive stochastic force is neglected.

As $\langle y^2\rangle$ increases, the reactant equilibrium distribution shifts towards the center of the barrier which separates the reactant from the product regions until a sort of threshold is reached. After this threshold, the largest part of the reactant population is found to be close to the center of the barrier (on the reactant side). This is indeed a chemical activation which results in a dramatic increase of the chemical reaction rate when the additive stochastic force is properly taken into account.

In scheme B, both v and y are assumed to be fast variables when compared to x,

$$\Gamma_x \ll \Gamma_y, \gamma, \tag{2.4}$$

with Γ_x and Γ_y defined in Eq. (1.7). Starting from Eqs. (1.5), the AEP of paper I may be applied leading to

$$\gamma\frac{\partial}{\partial t}\rho(x,t) = -\frac{\partial}{\partial x}\left[-\Phi'(x) - \langle y^2\rangle\Psi'(x) + 2\frac{\langle y^2\rangle}{\omega_0^2}\Psi(x)\Psi'(x) \right.$$
$$+ \frac{\langle y^2\rangle^2}{R\gamma^2}\Psi'(x)\Psi''(x) - \frac{\partial}{\partial x}\left(\frac{\langle y^2\rangle^2}{R\gamma^2}[\Psi'(x)]^2 + \frac{\langle v^2\rangle}{\gamma} \right)$$
$$\left. - \frac{2\langle y^2\rangle^2}{\gamma^2(1+2R)}\Psi'(x)\Psi''(x) - \frac{4\langle y^2\rangle}{(\omega_0^2)^2}\Psi'(x)\Psi^2(x) \right]\rho(x,t). \tag{2.5}$$

To derive Eq. (2.5), terms up to the fourth order in the perturbation expansion[1] have to be used, while the same level of approximation is obtained in scheme A [Eq. (2.1)] with terms up to the second order only. Indeed, the assumption of no inertia implied in scheme A generates *ipso facto* second-order perturbation terms. Scheme B, however, generates two new terms, the last two on the right-hand side of Eq. (2.5). The first plays a major role, especially when the parameter

$\langle y^2\rangle$ is given large values. For vanishing small values of R, however, even this term becomes negligible compared to the fourth term of the same equation, thereby allowing the result of scheme A to be recovered. Hence, schemes A and B are equivalent in the region $R \ll 1$ and scheme B will be used to explore the region $R \sim 1$. For large R, the two terms cancel each other out in accordance with a similar result already obtained by Graham and Schenzle.[3] The effect of these new
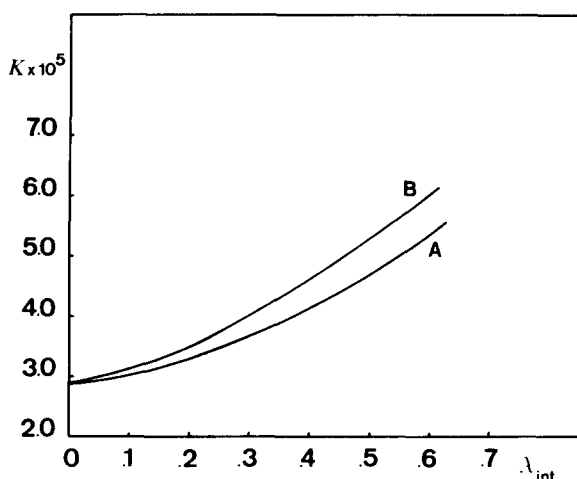
FIG. 1. Comparison between the decay rates K as calculated in the two schemes A and B using the continued fraction procedure. The parameters were given the values: $V_0 = 2 \times 10^{-7}$, $a^2 = 0.5$, $r = 0.5 \times a$, $R = \frac{1}{3}$, and $\langle y^2 \rangle \omega_0^2 = \langle w^2 \rangle = \langle v^2 \rangle = 1 \times 10^{-7}$. Atomic units are used throughout.

FIG. 2. Variation of the reaction rate K while increasing the energy in the nonreactive mode. A comparison is made between schemes A and B. The parameters were given the values: $\lambda_{int} = 0.5$, $V_0 = 2 \times 10^{-7}$, $\langle v^2 \rangle = 1 \times 10^{-7}$, $R = \frac{1}{3}$, $a = 0.5$, and $r = 2 \times a$. The threshold value of $\langle y^2 \rangle \omega_0^2$ for the noise-induced phase transition is about 6×10^{-6}. $K_0 = 1.2 \times 10^{-5}$ is the K value when $\langle w^2 \rangle = \langle v^2 \rangle$.

terms is reminiscent of the standard adiabatic effect introduced by the term (2.2). A detailed analysis shows that these terms cooperate to reduce the height of the effective barrier, thereby rendering the chemical reaction even faster. Results of calculations within schemes A and B are compared in Figs. 1 and 2. They show that the effect of the new terms obtained in scheme B becomes especially noticeable when the constraint of energy equipartition

$$\langle v^2 \rangle = \omega_0^2 \langle y^2 \rangle \qquad (2.6)$$

is released. This may be obtained by pumping energy in some way (e.g., by a selective radiation field) into the nonreactive mode only. On the other hand, this seems to be the only straightforward mechanism to reach the threshold for the noise-induced phase transition. Figure 2 shows in particular that the influence of the first new term is especially significant in the threshold region.
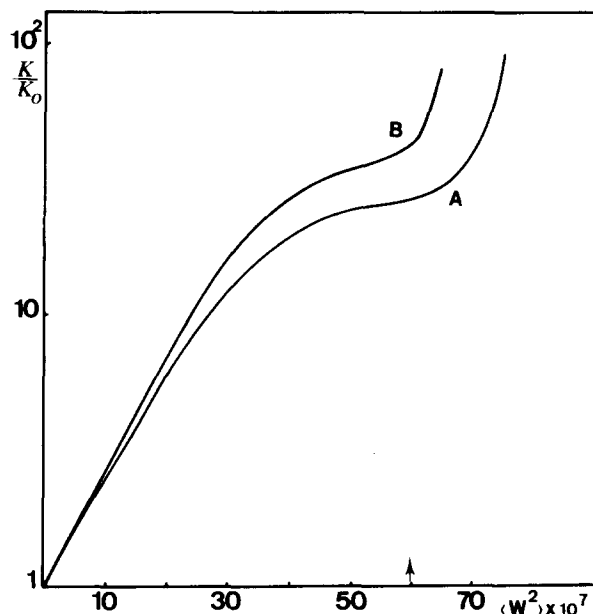
These interesting results stimulated us to explore the inertial regime, i.e., the region on $\gamma \sim \omega_0'$. Indeed, we are led to believe that the influence of multiplicative fluctuations on the reaction rate should be magnified in this regime. To this end, we introduce now scheme C (cf. Sec. I). Variables x and v are assumed to be slow when compared to y:

$$\Gamma_x, \gamma \ll \Gamma_y . \qquad (2.7)$$

Applying the AEP to Eqs. (1.5) we obtain the equation of motion of the joint probability distribution of the two slow variables:

$$\frac{\partial}{\partial t} \rho(x,v,t) = \left\{ - v \frac{\partial}{\partial x} + \frac{\partial}{\partial v} \Phi'(x) + \frac{\partial}{\partial v} \gamma v + \frac{\partial}{\partial v} \Psi'(x) \langle y^2 \rangle + \frac{\partial^2}{\partial v^2} \gamma \langle v^2 \rangle \right.$$
$$\left. - \frac{2}{\omega_0^2} \frac{\partial}{\partial v} \langle y^2 \rangle \Psi'(x) \Psi(x) + \frac{\partial^2}{\partial v^2} \langle y^2 \rangle \frac{\lambda}{\omega_0^2} [\Psi'(x)]^2 \right\} \rho(x,v,t) . \qquad (2.8)$$

The fourth term on the right-hand side of Eq (2.8) gives the standard adiabatic effect. The fifth and seventh terms give, in the overdamped region, the nonstandard adiabatic effects found in scheme B above.

In Fig. 3, the chemical rate K is displayed as a function of $R = (\omega_0^2/\lambda)/\gamma$. In the high-friction region (large γ, small R), we obtain a linear dependence on $1/\gamma$, in agreement with the classical Kramers result.[5]

As λ_{int} increases, we obtain straight lines of increasing slope. This is a further manifestation of the role played by inertia: The sensibility of the reaction rate K to λ_{int} increases as the reacting system becomes more inertial (smaller γ).

For large values of R, the lines start bending down, a

sign that the intermediate friction regime is being approached. Unfortunately, the method of computation used fails in that region. The numerical computations are made using a continued fraction procedure[6] which has convergence difficulties for large R.

III. THE ROLE OF NONREACTIVE MODES IN THE ENERGY-CONTROLLED REGIME

The energy-controlled regime is currently becoming of increasing interest as testified by Refs. 7 and 8 and many other papers quoted there. The important role played by the interaction between reactive and nonreactive modes can be assessed by some remarks on Eq. (2.8). Let us consider the
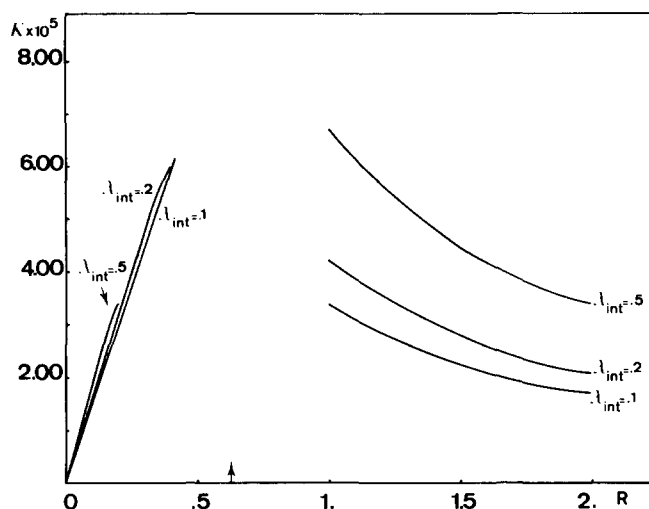
FIG. 3. Synergism of inertia and multiplicative fluctuation. Variation of the reaction rate throughout a wide domain, ranging from the high to the low-friction region. The curves on the left-hand side were obtained using the continued fraction procedure and those on the right-hand side were obtained by the first passage time technique. The arrow denotes the value of γ for which, in accordance with Larson and Kostin,[13] the diffusional regime ceases to be valid in the uncoupled case. The parameters were given the values: $V_0 = 2 \times 10^{-7}$, $a = 0.5$, $r = 2 \times a$, and $\langle y^2 \rangle \omega_0^2 = \langle v^2 \rangle = \langle w^2 \rangle = 1 \times 10^{-7}$.

case where $\langle y^2 \rangle = 0$. If $\gamma \langle v^2 \rangle$ is also assumed to vanish, Eq. (2.8) describes a purely deterministic process and the overcoming of the barrier is rigorously forbidden when the total energy of the reactant is lower than the barrier height. However, when the coupling between reacting and nonreacting modes is restored, the reactant undergoes the influence of the fluctuations acting on the nonreacting mode and this can supply enough energy for the reactant to overcome the barrier. Fluctuations become ineffective near the top of the barrier, where their intensity vanishes as implied by $\Psi'(0) = 0$ [cf. Eq. (1.3)]. This means that inertia is absolutely necessary for the barrier to be really overcome. As a result of such a synergism between inertia and multiplicative fluctuation, the chemical reaction can take place even when Kramers theory[5] predicts vanishingly small rates.

This is quite an interesting property, a quantitative discussion of which requires that a point of view completely different from that which inspired Sec. II be adopted. To derive a Fokker–Planck equation for the energy, we follow Lindenberg and Seshadri[9] who used energy and displacement as independent variables.

We define the energy E as follows:

$$E = \frac{v^2}{2} + \Theta(x),\tag{3.1}$$

where

$$\Theta(x) = \Phi(x) + \Psi(x)\langle y^2 \rangle - [\Psi(x)]^2 \frac{\langle y^2 \rangle}{\omega_0^2}.\tag{3.2}$$

After some manipulations, Eq. (2.8) can be rewritten in terms of the new pair of variables (x, E):

$$\frac{\partial}{\partial t}\rho(x,E,t) = \left[-\frac{\partial}{\partial x}[2(E - \Theta(x))] + \frac{\partial}{\partial E}\left\{ \gamma[2(E - \Theta(x))] - \gamma\langle v^2\rangle - [\Psi'(x)]^2\langle y^2\rangle^2\frac{\lambda}{\omega_0^2} \right\} \right.$$
$$\left. + \frac{\partial^2}{\partial E^2}\left\{ \left[\gamma\langle v^2\rangle + [\Psi'(x)]^2\langle y^2\rangle^2 \frac{\lambda}{\omega_0^2} \right][2(E - \Theta(x))] \right\} \right]\rho(x,E,t).\tag{3.3}$$

Note that, in the absence of the additive and multiplicative stochastic forces corresponding to the last two terms on the right-hand side of Eq. (2.8), E as defined by Eq. (3.1) would be a constant of the motion, rigorously independent of time.

Under the influence of these fluctuations, E becomes time dependent but its dynamics will certainly be very slow when compared to the dynamics of the variable x. This leads us to assume that

$$\rho(x,E,t) = \sigma(E,t)\frac{1}{2\varphi'(E)[E - \Theta(x)]^{1/2}},\tag{3.4}$$

where the prime denotes a derivative with respect to the argument and

$$\varphi(E) = \int dx(E - \Theta(x))^{1/2}\tag{3.5}$$

with the integration extending over a domain that includes all values of x for which $E \geqslant \Theta(x)$. The approximation behind Eq. (3.4) was suggested by the paper of Lindenberg and Seshadri,[9] who, in turn, followed a procedure introduced by Stratonovich.[10]

When replacing Eq. (3.4) into Eq. (3.3) and integrating the latter one over x, we obtain

$$\frac{\partial}{\partial t}\sigma(E,t) = \left\{ -\frac{\partial}{\partial E}\left[-\gamma\frac{\varphi(E)}{\varphi'(E)} + \gamma\langle v^2\rangle + \frac{\lambda_{int}^2}{r^4}\frac{\langle y^2\rangle^2}{\omega_0^2}\lambda\frac{\chi'(E)}{\varphi'(E)} \right] \right.$$
$$\left. + \frac{1}{2}\frac{\partial^2}{\partial E^2}\left[2\gamma\langle v^2\rangle\frac{\varphi(E)}{\varphi'(E)} + 2\frac{\lambda_{int}^2}{r^4}\langle y^2\rangle^2\frac{\lambda}{\omega_0^2}\frac{\chi(E)}{\varphi'(E)} \right] \right\}\sigma(E,t),\tag{3.6}$$

with

$$\chi(E) = \int dx \, x^2 e^{-2x^2/r^2} [E - \Theta(x)]^{1/2} , \qquad (3.7)$$

where the region of integration is the same as in Eq. (3.5) and the explicit form of $\Psi(x)$ as given by Eq. (1.3) is used.

To evaluate the chemical reaction rate via Eq. (3.6), we adopted the first-passage time method.[10,11] The mean first-passage time τ_{E_0} is calculated by

$$\tau_{E_0} = 2 \int_{E_0}^{V_{max}} e^{-U(E)} dE \int_0^E \frac{e^{U(E')}}{K_2(E')} dE' , \qquad (3.8)$$

where

$$U(E) = 2 \int_0^E \frac{K_1(E')}{K_2(E')} dE' , \qquad (3.9)$$

$$K_1(E) = -\gamma \frac{\varphi(E)}{\varphi'(E)} + \gamma\langle v^2 \rangle + \frac{\lambda_{int}^2}{r^4} \langle y^2 \rangle^2 \frac{\lambda}{\omega_0^2} \frac{\chi'(E)}{\varphi'(E)} , \qquad (3.10)$$

$$K_2(E) = 2\gamma\langle v^2 \rangle \frac{\varphi(E)}{\varphi'(E)} + 2 \frac{\lambda_{int}^2}{r^4} \langle y^2 \rangle^2 \frac{\lambda}{\omega_0^2} \frac{\chi(E)}{\varphi'(E)} , \qquad (3.11)$$

and V_{max} is the height of the barrier as given by the effective potential of Eq. (3.2).

As stressed by the recent work of Garrity and Skinner[12] and references therein, the classical transition state theory, being based on the assumption of no recrossing after the first crossing of the barrier, appears to overestimate (by nearly one order of magnitude in the conditions of Ref. 12) the chemical reaction rate when dealing with flat, wide barriers. Similar features will develop within the context of our model as $\langle y^2 \rangle$ increases. As Christoffel and Bowman[2] have discussed, the coupling to a transverse mode may create an effective potential in which the potential barrier is deformed to show a plateau or even a third well at the center. As $\langle y^2 \rangle$ increases, this may develop into a "wedge" driven into the double well potential that progressively widens and deepens, thereby acting as an even more effective reservoir for recrossing processes. In these conditions our first-passage method would also overestimate the chemical reaction rate.

In the right-hand side of Fig. 3 and in Fig. 4, results obtained by the first-passage time technique are displayed. The rate K is taken as the inverse of τ_{E_0} given by Eq. (3.8); a numerical procedure was used throughout.

In the situations considered here, the difficulty mentined above of gross overestimates is not expected to occur. The results illustrated on the right-hand side of Fig. 3 show that, in this region, the increase in K is much more sensitive
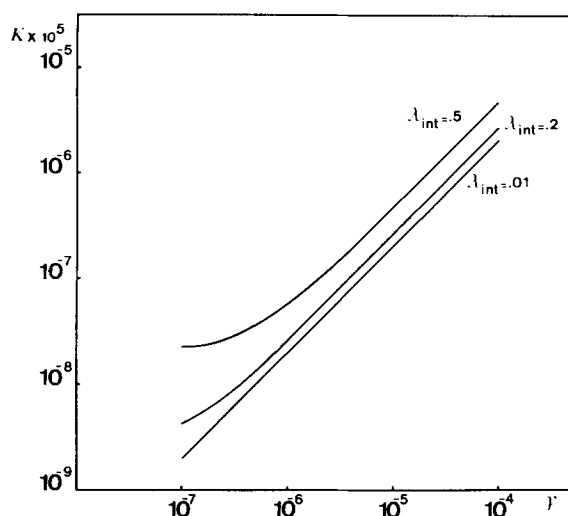

FIG. 4. Variation of the reaction rate in the low friction region $\gamma \rightarrow 0$. These results were obtained using the first-passage time method. Parameters were given the same values as in Fig. 3.

to the increases in λ_{int} than it is in the high-friction region, thereby corroborating our statements on the role of inertia. In Sec. II, we remarked that K shows a more and more sensitive dependence on the coupling between reactive and non-reactive modes as inertia increases. This appears now to be a general trend, especially emphasized at $\gamma \rightarrow 0$. This is better seen in Fig. 4. In accordance with what was noted at the very beginning of this section, the rate stays finite in this zero-friction limit counter to Kramers' prediction.

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