Interference of stochastic resonances: Splitting of Kramers' rate

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We consider the escape of particles located in the middle well of a symmetric triple well potential driven sinusoidally by two forces such that the potential wells rock as in stochastic resonance and the height of the potential barrier oscillates symmetrically about a mean as in resonant activation. It has been shown that depending on their phase difference the application of these two synchronized signals may lead to a splitting of time averaged Kramers' escape rate and a preferential product distribution in a parallel chemical reaction in the steady state.

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The escape of a particle from a metastable state due to thermal activation has been a major issue in chemical dynamics and condensed matter physics for several decades [1–5]. As a typical paradigm in this context, consider a Brownian particle in the middle well of a symmetric triple well potential which diffuses symmetrically to the left and the right well. At a finite temperature and in absence of any bias force the particles are activated only by inherent thermal fluctuation resulting in equalization of population in the two side wells. However, if, in addition, the potential is driven by an external periodic signal, the escape over the potential barrier is modified by the interplay of the thermal fluctuations and coherent external signal, due to *stochastic resonance* [6–9]. On the other hand, when the height of the potential barrier is made to oscillate symmetrically or fluctuates around a mean value by the action of an external input signal the mean escape time over the fluctuating barrier exhibits a minimum at a particular value of frequency or correlation time of the external source due to *resonant activation* [10–13]. In both of these cases the time averaged escape rates from the middle well are equal and the stationary population of the left and right wells remains the same.

Our aim of this paper is to explore a possible route leading to a splitting of the time averaged Kramers' escape rate from the middle well due to the interference of these two resonances and to propose a convenient method for controlling the pathways of a parallel reaction for which the barrier heights corresponding to two product states are equal. For example, take the case of nucleophilic attack by X^- (a halide ion of HX) at the carboxyl group of a ketone, say, $R_1(R_2)C=O$ producing $D-R_1(R_2)C(OH)X$ and $L-R_1(R_2)C(OH)X$, two optical isomers (enantiomers) having the same energy and stability but differing in their optical properties and hence biochemical activities. The middle well of the potential signifies the reactant state and the terminal wells represent the two product states of the parallel reaction. Specifically, our objective here is twofold: first, to understand how the asymmetry in the time averaged dynamics of the triple well potential driven simultaneously by two sinusoidal forces results in differential average escape rate to two product states and unequal distribution of stationary population densities between them. The second objective, is to explore the role of phase difference of the two interfering forces in determining asymmetric diffusion of the particles from the middle well and resulting localization in one state. In other words we look for a strategy for coherent control of pathways of a parallel reaction. As an interesting offshoot of the analysis a selective process of enrichment of one of the two isoenergetic isomers under appropriate thermal condition is also explored.

To illustrate the basic idea we begin with an overdamped Brownian particle in a symmetric triple well potential $V(x)$ (Fig. 1) kept in a thermal bath at temperature T and subjected to two sinusoidal signals $a_1(t)=A_1\sin(\omega_1 t+\phi_1)$ and $a_2(t)=A_2\sin(\omega_2 t+\phi_2)$. The governing Langevin equation is given by

$$\gamma\dot{x} = -V'(x) + A_1\sin(\omega_1 t + \phi_1) + A_2 x\sin(\omega_2 t + \phi_2) + \Gamma(t), \tag{1}$$

where $V(x)=x^2(bx^2-c)^2$; b and c are the parameters of the potential [Fig. 1(a)] and γ is the dissipation constant. ω_i and ϕ_i $(i=1,2)$ are the frequency and phase of the signals. Thermal fluctuation of the bath is modeled by zero mean $[\langle\Gamma(t)\rangle=0]$ and delta correlation of noise, $\langle\Gamma(t)\Gamma(t')\rangle=2D\delta(t-t')$, D being the strength of the thermal fluctuation and is given by $D=kT/\gamma$. Here the additive signal $a_1(t)$ rocks the potential wells sidewise [Fig. 1(b)], whereas the multiplicative signal $a_2(t)$ sets a symmetric oscillation [Fig. 1(c)] of the barrier height around ΔV_0 $(=4c^3/27b)$ with an amplitude $\pm A_2 x_b^2/2$ at $\pm x_m$, respectively (since the fluctuation is space dependent the amplitude of fluctuation of the barrier height around ΔV_0 is $\pm A_2(x_m^2-x_b^2)/2$ for terminal wells to the middle well), where $\pm x_b$ and $\pm x_m$ are the coordinates of two barrier tops and two terminal potential minima, respectively. The two configurations of the potential under simultaneous action of the two signals $a_1(t)$ and $a_2(t)$ are schematically illustrated in Fig. 1(d) for $\Delta\phi=\phi_1-\phi_2=0$ and synchronized frequencies $\omega_1=\omega_2$. As shown, the barrier height for the transition from the middle to right well fluctuates with an amplitude $\pm(A_2x_b^2/2+A_1x_b)$ whereas for the middle to left well the amplitude of fluctuation of the barrier height is $\pm(A_2x_b^2/2-A_1^0x_b)$. If the external modulations $a_1(t)$ and $a_2(t)$ are small and very slow implying $\Delta V_0 \gg A_2, A_1$ and the Kramers' es-

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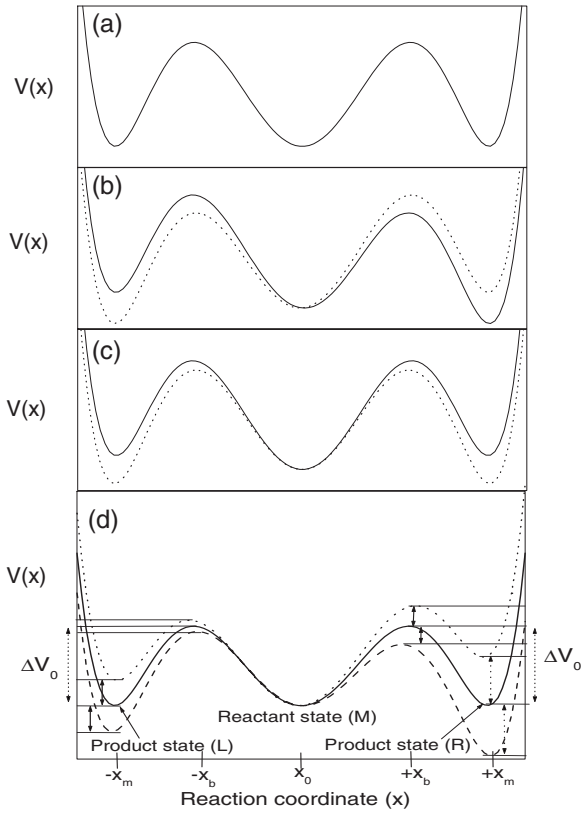

FIG. 1. (a) A schematic illustration of a symmetric triple-well potential. (b) The potential is acted upon by the sinusoidal force $a_1(t)$ resulting in rocking of the side wells with respect to middle well as in stochastic resonance. (c) The potential is acted upon by the sinusoidal force $a_2(t)$ which sets a symmetric oscillation of the barrier height as in resonant activation. (d) The two configurations of the potential under simultaneous action of the two signals $a_1(t)$ and $a_2(t)$ for $\Delta\phi=\phi_1-\phi_2=0$ and synchronized frequencies $\omega_1=\omega_2$.

cape time $(1/r_k)$ for the unperturbed system is much smaller than the time period of the external input signals $(1/r_k \ll 2\pi/\omega_1=2\pi/\omega_2)$ one may consider the expressions for the time dependent transition rates from the middle to left and right wells as follows:

$$W_M^L(t) = r_k \exp\{-[A_1 x_b \sin(\omega_1 t + \phi_1) - (A_2 x_b^2/2)\sin(\omega_2 t + \phi_2)]/D\}, \quad (2)$$

$$W_M^R(t) = r_k \exp\{+[A_1 x_b \sin(\omega_1 t + \phi_1) + (A_2 x_b^2/2)\sin(\omega_2 t + \phi_2)]/D\}, \quad (3)$$

respectively. Here $r_k=\frac{\omega_0\omega_b}{2\pi\gamma}\exp\left(-\frac{\Delta V_0}{D}\right)$ is the transition rate from the middle well for the unperturbed system; ω_0, ω_b are the frequencies corresponding to the potential minimum (x_0) and barrier top (x_b), respectively. Following McNamara and Wiesenfeld [8] if we expand the exponential term of the time dependent transition rate and keep the leading terms up to second order, the time averaged transition rates for $\omega_1=\omega_2$ and $\phi_1=\phi_2=0$ are given by

$$\langle W_M^L(t)\rangle_t = r_k\{1 + (1/4D^2)[A_1 x_b - (A_2/2)x_b^2]^2\}, \quad (4)$$

$$\langle W_M^R(t)\rangle_t = r_k\{1 + (1/4D^2)[A_1 x_b + (A_2/2)x_b^2]^2\}. \quad (5)$$

It is apparent from the above expressions that as a result of interplay of two resonances the period averaged transition rates from the middle to left and right wells significantly differ from each other at very low temperature and tend to equalize in the high temperature limit. In Fig. 2 we present two representative plots for the ratio of transition rate to the right and left wells as a function of temperature and compare the result with simulations in the adiabatic regime $1/r_k \ll 2\pi/\omega_1=2\pi/\omega_2$. We estimate the ratio W_r $(=\langle W_M^R\rangle/\langle W_M^L\rangle)$of the transition rate as a function of external driving frequencies (synchronized frequencies, $\omega_1=\omega_2$) by standard numerical simulation of the Langevin equation (1) using Huen's algorithm. We allow 10 000 test particles to move from the middle well in either direction and count the number of particles which arrive in the left well (n_L) and the right well (n_R), to calculate the ratio of the transition as given by $W_r=\langle W_M^R\rangle/\langle W_M^L\rangle=n_R/n_L$. It is apparent from Fig. 2 that the numerical analysis matches fairly well with our theoretical result. As a result of fluctuation of the barrier heights for both left and right wells, the transition rates $\langle W_M^L\rangle$ and $\langle W_M^R\rangle$ exhibit resonant activation independently as expected (when the Kramers' escape time coincides with $2\pi/\omega_2$). Moreover, as the amplitude of fluctuation of the barrier height corresponding to the right well is larger [see Fig. 1(d)], the ratio W_r differs significantly from unity and exhibits a resonance when the latter is plotted as a function of the frequency under a phase matched condition $\phi_1=\phi_2$. In Fig. 3(a) we plot this ratio as a function of frequency between the synchronized input signals for several values of temperature to exhibit this asymmetry in resonant activation due to differential transition rate. In Fig. 3(b) we plot the ratio of the transition rate as a function of the phase difference of the two input signals for different values of strength of the input signal (A_2). It is observed that the transition rates toward the side wells are equal $(W_r=1)$ for the phase difference $\phi_1-\phi_2=\pi/2$. The ratio of the rates W_r can be inverted by reversing the phase difference from $\phi_1-\phi_2=0$ to $\phi_1-\phi_2=\pi$. Therefore by controlling the phase of the input signals $a_1(t)$ and $a_2(t)$, it is possible to manipulate the transition of particles from the middle well to the product states and hence the course of the parallel reaction.

The above analysis is based on kinetic considerations. It is also worthwhile to turn our attention to the time averaged distribution of the particles in the two wells and the associated aspects of localization [14]. This is in the spirit of stationary product distribution of a parallel reaction. In this case we allow the trajectories to evolve dynamically for a long time starting from an arbitrary initial position in the well. Numerical simulation results show that the residential time distribution (Fig. 4) bears a marked asymmetry corresponding to a stochastic localization of the particles in the right well for $\phi_1-\phi_2=0$ and in the left well for $\phi_1-\phi_2=\pi$. For $\phi_1-\phi_2=\pi/2$, the distribution of $x(t)$ over time is more or less even for both the wells. In view of the input signal synchronization, a qualitative interpretation of this type of localization may be given as follows: so long as the force

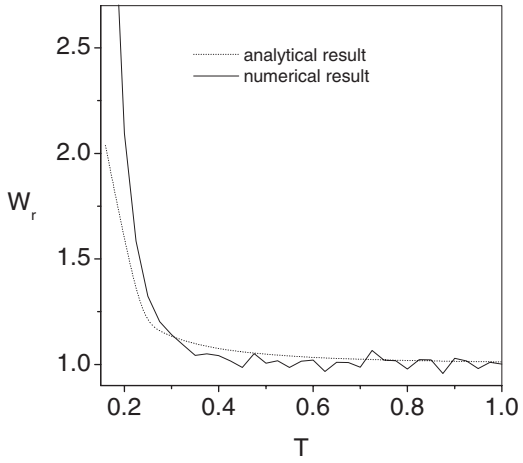

FIG. 2. A comparison between analytical result [based on analytical expressions (2) and (3)] and numerical simulation plotting W_r as a function of temperature for the parameter set $\Delta\phi=0$, $\omega_1=\omega_2=0.0005$, $A_1=0.1$, $A_2=0.2$, $b=0.1$, and $c=1.0$ (all the quantities are dimensionless).

$a_2(t)$ causing symmetric oscillation of the barrier height attains its lower value, the tilting force $a_1(t)$ points to the right well, so that the particle in the middle well move toward the right well very quickly. On the other hand as the tilting force points to the left $a_2(t)$ sets the barrier height at a larger value and consequently the particle in the middle well takes a relatively larger time to speed up from the middle to left well for the simultaneous action of the synchronized signals. The particles in the middle well therefore have a greater chance to cross the right-hand barrier. In the right well, the amplitude of oscillation of the barrier height is much larger and so the particle coming into the right well escapes from it more quickly and on returning back to the middle well it has again two options to cross the barrier as it was initially. Thus the particle dynamically spends most of the time in between the middle and the right wells. To proceed further we require a quantifier which measures the asymmetry in localization in the two wells. To this end we choose the mean position of the particle as a measure of asymmetry. For a symmetric distribution mean position $\langle x\rangle=0$ and for the localization of the

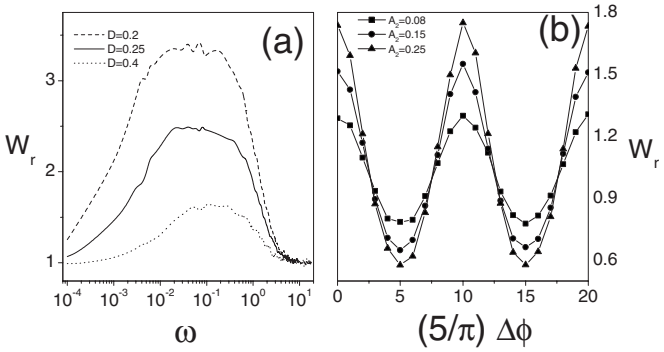

FIG. 3. (a) Variation of W_r as function of frequency for different values of temperature $T=0.2$ (dashed line), $T=0.25$ (solid line), and $T=0.4$ (dotted line), and for the parameter set $\Delta\phi=0$, $A_1=0.1$, $A_2=0.2$, $b=0.1$, $c=1.0$. (b) W_r vs phase difference $\Delta\phi$ plot for different values of A_2 and for the same parameter set as (a) but for $\omega_1=\omega_2=0.05$ and $T=0.2$ (all the quantities are dimensionless).

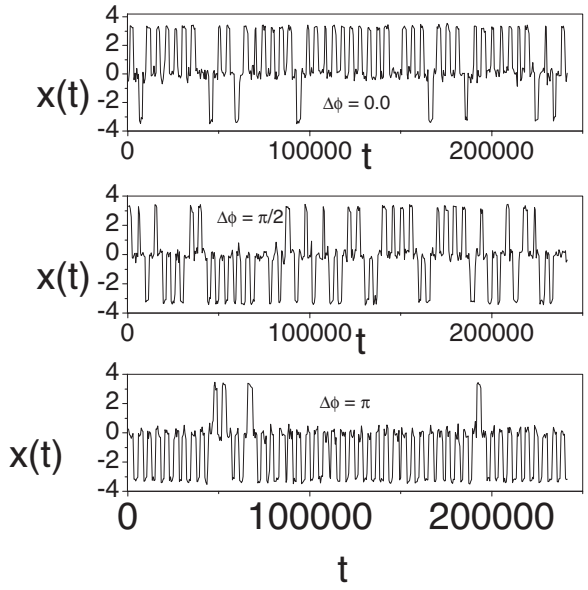

FIG. 4. Residential time distribution for several values of phase difference [$\Delta\phi=0$ (upper panel), $\Delta\phi=\pi/2$ (middle panel), $\Delta\phi=\pi$ (lower panel)] between two input signals, for the parameter set $\omega_1=\omega_2=0.0013$, $A_1=0.1$, $A_2=0.25$, $T=0.155$, $b=0.1$, and $c=1.0$ (all the quantities are dimensionless).

particles to the left or right well, the value of mean position is negative or positive, respectively. In Fig. 5(a) we present the variation of mean position as a function of synchronized input signal frequencies. With increase of the input signal frequency the mean position gradually shifts to a maximum positive value followed by a decrease to zero at high frequency. In Fig. 5(b) we show the mean position as a function of phase difference between the two input signals. The mean position is zero for $\Delta\phi=\pi/2$ and it departs from zero as the phase difference differs from $\pi/2$. For a phase matched condition $\phi_1=\phi_2$ the particles are localized in the right well while for a phase reversal $\Delta\phi=\pi$ localization takes place in the left well.

Can temperature influence the product distribution of a parallel reaction at the steady state? This question is intimately related to the manipulation of incoherent condition

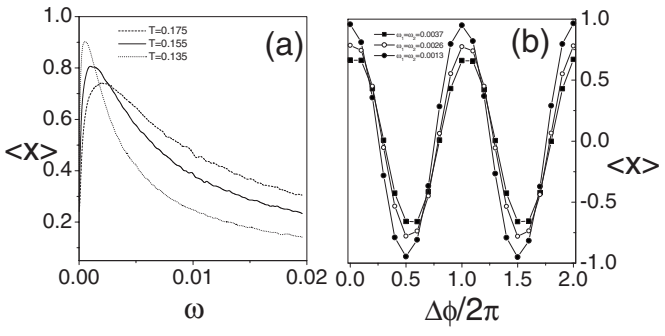

FIG. 5. (a) Mean position ($\langle x\rangle$) vs frequency plot for several values of temperature and for the parameter set $\Delta\phi=0$, $A_1=0.1$, $A_2=0.25$, $b=0.1$, and $c=1.0$. (b) Mean position ($\langle x\rangle$) vs phase difference ($\Delta\phi$) plot for different input signal frequencies and for the same parameter set as (a) but for $T=0.155$ (all the quantities are dimensionless).

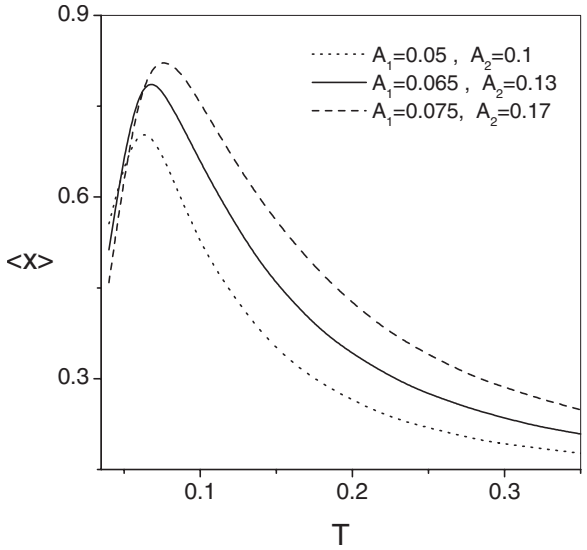

FIG. 6. Mean position ($\langle x\rangle$) vs temperature plot for different values of amplitude of the synchronized external signals and for the parameter set $\Delta\phi=0$, $\omega_1=\omega_2=0.0005$, $b=0.1$, and $c=0.6$ (all the quantities are dimensionless).

rather than coherence in selecting and controlling the reaction pathways. To have a closer look into this aspect we examine the variation of mean position $\langle x\rangle$ with temperature with the help of a discrete three-state model for the triple well potential. Three states are denoted by x_0, $\pm x_m$ for the symmetric unperturbed system corresponding to three minima. The diffusional motion causes transitions between them and it is schematically presented as

$$L \underset{\langle W_M^L\rangle}{\overset{k_L}{\rightleftharpoons}} M \underset{k_R}{\overset{\langle W_M^R\rangle}{\rightleftharpoons}} R$$

k_L, k_R, $\langle W_M^R\rangle$, $\langle W_M^L\rangle$ denote the time averaged rate of transition from left to middle well, right to middle well, middle to right well, and middle to left well, respectively. The number of particles in the three states at time t are denoted by n_L, n_R, and n_L. The governing master equations for n_i $(i=L,R,M)$ read as

$$dn_L/dt = -k_L n_L + \langle W_M^L\rangle n_M, \tag{6}$$

$$dn_R/dt = -k_R n_R + \langle W_M^R\rangle n_M, \tag{7}$$

$$dn_M/dt = k_L n_L + k_R n_R - (\langle W_M^L\rangle + \langle W_M^R\rangle) n_M. \tag{8}$$

At the steady state ($\dot{n_L}=\dot{n_M}=\dot{n_R}=0$) the probability of finding the particles at the three wells P_i $(i=L,R,M)$ are $P_L = \langle W_M^L\rangle k_R/P$, $P_R=\langle W_M^R\rangle k_L/P$, and $P_M=k_L k_R/P$ where $P = k_R\langle W_M^L\rangle + k_R k_L + k_L\langle W_M^R\rangle$. The expression for the mean position is then given by

$$\langle x\rangle = \int_{-\infty}^{+\infty} xP(x)dx = x_m P_R + x_0 P_M - x_m P_L$$

$$= \left(\frac{\sqrt{27\Delta V_0}}{2c}\right)\frac{\langle W_M^R\rangle k_L - \langle W_M^L\rangle k_R}{k_R\langle W_M^L\rangle + k_R k_L + k_L\langle W_M^R\rangle}. \tag{9}$$

The above expression clearly shows the dependence of mean position and probability on four time averaged rate constants. Furthermore, if we assume that k_R and k_L do not differ significantly then $\langle x\rangle$, in general, turns out to be positive since by Eqs. (4) and (5) $\langle W_M^R\rangle$ is greater than $\langle W_M^L\rangle$. Keeping in view of the Arrhenius temperature dependence of the individual rate constants, the variation of $\langle x\rangle$ with temperature is therefore expected to show a bell-shaped curve. The departure of $\langle x\rangle$ from zero toward positive direction indicates the preferential distribution of the product in the right well. The numerical simulation of the variation of mean position $\langle x\rangle$ as a function of temperature for synchronized input signals under phase matched condition as shown in Fig. 6 corroborates this assertion.

In summary, we have shown that depending on their phase difference, an application of two synchronized signals on a particle in a triple well potential may lead to a splitting of the time averaged Kramers' escape rate due to an interference of stochastic resonance and resonant activation. This allows us to realize a strategy for achieving a preferential product distribution in the steady state of a parallel reaction. The present analysis thus reveals that stochastic energetics [15] can be utilized to control kinetically the pathways of a chemical reaction by appropriate manipulation of coherence and/or inherent thermal condition.

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