Communication: Transition state trajectory stability determines barrier crossing rates in chemical reactions induced by time-dependent oscillating fields

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When a chemical reaction is driven by an external field, the transition state that the system must pass through as it changes from reactant to product—for example, an energy barrier—becomes time-dependent. We show that for periodic forcing the rate of barrier crossing can be determined through stability analysis of the non-autonomous transition state. Specifically, strong agreement is observed between the difference in the Floquet exponents describing stability of the transition state trajectory, which defines a recrossing-free dividing surface [G. T. Craven, T. Bartsch, and R. Hernandez, “Persistence of transition state structure in chemical reactions driven by fields oscillating in time,” Phys. Rev. E 89, 040801(R) (2014)], and the rates calculated by simulation of ensembles of trajectories. This result opens the possibility to extract rates directly from the intrinsic stability of the transition state, even when it is time-dependent, without requiring a numerically expensive simulation of the long-time dynamics of a large ensemble of trajectories. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4891471]

Controlling the rate at which reactants transform to products, either to accelerate a chemical process or to bias a reaction toward a certain pathway, is fundamental to chemical physics. Such kinetic control can be achieved through forcing from an external field, leading to emergent behavior in molecular structure assembly,1–4 organic synthesis,5 ultracold ing from an external field, leading to emergent behavior in physics. Such kinetic control can be achieved through forc-

An example of a molecular process where an external force influences the transition state (TS) geometry, and thus reaction rates, is the photoinduced isomerization between cis and trans stilbene (Ph-C=C-Ph).32–34 Its unimolecular reaction path can be parameterized through the torsion angle of the C=C double bond. Changing the energetics along this path through photoinduction alters the isomerization reaction rate.

We show here that when a chemical reaction is periodically forced by an external field (such as a laser), the reaction rates are determined directly by the stability of the transition state. We calculate the reaction rate of a model system by simulating large ensembles of trajectories and compare this result with the rate predicted by Floquet analysis of the transition state trajectory. Corresponding to the “chemical method” where the reactant concentration is followed as a function of time,35 we obtain reaction rates from the decay of a given initial distribution. These rates are well-defined because the decay is exponential when averaged over a period of the driving and independent of the choice of distribution. A major result of this work is that the rates can be obtained from a Floquet analysis of the transition state trajectory, an unstable periodic orbit (PO) close to the barrier top. This agreement suggests that chemical reaction rates can be extracted directly from the transition state without knowledge of the dynamics of the reactive population. This general result could have been anticipated from the known connection between the stability of periodic orbits of Hamiltonian systems and rates,36–38 but is here established even in the case of driven systems.

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To model barrier crossings in chemical reactions driven by a time-dependent external field $E(t)$ we consider a particle of unit mass with an initial position $x_0$ on the reactant side of a moving energy barrier. The chosen barrier is a quartic potential of the form

$$U(x) = -\frac{1}{2} \omega_b^2 (x - E(t))^2 - \frac{1}{4} \epsilon (x - E(t))^4,$$

which leads to the equations of motion

$$\dot{x} = v,$$

$$\dot{v} = -\gamma v + \omega_b^2 (x - E(t)) + \epsilon (x - E(t))^3,$$

where $\gamma$ is a dissipative emission parameter, $\omega_b$ is the barrier frequency, and $\epsilon$ is an anharmonic coefficient. The anharmonic coefficient is restricted to values $\epsilon \geq 0$ such that there is a single maximum in the potential located at the barrier top (BT). The time dependent, instantaneous position of the BT is specified by $E(t)$. Figure 1 shows the time evolution of $x(t)$ for an ensemble of trajectories following Eq. (2). Each trajectory either crosses the energy barrier forming product or remains on the reactant side, never surmounting the barrier. The normalized flux of reactive trajectories through the phase-space bottleneck—the TS—is the reaction rate.\(^8\)

Every realization of the forcing $E(t)$ has a special trajectory imbedded in the dynamics (2) that remains close to the BT. It is instead a specific trajectory that responds to motion of the BT in such a way that it remains bounded for all time. For the case of a harmonic barrier ($\epsilon = 0$), $x(t)$ follows the time evolution of the energetic maximum given by $E(t) = \cos(\Omega t + \phi)$ with creating a DS that is crossed once and only once by reactive trajectories and then evaluating the flux through that DS that is located at the instantaneous position of the TS trajectory. As shown previously by us,\(^29\) the configuration space projection of the TS trajectory is free of recrossings.

For the case of a harmonic barrier ($\epsilon = 0$), Eq. (2) can be solved analytically with eigenvalues $\lambda_{u,s} = -i/2(\gamma$}

\begin{align*}
\lambda_{u,s} &= \frac{\omega_b^2}{\lambda_u - \lambda_s}, \\
\mu &= \frac{\omega_b^2}{\Omega_1}, \\
\gamma &= \epsilon = 4, \\
S &= \frac{\mu}{\Omega_1 - \gamma}, \\
V &= \frac{1}{2} \epsilon (x - E(t))^4.
\end{align*}

The initial position for every trajectory, $x(0)$, is shown in black. The critical velocity $V^*$ is indicated by a red circle at the intersection of the dashed red line and $x_0$. The initial velocities are sampled from $\eta_R$. Parameters are $\epsilon = 1$, $\Omega = 3$, $\gamma = 4$, and $\phi = 0$.\(^9\)
external driving. The anharmonic equations of motion (2) are not amenable to an exact analytical solution, although approximate analytical methods have previously been employed. Instead, we obtain the TS trajectory $\Gamma^\dagger = (x^\dagger(t), v^\dagger(t))$ in phase space numerically as the periodic solution to the system of Eqs. (2). A DS that is attached to $\Gamma^\dagger$ will be recrossing free. Phase space portraits of $\Gamma^\dagger$ are shown in Fig. 2.

The barrier crossing rates for Eq. (1) were calculated by simulating ensembles of trajectories driven by an external field of the form $E(t) = \sin(\Omega t + \varphi)$. For single mode sinusoidal driving, the TS trajectory is a PO with period $2\pi/\Omega$. Physical units were set by normalizing $a$ and $\omega_0$, to unity, making all other parameters dimensionless. Each trajectory was given an initial position $x_0 = -0.1$ to the left of the instantaneous barrier top and $v_0$ was sampled from two separate distributions: (1) a Boltzmann distribution $q_B$ with $k_B T = 1$, and (2) a uniform distribution $q_U$ (bounded over the region $[1^\dagger - 1/2, 1^\dagger + 1/2]$). For each parameter set $(\Omega, \gamma, \epsilon)$, $10^8$ trajectories were simulated. The normalized reactant population $P_R(t)$ is obtained from a histogram of those trajectories that are on the reactant side of the TS trajectory at time $t$. Assuming first order kinetics, the scaled logarithm of the reactant population

$$\ln \left[ \frac{1}{1 - P_R(t)} \right]$$

is the barrier crossing rate $k_r$, corresponding to a respective $\epsilon$ value. Parameters are $\gamma = 1$ and $\varphi = 0$.

The long-time decay rate of $P_R(t)$ is determined by the behavior of trajectories close to the stable manifold. Once a trajectory is sufficiently close to the TS trajectory, it can be described by a linearization of the equations of motion (6),

$$\Delta \dot{x} = \Delta v,$$

$$\Delta \dot{v} = -\gamma \Delta v - U'(\Delta x + x^\dagger(t)) + U'(x^\dagger(t)).$$

The last term represents a time-dependent driving for the relative dynamics that does not depend on the current trajectory. It ensures that the relative equations of motion have a fixed point $\Delta \Gamma^\ast$ at $\Delta x = \Delta v = 0$, i.e., on the TS trajectory.

For harmonic driving, the TS trajectory is a PO with period $2\pi$, and the positivity of the Floquet multipliers, the vectors $\Delta \Gamma(t)$ is the Jacobian of Eq. (6) about $\Delta \Gamma^\ast$. The linearity of Eq. (8) allows its solution to be expressed as

$$\Delta \Gamma(t) = \sigma(t) \Delta \Gamma(0),$$

where the fundamental matrix solution $\sigma(t)$ is a $2 \times 2$ matrix that satisfies

$$\dot{\sigma} = J(t) \sigma, \quad \sigma(0) = I,$$

where $I$ is the identity matrix.

The fundamental matrix for one period of $\Delta \Gamma^\dagger$ is the monodromy matrix $M = \sigma(T)$ whose eigenvalues $m_{u,s}$ are called Floquet multipliers. The Floquet exponents $\mu_{u,s} = 1/T \ln |m_{u,s}|$ give the rates by which nearby trajectories approach or recede from $\Delta \Gamma^\dagger$. For a harmonic barrier, the multipliers are bounded according to $0 < m_u < 1 < m_s$ giving rise to a positive Floquet exponent $\mu_u$ and a negative exponent $\mu_s$. We will assume that this qualitative condition is also satisfied for the anharmonic barriers; we neglect the possibility that for strong anharmonicities bifurcations of the TS trajectory might occur.

Let $u_{u,s}(0)$ be the eigenvectors of $M$. By Floquet’s theorem and the positivity of the Floquet multipliers, the vectors

$$u_{u,s}(t) = e^{-\mu_{u,s} t} \sigma(t) u_{u,s}(0)$$

are periodic in time with period $T$. In the coordinate system defined by these vectors,

$$\Delta \Gamma(t) = z_{u,s}(t) u_{u,s}(t) + z_{s,u}(t) v_{s,u}(t),$$

the linearized equations of motion (8) read

$$\dot{z}_{u,s} = \mu_{u,s} z_{u,s},$$

with the solution

$$z_{u,s}(t) = C_{u,s} e^{\mu_{u,s} t}. (15)$$
Therefore, the vectors $v_{u,s}(t)$ determine the instantaneous directions of the stable and unstable manifolds in the linear approximation. The actual stable and unstable manifolds are tangent to these directions at the TS trajectory.

According to Eq. (13), the dynamics of Eq. (7) is therefore given by

$$\Delta x(t) = C_u \alpha_u(t) e^{\mu_u t} + C_s \alpha_s(t) e^{\mu_s t},$$

(16)

where $\alpha_{u,s}$ are the first components of the vectors $v_{u,s}$. They are periodic with period $T$. A trajectory with given initial conditions $C_u$ and $C_s$ will cross the moving dividing surface $\Delta x = 0$ at time $t$ determined by

$$e^{(\mu_u - \mu_s)t} = -\frac{C_s}{C_u} \frac{\alpha_u(t)}{\alpha_s(t)}.$$  

(17)

If the initial condition $C_s$ is fixed and a trajectory with a certain value of $C_u$ crosses the moving DS at time $t$, Eq. (17) shows that a trajectory with initial value $C_u e^{-(\mu_u - \mu_s)t}$ will cross at time $t + T$. Iteration then leads to the existence of trajectories with initial values $C_u e^{-(\mu_u - \mu_s)nt}$ that cross at time $t + nT$.

Now consider an arbitrary ensemble of initial conditions with fixed $x(0)$ on the reactant side and with a fixed value $C_s < 0$ small enough to be in the region of phase space where the linear approximation (8) is accurate. In this region, the phase space density is constant up to linear corrections in the distance from the stable manifold and the number of trajectories that cross the DS in a given time interval is proportional to the width of the strip that contains these trajectories. From one period to the next this width decreases by a factor $e^{-(\mu_u - \mu_s)T}$. Thus, up to periodic modulation, the flux must decay by this same factor. The flux through the moving DS is the time derivative of the population, $F(M,t) = \dot{P}(t)$, and thus the decay of $P(R)(t)$ is proportional to $e^{-(\mu_u - \mu_s)T}$. From this decay rate it follows that, $k_f = \mu_u - \mu_s$, which states that the rate of barrier crossing is the difference in the Floquet exponents. Note that we have made no assumption for the energy distribution and thus this rate is independent of the ensemble of initial conditions.

A comparison between the rates calculated from numerical simulation $k_f$ for both the Boltzmann $q_B$ and uniform $q_U$ distributions, and rates predicted by the Floquet exponents $\mu_u - \mu_s$ is shown in Fig. 4. For all values of the forcing frequency $\Omega$, dissipative parameter $\gamma$, and anharmonic strength $\epsilon$, the numerical rate is in agreement with rate predicted by stability analysis. This result opens the possibility that when chemical reactions are forced by periodic external fields the reaction rates can be extracted from knowledge of the stability of the TS trajectory. The extension of TS trajectory stability analysis to aperiodically forced or thermally activated reactions is a focus of our future research.

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