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Quantum theory of enhanced unimolecular reaction rates below the ergodicity threshold

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Abstract

A variety of unimolecular reactions exhibit measured rates that exceed Rice–Ramsperger–Kassel–Marcus (RRKM) predictions. We show using the local random matrix theory (LRMT) of vibrational energy flow how the quantum localization of the vibrational states of a molecule, by violating the ergodicity assumption, can give rise to such an enhancement of the apparent reaction rate. We present an illustrative calculation using LRMT for a model 12-vibrational mode organic molecule to show that below the ergodicity threshold the reaction rate may exceed many times the RRKM prediction due to quantum localization of vibrational states.

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1. Introduction

Rice–Ramsperger–Kassel–Marcus (RRKM) theory [1] serves as the foundation for predicting rates of unimolecular reactions [2–4], such as the rate of isomerization of a polyatomic molecule. Still, some underlying assumptions of RRKM theory remain hard to justify, and deviations between calculations based on RRKM theory and measurement arise frequently [5–18]. In many cases [5–16], RRKM theory overestimates the reaction rate. RRKM theory assumes that re-equilibration of an ensemble of reactants and products occur extremely rapidly during the course of reaction, ignoring the actual time needed for energy redistribution. Addressing the issue of energy flow explicitly has proven a formidable challenge, requiring an understanding of the complex nature of quantum mechanical energy flow in sizable molecules. We have met this challenge in recent years by turning to a random matrix approach [19–25]. Random matrix theory [26–29]

has long been used to describe the complex spectra [30–37] and distribution of reaction rates [38,39] for nuclei and highly excited molecules. Unlike the random matrices adopted for describing complex molecular spectra of relatively small molecules with large amounts of excitation energy, however, at modest energies for sizable molecules [19–25] a large number of near-selection rules are required for describing energy flow quantum mechanically among the many vibrational degrees of freedom, greatly restricting equilibration. We have subsequently incorporated this information into calculation of chemical reaction rates [5–9]. These energy flow effects modify in particular the rates of isomerization of modest-sized organic molecules. We have called this approach local random matrix theory (LRMT), since it is a random matrix theory that accounts for the local coupling in the vibrational quantum number space of a large molecule.

Recently, Carpenter [17] has pointed out a number of reactions that occur with rates greater than predicted by RRKM theory. Using the computational work of Berblinger and Schlier [18] on H_3^+ dissociation as an example, Carpenter explains that the surprisingly fast rates of these

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reactions may arise because the phase space in which the reactions occur is non-ergodic, i.e., the volume of phase space actually contributing to reaction is smaller than in the ergodic limit, and thus is overestimated by RRKM theory. A dramatic example is provided by certain gas-phase S_N2 reactions. These reactions occur by formation of ion-dipole complexes [17]. In the reaction between X^- and CH_3Y to $XCH_3 + Y^-$, the ion-dipole complex that first forms is X^-CH_3Y . This then isomerizes unimolecularly to XCH_3-Y^- [40]. The rate of isomerization can be enhanced beyond that predicted by RRKM theory and the overall S_N2 reaction promoted if vibrational energy is first introduced into the neutral CH_3Y by irradiation of the CH_3-Y stretch with an IR laser. This enhancement has been explained by a quasi-partitioning of the rotational-vibrational phase space, where the energy deposited into the internal degrees of freedom upon forming the collision complex flows readily among some of the vibrational degrees of freedom, but only slowly or in a limited fashion into other vibrations or rotational degrees of freedom [17]. RRKM theory thus overestimates the overall phase space volume in which the energy is partitioned and so underestimates the reaction rate from the states formed in the collision complex.

Earlier work by Berne [41] provides a theoretical underpinning for the enhancement of the reaction rate when the phase space in which the reaction takes place is non-ergodic. Berne's theory and the related work of Berblinger and Schlier [18] are classical. In the present article, we describe a quantum mechanical theory within the framework of LRMT that predicts an enhancement of the rate predicted by RRKM theory in the quantum localized regime.

The microcanonical unimolecular reaction rate for a reaction at energy E over a barrier E_0 is given by RRKM theory as [1–4]

$$k_{RRKM}(E) = \frac{N^\#(E - E_0)}{h\rho_{total}(E)}, \quad (1)$$

where $\rho_{total}(E)$ is the total density of states of the reactant at energy, E ; $N^\#(E - E_0)$ is the number of states of the transition state with excess energy less than or equal to $E - E_0$; and h is Planck's constant. Dynamics in the phase space is assumed to be ergodic. Berne [41] put forth a classical theory for the microcanonical reaction rate when the phase space consists of some regions that are irregular (i.e., chaotic, ergodic) and others that are regular. The phase space volume, Ω , then has an irregular part, Ω_I , and regular part, Ω_R , such that $\Omega = \Omega_I + \Omega_R$. Only trajectories that lie in the irregular region can give rise to an exponential population decay when they cross a reaction barrier, and therefore to the existence of a finite reaction rate. If energy flow within the irregular region is very rapid, then an RRKM-like approach to calculating the rate can be followed for states within the irregular region. The initial excess population, $P^{(0)}(t)$, of a species decays with time, t , as

$$P^{(0)}(t) = \frac{\Omega_R(E)}{\Omega(E)} + \frac{\Omega_I(E)}{\Omega(E)} e^{-k(E)t}. \quad (2)$$

The rate coefficient is

$$k(E) = k_{NEST}(E) = \frac{\Omega(E)}{\Omega_I(E)} k_{RRKM}(E), \quad (3)$$

where NEST refers to “non-ergodic statistical theory” [41]. We shall now present a quantum mechanical formulation for $k_{NEST}(E)$, $k_{QunEST}(E)$, or a quantum non-ergodic statistical theory.

In the following section, we show how $k_{QunEST}(E)$ can be derived from local random matrix theory. In Section 3, we give an example to illustrate the enhancement of the isomerization rate for a model 12-vibrational mode organic molecule, for which the barrier to reaction lies in the quantum non-ergodic domain. The model contains parameters that characterize F^-CH_3Cl isomerization. We conclude in Section 4.

2. Quantum non-ergodic statistical theory

According to local random matrix theory (LRMT), the “limited ergodic” portion of the vibrational quantum number space corresponds to the vibrational states that lie in a volume of radius corresponding to the localization length. This length can be calculated within the theory [21]. The volume contains the number of zero-order vibrational states that effectively contribute to a vibrational eigenstate, or the participation number, p . We shall refer to the number of states in the “limited ergodic” region of the vibrational state space as $N_p(E)$. LRMT then gives the unimolecular reaction rate as

$$k_{QunEST}(E) = \kappa(E) \frac{v(E)N^\#(E - E_0)}{N_p(E)}, \quad (4a)$$

$$\kappa(E) = \frac{k_{IVR}(E)}{k_{IVR}(E) + v(E)}, \quad (4b)$$

where $\kappa(E)$ is a dynamical correction to the RRKM theory estimate for the rate due to sluggish IVR in the limited ergodic region of the vibrational state space, and depends on the intramolecular vibrational relaxation (IVR) rate from transition states to states outside the transition region, k_{IVR} , and the barrier crossing rate, $v(E)$, to go from reactant to product [5–8]. Eq. (4a) is just the RRKM rate, Eq. (1), when $\kappa(E) = 1$, and when the number of states of the limited ergodic region, $N_p(E)$, corresponds to the total number of states on the energy shell [1–4].

Each of the $N^\#(E - E_0)$ states of the vibrational state space that are associated with the activated complex, or the transition states, may be coupled to states outside the transition region of the state space. The number of such states is related to the participation number, p . In the D -dimensional quantum number space of the reactant, one of those dimensions corresponds to the reaction coordinate, and the other $D - 1$ to the relevant bath coordinates that comprise the limited ergodic region overlapping the

transition states. We can thus estimate, assuming isotropic energy flow, that the number of states in the limited ergodic region that overlap the transition state dividing surface is $N_p(E) = N^\#(E - E_0)p^{(D-1)/D}$. Inserting this estimate into Eq. (4) we have

$$k_{\text{QunEST}}(E) = \kappa(E) \frac{v(E)}{p^{(D-1)/D}} \quad (5)$$

Since the vibrational eigenstates below the ergodicity threshold are localized, and we are in the “limited ergodic” region, the participation number is smaller than the number of states on the energy shell, $N(E)$, so that $N_p(E) = N^\#(E - E_0)p^{(D-1)/D} < N(E)$. We may therefore have an enhancement of the unimolecular reaction rate over that predicted by RRKM theory. In the classical theory of Berne [41] $\kappa(E)$ is implicitly 1, so that there is always an enhancement. The size of the enhancement given by Eq. (5) depends on the transmission coefficient, $\kappa(E)$. If the energy flow rate, $k_{\text{IVR}}(E)$, between transition states and non-transition states within the limited ergodic region is slower than the barrier crossing frequency from reactant to product, $v(E)$, then

$$k_{\text{QunEST}}(E) \approx \frac{k_{\text{IVR}}(E)}{p^{(D-1)/D}}, \quad k_{\text{IVR}}(E) < v(E). \quad (6)$$

Even when energy flow within the limited ergodic region is limiting there can be significant enhancement of the reaction rate.

The participation number, p , can be calculated with LRMT. It is obtained from the inverse participation number, ϕ_x , for an eigenstate with energy, E_x , which is defined in terms of the sum of each eigenstate component, c_{xi} , $\phi_x = \sum_i c_{xi}^4$. LRMT predicts the probability distribution, P_ϕ , for the inverse participation number, ϕ , at a given energy, E , to be [21]

$$P_\phi(\phi) = \gamma \phi^{-1/2} (1 - \phi)^{-3/2} \exp\left(-\frac{\pi \gamma^2 \phi}{1 - \phi}\right), \quad (7)$$

where

$$\gamma(E) = \sqrt{\frac{3}{2\pi} T(E) (1 - T(E))^{-1}}, \quad T(E) < 1. \quad (8)$$

The parameter $\gamma(E)$ is defined in terms of the transition parameter, $T(E)$, which is defined by [20]

$$T(E) = \frac{2\pi}{3} \left[\sum_Q K_Q \langle |V_Q| \rangle D_Q(E) \right]^2, \quad (9)$$

where K_Q is the number of vibrational states in a tier a distance Q away in quantum number space coupled to a given state in the vibrational state space, and D_Q is the normalized density of states a distance Q away. The average matrix element coupling such states is $\langle V_Q \rangle$. If a coupling matrix element arises from a cubic anharmonic term, then Q is at most 3, since at most 3 quanta are exchanged by such a term.

We can calculate a representative value for the participation number, p , as

$$p = 1 / \langle \phi \rangle. \quad (10)$$

We have found [21]

$$\langle \phi \rangle = \int_0^1 d\phi P_\phi(\phi) = e^{\pi \gamma^2 / 2} D_{-2}(\sqrt{2\pi \gamma^2}), \quad (11)$$

where D_p is the parabolic cylinder function.

We can also use LRMT to estimate the rate of energy flow in the limited ergodic region. The long time energy flow rate is proportional to the imaginary part of the self-energy, Δ , for a state of the vibrational state space. Typically, a self-consistent analysis of LRMT yields 0 for the most-probable value, Δ_{mp} , the long time rate when $T < 1$ [19,20]. However, we need to recognize that over short times, energy can rapidly flow in the limited ergodic region of the vibrational state space, the extent of which is quantified by p , a region of measure 0 if there were an infinite number of vibrational states. For this limited ergodic region, where energy can flow among p states, we can use the golden rule rate, which is given by

$$k_{\text{IVR}} = \frac{2\pi}{\hbar} \sum_Q K_Q \langle |V_Q| \rangle^2 D_Q(E). \quad (12)$$

3. Illustrative example

In the following, we consider a simple, illustrative example using an approximate expression for T for a system of N coupled non-linear oscillators. We shall illustrate how the isomerization rate for such a system can be larger than that predicted by RRKM theory, which occurs when the vibrational states of the molecule are localized and vibrational energy flow thereby restricted.

Our estimate for $T(E)$ for a molecule with N vibrational modes begins with approximations to the connectivity, K_Q , between a state in the vibrational state space to states a distance Q away; D_Q , the local density of states; and V_Q , the local coupling, which appear in Eqs. (9) and (12). We have found that if N is moderately large and $Q < 2N^{1/2}$ we can approximate K_Q by [20]

$$K_Q \approx \frac{(2N)^Q}{Q!}. \quad (13)$$

Below and near the transition we can approximate $D_Q(E)$ by ($\hbar = 1$) [20]

$$D_Q(E) \approx (\pi Q^{1/2} \Omega_{\text{rms}})^{-1}, \quad (14)$$

where Ω_{rms} is the root mean square vibrational frequency. Finally, we use for V_Q the scaling relation adopted by us previously [20]

$$V_Q = \Phi_3 \sigma^{3-Q} M^{Q/2}, \quad Q \geq 3, \quad (15)$$

where Φ_3 is a representative cubic anharmonic constant and σ quantifies how higher order constants become smaller with the order [42]. The relevant parameters have ranges $0.1 \text{ cm}^{-1} < \Phi_3 < 10 \text{ cm}^{-1}$ and $3 < \sigma < 10$ for organic molecules.

Combining these, we have [20]

$$T(E) = \frac{2\pi}{3} \tilde{\phi}^2 \sigma^6 F^2(\kappa), \quad (16a)$$

$$F(\kappa) = (2\pi)^{-1/2} \left[\sum_{Q=3} \mathcal{Q}^{-1} \left(\frac{\kappa}{\mathcal{Q}} \right)^{\mathcal{Q}} e^{\mathcal{Q}} \right], \quad (16b)$$

$$\kappa = \frac{2NM^{1/2}}{\sigma}, \quad (16c)$$

$$\tilde{\phi} = \Phi_3(\pi\Omega_{\text{rms}})^{-1}, \quad (16d)$$

where Stirling's approximation has been used in the estimate for K_Q . For simplicity, we take the average number of quanta per mode, M , to be $M \approx E/N\Omega_{\text{rms}}$ at energy E .

Similarly, we can approximate Eq. (12) for the rate of energy flow as [20]

$$k_{\text{IVR}} = \frac{2\pi}{\hbar} \Phi_3 \tilde{\phi} \sigma^6 F(\tilde{\kappa}), \quad (17a)$$

$$\tilde{\kappa} = \kappa \frac{M^{1/2}}{\sigma}. \quad (17b)$$

We consider an example of a 12-vibrational mode molecule ($N=12$). The model can be viewed as a simplistic caricature of the $\text{F}^- - \text{CH}_3\text{Cl}$ complex that isomerizes to $\text{FCH}_3 - \text{Cl}^-$ during the $\text{F}^- + \text{CH}_3\text{Cl}$ $\text{S}_{\text{N}}2$ reaction. For simplicity, we take nine of the frequencies to be evenly distributed between 0 and 1500 cm^{-1} , and the other three to be 3000 cm^{-1} , a range similar to that for $\text{F}^- - \text{CH}_3\text{Cl}$ [43]. Only the nine vibrations in the lower “band” of vibrational frequencies participate in energy flow at the relatively low energies of isomerization, the barrier to which is about 3.5 kcal/mol [43]. This gives $\Omega_{\text{rms}} = 620 \text{ cm}^{-1}$. We take as a representative value for a cubic anharmonic constant, $\Phi_3 = 7 \text{ cm}^{-1}$, and a “decay rate constant” for higher order anharmonicity, $\sigma = 10$, both within the established limits for organic molecules [20,42]. We calculate $T(E)$ as a function of energy, E , with Eq. (16), then calculate the participation number, p , with Eqs. (7)–(11). Results for $T(E)$ and $p(E)$ are plotted in Fig. 1.

The participation number, p , is calculated to be finite for energies up to the quantum ergodicity threshold, which lies at 1690 cm^{-1} for the parameters used in the calculation. We note that this value is higher than estimates for the isomerization barrier for the reaction $\text{F}^- - \text{CH}_3\text{Cl}$ to $\text{FCH}_3 - \text{Cl}^-$, which are in the neighborhood of 1200 cm^{-1} [43]. There is thus a sizable region of energy above the barrier for which the vibrations of $\text{F}^- - \text{CH}_3\text{Cl}$ are non-ergodic. In this example, the rise in p towards the limit of the entire phase volume is seen in Fig. 1 to be quite sharp. Therefore, there can be an enhancement of the unimolecular reaction rate over a broad range in energy above the reaction barrier.

We take the isomerization barrier to be 1200 cm^{-1} , a reasonable estimate for the isomerization barrier for $\text{F}^- - \text{CH}_3\text{Cl}$ to $\text{FCH}_3 - \text{Cl}^-$ [43]. We also take for simplicity the vibrational frequencies in the transition state to be the same as those for the reactant, and the lowest frequency mode (167 cm^{-1}) to be that corresponding to the reaction

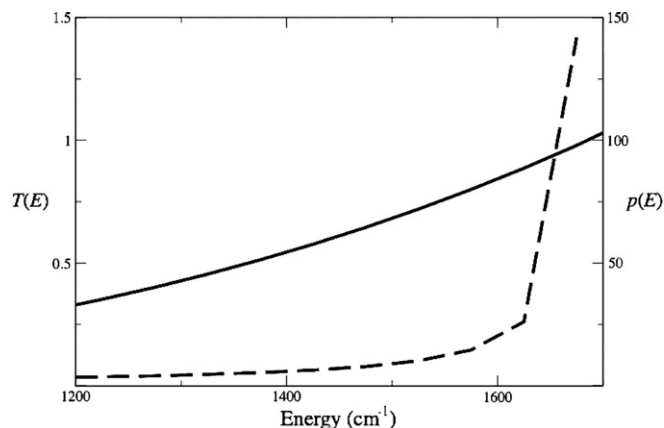


Fig. 1. Plot of the transition parameter, $T(E)$ (solid curve), and the participation number, $p(E)$ (dashed curve), calculated using local random matrix theory (LRMT), against total energy for the model 12-vibrational mode organic molecule of the illustrative example.

coordinate with frequency, ν . We calculate the total density of vibrational states, ρ_{total} , by direct count, which we then use to calculate the RRKM rate, k_{RRKM} , with Eq. (1). We then calculate the quantum non-ergodic statistical rate enhancement factor as $\frac{k_{\text{QunEST}}(E)}{k_{\text{RRKM}}(E)}$. The result of this calculation is plotted in Fig. 2. The bare enhancement of the reaction rate compared to the RRKM theory rate due to reduction of the vibrational state space, which is given by Eq. (5) with $\kappa(E) = 1$, is seen to be over an order of magnitude to about 1600 cm^{-1} , and is almost 2 orders of magnitude near the threshold energy. Introducing the

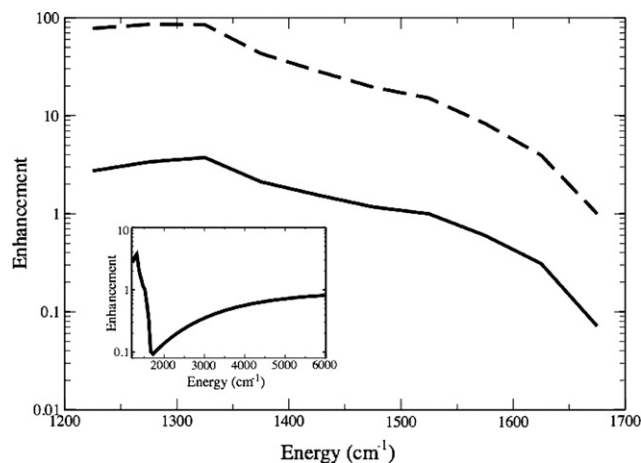


Fig. 2. Plot of the quantum non-ergodic statistical theory enhancement factor, $k_{\text{QunEST}}(E)/k_{\text{RRKM}}(E)$, for a model 12-vibrational mode organic molecule with 1200 cm^{-1} isomerization barrier at energies below the quantum ergodicity threshold, found to be 1690 cm^{-1} for this model. The dashed curve is the enhancement when k_{QunEST} is calculated with Eq. (5) assuming $\kappa(E) = 1$. The solid curve is the enhancement calculated with a correction, $\kappa(E)$ defined by Eq. (4), that accounts for the finite rate of energy flow between transition states and non-transition states of the limited ergodic region, which has been estimated using Eq. (17). The inset shows the rate up to 6000 cm^{-1} relative to the RRKM rate, which is calculated below the ergodicity threshold of 1690 cm^{-1} as $k_{\text{QunEST}}(E)/k_{\text{RRKM}}(E)$ including the correction, $\kappa(E)$, accounting for energy flow, and above the threshold is calculated as $\kappa(E)$.

transmission coefficient, $\kappa(E)$, which corrects for the finite rate of energy flow between transition states and non-transition states within the limited ergodic region diminishes the enhancement, which is seen in this example to be about a factor of 4 at energies close to the barrier energy. Above the ergodicity threshold of 1690 cm^{-1} , the ratio of the reaction rate to the RRKM theory estimate for the rate is $\kappa(E)$. We see in the inset of Fig. 2 that in this model $\kappa(E)$ will approach values close to 1 only at energies considerably higher than the ergodicity threshold, reaching 0.85 at 6000 cm^{-1} .

4. Concluding remarks

A variety of chemical reactions occur with rates larger than predicted by RRKM theory apparently because RRKM theory overestimates the volume of phase space in which the reaction takes place. Some time ago Berne developed a classical, non-ergodic statistical theory [41] describing how such an enhancement occurs. Here, we have put forth a quantum mechanical version of this theory describing the quantum mechanical energy flow in the vibrational state space using local random matrix theory. The reaction rate can be enhanced considerably if there is limited ergodicity at energies above the isomerization barrier. In a specific, illustrative example, we have shown that the rate may be many times faster than the RRKM prediction as a result of this effect.

We note that for the reactions discussed by Carpenter [17], for which RRKM theory overestimates the reaction rate, the discrepancy between the observed rate and the RRKM rate probably also involves incomplete mixing between rotations and vibrations. The present theory for the calculation of the reaction rate, $k_{\text{QunEST}}(E)$, quantifies the rate enhancement when the vibrations are themselves not ergodic and where energy flow is largely isotropic. The actual enhancement may be larger than in the calculation presented here when anisotropic flow or limited or sluggish energy flow between vibrations and rotations are taken into account, since the relative size of the limited ergodic portion of the state space to that assumed in an RRKM theory calculation is then even smaller.

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