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ABSTRACT

A series of experiments demonstrates that strong light–matter coupling between vibrational excitations in isotropic solutions of molecules and resonant infrared optical microcavity modes leads to modified thermally activated kinetics. However, Galego *et al.* [Phys. Rev. X **9**, 021057 (2019)] recently demonstrated that, within transition state theory, effects of strong light–matter coupling with reactive modes are mostly electrostatic and essentially independent of light–matter resonance or even of the formation of vibrational polaritons. To analyze this puzzling theoretical result in further detail, we revisit it under a new light, invoking a normal mode analysis of the transition state and reactant configurations for an ensemble of an arbitrary number of molecules in a cavity, obtaining simple analytical expressions that produce similar conclusions as Feist. While these effects become relevant in optical microcavities if the molecular dipoles are anisotropically aligned, or in cavities with extreme confinement of the photon modes, they become negligible for isotropic solutions in microcavities. It is concluded that further studies are necessary to track the origin of the experimentally observed kinetics.

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I. INTRODUCTION

Multiple experimental results show that reactions taking place inside of optical microcavities proceed with different kinetics than outside of them.^{1–6} Rate modification seems to require that the confined electromagnetic mode couples to one of the varieties of molecular vibrational modes present in the reactive medium.⁴ For reactions in solution, where molecules are isotropically distributed, this coupling is maximized under resonant conditions, i.e., when the cavity is tuned to a vibrational frequency in the molecules. In addition, the effect on the kinetics has been observed to increase as the collective coupling intensifies, as a consequence of the large number of molecules present in a sample.^{1,7} These observations are reminiscent of the description of light–matter coupling in terms of hybrid states known as polaritons,^{8–13} which successfully explains the optical properties of these systems.^{14–18} Recently, it has been suggested that a class of nonadiabatic charge transfer reactions would experience a catalytic effect from resonant collective coupling between high-frequency modes and infrared cavity modes; the mechanism relies on the formation of vibrational polaritons that feature reduced activation energies compared to the bare molecules.^{19,20}

However, a large class of reactions fall in the adiabatic regime, where the potential energy surfaces of the electronic ground and excited states are well-separated. These reactions should be accurately described by a transition state theory (TST)^{21–23} that accounts for vibrational strong coupling (VSC). Feist and co-workers, in fact, developed a theoretical framework with the essential ingredients to capture the action of a confined electromagnetic field on chemical processes such as nucleophilic substitution.^{24,25} Within this framework, they find that the presence of a cavity mode modifies the reactive potential energy surface, thus predicting conditions for the increase and decrease in reaction rates. However, according to their results, resonance is not essential for this modification to take place. Furthermore, the effect depends on the intensity of the single-molecule coupling, and cooperativity can only occur under conditions such as the anisotropic alignment of the permanent dipoles, an unlikely condition for the aforementioned reported experiments.²⁶ Remarkably, Feist's formalism excludes the language of polaritons. In fact, they concede that polaritonic degrees of freedom appear inconsequentially in the form of normal modes near the equilibrium configurations of the system and that the effects are of the Casimir–Polder type.²⁴ In this work, we restate their formalism bringing

the polaritonic modes into the limelight; we take advantage of the polaritonic framework to expand the formalism and obtain simple and physically intuitive analytical TST expressions that describe the modified collisional prefactors and activation energies in terms of light and matter parameters. Our results are in line with the predictions of Refs. 24 and 25, highlighting that further work must be carried out to understand the difference between experiment and theory in the context of thermally activated reactions under VSC.

II. THEORY

According to TST, the rate constant at temperature T is defined as^{27–31}

$$k_{\text{TST}} = \frac{k_B T}{2\pi\hbar} \frac{Z_{\ddagger}}{Z_{\text{eq}}} e^{-\frac{E_a}{k_B T}}, \quad (1)$$

where k_B and \hbar are the Boltzmann and reduced Planck constants, respectively. Z_{\ddagger} is the partition function of the transition state (TS) without the contribution of the reactive mode, and Z_{eq} is the total partition function of the reactant state. $E_a = V_{\ddagger} + \frac{1}{2} \sum_i \hbar \omega_{i,\ddagger} - V_{\text{eq}} - \frac{1}{2} \sum_j \hbar \omega_{j,\text{eq}}$ is the activation energy, where the frequency $\omega_{i,r}$ corresponds to the square root of the i th positive eigenvalue of the Hessian of the potential energy surface evaluated at the state r . We will determine how the rate constant changes for a thermally activated process in which the reactant is a heteronuclear diatomic molecule, when it takes place inside an optical microcavity. While the following analysis can be straightforwardly generalized for a multimode system, we will treat only the simplest case for the sake of conceptual clarity. Such a system with N identical reactant molecules can be described by the Hamiltonian^{24,32}

$$\hat{H} = \hat{H}_{\text{EM}} + \sum_{i=1}^N (\hat{H}_{\text{mol}}^{(i)} + \hat{V}_{\text{int}}^{(i)}), \quad (2)$$

where $\hat{H}_{\text{EM}} = \hbar \omega_0 (\hat{a}_0^\dagger \hat{a}_0 + \frac{1}{2})$ characterizes a confined electromagnetic field of frequency ω_0 , and creation and annihilation operators are \hat{a}_0^\dagger and \hat{a}_0 , respectively. $\hat{H}_{\text{mol}}^{(i)} = \hat{T}_{\text{nuc}}^{(i)} + \hat{V}_{\text{nuc}}^{(i)} + \hat{T}_{\text{elec}}^{(i)} + \hat{V}_{\text{elec}}^{(i)} + \hat{V}_{\text{nuc-elec}}^{(i)}$ is the Hamiltonian of the i th molecule containing the kinetic, \hat{T} , and potential, \hat{V} , energies of the nuclear and electronic degrees of freedom as well as their Coulomb interaction. The coupling between light and matter is given by $\hat{V}_{\text{int}}^{(i)} = g \omega_0 \hat{q}_0 \epsilon \cdot \hat{\mu}_i$, where $\hat{q}_0 = \sqrt{\frac{\hbar}{2\omega_0}} (\hat{a}_0^\dagger + \hat{a}_0)$ and $g = -(\mathcal{V}\epsilon_0)^{-1/2}$ is the coupling constant, where \mathcal{V} is the mode volume and ϵ_0 is the vacuum permittivity; ϵ is the polarization vector of the cavity field, and $\hat{\mu}_i$ is the molecular vibrational electric dipole moment. In the (cavity) Born–Oppenheimer approximation,^{12,33} the ground state potential energy for the electronic Schrödinger equation with Hamiltonian $\hat{H}_{\text{elec}} = \hat{H} - \sum_{i=1}^N \hat{T}_{\text{nuc}}$ can be parameterized in terms of the nuclear coordinates, \mathbf{R} , and the photon coordinate q_0 , which is an eigenvalue of the operator \hat{q}_0 . Thus, the potential energy surface governing the nuclear degrees of freedom (Fig. 1) becomes

$$V(\mathbf{R}, q_0) = \sum_{i=1}^N V_{\text{nuc}}(\mathbf{R}_i) + \frac{\omega_0^2}{2} q_0^2 + \omega_0 g q_0 \epsilon \cdot \sum_{i=1}^N \boldsymbol{\mu}(\mathbf{R}_i). \quad (3)$$

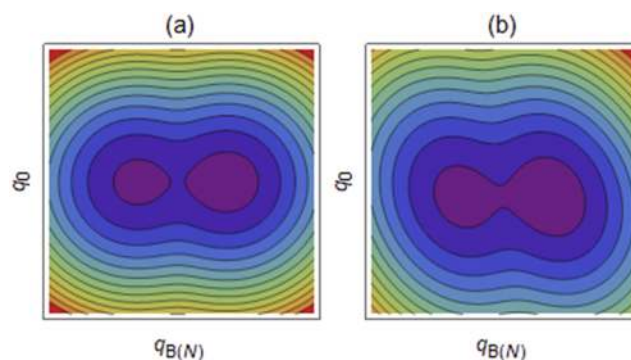


FIG. 1. Effect of VSC on a reactive potential energy surface. (a) Asymmetric double well potential uncoupled to an orthogonal harmonic cavity mode. (b) The same as in (a) but with non-zero light–matter coupling. The distortion of the wells reveals the redefinition of normal modes from the cavity and molecule to upper and lower polaritons.

Equation (3) implicitly assumes that the excited potential energy surfaces are well-separated in energy from the ground state. This is reasonable given that ω_0 is a frequency in the infrared region of the electromagnetic spectrum. In writing Eqs. (2) and (3), we have neglected the diamagnetic term arising from the Power–Zienau–Woolley transformation.³⁴ Its relevance for problems in the current context is explored in detail in Refs. 26 and 35. Nevertheless, since even in the ultrastrong regime, light–matter coupling *per molecule* is much smaller than the vibrational transition energies,³⁶ the inclusion of such a term should only account for slight modifications to the formalism that leave the findings unchanged.

In the neighborhood of the equilibrium configuration of the reactants, \mathbf{R}_{eq} , the potential is reasonably well described by a second order expansion, while the dipole moment can be approximated to first order,

$$V(\mathbf{R} \approx \mathbf{R}_{\text{eq}}, q_0) = \sum_{i=1}^N V_{\text{nuc}}(\mathbf{R}_{i,\text{eq}}) + \frac{\omega_{\text{eq}}^2}{2} \sum_{i=1}^N q_i^2 + \frac{\omega_0^2}{2} q_0^2 + \omega_0 g q_0 \sum_{i=1}^N (\mu_{i,\text{eq}} + \mu'_{i,\text{eq}} q_i), \quad (4)$$

where q_i is the mass-reduced bond elongation with respect to the equilibrium length of the i th molecule, $\omega_{\text{eq}}^2 = \left. \frac{\partial^2 V_{\text{nuc}}^{(i)}}{\partial q_i^2} \right|_0$, $\mu_{i,\text{eq}} = \epsilon \cdot \boldsymbol{\mu}(\mathbf{R}_{i,\text{eq}})$, and $\mu'_{i,\text{eq}} = \epsilon \cdot \left. \frac{\partial \boldsymbol{\mu}(\mathbf{R}_i)}{\partial q_i} \right|_0$. We note that this expansion excludes the polarizability term present in the perturbative treatment by Galego *et al.*;²⁴ however, as we shall see, this omission does not affect the main conclusions.

Differentiation of Eq. (4) yields

$$\frac{\partial V}{\partial q_0} = \omega_0^2 q_0 + \omega_0 g \sum_{i=1}^N (\mu_{i,\text{eq}} + \mu'_{i,\text{eq}} q_i), \quad (5a)$$

$$\frac{\partial V}{\partial q_j} = \omega_{\text{eq}}^2 q_j + \omega_0 g q_0 \mu'_{j,\text{eq}}, \quad 1 \leq j \leq N, \quad (5b)$$

and therefore, at the new minimum, $\mathbf{R}_{\text{eq}}^{\text{VSC}}$, close to \mathbf{R}_{eq} , the coordinates fulfill

$$\begin{pmatrix} \omega_0^2 & \omega_0 g \sqrt{N \langle \mu_{\text{eq}}^2 \rangle_N} \\ \omega_0 g \sqrt{N \langle \mu_{\text{eq}}^2 \rangle_N} & \omega_{\text{eq}}^2 \end{pmatrix} \begin{pmatrix} q_0 \\ q_{\text{B}(N)} \end{pmatrix} = -\omega_0 g N \langle \mu_{\text{eq}} \rangle_N \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (6)$$

where $\langle x \rangle_N = \frac{1}{N} \sum_{i=1}^N x_i$, and the bright molecular mode is given by $q_{\text{B}(N)} = \sqrt{\frac{N}{\langle \mu_{\text{eq}}^2 \rangle_N}} \langle \mu'_{\text{eq}} q \rangle_N$.

The coefficient matrix in Eq. (6) corresponds to the Hopfield-Bogoliubov form of the Dicke model in the normal phase,^{37,38} therefore, its diagonalization gives rise to polariton modes, as shown in Fig. 1. To be specific, Eq. (6) can be rewritten as

$$\begin{pmatrix} \omega_{+(N)}^2 & 0 \\ 0 & \omega_{-(N)}^2 \end{pmatrix} \begin{pmatrix} q_{+(N)} \\ q_{-(N)} \end{pmatrix} = -\omega_0 g N \langle \mu_{\text{eq}} \rangle_N \begin{pmatrix} \cos \theta_N \\ \sin \theta_N \end{pmatrix}, \quad (7)$$

where $\omega_{\pm(N)}^2 = \frac{1}{2} \left[\omega_0^2 + \omega_{\text{eq}}^2 \pm \sqrt{4\omega_0^2 g^2 N \langle \mu_{\text{eq}}^2 \rangle_N + (\omega_0^2 - \omega_{\text{eq}}^2)^2} \right]$ is the frequency squared of the upper(lower) polaritonic mode, $\begin{pmatrix} q_{+(N)} \\ q_{-(N)} \end{pmatrix}$

$= \begin{pmatrix} \cos \theta_N & -\sin \theta_N \\ \sin \theta_N & \cos \theta_N \end{pmatrix} \begin{pmatrix} q_0 \\ q_{\text{B}(N)} \end{pmatrix}$ are the polaritonic mode coordinates, and

$\theta_N = -\frac{1}{2} \arctan \frac{2\omega_0 g \sqrt{N \langle \mu_{\text{eq}}^2 \rangle_N}}{\omega_0^2 - \omega_{\text{eq}}^2}$ is the mixing angle.

Equation (4) can be recast using this new set of coordinates in the form

$$\begin{aligned} V(\mathbf{R} \approx \mathbf{R}_{\text{eq}}, q_0) &= \sum_{i=1}^N V_{\text{nuc}}(\mathbf{R}_{i,\text{eq}}) + \frac{\omega_{\text{eq}}^2}{2} \sum_{k=1}^{N-1} q_{\text{D}(N)}^{(k)2} \\ &+ \frac{\omega_{+(N)}^2}{2} q_{+(N)}^2 + \frac{\omega_{-(N)}^2}{2} q_{-(N)}^2 \\ &+ \omega_0 g N \langle \mu_{\text{eq}} \rangle_N (\cos \theta_N q_{+(N)} + \sin \theta_N q_{-(N)}), \quad (8) \end{aligned}$$

where $q_{\text{D}(N)}^{(k)} = \sum_{i=1}^N c_{ki} q_i$ are the dark vibrational modes, with the coefficients c_{ki} fulfilling $\sum_{i=1}^N \mu_{i,\text{eq}}' c_{ki} = 0$ and $\sum_{i=1}^N c_{k'i}^* c_{ki} = \delta_{k'k}$. Evaluating the potential in Eq. (8) at $\mathbf{R}_{\text{eq}}^{\text{VSC}}$ yields

$$V_{\text{eq}}^{\text{VSC}} = \sum_{i=1}^N V_{\text{nuc}}(\mathbf{R}_{i,\text{eq}}) - \left(\frac{\omega_0 \omega_{\text{eq}}}{\omega_{+(N)} \omega_{-(N)}} g N \langle \mu_{\text{eq}} \rangle_N \right)^2. \quad (9)$$

We note that the modification to the potential is proportional to the ratio of the determinants of the Hessian without and with light-matter coupling, which acts as a measure of the redefinition of the normal modes. Additionally, the presence of the permanent dipole reveals the largely electrostatic nature of this effect.

Without loss of generality, let us assume that the molecule with label N undergoes a reaction. The potential energy surface in the

neighborhood of the TS configuration, \mathbf{R}_{\ddagger} , is

$$\begin{aligned} V(\mathbf{R} \approx \mathbf{R}_{\ddagger}, q_0) &= \sum_{i=2}^N V_{\text{nuc}}(\mathbf{R}_{i,\text{eq}}) + V_{\text{nuc}}(\mathbf{R}_{N,\ddagger}) \\ &+ \frac{\omega_{\text{eq}}^2}{2} \sum_{i=1}^{N-1} q_i^2 + \frac{\omega_0^2}{2} q_0^2 + \frac{\omega_{\ddagger}^2}{2} q_N^2 \\ &+ \omega_0 g q_0 \left[\sum_{i=1}^{N-1} (\mu_{i,\text{eq}} + \mu'_{i,\text{eq}} q_i) + \mu_{\ddagger} + \mu'_{\ddagger} q_N \right]. \quad (10) \end{aligned}$$

Here, $\omega_{\ddagger}^2 = \frac{\partial^2 V_{\text{nuc}}^{(N)}}{\partial q_N^2} \Big|_{q_{\ddagger}} < 0$ is the squared frequency of the unstable mode, $\mu_{\ddagger} = \epsilon \cdot \boldsymbol{\mu}(\mathbf{R}_{N,\ddagger})$, and $\mu'_{\ddagger} = \epsilon \cdot \frac{\partial \boldsymbol{\mu}(\mathbf{R}_N)}{\partial q_N} \Big|_{q_{\ddagger}}$.

Applying the previous treatment to the potential energy surface in the saddle point, $\mathbf{R}_{\ddagger}^{\text{VSC}}$, the coordinates fulfill

$$\begin{pmatrix} \omega_0^2 & \omega_0 g \sqrt{(N-1) \langle \mu_{\text{eq}}^2 \rangle_{N-1}} & \omega_0 g \mu'_{\ddagger} \\ \omega_0 g \sqrt{(N-1) \langle \mu_{\text{eq}}^2 \rangle_{N-1}} & \omega_{\text{eq}}^2 & 0 \\ \omega_0 g \mu'_{\ddagger} & 0 & \omega_{\ddagger}^2 \end{pmatrix} \begin{pmatrix} q_0 \\ q_{\text{B}(N-1)} \\ q_N \end{pmatrix} = -\omega_0 g \left[(N-1) \langle \mu_{\text{eq}} \rangle_{N-1} + \mu_{\ddagger} \right] \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}. \quad (11)$$

For typical values of the transition dipole moments, the off-diagonal terms that depend on N remain significant since the number of molecules per cavity mode is estimated between 10^6 and 10^{10} .^{39,40} The term $g\omega_0\mu'_{\ddagger}$ is several orders of magnitude smaller, and we can neglect it to recover a polaritonic picture where

$$\begin{pmatrix} \omega_{+(N-1)}^2 & 0 & 0 \\ 0 & \omega_{-(N-1)}^2 & 0 \\ 0 & 0 & \omega_{\ddagger}^2 \end{pmatrix} \begin{pmatrix} q_{+(N-1)} \\ q_{-(N-1)} \\ q_N \end{pmatrix} \approx -\omega_0 g \left[(N-1) \langle \mu_{\text{eq}} \rangle_{N-1} + \mu_{\ddagger} \right] \begin{pmatrix} \cos \theta_{N-1} \\ \sin \theta_{N-1} \\ 0 \end{pmatrix} \quad (12)$$

at $\mathbf{R}_{\ddagger}^{\text{VSC}}$. Thus, the potential at the saddle point becomes

$$\begin{aligned} V_{\ddagger}^{\text{VSC}} &= \sum_{i=1}^{N-1} V_{\text{nuc}}(\mathbf{R}_{i,\text{eq}}) + V_{\text{nuc}}(\mathbf{R}_{N,\ddagger}) \\ &- \left(\frac{\omega_0 \omega_{\text{eq}}}{\omega_{+(N-1)} \omega_{-(N-1)}} g \left[(N-1) \langle \mu_{\text{eq}} \rangle_{N-1} + \mu_{\ddagger} \right] \right)^2. \quad (13) \end{aligned}$$

From Eqs. (4), (10), and (12), it follows that the step to the TS can be written as

$$\text{UP}_N + \text{LP}_N + \sum_{k=1}^{N-1} D_N^{(k)} \longrightarrow \text{UP}_{N-1} + \text{LP}_{N-1} + \sum_{k'=1}^{N-2} D_{N-1}^{(k')} + R_N^{\ddagger}, \quad (14)$$

where R_N^{\ddagger} represents the reactive molecule in the TS. Therefore, the rate constant should include the partition functions of the whole ensemble of molecules coupled to light; however, as we will see,

since only one molecule undergoes the reaction, the ratio of partition functions simplifies to an intelligible expression in terms of the single molecule k_{TST} .

Outside of the cavity, the rate constant takes the form

$$k_{\text{TST}} = \frac{k_B T}{\pi \hbar} \frac{Q_{\ddagger}}{Q_{\text{eq}}} \sinh\left(\frac{\hbar \omega_{\text{eq}}}{2k_B T}\right) \times \exp\left(-\frac{V_{\text{nuc}}(\mathbf{R}_{N,\ddagger}) - V_{\text{nuc}}(\mathbf{R}_{N,\text{eq}})}{k_B T}\right), \quad (15)$$

where the ratio $Q_{\ddagger}/Q_{\text{eq}}$ captures all the information from the translational and rotational degrees of freedom (for a 1D system comprised of the reactive mode only, $Q_{\ddagger} = Q_{\text{eq}}$). To characterize the effect of the cavity mode on the kinetics, we define

$$k_{\text{TST}}^{\text{VSC}} = \kappa_N k_{\text{TST}}, \quad (16)$$

where the ratio of rate constants is given by

$$\kappa_N = A_{\text{VSC}}(T) \exp\left(-\frac{\Delta V_{\text{VSC}} + \Delta E_0^{\text{VSC}}}{k_B T}\right) \quad (17a)$$

with prefactor

$$A_{\text{VSC}}(T) = \frac{\sinh(\hbar \omega_{+(N)})/2k_B T \sinh(\hbar \omega_{-(N)})/2k_B T}{\sinh(\hbar \omega_{+(N-1)})/2k_B T \sinh(\hbar \omega_{-(N-1)})/2k_B T}, \quad (17b)$$

cavity-induced potential energy difference

$$\Delta V_{\text{VSC}} = \omega_0^2 \omega_{\text{eq}}^2 g^2 \left[\left(\frac{N \langle \mu_{\text{eq}} \rangle_N}{\omega_{+(N)} \omega_{-(N)}} \right)^2 - \left(\frac{(N-1) \langle \mu_{\text{eq}} \rangle_{N-1} + \mu_{\ddagger}}{\omega_{+(N-1)} \omega_{-(N-1)}} \right)^2 \right], \quad (17c)$$

and zero-point-energy difference

$$\Delta E_0^{\text{VSC}} = \frac{\hbar \omega_{+(N-1)} + \hbar \omega_{-(N-1)} - \hbar \omega_{+(N)} - \hbar \omega_{-(N)}}{2}. \quad (17d)$$

As stated before, $N \gg 1$. In this limit, $A_{\text{VSC}}(T) \approx 1$, $\Delta E_0^{\text{VSC}} \approx 0$, and the ratio of rate constants becomes

$$\kappa_N \approx \exp\left[\frac{(\omega_{\text{eq}} g \mu_{\ddagger})^2}{(\omega_{\text{eq}}^2 - g^2 N \langle \mu_{\text{eq}}^2 \rangle) k_B T} \right], \quad (18)$$

where we have considered that, for typical reactions in liquid solution, the molecular dipoles are isotropically distributed; therefore, $\langle \mu_{\text{eq}} \rangle_N = 0$. Regarding collective effects, in Fig. 2, we show the ratio of rate constants as a function of the collective coupling and the permanent dipole moment of the TS. We can see that the variation of κ_N throughout the span of the weak and strong light-matter coupling regimes is negligible. Furthermore, even over a huge range of possible values of μ_{\ddagger} , the ratio of rate constants remains too close to 1 to imply any observable change in the reaction rate. In contrast, note that in a sample with perfectly aligned dipoles, $\langle \mu_{\text{eq}} \rangle_N \neq 0$, leading to substantial collective $O(N)$ contributions to ΔV_{VSC} [see Eq. (17c)]. Furthermore, regardless of dipole alignment, it can be shown that ΔV_{VSC} is independent of ω_0 and is therefore unable to describe a resonant effect.

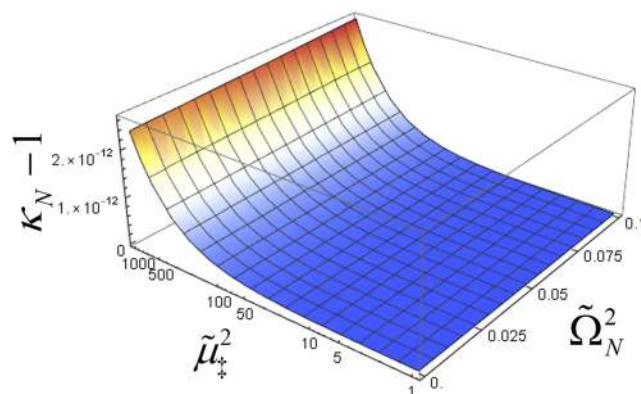


FIG. 2. Ratio of rate constants as a function of the permanent dipole in the TS and the collective light-matter coupling. $\tilde{\mu}_{\ddagger} = \mu_{\ddagger}/\langle(n+1)|\mu_{\text{eq}}|n\rangle$ is the permanent dipole moment in the TS normalized with respect to the transition dipole moment in the equilibrium configuration, and $\tilde{\Omega}_N = g\sqrt{N\langle\mu_{\text{eq}}^2\rangle}/\omega_{\text{eq}}$ is the light-matter coupling normalized with respect to the frequency in the same configuration. Over the span of the weak and strong coupling regimes and a wide range of values of the TS dipole, the transmission coefficient remains close to 1. For this calculation, $\omega_{\text{eq}} = 2000 \text{ cm}^{-1}$, $N = 10^9$, and $k_B T = 208.5 \text{ cm}^{-1}$.

III. CONCLUSIONS

From the previous analysis, we reach the same conclusions of Galego *et al.*:²⁴ the effects of resonance between the cavity and the vibrational modes cannot be captured in a description at the level of TST and the isotropic distribution of the permanent dipole moments negates the possibility of cooperative light-matter coupling effects. These results contrast with the situation of thermally activated non-adiabatic charge transfer reactions, where the role of collective light-matter resonance in isotropic media is more evident. While we agree that the role of the polaritonic picture in our present analysis is rather shallow, it undoubtedly simplifies and clarifies the theoretical analysis. In conclusion, our results restate that a TST that takes into account the strong coupling of the reactive mode to a resonant optical cavity mode is still insufficient to explain the experimental results involving thermally activated adiabatic reactions in Refs. 1–6.

Note added in proof. After submission, we became aware of a recent article that also provides a simplified TST picture of the thermally activated kinetics of reactions inside of optical microcavities.⁴¹ Despite the language of polariton normal modes not being central to its analysis, its conclusions are similar to ours.

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX: SINGLE-MOLECULE CASE

When there is a single molecule per cavity mode, the only surviving coupling in Eq. (11) is that between the TS and the photon. In this case, the saddle point condition can be recast in terms of the eigenmodes as

$$\begin{pmatrix} \omega_{-}^2 & 0 \\ 0 & \omega_{+}^2 \end{pmatrix} \begin{pmatrix} q_{+} \\ q_{-} \end{pmatrix} = -\omega_0 g \mu_{\pm} \begin{pmatrix} \cos \theta_{\pm} \\ \sin \theta_{\pm} \end{pmatrix}, \quad (\text{A1})$$

where $\omega_{-}^2 < 0 < \omega_{+}^2$. The potential energy evaluated at $\mathbf{R}_{\pm}^{\text{VSC}}$ is

$$V_{\pm}^{\text{VSC}} = V_{\text{nuc}}(\mathbf{R}_{\pm}) - \left(\frac{\omega_0 \omega_{\pm}}{\omega_{+} \omega_{-}} g \mu_{\pm} \right)^2, \quad (\text{A2})$$

which produces

$$A_{\text{VSC}} = \frac{\sinh(\hbar\omega_{+}/2k_B T) \sinh(\hbar\omega_{-}/2k_B T)}{\sinh(\hbar\omega_{+}/2k_B T) \sinh(\hbar\omega_{\text{eq}}/2k_B T)}, \quad (\text{A3a})$$

$$\Delta V_{\text{VSC}} = g^2 \omega_0^2 \left[\left(\frac{\omega_{\text{eq}} \mu_{\text{eq}}}{\omega_{+} \omega_{-}} \right)^2 - \left(\frac{\omega_{\pm} \mu_{\pm}}{\omega_{+} \omega_{-}} \right)^2 \right], \quad (\text{A3b})$$

$$\Delta E_0^{\text{VSC}} = \frac{\hbar\omega_{+} - \hbar\omega_{-} - \hbar\omega_{\text{eq}}}{2}. \quad (\text{A3c})$$

It is worth noting that, despite $A_{\text{VSC}}(T)$ and ΔE_0^{VSC} deviating from 1 to 0, respectively, in the single-molecule limit, the effect is still off-resonant, thus reinforcing the findings of Galego *et al.*²⁴ In any case, the mode volumes and transition dipole moments required to modify a reaction rate are unrealistic unless we consider nano- and picocavities.

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