The Journal of Chemical Physics

On the origin of ground-state vacuum-field catalysis: Equilibrium consideration

Cite as: J. Chem. Phys. **152**, 234107 (2020); https://doi.org/10.1063/5.0006472
Submitted: 02 March 2020 . Accepted: 27 May 2020 . Published Online: 15 June 2020

Tao E. Li, Abraham Nitzan, and Joseph E. Subotnik

COLLECTIONS

Paper published as part of the special topic on Photocatalysis and Photoelectrochemistry
Note: This paper is part of the JCP Special Topic on Photocatalysis and Photoelectrochemistry.

View Online Export Citation CrossMark

ARTICLES YOU MAY BE INTERESTED IN

State-pairwise decoherence times for nonadiabatic dynamics on more than two electronic states
The Journal of Chemical Physics **152**, 234105 (2020); https://doi.org/10.1063/5.0010081

Modeling voltammetry curves for proton coupled electron transfer: The importance of nuclear quantum effects
The Journal of Chemical Physics **152**, 234108 (2020); https://doi.org/10.1063/5.0010412

Polaritonic normal modes in transition state theory
The Journal of Chemical Physics **152**, 161101 (2020); https://doi.org/10.1063/5.0007547

Lock-in Amplifiers up to 600 MHz
Watch



© 2020 Author(s).

AIP Publishing

The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

On the origin of ground-state vacuum-field catalysis: Equilibrium consideration

Cite as: J. Chem. Phys. 152, 234107 (2020); doi: 10.1063/5.0006472
Submitted: 2 March 2020 • Accepted: 27 May 2020 •
Published Online: 15 June 2020

View Online Export Citation CrossMark

Tao E. Li,[1,a] Abraham Nitzan,[1,2,b] and Joseph E. Subotnik[1,c]

AFFILIATIONS

[1] Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA
[2] School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

Note: This paper is part of the JCP Special Topic on Photocatalysis and Photoelectrochemistry.
[a] **Author to whom correspondence should be addressed:** taoli@sas.upenn.edu
[b] **Electronic mail:** anitzan@sas.upenn.edu
[c] **Electronic mail:** subotnik@sas.upenn.edu

ABSTRACT

Recent experiments suggest that vibrational strong coupling (VSC) may significantly modify ground-state chemical reactions and their rates even without external pumping. The intrinsic mechanism of this "vacuum-field catalysis" remains largely unclear. Generally, modifications of thermal reactions in the ground electronic states can be caused by equilibrium or non-equilibrium effects. The former are associated with modifications of the reactant equilibrium distribution as expressed by the transition state theory of chemical reaction rates, while the latter stem from the dynamics of reaching and leaving transition state configurations. Here, we examine how VSC can affect chemical reactions rates in a cavity environment according to transition state theory. Our approach is to examine the effect of coupling to cavity mode(s) on the potential of mean force (PMF) associated with the reaction coordinate. Within the context of classical nuclei and classical photons and also assuming no charge overlap between molecules, we find that while the PMF can be affected by the cavity environment, this effect is negligible for the usual micron-length cavities used to examine VSC situations.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0006472

I. INTRODUCTION

Strong light–matter interactions can significantly modify the intrinsic properties of matter by forming hybrid light–matter states (i.e., polaritons).[1] The most common manifestation of this interaction is the Rabi splitting,[2–5]

$$\Omega_N = 2\sqrt{N}g_0, \tag{1}$$

where N is the number of closely spaced (relative to the wavelength) molecules, resulting from the coupling g_0 between the molecular transition and a resonant cavity mode. Moreover, due to the modification of the molecule's electronic levels, properties such as the energy transfer rate,[6] conductivity,[7] and the photochemical (i.e., light induced chemical change) reaction rates[8–11] can also be changed by strong light–matter interactions. The Rabi splitting in Eq. (1) was recently observed[12,13] in the case of vibrational strong coupling (VSC)—when an infrared cavity mode is resonantly coupled to a molecular vibrational mode. More intriguingly, it has been argued that the effect of VSC on the ground-state potential energy surface (PES) can result in an N-dependent modification of chemical reaction rates in the absence of external pumping, an effect termed vacuum-field catalysis.[14,15] Indeed, such behaviors were reported recently.[14,16–19]

This effect has attracted great attention of late as a novel manifestation of strong molecule–radiation field coupling with possible implications for catalysis. However, the physics underlying this behavior remains unclear. The difficulty is illustrated[20–23] by considering the following quantum Hamiltonian[24–26] used to analyze VSC effects (we set $\hbar = 1$):

$$\hat{H}_{\mathrm{RWA}} = \omega_0 \hat{a}^\dagger \hat{a} + \sum_{i=1}^{N} \omega_0 \hat{b}_i^\dagger \hat{b}_i + \sum_{i=1}^{N} g_0 (\hat{a}\hat{b}_i^\dagger + \hat{a}^\dagger \hat{b}_i), \tag{2}$$

where ω_0 denotes the energy of the cavity mode and molecular vibrations (assuming all are at resonance), and $\hat{a}$ ($\hat{a}^\dagger$) and $\hat{b}_i$ ($\hat{b}_i^\dagger$) denote the creation (annihilation) operators for the cavity mode and the ith

Published under license by AIP Publishing

vibrational mode, respectively. Note that the rotating-wave approximation (RWA) is taken in Eq. (2), which is a good approximation at resonance and when $\Omega_N \ll \omega_0$. Diagonalizing Eq. (2) leads to a pair of polariton states [known as the upper polariton (UP) and lower polariton (LP)] with a frequency difference Ω_N between them, and the remaining $N-1$ quantum states (known as the dark states) are totally decoupled from the cavity mode. Excitation from the ground state populates the polaritonic modes; however, it is not clear that these modes can affect the rate of a process in which a single molecule undergoes a chemical change. Put differently, at thermal equilibrium, most molecules are in the ground state and most of those with thermal energy of the order $\hbar\omega_0$ populate dark states, evolving just like bare molecules. Such a picture would not seem to agree with the experiments described above, and although a few theoretical studies have investigated VSC assisted vacuum-field catalysis,[15,23,27] to the best of our knowledge, a convincing and universal theory for the dependence on molecular density is still unavailable. For example, if one posits that an unknown mechanism were to force the UP or LP states to be a doorway to a chemical reaction, then the activation energy change should shift linearly with Ω_N,[15] in contrast to the recent studies demonstrating that both the entropy and enthalpy of chemical reactions vary *nonlinearly* as functions of Ω_N.[28]

Another way to look at the cavity effect on chemical reactions is to adhere to standard chemical rate theory when considering the possible effect of multimolecular coupling to cavity mode(s) on the chemical rate. Recent experiments indicate that "vacuum-field catalysis" is a collective effect, sometimes involving a macroscopic number of molecules.[14,16–18] For such system sizes, any full quantum treatment beyond the harmonic level is computationally very expensive. However, as often observed in chemical rate calculations, a classical picture should already contain the essence of the effect, with quantum effects providing additional corrections.

Chemical rate processes can be observed in different regimes. The simplest and most widely used picture is transition state theory (TST), which rests on the assumption that reactants maintain an equilibrium distribution in their configuration/velocity space even during the course of a rare event, e.g., a chemical reaction. In its classical unimolecular form, this theory assumes that a molecule undergoes the considered chemical change when its reaction coordinate x reaches a certain position ("transition configuration"). The probability to reach this configuration is determined, according to the equilibrium assumption, by the potential of mean force (PMF),[29,30] or free energy function, $F(x)$, defined by

$$e^{-\beta F(x)} \equiv \int d\mathbf{r}^N \int d\mathbf{p}^N \delta\big(x - \bar{x}(\mathbf{r}^N)\big) e^{-\beta H(\mathbf{p}^N, \mathbf{r}^N)}, \tag{3}$$

where $\beta = (k_B T)^{-1}$, $\mathbf{r}^N = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the configuration vector of the N-particle system, and $x = \bar{x}(\mathbf{r}^N)$ defines the reaction coordinate. At this level of description, assuming that the molecular reaction coordinate itself is the same inside and out of the cavity, the cavity effect on the reaction rate amounts to a change in the PMF and, in particular, the barrier height (i.e., activation energy) for the relevant potential.

In this paper, we investigate the implications of these considerations, as well as some of their quantum counterparts, for possible cavity effects on chemical rates. Within the context of classical nuclei and classical photons, we find that the PMF associated with the reaction coordinate of a single molecule can be modified by the cavity environment. However, the dependence of this modification on the number of molecules interacting with the cavity can result only from the cavity effect on intermolecular interactions. Such cavity effects are not necessarily related to the resonant interactions with a cavity mode and are identical to similar effects previously studied using image potential considerations.[31–35] Admittedly, there is one nuance here: one can separate the effects of intermolecular interactions from the effects of intramolecular interactions rigorously only within classical mechanics. Nevertheless, from the treatment below, we conclude that VSC catalysis cannot be directly explained through static equilibrium considerations when classical nuclei and photons are assumed. It should be emphasized that this conclusion does not preclude possible cavity effects as originating from inherently non-equilibrium effects that can dominate chemical rates in other dynamical regimes; as will be shown below, it is also possible that quantum mechanical effects could in principle lead to some collective effects on the PMF—though for now, we will hypothesize that such collective effects are unlikely.

A specific outline of the paper below is as follows: In Sec. II, we consider the implication of the interaction of N identical molecules with the cavity field *under the assumption that the cavity environment does not modify the direct intermolecular Coulombic interactions on the PMF associated with any single molecule*. Working in the Coulomb gauge, we show that while the cavity environment does modify the single-molecule PMF, this modification does not depend on N. This observation should not of course be gauge dependent, and indeed, we validate this observation in the equivalent dipole gauge (Power–Zienau–Woolley Hamiltonian[36,37]) representation, which provides a somewhat different perspective of this issue. Now, while disregarding cavity effects on the intermolecular Coulombic interactions may sometimes be a good approximation, it is fundamentally inconsistent with the theory of light–matter interaction, where a proper balance between such interactions and those mediated by the longitudinal part of the radiation field is required for achieving a fully retarded character of these interactions. Thus, in Sec. III, we re-examine this issue of intermolecular interactions by using a reasonable set of parameters and conclude that the cavity effects on intermolecular interactions are too small to explain observations of VSC-induced collective (namely N-dependent) effects on chemical rates (at least within the context of classical nuclei and photons). Finally, in the Appendix, we address the question of the PMF in the context of quantum nuclei and photons using a path-integral approach, but we are unable to establish with complete rigor whether the PMF is modified in any collective way; future numerical work will be needed in this regard.[38]

II. POTENTIAL OF MEAN FORCE

A. Single-cavity-mode approximation

We start with the standard Coulomb-gauge expression for the Hamiltonian of a system of charges interacting with the radiation field represented by a single cavity mode of frequency ω (the formulation remains the same if a sum over cavity modes is taken),

$$\hat{H} = \sum_i \frac{1}{2m_i}\big[\hat{\mathbf{p}}_i - Z_i e\hat{\mathbf{A}}(\hat{\mathbf{r}}_i)\big]^2 + \hat{V}_{\mathrm{Coul}}(\{\hat{\mathbf{r}}_i\}) + \hbar\omega\hat{a}^\dagger\hat{a}. \tag{4}$$

Published under license by AIP Publishing

Here, $\hat{a}^\dagger$ ($\hat{a}$) denotes the creation (annihilation) operator of the cavity mode; e denotes the electronic charge; and m_i, $\hat{\mathbf{p}}_i$, and $\hat{\mathbf{r}}_i$ are the mass, momentum, and position of the particle i of charge $Z_i e$, respectively. $\hat{V}_{\text{Coul}}(\{\hat{\mathbf{r}}_i\})$ denotes the electrostatic interaction between all charged particles, and

$$\hat{\mathbf{A}}(\mathbf{r}) = \sqrt{\frac{\hbar}{2\omega\Omega\epsilon_0}}\boldsymbol{\xi}\left[\exp(i\mathbf{k}\cdot\mathbf{r})\hat{a} + \exp(-i\mathbf{k}\cdot\mathbf{r})\hat{a}^\dagger\right] \tag{5}$$

denotes the vector potential of the electromagnetic field. ϵ_0 is the vacuum permittivity, while Ω, $\boldsymbol{\xi}$, and $\mathbf{k}$ denote the cavity volume, mode polarization, and wave vectors that satisfy $\boldsymbol{\xi}\cdot\mathbf{k} = 0$. Next, we make the long-wave approximation, assuming that the size of the molecular ensemble is much smaller than the wavelength of the cavity mode (or when many modes are considered—of all relevant modes). In this case, Eq. (5) can be approximated by

$$\hat{\mathbf{A}}(\mathbf{0}) = \sqrt{\frac{\hbar}{2\omega\Omega\epsilon_0}}\boldsymbol{\xi}\left(\hat{a} + \hat{a}^\dagger\right). \tag{6}$$

The molecular system is characterized by the total dipole moment

$$\hat{\boldsymbol{\mu}}_S = \sum_i Z_i e\hat{\mathbf{r}}_i, \tag{7}$$

which may be also grouped into the dipole moments of the individual molecules (indexed by n),

$$\hat{\boldsymbol{\mu}}_S = \sum_n \hat{\boldsymbol{\mu}}_n, \quad \hat{\boldsymbol{\mu}}_n = \sum_{j\in n} Z_j e\hat{\mathbf{r}}_j. \tag{8}$$

The molecules are assumed neutral, $\sum_{j\in n} Z_j = 0$; hence, $\hat{\boldsymbol{\mu}}_n$ does not depend on the choice of origin of coordinates. Next, we perform the unitary Göppert-Mayer transformation, $\hat{H}' = \hat{U}\hat{H}\hat{U}^\dagger$ with $\hat{U} = \exp\left[-\frac{i}{\hbar}\hat{\boldsymbol{\mu}}_S\cdot\hat{\mathbf{A}}(\mathbf{0})\right]$, leading to

$$\hat{H}' = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i} + \hat{V}_{\text{Coul}}(\{\hat{\mathbf{r}}_i\}) + \hbar\omega\hat{a}^\dagger\hat{a} - \hat{\boldsymbol{\mu}}_S\cdot\hat{\mathbf{E}} + \frac{1}{2\Omega\epsilon_0}\left(\hat{\boldsymbol{\mu}}_S\cdot\boldsymbol{\xi}\right)^2, \tag{9}$$

where $\hat{\mathbf{E}} = i\boldsymbol{\xi}\sqrt{\frac{\hbar\omega}{2\Omega\epsilon_0}}\left(\hat{a} - \hat{a}^\dagger\right)$ is the operator representing the electric field associated with the cavity mode.

Anticipating the possibility of making a classical approximation, it is also useful to recast the photon operators $\hat{a}$ and $\hat{a}^\dagger$ in Eq. (9) in terms of coordinate and momentum operators. Putting $\hat{a} = (2\hbar\omega)^{-1/2}(\omega\hat{q} - i\hat{p})$ and $\hat{a}^\dagger = (2\hbar\omega)^{-1/2}(\omega\hat{q} + i\hat{p})$ leads to $\hbar\omega\hat{a}^\dagger\hat{a} = \frac{1}{2}(\omega^2\hat{q}^2 + \hat{p}^2)$ and $\hat{\boldsymbol{\mu}}_S\cdot\hat{\mathbf{E}} = (\Omega\epsilon_0)^{-1/2}\left(\hat{\boldsymbol{\mu}}_S\cdot\boldsymbol{\xi}\right)\hat{p}$; the Hamiltonian (9) becomes

$$\hat{H}' = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i} + \hat{V}_{\text{Coul}}(\{\hat{\mathbf{r}}_i\}) + \frac{1}{2}\omega^2\hat{q}^2 + \frac{1}{2}\left(\hat{p} - \sqrt{\frac{1}{\Omega\epsilon_0}}\left(\hat{\boldsymbol{\mu}}_S\cdot\boldsymbol{\xi}\right)\right)^2. \tag{10}$$

More generally, the last two terms of Eq. (10) will be summed over all relevant cavity modes. Our focus is on the effects of vibrational strong coupling, where relevant cavity modes are assumed to evolve at time scales similar to molecular vibrational motions. The effect of faster modes, which under the Born–Oppenheimer time scale separation should be considered together with the electronic Hamiltonian, will be disregarded assuming that their energetic consequences (for electromagnetic vacuum) are small relative to electronic energy scales.

With this assumption, we may proceed to consider the potential energy surface associated with the ground electronic state of the Hamiltonian (10) assuming that the photon dynamics, namely, the evolution $[q(t), p(t)]$ takes place at a nuclear time scale. Disregarding intermolecular interactions embedded in $\hat{V}_{\text{Coul}}(\{\hat{\mathbf{r}}_i\})$, the ground-state nuclear/cavity photon Hamiltonian is

$$H_{\text{nuc}} = \sum_{n=1}^{N}\frac{P_n^2}{2M_n} + \frac{1}{2}\omega^2 q^2 + V(\{R_n\}, p), \tag{11}$$

where we now use capital P_n and R_n (rather than $\hat{\mathbf{p}}_i$ and $\hat{\mathbf{r}}_i$) to represent nuclear degrees of freedom (DOFs). The potential surface (electronic energy) for the N-molecule aggregate plus photon is

$$V(\{R_n\}, p) = \sum_{n=1}^{N} E_g(R_n) + \frac{1}{2}\left\langle\Psi_G\left|\left[p - \sqrt{\frac{1}{\Omega\epsilon_0}}\left(\sum_{n=1}^{N}\hat{\boldsymbol{\mu}}_n\cdot\boldsymbol{\xi}\right)\right]^2\right|\Psi_G\right\rangle. \tag{12}$$

Here, $E_g(R_n)$, the electronic ground-state energy of an individual molecule, is a function of its nuclear configuration (represented by R_n, with $\{R_n\}$ denoting the nuclear configurations of all N molecules), $P_n (n = 1, \ldots, N)$ denotes the nuclear momentum, and $\Psi_G(\{R_n\})$ denotes the ground-state electronic wave function for the molecular subsystem. Note that the designation of q or p as photon coordinate and momentum or vice versa is immaterial. In addition, note that for each molecule, the dipole operator $\hat{\boldsymbol{\mu}}_n = \hat{\boldsymbol{\mu}}_{ne} + \hat{\boldsymbol{\mu}}_{n,nuc}$ is a sum of electronic and nuclear terms, but these two terms should be considered together, otherwise each will depend on the choice of origin.

The second term in Eq. (12) should be handled with care because the square introduces bimolecular terms. According to the Hartree approximation, let $\Psi_G(\{R_n\}) = \prod_{n=1}^{N}\psi_{ng}(R_n)$ be a product of single-molecule electronic ground states and also denote $\hat{d}_n \equiv \hat{\boldsymbol{\mu}}_n\cdot\boldsymbol{\xi}$ and $d_{ng} \equiv \langle\psi_{ng}(R_n)|\hat{\boldsymbol{\mu}}_n|\psi_{ng}(R_n)\rangle\cdot\boldsymbol{\xi}$. The second term in Eq. (12) becomes

$$\begin{aligned}
&\frac{1}{2}\left\langle\Psi_G\left|\left[p - \sqrt{\frac{1}{\Omega\epsilon_0}}\left(\sum_{n=1}^{N}\hat{d}_n\right)\right]^2\right|\Psi_G\right\rangle \\
&= \frac{1}{2}\left[p - \sqrt{\frac{1}{\Omega\epsilon_0}}\left(\sum_{n=1}^{N} d_{ng}(R_n)\right)\right]^2 \\
&\quad + \frac{1}{2\Omega\epsilon_0}\left[\left\langle\Psi_G\left|\sum_{n=1}^{N}\left(\hat{d}_n - d_{ng}(R_n)\right)^2\right|\Psi_G\right\rangle\right] \\
&= \frac{1}{2}\left[p - \sqrt{\frac{1}{\Omega\epsilon_0}}\left(\sum_{n=1}^{N} d_{ng}(R_n)\right)\right]^2 \\
&\quad + \sum_{n=1}^{N}\frac{1}{2\Omega\epsilon_0}\left[\left\langle\psi_{ng}\left|\left(\hat{d}_n - d_{ng}(R_n)\right)^2\right|\psi_{ng}\right\rangle\right].
\end{aligned} \tag{13}$$

Note that in calculating Eq. (13), the main issue is how to calculate the expectation value of the self-dipole term $\langle\Psi_G|\left(\sum_n\hat{d}_n\right)^2|\Psi_G\rangle = \sum_{n,l}\langle\Psi_G|\hat{d}_n\hat{d}_l|\Psi_G\rangle$. For $n = l$, the expression becomes $\langle\psi_{ng}|\hat{d}_n^2|\psi_{ng}\rangle = d_{ng}^2 + \langle\psi_{ng}|(\hat{d}_n - d_{ng})^2|\psi_{ng}\rangle$. For $n \neq l$, the expression becomes $\langle\psi_{ng}\psi_{lg}|\hat{d}_n\hat{d}_l|\psi_{ng}\psi_{lg}\rangle = d_{ng}d_{lg}$.

Published under license by AIP Publishing

We then substitute Eq. (13) in Eqs. (12) and (11) to calculate the classical PMF according to [following Eq. (3)]

$$e^{-\beta F(R_j)} \equiv \int d\{P_n\} d'\{R_n\} dp dq e^{-\beta H_{\rm nuc}(\{P_n\},\{R_n\},p,q)}, \tag{14}$$

where $d'\{R_n\}$ denotes the integration of the nuclear coordinates of all molecules except molecule j. Note that in evaluating Eq. (14), the contribution from the first term on the bottom line of Eq. (13) will effectively disappear as it will be incorporated within the p integral, i.e., $\int_{-\infty}^{+\infty} dp\ \exp\left(-\beta\left[p - \sqrt{\frac{1}{\Omega\epsilon_0}}\left(\sum_{n=1}^{N} d_{ng}(R_n)\right)\right]^2/2\right)$ $= \int_{-\infty}^{+\infty} dp\ \exp\left(-\beta p^2/2\right) = \text{const}$. After the integrations over p, q, and $\{P_n\}$, Eq. (14) becomes (up to a constant)

$$\begin{aligned} e^{-\beta F(R_j)} &\sim \int d'\{R_n\} \prod_{n=1}^{N} \exp\Bigg[-\beta\Bigg(E_g(R_n) \\ &\quad + \frac{1}{2\Omega\epsilon_0}\left\langle \psi_{ng}(R_n)\left|\left(\hat{d}_n - d_{ng}(R_n)\right)^2\right|\psi_{ng}(R_n)\right\rangle\Bigg)\Bigg] \\ &\sim \exp\Bigg[-\beta\Bigg(E_g(R_j) \\ &\quad + \frac{1}{2\Omega\epsilon_0}\left\langle \psi_{jg}(R_j)\left|\left(\hat{d}_j - d_{jg}(R_j)\right)^2\right|\psi_{jg}(R_j)\right\rangle\Bigg)\Bigg]. \end{aligned} \tag{15}$$

We find that an effect on the PMF for a single molecule is

$$E_g(R) \to E_g(R) + \frac{1}{2\Omega\epsilon_0}\delta d^2(R). \tag{16}$$

Here, the self-dipole fluctuation terms are $\delta d^2(R) \equiv \left\langle \psi_g(R)\left|\left(\hat{d} - d_g(R)\right)^2\right|\psi_g(R)\right\rangle$ and $d_g(R) = \left\langle \psi_g(R)\left|\hat{d}\right|\psi_g(R)\right\rangle$.

The following points should be noted. First, for sufficiently small cavities ($\Omega \to 0$), the term $\frac{1}{2\Omega\epsilon_0}\delta d^2(R)$ can significantly modify the PMF and should be able to modify the ground-state chemistry. However, such an effect is not "collective" (that is, N-dependent), and for typical VSC experiments where micrometer-length cavities are used, the term $\frac{1}{2\Omega\epsilon_0}\delta d^2(R)$ should be negligible.

Second, a word is now appropriate vis-a-vis quantum vs classical mechanics. The term $\frac{1}{2\Omega\epsilon_0}\delta d^2(R)$ has a purely quantum origin and arises from the quantum treatment of the electron. When the molecules are treated entirely classically, the fluctuation $\delta d^2(R)$ would be zero, so the PMF would remain completely unchanged by the cavity. Such behavior is often discussed in the context of magnetism (denoted by $\mathbf{m}$), where the role of classical vs quantum mechanics is paramount.[39] According to the Bohr–van Leeuwen theorem, when molecules are treated classically, the evaluation of the momentum integral for the thermal-averaged magnetism [in a similar way as calculating Eq. (14)] leads to the conclusion $\langle \mathbf{m} \rangle = 0$, and therefore, one would predict a lack of magnetism. Of course, by symmetry, a fully quantum treatment of magnetism (that includes exchange) must also yield $\langle \mathbf{m} \rangle = 0$, but in practice, this result represents the average of two stable, symmetry-broken solutions with plus and minus magnetic moments. Thus, given the important distinction between classical and quantum mechanics, one may question our finding for the PMF above: even though we allowed for quantum *electrons*, we did rely on a classical assumption of *nuclear* and *photonic* DOFs. To that end, in the Appendix, we will present initial results for the fully quantum case as well.

Third and finally, yet another word of caution is also appropriate at this time. While the Hamiltonians (11) and (12) are often used to discuss molecular cavity QED phenomena, they constitute an approximation whose consistency has yet to be checked. In principle, within an exact quantum Hamiltonian for a system with light–matter interactions, all instantaneous Coulombic intermolecular interactions are canceled exactly by the presence of terms that arise from the self-interaction of dipoles arising from the last term in Eq. (12). This exact cancellation allows for causality to be enforced such that all intermolecular interactions are carried by the transverse photon field at the speed of light. However, to achieve this cancellation, one should sum contributions from all cavity modes. The approximation embedded in the Hamiltonians (4)–(10), such as in many other treatments of light–matter interactions in optical cavities, is to consider only such a cavity mode(s) that is (are) close to resonance with the molecular vibration(s) while keeping the intermolecular electrostatic interactions intact. While such an approximation appears reasonable when retardation effects are unimportant, it leaves open consistency issues that might arise in such systems. We note in passing that these intermolecular interactions [which are included within $\hat{V}_{\rm Coul}$ in Eq. (10)] are absent from Eq. (11) and in principle should be included, but we argue below that their dependence on the cavity environment is expressed only in cavity sizes much smaller than those actually used in the experimental work on VSC effects on ground-state chemical processes. Vice versa, if we did include these interactions, they will appear in the classical PMF in Eq. (15), but their form would not be altered by integration over the photon coordinates. For all of these reasons, we disregard them here.

B. Full consideration of causality

A somewhat different perspective on the third point above (i.e., the question of a proper light–matter Hamiltonian) can be obtained by examining the problem using another popular gauge, the dipole (or Power–Zienau–Woolley) gauge. This representation is particularly convenient when the system under study comprises neutral units (molecules), well separated relative to their size, that are characterized by their charge distributions, in particular, their dipoles.

Accordingly [and unlike Eq. (4) that starts from individual charged electrons and nuclei], our starting point focuses on such a system, and as before, we restrict ourselves to a classical description corresponding to the high temperature limit for the time and energy scales associated with nuclear motions and the corresponding electromagnetic modes. The Hamiltonian is taken to be[37]

$$\begin{aligned} H = &\sum_{n=1}^{N} H_n + \sum_{n<l} V_{\rm Coul}^{(nl)} + \frac{1}{2}\int d\mathbf{r}\left(\frac{1}{\epsilon_0}\mathbf{D}(\mathbf{r})\cdot\mathbf{D}(\mathbf{r}) + \frac{1}{\mu_0}\mathbf{B}(\mathbf{r})\cdot\mathbf{B}(\mathbf{r})\right) \\ &- \frac{1}{\epsilon_0}\int d\mathbf{r}\mathbf{D}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp(\mathbf{r}) + \frac{1}{2\epsilon_0}\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\perp(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp(\mathbf{r}), \end{aligned} \tag{17}$$

where H_n is the Hamiltonian for the nth molecule, $V_{\rm Coul}^{(nl)}$ are the Coulombic interactions between molecules that we assume to be dominated by dipole–dipole interactions,[40] $\mathbf{B}$ is the (transverse) magnetic field, and $\mathbf{D} = \mathbf{D}_\perp$ is the (transverse for a neutral system) displacement field. Here, we ignored magnetic and diamagnetic interactions with the material system. $\mathbf{D}$ and $\boldsymbol{\mathcal{P}}$ are related to the

Published under license by AIP Publishing

electric field according to $\mathbf{D} = \epsilon_0\mathbf{E}_\perp + \boldsymbol{\mathcal{P}}_\perp$ and $\epsilon_0\mathbf{E}_\parallel + \boldsymbol{\mathcal{P}}_\parallel = 0$. We also note that the dipole–dipole interactions between any two molecules can be written in terms of longitudinal polarizations associated with these molecules,

$$V_{\text{Coul}}^{(nl)} = \frac{1}{\epsilon_0}\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\parallel^{(n)}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\parallel^{(l)}(\mathbf{r}) \quad (\text{for } n \neq l), \tag{18}$$

so that using $\boldsymbol{\mathcal{P}}(\mathbf{r}) = \sum_{n=1}\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r}) = \sum_{n=1}\left(\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}) + \boldsymbol{\mathcal{P}}_\parallel^{(n)}(\mathbf{r})\right)$ and assuming we operate in the point-dipole approximation $\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r}) = \boldsymbol{\mu}^{(n)}\delta(\mathbf{r}-\mathbf{r}_n)$, we, thus, find

$$\begin{aligned}\sum_{n<l}V_{\text{Coul}}^{(nl)} + \frac{1}{2\epsilon_0}\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\perp(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp(\mathbf{r}) &= \frac{1}{\epsilon_0}\sum_{n<l}\int d\mathbf{r}\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}^{(l)}(\mathbf{r}) \\ &+ \frac{1}{2\epsilon_0}\sum_n\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}).\end{aligned} \tag{19}$$

The first term on the right-hand side of Eq. (19) vanishes by the assumption in our model that the charge distributions associated with different molecules do not overlap, which also reflects the retarded nature of light–matter interactions. Note that such a cancellation is valid both in free space and in cavities.[41] The Hamiltonian (17) then becomes

$$\begin{aligned}H = \sum_{n=1}^N H_n + \frac{1}{2\epsilon_0}\sum_n\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}) \\ + \frac{1}{2}\int d\mathbf{r}\left(\frac{1}{\epsilon_0}\mathbf{D}(\mathbf{r})\cdot\mathbf{D}(\mathbf{r}) + \frac{1}{\mu_0}\mathbf{B}(\mathbf{r})\cdot\mathbf{B}(\mathbf{r})\right) \\ - \frac{1}{\epsilon_0}\sum_{n=1}^N\int d\mathbf{r}\mathbf{D}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}).\end{aligned} \tag{20}$$

At this point, we explicitly assume the field is classical. We write $\mathbf{D}(\mathbf{r}) = \sum_{\mathbf{k},\xi} i\sqrt{\frac{\hbar\omega_k\epsilon_0}{2}}(a_k\mathbf{f}_k(\mathbf{r}) - a_k^*\mathbf{f}_k^*(\mathbf{r}))$, a (a^*) are the classical analogs of the quantum annihilation (creation) operators, and $\mathbf{f}_k(\mathbf{r})$ denotes the mode function which satisfies the Helmholtz equation with a certain boundary condition due to the cavity.[41] For example, in free space, $\mathbf{f}_k(\mathbf{r}) = \boldsymbol{\xi}\frac{1}{\sqrt{\Omega}}e^{i\mathbf{k}\cdot\mathbf{r}}$.

To arrive at a convenient Hamiltonian for studying the cavity effect, we rewrite the spatial integrations in Eq. (17) by the corresponding reciprocal-space integrations. For example, the free-field part is $\frac{1}{2}\int d\mathbf{r}\left(\frac{1}{\epsilon_0}\mathbf{D}(\mathbf{r})\cdot\mathbf{D}(\mathbf{r}) + \frac{1}{\mu_0}\mathbf{B}(\mathbf{r})\cdot\mathbf{B}(\mathbf{r})\right) = \sum_{\mathbf{k},\xi}\hbar\omega_k a_k^* a_k$. For point dipoles with $\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r}) = \boldsymbol{\mu}^{(n)}\delta(\mathbf{r}-\mathbf{r}_n)$, we have

$$\begin{aligned}\int d\mathbf{r}\mathbf{D}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}) &= \int d\mathbf{r}\mathbf{D}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r}) \\ &= \sum_{\mathbf{k},\xi} i\sqrt{\frac{\hbar\omega_k\epsilon_0}{2}}(a_k\mathbf{f}_k(\mathbf{r}_n) - a_k^*\mathbf{f}_k^*(\mathbf{r}_n))\cdot\boldsymbol{\mu}^{(n)}.\end{aligned}$$

Likewise,

$$\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}) = \int d\mathbf{r}d\mathbf{r}'\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r})\cdot\overleftrightarrow{\boldsymbol{\delta}}_\perp^{\text{cav}}(\mathbf{r}-\mathbf{r}')\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r}'),$$

because the transverse δ-function inside the cavity is a rank-two tensor defined as $\overleftrightarrow{\boldsymbol{\delta}}_\perp^{\text{cav}}(\mathbf{r}-\mathbf{r}') \equiv \sum_{\mathbf{k},\xi}\mathbf{f}_k(\mathbf{r})\mathbf{f}_k^*(\mathbf{r}')$ [where we take outer product of $\mathbf{f}_k(\mathbf{r})$ and $\mathbf{f}_k^*(\mathbf{r}')$],

$$\begin{aligned}\int d\mathbf{r}\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r})\cdot\boldsymbol{\mathcal{P}}_\perp^{(n)}(\mathbf{r}) &= \sum_{\mathbf{k},\xi}\left|\int d\mathbf{r}\boldsymbol{\mathcal{P}}^{(n)}(\mathbf{r})\mathbf{f}_k(\mathbf{r})\right|^2 \\ &= \sum_{\mathbf{k},\xi}\left|\boldsymbol{\mu}^{(n)}\cdot\mathbf{f}_k(\mathbf{r}_n)\right|^2.\end{aligned}$$

Therefore, we can rewrite Eq. (20) as

$$\begin{aligned}H = \sum_{n=1}^N H_n + \sum_{\mathbf{k}\in\text{supp},\xi}\Bigg[\hbar\omega_k a_k^* a_k \\ - \sum_{n=1}^N i\sqrt{\frac{\hbar\omega_k}{2\epsilon_0}}\left(a_k\mathbf{f}_k(\mathbf{r}_n) - a_k^*\mathbf{f}_k^*(\mathbf{r}_n)\right)\cdot\boldsymbol{\mu}^{(n)} \\ + \sum_{n=1}^N\frac{1}{2\epsilon_0}|\boldsymbol{\mu}^{(n)}\cdot\mathbf{f}_k(\mathbf{r}_n)|^2\Bigg],\end{aligned} \tag{21}$$

where $\mathbf{k}\in\text{supp}$ denotes that the summation includes all supported cavity modes. Equation (21) preserves causality exactly. Equivalently, when the photon modes are expressed as functions of positions and momenta such as $a_k = (2\hbar\omega_k)^{-1/2}(\omega_k q_k + ip_k)$, Eq. (21) reads

$$\begin{aligned}H = \sum_{n=1}^N H_n - \sum_{\mathbf{k}\in\text{supp},\xi}\sum_{n\neq l}\frac{1}{2\epsilon_0}\left(\boldsymbol{\mu}^{(n)}\cdot\mathbf{f}_k(\mathbf{r}_n)\right)\left(\boldsymbol{\mu}^{(l)}\cdot\mathbf{f}_k^*(\mathbf{r}_l)\right) \\ + \sum_{\mathbf{k}\in\text{supp},\xi}\Bigg[\frac{1}{2}\omega_k^2\left(q_k + \sum_{n=1}^N\frac{1}{\sqrt{\epsilon_0}\omega_k}\boldsymbol{\mu}^{(n)}\cdot\text{Im}[\mathbf{f}_k(\mathbf{r}_n)]\right)^2 \\ + \frac{1}{2}\left(p_k - \sum_{n=1}^N\frac{1}{\sqrt{\epsilon_0}}\boldsymbol{\mu}^{(n)}\cdot\text{Re}[\mathbf{f}_k(\mathbf{r}_n)]\right)^2\Bigg].\end{aligned} \tag{22}$$

Note that the second term in Eq. (22) is simply the modified dipole–dipole interaction between molecules in the cavity,

$$V_{\text{dd}}^{(nl)}(\Omega) = -\sum_{\mathbf{k}\in\text{supp},\xi}\frac{1}{2\epsilon_0}\left(\boldsymbol{\mu}^{(n)}\cdot\mathbf{f}_k(\mathbf{r}_n)\right)\left(\boldsymbol{\mu}^{(l)}\cdot\mathbf{f}_k^*(\mathbf{r}_l)\right) + \text{c.c.}, \tag{23}$$

which is a function of the cavity volume Ω and where c.c. denotes the complex conjugate. When $\Omega\to+\infty$, Eq. (23) reduces to the familiar free-space form,

$$V_{\text{dd}}^{(nl)} = -\frac{1}{\epsilon_0}\boldsymbol{\mu}_n\cdot\overleftrightarrow{\boldsymbol{\delta}}_\perp(\mathbf{r}_n-\mathbf{r}_l)\boldsymbol{\mu}_l = \frac{1}{\epsilon_0}\boldsymbol{\mu}_n\cdot\overleftrightarrow{\boldsymbol{\delta}}_\parallel(\mathbf{r}_n-\mathbf{r}_l)\boldsymbol{\mu}_l,$$

where $\overleftrightarrow{\boldsymbol{\delta}}_\perp$ and $\overleftrightarrow{\boldsymbol{\delta}}_\parallel$ denote the transverse and the longitudinal δ-functions in free space.

When Eq. (22) is used for calculating the PMF according to Eq. (3) (as what we did above), we see again that after integration over the radiation field DOFs (p_k and q_k), the only possible source of many-molecular contributions to the single-molecule PMF is through the remaining dipolar interaction terms represented by $\sum_{n<l}V_{\text{dd}}^{(nl)}(\Omega)$. In other words, the only way the cavity can exert a meaningful effect on a molecule is by dressing or modifying the dipole–dipole interactions, presumably through image charges, etc. We will discuss the size of these modifications in Sec. III.

Published under license by AIP Publishing

Before concluding this section, however, we note that all of the arguments so far have assumed a classical treatment of the nuclei and photons. In the Appendix, we will show that, if the quantum nature of the nuclei and photons is considered, a path-integral calculation does lead to an additional modification of the PMF [see Eqs. (A19) and (A20)]. However, we find that it is difficult to interpret the nature of this term even qualitatively with complete rigor, and future research will likely need to invoke numerical simulations with realistic parameters.

III. DISCUSSION

The analysis carried in Sec. II B indicates that for a system of N molecules that are coupled to each other through their interaction with cavity modes, the only possible source of the "collective" (N-dependent) effect at the single-molecular classical TST rate stems from the cavity effect on the intermolecular (assumed to be dominated by dipolar) interactions. Such effects were investigated in the past, where in the electrostatic (long-wave) limit, they can be described in terms of interaction of a given molecular dipole with the infinite number of images associated with each molecule positioned between cavity mirrors.[31–35] To estimate the magnitude of this effect, we consider a cavity bounded by perfect mirrors located at $z = 0$ and $z = L$, in which two point dipoles are positioned at $(0, 0, \frac{L+\Delta r}{2})$ and $(0, 0, \frac{L-\Delta r}{2})$. An analytical expression for the dipole–dipole interaction in such a configuration is provided in Ref. 31 [see Eq. (3.9) therein]. Figure 1 plots the normalized difference between the dipole–dipole interaction (v_{dd}) inside the cavity and that in free space,

$$\eta(L) \equiv \frac{v_{\mathrm{dd}}(L) - v_{\mathrm{dd}}(\infty)}{v_{\mathrm{dd}}(\infty)}, \tag{24}$$

as a function of the cavity length L. It is seen that when the cavity length is comparable with the separation between the dipoles (with $\Delta r = 1$ nm), the dipole–dipole interaction is affected significantly. Therefore, one may expect that for molecules located close to the cavity mirrors, the PMF of a single molecule can be modified because of the modification of intermolecular electrostatic interactions by the mirror as well as the trend for the molecules to collectively orient relative to the mirror, as recently demonstrated in Ref. 27 (using cavity lengths <10 nm). However, for cavities usually used in studies of VSC catalysis (with the cavity length of micrometers), the fraction of molecules in proximity to the cavity mirrors is not meaningful, nor are the molecules anisotropically oriented in liquid-phase reactions. Hence, one can conclude that the cavity effect on the intermolecular dipole interaction is negligible for typical liquid-phase VSC experiments.

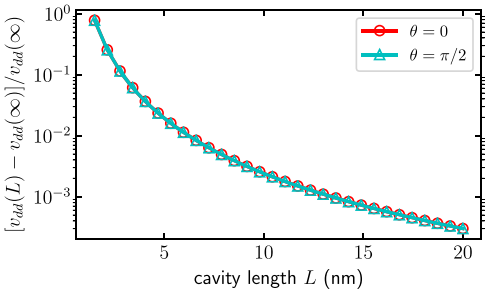


FIG. 1. The normalized difference between the dipole–dipole interaction inside a cavity and that in free space, Eq. (24), plotted against the cavity length L. The cavity mirrors are set at $z = 0$ and $z = L$, and two paralleled dipoles are located at $(0, 0, \frac{L+\Delta r}{2})$ and $(0, 0, \frac{L-\Delta r}{2})$ with an angle θ with respect to the z axis. The separation between the dipoles is set as $\Delta r = 1$ nm. Note that the dimensionless quantity $[v_{\mathrm{dd}}(L) - v_{\mathrm{dd}}(\infty)]/v_{\mathrm{dd}}(\infty)$ shows no dependence on the angle θ.

We conclude that, under the assumptions of classical nuclei and photons as well as no charge overlap between molecules, the cavity effects on the rate of chemical processes whose underlying nuclear dynamics takes place on the ground electronic potential surface cannot be accounted for at the level of classical transition state theory, where the rate is determined by the thermal distribution of nuclear configurations on the ground-state potential surface. While proximity to mirrors can affect intermolecular interactions, these effects are negligible for standard cavities used in VSC studies with L of the order of micrometers. This state of affairs then leaves us two options. First, quantum-mechanical features of the nuclei and photons could perhaps lead to important modifications of the PMF (though our hypothesis for now is that this is unlikely; see below). Second, experimentally observed cavity effects on ground (electronic) state reactions can also arise from other non-equilibrium physical effects that may have classical (excitation rates or barrier crossing efficiencies) or quantum (e.g., non-adiabatic transitions) origins.

ACKNOWLEDGMENTS

A.N. was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. J.E.S. was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0019397. T.E.L. thanks the Vagelos Institute for Energy Science and Technology at the University of Pennsylvania for a graduate fellowship. This research also used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-AC02-05CH11231. We thank A. Semenov and M. Dinpajooh for helpful discussions.

APPENDIX: PATH INTEGRAL TREATMENT

The calculation of the PMF above relies on an important assumption: the classical treatment of nuclei and photons. At this point, a natural question arises: will the quantum effects of nuclei and photons contribute to the PMF change? In fact, quantum effects may be relevant for VSC experiments, where the resonant mode frequency (800 cm^{-1}–4000 cm^{-1}) is much larger than room temperature (~200 cm^{-1}). Therefore, it is necessary to investigate the PMF change by considering quantum nuclei and photons.

In molecular dynamics simulations, the standard way to consider the quantum effects for nuclei is to perform path-integral calculations. For the system, we are interested in nuclei + photons in the electronic ground state; below, we will perform a path-integral calculation for the coupled photon–nuclear system characterized by the quantum Hamiltonian (10). Because the photon mode is a harmonic oscillator, we can rewrite Eq. (10) as

Published under license by AIP Publishing

$$\hat{H} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_i} + \hat{V}_{\mathrm{Coul}}(\{\hat{\mathbf{r}}_i\}) + \frac{1}{2}\omega^2\left(\hat{q} + \frac{1}{\sqrt{\Omega\epsilon_0}\omega}(\hat{\boldsymbol{\mu}}_S \cdot \boldsymbol{\xi})\right)^2 + \frac{1}{2}\hat{p}^2, \quad \text{(A1)}$$

where the potential is a function of coordinates only. Follow the derivations in Eqs. (12) and (13), after projecting the above Hamiltonian to the electronic ground state according to the Hartree approximation, Eq. (A1) becomes

$$\hat{H}^{\mathrm{G}} = \hat{H}_0^{\mathrm{G}} + \hat{H}_{\mathrm{F}}^{\mathrm{G}}. \quad \text{(A2a)}$$

Here, the nuclear part is defined as

$$\hat{H}_0^{\mathrm{G}} = \sum_{i=1}^{N_{\mathrm{nuc}}} \frac{\hat{\mathbf{P}}_i^2}{2M_i} + \hat{V}_{\mathrm{Coul}}(\{\hat{\mathbf{R}}_i\}). \quad \text{(A2b)}$$

The field-related part is

$$\hat{H}_{\mathrm{F}}^{\mathrm{G}} = \frac{1}{2}\hat{p}^2 + \frac{1}{2}\omega^2\left(\hat{q} + \frac{1}{\sqrt{\Omega\epsilon_0}\omega}\sum_{n=1}^{N}\hat{d}_{ng}\right)^2, \quad \text{(A2c)}$$

where $\hat{d}_{ng} \equiv \sum_n \langle\psi_{ng}|\hat{\boldsymbol{\mu}}_n|\psi_{ng}\rangle \cdot \boldsymbol{\xi}$ denotes the dipole moment operator for the nth molecule in the electronic ground state.

Note that the Hamiltonian (A2) contains operators for both the nuclei ($\hat{\mathbf{P}}_i$, $\hat{\mathbf{R}}_i$) and photons ($\hat{p}$, $\hat{q}$), and we have neglected the self-dipole fluctuation term [the last term in Eq. (13)].

The quantum canonical partition function ($\mathcal{Z}$) for Hamiltonian (A2) reads

$$\mathcal{Z} = \mathrm{Tr}_{\mathrm{np}}\left(e^{-\beta\hat{H}^{\mathrm{G}}}\right), \quad \text{(A3)}$$

where $\mathrm{Tr}_{\mathrm{np}}(\cdots)$ denotes the trace over both the nuclear and photonic DOFs. For performing a path-integral expansion,[30,42] we use a Trotter expansion such as $e^{-\beta\hat{H}} = \lim_{M\to+\infty}\prod_{\alpha=1}^{M} e^{-\beta_M\hat{V}/2}e^{-\beta_M\hat{T}}e^{-\beta_M\hat{V}/2}$. Here, we have split the exponential into M slices and $\beta_M \equiv \beta/M$. $\hat{T}$ and $\hat{V}$ denote the kinetic and potential parts of the coupled photon–nuclear system. After inserting M copies of the resolution of identity $I_{\mathbf{R}} = \int d\mathbf{R}_i^{(\alpha)}|\mathbf{R}_i^{(\alpha)}\rangle\langle\mathbf{R}_i^{(\alpha)}| \int dq^{(\alpha)}|q^{(\alpha)}\rangle\langle q^{(\alpha)}|$ and $I_{\mathbf{P}} = \int d\mathbf{P}_i^{(\alpha)}|\mathbf{P}_i^{(\alpha)}\rangle\langle\mathbf{P}_i^{(\alpha)}| \int dp^{(\alpha)}|p^{(\alpha)}\rangle\langle p^{(\alpha)}|$, we obtain a classical isomorphism for the partition function,

$$\mathcal{Z} = \lim_{M\to+\infty}\frac{1}{(2\pi\hbar)^f}\int d\{\mathbf{P}_i^{(\alpha)}\}d\{\mathbf{R}_i^{(\alpha)}\}d\{p^{(\alpha)}\}d\{q^{(\alpha)}\}e^{-\beta_M H^{\mathrm{rp}}}, \quad \text{(A4)}$$

where $f = M(N_{\mathrm{nuc}} + 1)$ and H^{rp} is the classical ring-polymer Hamiltonian for the coupled photon–nuclear system,

$$H^{\mathrm{rp}} = H_0^{\mathrm{rp}} + H_F^{\mathrm{rp}}. \quad \text{(A5)}$$

Here, H_0^{rp} denotes the conventional ring-polymer Hamiltonian for the nuclear part,

$$H_0^{\mathrm{rp}} = \sum_{\alpha=1}^{M}\sum_{i=1}^{N_{\mathrm{nuc}}}\left\{\frac{\left[\mathbf{P}_i^{(\alpha)}\right]^2}{2M_i} + V_{\mathrm{Coul}}(\{\mathbf{R}_i^{(\alpha)}\}) + \frac{1}{2}M_i\omega_M^2\left[\mathbf{R}_i^{(\alpha)} - \mathbf{R}_i^{(\alpha-1)}\right]^2\right\}, \quad \text{(A6)}$$

where $\omega_M \equiv 1/\beta_M\hbar$ and $\mathbf{R}_i^{(0)} = \mathbf{R}_i^{(M)}$. In Eq. (A6), M copies (aka M beads) of the classical nuclear Hamiltonian (the first two terms above) are coupled together by spring constants that capture the quantum effects of nuclei. Similarly, H_F^{rp} denotes the ring-polymer Hamiltonian for the photon-related part,

$$H_F^{\mathrm{rp}} = \sum_{\alpha=1}^{M}\left\{\frac{1}{2}\left[p^{(\alpha)}\right]^2 + \frac{1}{2}\omega^2\left[q^{(\alpha)} + \frac{1}{\sqrt{\Omega\epsilon_0}\omega}\sum_{n=1}^{N}d_{ng}^{(\alpha)}\right]^2 + \frac{1}{2}\omega_M^2\left[q^{(\alpha)} - q^{(\alpha-1)}\right]^2\right\}, \quad \text{(A7)}$$

where $q^{(0)} = q^{(M)}$. Note that, because the ground-state dipole moment for molecule n ($d_{ng}^{(\alpha)}$) is a function of nuclear coordinates, $d_{ng}^{(\alpha)}$ can take different values for different beads.

If $\hat{A}$ is a function of spatial coordinates only, the thermal average

$$\langle\hat{A}\rangle = \mathrm{Tr}\left(\hat{A}e^{-\beta\hat{H}^{\mathrm{G}}}\right) \quad \text{(A8)}$$

can be calculated by the following classical phase-space average:

$$\langle\hat{A}(\{\hat{\mathbf{R}}_i,\hat{q}\})\rangle = \lim_{M\to+\infty}\frac{1}{(2\pi\hbar)^f\mathcal{Z}}\int d\{\mathbf{P}_i^{(\alpha)}\}d\{\mathbf{R}_i^{(\alpha)}\}d\{p^{(\alpha)}\} \times d\{q^{(\alpha)}\}e^{-\beta_M H^{\mathrm{rp}}}\mathcal{A}_M, \quad \text{(A9)}$$

where

$$\mathcal{A}_M = \frac{1}{M}\sum_{\alpha=1}^{M}A(\{\mathbf{R}_i^{(\alpha)},q^{(\alpha)}\}). \quad \text{(A10)}$$

In order to calculate the PMF along a putative reaction pathway, let us make a simple assumption that $\hat{\mathbf{R}}_j$ is a reasonable reaction coordinate. Then,

$$\mathcal{A}_M = \frac{1}{M}\sum_{\alpha'=1}^{M}\delta(\mathbf{R}_j - \mathbf{R}_j^{(\alpha')}), \quad \text{(A11)}$$

and the PMF is calculated by

$$e^{-\beta F(\mathbf{R}_j)} = \lim_{M\to+\infty}\frac{1}{M}\sum_{\alpha'=1}^{M}\frac{1}{(2\pi\hbar)^f\mathcal{Z}} \times \int d\{\mathbf{P}_i^{(\alpha)}\}d'\{\mathbf{R}_i^{(\alpha)}\}d\{p^{(\alpha)}\}d\{q^{(\alpha)}\}e^{-\beta_M H^{\mathrm{rp}}}, \quad \text{(A12)}$$

where $d'\{\mathbf{R}_i^{(\alpha)}\}$ denotes excluding the integral over $\mathbf{R}_j^{(\alpha')}$.

To proceed with our calculation, let us make the replacement $q^{(\alpha)} \leftarrow q^{(\alpha)} + \frac{1}{\sqrt{\Omega\epsilon_0}\omega}\sum_{n=1}^{N}d_{ng}^{(\alpha)}$, so we find the above integral is equivalent to

$$e^{-\beta F(\mathbf{R}_j)} = \lim_{M\to+\infty}\frac{1}{M}\sum_{\alpha'=1}^{M}\frac{1}{(2\pi\hbar)^f\mathcal{Z}}\int d\{\mathbf{P}_i^{(\alpha)}\}d'\{\mathbf{R}_i^{(\alpha)}\} \times d\{p^{(\alpha)}\}d\{q^{(\alpha)}\}e^{-\beta_M\left(H_0^{\mathrm{rp}}+H_{F0}^{\mathrm{rp}}+V^{\mathrm{rp}}\right)}, \quad \text{(A13)}$$

where H_0^{rp} is defined in Eq. (A6), H_{F0}^{rp} denotes the ring-polymer Hamiltonian for a free photon,

Published under license by AIP Publishing

$$H_{F0}^{\mathrm{rp}} = \sum_{\alpha=1}^{M} \frac{1}{2}\left[p^{(\alpha)}\right]^2 + \frac{1}{2}\omega^2\left[q^{(\alpha)}\right]^2 + \frac{1}{2}\omega_M^2\left[q^{(\alpha)} - q^{(\alpha-1)}\right]^2, \quad \text{(A14)}$$

and V^{rp} arises from the quantum interbead interactions between nuclei and photons,

$$V^{\mathrm{rp}} = \sum_{\alpha=1}^{M} -\frac{\omega_M^2}{\sqrt{\Omega\epsilon_0}\omega}\left[q^{(\alpha)} - q^{(\alpha-1)}\right]\left[\sum_{n=1}^{N} d_{ng}^{(\alpha)} - d_{ng}^{(\alpha-1)}\right] + \frac{\omega_M^2}{2\Omega\epsilon_0\omega^2}\left[\sum_{n=1}^{N} d_{ng}^{(\alpha)} - d_{ng}^{(\alpha-1)}\right]^2. \quad \text{(A15)}$$

1. Exact solution

To further identify the effect of V^{rp} on the PMF, let us formally integrate out the photonic DOFs using the following identity:

$$\int d\{q^{(\alpha)}\}\, e^{-\frac{1}{2}\vec{q}^T\mathbf{A}\vec{q}+\vec{b}^T\vec{q}} = \sqrt{\frac{(2\pi)^M}{\det\mathbf{A}}}\, e^{\frac{1}{2}\vec{b}^T\mathbf{A}^{-1}\vec{b}}, \quad \text{(A16)}$$

where $\vec{q} = [q^{(1)}, q^{(2)}, \ldots, q^{(M)}]$. Given the definition of matrix $\mathbf{A}$ and vector $\vec{b}$ as

$$\mathbf{A}_{\alpha,\alpha'} = \begin{cases} \beta_M\left(\omega^2 + 2\omega_M^2\right), & \text{if } \alpha = \alpha' \\ -2\beta_M\omega_M^2, & \text{if } \alpha = \alpha' \pm 1 \\ 0, & \text{otherwise} \end{cases} \quad \text{(A17)}$$

and

$$b_\alpha = \beta_M\frac{\omega_M^2}{\sqrt{\Omega\epsilon_0}\omega}\left[\sum_{n=1}^{N} 2d_{ng}^{(\alpha)} - d_{ng}^{(\alpha-1)} - d_{ng}^{(\alpha+1)}\right], \quad \text{(A18)}$$

after the integration over the photonic DOFs, the PMF in Eq. (A13) is equivalent to

$$e^{-\beta F(\mathbf{R}_j)} = \lim_{M\to+\infty}\frac{1}{M}\sum_{\alpha'=1}^{M}\frac{1}{(2\pi\hbar)^f\mathcal{Z}_0} \times \int d\{\mathbf{P}_i^{(\alpha)}\}d'\{\mathbf{R}_i^{(\alpha)}\}e^{-\beta_M\left(H_0^{\mathrm{rp}}+V_{\mathrm{eff}}\right)}. \quad \text{(A19)}$$

Here, $\mathcal{Z}_0 = \lim_{M\to+\infty}(2\pi\hbar)^{-MN_{\mathrm{nuc}}}\int d\{\mathbf{P}_i^{(\alpha)}\}d\{\mathbf{R}_i^{(\alpha)}\}e^{-\beta_M H_0^{\mathrm{rp}}}$ denotes the partition function without the cavity mode. V_{eff} represents the effective cavity modification due to the quantum effects of nuclei and photons and is a function of the nuclear DOFs only,

$$V_{\mathrm{eff}} = \sum_{\alpha=1}^{M}\frac{\omega_M^2}{2\Omega\epsilon_0\omega^2}\left[\sum_{n=1}^{N} d_{ng}^{(\alpha)} - d_{ng}^{(\alpha-1)}\right]^2 + \frac{1}{2\beta_M}\vec{b}^T\mathbf{A}^{-1}\vec{b} - \frac{1}{\beta_M}\ln\left(\sqrt{\frac{(\beta_M\omega^2)^M}{\det\mathbf{A}}}\right). \quad \text{(A20)}$$

In general, due to a lack of symmetry in the path-integral form of the PMF in Eqs. (A19) and (A20), it is difficult to state definitively whether or not V_{eff} leads to a PMF change that depends on N (the number of molecules), and if it does – how will such dependence appear. Future numerical work will be necessary to address this point. That being said, before ending this paper, we note that for VSC experiments, the catalytic effect usually vanishes when the detuning (i.e., the frequency difference between the cavity mode and the vibrational frequency) increases.[14,16–18] In Eq. (A20), however, V_{eff} does not seem to show such a delta-function-like dependence on the detuning $(\omega - \omega_0)$. Therefore, at this point, even without any numerical evidence, one may hypothesize that the quantum modification V_{eff} on the PMF may not be responsible for VSC catalysis, but this hypothesis needs further numerical verification.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES

[1] F. Herrera and J. Owrutsky, "Molecular polaritons for controlling chemistry with quantum optics," J. Chem. Phys. **152**, 100902 (2020).
[2] Y. Kaluzny, P. Goy, M. Gross, J. M. Raimond, and S. Haroche, "Observation of self-induced Rabi oscillations in two-level atoms excited inside a resonant cavity: The ringing regime of superradiance," Phys. Rev. Lett. **51**, 1175–1178 (1983).
[3] J. M. Raimond, M. Brune, and S. Haroche, "Manipulating quantum entanglement with atoms and photons in a cavity," Rev. Mod. Phys. **73**, 565–582 (2001).
[4] P. Törmä and W. L. Barnes, "Strong coupling between surface plasmon polaritons and emitters: A review," Rep. Prog. Phys. **78**, 013901 (2015).
[5] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg, "Single-molecule strong coupling at room temperature in plasmonic nanocavities," Nature **535**, 127–130 (2016).
[6] X. Zhong, T. Chervy, S. Wang, J. George, A. Thomas, J. A. Hutchison, E. Devaux, C. Genet, and T. W. Ebbesen, "Non-radiative energy transfer mediated by hybrid light-matter states," Angew. Chem., Int. Ed. **55**, 6202–6206 (2016).
[7] E. Orgiu, J. George, J. A. Hutchison, E. Devaux, J. F. Dayen, B. Doudin, F. Stellacci, C. Genet, J. Schachenmayer, C. Genes, G. Pupillo, P. Samorì, and T. W. Ebbesen, "Conductivity in organic semiconductors hybridized with the vacuum field," Nat. Mater. **14**, 1123–1129 (2015).
[8] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, "Modifying chemical landscapes by coupling to vacuum fields," Angew. Chem. **124**, 1624–1628 (2012).
[9] F. Herrera and F. C. Spano, "Cavity-controlled chemistry in molecular ensembles," Phys. Rev. Lett. **116**, 238301 (2016).
[10] J. Galego, F. J. Garcia-Vidal, and J. Feist, "Suppressing photochemical reactions with quantized light fields," Nat. Commun. **7**, 13841 (2016).
[11] A. Mandal and P. Huo, "Investigating new reactivities enabled by polariton photochemistry," J. Phys. Chem. Lett. **10**, 5519–5529 (2019).
[12] J. P. Long and B. S. Simpkins, "Coherent coupling between a molecular vibration and Fabry–Perot optical cavity to give hybridized states in the strong coupling limit," ACS Photonics **2**, 130–136 (2015).
[13] T. Chervy, A. Thomas, E. Akiki, R. M. A. Vergauwe, A. Shalabney, J. George, E. Devaux, J. A. Hutchison, C. Genet, and T. W. Ebbesen, "Vibro-polaritonic IR emission in the strong coupling regime," ACS Photonics **5**, 217–224 (2018).
[14] H. Hiura, A. Shalabney, and J. George, "Cavity catalysis—Accelerating reactions under vibrational strong coupling," chemRxiv:7234721.v4 (2018).
[15] H. Hiura and A. Shalabney, "A reaction kinetic model for vacuum-field catalysis based on vibrational light-matter coupling," chemRxiv:9275777.v1 (2019).
[16] A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet, J. A. Hutchison, and T. W. Ebbesen, "Ground-state chemical reactivity under vibrational coupling to the vacuum electromagnetic field," Angew. Chem., Int. Ed. **55**, 11462–11466 (2016).
[17] J. Lather, P. Bhatt, A. Thomas, T. W. Ebbesen, and J. George, "Cavity catalysis by cooperative vibrational strong coupling of reactant and solvent molecules," Angew. Chem., Int. Ed. **58**, 10635–10638 (2019).

Published under license by AIP Publishing

[18]A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, "Tilting a ground-state reactivity landscape by vibrational strong coupling," Science **363**, 615–619 (2019).
[19]R. M. A. Vergauwe, A. Thomas, K. Nagarajan, A. Shalabney, J. George, T. Chervy, M. Seidel, E. Devaux, V. Torbeev, and T. W. Ebbesen, "Modification of enzyme activity by vibrational strong coupling of water," Angew. Chem., Int. Ed. **58**, 15324–15328 (2019).
[20]I. Imran, G. E. Nicolai, N. D. Stavinski, and J. R. Sparks, "Tuning vibrational strong coupling with co-resonators," ACS Photonics **6**, 2405–2412 (2019).
[21]B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. Wang, Y. Li, B. S. Simpkins, J. C. Owrutsky, J. Yuen-Zhou, and W. Xiong, "Two-dimensional infrared spectroscopy of vibrational polaritons," Proc. Natl. Acad. Sci. U. S. A. **115**, 4845–4850 (2018).
[22]J. D. Pino, J. Feist, and F. J. Garcia-Vidal, "Quantum theory of collective strong coupling of molecular vibrations with a microcavity mode," New J. Phys. **17**, 053040 (2015).
[23]J. A. Campos-Gonzalez-Angulo, R. F. Ribeiro, and J. Yuen-Zhou, "Resonant catalysis of thermally activated chemical reactions with vibrational polaritons," Nat. Commun. **10**, 4685 (2019).
[24]F. J. Hernández and F. Herrera, "Multi-level quantum Rabi model for anharmonic vibrational polaritons," J. Chem. Phys. **151**, 144116 (2019).
[25]A. Frisk Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, "Ultrastrong coupling between light and matter," Nat. Rev. Phys. **1**, 19–40 (2019).
[26]M. Du, L. A. Martínez-Martínez, R. F. Ribeiro, Z. Hu, V. M. Menon, and J. Yuen-Zhou, "Theory for polariton-assisted remote energy transfer," Chem. Sci. **9**, 6659–6669 (2018).
[27]J. Galego, C. Climent, F. J. Garcia-Vidal, and J. Feist, "Cavity Casimir-Polder forces and their effects in ground-state chemical reactivity," Phys. Rev. X **9**, 021057 (2019).
[28]A. Thomas, A. Jayachandran, L. Lethuillier-Karl, R. M. A. Vergauwe, K. Nagarajan, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, "Ground state chemistry under vibrational strong coupling: Dependence of thermodynamic parameters on the Rabi splitting energy," Nanophotonics **9**, 249 (2020).
[29]J. G. Kirkwood, "Statistical mechanics of fluid mixtures," J. Chem. Phys. **3**, 300–313 (1935).
[30]M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford University Press, New York, 2010).
[31]K. Takae and A. Onuki, "Applying electric field to charged and polar particles between metallic plates: Extension of the Ewald method," J. Chem. Phys. **139**, 124108 (2013).
[32]D. De Bernardis, T. Jaako, and P. Rabl, "Cavity quantum electrodynamics in the nonperturbative regime," Phys. Rev. A **97**, 043820 (2018).
[33]T. Kobayashi, Q. Zheng, and T. Sekiguchi, "Resonant dipole-dipole interaction in a cavity," Phys. Rev. A **52**, 2835–2846 (1995).
[34]M. Hopmeier, W. Guss, M. Deussen, E. O. Göbel, and R. F. Mahrt, "Enhanced dipole-dipole interaction in a polymer microcavity," Phys. Rev. Lett. **82**, 4118–4121 (1999).
[35]E. V. Goldstein and P. Meystre, "Dipole-dipole interaction in optical cavities," Phys. Rev. A **56**, 5135–5146 (1997).
[36]M. Babiker and R. Loudon, "Derivation of the power–Zienau–woolley Hamiltonian in quantum electrodynamics by gauge transformation," Proc. R. Soc. London, Ser. A **385**, 439–460 (1983).
[37]C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms: Introduction to Quantum Electrodynamics* (Wiley, New York, 1997), pp. 280–295.
[38]T. E. Li, A. Nitzan, and J. E. Subotnik, "Cavity molecular dynamics simulations of liquid water under vibrational ultrastrong coupling," arXiv:2004.04888 (2020).
[39]W. Nolting and A. Ramakanth, *Quantum Theory of Magnetism* (Springer, New York, 2009).
[40]Note that even if the molecule does not have a permanent dipole moment in its equilibrium configuration, a dipole may appear due to distortion resulting from nuclear motion.
[41]E. A. Power and T. Thirunamachandran, "Quantum electrodynamics in a cavity," Phys. Rev. A **25**, 2473–2484 (1982).
[42]S. N. Chowdhury and P. Huo, "Coherent state mapping ring polymer molecular dynamics for non-adiabatic quantum propagations," J. Chem. Phys. **147**, 214109 (2017).

Published under license by AIP Publishing