Controlling the electron-transfer-like reaction rate through molecular-vibration polaritons in the ultrastrong coupling regime

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Recent experiments showed that the chemical reaction rate is modified, either increased or decreased, by strongly coupling a nuclear vibration mode to the single mode of an optical cavity. Herein we investigate how the rate of electron-transfer-like reactions depends on the molecule-cavity coupling in the ultrastrong coupling regime, where the coupling strength is comparable in magnitude with both the vibrational and the cavity frequencies. We found two main factors that determine the modification of the reaction rate: the relative shifts of the energy levels induced by the coupling and the mixing of ground and excited states of molecular vibration in the ground state of the hybrid molecule-plus-cavity system through which the Franck-Condon factor between the initial and final states of the transition is altered. The former is the dominant factor if the molecule-cavity coupling strengths for the reactant and product states differ significantly from each other and gives rise to an increase in the reaction rate over a wide range of system’s parameters. The latter dominates if the coupling strengths and energy levels of the reactant and product states are close to each other and it leads to a decrease in the reaction rate. The effect of the mixing of molecular vibrational states on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton, and thus should be observed in a system containing a small number of molecules. In contrast, the effect of the relative shifts of the energy levels should be essentially independent of the number of molecules coupled to the cavity.

Keywords: polariton, ultrastrong coupling, molecular vibration, reaction rate

Controlling chemical reactions has always been an important goal in the field of chemistry. Over the last century, synthetic chemists have developed various kinds of catalysts to modify chemical reactions [1][2]. There are also physical methods to control chemical reactivity by using intense laser fields to excite the nuclear vibration to overcome the barrier of the reaction [3][4]. However, these approaches often require cryogenic temperature as the excitation energy can be redistributed to other vibrational degrees of freedom. One way to overcome this challenge is to control the chemical reaction by strongly coupling the molecular vibration to the vacuum field of a cavity mode [7][10]. Strong coupling of both electronic and vibrational degrees of freedom of molecules to an optical cavity has already been realized in various experimental platforms involving both an ensemble of molecules [7][17] as well as a single molecule [18]. It gave rise to a variety of interesting phenomena and important applications including the control of chemical reactivity [19][20], enhancement of transports [27][32], nonlinear optical properties with applications to optoelectronic devices [33][36], polariton lasing and condensate [37][40], and precise measurement of molecular excitation energies [41].

In particular, the interaction of the zero-point energy fluctuations of the cavity mode with the molecular vibration is expected to modify the chemical reactivity, which has recently been demonstrated experimentally [23][26]. Surprisingly, in Refs. [23][24] the reaction rate is found to decrease whereas in Refs. [25][26] the reaction rate increases if a molecular vibration is strongly coupled to the cavity mode. Theoretical investigations of the effect of the coupling between molecular vibrations and the optical cavity mode on the chemical reaction rate have also been done for the ab initio model of a simple molecule [12] and the model of an electron-transfer-like reaction [43]. However, the physical mechanism underlying the modification of the chemical reactivity induced by the molecule-cavity coupling is not fully understood. In particular, the change of the ground state of the total system by the molecule-cavity coupling has been ignored when applying the rotating-wave approximation [43]. The mixing of ground and excited states of molecular vibration in the ground state of the hybrid system can, in principle, significantly affect the chemical reactivity in a way similar to the excitation of nuclear vibrations done by an intense laser. The only difference is that here the excitation is induced by the quantum fluctuation in the vacuum field of the cavity rather than by a strong laser field.

In this paper, we extend the investigation of the effect of vibrational polariton on the chemical reaction rate to the so-called ultrastrong coupling regime, where the molecule-cavity coupling strength is comparable in mag-
nitude with both the vibrational and the cavity frequencies [44]. The ultrastrong coupling has already been realized in various kinds of systems including intersubband polaritons [45, 46], superconducting circuits [47, 48], Landau polaritons [49, 50], optomechanics [51] as well as organic molecules [52–59]. In particular, the ultrastrong coupling between molecular vibrations and the cavity field has been realized in the experiment of Ref. [25]. In the ultrastrong coupling regime, the rotating-wave approximation is no longer valid and the optical diamagnetic term, which is proportional to $A^2$ where $A$ is the vector potential of the cavity field, cannot be neglected. As a result, the ground state of the total system can be strongly modified as it now involves virtual photons and molecule’s vibrational excitations [44].

In the following, we investigate how the ultrastrong coupling between molecular vibrations and an optical cavity can affect the electron-transfer-like reaction rate. There exist both regions of parameters for which the reaction rate increases or decreases by coupling the molecular vibration to the cavity field. The modification of the reaction rate by the molecule-cavity coupling is determined by two main factors: the relative shifts of the energy levels induced by the coupling, and the mixing of ground and excited states of molecular vibration in the ground state of the hybrid system through which the Franck-Condon factor between the initial and final states of the transition is altered. The former is the dominant factor if the molecule-cavity coupling strengths for the reactant and product states differ significantly from each other. It increases the reaction rate over a wide range of system’s parameters. Conversely, the latter dominates if the coupling strengths and energy levels of the reactant and product states are close to each other, and it counter-intuitively leads to a decrease in the reaction rate. This is in contrast to the normal expectation that the reaction rate would increase due to the molecule’s vibrational excitations. The result, however, can be understood as a consequence of the minus sign of the coefficient of the molecular vibration’s excited state induced by coupling with the cavity. We also investigate how the effect of vibrational polariton on the reaction rate changes for a variable number of molecules coupled to the cavity. The effect of the mixing of vibrational excitations on the reaction rate is suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton, while the effect of the relative shifts of the energy levels is essentially independent of the number of molecules. It should be expected that in addition to the electron-transfer reaction, the results obtained herein can also be applied to similar types of reactions including the excitation-energy transfer and the spin-singlet fission processes.

FIG. 1: Control of electron-transfer chemical reaction by ultrastrongly coupling a vibration mode of a molecule to a single mode of an optical cavity (magenta). Top: Schematic illustration of the configuration taken by the surrounding molecular environment (blue ellipsoids) in accordance with the charge distribution of the molecule (yellow ellipsoid). Bottom: Formation of energy eigenstates of the hybrid system by an ultrastrong coupling between the molecular vibration and the cavity mode. The ultrastrong coupling regime refers to the case that the coupling strength is comparable in magnitude with both the vibration and the cavity frequencies. The lowest-energy eigenstate of the hybrid system is a superposition of $|n_v, n_c\rangle$ states with $n_v, n_c = 0, 1, 2, \ldots$ representing the numbers of vibrational quanta and photons, respectively.

I. ULTRASTRONG COUPLING BETWEEN A MOLECULAR VIBRATION AND AN OPTICAL CAVITY

We consider an electron-transfer-like chemical reaction in a system of $N$ identical molecules whose nuclear vibrations are coupled to an optical cavity. As described by the Marcus-Levich-Jortner model [60,62], the reactant (R) and product (P) electronic states of each molecule are coupled to a single high-frequency vibrational mode, which is further coupled to a single mode of the optical cavity as illustrated in Fig. 1. The molecule’s electronic states are also coupled to a continuum of low-frequency vibrational modes, which stem from the intermolecular vibrations of the surrounding molecular environment such as the solvent. The low-frequency vibrational modes are modeled by the annihilation operators $\hat{b}_\xi^{\dagger}$ and the Hamiltonian $H_e^{(i)} = \sum_\xi \hbar \omega_\xi (\hat{b}_\xi^{\dagger})^{\dagger}\hat{b}_\xi^{\dagger}$ (for the $i$th molecule).

The total Hamiltonian of the molecular system is given
\[
\hat{H}_m = \sum_{i=1}^{N} \left[ \hat{H}_R^{(i)} |R_i\rangle \langle R_i| + \hat{H}_P^{(i)} |P_i\rangle \langle P_i| \right] + (V_{RP}|P_i\rangle \langle R_i| + \text{h.c.}),
\]
(1)

where \( V_{RP} \) represents the coupling between the reactant and product states, and h.c. stands for Hermitian conjugate. The Hamiltonians \( \hat{H}_R^{(i)} \) and \( \hat{H}_P^{(i)} \) are given by

\[
\hat{H}_R^{(i)} = \hbar \omega_R \left( \hat{a}_R^{(i)\dagger} \hat{a}_R^{(i)} + \Delta E_{RP} \right)
\]
(2)
and

\[
\hat{H}_P^{(i)} = \hbar \omega_P \left( \hat{a}_P^{(i)\dagger} \hat{a}_P^{(i)} + \frac{g_k}{\hbar \omega_c} \right)
\]
(3)

Here, \( \omega_R \) and \( \omega_P \) are the frequencies of the harmonic potentials associated with the high-frequency vibrational mode near the equilibrium positions of the reactant and product states, respectively. The annihilation operators \( \hat{a}_R^{(i)} \) and \( \hat{a}_P^{(i)} \) correspond to the nuclear vibrational motions in these harmonic potentials. The energy difference \( \Delta E_{RP} = E_{R\mu} - E_{P\nu} \) is between two vibrational ground states \( |\mu\rangle \) and \( |\nu\rangle \) associated with R and P. The coupling strength to the low-frequency \( \xi \)-mode is denoted by \( g_k \)

The operators \( \hat{a}_R^{(i)} \) and \( \hat{a}_P^{(i)} \) of the two harmonic potentials are related to each other by \( \hat{a}_P^{(i)} = \hat{D}_i \hat{a}_R^{(i)} \hat{S}_i \), where

\[
\hat{S}_i = \exp \left\{ \frac{1}{2} \ln \left( \frac{\omega_P}{\omega_R} \right) \left[ (\hat{a}_R^{(i)})^2 - (\hat{a}_R^{(i)})^2 \right] \right\}
\]
(4)

and

\[
\hat{D}_i = \exp \left\{ -\frac{g_{RP}}{\sqrt{2}} \left[ (\hat{a}_R^{(i)})^2 - (\hat{a}_R^{(i)})^2 \right] \right\}
\]
(5)

are the squeezing and displacement operators, respectively. Here, \( d_{RP} \) is the dimensionless distance (normalized a factor proportional to \( 1/\sqrt{\omega_R} \)) between the two equilibrium positions of R and P along the high-frequency vibrational mode. For simplicity, however, in the following numerical calculations \( \omega_R = \omega_P \) was set.

The general coupling \( \mathbf{p} \cdot \mathbf{A} \) between the molecular vibration and the single mode of the optical cavity is given in the Coulomb gauge by

\[
\hat{H}_{\text{int}} = \hbar \sum_{i=1}^{N} \left\{ g_R \left[ (\hat{a}_R^{(i)})^\dagger - \hat{a}_R^{(i)} \right] |R_i\rangle \langle R_i| \right.
+ g_P \left[ (\hat{a}_P^{(i)})^\dagger - \hat{a}_P^{(i)} \right] |P_i\rangle \langle P_i| \left. \right\} \left( \hat{c}^\dagger + \hat{c} \right),
\]
(6)

where \( g_R \) and \( g_P \) denote the coupling strengths for the reactant and product states, respectively. Here, the momentum operator \( \mathbf{p} \) associated with the high-frequency vibrational mode is proportional to \( i \left[ (\hat{a}_R^{(i)})^\dagger - \hat{a}_R^{(i)} \right] \) and \( i \left[ (\hat{a}_P^{(i)})^\dagger - \hat{a}_P^{(i)} \right] \), while the vector potential operator \( \mathbf{A} \) is proportional to \( \hat{c}^\dagger + \hat{c} \), where \( \hat{c} \) is the cavity field operator.

It is noteworthy that in the ultrastrong coupling regime under consideration, where the coupling strength \( g_{RP} \) is comparable in magnitude with both the molecule’s vibrational frequency \( \omega_{R,P} \) and the cavity frequency \( \omega_c \), the rotating-wave approximation is no longer valid and the counter-rotating terms \( (\hat{a}_R^{(i)})^\dagger \hat{c} \) and \( (\hat{a}_P^{(i)})^\dagger \hat{c}^\dagger \) must be considered as they are included in Eq. (6). Moreover, in the ultrastrong coupling regime, the optical dipole magnetic term proportional to \( \mathbf{A}^2 \) also becomes comparable in magnitude with the light-matter interaction, and thus cannot be neglected [44, 64, 65]. Consequently, the total photonic Hamiltonian is given by

\[
\hat{H}_{\text{ph}} = \hbar \omega_c \hat{c}^\dagger \hat{c} + \hbar \sum_{i=1}^{N} \left( J_R |R_i\rangle \langle R_i| + J_P |P_i\rangle \langle P_i| \right) \left( \hat{c}^\dagger + \hat{c} \right)^2.
\]
(7)

According to the Thomas-Reiche-Kuhn sum rule [44, 64, 65], \( J_{RP} = g_{RP} \omega_c / \omega_{R,P} \). In the alternative dipole gauge, which can be obtained from the Coulomb gauge by making the Goppert-Mayer gauge transformation, in addition to the conventional dipole interaction, the so-called dipole self-energy also exists, which is comparable in magnitude with the dipole interaction in the ultrastrong coupling regime and needs to be considered.

Using the Fermi’s golden rule, the reaction rate is obtained as

\[
k = N \sum_{\mu} f_{\mu} \sum_{\nu} k_{\mu \rightarrow \nu},
\]
(8)

where \( \mu \) and \( \nu \) label all energy eigenstates of the hybrid molecule-plus-cavity system in the initial configuration, in which all molecules are in the R state, and in the final configuration, in which one molecule changes to the P state and the others remain in the R state, respectively. The factor of \( N \) in Eq. (8) accounts for the fact that each molecule can make a transition from R to P with equal probability. The Boltzmann distribution function for the initial state \( |\mu\rangle \) is given by \( f_{\mu} = e^{-E_{\mu}/k_B T} / Z \), where \( E_{\mu} \) is the energy of the \( |\mu\rangle \) state, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( Z = \sum_{\mu} e^{-E_{\mu}/k_B T} \) is the partition function. The rate \( k_{\mu \rightarrow \nu} \) in Eq. (8) is given by

\[
k_{\mu \rightarrow \nu} = \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{\nu}}} |V_{\mu,\nu}|^2 \exp \left\{ -\frac{(\Delta E_{\mu,\nu} - \lambda)^2}{4 \lambda k_B T} \right\},
\]
(9)

where \( \Delta E_{\mu,\nu} = E_{\mu} - E_{\nu} \) is the energy difference between the initial state \( |\mu\rangle \) and the final state \( |\nu\rangle \). Under the Condon approximation, the coupling \( V_{\mu,\nu} \) can be expressed in terms of the Franck-Condon factor as \( V_{\mu,\nu} = V_{RP} \langle \chi_{\mu} | \chi_{\nu} \rangle \), where \( \chi_{\mu} \) and \( \chi_{\nu} \) represent the nuclear wavefunctions of the \( |\mu\rangle \) and \( |\nu\rangle \) states along the high-frequency vibrational mode.
the reaction rate given by Eq. (8) is calculated for a vari-
by coupling the molecular vibration to the cavity mode,
ered. To investigate the modification of the reaction rate

\[ \frac{k(g_R)}{k(g_R = 0)} \]

as a function of the coupling strength \( g_R \) (normalized by the vibrational frequency \( \omega_R \)) for the two different cases of \( g_P = g_R \) (black) and \( g_P = 0 \) (red).

II. SINGLE-MOLECULE SYSTEM

A single-molecule system, i.e., with \( N = 1 \), is consid-
ered. To investigate the modification of the reaction rate
by coupling the molecular vibration to the cavity mode, the reaction rate given by Eq. (8) is calculated for a vari-
able coupling strength \( g_R \). Two different situations, in
which the coupling strengths \( g_R \) and \( g_P \) are nearly equal
to each other in one case and differ significantly in the
other case, are examined. Figure 2 shows the relative
change \( k(g_R)/k(g_R = 0) \) of the reaction rate as a func-
tion of the normalized coupling strength \( 0 \leq g_R/\omega_R \leq 1 \)
for the two different cases of \( g_P = g_R \) and \( g_P = 0 \). Here,
both of the energy difference \( \Delta E_{RP} \) and the detuning
\( \delta = \omega_c - \omega_R \) are set to be zero. The other parameters of
the system are \( \omega_R = \omega_P = 1000 \text{ cm}^{-1} \) corresponding to the
typical order of magnitude of molecular vibration fre-
quency, \( \lambda = 0.5 \text{ eV} \), and \( T = 300 \text{ K} \). The reorganization
energy associated with the high-frequency vibrational
mode is set to be \( \lambda_v = \hbar \omega_R^2 \omega_{RP}/2 = 0.5 \text{ eV} \), which corre-
sponds to \( \omega_{RP} \approx 2 \) for \( \omega_R = 1000 \text{ cm}^{-1} \). From Fig. 2, it is
evident that up to the coupling strength \( g_R \lesssim \omega_R \), which
is the largest coupling strength realized in experiments
thus far (\( \approx 740 \text{ cm}^{-1} \) in Ref. [25]), the reaction rate
can either increase or decrease by coupling the molecular
vibration to the cavity mode. The decrease in the reac-
tion rate is observed when the coupling strengths \( g_R \) and \( g_P \)
for the reactant and product states are close to each
other; the reverse is true when the coupling strengths
differ significantly from each other. It should, however,
be expected that for sufficiently stronger couplings,
the reaction rate would increase regardless of the relative
coupling strength \( g_P/g_P \), owing to the excitation of a large
fraction of high-energy vibrational states.

At first sight, the decrease in the reaction rate by the
colour-cavity coupling is counterintuitive as it is ex-
pected that the excitation of high-energy vibrational
states in the molecule would facilitate the chemical re-
action. To obtain physical insights into this behavior of
the reaction rate, we performed the following analysis.
In the case of equal coupling strengths \( g_R = g_P \) and zero
energy difference, \( \Delta E_{RP} = 0 \), the energy shifts induced
by the molecule-cavity coupling are the same for the re-
actant and product states. As a result, from Eq. (9), the
modification of the reaction rate can primarily be at-
tributed to the change in the Franck-Condon factor due
in the mixing of ground and excited states of molecular
vibration in the ground state of the hybrid system. In-
deed, the ground states \( |\mu_R = 0 \rangle \) and \( |\nu_P = 0 \rangle \) formed
by the coupling of the molecular vibration to the cav-
ity mode when the molecule is in the reactant and the
product states, respectively, can be expanded in terms of
the molecule’s vibrational states and the photonic Fock
states as

\[
|\mu_R = 0 \rangle = c_0 |n_R = 0, n_c = 0 \rangle + c_1 |n_R = 1, n_c = 1 \rangle \\
+ c_2 |n_R = 2, n_c = 0 \rangle + c_3 |n_R = 0, n_c = 2 \rangle \\
+ \cdots \tag{10}
\]

and

\[
|\nu_P = 0 \rangle = c_0 |n_P = 0, n_c = 0 \rangle + c_1 |n_P = 1, n_c = 1 \rangle \\
+ c_2 |n_P = 2, n_c = 0 \rangle + c_3 |n_P = 0, n_c = 2 \rangle \\
+ \cdots \tag{11}
\]

where \( n_{R,P} \) and \( n_c \) denote the number of molecular vibra-
tion’s quanta and that of cavity photons, respectively. It
can be seen from Eqs. (10) and (11) that only states with
an even total number of vibrational and photonic quanta
appear in the expansions of the ground states \( |\mu_R = 0 \rangle \)
and \( |\nu_P = 0 \rangle \) of the hybrid system. This is because of
the structure of the interaction Hamiltonian (6), in which
particles are either created or annihilated in pairs.

More importantly, the coefficients \( c_0 \) and \( c_2 \) in the ex-
trusions (10) and (11) have opposite signs. This can be
understood by the perturbation theory, which is valid
in the perturbation regime, as stemming from the nega-
tive factor of \( (i\hbar g_{R,P})^2 < 0 \), which is the product of the
amplitudes of two operators \( \hat{a}_{R,P}^{\dagger} \hat{c}^{\dagger} \) and \( \hat{a}_{R,P}^{\dagger} \hat{c} \) that con-
nect the unperturbed ground state \( |n_{R,P} = 0, n_c = 0 \rangle \) to
the vibrational excited state \( |n_{R,P} = 2, n_c = 0 \rangle \). How-
ever, it turns out that this is still valid for the ultra-
strong coupling regime \( g_{R,P} \sim \omega_{RP} \sim \omega_c \) under con-
der consideration. Numerically, we found that \( c_0 \approx 0.91 \)
and \( c_2 \approx -0.19 \) for \( g_{R,P} = \omega_{RP} \). It can be seen from
Eqs. (10) and (11) that the modification of the Franck-
Condon factor due to the change of the ground state of
the hybrid system from \( |n_R = 0 \rangle \) \( (|n_P = 0 \rangle) \) to
\( |\mu_R = 0 \rangle \) \( (|\nu_P = 0 \rangle) \) is mainly determined by the fac-
tor of \( |n_R = 2 \rangle |n_P = 0 \rangle = (|n_R = 0 \rangle |n_P = 2 \rangle \) multiplied
by the coefficient \( c_0 c_2 \). On the other hand, the factor of
\( |n_R = 2 \rangle |n_P = 0 \rangle = (|n_R = 0 \rangle |n_P = 2 \rangle \) is a positive real
number for a broad range of parameters around \( \omega_R \approx \omega_P \).
This can be deduced from the following relations between

![FIG. 2: Relative change of the reaction rate \( k(g_R)/k(g_R = 0) \) as a function of the coupling strength \( g_R \) (normalized by the vibrational frequency \( \omega_R \)) for the two different cases of \( g_P = g_R \) (black) and \( g_P = 0 \) (red).](image-url)
the Franck-Condon factors \[63\]

\[
(n_R = 0|n_P = 1) = -\frac{d_{RP}\sqrt{2}\epsilon}{1 + \epsilon} (n_R = 0|n_P = 0),
\]

\[
(n_R = 0|n_P = 2) = \frac{1 - \epsilon}{\sqrt{2}(1 + \epsilon)} (n_R = 0|n_P = 0) - \frac{d_{RP}\sqrt{2}\epsilon}{1 + \epsilon} (n_R = 0|n_P = 1),
\]

\[
(n_R = 1|n_P = 0) = \frac{2\sqrt{2}d_{RP}}{1 + \epsilon} (n_R = 0|n_P = 0),
\]

\[
(n_R = 2|n_P = 0) = \frac{\epsilon - 1}{\sqrt{2}(1 + \epsilon)} (n_R = 0|n_P = 0) + \frac{2d_{RP}}{1 + \epsilon} (n_R = 1|n_P = 0),
\]

where \(\epsilon \equiv \omega_R/\omega_P\). Combining the facts that \(c_0 c_2 < 0\) and \(\langle n_R = 2|n_P = 0 \rangle = \langle n_R = 0|n_P = 2 \rangle > 0\), we obtain a negative change in the value of the Franck-Condon factor due to the mixing of molecular vibration’s ground and excited states in the ground state of the hybrid system. This, in turn, results in a decrease in the reaction rate by coupling the molecular vibration to the cavity mode.

To investigate the effect of energy resonance, we calculated the relative change of the reaction rate \(k(g_R = \omega_R)/k(g_R = 0)\) for a variable energy difference \(\Delta E_{RP}\). The result is shown in Fig. 3 for the case that coupling strengths \(g_R\) and \(g_P\) are equal and in Fig. 3b for the case of \(g_P = 0\). In either case, both regions of \(\Delta E_{RP}\) exist for which the reaction rate increases or decreases by the molecule-cavity coupling. However, the region of \(\Delta E_{RP}\) for which the reaction rate decreases, i.e., \(k(g_R = \omega_R) < k(g_R = 0)\), is much broader in the case of \(g_R = g_P\) than in the case of \(g_P = 0\). The amount of decrease of the reaction rate is also much larger in the case of \(g_R = g_P\). In particular, in the case of \(g_R = g_P\) the minimum of the reaction rate is located at \(\Delta E_{RP} = 0\), regardless of the detailed values of the other parameters of the system, as opposed to the case of \(g_P = 0\). This reflects that the modification of the reaction rate by the molecule-cavity coupling is mainly governed by the mixing of ground and excited states of molecular vibration in the ground state of the hybrid system if the coupling strengths \(g_R\) and \(g_P\) are close to each other. In contrast, if the two coupling strengths differ significantly from each other, the modification of the reaction rate is mainly attributed to the relative shifts of the energy levels in the system induced by the molecule-cavity coupling. This is also supported by the fact that the value of \(\Delta E_{RP}\) at the minimum of the reaction rate in Fig. 3b is close to the resonance peak of the reaction rate \(k(g_R = 0)\) for the bare molecule (see Supplementary Information).

We also investigated the dependence of the reaction rate \(k(g_R = \omega_R)\) of the coupled molecule-cavity system on the detuning \(\delta = \omega_c - \omega_R\) of the cavity frequency relative to the molecule’s vibrational frequency (while keeping the energy difference \(\Delta E_{RP} = 0\) constant). The result is shown in Fig. 4a and Fig. 4b for the cases of \(g_P = g_R\)
and \( g_P = 0 \), respectively. It can be seen that there is a broad dip near \( \delta = 0 \) in the case of \( g_P = g_R \). In this case the reaction rate decreases by the molecule-cavity coupling (Fig. 2). In contrast, in the case of \( g_P = 0 \), for which the reaction rate increases by the molecule-cavity coupling (Fig. 2), no peak is observed around \( \delta = 0 \). The absence of a sharp resonance behavior here can be attributed to the system being in the ultrastrong coupling regime, where the coupling strength is comparable in magnitude with the other characteristic energies of the system and thus can compensate for a large energy detuning. For a comparison with experimental results, it should be noted that except for Ref. [26] where \( g \simeq 740 \) cm\(^{-1}\), all other experiments of molecular vibration polariton were not in the ultrastrong coupling regime as the Rabi frequency is less than 100 cm\(^{-1}\), an order of magnitude smaller than the vibrational frequency. Due to such a small ratio of the coupling strength to the vibrational frequency, a sharp resonance was observed in these experiments [23, 24]. It should be expected that by going closer to the ultrastrong coupling regime \( g \simeq \omega \), the broadening of the resonance would be observed in experiments.

### III. MULTI-MOLECULE SYSTEM

To investigate the collective effect in a system of identical molecules coupled to a common mode of an optical cavity, we numerically calculated the reaction rate for a system of \( N = 2 \) molecules. The obtained dependences of the reaction rate on the coupling strength \( g_R \), the energy difference \( \Delta E_{\text{RP}} \) and the detuning \( \delta = \omega_c - \omega_R \) are qualitatively similar to those of the single-molecule system (see Supplementary Information).

To examine the quantitative difference between the multi-molecule system and the single-molecule system, we compared the relative change \( k(g_R)/k(g_R = 0) \) of the reaction rate as a function of the normalized coupling strength \( 0 \leq g_R \sqrt{N}/\omega_R \leq 1 \) for the case of \( g_P = g_R \) and \( \Delta E_{\text{RP}} = 0 \) in the two systems. Here, \( g_R \sqrt{N} \) is the collective Rabi frequency (or coupling strength) and it reduces to the single-emitter Rabi frequency (or coupling strength) \( g_R \) if \( N = 1 \). The result is shown in Fig. 5. It is evident that in both systems, the reaction rate decreases by coupling the molecular vibration to the optical cavity mode. However, the amount of decrease is smaller in the system of \( N = 2 \) molecules than in the single-molecule system by a factor of approximately \( 1/2 \).

To obtain physical insights into this behavior, we examined how the Franck-Condon factor between the ground states of the hybrid molecule-plus-cavity system in the initial and final configurations changes with the variation of the number of molecules. As shown in the single-molecule system, when the coupling strengths \( g_R \) and \( g_P \) are close to each other and \( \Delta E_{\text{RP}} \simeq 0 \), the modification of the reaction rate by the molecule-cavity coupling is mainly determined by the change of the Franck-Condon factor between the ground states of the hybrid system in the initial and final configurations. For the system of identical molecules, the initial configuration consists of all molecules in the reactant states while in the final configuration one molecule changes to the product state.

If a system of \( N \) identical molecules is coupled to a common optical cavity mode, only a single molecular collective mode fully symmetric with respect to the exchange of any pair of molecules is coupled to the optical cavity, while a total number of \( N - 1 \) other molecular collective modes are not coupled to the cavity mode as they are in dark states. The fully symmetric molecular collective mode for the initial configuration, in which all molecules are in the reactant state, is given by \( \hat{A}^+_i = (1/\sqrt{N}) \sum_{j=1}^{N} a_R^{(j)} \), while that for the final configuration with one molecule, say the
$N$th molecule being in the product state, is given by $\hat{A}_i^\dagger = (1/\sqrt{N}) \left[ \sum_{j=1}^{N-1} \hat{a}_R^{(j)} + \hat{a}_P^{(N)} \right]$. The other $N-1$ collective molecular modes are denoted by a set of annihilation operators $\{ \hat{A}_i^\dagger \}$. The ground states $|\mu_i = 0 \rangle$ and $|\nu_i = 0 \rangle$ of the hybrid molecule-plus-cavity system in the initial and final configurations, respectively, can be expanded in terms of the molecular and photonic Fock states as

$$
| \mu_i = 0 \rangle = c_0 | n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle \\
+ c_1 | n_{A_i^+} = 1, n_c = 1, \{ n_{A_i^-} = 0 \} \rangle \\
+ c_2 | n_{A_i^+} = 2, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle \\
+ c_3 | n_{A_i^+} = 0, n_c = 2, \{ n_{A_i^-} = 0 \} \rangle \\
+ \cdots 
$$

and

$$
| \nu_i = 0 \rangle = c_0 | n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle \\
+ c_1 | n_{A_i^+} = 1, n_c = 1, \{ n_{A_i^-} = 0 \} \rangle \\
+ c_2 | n_{A_i^+} = 2, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle \\
+ c_3 | n_{A_i^+} = 0, n_c = 2, \{ n_{A_i^-} = 0 \} \rangle \\
+ \cdots,
$$

(16)

$$
\langle n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} | n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle = \langle n_R = 0 | n_P = 0 \rangle,
$$

(18)

$$
\langle n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} | n_{A_i^+} = 2, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle = \frac{1}{N} \langle n_R = 0 | n_P = 2 \rangle,
$$

(19)

$$
\langle n_{A_i^+} = 2, n_c = 0, \{ n_{A_i^-} = 0 \} | n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle = \frac{1}{N} \langle n_R = 2 | n_P = 0 \rangle.
$$

(20)

It is clear that compared to the single-molecule system, there appears an additional factor of $1/N$ in the expressions of $\langle n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} | n_{A_i^+} = 2, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle$ and $\langle n_{A_i^+} = 2, n_c = 0, \{ n_{A_i^-} = 0 \} | n_{A_i^+} = 0, n_c = 0, \{ n_{A_i^-} = 0 \} \rangle$. As a result, the change of the Franck-Condon factor between the ground states of the hybrid system in the initial and final configurations is given by

$$
\langle \mu_i = 0 | \nu_i = 0 \rangle \simeq c_0^2 \langle n_R = 0 | n_P = 0 \rangle + \frac{2 c_0 c_2}{N} \langle n_R = 0 | n_P = 2 \rangle,
$$

(21)

where we used the fact that $\langle n_R = 0 | n_P = 2 \rangle = \langle n_R = 2 | n_P = 0 \rangle$ for $\omega_R = \omega_P$. Since $|c_2| \ll |c_0|$ for $g_R \sqrt{N} \lesssim \omega_R$ (see Sec. 11), the change of the square of the Franck-Condon factor appearing in Eq. (9) for the reaction rate is found to be

$$
\langle \mu_i = 0 | \nu_i = 0 \rangle^2 \simeq c_0^4 \langle n_R = 0 | n_P = 0 \rangle^2 + \frac{2 c_0^2 c_2}{N} \langle n_R = 0 | n_P = 2 \rangle \langle n_R = 0 | n_P = 0 \rangle \langle n_R = 0 | n_P = 2 \rangle.
$$

(22)

It is evident that compared to the single-molecule system the decrease ($c_0 c_2 < 0$) of the reaction rate by the molecule-cavity coupling is reduced approximately by a factor of $1/N$. This is in agreement with the numerical result shown in Fig. 3 for $N = 2$. Consequently, it should be expected that the effect on the reaction rate of the mixing of ground and excited states of molecular vibration in the ground state of the hybrid system, through which the Franck-Condon factor between the initial and final states of the transition is altered, would be large for a system with a few molecules but would decrease to extremely small in a system containing a large number of molecules.
On the other hand, if the coupling strengths $g_R$ and $g_P$ for the reactant and product states differ significantly from each other, the relative shift of the energy levels induced by the molecule-cavity coupling should play the dominant role in the modification of the reaction rate, as already demonstrated for the single-molecule system. In the case of a collection of $N$ identical molecules coupled to a common cavity mode, the energy shift of the formed polariton state relative to the bare molecular energy is given by the collective Rabi frequency (or coupling strength) $g_{R,P} \sqrt{N}$. Therefore, as long as the collective coupling strength is kept fixed as the number of molecules is varied (i.e., the single-emitter coupling strength $g_{R,P}$ is proportional to $1/\sqrt{N}$), it can be expected that the effect of the energy shifts in the system on the reaction rate would not disappear in a system containing a large number of molecules.

**IV. DISCUSSION**

We investigated how the rate of an electron-transfer-like chemical reaction is modified by coupling the molecular vibrations to an optical cavity mode in the ultrastrong coupling regime, where the coupling strength is comparable in magnitude with both the vibrational and cavity frequencies. It was found that the modification of the reaction rate is determined by two main factors: the relative shifts of the energy levels induced by the molecule-cavity coupling and the mixing of ground and excited states of molecular vibration in the ground state of the hybrid system, through which the Franck-Condon factor between the initial and final states of the transition is altered. The former factor dominates if there is a significant difference between the molecule-cavity coupling strengths for the reactant and product states, giving rise to an increase in the reaction rate over a wide range of system's parameters. In contrast, if the coupling strengths and energy levels of the reactant and product states are close to each other, the latter factor becomes predominant and counterintuitively leads to a decrease in the reaction rate.

It is noteworthy that the mixing of ground and excited states of molecular vibration in the ground state of the hybrid system is an effect unique to the ultrastrong coupling regime, as opposed to the effect of energy shift which exists in both strong and ultrastrong coupling regimes. The effect of the mixing of vibrational excitations on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton. Therefore, this effect should be observed in a system containing a small number of molecules. A strong coupling between the electronic excitation of a single molecule and an optical nanocavity has been observed in Ref. \[18\]. The Rabi frequency attained in this experiment ($\approx 740 \text{ cm}^{-1}$) is comparable in magnitude with the typical molecular vibration frequency. It can be expected that with the rapid advancement of experimental techniques the ultrastrong coupling for vibrational polariton will be realized in a system containing a small number of molecules, which would be a suitable platform for observing the effect predicted in this paper.

On the other hand, the effect of the relative shifts of the energy levels is essentially independent of the number of molecules and therefore should be dominant in a system containing a large number of molecules. Even though the result obtained in this paper cannot be used to make a direct comparison with the experimental results in Refs. \[23,24\] because of different kinds of chemical reactions having been investigated, the result shown in Fig. \[5\] agrees at least qualitatively with what were observed in the experiments: the reaction rate can either decrease \[23,24\] or increase \[25,26\], and the amount of increase is several orders of magnitude larger than that of decrease.

The rapid progress in the realization of strong and ultrastrong couplings of both electronic and vibrational degrees of freedom of molecules to an optical cavity is expected to open new avenues regarding the physical control of various kinds of chemical reactions and dynamical processes \[11,67–69\] that, unlike other controlling approaches using intense laser fields such as the Floquet engineering \[70,71\], is based on the zero-point quantum fluctuation of the vacuum state of the cavity field.

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