A Reaction Kinetic Model for Vacuum-Field Catalysis Based on Vibrational Light-Matter Coupling

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Abstract

Since conventional catalysts are materials-based, they are effective only for particular chemical reactions. Recent studies suggest that vacuum-field catalysis (or cavity catalysis) based on vibrational light-matter coupling can boost reactions without the above constraint. Hence, we propose a reaction kinetic model for such vacuum-field-catalyzed reactions. Vibrational light-matter coupling is an interaction in which a molecular vibration and infrared (IR) vacuum field are coupled in resonance, consequently creating a pair of Rabi-split vibro-polaritonic states. Our kinetic model hypothesizes that vibrational light-matter coupling reshapes the reaction potential surface, thereby changing its reaction barrier height. We translate such a qualitative picture into two kinds of analytical equations derived from the Arrhenius and Eyring–Polanyi theories: both the equations are obtained as a function of the coupling ratio ΩR/2ω0 of vibro-polaritons (ΩR: Rabi frequency between a pair of vibro-polaritons, ω0: vibrational frequency of reactants), indicating that ΩR/2ω0 is a decisive quantity to define the catalytic activity of vacuum-field catalysis. Our numerical calculation shows that when ΩR/2ω0 ≥ 0.1, reactions may be accelerated by several orders of magnitude. Most importantly, our kinetic model can account well for rate enhancements ranging from ~106 to ~104 observed for vacuum-field-catalyzed reactions. We expect that our findings will bring fresh perspectives not only to chemistry but also to the broad fields of science and technology.

1. Introduction

Over the past quarter of a century, strong and ultra strong coupling between light and matter has been realized for a number of chemical and physical systems and used to create half-matter and half-light quantum states with novel properties.2,3 Such studies in light-matter interactions open up brand-new fields of science, as reviewed recently.1‒4 In 2015, Shalabney et al. demonstrated vibrational strong coupling (V-SC) between the C≡O stretching mode in solid poly(vinyl acetate) and infrared (IR) vacuum fields (electromagnetic zero-point field of the quantum vacuum)4 in a Fabry-Pérot (FP) cavity, with a Rabi frequency ΩR of 167 cm−1.5 As shown in Fig. 1, V-SC is a light-matter interaction in which the vibrational mode of molecules is resonantly coupled with the optical mode of an IR cavity in such a way that ΩR can exceed the sum of the loss rates of the vibrational and optical modes.1,4 To date, V-SC has been observed for many molecular systems with FP cavities6-19 and investigated theoretically20-32 to understand the fundamental properties of V-SC. George et al. reported vibrational ultra-strong coupling (V-USC) for the first time for degenerate C≡O stretching modes of liquid iron pentacarbonyl Fe(CO)5 (ΩR = 480 cm−1) with multiple Rabi splittings.8 More recently, giant Rabi splitting under V-USC was found in water and ice17,18 with ΩR = 740 cm−1 for the OH stretching mode of H2O water and ΩR = 820 cm−1 for the OH stretching mode of H2O ice. These values of ΩR are the largest ever reported in the literature.

The most recent studies of vibrational light-matter coupling have focused on polaritonic chemistry34 (or polariton chemistry),3,4,23-32 since V-SC or V-USC can have an obvious influence on the chemical reactivity in bond-cleavage11,18 and solvolysis reactions.17,19 Impressively, for such reaction systems under V-SC or V-USC, diametrically opposed effects on reaction rates have been observed: deceleration11,18 and acceleration.16,17,19 The latter rate accelerating action has been called vacuum-field catalysis (or cavity catalysis)16,17,19 because V-SC or V-USC with the FP cavity lowers the reaction barrier (Fig. 2(b)). In practice, it has been reported that some vacuum-field catalysts can give rise to a significantly large increase in the reaction rate constant:17,19 e.g., ~10 times the rate for solvolysis (ethyl acetate) of para-nitrophenyl acetate,19 ~102 times the rate for hydrolysis (H2O) of ammonia borane (NH3BH3).17 Nevertheless, no kinetic model for V-SC and V-USC has yet succeeded in accounting for such large reaction rate enhancements.27-30 Considering that vacuum-field catalysis could have a potential impact on science and technology, a new kinetic model is desired to clarify the mechanism of vacuum-field catalysis and to predict its catalytic action properly.

The purpose of this paper is to provide a reaction kinetic model under V-SC or V-USC, thereby trying to give a simple but comprehensive explanation for all the reported experimental results of vacuum-field-catalyzed reactions. First, we explain vibrational light-matter coupling and consider how vacuum-field catalysis works from the viewpoint of standard physical chemistry, wherein we hypothesize that vibrational light-matter coupling may reshape a reaction potential involved in the vibro-polaritons of reactants and thereby modify the reaction barrier height. Second, we show how to introduce such a bold hypothesis into the Arrhenius and Eyring–Polanyi equations, thereby obtaining two analytical formulas as a function of the coupling ratio ΩR/2ω0. Third, we estimate the potential performance of vacuum-field catalysis by numerical calculations using the obtained formulas and compare our calculations with reported observations of vacuum-field-catalyzed reactions.
2. Theory

2.1. Vibrational light-matter coupling

Figure 1 represents energy diagrams of vibrational light-matter coupling. For simplicity, vibrational potentials are drawn as a quadratic curve under the harmonic oscillator approximation. If the optical energy of a cavity $\hbar \omega_0$ ($\hbar$: reduced Planck constant) is exactly tuned to the vibrational energy of given molecules $\hbar \omega_0$, that is, $\hbar \omega_0 \approx \hbar \omega_0$, Rabi splitting occurs through hybridizing the molecular vibration and IR vacuum field. As a result, a pair of Rabi-split vibro-polaritonic states is formed as shown in Fig. 1(b). Such a pair of vibro-polaritons is often denoted as a light-matter hybrid;\textsuperscript{1,4} and composed of the upper vibro-polariton $P_+$ with an energy of $\hbar \omega_0$ and the lower vibro-polariton $P_-$ with an energy of $\hbar \omega_0$. The difference in energy between $P_+$ and $P_-$ is called the Rabi splitting energy $\hbar \Omega_R$ and described as follows:\textsuperscript{1,5}

$$\hbar \Omega_R = 2\sqrt{N E_d} = 2\sqrt{N} \frac{\hbar a_0}{2\pi V} \sqrt{n_{ph} + 1}$$

(1)

where $N$ is the number of molecules coupled to the cavity mode, $E$ is the amplitude of the electric field of light, $d$ is the transition dipole moment of the molecules, $n_{ph}$ is the number of photons populating the cavity mode, $a_0$ is the dielectric constant of vacuum and $V$ is the mode volume. The most striking aspect of Eq. 1 is that even if $n_{ph} = 0$, $\hbar \Omega_R$ may have a finite value due to the quantum vacuum fluctuation of electromagnetic field.\textsuperscript{1,4} The presence of such residual $\hbar \Omega_R$ is crucial for vacuum-field catalysis because it ensures that vacuum-field catalysis works as a reaction booster even without any photons. Moreover, in common with conventional catalysts, vacuum-field catalysis requires no additional energy to function as a catalyst.

Table 1. Physical quantities of vibrational vacuum Rabi Splitting

<table>
<thead>
<tr>
<th>molecule</th>
<th>vibrational mode</th>
<th>$[\hbar d] [D]$</th>
<th>$\omega_0$ [cm$^{-1}$]</th>
<th>$\Omega_R$ [cm$^{-1}$]</th>
<th>$\Omega_R/2\omega_0$</th>
<th>$E \times 10^{-4}$ [MV·cm$^{-1}$]</th>
<th>$N \times 10^{11}$</th>
<th>coupling regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a] acetonitrile</td>
<td>C≡N str.</td>
<td>0.061</td>
<td>2255</td>
<td>41</td>
<td>0.0091</td>
<td>0.83</td>
<td>0.59</td>
<td>V-SC</td>
</tr>
<tr>
<td>[b] toluene</td>
<td>C–H str.</td>
<td>0.14</td>
<td>3041</td>
<td>87</td>
<td>0.014</td>
<td>1.7</td>
<td>0.11</td>
<td>V-SC</td>
</tr>
<tr>
<td>[c] poly(vinyl acetate)</td>
<td>C≡O str.</td>
<td>0.24</td>
<td>1740</td>
<td>167</td>
<td>0.048</td>
<td>0.60</td>
<td>1.2</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] phenyl isocyanate</td>
<td>N=O=O str.</td>
<td>0.51</td>
<td>2272</td>
<td>308</td>
<td>0.068</td>
<td>1.0</td>
<td>0.32</td>
<td>V-SC</td>
</tr>
<tr>
<td>[e] H$_2$O water</td>
<td>O–H str.</td>
<td>0.34</td>
<td>3400</td>
<td>740</td>
<td>0.11</td>
<td>1.8</td>
<td>1.3</td>
<td>V-USC</td>
</tr>
<tr>
<td>[f] Fe(CO)$_5$</td>
<td>C≡O str.</td>
<td>0.88</td>
<td>2000</td>
<td>480</td>
<td>0.12</td>
<td>0.79</td>
<td>0.42</td>
<td>V-USC</td>
</tr>
<tr>
<td>[g] H$_2$O ice</td>
<td>O–H str.</td>
<td>0.41</td>
<td>3250</td>
<td>820</td>
<td>0.13</td>
<td>1.7</td>
<td>1.3</td>
<td>V-USC</td>
</tr>
</tbody>
</table>

[a] Ref. 33. [b] Refs. 5, 33. [c] Refs. 9, 33. [d] The unit is in debye (D), where 1 D = $3.33564 \times 10^{-30}$ C·m.

The absolute value of $\hbar \Omega_R$ varies from system to system. For comparison of such systems with different energy scales, the coupling ratio (or coupling strength) is defined as the ratio of half $\hbar \Omega_R$ to $\hbar \omega_0$, i.e., $\Omega_R/2\omega_0$.\textsuperscript{35,36} The boundary between the strong and ultra strong coupling regimes is most often set at $\Omega_R/2\omega_0 = 0.1, 3, 35–38$ whereas if $\Omega_R/2\omega_0 \geq 1$, the regime of the light-matter interaction is called deep strong coupling.\textsuperscript{39,40} However, no vibrational deep strong coupling has been found so far: the largest $\Omega_R/2\omega_0$ was $0.13$ observed for the OH stretch of ice.\textsuperscript{33}

The ratio of vibro-polariton energy $\hbar \omega_0$ to the original vibrational energy $\hbar \omega_0$ is expressed as a function of $\Omega_R/2\omega_0$ as follows:\textsuperscript{35,41}

$$\frac{\omega_+}{\omega_0} = \left( 1 \pm \frac{\Omega_R}{2 \omega_0} \right)$$

(2)

$$\frac{\omega_-}{\omega_0} = \sqrt{1 + \left( \frac{\Omega_R}{2 \omega_0} \right)^2} \pm \frac{\Omega_R}{2 \omega_0}$$

(3)

Both Eqs. 2 and 3 are derived from eigenvalues of Hopfield’s Hamiltonian:\textsuperscript{3,35} on the one hand, the former may be valid only if $\Omega_R/2\omega_0 \ll 1$, wherein the anti-resonance term of the light-matter coupling is neglected in the Hamiltonian (rotational wave approximation). On the other hand, the latter may be valid even if $\Omega_R/2\omega_0$ is nonnegligible compared to unity ($\Omega_R/2\omega_0 \approx 1$), wherein the anti-resonance term is included.\textsuperscript{39} Eq. 3 is thus more generic than Eq. 2 in that the former is valid for multiple regimes from weak to deep strong coupling. We henceforth utilize Eq. 3 for the following discussion.
2.2. Qualitative picture of vacuum-field catalysis

Figure 2(a) displays a schematic comparison of reaction potentials with and without vibrational light-matter coupling: the original potential is drawn as a black curve, whereas light-coupled \( P^+ \) and \( P^- \) potentials, which are derived from the upper and lower vibro-polarations, are drawn as blue and red curves, respectively. Here, we suppose that vibrational light-matter coupling is applied to a certain vibrational mode directly relevant to the bond-cleavage of the given reaction. In the same fashion as discussed before, when transitioning from the original potential to the light-coupled potentials, the force constant changes from \( k_0 \) to \( k \), in accordance with a frequency change from \( \omega_0 \) to \( \omega \). We hypothesize that such changes in force constant reshape the original reaction potential, resulting in the formation of the steeper \( P^- \) potential (colored in blue) and the shallower \( P^+ \) potential (colored in red). As mentioned above, the origin of the reshape in potential is due to the apparent giant IR vacuum field \( \sqrt{\mathcal{N}E} \) or the apparent giant transition dipole moment \( \sqrt{\mathcal{N}d} \). Such reshape in potential further make a difference in activation energy: the \( P^- \) potential has a high activation energy \( E_r^- \), whereas the \( P^+ \) potential has a low activation energy \( E_r^+ \). In comparison to the \( P_0 \) potential with an original activation energy \( E_0 \), thus, chemical reactions under vibrational light-matter coupling proceed more slowly or more rapidly when passing through the \( P^- \) or \( P^+ \) potential, respectively. In other words, \( \kappa^- < \kappa_0 \) and \( \kappa^+ > \kappa_0 \), where \( \kappa^- \) is the reaction rate constant via the \( P^- \) potential, \( \kappa_0 \) is the original reaction rate constant, and \( \kappa^+ \) is the reaction rate constant via the \( P^+ \) potential. Since \( \kappa^- < \kappa_0 < \kappa^+ \), the reaction on the \( P^+ \) potential dominates that on the \( P^- \) potential. As a result, the reactants on the \( P^+ \) potential act a rate enhancer.

Figure 2(b) illustrates a basic design of the vacuum-field catalyst using an FP cavity. If a certain vibrational mode involved in the bond-cleavage is coupled to IR vacuum field, the catalytic space may be spanned between a pair of mirrors of an FP cavity. The resonance can be tuned simply by adjusting the cavity length and the coupling ratio \( \Omega_R/2 \). Moreover, the original reaction potential \( U_0(r) \) is expressed as \( U_0 = U_0^0(r) + \hbar \Omega_R \mathcal{N} \mathcal{D}_0(r) \), where \( \mathcal{D}_0(r) \) is the original dissociation energy of A-B, and \( \mathcal{N} \) is the reduced mass of A-B and \( \omega_0 \) is the original molecular frequency of the A-B stretching mode, hence, \( \hbar \Omega_R \mathcal{D}_0(r) \) is the original activation energy \( E_0 \). Taking into account that \( U_0(n)(r) = (-\alpha)^nD_0(2^n - 2)/n! \), the original activation energy \( E_0 \) may be given by a Taylor expansion of Eq. 4 about a point of \( r_0 \) as

\[
E_0 = U_0(a_0) - U_0(r_0) = D_0 \sum_{n=1}^{\infty} \frac{\alpha^n(2^n - 2)}{n!}(r_0 - a_0)^n
\]

where \( \omega_0 \) is the original coordinate at the transition state of the original reaction. Note that the series in Eq. 6 converges for all \( \omega_0 \) since the Cauchy root test gives \( \lim_{n \to \infty} \frac{(2^n-2)!}{n!} > 0 \) for all \( n < 1 \). Thus, Eq. 6 can be simplified by the harmonic oscillator approximation as

\[
E_0 \approx \alpha_0^2D_0(a_0 - r_0)^2
\]

If the same manner is applied to the light-coupled reaction, the activation energy for the \( P^- \) potentials \( E_r^- \) may be written as

\[
E_r^- \approx \alpha_0^2D_0(a_0 - r_0)^2
\]

(3) The catalytic action of vacuum-field catalysis is dependent on the cavity length and the coupling ratio \( \Omega_R/2\omega_0 \) of the vibration involved in the reaction. The rate-enhancement is a function of \( \Omega_R/2\omega_0 \) as shown below.

Figure 2. (a) Schematic comparison of reaction potentials with and without vibrational light-matter coupling. (b) Basic design of vacuum-field catalysis using an FP cavity.
where $D_{\text{A}}$, $a_{\text{A}}$, $r_{\text{A}}$, and $k_0$ are, respectively, the dissociation energy of $\text{A}-\text{B}$, the coordinate at the transition state, the interatomic distance of $\text{A}-\text{B}$ at equilibrium, and the force constant of the $\text{A}-\text{B}$ stretching mode, all of which are defined under vibrational light-matter coupling. We assume here that the reduced mass $m$ remains intact regardless of the presence and absence of vibrational light-matter coupling.

If dividing Eq. 8 by Eq. 7, then introducing Eq. 3, the relative activation energy $E_+/E_0$ may be obtained as follows:

$$
\frac{E_+}{E_0} = \frac{a_+^2 D_+}{a_0^2 D_0} = \left(1 + \frac{1}{2} \frac{\Omega_R}{\omega_0} \right)^2 \frac{\omega_0}{\omega_0}.
$$

(9)

wherein we assume that $(a_+ - r_0)/(a_0 - r_0) \approx 1$ because the coordinate of the transition state point is moved nearly parallel to that of the equilibrium point when transitioning from the original potential to the $P_r$ potentials.

We next incorporate $\Omega_R/\omega_0$ into the Arrhenius and Eyring–Polanyi equations using Eq. 9, thereby obtaining the relative reaction rate constant $k_+/k_0$ as a function of $\Omega_R/\omega_0$. In general, the Arrhenius equation is regarded as an empirical relation between $k_0$ and $E_0$.53,55 whereas the Eyring–Polanyi equation is deductively derived from transition state theory.55,56

Figure 3. Original reaction potential $U_0(r)$ of a simple dissociation, $\text{AB}+\text{C} \rightarrow \text{A}+\text{BC}$, as a function of the reaction coordinate $r$.

Next, we compare $k_+/k_0$ and $k_-/k_0$ in Eqs. 14 and 15. Notice that $k_+/k_0$ and $k_-/k_0$ correspond to the decelerated and accelerated reactions because $k_+/k_0 < 1$ and $k_-/k_0 > 1$, respectively. Let us consider $\kappa/k_0$, which may be obtained if using Eq. 14 as

$$
\frac{\kappa}{k_0} = \exp \left( 4 \frac{E_0}{k_B T} \frac{1 + 1/2 \Omega_R^2}{\omega_0^2} \right).
$$

(16)

On the one hand, if assuming a typical reaction under V-SC, for example, $E_0 = 0.5$ eV, $T = 300$ K, and $\Omega_R/\omega_0 = 0.05$, Eq. 16 gives $\kappa/k_0 \approx 0.02$, indicating that compared to $k_-$, $k_+$ contributes little to total reaction rate constant as qualitatively discussed before. More generally, if assuming that the reactants lie on the $P_r$ and $P_\omega$ potentials with equal probability, the total reaction rate constant under V-SC or V-USC $\kappa_{\text{total}}$ may be expressed as

$$
\kappa_{\text{total}} = \frac{1}{2} \left( k_+ + k_- \right) = \frac{1}{2} \kappa_+ \left( 1 + \frac{1}{2} \kappa_- \right).
$$

(17)

Eq. 17 teaches us that $\kappa_+$ may determine $\kappa_{\text{total}}$ unless $\Omega_R/\omega_0$ is too small. On the other hand, if assuming that the access routes to the $P_r$ and $P_\omega$ potentials are not equiprobable, the situation may change, e.g., if the access to the $P_w$ potential occurs with zero probability, $\kappa_-$ may inevitably determine $\kappa_{\text{total}}$. We suspect that such situations might happen to the decelerated reactions under V-SC,11,18 but we have no particular idea how the reaction path on the $P_\omega$ potential could be closed. Since our aim is to explain the catalytic action of vacuum-field catalysis, we hereafter focus on $k_+/k_0$ for accelerated reactions and evaluate the performance of vacuum-field catalysis based on Eqs. 14 and 15 with $\kappa_+/k_0$.35,56
3. Results and Discussion

3.1. Performance of vacuum-field catalysis predicted by the reaction kinetic model in this study

Figure 4 depicts the comparison of $\kappa/\kappa_0$ versus $\Omega_R/2\omega_0$ with various $E_0$ when $T = 300$ K (room temperature). The values of $\kappa/\kappa_0$ were numerically calculated using Eqs. 14 (Arrhenius-type) and 15 (Eyring–Polanyi-type). The characteristics of Fig. 4 are summarized as follows:

![Figure 4. Comparison of relative reaction rate constant $\kappa/\kappa_0$ versus coupling ratio $\Omega_R/2\omega_0$ with various activation energies $E_0$](image)

(1) In all cases in both the Arrhenius-type and Eyring–Polanyi-type, $\kappa/\kappa_0$ is always larger than unity for any $\Omega_R/2\omega_0$ and $E_0$, manifesting that the vibrational light-matter coupling can promote any reactions. In other words, vacuum-field catalysts functions as a universal rate-accelerator. Nonetheless, we emphasize that there are several limitations to vacuum-field catalysis as explained in the following (2) - (4).

(2) In all cases, $\kappa/\kappa_0$ increases exponentially with an increase of $\Omega_R/2\omega_0$. This trend means that $\Omega_R/2\omega_0$ is a decisive factor to define the catalytic action of vacuum-field catalysis as mentioned earlier. On the one hand, if taking a close look at the case of $E_0 = 0.5$ eV, the value of which is typical as an activation energy, the acceleration in rate is not more than 50 under V-SC. On the other hand, for example, under the V-USC with $\Omega_R/2\omega_0 = 0.3, \kappa/\kappa_0$ increases above $10^4$. Thus, if a drastic acceleration is desired, the vacuum-field catalyst should be used under V-USC.

(3) For both the Arrhenius-type and Eyring–Polanyi-type, if $\Omega_R/2\omega_0$ is fixed, $\kappa/\kappa_0$ may increase as $E_0$ increases. This trend is explained in terms of the absolute reduction in activation energy $E_0 - E$. This value is always larger for the vacuum-field-catalyzed reaction with high $E_0$ than for that with low $E_0$, even though both the high-$E_0$ and low-$E_0$ reactions receive the same relative reduction in activation energy $E_0 - E$ according to Eq. 9. From the reverse point of view, vacuum-field catalysis may be almost useless if the absolute value of $E_0$ is too small: if $E_0$ is near and below the thermal energy of the reaction environment (e.g., $\sim 0.025$ eV at 300K), $\kappa/\kappa_0 < 2$ according to Eqs. 14 and 15.

(4) Since $\Omega_R/2\omega_0$ is proportional to the product of three quantities $\sqrt{N}$ (or $\sqrt{N/V}$), $d$, and $E$ according to Eq. 1, Eqs. 14 and 15 indicate that they should be made as large as possible for gaining large rate enhancement. On the one hand, although the confinement of $V$ brings about an increase of $E$, it causes a decrease in $\sqrt{N/V}$ at the same time. Namely, the changes in $E$ and $\sqrt{N/V}$ get cancelled out in total, implying that for the purpose of making $\Omega_R/2\omega_0$ larger, it is ineffective to improve the quality of an FP cavity. On the other hand, molecules with large $d$ are few in number. Moreover, it is rather hard to find a suitable combination of $d$ and $\sqrt{N/V}$ in molecular liquids.\(^\text{30}\) V-USC has been realized solely for Fe(CO)\(_5\), H\(_2\)O\(_2\),\(^\text{17,31}\) and D\(_2\)O\(_2\)\(^\text{17,30}\) among pure (neat) liquids. Furthermore, $\sqrt{N/V}$ must be treated as a variable quantity for solution reactions, where light-coupled reactants may be diluted with a reaction solvent: a possible way to reduce such a depletion effect in $\Omega_R/2\omega_0$ is to utilize light-coupled molecules that act both a reactant and a solvent, like water for hydrolysis\(^\text{17}\) and ethyl acetate for solvolysis\(^\text{19}\). Water is especially invaluable for vacuum-field catalysis because it has the largest $\Omega_R/2\omega_0$ among molecular liquids\(^\text{17,33}\) and engages in diverse reaction systems, including biological and environmental systems. Because of the intrinsically dilute nature of gases, vacuum-field catalysis is unsuitable for gaseous reactions.

(5) Although the Arrhenius-type and Eyring–Polanyi-type equations behave very similarly, the former always gives larger $\kappa/\kappa_0$ than the latter does at the same $E_0$ and $\Omega_R/2\omega_0$. The difference between them becomes manifested when $E_0 \lesssim 0.25$ eV. Such differences stem from the presence of the pre-exponential term of Eq. 15, $\sqrt{\Omega_R/2\omega_0} + \Omega_R/2\omega_0$. For example, when $\Omega_R/2\omega_0 = 0.01, 0.1$, and 1, the damping ratio of the Eyring–Polanyi-type to the Arrhenius type is determined as approximately 0.01, 0.1, and 0.4, respectively. Considering this trend, as long as vacuum-field-catalyzed reactions undergo V-SC ($\Omega_R/2\omega_0 \lesssim 0.1$), there is little difference between values of $\kappa/\kappa_0$ predicted by Eqs. 14 (Arrhenius-type) and 15 (Eyring–Polanyi-type).

3.2. Comparison between the kinetic-model calculations and the experimental observations

Figure 5(a) represents $\ln(k/\kappa_0)/E_0/k_B T$ versus $\Omega_R/2\omega_0$, where $\ln(k/\kappa_0)/E_0/k_B T$ denotes the natural logarithm of $k/\kappa_0$ normalized by $E_0/k_B T$ and can be obtained by taking the logarithm of both sides of Eq. 14 as follows:

$$
\ln \left( \frac{k}{\kappa_0} \right) = 1 - \left( \sqrt{1 + \frac{1}{2} \frac{\Omega_R^2}{\omega_0^2}} - 1 \right) \left( \Omega_R/2\omega_0 \right) \quad (18)
$$

Eq. 18 manifests that $\ln(k/\kappa_0)/E_0/k_B T$ depends only on $\Omega_R/2\omega_0$, thereby enabling us to simultaneously compare various vacuum-field-catalyzed reactions with different values of $k/\kappa_0$ and $E_0$.

In Fig. 5(a), the solid curve is theoretically drawn on the basis of Eq. 18, whereas the experimental points are plotted as denoted by (i) to (vi). The experimental data were taken from Refs. 17 and 19, in which a detailed description of vacuum-field-catalyzed reactions are found. The key parameters used in Fig. 5 are summarized in Table 2. In brief, (i) and (ii) are the addition reactions of phenyl isocyanate (Ph-NCO) with alcohols (methanol (MeOH) and 2-propanol (iPrOH), respectively) when the N=C=O stretching mode is light-coupled under V-SC, (iii) is a series of solvolyses (ethyl acetate (EtOAc)) of para-nitrophenyl acetate (O-N=Ph-COOCH\(_3\)) with various $\Omega_R/2\omega_0$ when the N=C-O stretching mode is light-coupled under V-SC, (iv) and (v) are a series of deuterolyses/hydrolyses (D\(_2\)O/H\(_2\)O) of OCN\(^-\) ions with various $\Omega_R/2\omega_0$ when the O–D (O–H) stretching mode is light-coupled under V-USC, and (vi) is a hydrolysis (H\(_2\)O) of NH\(_3\)BH\(_3\) when the O–H stretching mode is light-coupled under V-USC, and (vi) is a hydrolysis (H\(_2\)O) of NH\(_3\)BH\(_3\) when the O–H stretching mode is light-coupled under V-USC.
light-coupled under V-USC. In all cases, the vibrational mode directly relevant to the key bond-cleavage was chosen for the vibrational light-matter coupling. Note that for (ii) to (v), since the light-coupled molecules serve both as a reactant and a solvent, it is possible to maintain high $\Omega_R/2\omega_0$ during the reaction. Although some experimental points deviate from the theoretical curve, taken as a whole, Eq. 18 is capable of properly reproducing the observed dependence of $\ln(k_\text{cal}/k_\text{obs})/(E_\text{bind}/k_\text{B}T)$ on $\Omega_R/2\omega_0$. In particular, two series of experimental points in (iv) and (v) are rather well fit to the theoretical curve.

Figure 5(b) compares the calculated and observed $k_\text{cal}/k_\text{obs}$ thereby enabling us to verify our model more straightforwardly. The observed values of $k_\text{cal}/k_\text{obs}$ are likewise taken from the literature\textsuperscript{17,19}, while Eq. 15 (Arrhenius–Polanyi-type) provides the calculated values of $k_\text{cal}/k_\text{obs}$. Notably, the observed values of $k_\text{cal}/k_\text{obs}$ are in a good agreement with the calculated values in a wide range from $10^0$ to $10^3$, although the observed data are lacking around $10^3$. More quantitatively, the logarithmic conversion of both the calculated and observed values of $k_\text{cal}/k_\text{obs}$ gives a positive correlation coefficient of 0.97, implying that there is a strong linear correlation between the calculated and observed $k_\text{cal}/k_\text{obs}$. The same tendency with a correlation coefficient of +0.96 was seen if using Eq. 14 (Arrhenius-type). From the results, the kinetic model in this study can rather well account for the experimental vacuum-field-catalyzed reactions reported so far in that the catalytic action rises exponentially with an increase of $\Omega_R/2\omega_0$.

Finally, taking into account that numerous chemical reactions exist and exert diverse characteristics, the kinetic model in this study should be further evaluated by more different kinds of vacuum-field-catalyzed reactions. More fundamentally, since our kinetic model is built on a classical and phenomenological foundation of physical chemistry, some sort of quantum-electrodynamical description of kinetic models will be needed in future studies to understand vacuum-field catalysis more intrinsically from the viewpoint of first principles.

Table 2. Summary of key parameters for various vacuum-field-catalyzed reactions.

<table>
<thead>
<tr>
<th>reactants</th>
<th>coupled vibration</th>
<th>$E_0$ [eV]</th>
<th>$\Omega_R/2\omega_0$</th>
<th>$[a] \text{ observed } k_\text{cal}/k_\text{obs}$</th>
<th>calculated $k_\text{cal}/k_\text{obs}$ ((2\omega_0/\omega_0)_\text{Arrhenius})</th>
<th>calculated $k_\text{cal}/k_\text{obs}$ ((2\omega_0/\omega_0)_\text{Eyring-Polanyi})</th>
<th>coupling regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a] Ph-N=NC=O + MeOH</td>
<td>N=C=O str.</td>
<td>0.39</td>
<td>0.023</td>
<td>3.12</td>
<td>1.97</td>
<td>1.93</td>
<td>V-SC</td>
</tr>
<tr>
<td>[a] Ph-N=NC=O + iPrOH</td>
<td>N=C=O str.</td>
<td>0.51</td>
<td>0.023</td>
<td>3.80</td>
<td>2.43</td>
<td>2.37</td>
<td>V-SC</td>
</tr>
<tr>
<td>[b] EtOAc + O2N-Ph-COOCH3</td>
<td>C=O str.</td>
<td>0.77</td>
<td>0.020</td>
<td>2.2</td>
<td>3.22</td>
<td>3.16</td>
<td>V-SC</td>
</tr>
<tr>
<td>[b] EtOAc + O2N-Ph-COOCH3</td>
<td>C=O str.</td>
<td>0.77</td>
<td>0.029</td>
<td>3.2</td>
<td>5.51</td>
<td>5.35</td>
<td>V-SC</td>
</tr>
<tr>
<td>[c] D2O + OCN−</td>
<td>O–D str.</td>
<td>0.51</td>
<td>0.037</td>
<td>6.0</td>
<td>8.47</td>
<td>8.16</td>
<td>V-SC</td>
</tr>
<tr>
<td>[c] D2O + OCN−</td>
<td>O–D str.</td>
<td>0.51</td>
<td>0.043</td>
<td>2.0×10</td>
<td>1.16×10</td>
<td>1.11×10</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + OCN−</td>
<td>O–H str.</td>
<td>0.69</td>
<td>0.055</td>
<td>7.18</td>
<td>7.74</td>
<td>7.32</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + OCN−</td>
<td>O–H str.</td>
<td>0.69</td>
<td>0.079</td>
<td>1.86×10</td>
<td>1.77×10</td>
<td>1.64×10</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + OCN−</td>
<td>O–H str.</td>
<td>0.69</td>
<td>0.093</td>
<td>3.30×10</td>
<td>2.88×10</td>
<td>2.62×10</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + OCN−</td>
<td>O–H str.</td>
<td>0.69</td>
<td>0.102</td>
<td>5.26×10</td>
<td>3.87×10</td>
<td>3.49×10</td>
<td>V-USC</td>
</tr>
<tr>
<td>[d] H2O + NH3BH3</td>
<td>O–H str.</td>
<td>1.17</td>
<td>0.052</td>
<td>1.10×10</td>
<td>1.40×10</td>
<td>1.32×10</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + NH3BH3</td>
<td>O–H str.</td>
<td>1.17</td>
<td>0.074</td>
<td>3.64×10</td>
<td>3.92×10</td>
<td>3.64×10</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + NH3BH3</td>
<td>O–H str.</td>
<td>1.17</td>
<td>0.090</td>
<td>7.84×10</td>
<td>8.08×10</td>
<td>7.38×10</td>
<td>V-SC</td>
</tr>
<tr>
<td>[d] H2O + NH3BH3</td>
<td>O–H str.</td>
<td>1.17</td>
<td>0.104</td>
<td>2.28×10</td>
<td>1.49×10</td>
<td>1.34×10</td>
<td>V-USC</td>
</tr>
</tbody>
</table>

[a], [b] Experimental data were taken from Refs. 17 and 19, respectively. [c] The observed $k_\text{cal}/k_\text{obs}$ was obtained by doubling the observed $k_\text{cal}/k_\text{obs}$ according to Eq. 17.

4. Conclusion

We have proposed the reaction kinetic model for vacuum-field catalysis under vibrational light-matter coupling. We have shown two kinds of analytical equations based on the Arrhenius and Eyring–Polanyi theories. We have further demonstrated that the obtained reaction-kinetic equations can properly account for the experimental results of vacuum-field-catalyzed reactions reported so far. Furthermore, we have discussed characteristics
of vacuum-field catalysis: vacuum-field catalysts may act as a versatile rate-accelerator to promote reactions and their catalytic power is determined predominantly by the coupling ratio of Rabi frequency to molecular frequency, namely, $\frac{\Omega}{2\omega_0}$. In particular, under the V-USC regime, the kinetic model predicts that vacuum-field catalysts can enhance the reaction rate constant by several orders of magnitude. Nevertheless, we have found from our model that if the coupling ratio is too small ($\Omega/2\omega_0 \ll 0.1$) or the activation energy approaches less than the thermal energy of the reaction environment, vacuum-field catalysts may be basically ineffective as a chemical booster.

Considering the very simple structure of vacuum-field catalysts, we envision that they will find many different applications in industry. When reflecting on past views on catalysts, we envision that they will find many different vacuurn-field catalysis, a few unusual ideas may come to mind: e.g., a conventional catalyst whose catalytic mechanism is used for human activities without the least awareness of them, first, by some chance, vacuum-field catalysts might have been catalyze such prospective and retrospective studies that can build a new dimension in science and technology.

Acknowledgements

H.H. acknowledges Professor Thomas W. Ebbesen for valuable discussions.

References


34. Strictly speaking, “polariton chemistry” and “polaritonic chemistry” are distinguished as follows: the former is real light and a polariton is formed, whereas the latter is chemistry in the ground state under vibrational light-matter coupling.


54. If using Eq. 2, the relative activation energy $E_c/E_0$ may be expressed as follows:

$$\frac{E_c}{E_0} \approx \left(1 \pm \frac{1}{2w_0}\right)^2$$

(9')


57. If using Eq. 2, the Arrhenius type $\kappa_0/\kappa_0$ may be expressed as follows:

$$\frac{\kappa_0}{\kappa_0} \approx \exp \left(\frac{-E_c}{k_B T}\right) \left(1 \pm \frac{1}{2w_0}\right)^2 - 1$$

(14')

58. If using Eq. 2, the Eyring–Polanyi type $\kappa_0/\kappa_0$ may be expressed as follows:

$$\frac{\kappa_0}{\kappa_0} \approx \left(1 \pm \frac{1}{2w_0}\right) \exp \left(\frac{-E_c}{k_B T}\right) \left(1 \pm \frac{1}{2w_0}\right)^2 - 1$$

(15')