

# RRKM theory

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# RRKM Theory



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# 1.1 calculation of partition functions and state densities

Boltzmann distribution at temperature T:

$$\frac{N_i}{N} = \frac{g_i e^{-\varepsilon_i/kT}}{Q}, Q = \sum g_i e^{-\varepsilon_i/kT}$$

The equilibrium constant for isomerization  $A^* \rightleftharpoons A^+$  :

$$K = \frac{Q^+ \exp(-\epsilon_0/kT)}{Q^*}$$

We can easily get:

$$Q_{\text{trans}} = \frac{(2\pi mkT)^{1/2} l}{h} \quad (\text{one dimension}) \quad Q_{\text{rot}} = \frac{8\pi^2 IkT}{h^2} \quad (\text{linear molecule})$$

and

$$Q_{\text{vib}} = \{1 - \exp(-h\nu/kT)\}^{-1}$$

If  $h\nu \ll kT$ , then  $Q_{\text{vib}} = kT/h\nu$ .

# 1.1 calculation of partition functions and state densities

For one-dimensional translation,

$$\varepsilon = \frac{n^2 h^2}{8ml^2}$$

Thus

$$\Omega(\varepsilon) = \frac{\partial n}{\partial \varepsilon} = \left( \frac{2m}{\varepsilon} \right)^{1/2} \frac{l}{h}$$

Similarly, for a single classical harmonic oscillator:

$$\Omega(\varepsilon) = (h\nu)^{-1}$$



# 1.1 calculation of partition functions and state densities

Total number of states  $W(\epsilon)$  of the molecule for  $H \leq \epsilon$  is:

$$W(\epsilon) = \frac{1}{h^n} \int \dots \int dq_1 \dots dp_n$$

For 1D translation,

$$W(\epsilon) = \frac{1}{h} \int_{x=0}^l \int_{p=-\sqrt{2m\epsilon}}^{+\sqrt{2m\epsilon}} dx dp = \frac{(8m\epsilon)^{1/2} l}{h}$$

For a system of 2 oscillators:

$$W^{s=2}(\epsilon) = \int_0^\epsilon [(h\nu)^{-1} d\epsilon_1][(\epsilon - \epsilon_1)/h\nu_2] = \frac{\epsilon^2}{2h\nu_1 h\nu_2}$$

Similarly, for a system of  $s$  oscillators:

$$W^s(\epsilon) = \frac{\epsilon^s}{s! \prod_{i=1}^s h\nu_i}$$

# 1.1 calculation of partition functions and state densities

So, the density of states for  $s$  classical harmonic oscillators at energy  $\epsilon$  is:

$$\Omega^s(\epsilon) = \frac{\partial W^s(\epsilon)}{\partial \epsilon} = \frac{\epsilon^{s-1}}{(s-1)! \pi h \nu_i}$$

The probability  $P(\epsilon)$  of this system carrying energy  $\epsilon$  is:

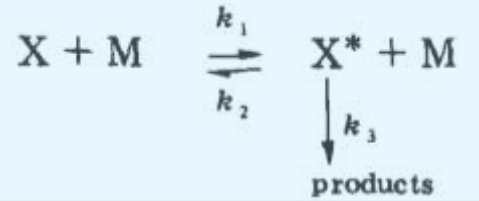
$$P(\epsilon) d\epsilon = \frac{\Omega(\epsilon) d\epsilon \exp(-\epsilon/kT)}{Q_{\text{vib}}} = \frac{(\epsilon/kT)^{s-1} \exp(-\epsilon/kT)}{kT(s-1)!}$$

# 1.2 Early theories

## --The Lindemann Type Model

Consider the thermal decomposition of molecules X in a large excess of inert gas M, a small fraction of collisions are highly energetic and produce excited molecules X\*, which have sufficient energy to decompose.

Neglecting any energy dependence of the microscopic rate coefficients:



Considering [X\*] unchanged:

$$-\frac{d[\text{X}]}{dt} = \frac{k_1 k_3 [\text{X}] [\text{M}]}{k_2 [\text{M}] + k_3}$$

The **unimolecular rate coefficient**  $k_{uni}$  is defined as:

$$k_{uni} = -\frac{\partial \ln[\text{X}]}{\partial t} = \frac{k_1 k_3 [\text{M}]}{k_2 [\text{M}] + k_3}$$



# 1.2 Early theories

## -Kassel's Theory

In Kassel's theory,  $k_1$  and  $k_3$  are evaluated as a function of energy. Kassel treats a system of  $s$  coupled, harmonic oscillators. For a non-linear system,  $s=3n-6$ .

Consider isomerization of  $X^*$  to a transition complex  $X^+$ ,

$$\frac{[X^+]}{[X^*]} = \frac{(\epsilon - \epsilon_0)^{s-1} / (s-1)! \prod_i h\nu_i^+}{\epsilon^{s-1} / (s-1)! \prod_i h\nu_i^*} = \frac{\prod_i \nu_i^*}{\prod_i \nu_i^+} \left( \frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1} = \frac{Q_{\text{vib}}^+}{Q_{\text{vib}}^*} \left( \frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1}$$

Therefore,  $k_3$  becomes  $k(\epsilon) = A \left( \frac{\epsilon - \epsilon_0}{\epsilon} \right)^{s-1}$ , where  $A$  is the reciprocal mean lifetime of the transition complex multiplied by the ratio of the partition functions.

# 1.2 Early theories

Take  $k_2[M] = \omega$ , and we have Boltzmann contribution :

$$\frac{[X^*]_{\epsilon, \epsilon + d\epsilon}}{[X]} = P(\epsilon) d\epsilon \quad [k_1]_{\epsilon, \epsilon + d\epsilon} [M] [X] = k_2 [M] [X^*]_{\epsilon, \epsilon + d\epsilon}$$

Hence,

$$[k_1]_{\epsilon, \epsilon + d\epsilon} [M] = \omega P(\epsilon) d\epsilon$$

So, the unimolecular rate coefficient obtained in the previous model becomes:

$$k_{\text{uni}} = \int_{\epsilon = \epsilon_0}^{\infty} \frac{k(\epsilon) P(\epsilon) d\epsilon}{1 + k(\epsilon)/\omega} \quad (\text{Kassel})$$

# 1.2 Early theories

At high pressure ( $\omega = \infty$ ),

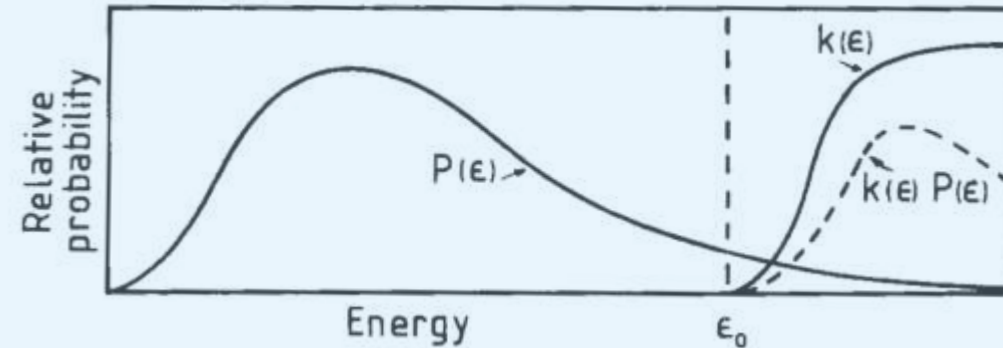
$$k_{\infty} = \int_{\epsilon = \epsilon_0}^{\infty} k(\epsilon) P(\epsilon) d\epsilon$$

For  $s$  harmonic oscillators,

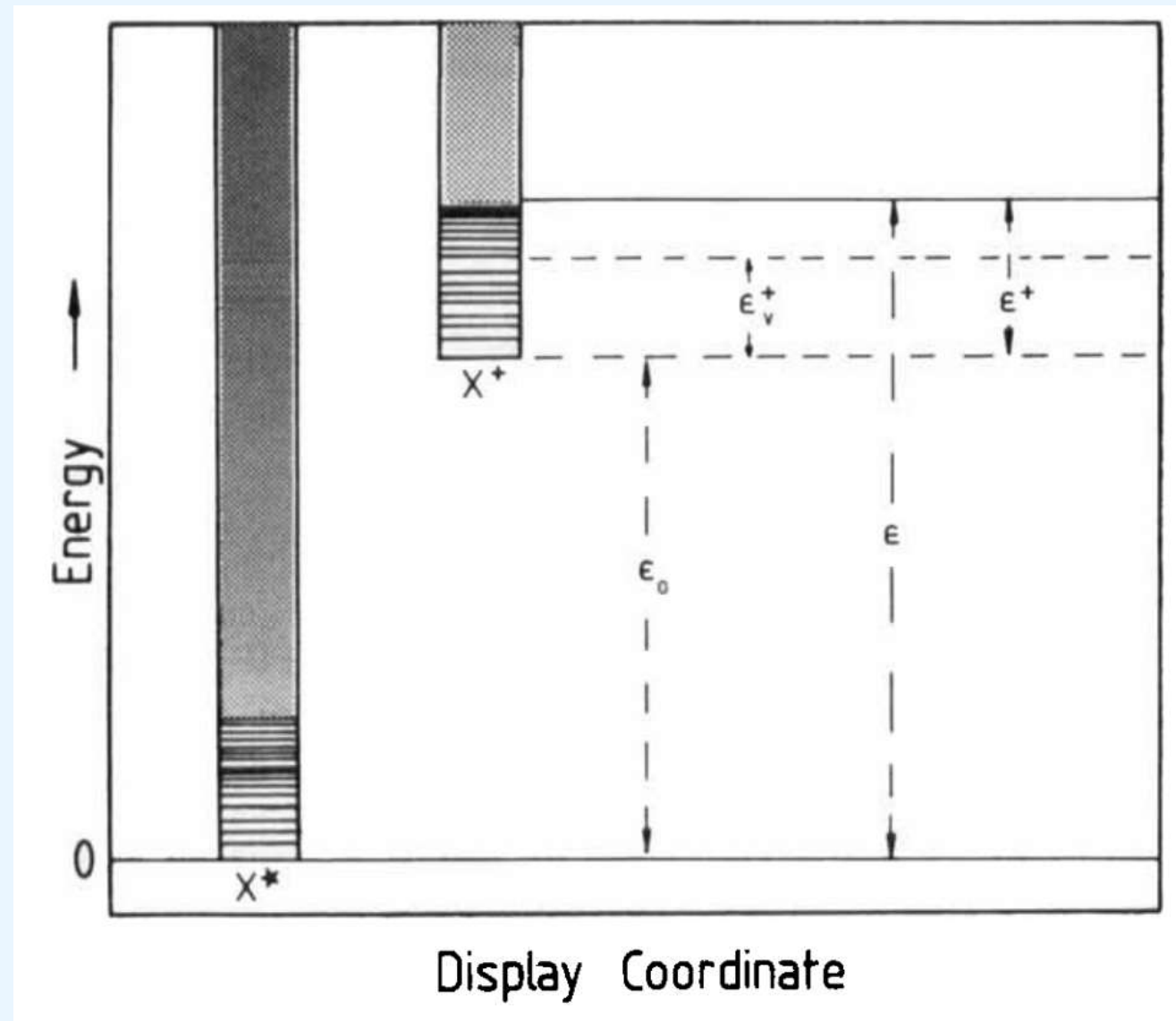
$$k_{\infty} = A \exp(-\epsilon_0/kT)$$

Fails because:

The density of states obtained by the classical method is an underestimate at low energy.



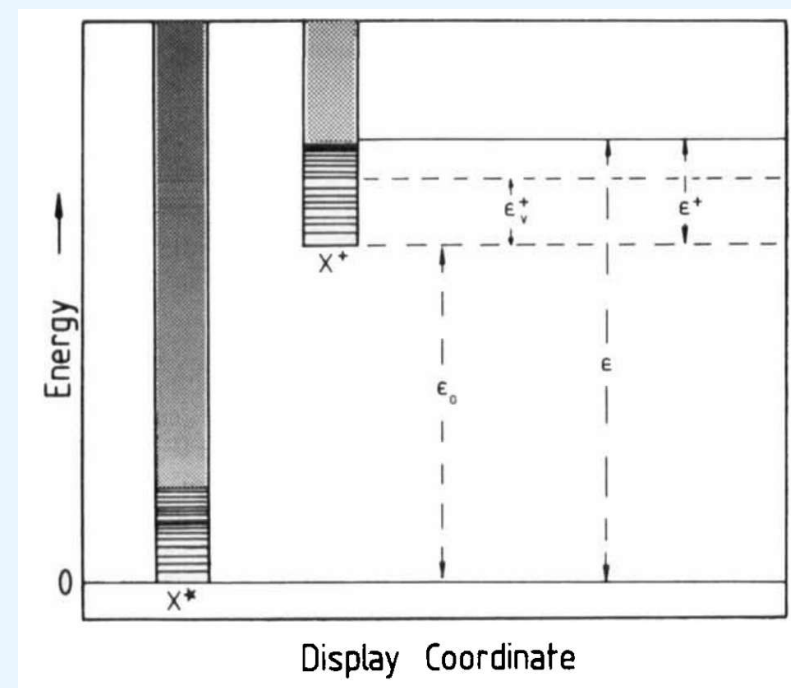
# 1.3 Marcus-Rice theory



# 1.3 Marcus-Rice theory

Within the interval  $\epsilon, \epsilon + d\epsilon$ ,

$$[X^+(\epsilon_v^+)]/[X^*(\epsilon)] = \frac{\Omega(\epsilon^+ - \epsilon_v^+)d\epsilon}{\Omega(\epsilon)d\epsilon}$$



So the contribution to the rate of decomposition of  $X^*$ , from the flux proceeding through a particular vibrational state is:

$$\begin{aligned} \text{Rate}(\epsilon, \epsilon_v^+) &= k(\epsilon, \epsilon_v^+)[X^*(\epsilon)] \\ &= \frac{\frac{1}{2}[X^*(\epsilon)]\{2\mu/(\epsilon^+ - \epsilon_v^+)\}^{1/2}\{2(\epsilon^+ - \epsilon_v^+)/\mu\}^{1/2}}{h\Omega(\epsilon)} \\ &= \frac{[X^*(\epsilon)]}{h\Omega(\epsilon)} \end{aligned}$$

$$k=v/L$$

# 1.3 Marcus-Rice theory

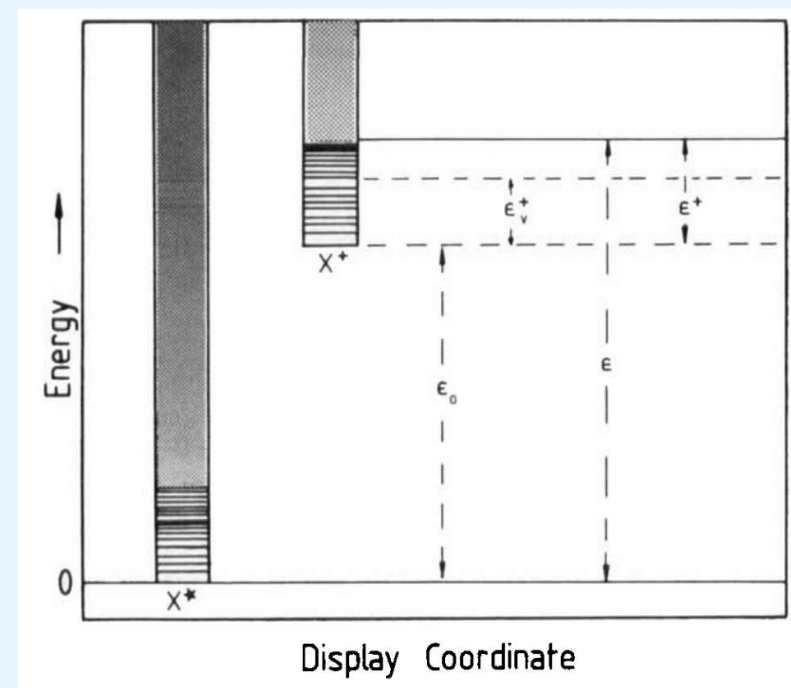
Hence,

$$k(\varepsilon, \varepsilon_v) = \frac{1}{h\Omega(\varepsilon)}$$

So,

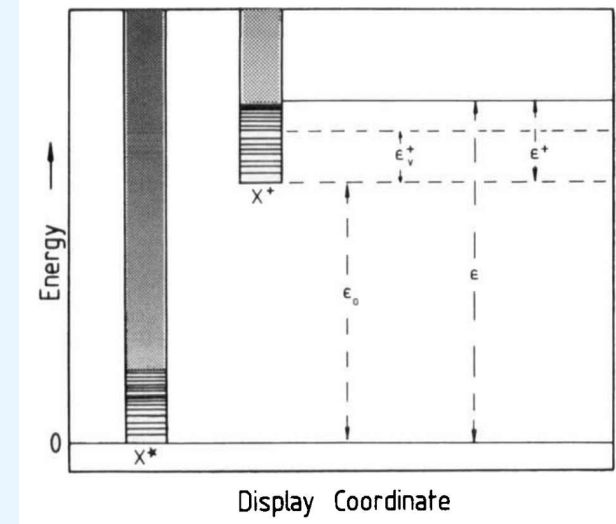
$$k(\varepsilon) = \sum_{0 \leq \varepsilon_v^+ \leq \varepsilon^+} \frac{1}{h\Omega(\varepsilon)} = \frac{W(\varepsilon^+)}{h\Omega(\varepsilon)}$$

- (1). If we also consider internal rotation, then  $W(\varepsilon^+)$  is the total number of states of vibration and internal rotation with energy no greater than  $\varepsilon^+$ .
- (2). The RRKM theory is expected to give **an upper bound of the rate coefficient**, ignoring the tunneling through the potential energy barrier.





# 1.3 Marcus-Rice theory



Consider  $s$  coupled, classical simple harmonic oscillators:

$$\Omega(\varepsilon) = \frac{\varepsilon^{s-1}}{(s-1)! \prod_{i=1}^s h\nu_i}, W(\varepsilon^+) = \frac{\varepsilon^{s-1}}{(s-1)! \prod_{i=1}^{s-1} h\nu_i^+}$$

Thus,

$$k(\varepsilon) = \frac{1}{h} \frac{\prod_{i=1}^s (h\nu_i)}{\prod_{i=1}^{s-1} (h\nu_i^+)} \left( \frac{\varepsilon - \varepsilon_0}{\varepsilon} \right)^{s-1} = \frac{kT}{h} \frac{Q_{\text{vib}}^+}{Q_{\text{vib}}} \left( \frac{\varepsilon - \varepsilon_0}{\varepsilon} \right)^{s-1}$$

Further,

$$k_{\infty} = \int_{\varepsilon = \varepsilon_0}^{\infty} k(\varepsilon) P(\varepsilon) d\varepsilon = \frac{kT}{h} \frac{Q_{\text{vib}}^+}{Q_{\text{vib}}} \exp(-\varepsilon_0/kT)$$

# 1.3 Marcus-Rice theory

Taking overall rotation into account, then the rotational energy decreases due to larger atom distances in the complex.

$$\epsilon + \epsilon_j = \epsilon^+ + \epsilon_0 + \epsilon_j^+ \quad \langle \Delta \epsilon_l \rangle = \frac{kT\Delta I}{I^+}$$

So:

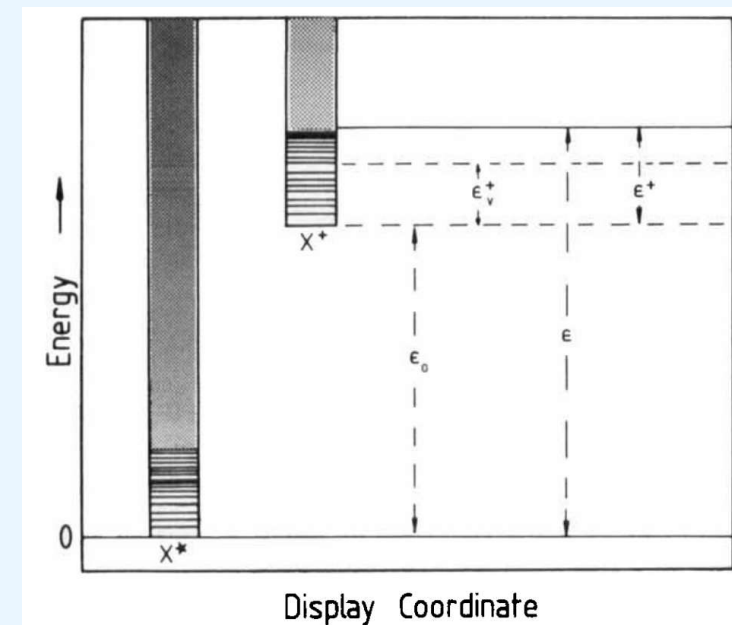
$$k_\infty = \sum_j \int_{\epsilon} \frac{1}{h} \frac{W(\epsilon^+)}{\Omega(\epsilon)} P(\epsilon, \epsilon_j) d\epsilon$$

Substituting

$$P(\epsilon, \epsilon_j) = \frac{g_j \Omega(\epsilon) \exp [-(\epsilon + \epsilon_j)/kT]}{Q_{\text{vib}} Q_{\text{rot}}}$$

We get

$$k_\infty = \left( \frac{kT}{h} \right) \frac{Q_{\text{vib}}^+ Q_{\text{rot}}^+}{Q_{\text{vib}} Q_{\text{rot}}} \exp (-\epsilon_0/kT)$$





02

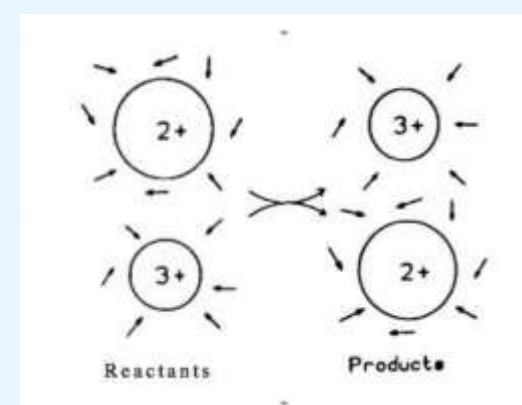
# Marcus theory for electron transfer



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## 2. Marcus theory for electron transfer



**History:** Libby's paper explaining why reactions between pairs of small cations in aqueous solution (e.g.  $Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3+} + Fe^{*2+}$ ) are relatively slow with respect to the same electron transfer reactions involving larger ions, such as  $Fe(CN)_6^{4-}$ .

**Why?**

Electron transfer is much faster than the changing of the ions' surroundings, which introduce a "solvation energy barrier" for the process. For large ions, the influence is smaller, so is the barrier. (**Frank-Condon principle**)

**Problem:**

Unable to satisfy **the Frank-Condon principle** and **energy conservation** at the same time!

**Solution by Marcus:**

Introduce fluctuations from the original equilibrium ensemble of configurations.

## 2. Marcus theory for electron transfer

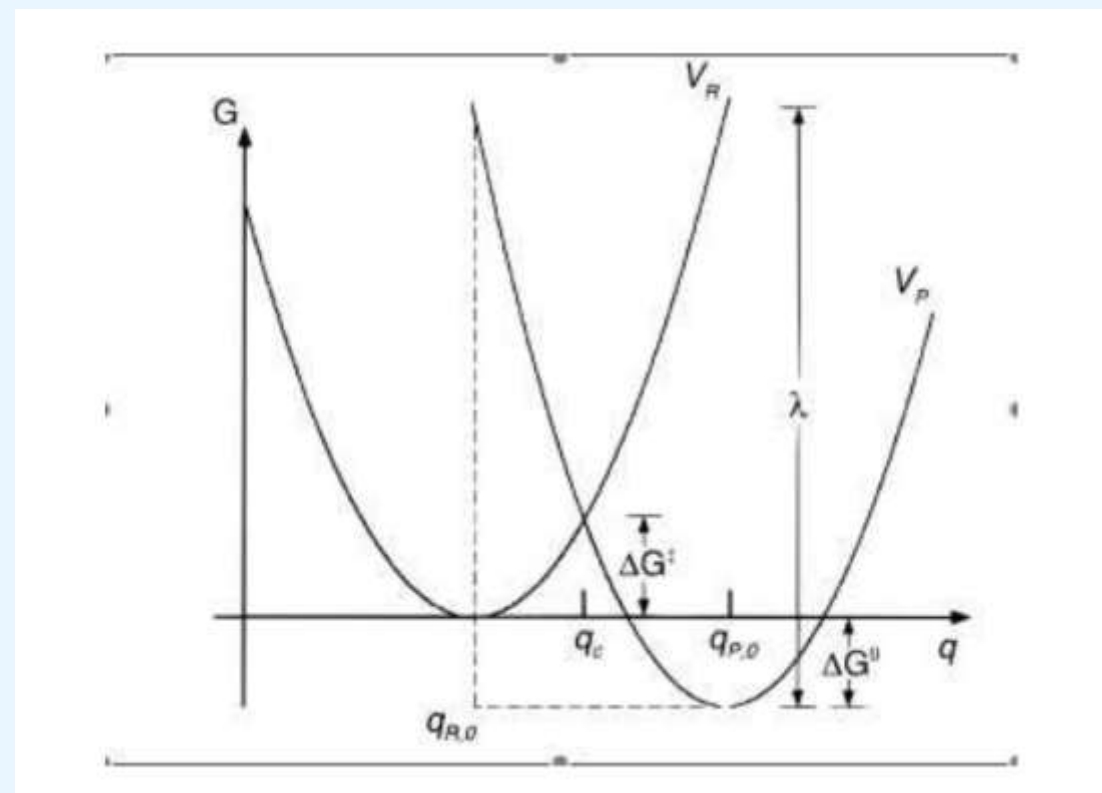
Treat the potential energy of the reactant and the product as two functions of the translational, rotational, and vibrational coordinates of the ions and its surroundings.

Reactant:  $V_R(q) = \frac{f}{2}(q - q_R)^2$

Product:  $V_P(q) = \Delta G_0 + \frac{f}{2}(q - q_P)^2$

If the entropy changes are ignored, then the free energy becomes energy. At the crossing:

$$V_R(q_c) = V_P(q_c)$$

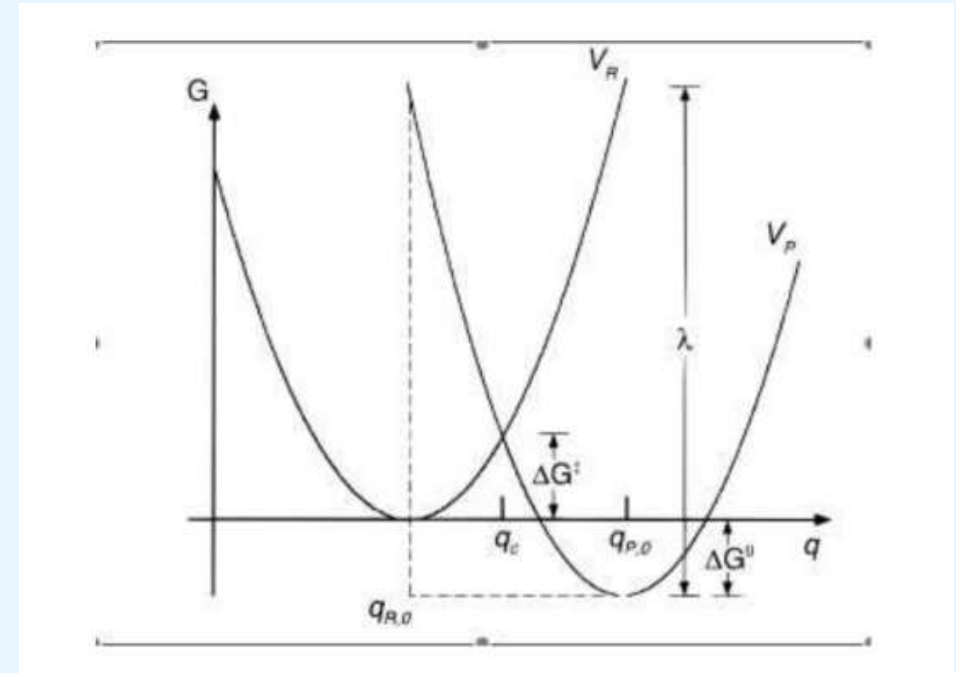


## 2. Marcus theory for electron transfer

We get:  $q_c = \frac{\Delta G_0}{f(q_P - q_R)} + \frac{q_P + q_R}{2}$

Reorganization energy:  $\lambda = \frac{f}{2} (q_R - q_P)^2$

Energy barrier:  $\Delta G^* = V_R(q_c) - V_R(q_R) = \frac{\lambda}{4} \left(1 + \frac{\Delta G_0}{\lambda}\right)^2$





## 2. Marcus theory for electron transfer

The rate constant of electron transfer is given by (known that  $\Delta G^* = \frac{\lambda}{4} (1 + \frac{\Delta G_0}{\lambda})^2$ ):

$$k_{et} = A \exp \left[ \frac{-\Delta G^*}{K_B T} \right]$$

While  $\lambda$  is the “reorganization term” composed of solvational ( $\lambda_0$ ) and vibrational ( $\lambda_i$ ) components:

$$\lambda = \lambda_0 + \lambda_i$$

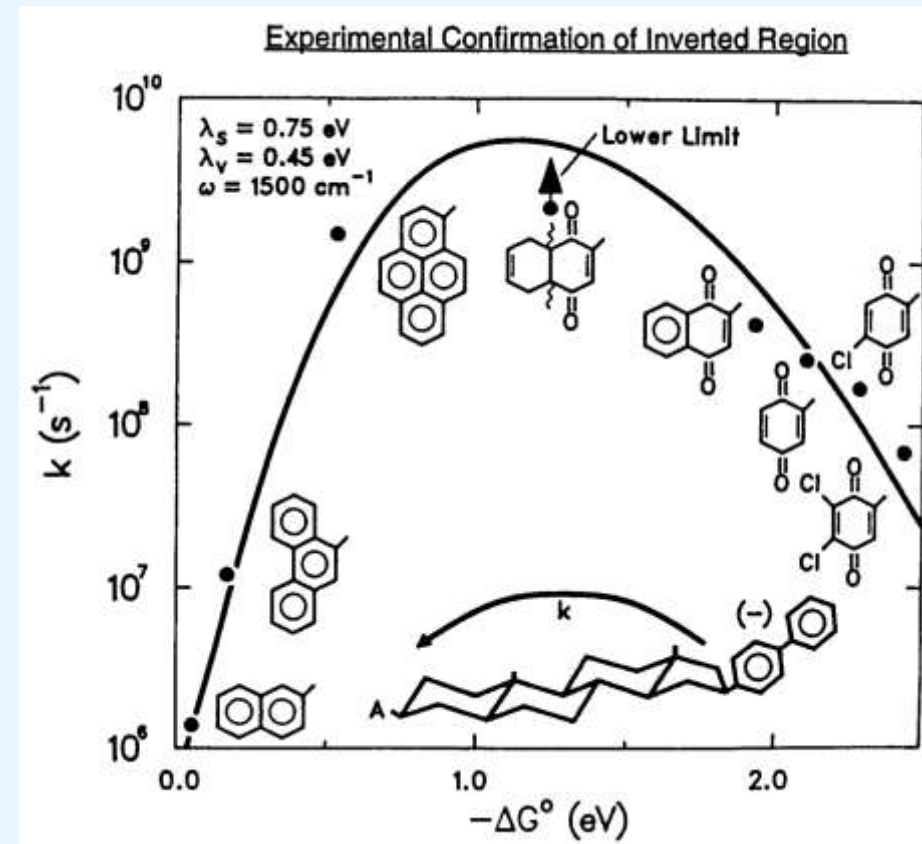
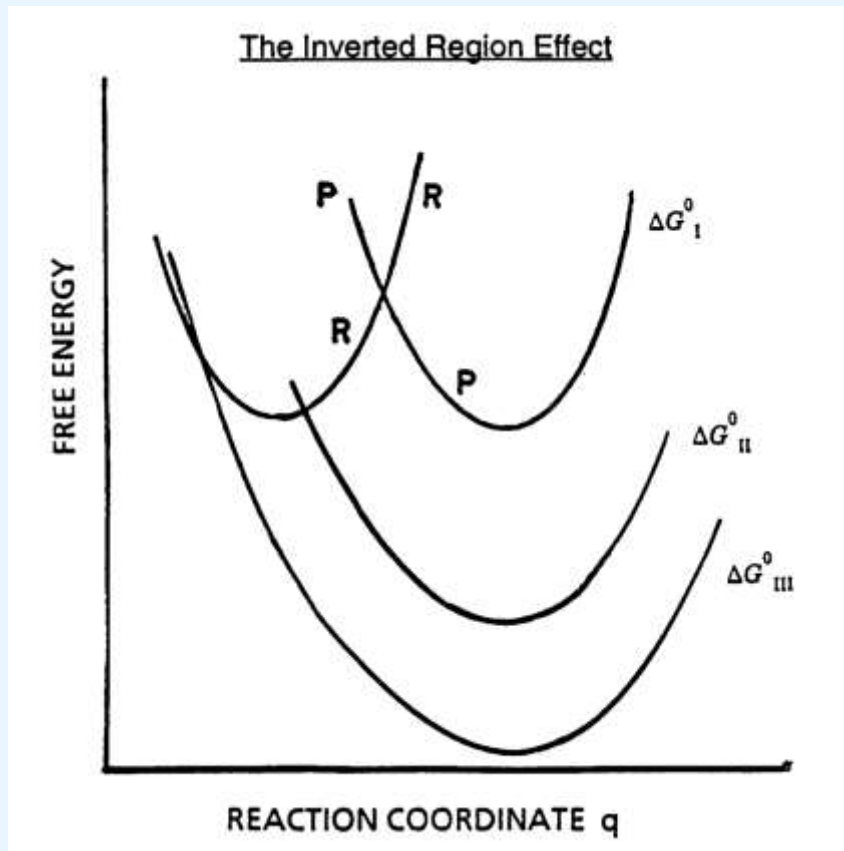
$$\lambda_0 = (\Delta e)^2 \left[ \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right] \left[ \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right]$$

$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2} \sum_l f_l (\Delta q_{e,l})^2$$

## 2. Marcus theory for electron transfer

Important prediction: inverted region

When  $\Delta G_0 = -\lambda$ ,  $k$  reaches its maximum.





03

# Application 1

Theory of Mode-Selective Chemistry through  
Polaritonic Vibrational Strong Coupling



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# Theory of Mode-Selective Chemistry through Polaritonic Vibrational Strong Coupling

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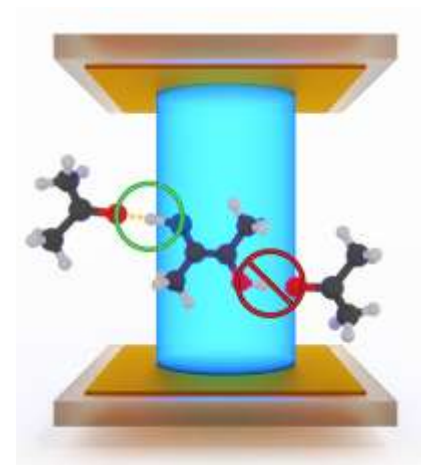


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By hybridizing the **vibrational excitations of a molecule** with the **photonic excitation of the radiation inside the cavity**, new light-matter entangled states, so-called **polariton states**, are generated.

Through the **resonant coupling** between the cavity and vibrational degrees of freedom (DOF) of the molecules, it has been demonstrated that it is possible to **suppress or enhance ground-state chemical reactivities**.

This so-called **vibrational strong coupling (VSC)** regime operates in the absence of any light source.

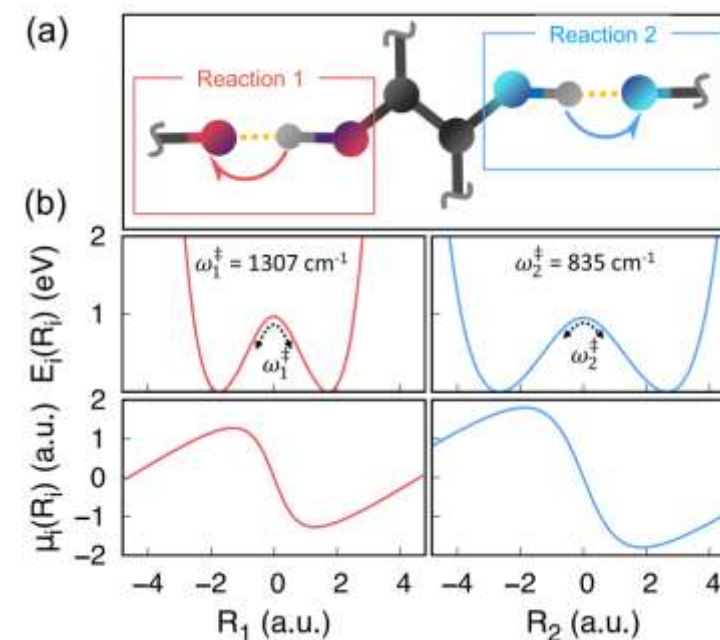
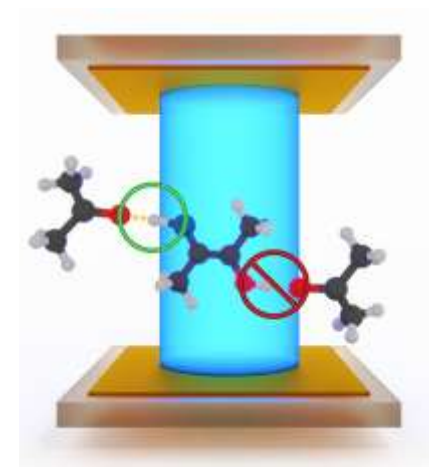




In this work, a model molecular system that has two competing reaction pathways (Reaction 1 and 2), with a **nearly identical potential energy barrier height** (with a difference less than 0.4 kcal/mol), but **different imaginary barrier frequencies** is considered.

Outside the cavity, Reaction 2 is preferred compared to Reaction 1, and by coupling the molecule to the cavity mode within a particular range of frequencies, Reaction 1 is preferred over Reaction 2, similar behavior has been also observed by recent experiments.

However, it should be emphasized that the theoretical study is limited to **a single molecule coupled to the cavity**, whereas the experiment is operated under the collective coupling condition that many molecules are coupled to the cavity.



The **matter Hamiltonian** and the corresponding total dipole operator are defined as follows:

$$\hat{H}_M = \hat{T} + \hat{V}(\hat{\mathbf{x}}) = \sum_j \frac{1}{2m_j} \hat{\mathbf{p}}_j^2 + \hat{V}(\hat{\mathbf{x}}); \quad \hat{\boldsymbol{\mu}} = \sum_j z_j \hat{\mathbf{x}}_j \quad \hat{\mathbf{x}} \equiv \{\hat{\mathbf{x}}_j\} = \{\hat{\mathbf{R}}, \hat{\mathbf{r}}\}$$

Where R and r represents the **nuclear and electronic coordinates**.

The **cavity photon field Hamiltonian** under the single mode assumption can be expressed as:

$$\hat{H}_{ph} = \hbar\omega_c \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right) = \frac{1}{2} (\hat{p}_c^2 + \omega_c^2 \hat{q}_c^2)$$

$$\hat{q}_c = \sqrt{\hbar/2\omega_c} (\hat{a}^\dagger + \hat{a})$$

$$\hat{p}_c = i\sqrt{\hbar\omega_c/2} (\hat{a}^\dagger - \hat{a})$$

The vector potential operator can be written as:

$$\hat{\mathbf{A}} = \mathbf{A}_0 (\hat{a} + \hat{a}^\dagger) = \mathbf{A}_0 \sqrt{2\omega_c/\hbar} \hat{q}_c$$

$$\mathbf{A}_0 = \sqrt{\frac{\hbar}{2\omega_c \epsilon_0 V}} \hat{\mathbf{e}} \equiv A_0 \hat{\mathbf{e}}$$

Coulomb gauge:  $\nabla \cdot \hat{\mathbf{A}} = 0 \Rightarrow \hat{\mathbf{A}}$  becomes purely transverse.  $\hat{\mathbf{A}} = \hat{\mathbf{A}}_\perp$

$$\therefore \vec{A}(\vec{r}, t) = \sum_{\vec{k}, \mu} (e^{i\mu(\vec{k})} a_{\vec{k}}^{(\mu)}(t) e^{i\vec{k} \cdot \vec{r}} + h.c.) \quad , \quad a_{\vec{k}}^{(\mu)}(t) = a_{\vec{k}}^{(\mu)} e^{-i\omega t}$$

$$\Rightarrow \left\{ \begin{array}{l} \vec{B} = \nabla \times \vec{A} = \sum_{\vec{k}, \mu} [i(\vec{k} \times e^{i\mu(\vec{k})}) a_{\vec{k}}^{(\mu)}(t) e^{i\vec{k} \cdot \vec{r}} + h.c.] \\ \vec{E}(\vec{r}, t) = \sum_{\vec{k}, \mu} [i\omega e^{i\mu(\vec{k})} a_{\vec{k}}^{(\mu)}(t) e^{i\vec{k} \cdot \vec{r}} + h.c.] \end{array} \right.$$

$$\text{Quantization: } a_{\vec{k}}^{(\mu)}(t) \rightarrow \sqrt{\frac{\hbar\epsilon_0}{2\omega V}} \cdot a_{\vec{k}}^{(\mu)}(\vec{k}) \quad , \quad [a_{\vec{k}}^{(\mu)}(t)]^\dagger = \sqrt{\frac{\hbar\epsilon_0}{2\omega V}} \cdot a_{\vec{k}}^{\dagger(\mu)}(\vec{k})$$

$$\Rightarrow \vec{E}(\vec{r}, t) = \sum_{\vec{k}, \mu} \sqrt{\frac{\hbar\omega}{2V\epsilon_0}} \cdot [i e^{i\mu(\vec{k})} a_{\vec{k}}^{(\mu)}(\vec{k}) e^{i\vec{k} \cdot \vec{r}} + h.c.]$$

$$H = \frac{1}{2} \epsilon_0 \int_V (|\vec{E}(\vec{r}, t)|^2 + c^2 |\vec{B}(\vec{r}, t)|^2) d^3\vec{r} = \hbar\omega \sum_{\vec{k}, \mu} (a_{\vec{k}}^{\dagger(\mu)}(\vec{k}) a_{\vec{k}}^{(\mu)}(\vec{k}) + \frac{1}{2})$$

$$\text{Long-wavelength approximation: } e^{i\vec{k} \cdot \vec{r}} \sim 1 \quad , \quad \vec{A} = \sum_{\vec{k}, \mu} \sqrt{\frac{\hbar\epsilon_0}{2\omega V}} \cdot (a + a^\dagger)$$

$$\text{Single-mode assumption: } \vec{A} = \sqrt{\frac{\hbar\epsilon_0}{2\omega V}} \cdot (a + a^\dagger) \quad , \quad [a, a^\dagger] = 1$$



P.A form:  $H_c = \sum_j \frac{1}{2m_j} (\hat{p}_j - q_j \hat{A})^2 + \hat{V}(\hat{x}) + \hat{H}_{ph}$

① PZW gauge transformation operator  $\hat{U} = \exp[-\frac{i}{\hbar} \hat{\mu} \hat{A}] = \exp[-\frac{i}{\hbar} \hat{\mu} \hat{A}_0 (\hat{a} + \hat{a}^\dagger)] = \exp[-\frac{i}{\hbar} \hat{\mu} \cdot \vec{A}_0 \sqrt{\frac{2m\omega_c}{\hbar}} \hat{q}_c]$

若  $\hat{U}_p = e^{-i\hat{p}\hat{q}}$   $\hat{U}_p \hat{O}(\hat{p}) \hat{U}_p^\dagger = \hat{O}(\hat{p} + \hat{p}_0)$  而  $\hat{\mu} = \sum_j q_j \hat{x}_j$

$\rightarrow \hat{H}_D = \exp[-\frac{i}{\hbar} \hat{\mu} \cdot \vec{A}_0 (\hat{a} + \hat{a}^\dagger)] \left[ \sum_j \frac{1}{2m_j} (\hat{p}_j - q_j \hat{A})^2 + \hat{V} + \hat{H}_{ph} \right] \exp[\frac{i}{\hbar} \hat{\mu} \cdot \vec{A}_0 (\hat{a} + \hat{a}^\dagger)]$

$= \hat{H}_M + \exp[-\frac{i}{\hbar} \hat{\mu} \cdot \vec{A}_0 \sqrt{\frac{2m\omega_c}{\hbar}} \hat{q}_c] \cdot (\frac{1}{2} \hat{p}_c^2 + m^2 \hat{q}_c^2) \exp[\frac{i}{\hbar} \hat{\mu} \cdot \vec{A}_0 \sqrt{\frac{2m\omega_c}{\hbar}} \hat{q}_c]$

$= \hat{H}_M + \frac{1}{2} m^2 \hat{q}_c^2 + \frac{1}{2} (\hat{p}_c + \sqrt{\frac{2m\omega_c}{\hbar}} \hat{\mu} \cdot \vec{A}_0)^2$

$= \hat{H}_M + \hbar\omega_c (\hat{a}^\dagger \hat{a} + \frac{1}{2}) + i\omega_c \hat{\mu} \cdot \vec{A}_0 (\hat{a}^\dagger - \hat{a}) + \frac{\omega_c}{\hbar} (\hat{\mu} \cdot \vec{A}_0)^2$

② PF gauge transformation

$\hat{U}_\phi = \exp[-i\phi \hat{a}^\dagger \hat{a}]$

$\hat{U}_\phi \hat{a}^\dagger \hat{U}_\phi^\dagger = e^{-i\phi \hat{a}^\dagger \hat{a}} \hat{a}^\dagger e^{i\phi \hat{a}^\dagger \hat{a}} = \hat{a}^\dagger + [-i\phi \hat{a}^\dagger \hat{a}, \hat{a}^\dagger] + \frac{1}{2} [-i\phi \hat{a}^\dagger \hat{a}, -i\phi \hat{a}^\dagger \hat{a}] + \dots = e^{-i\phi} \hat{a}^\dagger$

$\hat{U}_\phi \hat{a} \hat{U}_\phi^\dagger = e^{-i\phi \hat{a}^\dagger \hat{a}} \hat{a} e^{i\phi \hat{a}^\dagger \hat{a}} = \hat{a} + [-i\phi \hat{a}^\dagger \hat{a}, \hat{a}] + \dots = e^{i\phi} \hat{a}$

$\hat{U}_\phi (\hat{a}^\dagger \hat{a}) \hat{U}_\phi^\dagger = \hat{a}^\dagger \hat{a}$   $\hat{U}_\phi (\hat{a}^\dagger - \hat{a}) \hat{U}_\phi^\dagger = e^{-i\phi} \hat{a}^\dagger - e^{i\phi} \hat{a}$

$\Rightarrow \hat{H}_{PF} = \hat{U}_\phi \hat{H}_D \hat{U}_\phi^\dagger = \hat{H}_M + \hbar\omega_c (\hat{a}^\dagger \hat{a} + \frac{1}{2}) + i\omega_c (\hat{\mu} \cdot \vec{A}_0) \cdot (-i) (\hat{a}^\dagger + \hat{a}) + \frac{\omega_c}{\hbar} (\hat{\mu} \cdot \vec{A}_0)^2$

$= \hat{H}_M + \frac{1}{2} (\hat{p}_c^2 + m^2 \hat{q}_c^2) + m (\hat{\mu} \cdot \vec{A}_0) \sqrt{\frac{2m\omega_c}{\hbar}} \hat{q}_c + \frac{\omega_c}{\hbar} (\hat{\mu} \cdot \vec{A}_0)^2$

$= \hat{H}_M + \frac{1}{2} \hat{p}_c^2 + \frac{1}{2} m^2 (\hat{q}_c + \sqrt{\frac{2}{\hbar\omega_c}} \hat{\mu} \cdot \vec{A}_0)^2$

In this work, it's assumed that  $\hat{\mu} \parallel \vec{A}_0$

$\Rightarrow \hat{\mu} \cdot \vec{A}_0 = \hat{\mu} A_0 = \hat{\mu} \cdot \sqrt{\frac{\hbar}{2m\omega_c \epsilon_0 V}}$

$\therefore \hat{H}_{PF} = \hat{H}_M + \frac{\hat{p}_c^2}{2} + \frac{1}{2} m^2 (\hat{q}_c + \sqrt{\frac{2}{\hbar\omega_c}} A_0 \hat{\mu}(\mathbf{R}))^2$

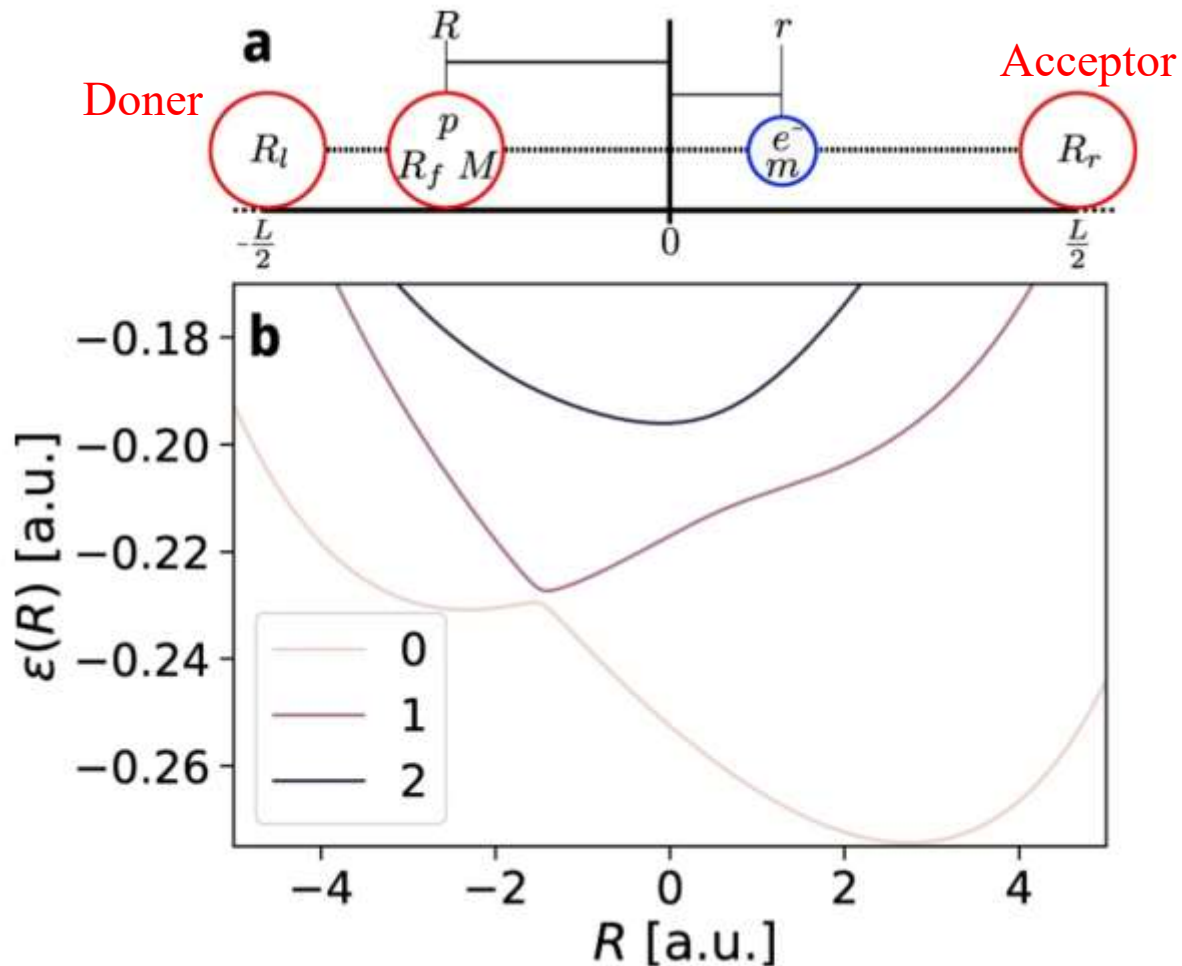
In this work, only electronic ground state is considered:

$$(\hat{H}_M - \hat{T}_R) |\Psi_g\rangle = E_g(\mathbf{R}) |\Psi_g\rangle$$

So we obtain the model Hamiltonian:

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + E_g(\mathbf{R}) + \frac{\hat{p}_c^2}{2} + \frac{1}{2} \omega_c^2 \left( \hat{q}_c + \sqrt{\frac{2}{\hbar\omega_c}} A_0 \cdot \mu(\mathbf{R}) \right)^2$$

# The Shin-Metiu Model



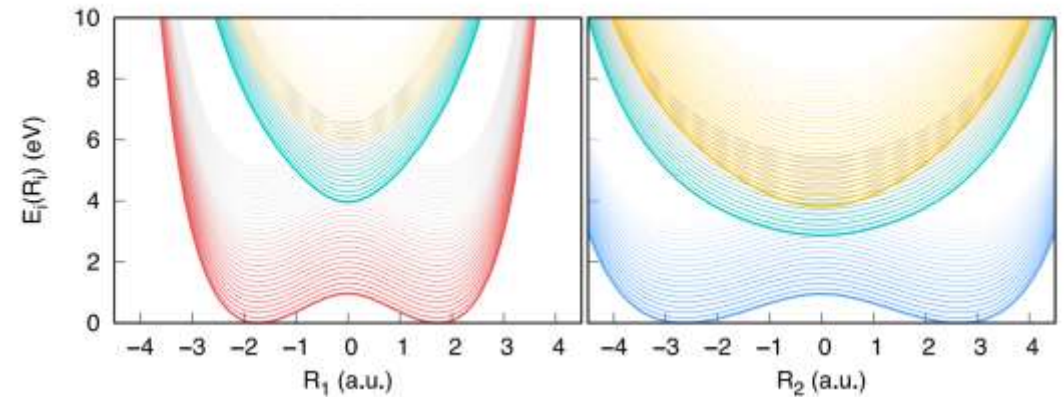
The Hamiltonian of the system reads:

$$\hat{H}_M = \frac{\hat{P}^2}{2M} + \hat{H}_{\text{el}},$$

with the electronic part being:

$$\hat{H}_{\text{el}} = \hat{T}_r + \hat{V}_{\text{eN}} + \hat{V}_{\text{NN}}$$

$$\hat{V}_{\text{eN}} = -z_p e^2 \frac{\text{erf}(\frac{|r-R|}{R_c})}{|r-R|} - \sum_{\alpha \in \text{D,A}} z_\alpha e^2 \frac{\text{erf}(\frac{|r-R_\alpha|}{R_c})}{|r-R_\alpha|} \quad V_{\text{NN}} = \frac{z_p z_D e^2}{|R-R_D|} + \frac{z_p z_A e^2}{|R-R_A|}$$



Bold curves: solution of  $\hat{H}_{\text{el}}|\Psi_i^\alpha\rangle = E_i^\alpha(R)|\Psi_i^\alpha\rangle$

Thin curves: photon dressed potentials  $E_i^\alpha(R) + n\hbar\omega_c$

So, the molecular Hamiltonian is expressed as:

$$\hat{H}_m = \sum_{i=1}^2 \frac{\hat{P}_i^2}{2M_i} + E(R_1, R_2) + \hat{H}_{\text{vib}}(\mathbf{R}, \mathbf{x})$$

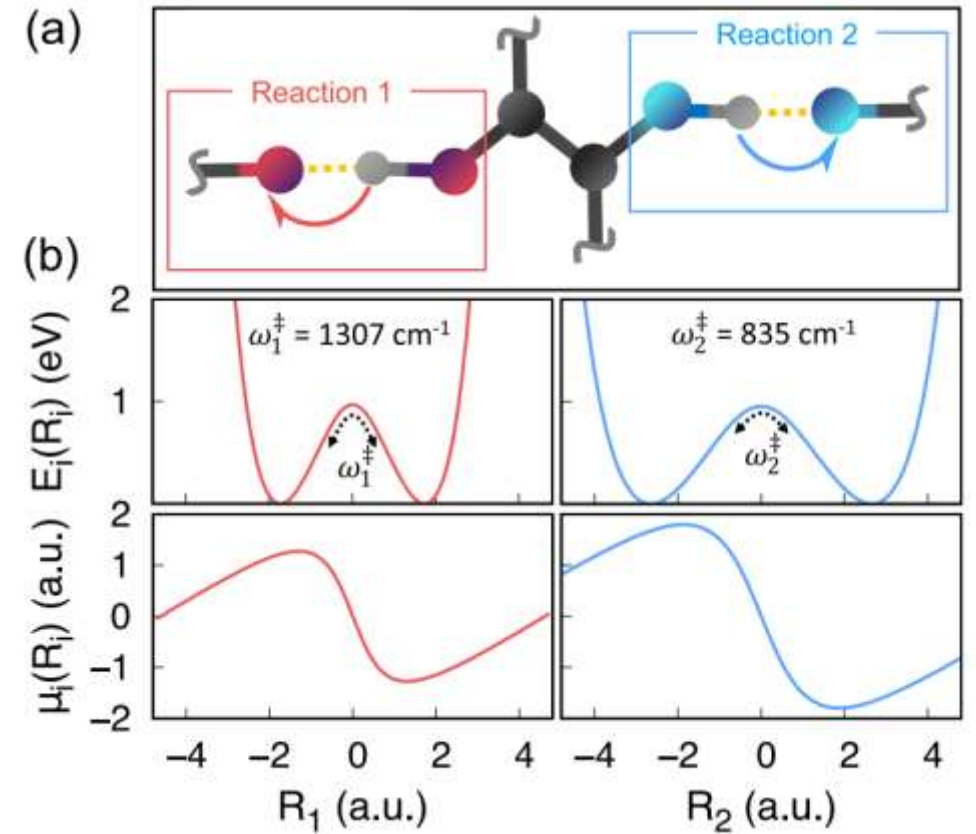
where  $E(R_1, R_2)$  is the ground electronic state potential energy surface for two uncoupled Shin-Metiu model.

The bottom of the well position for the reactant is  $R_i^0$  and the dividing surface position is  $R_i^\ddagger$ . The reactant well frequency is defined as

$$(\omega_i^0)^2 = \frac{\partial^2 E_i(R_i)}{M_i \partial R_i^2} \Big|_{R_i=R_i^0}$$

The imaginary part:  $(\omega_i^\ddagger)^2 = -\frac{\partial^2 E_i(R_i)}{M_i \partial R_i^2} \Big|_{R_i=R_i^\ddagger}$

The total dipole moment is modeled as  $\mu(\mathbf{R}) = \mu_1(R_1) + \mu_2(R_2)$ .  $\mu_i(R_i)$  is the ground state permanent dipole moment of the  $i$ th reaction coordinate



The VSC polariton chemical kinetics can be viewed as a barrier crossing process on the cavity Born-Oppenheimer surface(CBO).

$$V_{\text{CBO}}(\mathbf{R}, q_c) = \sum_{i=1}^2 E_i(R_i) + \frac{1}{2} \omega_c^2 \left( q_c + \sqrt{\frac{2}{\hbar \omega_c}} A_0 \cdot \sum_{i=1}^2 \mu_i(R_i) \right)^2$$

Define a normalized coupling strength(**cavity frequency independent**):

$$\tilde{\eta} = \frac{A_0}{\sqrt{M} \hbar}$$

In this work, the coupling strength is fixed at 0.047 au.

**Note: the molecule-cavity coupling strength per molecule used in this work is much stronger than the realistic coupling strength in the VSC experiments that include many molecules.**

# Reaction rate constant:

Method 1. numerical simulation.

$$k = \lim_{t \rightarrow t_p} k(t) \cdot k^{TST},$$

$k(t)$ : transmission coefficient.  $k^{TST}$ : transition state theory rate

$$k^{TST} = \nu \cdot K_c = \frac{\omega^0}{2\pi} e^{-\beta E^\ddagger} \quad \text{where } E^\ddagger = E(R^\ddagger) - E(R_0).$$

when treated classically,  $E^\ddagger$  is independent of  $\omega_c$

calculation of  $k(t)$ :

the flux passing through  $x=s$ :  $\hat{F}(s) = \frac{i}{\hbar} [\hat{H}, h(x-s)]$ .  $h(x-s) = \begin{cases} 1, & \text{if } x > s \\ 0, & \text{if } x < s \end{cases}$

$$H = \frac{\hat{p}^2}{2m} + \hat{V}(x) \Rightarrow \hat{F}(s) = -\frac{i\hbar}{2m} \left\{ \delta(x-s) \frac{d}{dx} + \frac{d}{dx} \delta(x-s) \right\}$$

$$K(t) = \frac{\langle \hat{F}(0) \cdot h(R(t) - R^\ddagger) \rangle}{\langle \hat{F}(0) \cdot h(R^\ddagger(0)) \rangle}$$

Method 2. Analytical expression.  $k^{GH} = \frac{1}{2\pi} \frac{\prod_{\nu=1}^N \Omega_\nu^0}{\prod_{\nu=2}^N \Omega_\nu^\ddagger} e^{-\beta E^\ddagger}$

focus on transition state configuration  $\{R_1^\ddagger, R_2^0, q_c(R_1^\ddagger, R_2^0)\}$

$$\text{where } q_c(R_1, R_2) = -\sqrt{\frac{2}{\hbar \omega_c}} A_0 [\mu_1(R_1) + \mu_2(R_2)]$$

Using  $(\Omega_1^\ddagger, \Omega_2^\ddagger, \Omega_3^\ddagger)^2 = -(\omega_1^\ddagger, \omega_2^\ddagger, \omega_c)^2$ ,  $(\Omega_1^0, \Omega_2^0, \Omega_3^0)^2 = (\omega_1^0, \omega_2^0, \omega_c)^2$ :

$$k_1 = \frac{1}{2\pi} \frac{\prod_{\nu=1}^N \Omega_\nu^0}{\prod_{\nu=2}^N \Omega_\nu^\ddagger} e^{-\beta E^\ddagger} = \frac{\sqrt{(\Omega_1^\ddagger)^2}}{\omega_1^\ddagger} \cdot \frac{\omega_1^0}{2\pi} \cdot e^{-\beta E^\ddagger}$$

Diagonalizing  $H(R_1^\ddagger, R_2^0, q_c)$ . one can get  $\Omega_1^\ddagger$ . and there is a  $\omega_1^\ddagger$  that minimizes  $\Omega_1^\ddagger$ :

$$\omega_1^\ddagger = -\frac{\hbar}{2} \tilde{\eta}^2 (\mu_1^\ddagger)^2 + \frac{1}{2} \sqrt{\hbar^2 \tilde{\eta}^4 (\mu_1^\ddagger)^4 + 4\omega_1^{\ddagger 2}}, \quad \mu_1^\ddagger = \frac{\partial \mu_1(R_1^\ddagger)}{\partial R_1}$$

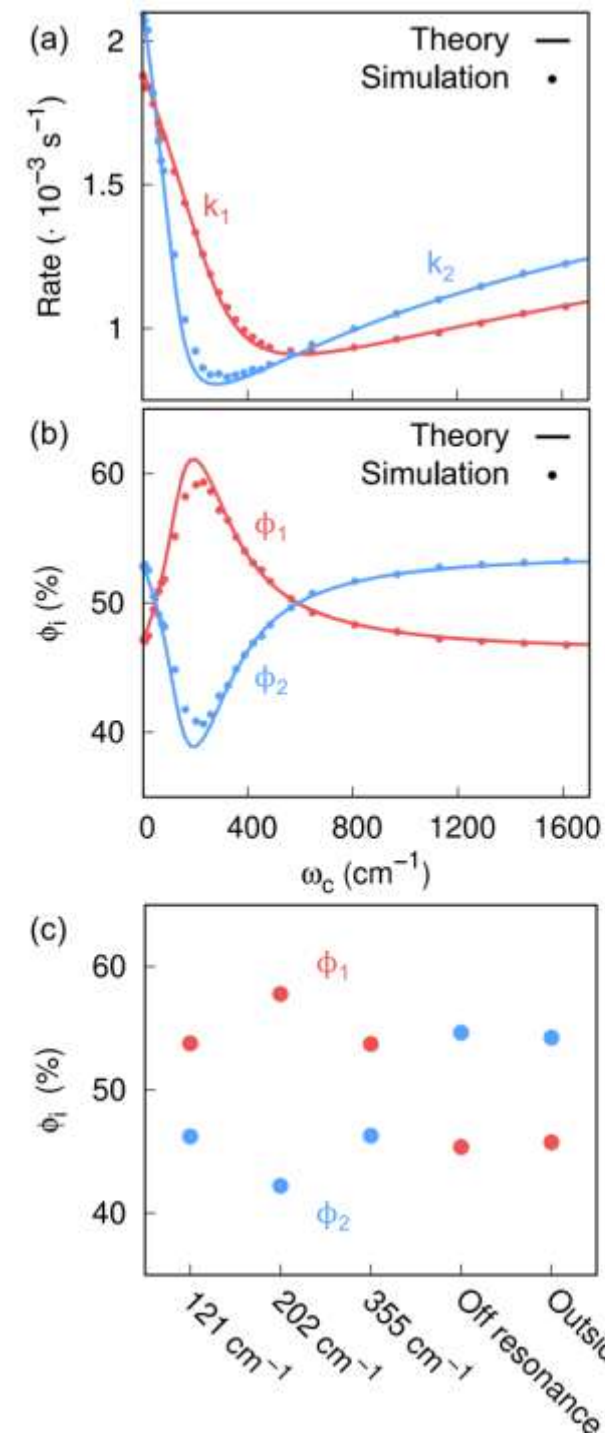
Yield of reaction  $i$ :

$$\phi_i = \frac{k_i}{k_1 + k_2}$$



## Results and discussion:

1. The suppression completely originates from the reduction of the transmission coefficient  $\kappa$ , not from the TST rate constant, as the classical barrier height is independent of the cavity frequency.
2. The maximum suppression of  $k_i$  occurs at two different frequencies.
3. From last page, we can get the maximum suppression frequency for reaction  $i$ : 
$$\omega_i^* = -\frac{\hbar}{2}\bar{\eta}^2(\mu_i^{\ddagger})^2 + \frac{1}{2}\sqrt{\hbar^2\bar{\eta}^4(\mu_i^{\ddagger})^4 + 4\omega_i^{\ddagger 2}}$$
 For small  $\eta$ , the maximum suppression frequency is close to the barrier frequency.
4. The reverted preference occurs at a range of different frequencies ( $[49\text{cm}^{-1}, 565\text{cm}^{-1}]$ ), and the maximum reverted preference at  $201.6\text{ cm}^{-1}$ .





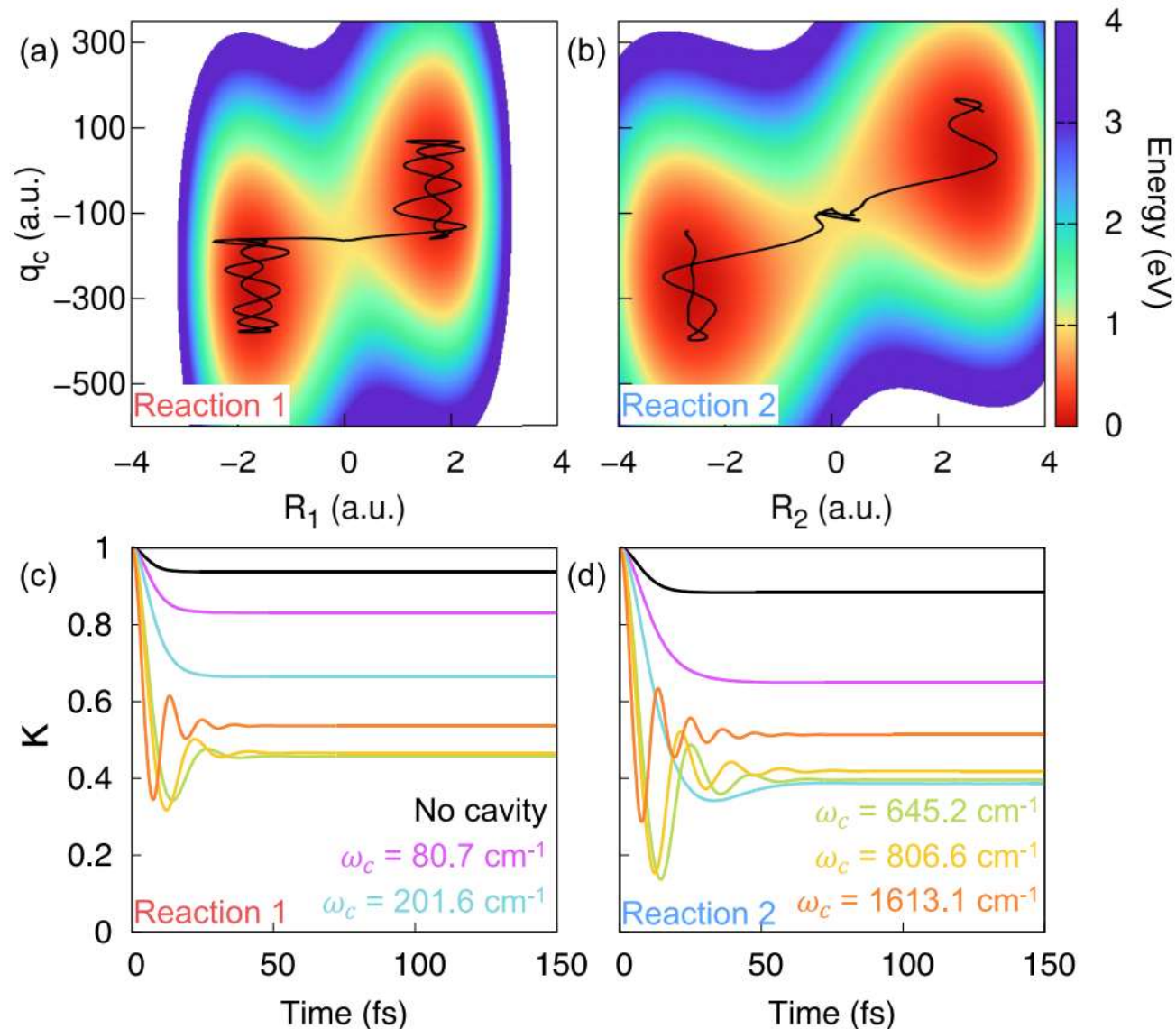
## Further explanation: **caging effect**

(a)(b): representative reaction trajectories on the CBO surface for reaction 1&2.

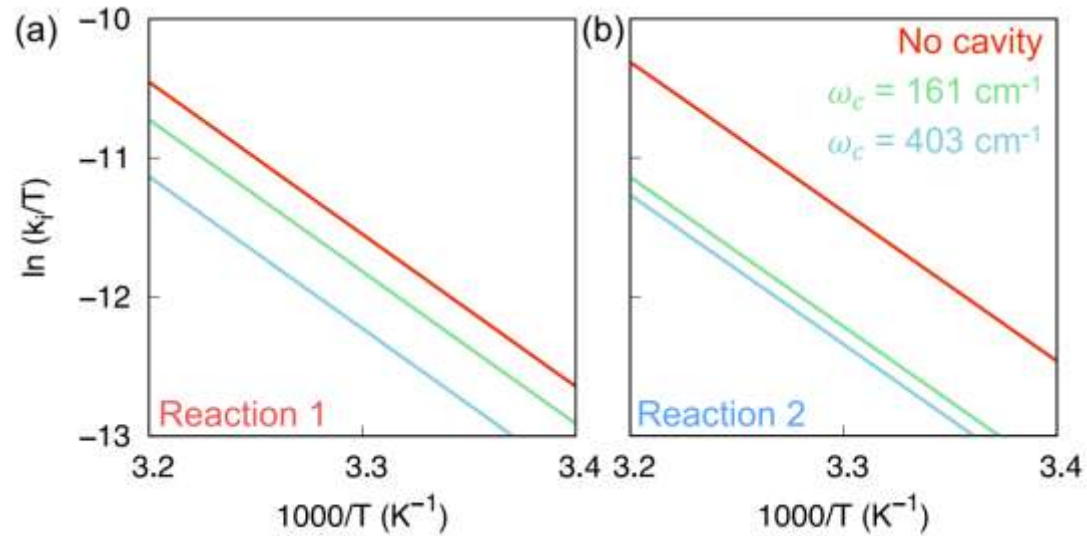
(c)(d): transmission coefficients at various cavity frequencies.

1. The maximum reverted preference ( $201.6\text{ cm}^{-1}$ ) is far from the maximum suppression frequency of reaction 1, but close to which of reaction 2, hence significantly lowering  $\kappa_2$  through multiple recrossing dynamics. Together we can see that the *fundamental mechanism* of the cavity-enhanced selectivities originates from a *selective dynamical caging effect*.

2. As  $\omega_c$  increases,  $\kappa(t)$  for both reactions becomes more oscillatory. The long-time plateau values of  $\kappa(t_p)$  decrease with increasing cavity frequency. After reaching a minimum (when  $\omega_c = \omega_i^s$  for a given reaction),  $\kappa(t_p)$  starts to increase again.



Temperature dependence:



The simple Eyring theory gives:

$$\ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{k_B} \cdot \frac{1}{T} + \frac{\Delta S^\ddagger}{k_B} + \ln \frac{k_B}{h}$$

Cannot explain the change of slope in the Eyring plot observed in the experiments!

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## Application 2

Catalysis by Dark States in  
Vibropolaritonic Chemistry



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# Catalysis by Dark States in Vibropolaritonic Chemistry

Matthew Du<sup>ID</sup> and Joel Yuen-Zhou<sup>ID\*</sup>

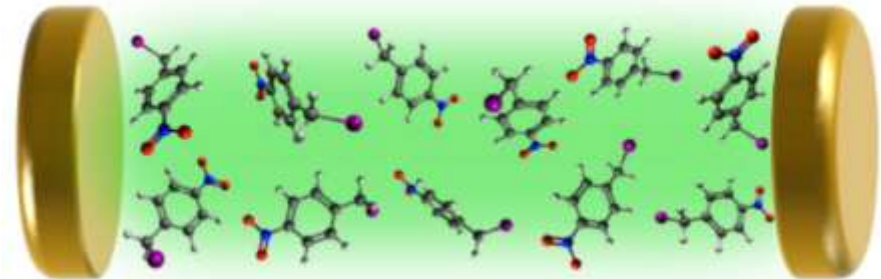
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## System Hamiltonian:

Consider **a disordered ensemble of N molecular vibrations**, respectively, corresponding to N independent molecules, inside an optical cavity. The system is described by the Hamiltonian:

$$H = \hbar\omega_c a_0^\dagger a_0 + \hbar \sum_{i=1}^N \omega_i a_i^\dagger a_i + \hbar \sum_{i=1}^N g_i (a_i^\dagger a_0 + H.c.).$$

Vibrational mode  $i$  is represented by annihilation operator  $a_i$  and has frequency  $\omega_i = \overline{\omega_v} + \delta\omega_i$ . The cavity mode has frequency  $\omega_c$  and couples to vibration  $i$  with strength  $g_i$ . Here  $g_i = g$  for all  $i$ , and  $\delta\omega_i$  is normally distributed with mean zero and standard deviation  $\sigma_v$ .



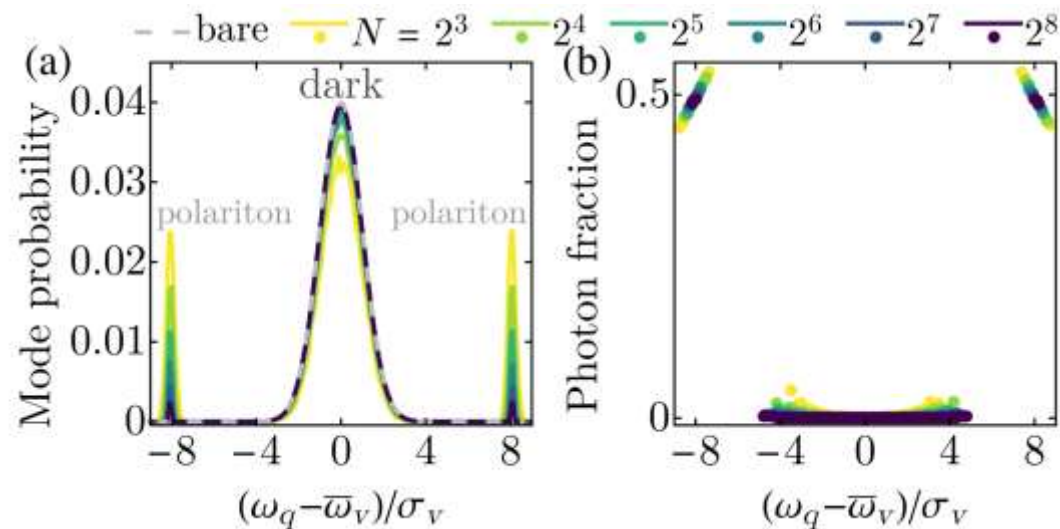
The physicochemical properties of a disordered molecular system under VSC:

Calculations take  $\omega_c = \overline{\omega_v}$ ,  $g\sqrt{N} = 8\sigma_v$  (for all N).

*The eigenmodes of H*: mode  $q = 1, \dots, N + 1$  is represented by operator  $\alpha_q = \sum_{i=0}^N c_{qi} a_i$  and has frequency  $\omega_q$ .

(a): Probability distribution of  $\omega_q$ .

(b): Photon fraction ( $|c_{q0}|^2$ ) vs. eigen frequency



# The delocalization of dark modes:

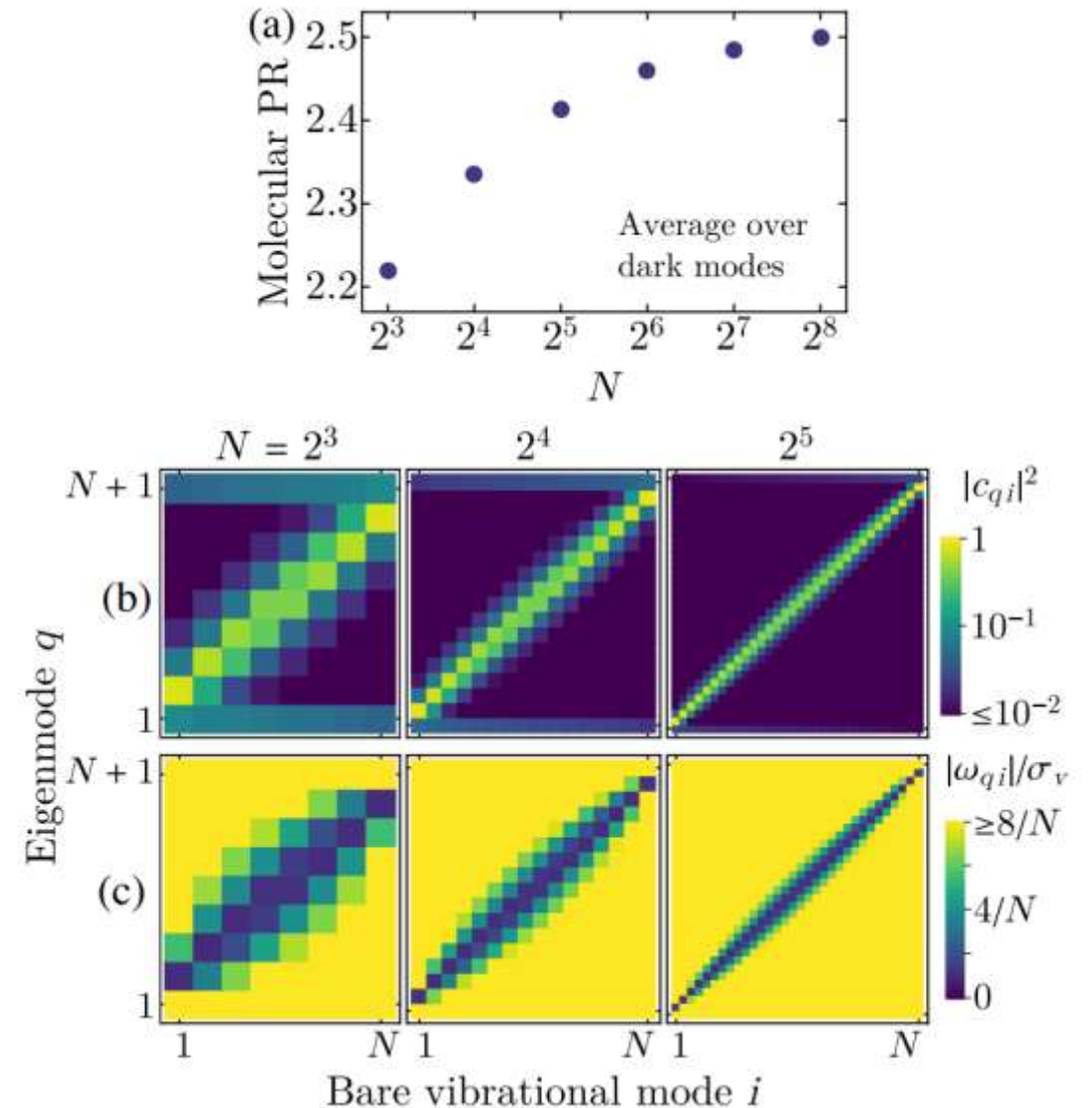
First define the *molecular participation ratio (PR)* as:

$$PR = 1 / \sum_{i=1}^N \left| \frac{c_{qi}}{\sqrt{\sum_{i=1}^N |c_{qi}|^2}} \right|^4.$$

PR estimates the number of molecules over which eigenmode  $q$  is delocalized

(a): The average molecular PR of dark modes.

(b)(c): The squared overlap ( $|c_{qi}|^2$ ) and frequency difference  $\omega_{qi} = \omega_q - \omega_i$  between each dark mode and vibrational mode.



VSC's influence on the *kinetics* of a thermally activated chemical reaction:

Consider a reactive molecule (*only 1 molecule!*) that undergoes nonadiabatic intramolecular electron transfer under collective VSC. To model the reaction(rxn) of one molecule in the ensemble:

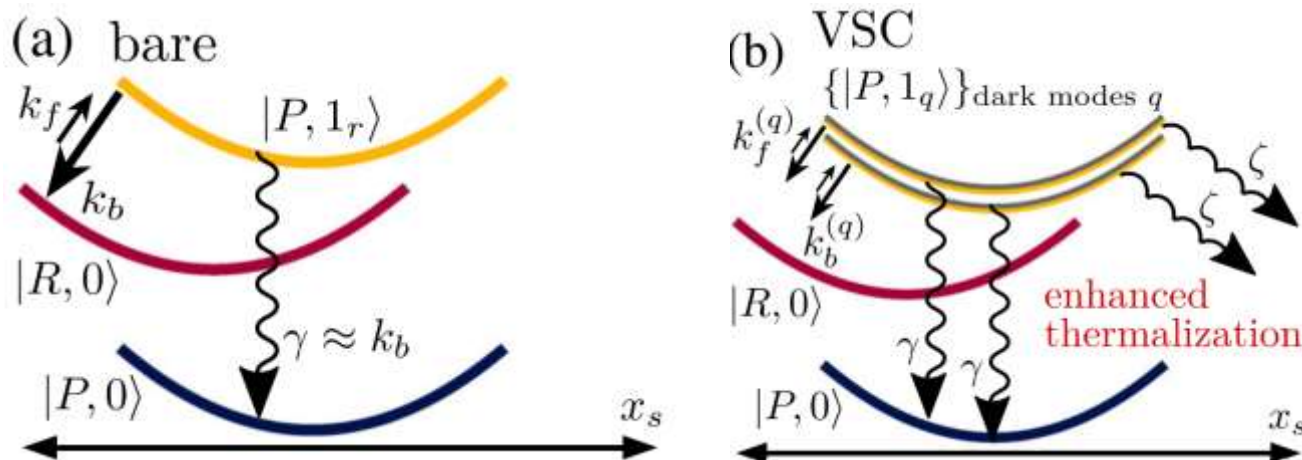
$$H_{rxn} = H + \sum_{X=R,P} |X\rangle\langle X| \{E_X + \hbar\omega_r [\lambda_X (a_r + a_r^\dagger) + \lambda_X^2]\} + V + H_S^{(l)}$$

$$V = J_{RP}(|R\rangle\langle P| + H.c.)$$

Here, we have changed the numerical index of the bare vibrational mode ( $i=1$ ) involved in the reaction to the letter  $r$  (i.e.,  $\omega_1 \rightarrow \omega_r$ ,  $a_1 \rightarrow a_r$ ).

Eigenstates:  $|X, \chi\rangle = |X\rangle \otimes |\tilde{\chi}_{(X)}\rangle$ , where  $|\tilde{\chi}_{(X)}\rangle = (\prod_{q=1}^{N+1} D_q^\dagger(\lambda_{Xq}))|\chi\rangle$ ,  $D_q(\lambda) = \exp(\lambda\alpha_q^\dagger - \lambda^*\alpha_q)$ ,  $\lambda_{Xq} = \lambda_X c_{qr}(\omega_r/\omega_q)$

Reaction rate:  $k_{(R,\chi) \rightarrow (P,\chi')} = \mathcal{A} F_{\chi,\chi'} \exp(-\beta E_a^{\chi,\chi'})$   $F_{\chi,\chi'} = |\langle \tilde{\chi}_{(R)} | \tilde{\chi}'_{(P)} \rangle|^2$





Approximate models: only  $\chi = 0$  and  $\chi = 1_q$  are considered.

Bare:

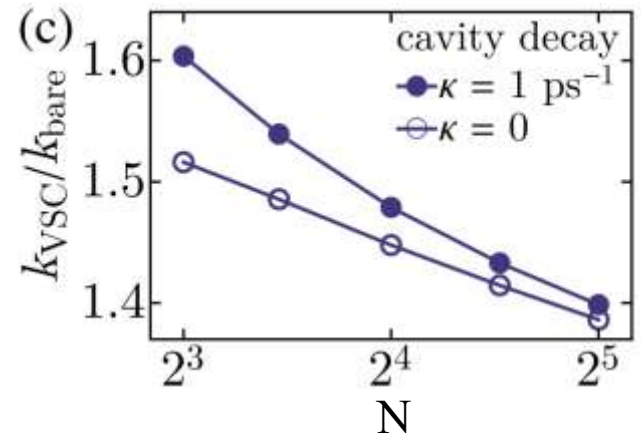
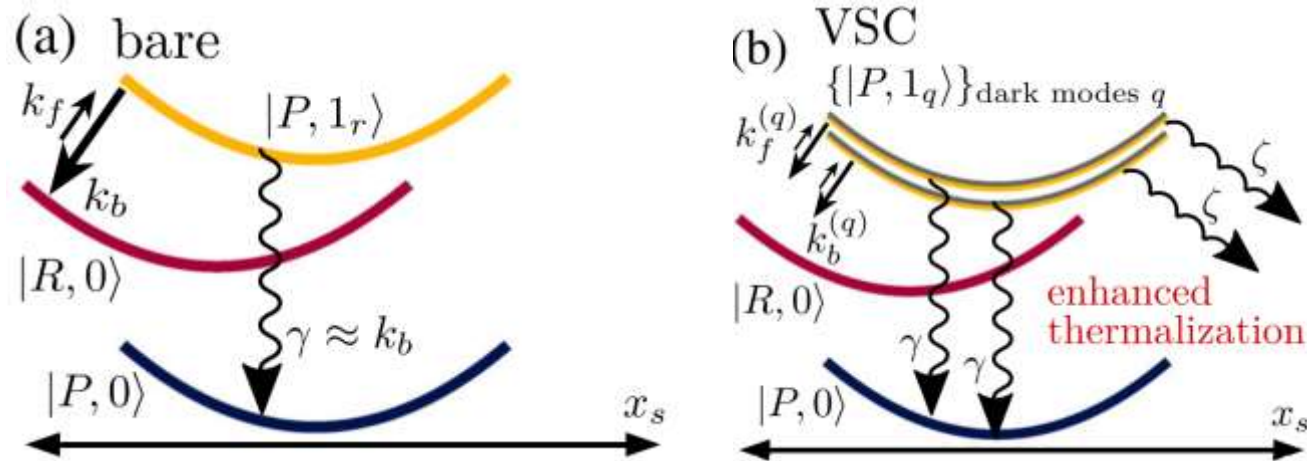
$$k_f = \mathcal{A}F_{0,1_r} \exp(-\beta E_a) \quad k_b = k_f \exp[\beta(E_P + \hbar\omega_r - E_R)] \quad \gamma \approx k_b$$

$$\begin{aligned} \frac{dp_{(R,0)}}{dt} &= -k_f p_{(R,0)} + k_b p_{(P,1_r)}, \\ \frac{dp_{(P,1_r)}}{dt} &= -(k_b + \gamma) p_{(P,1_r)} + k_f p_{(R,0)} \end{aligned} \quad \xrightarrow{\text{yields}} \quad k_{\text{bare}}^{(\text{analytical})} = k_f \left( \frac{\gamma}{\gamma + k_b} \right)$$

VSC:

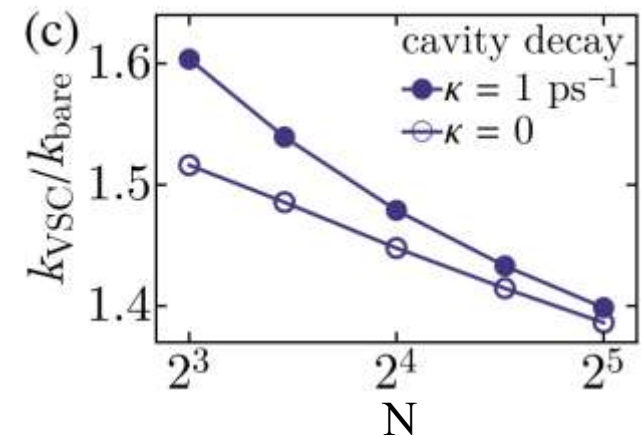
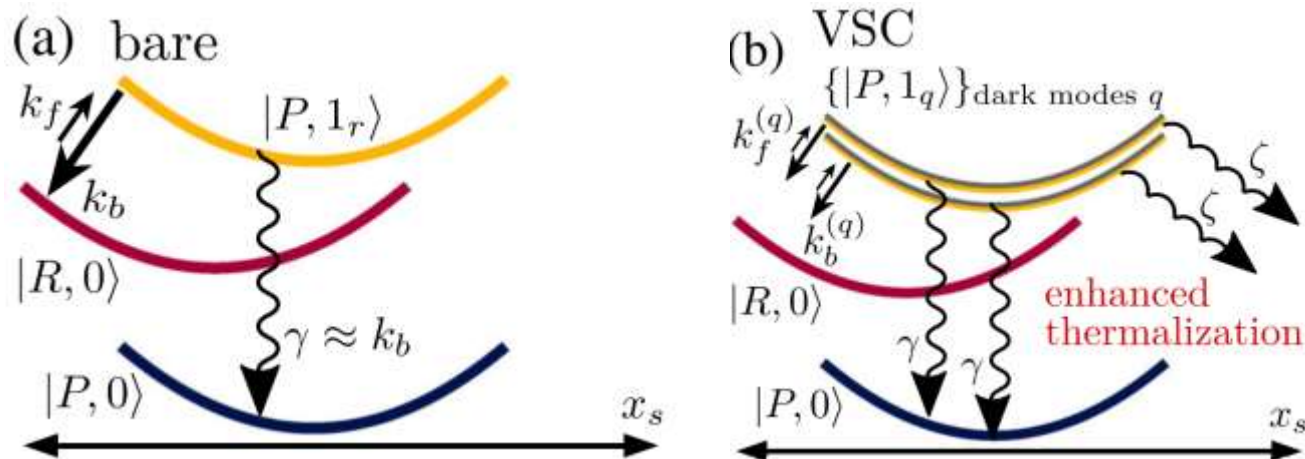
$$k_f^{(q)} = \mathcal{A}F_{0,1_q} \exp(-\beta E_a^{(q)}) \quad k_b^{(q)} = k_f^{(q)} \exp\{\beta[E_P + \hbar\omega_q + \Delta_P - (E_R + \Delta_R)]\}$$

$$F_{0,1_q} \approx |c_{qr}|^2 F_{0,1_r} \quad \rightarrow \quad k_{f/b}^{(q)} \approx |c_{qr}|^2 k_{f/b} \quad \xrightarrow{\text{yields}} \quad k_{\text{VSC}}^{(\text{analytical})} = k_f \left\langle \frac{\gamma}{\gamma + |c_{qr}|^2 k_b} \right\rangle_{\text{dark modes } q}$$



## Analysis:

1. We can see that the major contributions to the average come from dark modes that are closest to the bare reactive mode.
2. Further enhancement of the VSC reaction, beyond that given by  $k_{VSC}^{(analytical)}$ , occurs via dissipative scattering from these dark modes to those with  $c_{qr} \approx 0$ .
3. From (c), we can see that VSC significantly accelerates the reaction compared to the bare case (roughly 50% for  $8 \leq N \leq 32$ ).

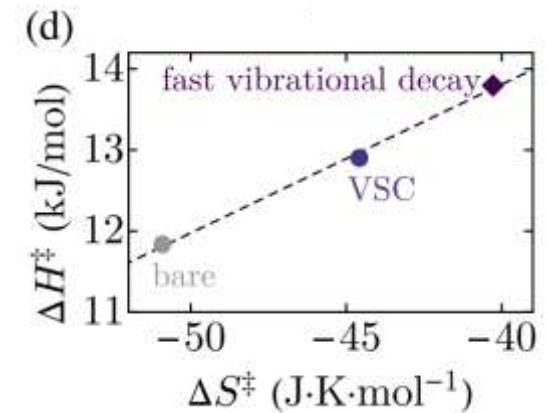
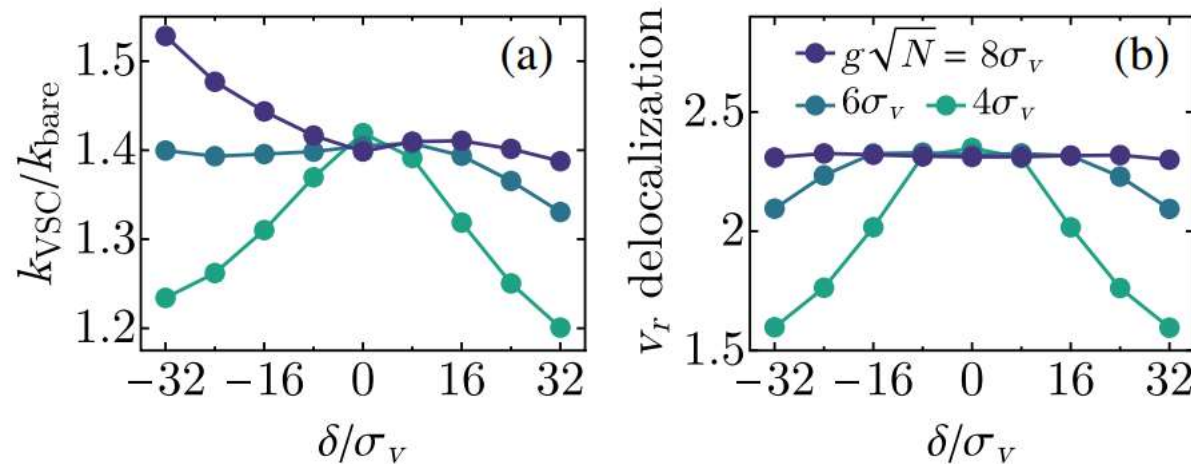


Dependence on cavity detuning:

Now that  $\delta = \omega_c - \overline{\omega_v}$ , consider the reaction rate and reactive delocalization  $1/\sum_{i=1}^N |c_{qr}|^4$  (the PR of  $v_r$  when the mode is expressed in the eigenbasis of H).

1. The observed correlation between reactivity under VSC and delocalization of the reactive mode corroborates that the reaction is sped up by dark-mode semilocalization.

2. By fitting apparent reaction rates to the Eyring-Polanyi equation, we can see that changes in effective parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  can result from dynamical effects such as accelerated vibrational decay, rather than from potential energy changes.







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## •Application 3

Shining light on the microscopic resonant mechanism responsible for cavity-mediated chemical reactivity



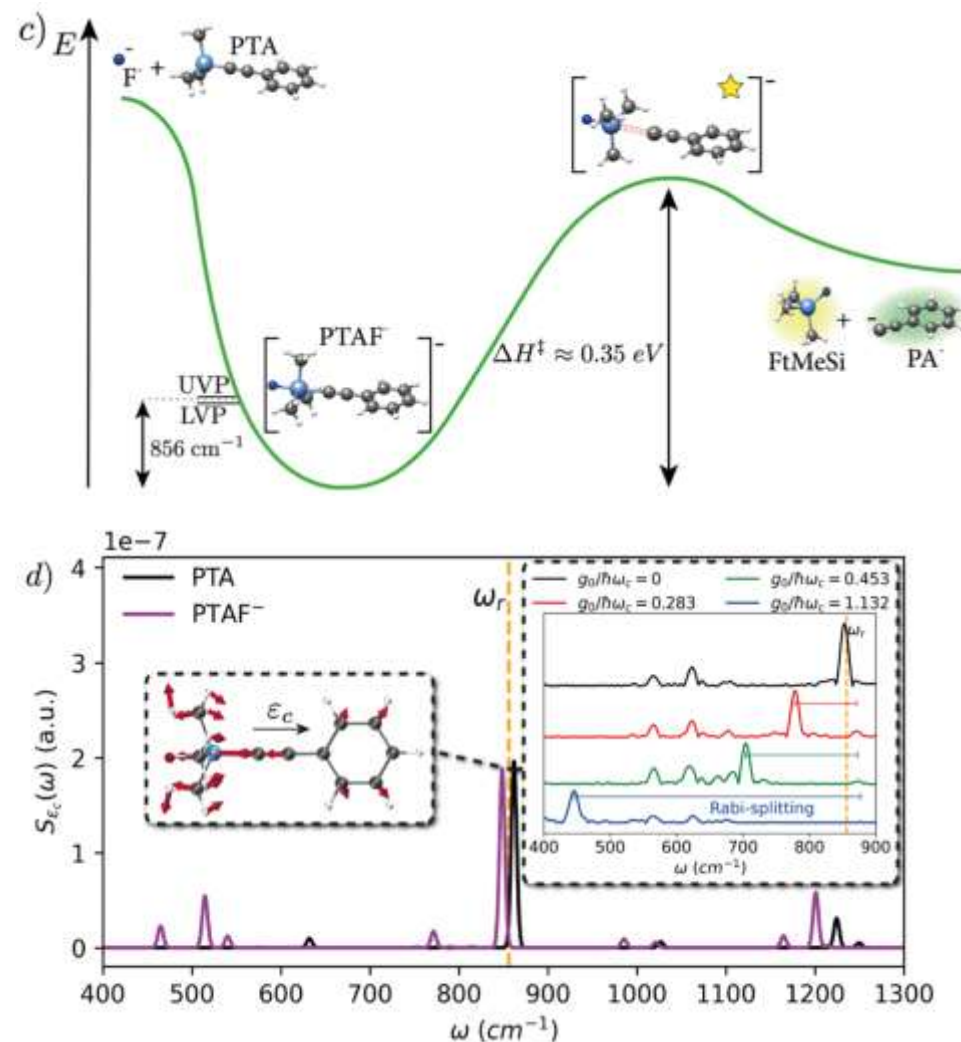
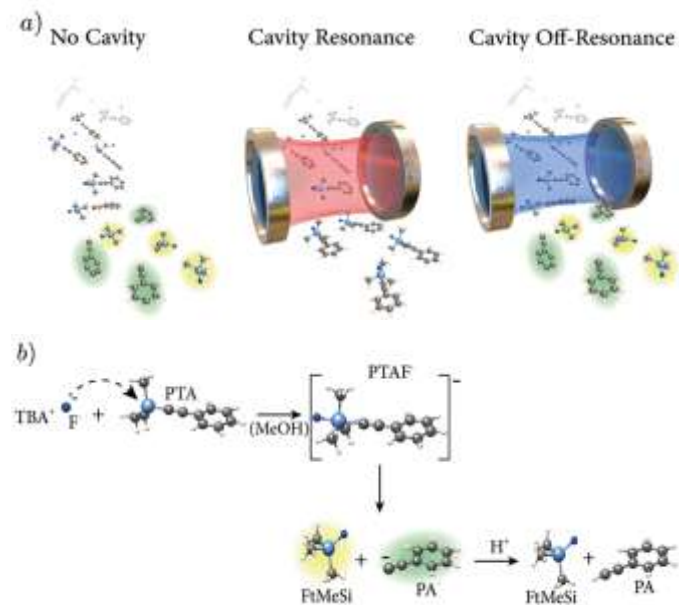
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# Shining light on the microscopic resonant mechanism responsible for cavity-mediated chemical reactivity

Received: 31 May 2022

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Prineha Narang<sup>6,10</sup> & Angel Rubio<sup>1,2,5</sup>

Accepted: 28 November 2022



(a): Strong coupling can selectively inhibit a chemical reaction

(b): Illustration of the reaction mechanism for the deprotection of PTA.

(c): Energy of the reaction in free space.

(d): Vibrational absorption spectrum of PTA and PTAF<sup>-</sup>.

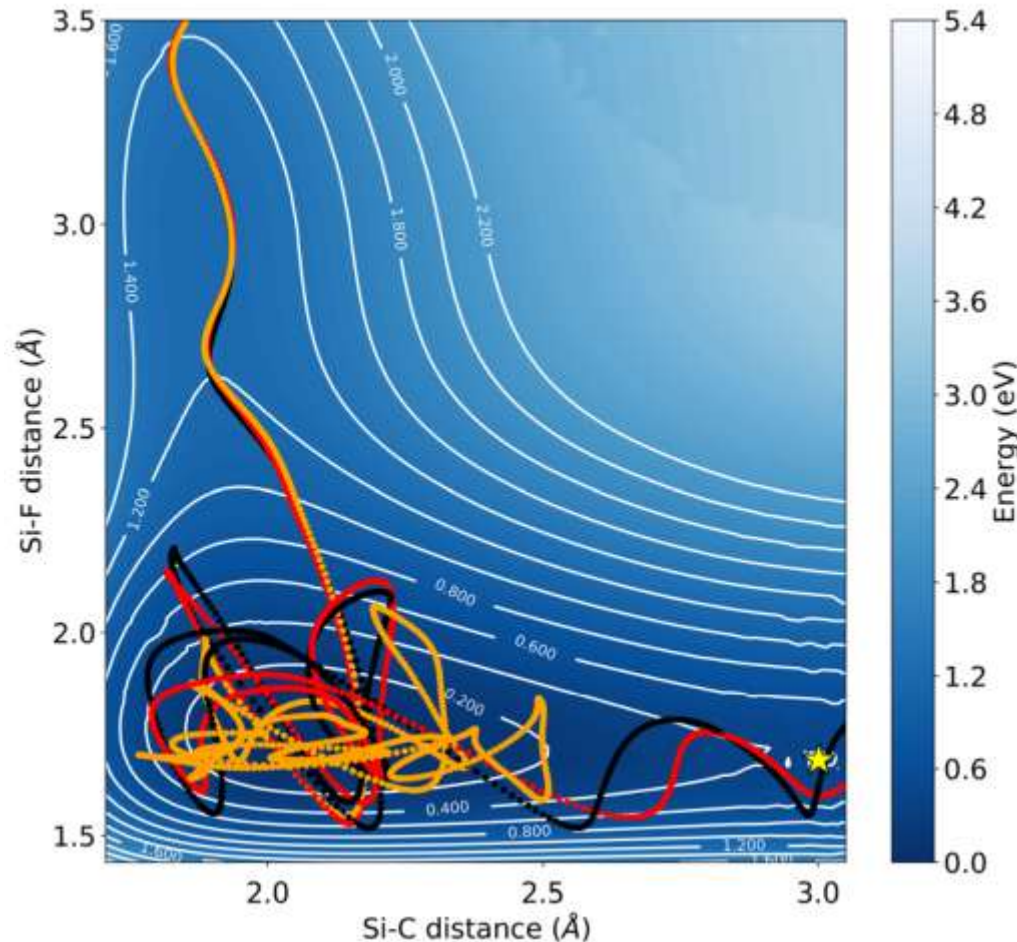


Similar to the first article, we get:

$$\hat{H} = \hat{H}_{\text{Matter}} + \hbar\omega_c(\hat{a}^\dagger\hat{a} + \frac{1}{2}) + \sqrt{\frac{\hbar\omega_c}{2\varepsilon_0 V_c}}(\boldsymbol{\varepsilon}_c \cdot \hat{\mathbf{R}})(\hat{a}^\dagger + \hat{a}) + \frac{1}{2\varepsilon_0 V_c}(\boldsymbol{\varepsilon}_c \cdot \hat{\mathbf{R}})^2$$

Light-matter coupling

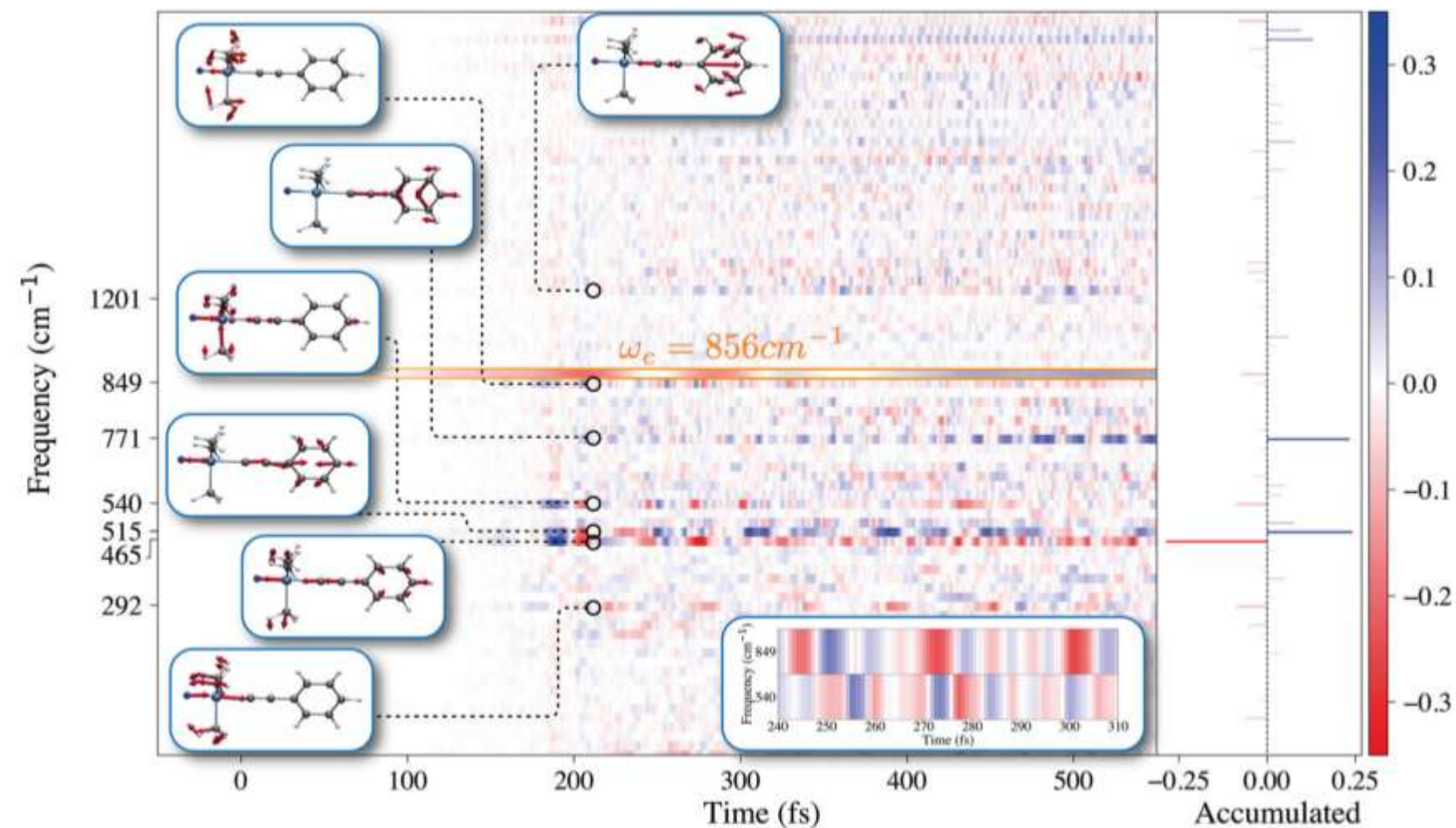
Dipole self-energy



Exemplary trajectory:

1. Outside the cavity  $g_0/\hbar\omega_c = 0$  (black)
2. on resonance  $g_0/\hbar\omega_c = 1.132$ ,  $\omega_c = 856 \text{ cm}^{-1}$  (orange)
3. off-resonant  $g_0/\hbar\omega_c = 1.132$ ,  $\omega_c = 1712 \text{ cm}^{-1}$  (red)

## Cavity-mediated redistribution of vibrational energy:



1. a coherent exchange of occupation between the coupled mode at  $849 \text{ cm}^{-1}$  and the vibration at  $540 \text{ cm}^{-1}$ . (Similar structures)
2. the strongest changes appear for the modes at 771, 515, and  $465 \text{ cm}^{-1}$ , all characterized by strong F-Si-C contributions and with minor or no methyl (甲基) contribution

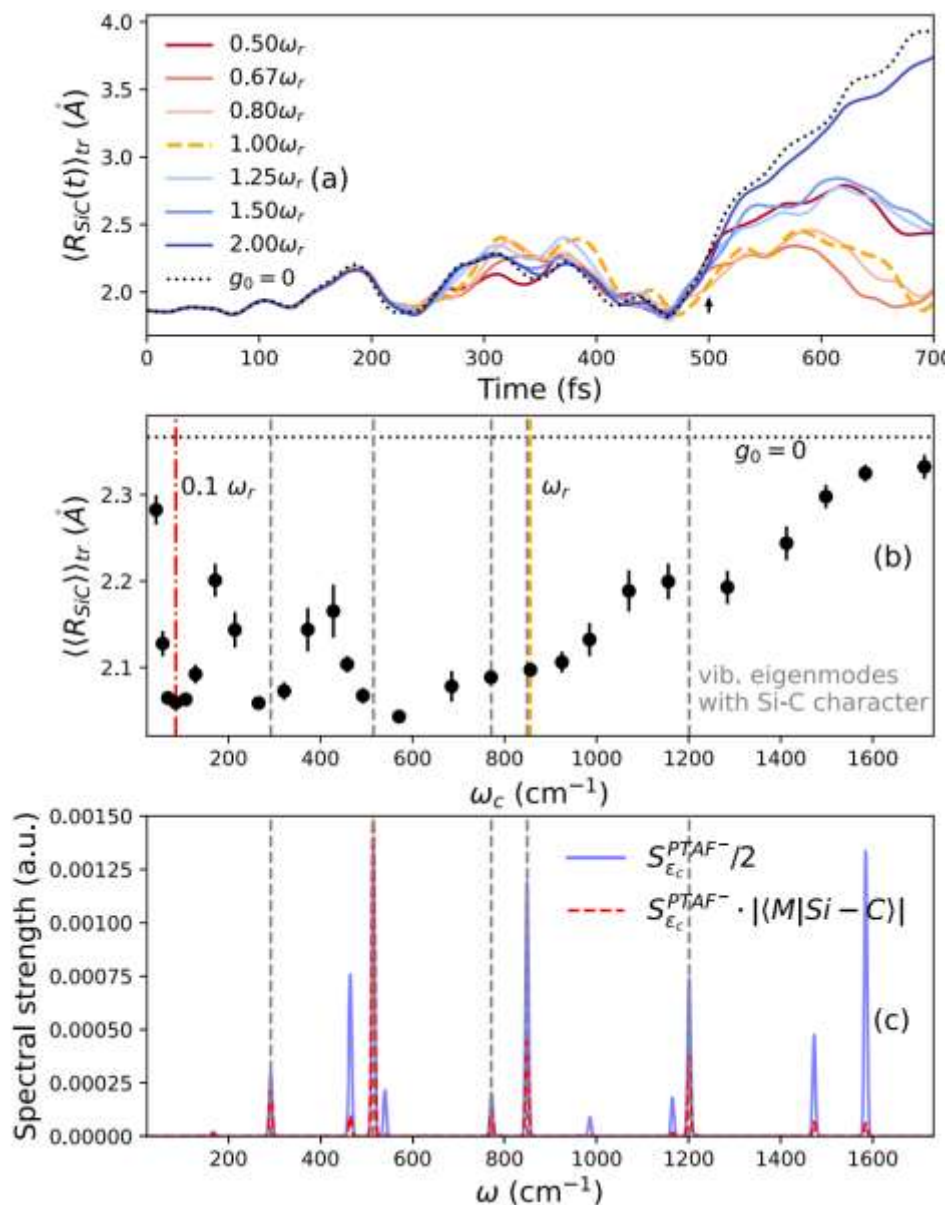
## Frequency dependency of cavity-mediated chemical inhibition

- (a) the time-averaged Si-C distance
- (b) the spectrum along the cavity polarization of PTAF<sup>-</sup>
- (c) the spectrum weighted with its Si-C contribution

Clear resonant features appear around 86 (red dashed-dotted vertical line), 290, 570, and 1200 cm<sup>-1</sup> in addition to a broad shoulder between 600 and 1000 cm<sup>-1</sup>.

86 cm<sup>-1</sup> : dynamical caging effect

290, 570, 1200 cm<sup>-1</sup> : redistribution between vibrational modes





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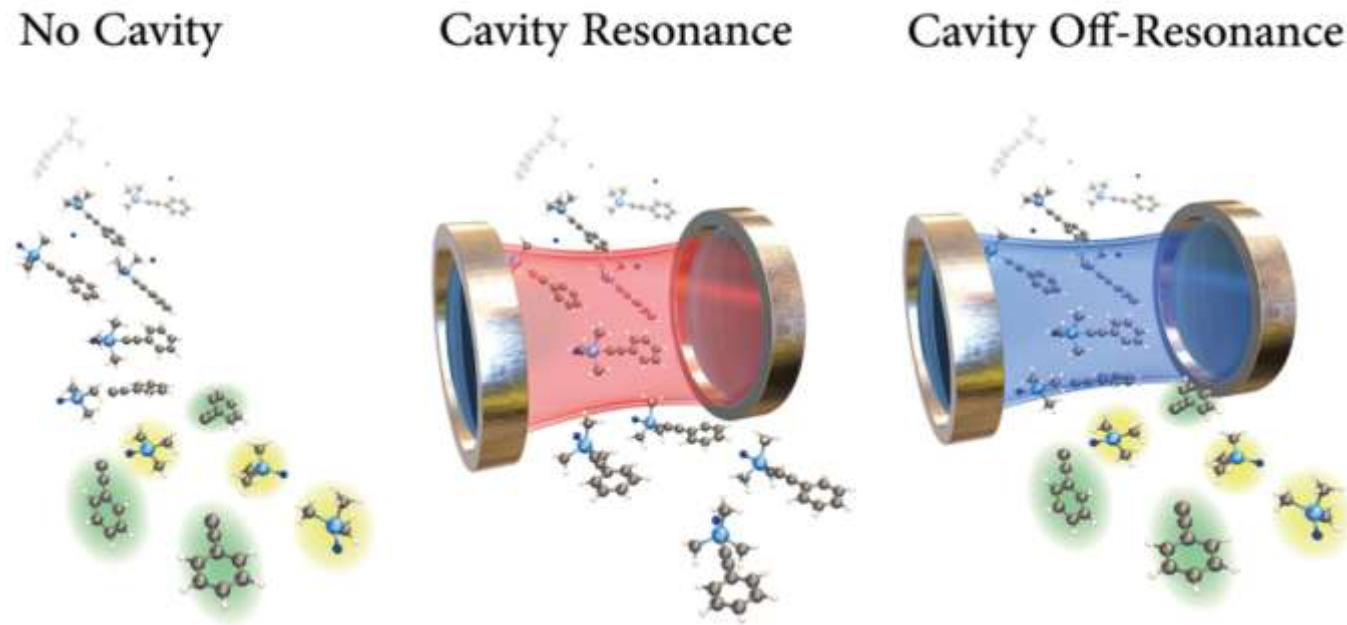
# Conclusion



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# Conclusion:

1. *Dynamic features* (i.e. dynamical caging effect & energy redistribution) play a much more pronounced role under strong light-matter coupling than commonly assumed by standard transition-state theory for ground-state chemical reactivity.
2. Limitations: All three articles focus only on *one-molecule reaction*, which results in considerably broader resonances than experimentally observed.





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# Thank you!