

Investigate New Reactivities Enabled by Polariton Photochemistry

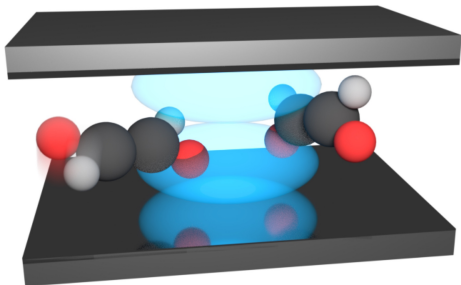
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Abstract

We perform quantum dynamics simulations to investigate new chemical reactivities enabled by cavity quantum electrodynamics. The quantum light-matter interactions between the molecule and the quantized radiation mode inside an optical cavity create a set of hybridized electronic-photonic states, so-called polaritons. The polaritonic states adapt the curvatures from both the ground and the excited electronic states, opening up new possibilities to control photochemical reactions by exploiting intrinsic quantum behaviors of light-matter interactions. With direct quantum dynamics simulations, we demonstrate that the selectivity of a model photo-isomerization reaction can be controlled by tuning the photon frequency of the cavity mode or the light-matter coupling strength, providing new ways to manipulate chemical reactions via light-matter interaction. We further investigate collective quantum effects enabled by coupling quantized radiation mode to multiple molecules. Our results suggest that in the resonance case, a photon is recycled among molecules to enable multiple excited state reactions, thus effectively functioning as a catalyst. In the non-resonance case, molecules emit and absorb virtual photons to initiate excited state reactions through fundamental quantum electrodynamics processes. These results from direct quantum dynamics simulations reveal basic principles of polariton photochemistry as well as promising reactivities that take advantage of intrinsic quantum behaviors of photons.



Introduction. Coupling molecules to a quantized radiation field inside an optical cavity creates a set of photon-matter hybrid states, so-called polaritons. These polariton states hybridize the curvatures from both the ground and the excited electronic states and have shown a great promise to alter the photochemistry of molecules.^{1–4} Unlike traditional photochemistry which uses light as an energy source, polariton chemistry uses quantized photons as active chemical catalysts to significantly change the shape of the potential energy surface in molecular systems, and thus, open up new possibilities to tune and control chemical reactions.^{5–8}

Theoretical investigations play a vital role in understanding the fundamental limits and the basic principle of new chemical reactivities achieved by polariton chemistry.^{7–10} It has been shown that the presence of the cavity can suppress¹¹ or enhance^{8,12} photoisomerizations,^{11–13} increase charge transfer rates by orders of magnitude,^{14–16} modify potential energy landscapes even with no photon in the cavity,^{8,11,17–19} enhance electron-phonon coupling strength,²⁰ accelerate singlet fission kinetics,²¹ remotely control chemical reactions,²² enhance excitation energy transfer processes,^{16,23,24} and create new polariton induced conical intersections.^{8,18,25,26}

All of these emerging features of the polariton chemistry demonstrate a great promise to control and tune chemical reactivities, as the cavity quantum electrodynamics (QED) processes take advantages of the quantum nature of the light and its interaction with the molecular system. Simulating the time-dependent polariton quantum dynamics of such hybrid matter-field systems is an essential task, as these polariton photochemical reactions often involve a complex dynamical interplay between the electronic, nuclear, and photonic degrees of freedom. Despite encouraging recent progress,^{9,17,19,27–30} the polariton non-adiabatic dynamics remains to be clarified, which are beyond the usual paradigm of photochemistry that does not include the quantum state of photon nor explicitly consider spontaneous emission, or quantum optics that does not study molecules.

In this letter, we perform direct quantum dynamics simulations to investigate the quantum transitions in a molecule-cavity hybrid system. We describe the quantized photon mode with its Fock states and explicitly treat the polaritonic non-adiabatic transitions through an accurate real-time path-integral approach. With a model photo-isomerization reaction, our numerical results suggest that it can be controlled by tuning the photon frequency of the cavity mode or the light-matter coupling strength, providing new ways to manipulate chemical reactions via light-matter interactions. Further, we demonstrate collective quantum effects enabled by coupling quantized radiation mode to multiple molecules. This study demonstrates the possibilities to exploit intrinsic quantum behaviors of photons to enable new photochemical reactivities.

Theory and Model. We use the generalized Jaynes-Cummings (JC) model^{10,17–19,26–30} to describe the molecule-cavity hybrid system. The total Hamiltonian is

$$\hat{H} = \hat{H}_e + \hat{H}_{sb} + \hat{H}_p + \hat{H}_{ep}, \quad (1)$$

where $\hat{H}_e + \hat{H}_{sb}$ is the molecular Hamiltonian, \hat{H}_p is the Hamiltonian of the quantized photon mode inside the cavity, and \hat{H}_{ep} describes the molecule-photon interaction.

The electronic Hamiltonian \hat{H}_e is described by a model system that undergoes isomerization reaction¹²

$$\hat{H}_e = \hat{T}_R + E_g(R)|g\rangle\langle g| + E_e(R)|e\rangle\langle e|. \quad (2)$$

Here, $|\alpha\rangle \in \{|g\rangle, |e\rangle\}$ represents the electronic ground or excited state, R represents the reaction coordinate, \hat{T}_R is the nuclear kinetic energy operator associated with R . The detailed expression of $E_\alpha(R)$ is provided in the Supporting Information, and the corresponding potentials are depicted in Fig. 1. To clearly demonstrate the quantum dynamics from the light-matter interaction, we choose to omit¹² the non-adiabatic coupling $\langle g|\nabla_R|e\rangle$ in our model system, thus effectively turning off the electronic non-adiabatic transitions between the $|g\rangle$ and $|e\rangle$ states. With this assumption, both $|g\rangle$ and $|e\rangle$ states effectively become diabatic states.

The reaction coordinate R is coupled to the other vibrational modes $\mathbf{r} = \{r_k\}$ in the molecule, modeled by a system-bath Hamiltonian \hat{H}_{sb} as follows

$$\hat{H}_{sb} = \hat{T}_{\mathbf{r}} + \sum_k \frac{1}{2} \omega_k^2 \left[r_k + \frac{c_k R}{\omega_k^2} \right]^2. \quad (3)$$

In the above equation, $\hat{T}_{\mathbf{r}}$ represents the kinetic energy of the phonon modes, r_k is the k_{th} phonon mode with the corresponding coupling constant c_k and frequency ω_k . The details of the bath parameters and the spectral density discretization procedure are provided in the Supporting Information.

The quantized radiation mode inside the optical cavity is described as

ity is described as

$$\hat{H}_p = \hbar\omega_c \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) = -\frac{\hbar^2}{2} \frac{d^2}{dq^2} + \frac{1}{2} \omega_c^2 q^2, \quad (4)$$

where \hat{a}^\dagger and \hat{a} are the photon creation and annihilation operators, respectively, and the photon displacement coordinate is $\hat{q} = \sqrt{\frac{\hbar}{2\omega_c}} (\hat{a} + \hat{a}^\dagger)$.

The light-matter interaction between the electronic and photonic DOF is expressed as

$$\hat{H}_{ep} = \hbar g_c (\hat{a} + \hat{a}^\dagger) (\hat{\sigma}^\dagger + \hat{\sigma}) = g_c \sqrt{2\hbar\omega_c} \hat{q} (|e\rangle\langle g| + |g\rangle\langle e|). \quad (5)$$

Here, $\hat{\sigma}^\dagger = |e\rangle\langle g|$ and $\hat{\sigma} = |g\rangle\langle e|$ are the molecular exciton creation and annihilation operators, respectively. The light-matter interaction strength is

$$\hbar g_c = \boldsymbol{\mu}_{eg} \cdot \hat{\mathbf{e}} \sqrt{\frac{\hbar\omega_c}{2V_c\epsilon_0}}, \quad (6)$$

where $\boldsymbol{\mu}_{eg}$ is the transition dipole moment vector between electronic states $|g\rangle$ and $|e\rangle$, $\hat{\mathbf{e}}$ represents the unit vector along the direction of the cavity polarization mode, V_c is the active volume of the cavity mode. In this study, we treat $\hbar g_c$ as a constant.

We further denote the polariton Hamiltonian \hat{H}_{pl} as follows

$$\hat{H}_{pl} = \hat{H} - \hat{T}_R - \hat{H}_{sb} = (\hat{H}_e - \hat{T}_R) + \hat{H}_p + \hat{H}_{ep}, \quad (7)$$

which includes the electronic part of the molecular Hamiltonian, the kinetic and potential energy of the quantized photon mode, as well as the interaction between the molecular and photonic DOFs. Representing the radiation field in its Fock state (the photon number state), and the molecule in its electronic states, the polariton Hamiltonian \hat{H}_{pl} is expressed as

$$\begin{aligned} \hat{H}_{pl} = & \sum_{\alpha n} \left(E_\alpha(R) + \left(n + \frac{1}{2} \right) \hbar\omega_c \right) |\alpha, n\rangle\langle \alpha, n| \\ & + \sum_n g_c (\hat{\sigma}^\dagger + \hat{\sigma}) (|n\rangle\langle n+1| + |n\rangle\langle n-1|), \end{aligned} \quad (8)$$

where $|\alpha, n\rangle = |\alpha\rangle \otimes |n\rangle$ is the electronic-photonic basis (or exciton-Fock basis), with $|\alpha\rangle \in \{|g\rangle, |e\rangle\}$, and $|n\rangle$ is the Fock state of the radiation mode with n photons in the cavity. The eigenstate of \hat{H}_{pl} is so-called the polariton state, which satisfies the following eigenequation

$$\hat{H}_{pl} |\Phi_\mu(R)\rangle = E_\mu(R) |\Phi_\mu(R)\rangle. \quad (9)$$

The polariton states $|\Phi_\mu(R)\rangle$ can be expressed as linear combinations of the exciton-Fock basis

$$|\Phi_\mu(R)\rangle = \sum_{\alpha, n} c_{\alpha n}^\mu(R) |\alpha, n\rangle. \quad (10)$$

The polariton energies and eigenvectors can be obtained by diagonalizing \hat{H}_{pl} 's matrix under the $\{|\alpha, n\rangle\}$ basis.

For the quantum dynamics simulation of a single

molecule coupled to the cavity, the initial excitation is chosen to be $|e, 0\rangle$ state, which is directly coupled to the $|g, 1\rangle$ state through the $\hat{a}\hat{\sigma}^\dagger$ and $\hat{a}^\dagger\hat{\sigma}$ terms in \hat{H}_{ep} (Eqn 5). Because we do not include the non-adiabatic coupling $\langle g|\nabla_R|e\rangle$ in the model system, $|e, 0\rangle$ does not directly couple to the $|g, 0\rangle$ state. Further, $|e, 2\rangle$ is coupled to the $|g, 1\rangle$ state through $\hat{a}\hat{\sigma}$ and $\hat{a}^\dagger\hat{\sigma}^\dagger$ terms, with far off-resonance energy from $|e, 0\rangle$ and $|g, 1\rangle$ state. Thus the polariton dynamics is confined within the $|e, 0\rangle$ and $|g, 1\rangle$ Hilbert subspace in this case. This allows one to analyze the Hamiltonian in the $|e, 0\rangle$ and $|g, 1\rangle$ subspace, although our numerical simulation does not make such assumption. The polariton Hamiltonian within this subspace is expressed as follows

$$\hat{H}_{\text{pl}} = \begin{bmatrix} E_g(R) + \hbar\omega_c & \hbar g_c \\ \hbar g_c & E_e(R) \end{bmatrix} + \frac{1}{2}\hbar\omega_c\mathbb{1}, \quad (11)$$

where $\mathbb{1}$ is the identity operator (in this subspace) and $\frac{1}{2}\hbar\omega_c$ is the zero point energy of the quantized photon mode inside the cavity. The light-matter coupling $\hbar g_c$ induces a Rabi splitting between two polariton states, given by

$$\hbar\Omega_c = \sqrt{4\hbar^2 g_c^2 + [E_e(R) - E_g(R) - \hbar\omega_c]^2}. \quad (12)$$

Under the *resonance* condition where $E_e(R) - E_g(R) = \hbar\omega_c$, the Rabi splitting becomes $\hbar\Omega_c = 2\hbar g_c$.

For the case of many molecules coupled to a common quantized radiation mode, the total Hamiltonian for the molecules-cavity hybrid system is given by

$$\hat{H} = \sum_{\nu} \hat{H}_e(R_{\nu}) + \hat{H}_{\text{sb}}(R_{\nu}, \mathbf{r}_{\nu}) + \hat{H}_p(\hat{q}) + \sum_{\nu} \hat{H}_{\text{ep}}(\sigma_{\nu}^\dagger, \sigma_{\nu}, \hat{q}), \quad (13)$$

where $\hat{H}_e(R_{\nu}) + \hat{H}_{\text{sb}}(R_{\nu}, \mathbf{r}_{\nu})$ is the ν_{th} molecule's Hamiltonian (Eqn.2), \hat{H}_p is the Hamiltonian of the quantized photon mode (Eqn.4), and $\hat{H}_{\text{ep}}(\sigma_{\nu}^\dagger, \sigma_{\nu}, \hat{q})$ describes the interaction between the photon mode \hat{q} and the ν_{th} molecule (Eqn.5). This model can be viewed as a generalization of the Tavis-Cummings model^{10,31,32} in quantum optics. To clearly demonstrates the essential feature of the collective behavior, we consider the case of two molecules coupled to one quantized radiation mode in this work. The above Hamiltonian is evaluated in the electronic-photonic basis $|\alpha, \gamma, n\rangle$, where $|\alpha\rangle$ and $|\gamma\rangle$ denote the electronic state of the first and second molecule, respectively, and $|n\rangle$ denotes the Fock state of the quantized mode inside the cavity.

In this study, we do not include the decay mechanism that accounts for cavity loss. The decay rate, $\hbar\Gamma_c$ is related to the cavity finesse. The strong coupling regime is usually referred as $\hbar\Omega_c > \hbar\Gamma_c$ (more generally, it refers to a Rabi frequency higher than all decay rates of polariton). While the typical cavity photon lifetime in a cavity is around 100 fs,³³⁻³⁵ recent experimental setup has indicated polariton lifetime of 100 ps³⁶⁻³⁸ in a high quality cavity, which far exceeds the typical nuclear relaxation time presented in this studies. In addition,

during the polariton photochemistry events, there will be multiple inter-conversions between the electronic excitation in molecules and photonic excitation in the cavity. Once the excitation is localized on the molecule, it is robust to the photonic loss.²⁹ Further, for the polariton quantum dynamics presented here, the wavepacket transiently travels on the photon dressed state to alter the course of chemical reactions. The transient presence of the photon inside the cavity can also significantly reduce the cavity loss. The influence of the cavity loss on polariton quantum dynamics will subject to future investigations, although we do not expect a major impact on the isomerization reaction reactions.²⁹

To simulate the polariton quantum dynamics, We apply Partial Linearized Density Matrix Dynamics (PLDM) path-integral approach.^{39,40} PLDM is an approximate real-time path-integral approach that has been successfully applied to investigate various non-adiabatic processes.⁴¹⁻⁴⁵ A brief summary of this approach, together with the numerical details of the simulations are provided in the Supporting Information.

In this letter, we compute the time-dependent reduced density matrix of the light-matter hybrid system

$$\rho_{ij}(t) = \text{Tr}_{\text{R},\mathbf{r}} \left[\hat{\rho}(0) e^{i\hat{H}t/\hbar} |i\rangle \langle j| e^{-i\hat{H}t/\hbar} \right]. \quad (14)$$

In the above expression, \hat{H} is the total Hamiltonian (Eqn. 1), and $\text{Tr}_{\text{R},\mathbf{r}}$ represents the trace over the nuclear DOF, including the nuclear coordinate R and the bath coordinate \mathbf{r} . In addition, $\{|i\rangle, |j\rangle\} \in \{|\alpha, n\rangle\}$ for the single molecule case, and in the two molecule case $\{|i\rangle, |j\rangle\} \in \{|\alpha, \gamma, n\rangle\}$. We further compute the time-dependent population of the cis isomer state, defined as $|C\rangle\langle C| \equiv 1 - h(R - R_0)$, and the trans states $|T\rangle\langle T| \equiv h(R - R_0)$, correspondingly. Here, $h(R - R_0)$ is the Heaviside function, and $R_0 = -0.045$ a.u. that corresponds to both the maximum of $E_g(R)$ and the minimum of $E_e(R)$ is chosen to be the dividing surface of the reaction.¹² The time-dependent population of the I isomer (C or T) is computed as

$$P_I(t) = \text{Tr}_{\text{R},\mathbf{r}} \left[\hat{\rho}(0) e^{i\hat{H}t/\hbar} |I\rangle \langle I| e^{-i\hat{H}t/\hbar} \right]. \quad (15)$$

The yield of the isomer I is defined as

$$Y_I = \lim_{t \rightarrow t_p} P_I(t), \quad (16)$$

where t_p is the plateau time of the population $P_I(t)$. For the model system investigated in this study, $t_p \approx 5 \sim 10$ ps. The details of the numerical simulations are provided in the Supporting Information.

Results and Discussions. Fig. 1 presents the model system and demonstrates the basic principle of polariton photochemistry. Fig. 1a depicts the potential of \hat{H}_{pl} (Eqn. 8) in the electronic-photonic basis $\{|\alpha, n\rangle\}$, where $|g, 0\rangle$ (black) and $|e, 0\rangle$ (blue) represent the ground and excited states of the molecule with zero photon (vacuum state) in the cavity, $|g, 1\rangle$ (red) repre-

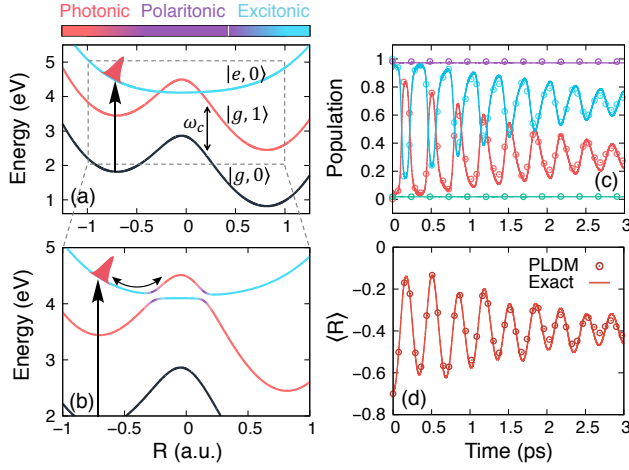


Figure 1: The polariton Hamiltonian \hat{H}_{pl} in (a) the electronic-photonic basis $\{|\alpha, n\rangle\}$ and (b) the polariton states $\{|\Phi_\mu(R)\rangle\}$, with the color coding (top) that represents the excitation character. Upon photoexcitation (black arrow), the wavepacket (red) is placed on the $|e, 0\rangle$ state. (c) Polariton quantum dynamics governed by $\hat{H} - \hat{H}_{\text{sb}}$ at $T = 0\text{K}$. The populations of the $|e, 0\rangle$ (red) and $|g, 1\rangle$ (blue), as well as the adiabatic polariton populations $|+\rangle$ (magenta) and $|-\rangle$ (green) are obtained from the PLDM approach (open circles) and the numerically exact calculation (solid line). (d) Time-dependent expectation value of the nuclear reaction coordinate.

sents a photon dressed state, where molecule is in the ground electronic state and the cavity contains one photon. Thus, $|g, 1\rangle$ adapts the potential of the molecular ground state, with a vertical energy shift with the photon frequency, which is $\hbar\omega_c = 2.18\text{ eV}$ in this particular example.

Fig. 1b depicts the light-matter interaction induced hybridization among the $|g, 1\rangle$ and $|e, 0\rangle$ state. Because of the transition dipole between the molecular ground $|g\rangle$ and excited $|e\rangle$ states, the $|g, 1\rangle$ and $|e, 0\rangle$ states are coupled to each other through the light-matter interaction Hamiltonian \hat{H}_{ep} (Eqn. 5), and hybridized to form the upper polariton state $|+\rangle$ and the lower polariton state $|-\rangle$, which are the eigenstates of \hat{H}_{pl} (Eqn. 8). The coupling strength (Eqn. 6) between $|g, 1\rangle$ and $|e, 0\rangle$ used here is assumed to be a constant $\hbar g_c = 0.136\text{ eV}$, which creates a large Rabi splitting between two polariton surfaces. The curves are color coded with the scheme (on top of Fig. 1a) that represents the character of excitation based on the number of photons inside the cavity, $\langle \hat{a}^\dagger \hat{a} \rangle = \langle \Phi_\mu(R) | \hat{a}^\dagger \hat{a} | \Phi_\mu(R) \rangle$, where $|\Phi_\mu(R)\rangle \in \{|+\rangle, |-\rangle\}$ (see Eqn. 10). When the excitation is purely localized on the molecule with no photon inside the cavity, $\langle \hat{a}^\dagger \hat{a} \rangle = 0$, and the character of the excitation is purely excitonic (blue). Conversely, when the excitation is purely localized on the radiation mode inside the cavity (*i.e.*, molecule is in the ground electronic state and the cavity contains 1 photon), $\langle \hat{a}^\dagger \hat{a} \rangle = 1$, and the character of excitation is purely photonic (red). When the energies of $|g, 1\rangle$ and $|e, 0\rangle$ are in resonance

($E_e(R) - E_g(R) \approx \hbar\omega_c$), the light-matter interaction (\hat{H}_{ep} in Eqn. 5) causes a strong mixing of the two states and a splitting (avoided crossings) between them. The resulting polariton states, which are hybrid excitation of both the molecule and the cavity (magenta) adapts a value of average photon $\langle \hat{a}^\dagger \hat{a} \rangle$ between 0 and 1. Thus, depending on the nuclear position R , the character of the excitation for the hybrid system can be excitonic (blue), photonic (red) or polaritonic (magenta).

Fig. 1c presents the polariton quantum dynamics obtained from numerically exact split-operator method (solid lines) and the PLDM approach (open circles). Here, we consider the dynamics governed by $\hat{H} - \hat{H}_{\text{sb}}$ at $T = 0\text{ K}$, where the numerically exact results can be easily obtained. The initial condition is modeled as the Franck-Condon excitation from $|g, 0\rangle$ to $|e, 0\rangle$ state, indicated by the vertical black arrow in panels (a) and (b). The polariton wavepacket moves adiabatically (due to the large Rabi-splitting) on the upper polariton surface, as depicted by the curved arrow in panel (b). This is reflected in the time-dependent polariton populations, where the upper polariton state $|+\rangle$ (magenta) remain a unitary population, indicating no non-adiabatic transitions between the upper and the lower polariton state. On the other hand, the rapid population oscillations of the $|g, 1\rangle$ (red) and $|e, 0\rangle$ (blue) states reflect a change of the character of the polariton states, from excitonic to photonic, then back and forth. These processes occur by exchanging excitations between the molecule and the quantized photon mode inside the cavity, through the spontaneous emission (that the molecule emits one photon into the cavity) and absorption process (that the molecule absorbs one photon from the cavity and gets electronically excited). The population of $|g, 1\rangle$ (red curve in (c)) also indicates the time-dependent expectation number of photon inside the cavity, which clearly demonstrates the alternating emission and absorption processes. It is worth noting that spontaneous emission is usually induced due to the vacuum fluctuations from other non-cavity modes. Here, it is induced due to the molecular vibration that changes the character of the polariton wavefunction. Further, the inter-conversions between the electronic excitation in molecule and photonic excitation in the cavity help to protect against the cavity loss, because the $|e, 0\rangle$ state contains 0 photon and is free from the photon loss.²⁹ This gives rise a much longer polariton lifetime compare to the typical lifetime of a photon, as been observed in both experiments¹ and theoretical simulation.²⁹

Fig. 1d presents the time-dependent expectation value of the nuclear position $\langle R \rangle$ obtained from the numerically exact result (solid line) and PLDM (open circles). The adiabatic motion of the wavepacket on the upper polariton surface results in an oscillatory behavior of $\langle R \rangle$. This motion of R also changes the character of the polariton state, causing the oscillatory populations in panel (c). In Fig.1c-d, PLDM provides nearly identical results compared to the numerically exact approach, demonstrating the accuracy of using such approach to

simulate the polariton quantum dynamics. We will use it to explore new chemical reactivities enabled by quantum light-matter interactions in the rest of this study.

Fig. 2 demonstrates the control of chemical reactivities by changing the frequency of the photon $\hbar\omega_c$ inside the cavity, with a strong light-matter coupling strength $\hbar g_c = 0.136$ eV, such that $\beta\hbar\Omega_c \gg 1$, where $\beta = 1/k_B T$ corresponds to 300 K in this study. The initial excitation is chosen as $|e, 0\rangle$. The schematic illustration of the dynamics for an isolated molecular system is presented in Fig. 2(a), whereas the schematics of the polariton dynamics for the molecule-cavity hybrid system at two different photon frequencies are presented in Fig. 2(b)-(c). The yield (Eqn. 16) of the cis and trans isomer as a function of the photon frequency $\hbar\omega_c$ are presented in Fig. 2(d). The corresponding time-dependent polariton population dynamics, as well the trans state populations are provided in the supporting information.

In Fig. 2a, the photoexcited initial wavepacket in the bare molecular system can freely explore the relatively flat $|e, 0\rangle$ surface along the reaction coordinate R . Due to the presence of other vibrational modes (described by \hat{H}_{sb} in Eqn. 3) serving as the dissipative bath, the wavepacket eventually relaxes. Through the non-radiative decay channels (*i.e.*, non-adiabatic coupling $\langle e|\nabla_R|g\rangle$ which is not modeled in our study) between the $|e\rangle$ and $|g\rangle$ state, the system relaxes back to the ground electronic state $|g\rangle$, producing a nearly equal mixture of cis and trans isomer.

In Fig. 2b, the molecule is coupled with the quantized photon mode with a frequency of $\hbar\omega_c = 2.18$ eV, causing a hybridization between the $|e, 0\rangle$ and $|g, 1\rangle$ states, and creating a sizable barrier which is higher than the Franck-Condon initial excitation position. As a result, the wavepacket is confined within this cavity-induced minimum on the upper polariton surface. Further, the large light-matter coupling strength $\hbar g_c = 0.136$ eV suppresses non-adiabatic transitions between polaritonic states. The system eventually decays to the ground state $|g, 0\rangle$ through both the radiative and non-radiative channels, leading to a nearly 100% yield of the cis isomer. This provides a robust control to suppress photochemical isomerization (from cis to the trans configuration),^{8,11} as has been recently discovered experimentally.¹

In Fig. 2c, the molecule is coupled to the photon mode which has a larger frequency $\hbar\omega_c = 3.13$ eV, and the $|g, 1\rangle$ state is now above the position of the Franck-Condon excitation. The wavepacket thus travels adiabatically on the lower polariton surface and relaxes to the minimum at $R \approx 0.75$ a.u. The system eventually decays to the ground state $|g, 0\rangle$ through radiative or non-radiative decay channels, yielding a nearly 100% trans isomer.¹²

Fig. 2d presents the yield as a function of the photon frequency. The yield at two specific $\hbar\omega_c$ are circled and labeled corresponding to the schematics presented in Fig. 2b-c. Between these two regimes, the initial excitation in the $|e, 0\rangle$ state corresponds to a linear com-

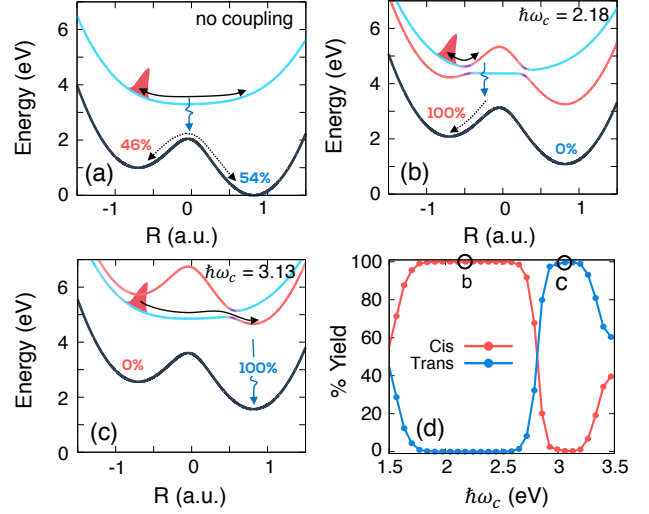


Figure 2: Control of the reactivities by changing the photon frequency $\hbar\omega_c$. Schematic illustrations of the polariton quantum dynamics are presented for (a) the bare molecular system and (b)-(c) the molecule-cavity hybrid system at various photon frequencies. (d) Quantum yield of the cis and trans isomer as a function of $\hbar\omega_c$.

bination of $|+\rangle$ and $|-\rangle$ states. The wavepacket on each of the polariton surface moves adiabatically, resulting in both the cis conformer (for the upper polariton component) and the trans conformer (for the lower polariton component). Increasing the photon frequency $\omega_c > 3.5$ eV drives the $|e, 0\rangle$ state off-resonance with the $|g, 1\rangle$ state, and $|+\rangle$ becomes nearly identical to $|e, 0\rangle$. As a result, the dynamics remains almost identical to bare molecular case, leading to the nearly equal mixture of the cis and trans isomers.

We emphasize that the above control scheme utilizes the presence of dressed levels from quantum light-matter interactions and the hybridization of different potential energy curvatures from both the ground and the excited states. In that sense, it is akin to the recently proposed Stark control⁴⁶⁻⁴⁹ that uses classical laser-field. Just like the Stark control, the scheme presented here is robust to decoherence because it does not rely on the fragile coherence properties of superposition states.^{46,49} The cavity QED process relies on the transient presence of the polariton states to alter the course of chemical reactions. On the other hand, the difference between the cavity QED scheme and the classical Stark control is that, the former operates at the low photon limit ($0 \sim 1$ photon inside the cavity), whereas the latter relies on a large number of photons.⁷ Finally, when the polariton wavepacket reaches to the desired nuclear region of the product state, the radiative and non-radiative decay channels enforce the final selection of various isomers. Thus, the scheme presented here is at least robust to the radiative decay channel for the model system studied in this work.

The polariton quantum dynamics can also be con-

trolled by the light-matter coupling strength $\hbar g_c$, which dictates the non-adiabaticity of the polariton quantum dynamics. As we have already seen in Fig. 1-2, the “strong coupling regime” where the large g_c causes a sizable Rabi splitting turns off non-adiabatic transitions between polariton states, and confines the wavepacket in one polariton surface.^{1,2,8,11,12,50} The intermediate coupling, which is weak enough to allow non-adiabatic transitions among polariton states, but still strong enough to mix the $|e, 0\rangle$ and $|g, 1\rangle$ states, can potentially offer new reactivities compared to the strong coupling regime. Here, we explore such possibility by changing $\hbar g_c$. This coupling strength (see Eqn. 6) can be experimentally tuned by changing (i) the effective quantization volume V_c (by changing the lateral dimensions of the mirrors in a planar Fabry-Pérot cavity^{38,51}), (ii) the permittivity ϵ_0 (by changing the types of the hosting polymer¹ inside the cavity), or (iii) the relative alignment between the molecular transition dipole moment and radiation mode which has been recently accomplished in the plasmonic nano-cavity at the single-molecule level.⁵⁰

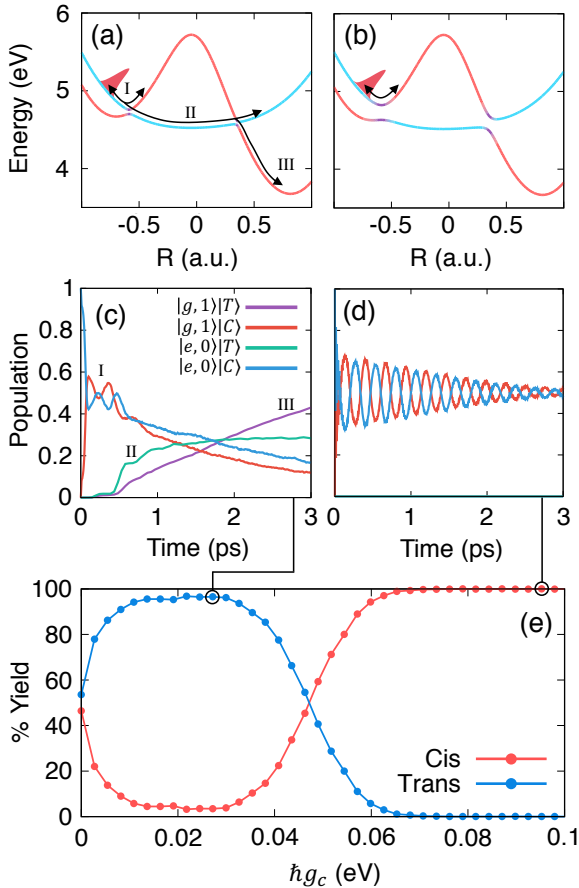


Figure 3: Control of the reactivities by changing the light-matter coupling strength $\hbar g_c$, with a fixed photon frequency $\omega_c = 2.45$ eV. Polariton dynamics at (a) $\hbar g_c = 0.0271$ eV and at (b) $\hbar g_c = 0.0957$ eV, with the corresponding population dynamics provided in (c) and (d). (e) Quantum yield of the cis and trans isomers as a function of $\hbar g_c$.

Fig. 3a-b presents the schematics of the polariton quantum dynamics with two different light-matter coupling strength at (a) $\hbar g_c = 0.0271$ eV, and (b) $\hbar g_c = 0.0957$ eV, respectively, with the photon frequency $\hbar\omega_c = 2.45$ eV. The polariton dynamics in Fig. 3b is adiabatic due to the large coupling strength that suppresses non-adiabatic transitions among polariton states, such that the wavepacket is confined on the cis side of the dividing surface. Fig. 3a presents the polariton dynamics with an intermediate coupling strength, such that $\beta\hbar\Omega_c \approx 1$. Under this condition, the wavepacket branches to the trans configurations of the $|g, 1\rangle$ and $|e, 0\rangle$ states through non-adiabatic transitions. As a result, the molecule can access the global potential minimum of the hybrid system on the trans side of the $|g, 1\rangle$ surface, leading to nearly 100% trans isomer for the product. This completely alters the selectivity of the product, compared to the large coupling strength scenario presented in panel (b), even though the same photon frequency is used.

Fig. 3c-d presents the population dynamics of the conformation specific states $|e, 0\rangle|C\rangle$, $|g, 1\rangle|C\rangle$, $|e, 0\rangle|T\rangle$, and $|g, 1\rangle|T\rangle$, corresponding to the schematics presented in Fig. 3a-b. The oscillations between $|e, 0\rangle|C\rangle$ and $|g, 1\rangle|C\rangle$ states in Fig. 3d reflect the adiabatic dynamics on the upper polariton surface $|+\rangle$, similar to those presented in Fig. 1. Meanwhile, $|e, 0\rangle|T\rangle$ and $|g, 1\rangle|T\rangle$ states remain unpopulated, as the wavepacket is adiabatically confined on the cis conformer side of the upper polariton surface. On the other hand, Fig. 3c shows several interesting features of the population dynamics, which can be characterized into three stages. In stage I, the wavepacket moves to the light-induced avoided crossing at $R \approx 0.5$ a.u., causing the change of the character of the polariton wavefunction, and the oscillations between $|e, 0\rangle|C\rangle$ and $|g, 1\rangle|C\rangle$ in a short period of time (≈ 300 fs). This is followed by a sharp population increase of $|e, 0\rangle|T\rangle$ in stage II, as the wavepacket undergoes non-adiabatic transitions between the upper and lower polariton surfaces and across the dividing surface ($R_0 = -0.045$ a.u.) of the isomerization reaction on the $|e, 0\rangle$ state. Finally, in stage III, a steady increasing $|g, 1\rangle|T\rangle$ population indicates the non-adiabatic transitions between the upper and lower polariton surfaces at $R \sim 0.4$ a.u., leading to the trans isomer. These three stages of the population dynamics are labeled in panel (a) and (c). During this process, the hybrid matter-field system experiences a rich dynamical interplay among the electronic, nuclear, and photonic DOFs. Its excitation character starts with a molecular exciton, then changes to polariton and back to exciton (during I to II), and changes again to polariton and finally to an almost photonic excitation (during II to III). Thus, inside such molecule-cavity hybrid system, the motion of the nuclei significantly impacts the quantum state of the photon as well as the nature of the excitation. On the other hand, the time-dependent quantum mechanical state of the photon also exerts different forces on nuclear DOF (by changing the curvature of the excited states), influ-

encing its motion and opening up new possibilities to alter the course of chemical reactions.

Fig. 3e presents the yield of the isomerization reaction by changing the light-matter coupling strength $\hbar g_c$. At a nearly zero coupling strength, the hybrid molecule-cavity system reduces to the uncoupled case, resulting in a nearly equal amount of cis and trans isomers. A small increase of $\hbar g_c$ (≈ 0.005 eV) significantly enhances the selectivity towards to the trans isomer, as it enables the non-adiabatic branching channels among different polariton surfaces. The trans yield reaches to nearly 100% in the range of $\hbar g_c \in [0.01, 0.03]$ eV. The polariton quantum dynamics in this region corresponds to the schematic illustration in Fig 3a. Further increasing $\hbar g_c$ leads to the adiabatic polariton quantum dynamics and a switching of the selectivity for the isomerization reaction. For $\hbar g_c > 0.06$ eV, the yield of the cis isomer reaches nearly 100%, corresponding to the adiabatic dynamics presented in Fig 3b.

Fig. 4 presents the polariton dynamics of the hybrid system that contains two molecules inside an optical cavity. Fig. 4a presents the lower polariton surface, with the black dots indicates one of the two equivalent minimum energy paths. Both molecules are coupled to a common quantized radiation mode (through \hat{H} described in Eqn. 13). The photon frequency in this calculation is set to be $\omega_c = 2.585$ eV and it is in resonance with the excitation energy of both molecules at the position of their Franck-Condon points, such that $E_{ge0} - E_{gg0} = E_{eg0} - E_{gg0} \approx \hbar\omega_c$. The light-matter coupling strength is set to be $\hbar g_c = 0.136$ eV, causing a large Rabi splitting between different polariton states. The initial photoexcitation is prepared on the lower polariton state of the molecule-cavity system by a vertical photo-excitation from the ground state $|g, g, 0\rangle$ at the cis nuclear configurations for both molecules.

Fig. 4b presents the reaction path specific expectation value of the reaction coordinate (black solid line) on the lower polariton surface. It is classified as molecule 1 isomerizing prior to molecule 2 (upper off-diagonal), or molecule 2 isomerizing prior to molecule 1 (lower off-diagonal). They are equivalent paths for this bi-molecular reaction and equally likely appear in our simulation, as one expected due to the symmetry of the Hamiltonian.

Fig. 4c presents the polariton population dynamics corresponding to the upper off-diagonal path in Fig. 4b, *i.e.*, molecule 1 isomerizes prior to molecule 2. The wavepacket propagates adiabatically on the lower polariton surface, following the barrier-less reaction path and relaxes to the minimum that corresponds to the trans configuration of both molecules. The initial polaritonic state corresponds to a superposition of excitation on both molecules and the radiation mode, resulting a non-zero number of photon inside the cavity. The superposition of the excitation quickly collapses onto molecule 1 during the first 200 fs, as indicated by the sharp increase in the $|e, g, 0\rangle$ population. The excited

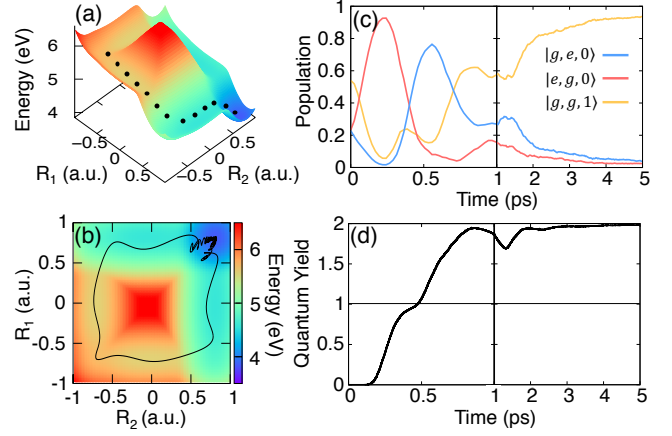


Figure 4: Polariton dynamics of two molecules coupled to a resonant radiation mode. (a) Adiabatic polariton surface, with black dots indicating one of two equivalent minimum energy paths. (b) Expectation value of the nuclear position on adiabatic polariton potential. (c) The population dynamics corresponding to the upper reaction paths. (d) Time- dependent quantum yield of the trans isomer.

molecule 1 undergoes cis to trans isomerization, leading to a quantum yield of nearly 100% for the trans isomer at $t = 0.4 - 0.5$ ps. Following the isomerization reaction of molecule 1, the hybrid molecules-cavity system releases a photon back to the cavity, indicated by an increase in $|g, g, 1\rangle$ population at $t = 0.4$ ps. The photon is immediately absorbed by molecule 2 (which is still in the cis configuration at that moment), causing the increase in the $|g, e, 0\rangle$ population at $t = 0.6$ ps. Following this excitation, molecule 2 undergoes cis to trans isomerization and then releases the photon back to the cavity, leading to the increasing $|g, g, 1\rangle$ population at a longer time.

Fig. 4d presents the time-dependent quantum yield of the trans isomer in this hybrid system. By coupling to the common quantized radiation mode, two molecules undergoes chemical reactions with one photon inside the optical cavity, leading to a quantum yield of nearly 200%. This process overcomes the Stark-Einstein limit^{8,12} which requires one photon per molecular photo-reaction. With the presence of the cavity, the photon is recycled among multiple molecules which enables excited state reactions, thus enabling the hybrid system to go beyond the Stark-Einstein limits through a novel collective excitation.^{8,12} In that sense, quantized photon is used as a *catalyst* (participate the reaction without being consumed) in this case, as opposed to an energy source to excited the system in traditional photochemistry.

Fig. 5 presents the polariton dynamics with two molecules coupled to an *off-resonant* quantized radiation mode inside the optical cavity. Fig. 5a presents the PES of the $|e, g, 1\rangle$ state (red) and $|g, e, 1\rangle$ state (blue). In this example, the photon frequency is $\hbar\omega_c = 7.62$ eV

$\gg E_{ge0} - E_{gg0} = E_{eg0} - E_{gg0}$, such that the $|g, g, 1\rangle$ states (not shown in this figure) lies well above both the $|g, e, 0\rangle$ and the $|e, g, 0\rangle$ state. Further, the two molecules are not directly coupled to each other through the electronic interaction, *i.e.*, $\langle g, e, 0 | \hat{V} | e, g, 0 \rangle = 0$, where $\hat{V} = \sum_{\nu} \hat{H}_{ep}(\sigma_{\nu}^{\dagger}, \sigma_{\nu}, \hat{q})$ is the light-matter interaction Hamiltonian in Eqn. 13, with \hat{H}_{ep} defined in Eqn. 5. On the other hand, they are both strongly coupled to the $|g, g, 1\rangle$ state, with a strength of $\hbar g_c = 0.2714$ eV. Due to these off-resonance interactions, the $|g, e, 0\rangle$ and $|e, g, 0\rangle$ states start to mix with the $|g, g, 1\rangle$ component, allowing them to effectively interact with each other. This effective coupling can be understood from the following perturbative analysis, which is not assumed in our quantum dynamics simulations. The light-matter interaction generates the perturbed state $|g, e, 0'\rangle = |g, e, 0\rangle + \hbar g_c |g, g, 1\rangle / [E_{ge0} - E_{gg1}]$, and $|e, g, 0'\rangle$ state with a similar expression. Because of the presence of the $|g, g, 1\rangle$ component, an effective coupling between these two perturbed states is

$$\langle g, e, 0' | \hat{V} | e, g, 0' \rangle = \frac{\hbar^2 g_c^2}{E_{ge0} - E_{gg1}} + \frac{\hbar^2 g_c^2}{E_{eg0} - E_{gg1}} \quad (17)$$

$$+ \frac{\hbar^2 g_c^2 E_{gg1}}{(E_{eg0} - E_{gg1})(E_{ge0} - E_{gg1})}.$$

Fig. 5b presents the population dynamics (red and blue) as well as the time-dependent quantum yield (black). Here, the system is initially excited to the $|e, g, 0\rangle$ state. While population is transferred from the $|e, g, 0\rangle$ state (red) to the $|g, e, 0\rangle$ state (blue), the $|g, g, 1\rangle$ state (yellow) is only virtually populated (with no apparent population). Meanwhile, the quantum yield (black) reaches a value of 1.2, higher than the Stark-Einstein limit. This process is usually referred as the “super-exchange” mechanism in chemical kinetics, where the $|g, e, 0\rangle$ state is only virtually populated to facilitate the quantum transitions between the $|e, g, 0\rangle$ and $|g, e, 0\rangle$ states. During the reaction course, the system evolves on the $|e, g, 0\rangle$ surface (red), makes a non-adiabatic transition to the $|g, e, 0\rangle$ surface (blue) due to the effective coupling (Eqn. 17), and eventually relaxes at the middle of $|g, e, 0\rangle$ surface. Meanwhile, $|g, g, 1\rangle$ only acts as a virtual state to mediate the non-adiabatic transitions between the $|e, g, 0\rangle$ and $|g, e, 0\rangle$ states. This off-resonant case can significantly suppress the cavity loss which leaks the photon population to the other non-cavity modes, due to the nearly zero photon population during the polariton dynamics. Note that this mechanism is different than the “sequential” one presented in Fig. 4 where the population is sequentially transferred between molecular excitations and the photonic excitation. Similar sequential and super-exchange mechanisms have been recently discussed in the context of singlet fission,^{52,53} where the charge transfer states are used as the intermediate or virtual state to connect the singlet and triplet-triplet pair states.

Fig. 5c presents the nuclear position distribution at

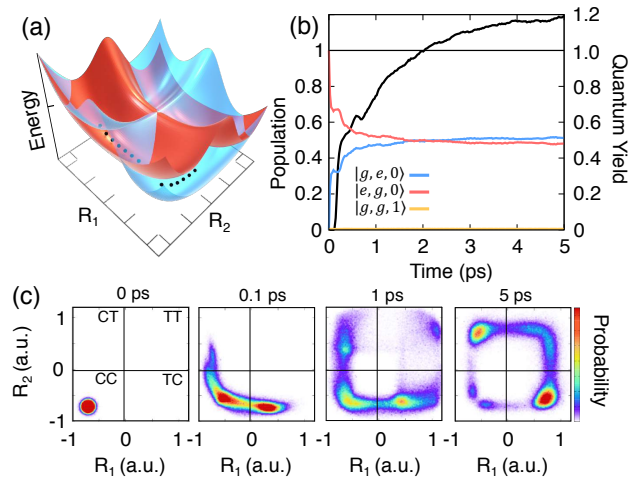


Figure 5: Polariton dynamics of two molecules coupled to an off-resonant radiation mode. (a) PES for $|g, e, 0\rangle$ (blue) and $|e, g, 0\rangle$ with black dots indicating a schematic nuclear path. (b) Population dynamics and corresponding time dependent quantum yield. (c) Histogram of the nuclear distribution at various times during the reaction, with red represent a higher probability density.

various times during the polariton photochemical reaction. Four distinct regions are defined with the dividing surface at $R_i = -0.045$ a.u. ($i = 1, 2$) along each isomerization coordinate. These regions are labeled as CC, CT, TC and TT, where each letter corresponds to either cis or trans configuration indicated for the first and second molecule, respectively. The time-dependent nuclear distribution demonstrates that at longer times the nuclear distribution is localized in the TC, CT and TT regions; the overall yield of trans isomer at a longer time is then higher than 100% because of the non-zero probability density in the TT region.

Again, we emphasize that there is no photonic population accumulated for the $|g, g, 1\rangle$ state in the above off-resonance polariton photochemical process. The chemical reactions of the molecules occur through emitting and absorbing the *virtual* photon. Similar physical processes that exchange virtual photons have been extensively discussed in the context of quantum electrodynamics and atomic quantum optics.^{54–58} Here, we provide an interesting example of the photochemical reactions of molecules, where exchanging virtual photons can exert additional force on the nuclei and alter the course of chemical reactions. This perhaps marks the most fundamental difference between polariton photochemistry which in this case operates at the zero-photon limit, compared to the classical laser-matter interaction scenario which operates at the limit with a large number of photons. In general, cavity enables the hybrid system to explore Fock states that are close to the vacuum state, opening up new possibilities that are not available or difficult to access to at the large photon number limit.^{6–8}

Conclusions. We investigate the real-time polariton quantum dynamics for a model isomerization molecule coupled to an optical cavity. The quantum light-matter interactions hybridize the molecular excitation and the photonic excitation, creating a set of light-matter hybrid states, so-called the polaritons. These polariton states hybridize the curvatures from both the ground and the excited electronic states.^{1,5,7,8} For such molecule-cavity hybrid system, the time-dependent quantum mechanical state of the photon exerts different forces on nuclear DOF (by changing the curvature of the polariton states), influencing its motion and thus opening up new possibilities to tune and control photochemical reactions.

Our numerical results demonstrate that by changing the frequency of the photon inside the cavity, one can selectively modify the polaritonic potential energy surface, allowing the wavepacket to relax to different nuclear configurations and thus control the outcome of the model isomerization reactions. Further, by tuning the light-matter coupling strength, and hence the non-adiabaticity of the polariton quantum dynamics, the wavepacket can either be confined on one polariton surface or allowed to explore multiple surfaces through non-adiabatic transitions, resulting in different preference of the product.

Further, we explore the collective behavior of molecules that stems from strong coupling to a common quantized radiation mode inside the cavity. This forms a polaritonic “super-molecule” that spans across many molecules and the cavity.^{8,12} For the resonance case, our quantum dynamics results reveal a sequential transfer of the population among molecular excitonic states and the cavity photonic state, where one molecule absorbs photon and undergoes excited state isomerization reaction, emit photon back to the cavity, then the second molecule absorbs it and react. During this process, the photon is recycled among different molecules and the cavity, effectively serving as a *catalyst* for the photochemical reactions. In the off-resonance case, molecular excitonic states transfer population by using the off-resonant photonic state as a virtual state, thus emitting and absorbing the *virtual* photon to react. Both cases lead to a quantum yield beyond the Stark-Einstein limit.

Through direct quantum dynamics simulations, this work reveals and clarifies several basic principles of polariton photochemistry. Future investigations will focus on providing the fundamental understanding of cavity quantum electrodynamics induced chemistry, as well as new reactivities that exploit intrinsic quantum behaviors of photons, facilitating the merger of quantum optics and photochemistry.

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