Superreaction: the collective enhancement of a reaction rate by molecular polaritons in the presence of energy fluctuations

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Recent experiments have demonstrated that molecular polaritons, hybrid states of light and matter formed by the strong coupling between molecular electronic or vibrational excitations and an optical cavity, can substantially modify the physical and chemical properties of molecular systems. Here, we show that, by exploiting the collective character of molecular polaritons in conjunction with the effect of polaron decoupling, i.e., the suppression of environmental influence on the polaron, a superreaction can be realized, involving a collective enhancement of charge or excitation-energy transfer reaction rate in a system of donors all coupled to a common acceptor. This effect is analogous to the phenomenon of superradiation. Since the polaron is a superposition state of excitations of all the molecules coupled to the cavity, it is vulnerable to the effect of decoherence caused by energy fluctuations in molecular systems. Consequently, in the absence of a strong light-matter interaction, the reaction rate decreases significantly as the number of molecules increases, even if the system starts from the polaron state. By turning on the light-matter interaction, the dynamic behavior of the system changes dramatically, and the reaction rate increases with the number of molecules, as expected for a superreaction. The underlying mechanism is shown to be the enhancement of quantum coherence between different donors as the light-matter interaction becomes stronger.

Keywords: molecular polariton, reaction rate, collective effect, energy fluctuation

Introduction – The last decade has witnessed the emergence of a new field of study around molecular polaritons. Polaritons modify the physical and chemical properties of molecular systems significantly through the strong coupling of electronic or vibrational molecular excitations to an optical cavity. This coupling leads to the formation of a hybrid state of light and matter, resulting in various interesting phenomena. Important applications have been proposed and demonstrated, including the manipulation of chemical landscapes, the modification of chemical reactivity by molecular-vibration polaritons, cavity-enhanced energy transfer and conductivity in organic media. Further applications include polariton lasing and Bose-Einstein condensates, and nonlinear optical properties with applications in optoelectronic devices.

In the absence of interaction with the environment, the molecular polaron has the form of a superposition state in which all the molecules coupled to the cavity are collectively excited. However, recent studies have shown that, in most cases, the collective effect displayed by a molecular polaron does not prominently influence chemical reactivity, except for its contribution to the collective coupling strength between the polaron and the cavity. In some cases, no collective effect is observed; the collective coupling can even lead to the suppression of an effect that scales as \(1/N\), where \(N\) is the number of molecules. Therefore, it is unclear whether the inherent collective excitation in the polaron state can play a key role in chemical reactions or not. On the other hand, the collective coupling reportedly produces dramatic changes in physical system properties.

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dramatic change in the system dynamics. In this case, the reaction rate increases with the number of molecules coupled to the cavity, as expected for a superreaction. We show that the underlying mechanism of this change in behavior is the enhancement of quantum coherence between donors as the light-matter interaction becomes stronger. The effect of polaron decoupling is thus demonstrated in a dynamic context. This is in contrast to its static manifestation in optical spectroscopy, which was first studied for a molecular aggregate with electronic excitation coupled to a single vibration mode \(^{35}\). The effect of polaron decoupling is thus demonstrated in a dynamic context. This is in contrast to its static manifestation in optical spectroscopy, which was first studied for a molecular aggregate with electronic excitation coupled to a single vibration mode \(^{35}\). The collective coupling between the molecules and the cavity produces a molecular polariton, a hybrid state of light and matter. The blue ellipsoids surrounding the donors represent the molecular environments whose thermal dynamics give rise to strong energy fluctuations in the molecular system.

\[ |g\rangle = \prod_{j=1}^{N} |0\rangle \otimes |g_j\rangle \]

FIG. 1: Schematic illustration of a superreaction, involving the collective enhancement of the electronic or exciton transfer reaction rate in a system of donors (green) coupled to a common acceptor (yellow), all located inside an optical cavity. The collective coupling between the molecules and the cavity field (light magenta) produces a molecular polariton, a hybrid state of light and matter. The blue ellipsoids surrounding the donors represent the molecular environments, whose thermal dynamics give rise to strong energy fluctuations in the molecular system.

\[ |p\rangle = \frac{1}{\sqrt{2}} \left( |1\rangle \otimes |g\rangle + |0\rangle \otimes \sum_{j=1}^{N} |e_j\rangle \right), \]

where \(|0\rangle\) and \(|1\rangle\) denote the photon-number states with zero and one cavity photon, respectively. We first make the \textit{a priori} assumption that environmental energy fluctuations negligibly affect the polariton state, so that the polariton state is maintained throughout the transfer reaction. Then, by Fermi’s golden rule, the transfer rate in the weak-coupling and high-temperature limit is given by

\[ \lambda_{\text{ex}} = \sum_{\chi} (g_{\chi}^{\text{ex}})^2 / (\hbar \omega_\chi). \]

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by
\[ k_{J}^{\text{transfer}} = \sqrt{\frac{\pi}{\hbar k_{B} T \lambda_{\text{PA}}}} \left| \langle p | \hat{H}_{\text{DA}} | a \rangle \right|^2 \times \exp \left[ -\frac{(\Delta E_{\text{PA}} - \lambda_{\text{PA}})^2}{4 \lambda_{\text{PA}} k_{B} T} \right], \] (7)

where \( \Delta E_{\text{PA}} \) denotes the energy difference between the polaron and acceptor states, and \( \lambda_{\text{PA}} \) is the reorganization energy associated with the transfer from the polaron to the acceptor. If the displacements of the potential energy surfaces associated with the electronic excitations in the system of \( N \) donors is small compared with those associated with the transfer from the donors to the acceptor, we have an approximate relation \( \lambda_{\text{PA}} \approx N \lambda_{\text{DA}} \). On the other hand, Eqs. (8) and (9) give
\[ \langle p | \hat{H}_{\text{DA}} | a \rangle = -\hbar V_{\text{DA}} \sqrt{\frac{N}{2}}. \] (8)

Therefore, the maximum transfer rate, obtained for \( \Delta E_{\text{PA}} = \lambda_{\text{PA}} \), scales as \( N^{1/2} \). On the other hand, if the donor system is independent and one donor is initially excited, the maximum transfer rate scales as \( N^{-1/2} \). This factor is explained by the fact that, when the transfer is accomplished, changes in the environment configurations become associated with all of the donors, such that the reorganization energy \( \lambda_{\text{DA}} \) is multiplied by \( N \).

The above analysis suggests that a system initially prepared in the molecular polaron state can produce a superreaction whose rate is greater than that of a system of independent donors and increases with the number of molecules. This is true provided that the influence of energy fluctuations from the environment on the polaron state can be ignored. On the other hand, because the molecular polaron is a superposition state involving collective excitation from all molecules coupled to the cavity (as expressed in Eq. (6)), it is conventionally argued that the polaron state is vulnerable to decoherence, namely the loss of quantum coherence due to energy fluctuations. Therefore, it is highly nontrivial whether a superreaction can be achieved or not. To examine the prediction of the above analysis, we numerically simulated the dynamics of the system described by the above set of Hamiltonians. To limit the computational workload (which increases exponentially with the number of independent environments), the environments associated with the electronic excitation of each donor and with the transfer from the donor to the acceptor are described by a common set of harmonic oscillators \( \xi = \chi \). We also assumed that the coupling strengths are related by a constant \( \eta \), that is, \( g_{\xi}^{\text{DA}} = \eta g_{\xi}^{\text{DA}} = \eta g_{\xi} \). The environmental dynamics are characterized by their correlation functions
\[ C(t) = \int_{0}^{\infty} d\omega J(\omega) \left[ \coth \left( \frac{\beta \omega}{2} \right) \cos \omega t - i \sin \omega t \right], \] (9)

where \( \beta = 1/(k_{B} T) \) and \( J(\omega) = \sum_{\xi} g_{\xi}^{2} \delta(\omega - \omega_{\xi}) \) is the environmental spectral density. Considering the Drude-Lorentz spectral density \( J(\omega) = 2\lambda \tau / (\tau^2 \omega^2 + 1) \) in the high-temperature limit \( (k_{B} T/\hbar \gg 1) \), the correlation function \( C(t) \) becomes exponential. Here, \( \lambda = \sum_{\xi} g_{\xi}^2 / (\hbar \omega_{\xi}) \) is the reorganization energy, and \( \tau \) is the relaxation time of the environment. In this case, the dynamics of the reduced system can be obtained by integrating out the environmental degrees of freedom. The resulting hierarchical equation of motion describes the dynamics of open quantum systems for a wide range of coupling strengths \( g_{\xi} \). Our numerical simulation set the following parameter values for the molecular system and environment: \( V_{\text{DA}} = 10 \text{ cm}^{-1} \), \( T = 300 \text{ K} \), \( \tau = 250 \text{ fs} \), \( \lambda = 10 \text{ cm}^{-1} \), and \( \eta = 1 \), which correspond to the high-temperature and strong-energy-fluctuation limits \( (V_{\text{DA}} < \sqrt{\lambda \hbar \omega_{\xi}}) \). For the initial state, we consider the case in which the system is initially prepared in the molecular polaron state \( |\text{Eq. (6)}\rangle \) by a vertical excitation under the Condon approximation, that is, the environments are at the equilibrium positions of the potential energy surfaces associated with the donor electronic ground states.

Figure 2 compares the transfer dynamics in the absence and presence of energy fluctuations if the molecules and the cavity are uncoupled, i.e., \( \Omega_{R} = 0 \). Here, the time-dependent probability \( p_{\text{DA}}(t) \) of finding an electron/exciton at the acceptor is calculated for systems with different numbers of donors \( 1 \leq N \leq 4 \). Evidently, despite the initial increase in transfer rate with the number of molecules due to the collective effect of the polaron state, the transfer rate rapidly changes its behavior as a result of energy fluctuations, becoming smaller for systems with many molecules. This change in behavior can be attributed to decoherence.

Figure 3 shows the transfer dynamics for systems with different numbers \( N \) of molecules if the coupling between the molecules and the cavity is set to the collective Rabi frequency \( h\Omega_{R} \sqrt{N} = 20 \text{ meV} \). Here, the single-emitter Rabi frequency \( \Omega_{R} \) is changed while keeping the collective Rabi frequency fixed to the above value as \( N \) is varied. The collective Rabi coupling is strong in the sense that it is greater than the energy fluctuation amplitude characterized by \( \sqrt{\lambda \hbar \omega_{\xi}} \). It is clear from the numerical result that the transfer rate of transfer increases with \( N \), as expected for a superreaction. By comparing this result with that in Fig. 2, when the light-matter interaction is turned off, it can be inferred that the effect of decoherence is suppressed when the molecular system is strongly coupled to the cavity. This in turn leads to an increase in the transfer rate for systems with large \( N \). This demonstrates the effect of polaron decoupling in a dynamic context, as opposed to its static manifestation in optical spectroscopy [32, 37].

To justify the above prediction of the polaron decoupling mechanism for realizing a superreaction, we investigated the dependence on the Rabi coupling strength of the transfer dynamics and quantum coherence between different donors. Figure 4 plots the time-dependent electron/exciton population \( p_{\text{DA}}(t) \) at the acceptor, and the quantum coherence between two different donors \( i \neq j \),
FIG. 2: Comparison of electron/exciton transfer dynamics from a system of donors to an acceptor in the (a) absence and (b) presence of energy fluctuations when there is no coupling between the molecules and the cavity, namely $\Omega_R = 0$. The probability $p_A$ of finding an electron/exciton at the acceptor is plotted as a function of time for systems with different numbers $N$ of donors. In both cases, the system is initially prepared in the molecular polariton state given by Eq. (6). The parameters of the molecular system and environment are given in the text.

In conclusion, we have shown that, by exploiting the collective character of the molecular polariton state, a superreaction with a collective enhancement of the electron/exciton transfer reaction rate can be obtained in a system of donors coupled to a common acceptor. Such a superreaction requires the persistence of quantum coherence between different donors in the presence of strong energy fluctuations. This condition can be fulfilled by the effect of polaron decoupling, provided that the light-matter interaction is sufficiently strong. Finally, it is worth noting that the transfer dynamics considered in this study and their timescales depend on the coupling between the system and the environment as the system eventually approaches the thermal equilibrium state. Therefore, the dependence of the transfer rate with respect to the number $N$ of molecules coupled to the cavity, which is obtained by numerical simulations, should differ from the power scaling law obtained by the Fermi's golden rule analysis. Remaining avenues for future work include a quantitative investigation of the scaling power in the thermodynamic limit, that is, when $N \rightarrow \infty$, and in a nonequilibrium steady state.

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FIG. 4: (a) Electron/exciton transfer dynamics from a system of donors to an acceptor, and (b) the quantum coherence between different donors for different values of the collective Rabi coupling strength $\Omega_R \sqrt{N}$. The quantum coherence between donors is quantified by $|\rho_{ij}(t)|/\sqrt{p_i(t)p_j(t)}$, where $\rho_{ij}$ ($i \neq j$) is the off-diagonal matrix element of the density matrix of the system, and $p_i, p_j$ are the probabilities of finding an electron/exciton at the $i, j$th donors.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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