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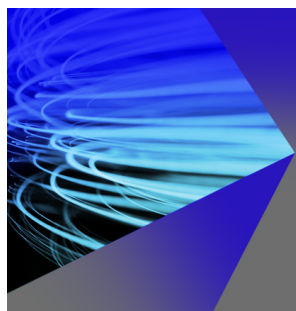
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# Molecular electron transfer in optical cavities: From excitonic to vibronic polaritons

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## ABSTRACT

Strong coupling between molecular excitations and quantized electromagnetic fields in optical cavities provides a powerful means to control the physical and chemical properties of molecular systems. Here, we study electron transfer (ET) dynamics in cavity-coupled molecules using the numerically exact hierarchical equations of motion method, which captures nonperturbative and non-Markovian effects beyond standard perturbative theories. We identify distinct resonance and collective effects associated with polariton formation and show that the ET rate saturates in the strong-coupling regime, a feature not captured by perturbative approaches. We further extend the cavity-modified ET model by incorporating the nuclear-coordinate dependence of molecular electric dipole moments, which gives rise to a three-body interaction involving molecular electronic and vibrational degrees of freedom and cavity photons. This vibronic polariton formation leads to non-monotonic, oscillatory dependencies of the ET rate on the light-matter coupling strength and cavity frequency, which we attribute to quantum interference among multiple transfer pathways. These findings establish cavity-modified electron transfer as a multichannel quantum process governed by the interplay of electronic, vibrational, and photonic degrees of freedom.

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## I. INTRODUCTION

Recent advances in cavity quantum electrodynamics have established that confining molecules within tailored electromagnetic environments can strongly couple their internal excitations to quantized light fields, opening new routes to control material properties and chemical reactivity.<sup>1</sup> In this strong-coupling regime, the hybridization of optical cavity modes with molecular excitations gives rise to light-matter eigenstates known as molecular polaritons.<sup>2,3</sup> Depending on whether the cavity couples predominantly to electronic or vibrational molecular transitions, one distinguishes exciton polaritons and vibrational polaritons, respectively. The latter, formed under vibrational strong coupling, has been reported to influence ground-state chemical reactivity<sup>4–7</sup> and has been linked to enhanced intermolecular vibrational energy transfer<sup>8</sup> and accelerated intramolecular vibrational relaxation.<sup>9</sup>

Electronic strong coupling and the resulting exciton polaritons have been widely explored as platforms to reshape

exciton migration, nonadiabatic dynamics, photochemical transformations,<sup>10–19</sup> and spin transport.<sup>20</sup> Among the processes amenable to cavity control, condensed-phase electron transfer (ET) is of particular importance, as it underpins charge separation and transport in organic electronics, redox chemistry, and numerous biological functions.<sup>21,22</sup>

In condensed-phase ET, the transfer rate is governed by the interplay among three key elements: (i) the electronic coupling between donor and acceptor states; (ii) the energetic driving force and activation barrier, shaped by solvent and intramolecular reorganization; and (iii) the thermal fluctuations and dissipation induced by the molecular environment. Optical cavities can, in principle, modify each of these elements. Hybridizing electronic states with a cavity mode creates polaritonic manifolds that reshape energy gaps and effective couplings. Additional radiative and dissipative channels introduced by cavity leakage alter the competition between coherent and incoherent dynamics. Furthermore, collective light-matter coupling in molecular ensembles can renormalize

effective interactions and change how disorder and fluctuations impact reaction kinetics. Together, these mechanisms make cavity-modified ET a rich arena for controlling charge transport and chemical reactivity in nanophotonic environments.<sup>23</sup> Despite growing theoretical interest in cavity-modified condensed-phase ET,<sup>24–33</sup> most existing studies have relied on perturbative rate expressions, typically within the Fermi's golden rule (FGR) framework, which are rigorously justified only in the linear response regime. However, experimentally relevant cavity QED settings can involve strong light–matter coupling and structured vibrational environments, where nonperturbative and non-Markovian effects may be essential for accurate quantitative predictions and mechanistic understanding.

In this work, we employ the hierarchical equations of motion (HEOM)<sup>34</sup> to simulate the quantum dynamics of cavity-modified ET beyond the perturbative regime. Effective transfer rates are extracted by exponential fitting of the time-evolving donor and acceptor populations computed from HEOM. We organize our investigation as follows. We begin with the minimal model of cavity-modified ET, in which the nuclear-coordinate dependence of the molecular electric dipole moments is neglected, so that the cavity couples exclusively to the electronic degrees of freedom. Within this model, we characterize ET rate modification as a function of the driving force and reorganization energy for two distinct coupling channels: direct transition coupling and energy fluctuation coupling. We examine the effect of strong light–matter coupling on coherence dynamics by comparing the system's time evolution with and without cavity coupling. Resonance and collective effects arising from polariton formation are investigated by varying the cavity frequency and the number of molecules coupled to a single cavity mode, respectively. The role of cavity loss is assessed by augmenting the HEOM with a Lindblad-form dissipation term. We then generalize the model to include the nuclear-coordinate-dependent molecular dipole moments, which introduces a three-body interaction coupling the molecular electronic and vibrational degrees of freedom to the cavity photons. The influence of the vibronic polariton formation on ET dynamics is investigated for environments characterized by both Drude–Lorentz and underdamped spectral densities, revealing a rich interplay of quantum interference and nonlinear coupling effects.

## II. SYSTEM MODEL

We consider  $N_{\text{mol}}$  identical molecules in the condensed phase strongly coupled to a single mode of an optical cavity. In the dipole gauge, the light–matter interaction is described by the Hamiltonian<sup>24</sup>

$$\hat{H} = \sum_{n=1}^{N_{\text{mol}}} \left( \hat{H}_{\text{M}}^{(n)} + \hat{H}_{\text{B}}^{(n)} + \hat{H}_{\text{MB}}^{(n)} \right) + \hbar\omega_c \hat{a}^\dagger \hat{a} - \sum_{n=1}^{N_{\text{mol}}} \hat{\boldsymbol{\mu}}^{(n)} \cdot \hat{\mathbf{E}} + \frac{1}{2\mathcal{V}\epsilon_0} \left( \sum_{n=1}^{N_{\text{mol}}} \hat{\boldsymbol{\mu}}^{(n)} \cdot \boldsymbol{\epsilon} \right)^2, \quad (1)$$

where  $\hat{H}_{\text{M}}^{(n)}$ ,  $\hat{H}_{\text{B}}^{(n)}$ , and  $\hat{H}_{\text{MB}}^{(n)}$  represent the molecular, bath (environment), and molecule–bath interaction Hamiltonians, respectively, of the  $n$ th molecule. The cavity mode, characterized by frequency  $\omega_c$ , polarization unit vector  $\boldsymbol{\epsilon}$ , and effective mode volume  $\mathcal{V}$ , is

described by photonic creation and annihilation operators  $\hat{a}^\dagger$  and  $\hat{a}$ . Light–matter interaction enters through the coupling between the total molecular electric dipole moment  $\hat{\boldsymbol{\mu}}^{(n)}$  and the cavity electric field operator,

$$\hat{\mathbf{E}} = i\epsilon\sqrt{\frac{\hbar\omega_c}{2\mathcal{V}\epsilon_0}} (\hat{a} - \hat{a}^\dagger), \quad (2)$$

where  $\epsilon_0$  is the vacuum permittivity. The final term in Eq. (1) is the dipole self-energy, which ensures gauge invariance and becomes significant in the ultrastrong coupling regime where the light–matter coupling strength is comparable to the characteristic molecular energy scales and the cavity frequency.<sup>35</sup> This dipole gauge Hamiltonian is obtained via the Power–Zienau–Woolley unitary transformation from the minimal coupling Hamiltonian in the Coulomb gauge.<sup>36</sup>

We first consider a single molecule ( $N_{\text{mol}} = 1$ ) strongly coupled to a single cavity mode. To model electron transfer, we project the molecular Hamiltonian onto the two relevant electronic states: the donor state  $|D\rangle$  and acceptor state  $|A\rangle$ . The environment is represented as a collection of harmonic oscillators with frequencies  $\nu_j$  and annihilation operators  $\hat{b}_j$ , yielding the combined molecular and bath Hamiltonian,

$$\hat{H}_{\text{M}} + \hat{H}_{\text{B}} + \hat{H}_{\text{MB}} = E_{\text{D}}|D\rangle\langle D| + \left[ E_{\text{A}} + \sum_j \lambda_j (\hat{b}_j + \hat{b}_j^\dagger) \right] |A\rangle\langle A| + \sum_j \hbar\nu_j \hat{b}_j^\dagger \hat{b}_j + H_{\text{DA}}|D\rangle\langle A| + H_{\text{AD}}|A\rangle\langle D|, \quad (3)$$

where  $E_{\text{D}}$  and  $E_{\text{A}}$  are the donor and acceptor energies, respectively;  $H_{\text{DA}}$  and  $H_{\text{AD}}$  characterize the electronic coupling between states; and  $\lambda_j$  represents the vibronic coupling strength of the  $j$ th bath mode. Throughout our numerical calculations, we set  $H_{\text{DA}} = H_{\text{AD}} = 30 \text{ cm}^{-1}$ .

Expressing the full Hamiltonian in the donor–acceptor basis in terms of dipole matrix elements yields<sup>24</sup>

$$\begin{aligned} \hat{H} = & E_{\text{D}}|D\rangle\langle D| + \left[ E_{\text{A}} + \sum_j \lambda_j (\hat{b}_j + \hat{b}_j^\dagger) \right] |A\rangle\langle A| \\ & + \sum_j \hbar\nu_j \hat{b}_j^\dagger \hat{b}_j + H_{\text{DA}}|D\rangle\langle A| + H_{\text{AD}}|A\rangle\langle D| + \hbar\omega_c \hat{a}^\dagger \hat{a} \\ & + \hbar\omega_c (\hat{a} - \hat{a}^\dagger) (g_{\text{D}}|D\rangle\langle D| + g_{\text{A}}|A\rangle\langle A| + t_{\text{DA}}|D\rangle\langle A| \\ & + t_{\text{AD}}|A\rangle\langle D|) + \hbar\omega_c [|g_{\text{D}}|^2|D\rangle\langle D| + |g_{\text{A}}|^2|A\rangle\langle A| \\ & + |t_{\text{DA}}|^2 - (g_{\text{D}} + g_{\text{A}})(t_{\text{DA}}|D\rangle\langle A| + t_{\text{AD}}|A\rangle\langle D|)], \end{aligned} \quad (4)$$

where the coupling parameters are defined by projections of the molecular dipole operator onto the donor–acceptor basis,

$$g_{\text{D}} = i\sqrt{\frac{1}{2\hbar\omega_c \mathcal{V}\epsilon_0}} \boldsymbol{\mu}_{\text{DD}} \cdot \boldsymbol{\epsilon}, \quad (5)$$

$$g_{\text{A}} = i\sqrt{\frac{1}{2\hbar\omega_c \mathcal{V}\epsilon_0}} \boldsymbol{\mu}_{\text{AA}} \cdot \boldsymbol{\epsilon}, \quad (6)$$

$$t_{\text{DA}} = i\sqrt{\frac{1}{2\hbar\omega_c\mathcal{V}\epsilon_0}}\boldsymbol{\mu}_{\text{DA}}\cdot\boldsymbol{\epsilon}, \quad (7)$$

with  $\boldsymbol{\mu}_{\text{DD}} = \langle \text{D} | \hat{\boldsymbol{\mu}} | \text{D} \rangle$  and  $\boldsymbol{\mu}_{\text{AA}} = \langle \text{A} | \hat{\boldsymbol{\mu}} | \text{A} \rangle$  denoting the diagonal (permanent) dipole matrix elements and  $\boldsymbol{\mu}_{\text{DA}} = \langle \text{D} | \hat{\boldsymbol{\mu}} | \text{A} \rangle$  denoting the off-diagonal (transition) dipole matrix element. In the minimal model formulation, we treat the dipole matrix elements as constants, independent of nuclear coordinates. This approximation is valid when the Born–Oppenheimer separation holds and the electronic charge distribution is only weakly modulated by vibrational motion. We will relax this constraint in the generalized model presented later, where nuclear-coordinate dependence of the dipole moments gives rise to a three-body electronic–vibrational–photonic interaction. The final term in Eq. (4) accounts for dipole self-energy contributions.

This formulation reveals two distinct coupling channels through which the cavity mode influences electron transfer. The first channel, characterized by  $g_{\text{D}}$  and  $g_{\text{A}}$ , corresponds to the cavity-induced fluctuations of the donor and acceptor state energies (energy-fluctuation coupling). The second channel, characterized by  $t_{\text{DA}} = -t_{\text{AD}}^*$ , couples the cavity field directly to the electronic transition between donor and acceptor states (direct transition coupling).

The influence of the environment on the system dynamics is encoded in the spectral density  $J(\omega) = (2\pi/\hbar)\sum_j \lambda_j^2 \delta(\omega - \nu_j)$ , with the overall system–environment coupling strength quantified by the reorganization energy  $\lambda_0 = \sum_j \lambda_j^2 / (\hbar\nu_j)$ . Unless otherwise stated, we employ a Drude–Lorentz spectral density representing a collection of low-frequency intermolecular vibrational modes,

$$J_{\text{DL}}(\omega) = \frac{4\lambda_0 W \omega}{\omega^2 + W^2}, \quad (8)$$

where the cutoff frequency  $W = \tau_b^{-1}$  is inversely related to the bath relaxation time, which we set to  $\tau_b = 100$  fs.

The parameter regime considered in this work is broadly representative of two well-studied classes of condensed-phase electron-transfer systems. One example is primary charge separation in photosynthetic reaction centers, where the relevant electronic couplings, environmental reorganization energies, and energy gaps are often comparable to the scales used in the present model. In particular, recent quantum-chemical and quantum-dynamical studies of bacterial reaction centers and photosystem II explicitly treat the associated energetics, electronic couplings, and vibronic couplings in the protein environment.<sup>37</sup> For bacterial reaction centers, molecular-dynamics simulations have reported reorganization energies on the scale of a few hundred  $\text{cm}^{-1}$  for the low-frequency membrane/protein environment,<sup>38</sup> while open-quantum-dynamics modeling of pigment–protein complexes commonly employs Drude-type bath parameters of order  $10^2 \text{ cm}^{-1}$ , consistent with the effective low-frequency bath description adopted here.<sup>39,40</sup> Driving-force scales of several hundred  $\text{cm}^{-1}$  are likewise common in photosynthetic charge-separation chains.<sup>41</sup>

A second important class is provided by organic donor–acceptor and mixed-valence compounds described within the Marcus–Levich–Jortner framework, where the reorganization energy is commonly partitioned into a classical low-frequency component and one or a few high-frequency intramolecular

quantum modes.<sup>42,43</sup> In that context, the low-frequency sector is naturally modeled by a Drude–Lorentz-type spectral density such as Eq. (8), whereas the higher-frequency sector may be represented by effective skeletal, ring-deformation, or bond-stretching modes. For the prototypical Creutz–Taube ion, recent *ab initio* work and earlier resonance-Raman studies both support the involvement of multiple ET-active vibrations spanning the few-hundred- $\text{cm}^{-1}$  region up to  $\sim 1600 \text{ cm}^{-1}$ .<sup>44,45</sup> Our choice  $\omega_0 = 500 \text{ cm}^{-1}$  in Sec. III C is intended to represent such a skeletal or ring-deformation mode. Electronic couplings likewise span a broad range across this class, from very small values in long molecular-wire systems to  $\sim 10^2 \text{ cm}^{-1}$  in moderately coupled bridged systems and much larger values in strongly mixed-valence compounds.<sup>46–48</sup> Our choice of  $H_{\text{DA}} = 30 \text{ cm}^{-1}$ , therefore, lies naturally in the weakly to moderately coupled, nonadiabatic regime for which the present analysis is most directly applicable.

The parameter values adopted in this work were thus chosen to capture the essential physics of cavity-modified ET in this broad condensed-phase regime rather than to reproduce a single specific compound. In particular,  $\lambda_0$  should be viewed as an effective low-frequency environmental parameter, while the high-frequency mode introduced in Sec. III C is intended to represent a representative intramolecular vibration in the spectral window relevant to vibronic ET.

To capture the quantum dynamics in such parameter regimes, we employ the hierarchical equations of motion (HEOM),<sup>34</sup> which provides numerically exact solutions for open quantum systems across arbitrary coupling strengths. The HEOM approach proceeds by first expanding the bath correlation function,

$$C(t) = \int_0^\infty d\omega J(\omega) \left[ \coth\left(\frac{\beta\omega}{2}\right) \cos \omega t - i \sin \omega t \right], \quad (9)$$

into a sum of exponential functions, exploiting the structure of the spectral density  $J(\omega)$  and temperature-dependent factors. After formally integrating out the bath degrees of freedom, one obtains a hierarchical set of coupled differential equations governing not only the reduced density matrix of the system but also a hierarchy of auxiliary density operators (ADOs). These ADOs encode the complete memory of past system–bath interactions at different time depths. Each level of the hierarchy captures correlations extending further back in time, with higher-level ADOs representing increasingly long-lived memory effects. The coupled evolution of the system density operator and the ADO hierarchy enables exact treatment of non-Markovian dynamics, capturing memory effects that persist when the bath relaxation timescale is comparable to or longer than the characteristic timescales of the system's evolution.

We solve the HEOM to obtain the time evolution of the donor and acceptor populations,  $p_{\text{D}}(t)$  and  $p_{\text{A}}(t) = 1 - p_{\text{D}}(t)$ , with initial conditions corresponding to the molecule in the donor state and the environment in thermal equilibrium:  $p_{\text{D}}(0) = 1$  and  $p_{\text{A}}(0) = 0$ . Effective transfer rates are extracted by fitting the computed population dynamics to the kinetic rate equations,

$$\frac{dp_{\text{D}}}{dt} = -k_{\text{DA}} p_{\text{D}} + k_{\text{AD}} p_{\text{A}}, \quad (10)$$

$$\frac{dp_A}{dt} = k_{DA}p_D - k_{AD}p_A, \quad (11)$$

where  $k_{DA}$  and  $k_{AD}$  denote the forward and backward transfer rates, respectively. The solution to these equations yields

$$p_D(t) = \frac{k_{AD}}{k_{AD} + k_{DA}} + \frac{k_{DA}}{k_{AD} + k_{DA}} e^{-(k_{AD} + k_{DA})t}, \quad (12)$$

from which  $k_{DA}$  is determined via an effective exponential fit to the HEOM population dynamics. Here, Eq. (12) is used to extract an effective kinetic rate from the overall donor-population relaxation, rather than to imply that the full time-domain dynamics are strictly monoexponential at all times. In particular, short-time coherent oscillations may be present in the HEOM dynamics, and such oscillatory features are not expected to be captured by a simple monoexponential form.

### III. RESULTS AND DISCUSSION

#### A. Minimal model: Cavity-electronic coupling

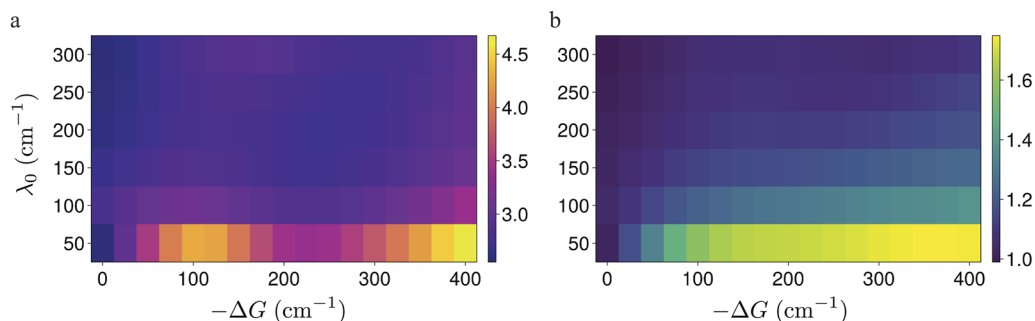
We begin by introducing the quantities used in Fig. 1. Here,  $k_{\text{cav}}$  and  $k_{\text{non-cav}}$  denote the effective forward electron-transfer (ET) rates extracted from the HEOM population dynamics with and without cavity coupling, respectively, using the fitting procedure described in Eq. (12). The relative rate change is measured by the ratio  $k_{\text{cav}}/k_{\text{non-cav}}$ . The horizontal axes in Fig. 1 are the reorganization energy  $\lambda_0$ , which characterizes the overall coupling strength to the low-frequency bath [Eq. (8)], and the driving force  $-\Delta G = E_D - E_A$ , which measures the donor-acceptor energy bias in the absence of cavity coupling. The cavity mode frequency is denoted by  $\omega_c$ . As introduced in Eqs. (5)–(7),  $t_{DA}$  describes the direct transition-coupling channel between the donor and acceptor states mediated by the cavity field, whereas  $g_D$  and  $g_A$  describe the energy-fluctuation coupling channel through the diagonal dipole couplings of the donor and acceptor states.

Figure 1 displays the relative change in ET rate,  $k_{\text{cav}}/k_{\text{non-cav}}$ , as a function of  $\lambda_0$  and  $-\Delta G = E_D - E_A$  for a single molecule ( $N_{\text{mol}} = 1$ ). Figure 1(a) shows the case where light-matter interaction occurs exclusively through the direct transition coupling channel, i.e.,  $t_{DA} \neq 0$  and  $g_D = g_A = 0$ . Here, we set  $\hbar\omega_c = 100 \text{ cm}^{-1}$  and  $|t_{DA}| = 0.5$ . The cavity coupling produces substantial rate

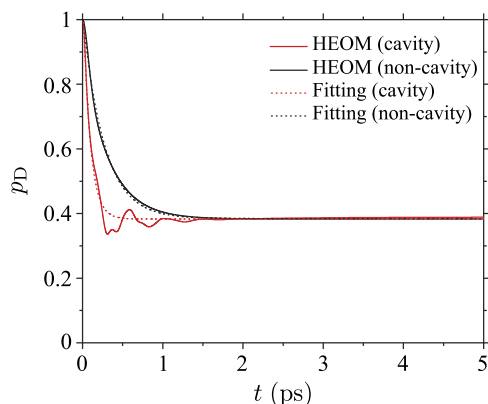
enhancement across a broad parameter space, with increases exceeding fourfold under optimal conditions. This pronounced effect arises because the cavity field couples directly to the transition dipole moment, effectively opening a new coherent pathway for electron transfer. Figure 1(b) presents the corresponding results when interaction occurs solely through the energy-fluctuation coupling channel, i.e.,  $t_{DA} = 0$  and  $g_D, g_A \neq 0$ , with parameters  $\hbar\omega_c = 100 \text{ cm}^{-1}$ ,  $|g_D| = 0.6$ , and  $|g_A| = 0.1$ . While this channel also yields rate enhancement, the effect is less pronounced than for the  $t_{DA}$  channel. Here, the cavity modulates the energies of the donor and acceptor states rather than directly facilitating the electronic transition, resulting in a qualitatively different enhancement mechanism with generally smaller magnitude.

To examine how cavity coupling affects the temporal dynamics of electron transfer, we plot the time evolution of the donor population in Fig. 2 for the direct transition coupling channel only, i.e.,  $t_{DA} \neq 0$  and  $g_D = g_A = 0$ . The parameters are  $\lambda_0 = 50 \text{ cm}^{-1}$ ,  $-\Delta G = 100 \text{ cm}^{-1}$ ,  $\hbar\omega_c = 100 \text{ cm}^{-1}$ , and  $|t_{DA}| = 0.5$ , corresponding to an effective coupling  $\hbar\omega_c |t_{DA}| = 50 \text{ cm}^{-1}$ . This parameter set corresponds to a case in which the relative rate enhancement shown in Fig. 1(a) is close to its maximum. In the figure, we also show the corresponding effective fits based on Eq. (12). Comparison between cavity-coupled and uncoupled cases reveals two distinct effects of the light-matter interaction. First, the cavity accelerates the transfer process, as evidenced by the faster decay of the donor population toward its equilibrium value. Second, the cavity-coupled system exhibits pronounced oscillatory behavior that persists over significantly longer timescales, indicating an extended coherence time compared to the bare molecular system. At the same time, the fitted curves make clear that Eq. (12) is used only to characterize the overall relaxation kinetics and extract an effective transfer rate, rather than to reproduce the short-time coherent oscillations in detail.

This prolonged coherence can be understood through the dynamic polaron decoupling effect.<sup>49–54</sup> When light-matter coupling is sufficiently strong, the formation of delocalized polariton states effectively reduces the local system-environment interaction. The polariton, being a hybrid light-matter excitation distributed across both photonic and molecular components, is less susceptible to environmental fluctuations that would otherwise rapidly dephase purely molecular transitions. This decoherence protection



**FIG. 1.** Relative change  $k_{\text{cav}}/k_{\text{non-cav}}$  in electron transfer rate as a function of reorganization energy  $\lambda_0$  and driving force  $-\Delta G$  for a single molecule ( $N_{\text{mol}} = 1$ ). (a) Direct transition coupling only ( $t_{DA} \neq 0$ ,  $g_D = g_A = 0$ ). (b) Energy-fluctuation coupling only ( $t_{DA} = 0$ ,  $g_D, g_A \neq 0$ ).



**FIG. 2.** Time evolution of the donor population  $p_D(t)$  for the direct-transition-coupling case only, with  $g_D = g_A = 0$ ,  $\lambda_0 = 50 \text{ cm}^{-1}$ ,  $-\Delta G = 100 \text{ cm}^{-1}$ ,  $\hbar\omega_c = 100 \text{ cm}^{-1}$ , and  $|t_{DA}| = 0.5$  (equivalently,  $\hbar\omega_c|t_{DA}| = 50 \text{ cm}^{-1}$ ). This parameter set corresponds to a case for which the relative rate enhancement is close to maximal in Fig. 1(a). Solid curves: HEOM population dynamics. Dotted curves: effective fits based on Eq. (12) used to extract the transfer rates. Red: cavity-coupled system. Black: uncoupled system. The figure illustrates that cavity coupling both accelerates transfer and extends coherence time, while the fit captures the overall relaxation dynamics rather than the short-time oscillatory structure.

mechanism allows coherent dynamics to survive longer, manifesting as sustained oscillations in the population dynamics.

To assess the validity of perturbative approaches, we compare our numerically exact HEOM results with analytic expressions derived from Fermi's golden rule (FGR).<sup>24</sup> FGR provides a widely used perturbative framework for calculating transition rates, treating the donor-acceptor coupling to the second order. For cavity-modified ET, the FGR expressions take different forms depending on the coupling channels. For the energy-fluctuation coupling channel ( $g_{DA}$  channel), the FGR rate is

$$k_{DA}^{\text{FGR}} = \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_0}} H_{DA}^2 e^{-|g_D - g_A|^2} \sum_{m=0}^{\infty} \frac{|g_D - g_A|^{2m}}{m!} \times \exp \left\{ -\frac{(-\Delta G - \lambda_0 - m\hbar\omega)^2}{4k_B T \lambda_0} \right\}, \quad (13)$$

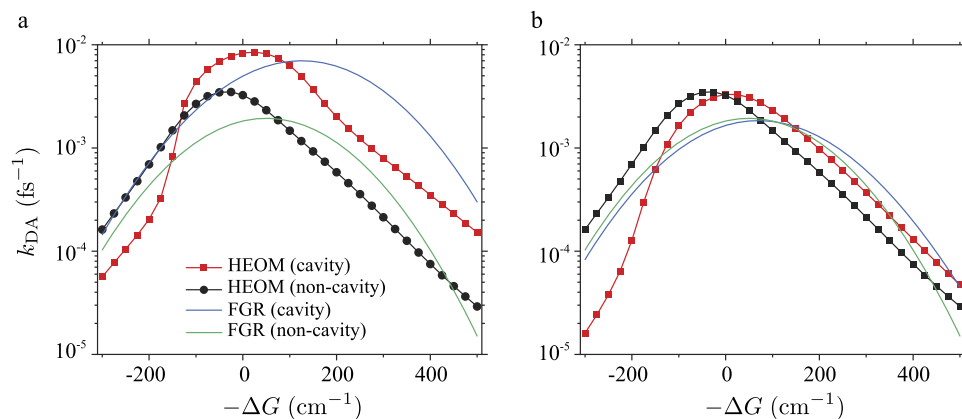
where the summation over photon number states  $m$  reflects the cavity-induced modulation of the activation barrier. For the direct transition coupling channel ( $t_{DA}$  channel), the FGR rate is

$$k_{DA}^{\text{FGR}} = \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_0}} \left[ H_{DA}^2 \exp \left\{ -\frac{(-\Delta G - \lambda_0)^2}{4k_B T \lambda_0} \right\} + |\hbar\omega t_{DA}|^2 \exp \left\{ -\frac{(-\Delta G - \lambda_0 - \hbar\omega)^2}{4k_B T \lambda_0} \right\} \right], \quad (14)$$

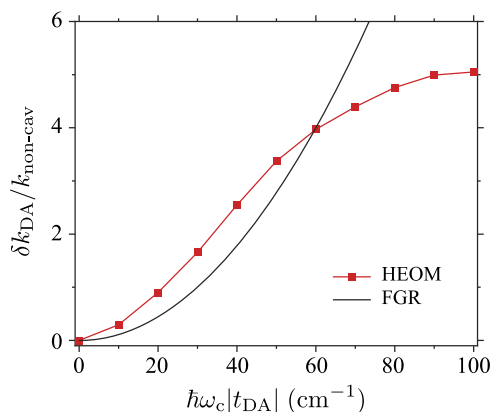
where the two terms represent the bare molecular transfer and the cavity-mediated transfer pathway, respectively.

Figure 3 compares these FGR predictions (solid lines) with HEOM results (dots), as a function of driving force  $-\Delta G$  for  $\lambda_0 = 50 \text{ cm}^{-1}$ . Although FGR reproduces the overall dependence of the ET rate on the driving force, the HEOM results exhibit systematically narrower profiles and a noticeable shift of the peak position relative to the FGR curves. These discrepancies stem from the perturbative nature of FGR. In contrast, HEOM fully captures nonperturbative couplings as well as non-Markovian memory effects that arise when the bath relaxation timescale is comparable to the characteristic timescale of electron transfer dynamics. These memory effects manifest as correlations between the system's past and present states, leading to rate modifications and spectral narrowing that cannot be predicted by time-local, perturbative theories.

The limitations of perturbative theory become most pronounced when examining the dependence of the ET rate on light-matter coupling strength. According to Eq. (14), FGR predicts a quadratic scaling of the cavity-induced rate enhancement:  $\delta k_{DA} \propto |t_{DA}|^2$ , where  $\delta k_{DA} = k_{\text{cav}} - k_{\text{non-cav}}$  represents the change in transfer rate upon cavity coupling. Figure 4 compares this FGR prediction (black curve) with HEOM results (red dots) as a function of the coupling strength  $|t_{DA}|$ . The quadratic scaling holds only in the weak and moderate coupling regimes. Beyond this threshold, the HEOM results deviate systematically from the perturbative prediction: the rate enhancement saturates rather than continuing to grow quadratically. This saturation signals entry into the ultrastrong coupling regime, where the light-matter interaction energy becomes comparable to other characteristic energy scales in the system. Notably, even within the moderate coupling window, the HEOM-predicted rate differs quantitatively from the FGR value. This discrepancy reflects the fact that FGR neglects non-Markovian bath correlations



**FIG. 3.** Comparison of ET rates as a function of driving force  $-\Delta G$  for (a) the direct transition coupling channel ( $t_{DA}$ ) and (b) the energy-fluctuation coupling channel ( $g_{DA}$ ), with  $\lambda_0 = 50 \text{ cm}^{-1}$ . Solid lines: Fermi's golden rule predictions. Dots: numerically exact HEOM results. While FGR captures qualitative trends, it fails to reproduce the quantitative rates and spectral widths due to neglect of nonperturbative and non-Markovian effects.

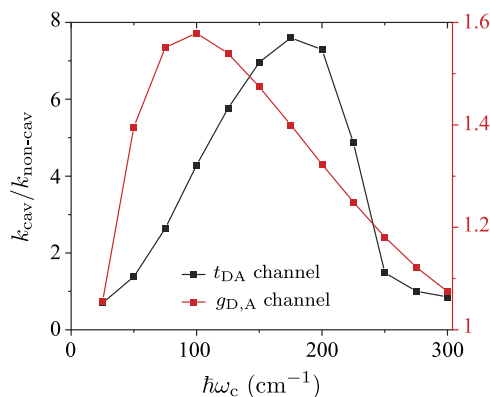


**FIG. 4.** Cavity-induced change in ET rate,  $\delta k_{DA} = k_{cav} - k_{non-cav}$  (normalized by  $k_{non-cav}$ ) as a function of direct transition coupling strength  $|t_{DA}|$  for  $\lambda_0 = 50 \text{ cm}^{-1}$  and  $-\Delta G = 100 \text{ cm}^{-1}$ . Red dots: HEOM results. Black solid curve: FGR prediction [Eq. (14)]. The rate saturates as the system enters the ultrastrong coupling regime.

and higher-order virtual processes that contribute to the effective rate even at modest coupling strengths.

## B. Resonance, loss, and collective effects

An important feature of cavity-modified ET is the resonance behavior that emerges when the cavity frequency is tuned relative to the molecular and environmental energies. Figure 5 shows the ET rate as a function of cavity frequency  $\omega_c$  for two channel-resolved cases plotted in a single figure at a fixed driving force of  $-\Delta G = 100 \text{ cm}^{-1}$ . The curve labeled  $t_{DA}$  channel corresponds to the direct-transition-coupling case, for which  $t_{DA} \neq 0$  and  $g_D = g_A = 0$ , whereas the curve labeled  $g_{D,A}$  channel corresponds to the energy-fluctuation-coupling case, for which  $t_{DA} = 0$  and  $g_D, g_A \neq 0$ . To



**FIG. 5.** Resonance behavior of the ET rate as a function of cavity frequency  $\omega_c$  at fixed driving force  $-\Delta G = 100 \text{ cm}^{-1}$ , with the nonzero coupling parameters rescaled as  $t_{DA}, g_{D,A} \propto 1/\sqrt{\omega_c}$  at fixed mode volume. The curve labeled  $t_{DA}$  channel corresponds to the direct-transition-coupling case ( $t_{DA} \neq 0$ ,  $g_D = g_A = 0$ ), while the curve labeled  $g_{D,A}$  corresponds to the energy-fluctuation-coupling case ( $t_{DA} = 0$ ,  $g_D, g_A \neq 0$ ). The different resonance frequencies underscore the distinct physical mechanisms of the two coupling channels.

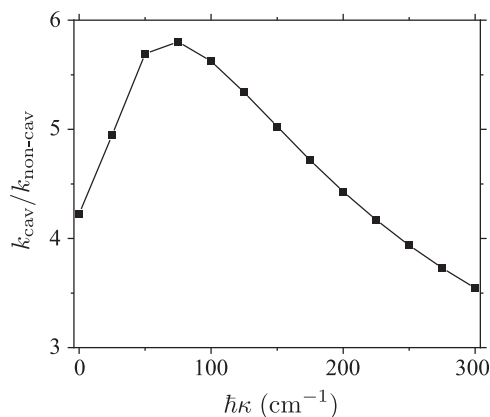
isolate the effect of cavity frequency from changes in coupling strength, we rescale the nonzero coupling parameters according to  $t_{DA}, g_{D,A} \propto 1/\sqrt{\omega_c}$  [see Eqs. (5)–(7)], keeping the effective light–matter interaction fixed at constant cavity mode volume  $\mathcal{V}$ . This normalization ensures that variations in the ET rate arise solely from energetic resonance conditions rather than from trivial changes in coupling magnitude.

Both channel-resolved cases exhibit clear resonance peaks where the ET rate is maximized, but the optimal frequencies differ significantly between the two mechanisms. For the curve labeled  $t_{DA}$  channel, the resonance occurs when the cavity frequency matches the effective energy gap between the donor and acceptor states. At this condition, the cavity mode is resonant with the electronic transition, enabling efficient cavity-mediated transfer through coherent emission and reabsorption of virtual photons. In contrast, for the curve labeled  $g_{D,A}$  channel, the resonance condition is more subtle, as it depends on the energetic overlap between cavity-shifted donor and acceptor potentials modulated by the reorganization energy and thermal fluctuations. The cavity effectively renormalizes the energetics of both states, and the optimal frequency reflects a balance between activation barrier reduction and thermal accessibility. These distinct resonance behaviors highlight the qualitatively different mechanisms by which the two coupling channels modify electron transfer: the  $t_{DA}$  channel opens a new coherent transfer pathway through direct cavity-mediated coupling, while the  $g_{D,A}$  channel reshapes the free energy landscape governing the transfer process.

In realistic experimental implementations, optical cavities have finite quality factors due to photon leakage into external electromagnetic modes. This cavity loss, characterized by a photon lifetime  $\tau_c$ , causes spectral broadening of the cavity resonance and introduces dissipation into the light–matter dynamics. To capture these effects, we extend our model by incorporating Lindblad dissipation into the quantum master equation for the reduced density operator  $\hat{\rho}$ ,

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + \frac{\kappa}{2}(2\hat{a}\hat{\rho}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}\hat{\rho} - \hat{\rho}\hat{a}^\dagger\hat{a}), \quad (15)$$

where  $\kappa = \tau_c^{-1}$  is the cavity loss rate and the Lindblad term describes Markovian photon leakage from the cavity mode. This dissipator models the irreversible decay of cavity photons while preserving the positivity and trace of the density operator, as required for a physically valid quantum evolution. Figure 6 reveals a non-monotonic dependence of the ET rate enhancement on the cavity loss rate  $\kappa$ . This behavior reflects a competition between two opposing effects. In the low-dissipation regime, increasing cavity loss actually enhances the ET rate. Here, dissipation plays a constructive role by broadening the cavity resonance, which relaxes stringent energy-matching requirements and enables fluctuation-assisted transport. This mechanism is analogous to environment-assisted quantum transport observed in other contexts, where moderate decoherence can facilitate incoherent hopping between states that would otherwise remain energetically misaligned.<sup>55–58</sup> The photon leakage effectively provides an additional pathway for energy dissipation that can help the system overcome activation barriers. However, in the high-dissipation regime, excessive cavity loss becomes detrimental. Strong damping suppresses the coherent light–matter dynamics necessary for polariton formation and cavity-mediated transfer. The



**FIG. 6.** ET rate enhancement  $k_{\text{cav}}/k_{\text{non-cav}}$  as a function of cavity loss rate  $\kappa$  for the direct transition coupling channel ( $t_{\text{DA}}$ ) with  $\lambda_0 = 50 \text{ cm}^{-1}$  and  $-\Delta G = 100 \text{ cm}^{-1}$ . The non-monotonic behavior reflects a competition between fluctuation-assisted transport in the low-dissipation regime and coherence suppression in the high-dissipation regime. The optimal enhancement occurs at intermediate loss rates where cavity-mediated coherent dynamics and dissipative broadening are balanced.

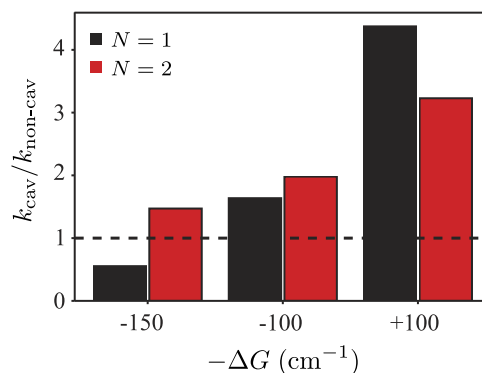
rapid photon decay prevents the buildup of coherent cavity excitation, essentially reverting the system toward the bare molecular limit. This inhibition resembles a quantum Zeno-like effect: frequent dissipative events disrupt the coherent evolution before it can facilitate electron transfer. The optimal cavity loss rate, corresponding to the peak in Fig. 6, represents a balance between these competing mechanisms: sufficient dissipation to enable flexible energy matching, but not so much as to destroy the coherent polariton dynamics underlying cavity-enhanced transfer.

The corresponding time-domain donor-population dynamics for different cavity-loss rates are shown in the [supplementary material](#) [Fig. S1(a)]. These results make clear that increasing cavity loss tends to damp the coherent oscillations visible in the direct-transition-coupling case of Fig. 2, because photon leakage suppresses sustained light-matter coherence. At the same time, this damping of oscillations does not preclude a moderate-loss enhancement of the effective ET rate, since intermediate cavity loss can still promote transfer through resonance broadening and fluctuation-assisted transport.

A distinctive feature of cavity QED is the emergence of collective effects when multiple emitters couple to a shared cavity mode. Whether such collective coupling can influence electron transfer—a fundamentally local process occurring at individual molecular sites—is a non-trivial question, especially when the per-molecule light-matter coupling strength is modest. The answer depends on whether collective polariton formation modifies the energy landscape and decoherence dynamics in ways that align favorably or unfavorably with the conditions for efficient ET. To investigate collective effects systematically, we compare systems with  $N_{\text{mol}} = 1$  and  $N_{\text{mol}} = 2$  molecules while maintaining fixed per-molecule coupling strength. This ensures that the light-matter interaction per molecule remains constant, allowing us to isolate purely collective phenomena arising from cooperative coupling to the same cavity mode. All molecules are initialized in their donor states with the cavity in the

vacuum state. In the absence of cavity coupling, ET occurs independently at each molecule, and the rate is naturally independent of  $N_{\text{mol}}$ . We neglect the dipole self-energy term in this analysis to focus on the essential collective physics.

Figure 7 displays the relative ET rate enhancement  $k_{\text{cav}}/k_{\text{non-cav}}$  for  $N_{\text{mol}} = 1$  and  $N_{\text{mol}} = 2$  across three different driving forces,  $-\Delta G$ . These numerically exact HEOM results provide small- $N$  benchmark evidence that cavity-modified ET can depend sensitively on the number of molecules coupled to the cavity, even at the smallest nontrivial ensemble size. At the same time, because only  $N_{\text{mol}} = 1$  and 2 are analyzed here, these results should be regarded as proof-of-principle evidence for parameter-dependent collectivity rather than as a definitive characterization of the large- $N$  limit. Within this small- $N$  benchmark, we identify three representative behaviors depending on the driving force: (i) An apparent positive collective trend ( $-\Delta G = -100 \text{ cm}^{-1}$ , center panel): Enhancement increases with molecular number, following  $k_{\text{non-cav}} < k_{\text{cav}}(N_{\text{mol}} = 1) < k_{\text{cav}}(N_{\text{mol}} = 2)$ . Collective coupling amplifies the cavity's beneficial influence on ET, with the two-molecule system exhibiting stronger rate enhancement than the single-molecule case. (ii) An apparent negative collective trend ( $-\Delta G = 100 \text{ cm}^{-1}$ , right panel): Enhancement decreases with molecular number, yielding  $k_{\text{non-cav}} < k_{\text{cav}}(N_{\text{mol}} = 2) < k_{\text{cav}}(N_{\text{mol}} = 1)$ . While both systems exhibit rate enhancement relative to the uncoupled baseline, collective coupling counterintuitively reduces the enhancement magnitude. The single molecule benefits more from cavity coupling than the two-molecule ensemble. (iii) A transition-like behavior ( $-\Delta G = -150 \text{ cm}^{-1}$ , left panel): The system changes from cavity-induced suppression to enhancement with increasing  $N_{\text{mol}}$ , following  $k_{\text{cav}}(N_{\text{mol}} = 1) < k_{\text{non-cav}} < k_{\text{cav}}(N_{\text{mol}} = 2)$ . For a single molecule, cavity coupling inhibits transfer below the uncoupled rate. However,



**FIG. 7.** Small- $N$  benchmark results for collective effects in cavity-modified ET for the direct transition coupling channel. Plotted is the rate enhancement  $k_{\text{cav}}/k_{\text{non-cav}}$ , comparing single-molecule ( $N_{\text{mol}} = 1$ , black) and two-molecule ( $N_{\text{mol}} = 2$ , red) systems at fixed per-molecule coupling strength for three driving forces: (center)  $-\Delta G = -100 \text{ cm}^{-1}$ , showing an apparent positive collective trend with  $k_{\text{non-cav}} < k_{\text{cav}}(N_{\text{mol}} = 1) < k_{\text{cav}}(N_{\text{mol}} = 2)$ ; (right)  $-\Delta G = 100 \text{ cm}^{-1}$ , showing an apparent negative collective trend with  $k_{\text{non-cav}} < k_{\text{cav}}(N_{\text{mol}} = 2) < k_{\text{cav}}(N_{\text{mol}} = 1)$ ; and (left)  $-\Delta G = -150 \text{ cm}^{-1}$ , showing transition-like behavior with  $k_{\text{cav}}(N_{\text{mol}} = 1) < k_{\text{non-cav}} < k_{\text{cav}}(N_{\text{mol}} = 2)$ . These numerically exact HEOM results demonstrate that cavity-induced collective effects can already emerge at the smallest nontrivial ensemble size, while their robustness in the large- $N$  limit remains to be established. Parameters:  $\lambda_0 = 50 \text{ cm}^{-1}$  and  $\hbar\omega_c = 100 \text{ cm}^{-1}$ .

adding a second molecule reverses this effect, restoring enhancement. This transition demonstrates that collective effects can qualitatively change the role of the cavity from inhibitor to facilitator. These results show that, already at small  $N_{\text{mol}}$ , the sign and magnitude of cavity-induced collective effects can depend sensitively on the driving force and resonance conditions.

The small- $N$  trends in Fig. 7 can be understood in terms of the interplay of two mechanisms associated with collective polariton formation. When  $N_{\text{mol}}$  molecules couple identically to a cavity mode, the effective light-matter coupling strength scales as  $\sqrt{N_{\text{mol}}}$ , producing a collective Rabi splitting that grows with ensemble size. This enhanced splitting can modify ET dynamics through complementary pathways. First, the larger Rabi splitting reshapes the polaritonic energy landscape, altering effective activation barriers and energy-matching conditions. Second, collective polaritons delocalized across multiple molecules can experience reduced coupling to local vibrational environments, which tends to enhance the dynamic polaron decoupling effect and protect coherent dynamics from decoherence. For the present  $N_{\text{mol}} = 1$  and 2 benchmarks, these competing effects can either favor or disfavor ET, depending on the driving force. Whether the positive or negative trends identified here remain robust at much larger  $N_{\text{mol}}$  is, however, an open question beyond the scope of the present work.

While our HEOM calculations for  $N_{\text{mol}} = 1$  and 2 provide rigorous benchmarks, they do not by themselves establish the asymptotic behavior of collective effects at much larger  $N_{\text{mol}}$ . Definitive assessment of the robustness of the positive and negative collective trends shown in Fig. 7 will require methods that remain accurate in the large- $N$  regime. Unfortunately, numerically exact quantum dynamics using HEOM becomes computationally prohibitive as Hilbert space dimensions grow exponentially with molecular number. A promising route forward is to combine these small- $N$  HEOM benchmarks with semiclassical approaches such as the truncated Wigner approximation (TWA), which can describe molecular polariton dynamics efficiently in the large- $N$  limit.<sup>50,59</sup>

The collective effects studied here connect to broader phenomena in polaritonic chemistry and condensed matter physics, including super-radiant reaction enhancement through constructive interference between spatially separated transfer pathways in molecular ensembles<sup>49</sup> and Bose enhancement of transport from polariton Bose-Einstein condensation under strong collective coupling.<sup>60</sup> These diverse manifestations underscore the rich physics accessible when multiple quantum emitters coherently share a photonic environment, revealing collective light-matter coupling as a multifaceted control mechanism whose influence depends critically on the interplay between polaritonic energy structure, decoherence dynamics, and molecular reaction energetics.

### C. Generalized model: Electronic-vibrational-photonic coupling

The minimal model discussed thus far neglects an important physical effect: the dependence of molecular dipole moments on nuclear coordinates. In realistic molecular systems, electronic charge distributions, and hence dipole moments, are modulated by vibrational motion. When a molecule vibrates, the spatial overlap between donor and acceptor electronic wavefunctions changes, causing the transition dipole moment  $\mu_{\text{DA}}$  to vary with nuclear

displacement. Similarly, the diagonal dipole moments  $\mu_{\text{DD}}$  and  $\mu_{\text{AA}}$  are also nuclear-coordinate-dependent. Incorporating this coordinate dependence into the cavity coupling leads to a qualitatively new interaction mechanism. Expanding the dipole moments to linear order in nuclear displacements and projecting onto the donor-acceptor basis yields a three-body interaction Hamiltonian,

$$\hat{H}_{\text{el-vib-ph}} = \eta (\hat{a} + \hat{a}^\dagger) [ |D\rangle\langle D| + |A\rangle\langle A| + |D\rangle\langle A| + |A\rangle\langle D| ] \sum_j \lambda_j (\hat{b}_j + \hat{b}_j^\dagger), \quad (16)$$

where  $\eta$  quantifies the strength of this electronic-vibrational-photonic coupling. This term simultaneously involves the cavity field operator ( $\hat{a} + \hat{a}^\dagger$ ), electronic state projectors, and vibrational bath coordinates ( $\hat{b}_j + \hat{b}_j^\dagger$ ), creating a fundamentally nonlinear interaction that cannot be factorized into pairwise couplings.

Physically, Eq. (16) describes a reciprocal modulation mechanism: vibrational motion alters the effective light-matter coupling strength, while the cavity field simultaneously influences the electronic-vibrational interaction. For instance, a vibrational displacement along coordinates coupled to the electronic transition can transiently enhance or suppress the transition dipole moment, thereby modulating the strength of cavity-mediated transfer. Conversely, photons in the cavity mode can modify the potential energy surfaces experienced by vibrations, effectively renormalizing vibronic coupling constants. This correlated interplay of electronic, vibrational, and photonic degrees of freedom creates a fundamentally nonlinear interaction that can generate multiple competing transfer pathways, leading to rich dynamical behavior absent in models where cavity and vibrational couplings remain independent.

To make the problem tractable while capturing the essential physics, we adopt several approximations. First, we truncate the dipole expansion at linear order in nuclear coordinates, which is justified when zero-point and thermal vibrational amplitudes remain small compared to the characteristic length scales over which the electronic wavefunctions vary. Second, we assume equal coupling strengths for all four electronic operators in Eq. (16). This assumption is introduced as a symmetry-based simplification to reduce the parameter space and to reveal the qualitative consequences of the three-body electronic-vibrational-photonic interaction. It is not meant to imply that the interfering pathways are controlled only by phases. In general, interference is determined by both amplitudes and phases, and relaxing the equal-coupling assumption would modify the quantitative weights of the competing pathways and may shift the positions and heights of the maxima and minima in the ET-rate profiles. Nevertheless, the central qualitative message of the present analysis—namely, that the three-body term introduces multiple competing pathways and can generate interference-driven non-monotonic ET behavior—does not rely on all amplitudes being equal.

Third, we neglect the dipole self-energy (DSE) contributions associated with this coordinate-dependent term. Here, we emphasize that the present analysis is restricted to a parameter regime chosen to remain outside the ultrastrong coupling limit, in which the DSE is expected to qualitatively modify the dynamics; in particular, we consider  $\eta \leq 0.3$ . We, therefore, treat the omission of the DSE

term as a modeling approximation adopted to keep the generalized three-body problem tractable and to isolate the qualitative role of the coordinate-dependent light–matter coupling. While the DSE term is essential for full gauge consistency and can become quantitatively important in the ultrastrong-coupling regime, the present calculations are intended as an exploratory study of the interference physics in a parameter regime where the three-body term is not assumed to place the system deep into a DSE-dominated regime.

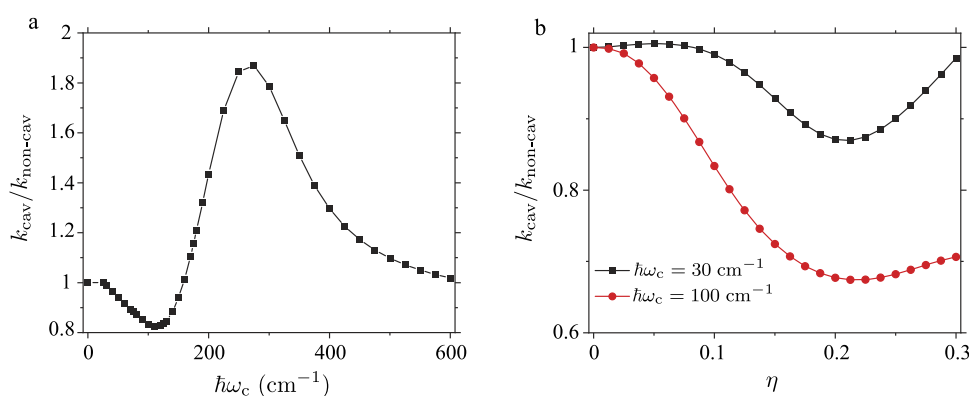
Finally, we assume that the spectral content of the three-body coupling parallels that of the standard vibronic coupling, characterized by the same spectral density  $J(\omega)$ . This implies that the vibrational modes that couple the donor and acceptor state energies to the bath also modulate the dipole moments with proportional strengths. While this assumption simplifies the analysis, it represents a physically reasonable scenario where the same nuclear coordinates that determine electronic energy gaps also control charge redistribution and hence dipole moments.

In principle, entanglement-based quantities such as reduced-subsystem von Neumann entropy, mutual information, or logarithmic negativity for selected bipartitions could provide additional insight into the correlated electronic–vibrational–photonic dynamics. However, the key issue is not merely the evaluation of such quantities, but rather how to relate them in a clear and physically meaningful way to the specific interfering transfer pathways discussed here. Establishing such a connection is highly nontrivial and is left for future studies.

The introduction of three-body electronic–vibrational–photonic coupling fundamentally alters how ET enhancement depends on cavity parameters. To isolate the effects of this interaction, we set the standard light–matter couplings to zero ( $t_{DA} = g_{DA} = 0$ ) so that cavity modification arises solely through the coordinate-dependent term characterized by  $\eta$ . Figure 8 displays the ET rate enhancement as a function of (a) the cavity frequency  $\omega_c$  at fixed  $\eta$  and (b) three-body coupling strength  $\eta$  for two different cavity frequencies, with the molecular environment modeled as a Drude–Lorentz bath. Both dependencies exhibit strikingly different

behavior compared to the minimal model. Instead of the simple resonance peak observed in the  $\omega_c$  dependence (Fig. 5) or the monotonic-to-saturating trend in the coupling strength dependence (Fig. 4), the three-body interaction induces pronounced oscillatory, non-monotonic behavior in both parameter scans. The ET rate alternates between enhancement and suppression as  $\omega_c$  or  $\eta$  varies, exhibiting multiple maxima and minima across the explored parameter ranges. At certain values, the cavity coupling enhances transfer beyond the uncoupled baseline; at others, it suppresses transfer below this baseline despite the presence of light–matter interaction.

This non-monotonic, oscillatory behavior is consistent with quantum interference between multiple competing pathways generated by the three-body coupling. In the presence of this interaction, electron transfer can proceed through several distinct channels: (i) direct electronic tunneling via  $H_{DA}$ ; (ii) vibrationally assisted transfer, where bath modes facilitate electronic transitions; and (iii) cavity–vibration-mediated transfer enabled by  $\eta$ , where photon exchange coupled with nuclear motion creates new transfer routes. Each pathway contributes a characteristic amplitude and phase determined by the energy matching condition, coupling strengths, and bath dynamics. The overall transfer rate reflects the quantum superposition of these pathways. The oscillations arise because varying  $\omega_c$  or  $\eta$  changes both the relative amplitudes and the relative phases of the competing pathways. When pathways combine constructively, the transfer rate is enhanced beyond what a single channel would achieve in isolation, whereas destructive combination suppresses the rate below the uncoupled limit. Our interpretation is thus based on the non-monotonic dependence of the ET rate on  $\omega_c$  and  $\eta$ , together with the structure of the three-body interaction. A more direct connection between entanglement-based observables and these interfering pathways would be very interesting but is left for future studies. The precise conditions for constructive vs destructive interference depend sensitively on multiple factors: the cavity frequency sets the energy scale for virtual photon exchange, the three-body coupling strength  $\eta$  determines the amplitude of



**FIG. 8.** Oscillatory quantum interference in cavity-modified ET with three-body electronic–vibrational–photonic coupling for a Drude–Lorentz environment. ET rate enhancement  $k_{\text{cav}}/k_{\text{non-cav}}$  as a function of (a) cavity frequency  $\omega_c$  at fixed  $\eta = 0.1$  and (b) three-body coupling strength  $\eta$  at two cavity frequencies: black,  $\hbar\omega_c = 30 \text{ cm}^{-1}$  and red,  $\hbar\omega_c = 100 \text{ cm}^{-1}$ . Standard light–matter couplings are turned off ( $t_{DA} = g_{DA} = 0$ ) to isolate the three-body effect. The oscillatory, non-monotonic dependencies contrast sharply with the simple resonance and saturation behaviors in the minimal model (cf. Figs. 5 and 4), reflecting quantum interference between direct molecular transfer, vibrationally assisted transfer, and cavity–vibration-mediated pathways. Parameters:  $\lambda_0 = 50 \text{ cm}^{-1}$  and  $-\Delta G = 100 \text{ cm}^{-1}$ .

cavity–vibration-mediated pathways, and the bath spectral density governs how nuclear motion correlates with electronic transitions. This interference-driven landscape contrasts fundamentally with the minimal cavity–electronic model, where optimization is straightforward: tune the cavity to resonance and increase coupling until saturation. With the three-body interaction, optimal ET enhancement requires navigating a complex multidimensional parameter space to identify constructive interference regimes. This suggests new design principles for cavity-controlled chemistry: rather than simply maximizing coupling strength or matching a resonance condition, one must engineer the relative phases of multiple quantum pathways to achieve desired reactivity outcomes.

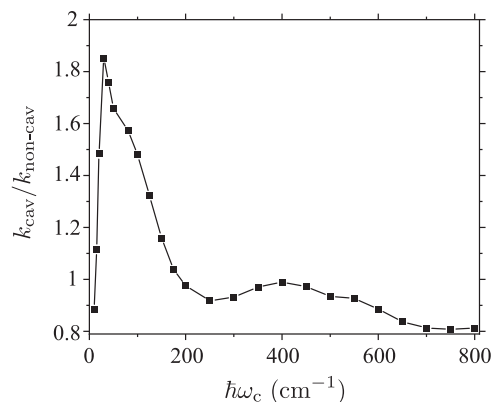
Representative donor–population dynamics for the generalized vibronic–polariton case with a Drude–Lorentz bath are shown in the [supplementary material](#) [Fig. 1S(b)] for several values of the three-body coupling strength  $\eta$ . In contrast to the direct electronic–photonic coupling case shown in Fig. 2, the short-time oscillations for  $\eta \leq 0.3$  are much less pronounced here. However, the deviation of the population dynamics from a simple monoexponential relaxation becomes increasingly significant as  $\eta$  increases. This provides a time-domain signature of the more complex multichannel dynamics induced by the three-body electronic–vibrational–photonic interaction.

To explore how the three-body interaction behaves when a high-frequency intramolecular vibrational mode is involved, we employ a spectral density structure that separates the roles of different vibrational modes. In particular, we assign an underdamped spectral density to the three-body interaction term while retaining the Drude–Lorentz form for the standard vibronic coupling. The underdamped spectral density

$$J_{\text{UD}}(\omega) = \frac{2\lambda_2^2 W_2 \omega}{(\omega^2 - \omega_0^2)^2 + W_2^2 \omega^2} \quad (17)$$

represents a localized vibrational resonance centered at frequency  $\omega_0 = 500 \text{ cm}^{-1}$  with coupling strength  $\hbar\lambda_2 = [1420 \text{ cm}^{-1}]^{3/2}$  and damping rate  $W_2 = \tau_d^{-1}$ , where  $\tau_d = 100 \text{ fs}$ . Since  $\eta$  serves as an overall amplitude factor that is now absorbed into the spectral density normalization, we set  $\eta = 1$  in this analysis. This model captures a physically motivated scenario: high-frequency intramolecular vibrations modulate the molecular transition dipole moment and, thus, couple to the cavity field through the three-body term, while low-frequency intermolecular vibrations described by the Drude–Lorentz bath primarily couple to the electronic state energies through standard vibronic interactions. The narrow linewidth of the underdamped mode (set by  $W_2$ ) creates a well-defined spectral feature that, in simple resonance models, would be expected to produce a pronounced peak when matched with the cavity frequency.

Figure 9 displays the ET rate enhancement  $k_{\text{cav}}/k_{\text{non-cav}}$  as a function of cavity frequency. In a conventional cavity–vibration coupling scenario, one would anticipate a resonance feature when the cavity frequency approaches the underdamped vibrational mode frequency ( $\hbar\omega_c \simeq \hbar\omega_0 = 500 \text{ cm}^{-1}$ ), corresponding to efficient resonant energy exchange between cavity photons and nuclear motion. However, the frequency dependence obtained in the present model deviates markedly from this simple expectation. Instead of a single resonance peak near  $\hbar\omega_c \simeq \hbar\omega_0$ , the enhancement exhibits a complex multi-featured profile, whose primary maximum appears at



**FIG. 9.** ET rate enhancement  $k_{\text{cav}}/k_{\text{non-cav}}$  as a function of cavity frequency  $\omega_c$  for a system in which a high-frequency underdamped vibrational mode ( $\omega_0 = 500 \text{ cm}^{-1}$ ,  $\hbar\lambda_2 = [1420 \text{ cm}^{-1}]^{3/2}$ ,  $\tau_d = 100 \text{ fs}$ ) couples through the three-body interaction to the cavity field, while a Drude–Lorentz bath ( $\lambda_0 = 50 \text{ cm}^{-1}$ ,  $\tau_b = 100 \text{ fs}$ ) couples to the molecular electronic states. Within the present linearized dipole-expansion model, the absence of a simple resonance peak at  $\hbar\omega_c \simeq \hbar\omega_0$  and the appearance of a strong low-frequency maximum near  $\hbar\omega_c \simeq 30 \text{ cm}^{-1}$  indicate that the frequency dependence is governed by interference among multiple coupled transfer pathways rather than by bare vibrational resonance alone. The precise position and magnitude of this low-frequency maximum may depend quantitatively on the linear-dipole approximation used here. Other parameters:  $-\Delta G = 100 \text{ cm}^{-1}$ .

$\hbar\omega_c \simeq 30 \text{ cm}^{-1}$ , followed by an oscillatory tail extending to higher frequencies with alternating regions of enhancement and suppression. Remarkably, certain frequency ranges show  $k_{\text{cav}}/k_{\text{non-cav}} < 1$ , indicating that the cavity coupling actually suppresses ET below the uncoupled baseline despite nominally providing an additional pathway for energy redistribution.

Within the present linearized dipole-expansion model, we do not interpret the strong low-frequency feature near  $\hbar\omega_c \simeq 30 \text{ cm}^{-1}$  as a simple resonance with the bare underdamped vibrational mode. Rather, we interpret it as a constructive-interference feature emerging from the coupled electronic–vibrational–photonic dynamics generated by the nonlinear three-body interaction in combination with the bath-assisted ET dynamics. In this view, the cavity-frequency dependence is governed by the combined pathway structure of the full model rather than by the bare vibrational resonance alone. The large downward shift of the dominant maximum relative to  $\hbar\omega_0$ , therefore, should not be read as an anomalous renormalized single-mode resonance but instead as a model-dependent consequence of interference among the available transfer pathways in the coupled electronic–vibrational–photonic landscape.

At the same time, we emphasize that this interpretation is made within the present approximation in which the dipole moments are expanded only to linear order in nuclear coordinates. We have not carried out a separate nonlinear-dipole analysis, and therefore we cannot make a definitive statement about how the precise position or magnitude of the low-frequency maximum would change when higher-order dipole-coordinate terms are included. Accordingly, the peak near  $\hbar\omega_c \simeq 30 \text{ cm}^{-1}$  should be viewed as a feature of the present model rather than as a universal prediction for all vibronic–polariton systems.

This nonresonant, oscillatory structure—similar to the behavior observed with the Drude–Lorentz spectral density for the three-body interaction [Fig. 8(a)]—is consistent with an interference-based interpretation rather than with a simple description based solely on classical resonant energy matching. The absence of a pronounced resonance at  $\hbar\omega_c \approx \hbar\omega_0$  indicates that the contribution of the underdamped vibrational mode cannot be understood in isolation as a single mode resonantly exchanging energy quanta with the cavity. Rather, within the present model, its effect is strongly mixed with the other system degrees of freedom through the nonlinear three-body term. The electronic states, continuous Drude–Lorentz bath modes, discrete high-frequency vibrational modes, and cavity photons, therefore, form a strongly correlated dynamical system in which conventional distinctions between resonant and off-resonant contributions become blurred. Under this vibronic polariton regime, the ET dynamics are most naturally interpreted in terms of collective interference among the available pathways in the coupled electronic–vibrational–photonic landscape.

#### IV. CONCLUSION

We have investigated electron transfer dynamics in cavity-coupled molecular systems using numerically exact HEOM simulations, revealing both fundamental insights and control mechanisms for polaritonic chemistry. Beginning with the minimal model, in which cavity fields couple exclusively to electronic degrees of freedom, we examined two distinct light–matter coupling channels: direct transition coupling ( $t_{DA}$ ) and energy-fluctuation coupling ( $g_{DA}$ ). Both channels enhance ET rates across wide ranges of driving forces and reorganization energies, with direct transition coupling generally providing stronger enhancement by creating coherent transfer pathways through virtual photon exchange. This acceleration is accompanied by extended coherence times, consistent with the dynamic polaron decoupling effect whereby strong light–matter coupling suppresses vibronic decoherence. The ET rate exhibits resonance behavior in both channels, although optimal cavity frequencies differ due to their distinct physical mechanisms: the  $t_{DA}$  channel resonates when the cavity matches the effective electronic transition energy, while the  $g_{DA}$  channel's resonance reflects optimal modulation of the activation barrier.

By comparing HEOM results against perturbative predictions from Fermi's golden rule (FGR), we found that while FGR captures qualitative trends, it fails quantitatively in the strong coupling regime: the predicted quadratic scaling of the rate with coupling strength breaks down beyond a threshold, and even in the moderate coupling regime, where quadratic scaling approximately holds, the prefactor differs significantly from the perturbative prediction. This saturation behavior underscores the necessity of non-perturbative methods for accurate quantitative predictions in the strong coupling limit. We identified additional phenomena within the minimal model framework. Collective effects emerge when multiple molecules couple to a single cavity mode: the ET rate changes with molecular number even at fixed per-molecule coupling strength, exhibiting parameter-dependent enhancement or suppression depending on how collective Rabi splitting and delocalization-induced decoherence protection align with energy matching

conditions. Cavity loss introduces competing mechanisms: moderate dissipation enhances transfer through fluctuation-assisted processes and resonance broadening, while excessive loss destroys the coherent polariton dynamics underlying cavity-mediated enhancement, resulting in non-monotonic rate dependence on the photon decay rate.

Our generalized model, incorporating the nuclear-coordinate dependence of transition dipole moments, unveils qualitatively new physics. This extension introduces a three-body electronic–vibrational–photonic interaction that fundamentally alters the nature of cavity control. Rather than the monotonic or saturating behaviors of the minimal model, the three-body coupling induces oscillatory, non-monotonic dependence of ET rates on both cavity frequency and coupling strength. These oscillations are consistent with quantum interference between multiple transfer pathways, whose relative weights and phases vary with system parameters. We demonstrated these interference-driven dynamics for both Drude–Lorentz environments representing continuous low-frequency modes and composite spectral densities including discrete high-frequency vibrations. Remarkably, even when a well-defined intramolecular mode couples through the three-body term, the ET enhancement exhibits complex multi-featured frequency dependence with the primary maximum shifted far from the vibrational resonance and followed by an oscillatory tail. This absence of simple resonance behavior confirms that nonlinear quantum interference, rather than conventional energy matching, governs the dynamics.

These findings establish that optical cavities provide a dual control mechanism for molecular reactivity: tuning electronic energy gaps via excitonic polaritons and modulating reaction pathways through vibronic polaritons. The oscillatory interference effects we identify suggest new strategies for cavity-mediated chemical control that exploit quantum coherence and many-body correlations, opening avenues for designing cavity-enhanced molecular devices and catalysts.

#### SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for representative time-domain donor-population dynamics for different values of  $\kappa$  and  $\eta$  (Fig. S1).

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#### AUTHOR DECLARATIONS

##### Conflict of Interest

The authors have no conflicts to disclose.

## Author Contributions

**Takumi Hidaka:** Data curation (equal); Formal analysis (supporting); Investigation (equal); Writing – original draft (supporting); Writing – review & editing (supporting). **Tomohiro Fukushima:** Formal analysis (supporting); Funding acquisition (supporting); Writing – review & editing (supporting). **Nguyen Thanh Phuc:** Conceptualization (lead); Data curation (equal); Formal analysis (lead); Funding acquisition (lead); Investigation (equal); Writing – original draft (lead); Writing – review & editing (lead).

## DATA AVAILABILITY

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

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