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Cavity-controlled chemistry in molecular ensembles

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The demonstration of strong and ultrastrong coupling regimes of cavity QED with polyatomic molecules has opened new routes to control chemical dynamics at the nanoscale. We show that strong resonant coupling of a cavity field with an electronic transition can effectively decouple collective electronic and nuclear degrees of freedom in a disordered molecular ensemble, even for molecules with high-frequency quantum vibrational modes having strong electron-vibration interactions. This type of polaron decoupling can be used to control chemical reactions. We show that the rate of electron transfer reactions in a cavity can be orders of magnitude larger than in free space, for a wide class of organic molecular species.

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The experimental realization of the strong [1–9] and ultrastrong [10–15] coupling regimes of cavity quantum electrodynamics (QED) with organic matter in optical cavities has stimulated interest in the development of hybrid quantum devices with enhanced energy and electron transport properties [16–19], tunable nonlinear optical response [20], and novel optomechanics [21]. The strong resonant coupling between a cavity mode and electronic [22, 23] or vibrational [24–27] molecular transitions is well-known to result in polariton formation [23, 28–32].

Recent experiments have shown the potential of cavity fields to alter chemical reactivity by manipulation of the reaction energy landscape [33], although the role of the coupling between nuclear and electronic degrees of freedom in an optical cavity is still not well understood. This topic has only recently been addressed for molecular aggregates [34] and single molecules [35]. Understanding the role that a cavity field can play in altering electron-vibration dynamics would help in developing tools for controlling a broad range of chemical reactions using cavity QED.

In this work, we show that the strong collective interaction of a molecular ensemble with the vacuum field of an optical cavity can in fact modify the nuclear dynamics of individual molecules in the ensemble. In free space, when an electron is optically excited, the nuclei in a molecule rearrange to a configuration that minimizes the electronic energy in the excited state. The excited nuclear configuration is typically different from the ground state equilibrium configuration. We find that in an optical cavity that can exchange energy with a collective electronic state faster than the timescales associated with nuclear motions, reorganization of the nuclei upon excitation is strongly suppressed. This effect is a type of polaron decoupling involving collective electronic degrees of freedom that are symmetric with respect to molecular permutations. Polaron decoupling can be understood as an extension of the concept of cavity-induced motional narrowing [36] to vibronic interactions, and resembles phenomena found in the nuclear dynamics of molecular junctions [37–40]. We show that the decoupling mechanism is robust with respect to energetic disorder in molecular ensembles.

The effective manipulation of intramolecular nuclear dynamics can be used to control chemical reactivity, for example, by controlling the reorganization energy in Marcus electron transfer reactions [41]. In order to illustrate this possibility, we show that strong cavity-matter coupling can significantly enhance the rate of intramolecular electron transfer (ET) reactions within individual molecules in the ensemble.

Polyatomic molecules with $z$ atoms have $3z - 6$ normal modes of vibration, each mode involving the coupled motion of multiple atoms within a molecule. Often only a few of these modes are needed to describe a chemical reaction [42]. These are known as the reaction coordinates (RC), associated with a mass-weighted superposition of the form $q_k = \sum_i \alpha_{ik} \sqrt{m_i} x_i$, where $k$ is a mode index and $x_i$ is the displacement of the $i$-th atom from the potential minimum. Each atomic displacement has a mass-weighted momentum $p_i/\sqrt{m_i}$. For a single reaction coordinate $q$ in the harmonic approximation for the potential, we can represent the ground state energy as $H_0(q) = (p^2 + \omega_q^2 q^2)/2$, where $\omega_q$ is the frequency of the intramolecular vibration and $p$ is the normal mode momentum. The nuclei have a reference equilibrium configuration $q_0 = 0$ in the ground state $|g\rangle$. The equilibrium nuclear configuration in an excited electronic state is however different from the ground state configuration. This difference is a manifestation of electron-vibration coupling, or vibronic coupling. In the harmonic approximation, the nuclear potential in an excited state $|e\rangle$ is given by

$$H_e(q) = \omega_e + \frac{1}{2} \left[ p^2 + \omega_q^2 (q - q_0^{(e)})^2 \right],$$

where $\omega_e$ is the electronic energy and $q_0^{(e)}$ is a state-dependent shift that quantifies the degree of vibronic coupling. We set $\hbar = 1$ throughout and assume that the vibrational frequency is the same in all electronic states. In Fig. 1a, we show the nuclear potentials for a molecule with a ground state $|g\rangle$ centered at $q_0 = 0$, as well as
obtained from the unshifted ground state oscillator mode states of the shifted harmonic potential are denoted by a similar Huang-Rhys factor $\lambda$. A similar definition holds for state $a$.

The nuclear displacement operator and the cavity field $\hat{a}$ couple to the transition $|g\rangle \leftrightarrow |e\rangle$ with a detuning $\Delta_e$ and Rabi frequency $\Omega_e$. For large enough $\Omega_e$, the cavity effectively shifts the potential minimum in state $|e\rangle$ to coincide with $|g\rangle$ (right grey arrow). State $|f\rangle$ does not couple to the cavity. Panel (b): Cavity-dressed spectrum for an ensemble of $N$ molecules with vibronic coupling, showing the splitting of the permutation-symmetric collective dressed states $|\pm, \tilde{m}\rangle$ from the cavity-free polaron eigensates $\mathcal{Q}|\Psi_N\rangle$. $\omega_v$ is the vibrational frequency.

Excited states $|e\rangle$ and $|f\rangle$, centered on opposite sides of the ground state minimum. This nuclear arrangement is relevant to describe electron transfer in substituted biphenyls [43, 44], where the RC represents a torsional angle between the electron donor and acceptor groups. In Fig. 1a, we also represent a quantized cavity mode $\hat{a}$ that induces Rabi oscillations between states $|g\rangle$ and $|e\rangle$ at frequency $\Omega_e$ with detuning $|\Delta_e| \ll \Omega_e$.

Shifted harmonic oscillator modes $\hat{b}$ for state $|e\rangle$ can be obtained from the unshifted ground state oscillator mode $b$ by a displacement along the RC, so that $\hat{b} = b + \lambda_e [45]$. A similar definition holds for state $|f\rangle$. The dimensionless Huang-Rhys factor $\lambda^2 = (\omega_v/2) \langle \delta(\varepsilon) \rangle^2$ characterizes the strength of vibronic coupling. The vibrational eigenstates of the shifted harmonic potential are denoted by $|\tilde{m}\rangle = \mathcal{D}(\lambda_e)|m\rangle$, where $\mathcal{D}(\lambda_e) = \exp[\lambda_e(b^\dagger - b)]$ is the nuclear displacement operator and $|m\rangle$ is a vibrational eigenstate for the reference mode $b$.

We are interested in the dynamics of an ensemble of $N$ identical molecules interacting with a single quantized electromagnetic mode of an optical cavity, having annihilation operator $\hat{a}$. The many-body Hamiltonian for the ensemble can be written in the interaction picture as

$$
\mathcal{H}_N = \omega_e \sum_{\nu} b^\dagger_{\nu} b_{\nu} + \sum_{\alpha\beta\nu} \left[ \delta_{\alpha\beta}\Delta + g_{\alpha\beta}\nu b^\dagger_{\nu} b^\dagger_{\nu} \right] |\alpha\rangle \langle \beta| + \sqrt{N} \left( \frac{\Omega_e}{2} \right) (|a\rangle \langle G| \hat{a} + |G\rangle \langle a| \hat{a}^\dagger),
$$

where $|G\rangle = |g_1, g_2, \ldots, g_N\rangle$ is the ensemble ground state, $|\alpha\rangle = \sum_\nu u_{\alpha\nu} |e\rangle$ one-excitation states and $b^\dagger_{\nu} = \sum_\nu c_{\nu\beta} b^\dagger_{\nu}$ creates a phonon in mode $\nu$. The detuning from the cavity frequency $\Delta = \Delta_c + \omega_v \lambda^2_e$, with $\Delta_c = \omega_c - \omega_c$ being the detuning from the zero-phonon line (0-0) transition and $\omega_v$ is the single-molecule Rabi frequency. We assume that $|\Delta_c|/\Omega_e \ll 1$. Other excited states (for example, $|f\rangle$ in Fig. 1a) are far detuned or weakly coupled to the cavity field and cannot exchange energy with the confined mode over the timescales of interest.

The electron-vibration coupling constant in eq. (2) is given by $g_{\alpha\beta}^\nu = \lambda_e \omega_v \sum_\nu u_{\alpha\nu}^* u_{\beta\nu}$. By defining the $\nu = 0$ phonon mode to be totally-symmetric with respect to particle permutations, i.e., $c_{0\alpha} = N^{-1/2}$, we have $g_{\alpha\beta}^{\nu=0} = \delta_{\alpha,\beta} \lambda_e \omega_v / \sqrt{N}$. In other words, the permutation-symmetric phonon mode does not couple different collective electronic states.

We refer to Hamiltonian $\mathcal{H}_N$ in eq. (2) as a Holstein-Jaynes-Cummings (HJC) model. It extends the model used in Ref. [35] to treat many particles with quantized molecular vibrations. In free space, we can set $\Omega_e \rightarrow 0$ and $\Delta_e \rightarrow \omega_v$ to recover a standard Holstein model with optical phonons [46], which is used to describe small polaron dynamics [45–47]. It is straightforward to generalize eq. (2) to include direct long-range interactions between molecules and energetic disorder. For an ensemble with translational symmetry in a lattice, we identify the mode indices $\alpha$ and $\nu$ with the quasi-momenta $k$ and $\mathbf{q}$ of electronic and phonon excitations, respectively. We use this $(k, \mathbf{q})$ lattice representation below for numerical diagonalization of eq. (2).

The cavity field profile is assumed to be constant over the volume occupied by the molecular ensemble. Therefore, the cavity mode can exchange energy efficiently only with the permutation-symmetric electronic state $|\alpha\rangle = \sum_\nu |e\rangle / \sqrt{N}$ (second line eq. (2)), with a size-enhanced Rabi frequency $\sqrt{N}\Omega_e$. We show in the Supplementary Material (SM) that we can exploit the selection of permutation-symmetric electronic states by the cavity to partition the electronic Hilbert space into a symmetric subspace $\mathcal{P} = |G\rangle \langle G| + |\alpha\rangle \langle \alpha|$ and a non-symmetric manifold $\mathcal{Q} = 1_N - \mathcal{P}$, where $1_N$ is the many-body identity. Equation (2) can be projected into these orthogonal manifolds to give

$$
\mathcal{H}_N = \mathcal{P}^\dagger \mathcal{H}_N \mathcal{P} + \mathcal{Q}^\dagger \mathcal{H}_N \mathcal{Q} + \mathcal{P}^\dagger \mathcal{H}_N \mathcal{Q} + \text{H.c.} \quad (3)
$$

The specific forms for each term in eq. (3) are given in the SM.

Electron-vibration coupling in the $\mathcal{P}$ manifold involves only the symmetric phonon ($\nu = 0$) with coupling constant $g_{\nu=0} = \lambda_e \omega_v / \sqrt{N}$. Vibronic coupling in the symmetric mode is suppressed by a factor of $1/\sqrt{N}$ with respect to single-molecule vibronic coupling, leading to an effective shift of the potential minima in excited state $|e\rangle$ in Fig. 1a towards the ground state minimum [34]. A similar idea could be used to interpret the single mo-
We illustrate the phenomenon of polaron decoupling in Fig. 2. We quantify the degree of vibronic decoupling in the eigenstates of the HJC model by the squared-overlap $P_0 \equiv |\langle \Phi_0 | \psi_-; m = 0 \rangle |^2$, where $|\Phi_0\rangle$ is the lowest polaronic eigenstate of $\mathcal{H}_N$ for a resonant cavity ($\Delta_c = 0$), and $|\psi_-; m = 0 \rangle \{0\}_\nu\rangle$ is defined in eq. (4) for $\lambda_c = 0$. As we mentioned above, periodic boundary conditions are used to represent collective electronic and vibrational states, including up to six vibrational quanta in the symmetric mode $b_0$ and up to two in the non-symmetric modes $b_\nu \neq 0$. We find that the squared-overlap satisfies $P_0 \leq \exp[-\lambda^2_c/4N]$ (see SM for a derivation). The upper bound corresponds an effective Franck-Condon overlap with Huang-Rhys factor $\lambda^2_c/4N$ between the collective nuclear states in state $|\alpha_0\rangle$ and those in state $|G\rangle$. This overlap becomes exponentially close to unity in the limit $N \gg \lambda^2_c$. The nuclear configuration of the collective excited electronic state $|\alpha_0\rangle$ is thus the same as the ground state equilibrium configuration, for all phonon modes $\nu$. In other words, when the collective Rabi oscillation period is shorter than the timescales for vibrational motion, the electron can exchange energy with the cavity mode many times before the nuclei have time to reorganize their configuration to the excited state potential. In practice, it may be challenging to reach this regime [48], although Rabi oscillation periods as fast as 5.9 fs ($\sqrt{N}\omega_c = 700$ meV) have been reported [10].

We now go beyond the restriction of identical molecules and consider an excited state energy $\omega_0(r_i)$ that depends on the position of the molecule $r_i$ in the ensemble. This type of static disorder in organic systems is typically taken into account by assuming that $\omega_0(r_i)$ has a Gaussian distribution with standard deviation $\sigma$ [34, 49]. For a linear array with $N = 10$ molecules, we show in Fig. 2b that the lowest eigenstate $|\Phi_0\rangle$ of the HJC Hamiltonian $\mathcal{H}_N$ with random detunings $\Delta_c(r_i)$ is accurately given by $|\Phi_0\rangle = \exp[-\lambda^2_c/4N]$ as the collective Rabi frequency exceeds the disorder strength ($\sqrt{N}\omega_c \gg \sigma$). In this limit, the upper bound for $P_0$ becomes tight for all disorder realizations, as observed by the narrowing of the distribution in Fig. 2b.

Having described polaron decoupling by energetic isolation of the permutation-symmetric $\mathcal{P}$-manifold, we now consider its effect on non-adiabatic unimolecular electron transfer (ET) reactions. In ET reactions, an excess electron is transferred from a donor (D) to an acceptor (A) group within a molecule. The coherent transfer rate $V$ is proportional to the orbital overlap between the D and A groups [41, 45]. For non-adiabatic ET reactions we have $V/h \sim \omega_0$.

The relative energy between donor and acceptor vibronic levels $\Delta E \equiv \omega_{DA} + (m_D - m_A)\omega_0$ is known as the driving force of an ET reaction [45]. $\omega_{DA} = \omega_D - \omega_A$ is the electronic transition frequency and $(m_D - m_A)\omega_0$ the vibrational transition frequency for the D-A pair. The reaction rate can be written using linear response theory...
Rabi splitting the energy of the upper dressed donor state \( \omega \) by eq. (4). For a vibrational frequency \( \omega_v \), states undergo polaron decoupling and can be represented for experimentally accessible Rabi frequencies along the reaction coordinate, significant polaron decoupling is related to polaron decoupling of the donor electronic state. As we discussed above, the collective coupling of donor groups to the same cavity mode effectively decouples the nuclear and the electronic modes.

We consider a cavity-driven ET reaction in an ensemble of \( N \) donor-acceptor complexes. The state \( |e\rangle \) from Fig. 1 takes the role of the donor and state \( |f\rangle \) becomes the acceptor. Outside the cavity, the ET reaction channel \( |e\rangle \rightarrow |f\rangle \) is strongly suppressed when \( \Delta E \) is away from a vibrational resonance between the donor and acceptor potentials. Inside the cavity, a confined photon can exchange energy resonantly with the transition \( |g\rangle \leftrightarrow |e\rangle \) at frequency \( \Omega_c \), which delocalizes the donor state over the ensemble. On the other hand, the acceptor state \( |f\rangle \) is assumed to have a weak transition dipole with \( |g\rangle \) and is far detuned to the blue of the cavity frequency. The acceptor wavefunction thus remains localized in each molecule. For \( \sqrt{N}\Omega_c \gg \omega_v \), the donor states undergo polaron decoupling and can be represented by eq. (4). For a vibrational frequency \( \omega_v \approx 0.1 \text{ eV} \) along the reaction coordinate, significant polaron decoupling can be expected for experimentally accessible Rabi frequencies of \( 0.2 - 0.6 \text{ eV} \). For a cavity with at most one confined photon, the polaronitons energies involved are far below typical molecular ionization thresholds \([50]\).

We can open the ET reaction channel \( |e\rangle \rightarrow |f\rangle \), by Rabi splitting the energy of the upper dressed donor state \( |\pm0; 0 \rangle_{\nu'} \) above the acceptor level. \( \nu_D = \frac{1}{2} \sqrt{N}\Omega_c/2 \) is the donor electronic energy in a frame rotating at the cavity frequency \( \omega_{\text{cav}} \). An electron placed in the dressed donor state \( |\pm0; 0 \rangle_{\nu'} \) by an electron beam or a weak laser probe far-detuned from the cavity mode frequency, is thus transferred via resonant tunneling to an acceptor state \( |f\rangle \) at the rate \( k_{ET}(\Delta E) \), where \( \Delta E \) is smaller than the vibrational linewidth \( \hbar\gamma_v \). In an optical cavity, the rate expression in eq. (6) is still valid for this process, but the lineshape function is not the same as in free space. In the SM, we derive the lineshape function for ET reactions in a cavity.

In general, the cavity-donor coupling has two main effects on the ET reaction rate \( k_{ET} \). The first effect is the Rabi splitting of the dressed donor energy \( \omega_D \) relative to the acceptor levels. This energy shift can change the driving force of the reaction \( \Delta E \) relative to its free-space value \( \Delta E_0 \). The cavity can thus resonantly enhance nuclear tunneling for ET reactions involving high-frequency modes.

The second effect of cavity-donor coupling on ET reactions is related to polaron decoupling of the donor electronic state. As we discussed above, the collective coupling of donor groups to the same cavity mode effectively preserves the nuclear configuration of the ground electronic state along the collective reaction coordinate. For donor and acceptor excited states that in free space have equilibrium nuclear configurations with shifts of opposite signs \( \lambda_D = -\lambda_A = \sqrt{2} \). Panel (b): \( k_{ET}/k_0 \) as a function of \( \lambda_D/\lambda_A \) for \( N = 10^4 \) molecules with \( \lambda_A = \sqrt{2} \) and \( \Delta E = 0 \) (circles). The solid line is the analytical bound in eq. (7). In both panels the vibrational linewidth is \( \hbar\gamma_v = 0.01 \hbar\omega_v \), where \( \omega_v \) is the vibrational frequency, and \( k_0 T = 0.1 \hbar\omega_v \). \( \Delta E \ll \omega_v \) is the donor-acceptor electronic transition frequency, taken to be the same in the cavity and in free space.

The ET rate has the same size scaling of \( V \) as in free space (see SM for details). Figure 3: Electron transfer (ET) rate \( k_{ET} \) in an optical cavity. Panel (a): Ratio \( k_{ET}/k_0 \) as a function of \( N \). \( k_0 \) is the ET rate in free space. Curves are shown for \( \Delta E = 0 \) (curve a), \( \Delta E = 2\gamma_v \) (curve b) and \( \Delta E = 5\gamma_v \) (curve c). We set \( \lambda_D = -\lambda_A = \sqrt{2} \). Panel (b): \( k_{ET}/k_0 \) as a function of \( \lambda_D/\lambda_A \) for \( N = 10^4 \) molecules with \( \lambda_A = \sqrt{2} \) and \( \Delta E = 0 \) (circles). The solid line is the analytical bound in eq. (7). In both panels the vibrational linewidth is \( \hbar\gamma_v = 0.01 \hbar\omega_v \), where \( \omega_v \) is the vibrational frequency, and \( k_0 T = 0.1 \hbar\omega_v \). \( \Delta E \ll \omega_v \) is the donor-acceptor electronic transition frequency, taken to be the same in the cavity and in free space.

The cavity rate \( k_{ET} \) for resonant tunneling \( \Delta E = 0 \) can be approximated by

\[
k_{ET} = \left( k_0/2 \right) \exp[\lambda_D^2 - 2\lambda_D\lambda_A],
\]

where \( k_0 \) is the resonant tunneling rate in free space. This expression is valid for \( N \gg \lambda_D^2 \). The ratio \( k_{ET}/k_0 \) therefore exceeds unity whenever the exponent exceeds \( \ln(2) \). This is illustrated in Fig. 3b. Equation (7) also predicts a region of suppressed reaction rates when \( \lambda_A \) is near \( \lambda_D \). The equation further shows that the cavity rate has the same size scaling of \( V \) as in free space (see SM for details).

In summary, we discuss a mechanism for cavity-assisted decoupling of the nuclear and the electronic molecular degrees of freedom in a molecular ensemble. This
type of polaron decoupling can enhance or suppress the rate of intramolecular electron transfer by orders of magnitude in comparison with free space. Since we only assume conditions of strong coupling of a single cavity mode with an electronic transition, our results are valid for organic systems in microcavities [5] and plasmonic nanocavities [9, 53]. The predicted enhancements should be observable for a wide class of electron transfer reactions that involve large nuclear rearrangements in excited electronic states [44]. In addition to intramolecular electron transfer, cavity-induced polaron decoupling can also be used to modify the photophysical response of molecular aggregates [54, 55], and to control bimolecular electron or energy transfer processes that involve nuclear rearrangements in excited electronic states, including Förster resonance energy transfer [16].

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