



Cavity-Controlled Chemistry in Molecular Ensembles

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(Received 16 December 2015; published 8 June 2016)

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.

DOI: 10.1103/PhysRevLett.116.238301

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 Letter, 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 time scales 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 (RCs) 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 $H_g(q) = (p^2 + \omega_v^2 q^2)/2$, where ω_v 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

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

where ω_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. 1(a), we show the nuclear potentials for a molecule with a ground state $|g\rangle$ centered at $q_0 = 0$, as well as excited states $|e\rangle$ and $|f\rangle$

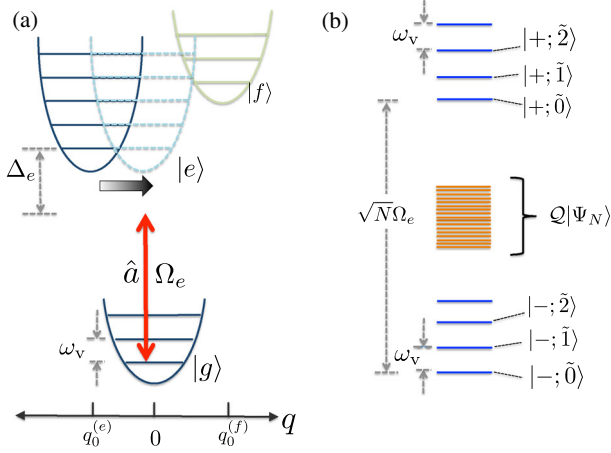


FIG. 1. (a) Nuclear potentials for a single molecule along the reaction coordinate q . Excited states $|e\rangle$ and $|f\rangle$ are shifted with respect to the ground state by $q_0^{(e)}$ and $q_0^{(f)}$ in free space. A cavity field \hat{a} couples to the transition $|g\rangle \leftrightarrow |e\rangle$ with a detuning Δ_e and Rabi frequency Ω_e . For large enough Ω_e , the cavity effectively shifts the potential minimum in state $|e\rangle$ to coincide with $|g\rangle$ (right gray arrow). State $|f\rangle$ does not couple to the cavity. (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 eigenstates $\mathcal{Q}|\Psi_N\rangle$. ω_ν is the vibrational frequency.

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. 1(a), we also represent a quantized cavity mode \hat{a} that induces Rabi oscillations between states $|g\rangle$ and $|e\rangle$ at frequency Ω_e with detuning $|\Delta_e| \ll \Omega_e$.

Shifted vibrational 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 $\hat{b} = \hat{b} + \lambda_e$ [45]. A similar definition holds for state $|f\rangle$. The dimensionless Huang-Rhys factor $\lambda_e^2 \equiv (\omega_\nu/2)[q_0^{(e)}]^2$ characterizes the strength of vibronic coupling. The vibrational eigenstates of the shifted harmonic potential are denoted by $|\tilde{m}_e\rangle \equiv D^\dagger(\lambda_e)|m\rangle$, where $D(\lambda_e) = \exp[\lambda_e(\hat{b}^\dagger - \hat{b})]$ is the nuclear displacement operator, and $|m\rangle$ is a vibrational eigenstate for the reference mode \hat{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

$$\mathcal{H}_N = \omega_\nu \sum_\nu \hat{b}_\nu^\dagger \hat{b}_\nu + \Delta \sum_\alpha |\alpha\rangle \langle \alpha| + \sum_{\alpha\beta\nu} g_{\alpha\beta}^\nu \hat{b}_\nu |\alpha\rangle \langle \beta| + \text{H.c.} \\ + \sqrt{N} \left(\frac{\Omega_e}{2} \right) (|\alpha_0\rangle \langle G| \hat{a} + |G\rangle \langle \alpha_0| \hat{a}^\dagger), \quad (2)$$

where $|G\rangle = |g_1, g_2, \dots, g_N\rangle$ is the ensemble ground state, $|\alpha\rangle = \sum_i u_{\alpha i} |e_i\rangle$ are one-excitation states, and $\hat{b}_\nu^\dagger = \sum_i c_{\nu i} \hat{b}_i^\dagger$ creates a phonon in mode ν . The detuning from the cavity frequency ω_{cav} is $\Delta = \Delta_e + \omega_\nu \lambda_e^2$, with $\Delta_e = \omega_e - \omega_{\text{cav}}$ being the detuning from the zero-phonon line (0-0) transition, and Ω_e is the single-molecule Rabi frequency. We assume that $|\Delta_e|/\Omega_e \ll 1$. Other excited states [for example, $|f\rangle$ in Fig. 1(a)] are far detuned or weakly coupled to the cavity field and cannot exchange energy with the confined mode over the time scales of interest.

The electron-vibration coupling constant in Eq. (2) is given by $g_{\alpha\beta}^\nu = \lambda_e \omega_\nu \sum_i u_{\alpha i}^* c_{\nu i} u_{\beta i}$. By defining the $\nu = 0$ phonon mode to be totally symmetric with respect to particle permutations, i.e., $c_{0i} = N^{-1/2}$, we have $g_{\alpha\beta}^{\nu=0} = \delta_{\alpha\beta} \lambda_e \omega_\nu / \sqrt{N}$. 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-Tavis-Cummings (HTC) 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 $\Delta_e \rightarrow \omega_e$ 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 α and ν with the quasimomenta \mathbf{k} and \mathbf{q} of electronic and phonon excitations, respectively. We use this (\mathbf{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 $|\alpha_0\rangle = \sum_i |e_i\rangle / \sqrt{N}$ [second line of Eq. (2)], with a size-enhanced Rabi frequency $\sqrt{N} \Omega_e$. We show in the Supplemental Material [48] that we can exploit the selection of permutation-symmetric electronic states by the cavity to partition the electronic Hilbert space into a symmetric subspace $\mathcal{P} = |G\rangle \langle G| + |\alpha_0\rangle \langle \alpha_0|$ and a nonsymmetric 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 Supplemental Material [48].

Electron-vibration coupling in the \mathcal{P} manifold involves only the symmetric phonon ($\nu = 0$) with coupling constant $g_{\alpha_0\alpha_0}^{\nu=0} = \lambda_e \omega_\nu / \sqrt{N}$. 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. 1(a) towards the ground state minimum [34]. A similar idea could be used to interpret the single-molecule absorption

spectra computed in Ref. [35]. In the Supplemental Material [48], we provide an equivalent derivation of the cavity-induced reduction of the Huang-Rhys factor for lattice vibrations using phonon modes in the site basis \hat{b}_i . We choose the collective phonon basis \hat{b}_ν here to make a clear connection with lattice systems that are relevant to describe molecular aggregates [20,34].

The permutation-symmetric electronic partition $\mathcal{P}^\dagger \mathcal{H}_N \mathcal{P}$ can be diagonalized to obtain dressed vibronic states of the form

$$|\pm; \tilde{m}; \{m\}_\nu\rangle = |\psi_\pm\rangle \otimes \hat{D}^\dagger(\lambda_e/2\sqrt{N})|m\rangle \otimes |\{m\}_\nu\rangle, \quad (4)$$

where $|\psi_\pm\rangle = \{|G\rangle|n_{\text{cav}} = 1\rangle \pm |\alpha_0\rangle|n_{\text{cav}} = 0\rangle\}/\sqrt{2}$ is the dressed state in the absence of vibrations. We have assumed that $\Delta = 0$ and $\sqrt{N}\Omega_e \gg \omega_v$. $|n_{\text{cav}}\rangle$ is a Fock state of the cavity mode, which we restrict here to $n_{\text{cav}} \leq 1$ to study cavity-vacuum effects only. State $|m\rangle$ is a vibrational eigenstate of the symmetric phonon mode $\hat{b}_{\nu=0}$ and $|\{m\}_\nu\rangle \equiv |m_{\nu=1}, \dots, m_{\nu=N-1}\rangle$ describes the vibrational state in nonsymmetric phonon modes. Dressed states in Eq. (4) have energies given by

$$\omega_{\pm, \tilde{m}; \{m\}_\nu} = \pm\sqrt{N}\Omega_e/2 + \omega_v \tilde{m} + \omega_v \sum_{\nu \neq 0} m_\nu, \quad (5)$$

where terms of order $1/N$ have been ignored. We illustrate the spectrum of the many-body Hamiltonian \mathcal{H}_N in Fig. 1(b). We show in the Supplemental Material [48] that as long as $\sqrt{N}\Omega_e \gg \omega_v$, the coupling between the \mathcal{P} and \mathcal{Q} manifolds through phonon absorption or emission becomes strongly suppressed. In this regime, the many-body states given in Eq. (4) become eigenstates of the HTC model with energies given by Eq. (5). We show below that polaron decoupling can have a significant impact on the chemical reactivity of molecular ensembles in optical cavities.

We illustrate the phenomenon of polaron decoupling in Fig. 2. We quantify the degree of vibronic decoupling in the eigenstates of the HTC model by the squared overlap $P_0 \equiv |\langle \Phi_0 | \psi_-; m = 0 \rangle \langle \{0\}_\nu \rangle|^2$, where $|\Phi_0\rangle$ is the lowest polaronic eigenstate of \mathcal{H}_N for a resonant cavity ($\Delta = 0$), and $|\psi_-; m = 0\rangle \langle \{0\}_\nu \rangle$ is defined in Eq. (4) for $\lambda_e = 0$. 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 \hat{b}_0 and up to two in the nonsymmetric modes $\hat{b}_{\nu \neq 0}$. We find that the squared overlap satisfies $P_0 \leq \exp[-\lambda_e^2/4N]$ (see the Supplemental Material [48] for a derivation). The upper bound corresponds an effective Franck-Condon overlap with the Huang-Rhys factor $\lambda_e^2/4N$ 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 $N \gg \lambda_e^2$. 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 ν . In other words, when the collective

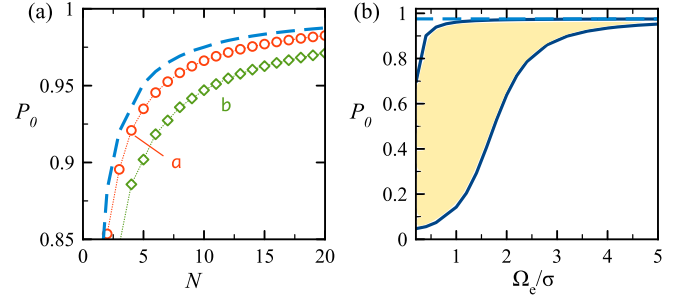


FIG. 2. Cavity-induced polaron decoupling. (a) Probability P_0 for the lowest many-body dressed state to be decoupled from molecular vibrations, as a function of the number of molecules N in a linear lattice. Several values of the Rabi frequency are shown: $\Omega_e/\omega_v = 4$ (curve *a*) and $\Omega_e/\omega_v = 2$ (curve *b*). ω_v is the vibrational frequency. (b) P_0 as a function of Ω_e/σ for a linear array of size $N = 10$ and disorder width σ . 2500 disorder realizations are included in the shaded area. Dashed lines in both panels correspond to $P_0 = \exp[-\lambda_e^2/4N]$, with $\lambda_e^2 = 1$.

Rabi oscillation period is shorter than the time scales 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 [49], although Rabi oscillation periods as fast as 5.9 fs ($\sqrt{N}\Omega_e = 700$ meV) have been reported [10].

We now go beyond the restriction of identical molecules and consider an excited state energy $\omega_e(\mathbf{r}_i)$ that depends on the position of the molecule \mathbf{r}_i in the ensemble. This type of static disorder in organic systems is typically taken into account by assuming that $\omega_e(\mathbf{r}_i)$ has a Gaussian distribution with standard deviation σ [34,50]. For a linear array with $N = 10$ molecules, we show in Fig. 2(b) that the lowest eigenstate $|\Phi_0\rangle$ of the HTC Hamiltonian \mathcal{H}_N with random detunings $\Delta_e(\mathbf{r}_i)$ is accurately given by $|-; \tilde{0}; \{0\}_\nu\rangle$ as the collective Rabi frequency exceeds the disorder strength ($\sqrt{N}\Omega_e \gg \sigma$). 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. 2(b).

Having described polaron decoupling by energetic isolation of the permutation-symmetric \mathcal{P} manifold, we now consider its effect on nonadiabatic unimolecular 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 nonadiabatic ET reactions, we have $V/\hbar \ll \omega_v$.

The relative energy between donor and acceptor vibronic levels $\Delta E \equiv \omega_{DA} + (m_D - m_A)\omega_v$ is known as the driving force of an ET reaction [45]. $\omega_{DA} = \omega_D - \omega_A$ is the electronic transition frequency and $(m_D - m_A)\omega_v$ the vibrational transition frequency for the *D-A* pair. The reaction rate can be written using linear response theory as [45] ($\hbar = 1$)

$$k_{\text{ET}}(\Delta E) = 2\pi V^2 \sum_{m_D} \sum_{m_A} \eta_{m_D}(T) \mathcal{D}(\Delta E), \quad (6)$$

where $\eta_{m_D}(T)$ is the Boltzmann distribution of nuclear states in the donor manifold $|m_D\rangle$ at temperature T , and $\mathcal{D}(\Delta E)$ is a Franck-Condon weighted line shape function, whose specific form depends on the model assumed for the system-environment interaction and the relative donor-acceptor shift $\lambda_{DA} \equiv \lambda_D - \lambda_A$. For a closed system, we have $\mathcal{D}(\Delta E) = |\langle m_D | m_A \rangle|^2 \delta(\Delta E)$, which gives the Fermi golden rule. We are interested in high-frequency internal vibrations for which $k_B T / \hbar \omega_v \ll 1$ at room temperature. In this case, ET reactions occur through nuclear tunneling, and the rate is strongly suppressed away from the resonance condition $\Delta E = 0$ [45].

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 ΔE 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 Ω_e , 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 wave function, thus, remains localized in each molecule. For $\sqrt{N}\Omega_e \gg \omega_v$, the donor states undergo polaron decoupling and can be represented by Eq. (4). For a vibrational frequency $\omega_v \approx 0.1$ eV along the reaction coordinate, significant polaron decoupling can be expected for experimentally accessible Rabi frequencies of 0.2–0.6 eV. For a cavity with at most one confined photon, the polariton energies involved are far below typical molecular ionization thresholds [51].

We can open the ET reaction channel $|e\rangle \rightarrow |f\rangle$ by Rabi splitting the energy of the upper dressed donor state $|+\tilde{0}; \{0\}_{\nu}\rangle$ above the acceptor level. $\omega_D = \sqrt{N}\Omega_e/2$ is the donor electronic energy in a frame rotating at the cavity frequency ω_{cav} . An electron placed in the dressed donor state $|+\tilde{0}; \{0\}_{\nu}\rangle$ 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 $k_{\text{ET}}(\Delta E)$, where ΔE 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 line shape function is not the same as in free space. In the Supplemental Material [48], we derive the line shape 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 ω_D relative to the acceptor levels. This energy shift can change the driving force of the reaction ΔE relative to its free-space value

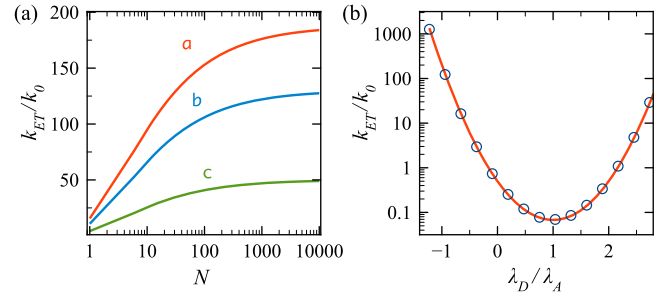


FIG. 3. ET rate k_{ET} in an optical cavity. (a) Ratio k_{ET}/k_0 as a function of N . k_0 is the ET rate in free space. Curves are shown for $\Delta E = 0$ (curve a), $\Delta E = 2\gamma_v$ (curve b), and $\Delta E = 5\gamma_v$ (curve c). We set $\lambda_D = -\lambda_A = \sqrt{2}$. (b) k_{ET}/k_0 as a function of λ_D/λ_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 ω_v is the vibrational frequency, and $k_B T = 0.1\hbar\omega_v$. $\Delta E \ll \omega_v$ is the donor-acceptor electronic transition frequency taken to be the same in the cavity and in free space.

ΔE_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 ($\lambda_D\lambda_A < 0$) relative to the $|g\rangle$, as in Fig. 1(a), polaron decoupling at low temperatures (or high vibrational frequencies) can increase the ET rate by orders of magnitude compared to the free space rate k_0 . This is illustrated in Fig. 3(a), where we show the ratio k_{ET}/k_0 as a function of N for fixed ΔE . We assume that ΔE is the same in the cavity and in free space, which can be achieved by tuning the acceptor energy ω_A through chemical substitution [52] or by changing the solvent polarity [53]. For low vibrational temperature, only $m_D = 0$ and $m_A = 0$ contribute to the rate for $\Delta E \ll \omega_v$. In this case, the cavity rate k_{ET} for resonant tunneling ($\Delta E = 0$) can be approximated by

$$k_{\text{ET}} = (k_0/2) \exp[\lambda_D^2 - 2\lambda_D\lambda_A], \quad (7)$$

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. 3(b). Equation (7) also predicts a region of suppressed reaction rates when λ_A is near λ_D . The equation further shows that the cavity rate has the same size scaling of V as in free space (see the Supplemental Material [48] 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 [9,54]. 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 [55,56] and to control bimolecular electron or energy transfer processes that involve nuclear rearrangements in excited electronic states, including Förster resonance energy transfer [16].

We thank Marina Litinskaya and Juan C. Retamal for helpful discussions. F.H. is supported by CONICYT through Grant No. PAI 79140030 and Fondecyt Iniciación Grant No. 11140158. F.C.S. is supported by the NSF, Grant No. DMR-1505437.

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- [1] D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, and D. M. Whittaker, *Nature (London)* **395**, 53 (1998).
- [2] D. G. Lidzey, D. D. C. Bradley, T. Virgili, A. Armitage, M. S. Skolnick, and S. Walker, *Phys. Rev. Lett.* **82**, 3316 (1999).
- [3] D. G. Lidzey, D. D. C. Bradley, A. Armitage, S. Walker, and M. S. Skolnick, *Science* **288**, 1620 (2000).
- [4] J. R. Tischler, M. S. Bradley, V. Bulovic, J. H. Song, and A. Nurmikko, *Phys. Rev. Lett.* **95**, 036401 (2005).
- [5] R. J. Holmes and S. R. Forrest, *Org. Electron.* **8**, 77 (2007).
- [6] S. Kéna-Cohen, M. Davanço, and S. R. Forrest, *Phys. Rev. Lett.* **101**, 116401 (2008).
- [7] S. Kéna-Cohen and S. R. Forrest, *Nat. Photonics* **4**, 371 (2010).
- [8] J. A. Hutchison, A. Liscio, T. Schwartz, A. Canaguier-Durand, C. Genet, V. Palermo, P. Samorì, and T. W. Ebbesen, *Adv. Mater.* **25**, 2481 (2013).
- [9] J. Bellessa, C. Symonds, J. Laverdant, J.-M. Benoit, J. C. Plenet, and S. Vignoli, *Electronics* **3**, 303 (2014).
- [10] T. Schwartz, J. A. Hutchison, C. Genet, and T. W. Ebbesen, *Phys. Rev. Lett.* **106**, 196405 (2011).
- [11] S. Kéna-Cohen, S. A. Maier, and D. D. C. Bradley, *Adv. Opt. Mater.* **1**, 827 (2013).
- [12] M. Mazzeo, A. Genco, S. Gambino, D. Ballarini, F. Mangione, O. Di Stefano, S. Patanè, S. Savasta, D. Sanvitto, and G. Gigli, *Appl. Phys. Lett.* **104**, 233303 (2014).
- [13] A. Cacciola, O. Di Stefano, R. Stassi, R. Saija, and S. Savasta, *ACS Nano* **8**, 11483 (2014).
- [14] J. George, S. Wang, T. Chervy, A. Canaguier-Durand, G. Schaeffer, J.-M. Lehn, J. A. Hutchison, C. Genet, and T. W. Ebbesen, *Faraday Discuss.* **178**, 281 (2015).
- [15] S. Gambino, A. Genco, G. Accorsi, O. Di Stefano, S. Savasta, S. Patan, G. Gigli, and M. Mazzeo, *Appl. Mater. Today* **1**, 33 (2015).
- [16] P. Andrew and W. L. Barnes, *Science* **290**, 785 (2000).
- [17] J. Feist and F. J. Garcia-Vidal, *Phys. Rev. Lett.* **114**, 196402 (2015).
- [18] J. Schachenmayer, C. Genes, E. Tignone, and G. Pupillo, *Phys. Rev. Lett.* **114**, 196403 (2015).
- [19] E. Orgiu *et al.*, *Nat. Mater.* **14**, 1123 (2015).
- [20] F. Herrera, B. Peropadre, L. A. Pachon, S. K. Saikin, and A. Aspuru-Guzik, *J. Phys. Chem. Lett.* **5**, 3708 (2014).
- [21] K. Hyun Kim, G. Bahl, W. Lee, J. Liu, M. Tomes, X. Fan, and T. Carmon, *Light Sci. Appl.* **2**, e110 (2013).
- [22] J. R. Tischler, M. Scott Bradley, Q. Zhang, T. Atay, A. Nurmikko, and V. Bulović, *Org. Electron.* **8**, 94 (2007).
- [23] P. Törmä and W. L. Barnes, *Rep. Prog. Phys.* **78**, 013901 (2015).
- [24] J. P. Long and B. S. Simpkins, *ACS Photonics* **2**, 130 (2015).
- [25] M. Muallem, A. Palatnik, G. D. Nessim, and Y. R. Tischler, *Ann. Phys. (Amsterdam)* **528**, 313 (2015).
- [26] J. George, A. Shalabney, J. A. Hutchison, C. Genet, and T. W. Ebbesen, *J. Phys. Chem. Lett.* **6**, 1027 (2015).
- [27] A. Shalabney, J. George, J. Hutchison, G. Pupillo, C. Genet, and T. W. Ebbesen, *Nat. Commun.* **6**, 5981 (2015).
- [28] H. Mabuchi and A. C. Doherty, *Science* **298**, 1372 (2002).
- [29] K. J. Vahala, *Nature (London)* **424**, 839 (2003).
- [30] M. Litinskaya, P. Reineker, and V. Agranovich, *J. Lumin.* **119–120**, 277 (2006).
- [31] G. Khitrova, H. M. Gibbs, M. Kira, S. W. Koch, and A. Scherer, *Nat. Phys.* **2**, 81 (2006).
- [32] R. Miller, T. E. Northup, K. M. Birnbaum, A. Boca, A. D. Boozer, and H. J. Kimble, *J. Phys. B* **38**, S551 (2005).
- [33] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, and T. W. Ebbesen, *Angew. Chem., Int. Ed. Engl.* **51**, 1592 (2012).
- [34] F. C. Spano, *J. Chem. Phys.* **142**, 184707 (2015).
- [35] J. Galego, F. J. Garcia-Vidal, and J. Feist, *Phys. Rev. X* **5**, 041022 (2015).
- [36] M. S. Skolnick, T. A. Fisher, and D. M. Whittaker, *Semicond. Sci. Technol.* **13**, 645 (1998).
- [37] T. Seideman, *J. Phys. Condens. Matter* **15**, R521 (2003).
- [38] R. Jörn and T. Seideman, *Acc. Chem. Res.* **43**, 1186 (2010).
- [39] J. W. Gadzuk, L. J. Richter, S. A. Buntin, D. S. King, and R. R. Cavanagh, *Surf. Sci.* **235**, 317 (1990).
- [40] J. W. Gadzuk, *Phys. Rev. B* **44**, 13466 (1991).
- [41] R. A. Marcus, *Rev. Mod. Phys.* **65**, 599 (1993).
- [42] W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.* **72**, 99 (1980).
- [43] M. Maus and W. Rettig, *J. Phys. Chem. A* **106**, 2104 (2002).
- [44] Z. R. Grabowski, K. Rotkiewicz, and W. Rettig, *Chem. Rev.* **103**, 3899 (2003).
- [45] V. May and O. Kuhn, *Charge and Energy Transfer Dynamics in Molecular Systems*, 3rd ed. (Wiley-VCH Verlag GmbH & Co., New York, 2011), Vol. 35, ISBN 3527403973.
- [46] T. Holstein, *Ann. Phys. (N.Y.)* **8**, 325 (1959).
- [47] E. K. Salje, A. Alexandrov, and W. Liang, *Polarons and Bipolarons in High-Tc Superconductors and Related*

- Materials* (Cambridge University Press, Cambridge, England, 2005).
- [48] See Supplemental Material <http://link.aps.org/supplemental/10.1103/PhysRevLett.116.238301> for the derivation of Eqs. (4)–(7) in the main text and the asymptotic bound shown in Fig. 2.
- [49] M. A. Koponen, U. Hohenester, T. K. Hakala, and J. J. Toppari, *Phys. Rev. B* **88**, 085425 (2013).
- [50] V. M. Agranovich, M. Litinskaia, and D. G. Lidzey, *Phys. Rev. B* **67**, 085311 (2003).
- [51] S. M. Hankin, D. M. Villeneuve, P. B. Corkum, and D. M. Rayner, *Phys. Rev. A* **64**, 013405 (2001).
- [52] G. L. Closs and J. R. Miller, *Science* **240**, 440 (1988).
- [53] M. Maroncelli, J. Macinnis, and G. R. Fleming, *Science* **243**, 1674 (1989).
- [54] A. González-Tudela, P. A. Huidobro, L. Martin-Moreno, C. Tejedor, and F. J. Garcia-Vidal, *Phys. Rev. Lett.* **110**, 126801 (2013).
- [55] M. Kasha, *Radiat. Res.* **20**, 55 (1963).
- [56] F. C. Spano, *Acc. Chem. Res.* **43**, 429 (2010).