Supplementary Information: Cavity-Modified Unimolecular Dissociation Reactions via Intramolecular Vibrational Energy Redistribution

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1. MODEL PARAMETERS

| $q_1^0$ | $q_2^0$ | $q_3^0$ |
|---------|---------|---------|
| 2.426   | 2.426   | 2.039   |

| $\alpha_1$ | $\alpha_2$ | $D_1$ | $D_2$ |
|------------|------------|-------|-------|
| 2.212      | 2.212      | 24    | 24    |

$G_{11}^{(0)} = G_{22}^{(0)} = G_{33}^{(0)} = G_{12}^{(0)} = G_{13}^{(0)} = G_{23}^{(0)}$

$6.85 \times 10^{-4} = 2.88 \times 10^{-4} = -1.54 \times 10^{-4} = 1.26 \times 10^{-4}$

TABLE I. Parameters for $H_{\text{mol}}$ in atomic units, except $D_i$, in kcal/mol, adapted from Ref. 1. These values result in local mode frequencies of $(\omega_1, \omega_2, \omega_3) = (1112, 1040, 632) \text{ cm}^{-1}$ for low vibrational excitations corresponding to the harmonic approximation.

2. DERIVATION OF THE LIGHT-MATTER HAMILTONIAN

In the main text we show the dynamics of the molecule (a classical mechanical three-body system) coupled with a single mode of an electromagnetic cavity. In this section, we show how these Hamiltonians can be derived from the classical Lagrangian formulation of electrodynamics. The Lagrangian of electromagnetic field coupled with mechanical degrees of freedom is [2]

\[
L = \int dr \left[ \frac{1}{2} \varepsilon_0 E^2 - \frac{1}{2 \mu_0} B^2 + \int dr \cdot A \right]_{\text{EM}} + \int dr \cdot A_{\text{LM}} + \sum_i \frac{1}{2} m_i \dot{r}_i^2 - V(r_1...r_i...),
\]

where $L_{\text{EM}}$ is the Lagrangian of the electromagnetic field, $L_{\text{LM}}$ is the light-matter coupling Lagrangian and $L_M$ is the matter Lagrangian. The electromagnetic field is described by the vectors of electric and magnetic field, $E$ and $B$, respectively, and the vector potential $A$. The positions $r_i$ of the mechanical degrees of freedom considered as three particles of respective masses $m_i$ determine the mechanical potential $V(r_1...r_i...)$. The electromagnetic fields are coupled to matter by the current density $J$.

We next consider that the electromagnetic field is described in the Coulomb gauge where the electrostatic interaction within the molecule is embedded in the potential $V(r_1...r_i...)$. We further consider that the electromagnetic field is represented by a sum over transverse modes of an electromagnetic cavity. The respective electromagnetic-field vectors can thus be expressed as:

\[
A = \sum_k A_k f_k(r),
\]

\[
E = -\sum_k \dot{A}_k f_k(r),
\]

\[
B = \sum_k A_k \nabla \times f_k(r).
\]

Here $A_k$ is the amplitude of the vector potential of mode $k$, and $f_k(r)$ is the corresponding vectorial mode profile. For concreteness, we consider $f_k = \sin(k \pi z / L) \xi$ (where $\xi$ is a unit vector transverse to $e_z$) which is confined in the $xy$ plane to a certain area $S_{xy}$. We note that this concrete definition is not central to the general conclusions of this derivation. The Lagrangian in Eq. (1) then becomes:

\[
L \approx \sum_k \left[ \frac{1}{2} \varepsilon_0 V_{\text{eff}} \left( \dot{A}_k^2 - \omega_k^2 A_k^2 \right) + s_k \mu \xi A_k \right] \\
+ \sum_i \frac{1}{2} m_i \dot{r}_i^2 - V(r_1...r_i...),
\]

where we have defined the cavity frequency as $\omega_k = k c \pi / L$ and the mode volume $V_{\text{eff}} = L S_{xy} / 2$. We have also used $j = \mu \delta(r - r_{\text{mol}})$, where $\mu$ is the dipole moment of the mechanical system (the molecule), and we have assumed that the molecule is a point-like object positioned at $r_{\text{mol}} = [x_{\text{mol}}, y_{\text{mol}}, z_{\text{mol}}]$. We have defined $\mu : \xi \equiv \mu \xi$ and $\sin(k \pi z_{\text{mol}}) \equiv s_k$.

The Lagrangian $L_M$ generally contains all nine mechanical degrees of freedom of the molecule. Cross et al. [3] have shown how the translational and rotational degrees of freedom can be eliminated using a series of transformations (assuming only 2D dynamics of the molecule, fixing the center of mass of the molecule, and removing...
the remaining rotational degree of freedom by setting the molecule’s angular momentum equal to zero). We note that this transformation neglects the effects of molecular angular momentum on the light-matter coupling. The reduced mechanical Lagrangian $R$ expressed in terms of the internal coordinates $q_i$ is:

$$ R = \frac{1}{2} \sum_{ij} \Gamma_{ij} \dot{q}_i \dot{q}_j - V(q_1, q_2, q_3), \quad (6) $$

where $\Gamma_{ij}$ are generally coordinate-dependent quantities playing the role of generalized masses. We neglect the coordinate-dependence of $\Gamma_{ij}$ and only consider its values at the equilibrium geometry of the molecule. This approximation neglects certain anharmonic interactions among the molecular internal degrees of freedom, but makes the numerical treatment of the system dynamics tractable.

The reduced Lagrangian of the molecule coupled with the electromagnetic cavity therefore becomes:

$$ L_R = \sum_k \left[ \frac{1}{2} \varepsilon_0 V_{\text{eff}} \left( \dot{A}_k^2 - \omega_k^2 A_k^2 \right) + s_k \mu_\xi (q_1, q_2, q_3) A_k \right] $$

$$ + \frac{1}{2} \sum_{ij} \Gamma_{ij} \dot{q}_i \dot{q}_j - V(q_1, q_2, q_3). \quad (7) $$

The Lagrangian $L_R$ could in principle be directly transformed into the corresponding Hamiltonian by the standard procedure. Although such a procedure is possible, the resulting Hamiltonian would have a complicated form not suitable for numerical treatment. Instead, it is more convenient to first transform $L_R$ by explicitly subtracting from it the total time derivative of $\sum_k s_k \mu_\xi A_k$:

$$ L_T = L_R - \frac{d}{dt} \left( \sum_k s_k \mu_\xi A_k \right) $$

$$ = \sum_k \left[ \frac{1}{2} \varepsilon_0 V_{\text{eff}} \left( \dot{A}_k^2 - \omega_k^2 A_k^2 \right) - s_k \mu_\xi \dot{A}_k \right] $$

$$ + \frac{1}{2} \sum_{ij} \Gamma_{ij} \dot{q}_i \dot{q}_j - V(q_1, q_2, q_3). \quad (8) $$

Notice that this transformation shifts the time derivative in the light-matter coupling Lagrangian from the dipole moment to the field coordinate. We now transform $L_T$ to the Hamiltonian picture. For further convenience we define the canonical coordinate $Q_k = \sqrt{\varepsilon_0 V_{\text{eff}}} A_k$ and obtain the conjugate momenta:

$$ p_i = \frac{\partial L_T}{\partial \dot{q}_i} = \sum_j \Gamma_{ij} \dot{q}_j, \quad (9) $$

$$ P_k = \frac{\partial L_T}{\partial \dot{Q}_k} = \sqrt{\varepsilon_0 V_{\text{eff}}} \dot{A}_k - \frac{\mu_\xi s_k}{\sqrt{\varepsilon_0 V_{\text{eff}}}}. \quad (10) $$

The Hamiltonian then becomes:

$$ H = \sum_i p_i \dot{q}_i + \sum_k P_k \dot{Q}_k - L_T $$

$$ = \frac{1}{2} \sum_{ij} G_{ij} p_i p_j + V(q_1, q_2, q_3) $$

$$ + \sum_k \left[ \frac{1}{2} \left( P_k + \frac{\mu_\xi s_k}{\sqrt{\varepsilon_0 V_{\text{eff}}}} \right)^2 + \frac{1}{2} \omega_k^2 Q_k^2 \right], \quad (11) $$

where $G_{ij}$ are the elements of the matrix inverse to $\Gamma_{ij}$. Finally, to obtain the Hamiltonian in the form expressed in the main text, we apply the canonical transformation (change of phase-space coordinates):

$$ Q_k = \frac{p_k}{\omega_k}, \quad (12) $$

$$ P_k = -\omega_k q_k, \quad (13) $$

and obtain

$$ H = \frac{1}{2} \sum_{ij} G_{ij} p_i p_j + V(q_1, q_2, q_3) $$

$$ + \sum_k \left[ \frac{1}{2} \omega_k^2 \left( q_k - \frac{\lambda_k}{\omega_k} \mu_\xi \right)^2 + \frac{1}{2} \mu_\xi^2 \right], \quad (14) $$

where we have identified $\lambda_k = s_k / \sqrt{\varepsilon_0 V_{\text{eff}}}$. Finally, it is interesting to consider the connection between the variables $p_k$ ($q_k$) and the original fields:

$$ p_k = \omega_k \sqrt{\varepsilon_0 V_{\text{eff}}} A_k, \quad (15) $$

$$ q_k = -\sqrt{\varepsilon_0 V_{\text{eff}}} A_k + \mu_\xi \frac{s_k}{\omega_k \sqrt{\varepsilon_0 V_{\text{eff}}}}. \quad (16) $$

We see that the momentum $p_k$ is proportional to the amplitude $\omega_k A_k / c$ of the magnetic field of mode $k$, and the coordinate $\omega_k q_k$ is proportional to the electric field plus the dipole moment (related to the polarization), and is thus resembling the displacement field of the cavity mode.

With this we can write the energy of the transverse electromagnetic field of a single cavity mode ($k = c$) as

$$ E_{\text{EM}} = \frac{1}{2} \varepsilon_0 V_{\text{eff}} \left( \dot{A}_c^2 + \omega_c^2 A_c^2 \right) $$

$$ = \frac{1}{2} \omega_c^2 \left( q_c - \frac{\lambda_c}{\omega_c} \mu_\xi \right)^2 + \frac{1}{2} \mu_\xi^2. \quad (17) $$

Interestingly, the coupling term is fully embedded in the energy of electromagnetic field. The mechanical energy of the system is

$$ E_M = \frac{1}{2} \sum_{ij} G_{ij} p_i p_j + V(q_1, q_2, q_3). \quad (18) $$

We find that there is no extra energy associated with the coupling between the molecule and the cavity field.
3. INITIAL STATES

We briefly review the method of generating initial molecular states, as originally described in Ref. 1, and discuss how it is generalized to initialize the cavity.

For a given molecule energy $E_{\text{mol}}$, we compute the minimum $m_{\text{min}}$ and maximum $m_{\text{max}}$ possible values of $m \in \{q_1, q_2, p_1, p_2, p_3\}$ corresponding to the cases when $E_{\text{mol}}$ is contained entirely within the potential or kinetic energy associated with $m$. Then, we generate all possible initial states from uniformly spaced arrays with $N$ values between $m_{\text{min}}$ and $m_{\text{max}}$. For each of these states with energy less than $E_{\text{mol}}$, we choose the positive root of $q_3 - q_0^2$ that results in a total energy of $E_{\text{mol}}$. To obtain converged results in this study, we choose $N$ between 15 and 23, where larger values are necessary for survival probabilities and smaller values are sufficient for Fourier spectra and time-dependent energy curves.

When the total field energy $E_{\text{EM}}$ is set to 0, $Q_c$ is fixed by the cavity strength $\lambda_c$ and $P_c$ is set vanishingly small to ensure numerical stability. To initialize the molecule-cavity system with a given $E_{\text{total}}$ dictated by $H_{\text{mol}} + H_F$, we adapt the procedure from the case of the bare molecule described above, except that we generate all possible initial states from uniformly spaced arrays of $q_1, q_2, q_3, p_1, p_2, p_3, Q_c$, and select the value of $P_c$ that gives the desired total energy.

To initialize the cavity with a given $E_{\text{cav}} = P_c^2/2 + \omega_c^2 Q_c^2/2$, we first compute the minimum $Q_{\text{min},c}$ and maximum $Q_{\text{max},c}$ possible values of $Q_c$ corresponding to $E_{\text{cav}} = \omega_c^2 Q_c^2/2$. For the study of $Q_c > 0$ ($Q_c < 0$), for each molecule initial state, there is only one initial cavity state with $Q_c = Q_{\text{max},c}$ ($Q_c = Q_{\text{min},c}$, $-Q_{\text{max},c}$) and $P_c = 0$. For the “uniform $Q_c$” studies, for each molecule initial state, we generate $N_c$ cavity states, where $Q_c$ is selected from a uniformly spaced array with $N_c$ points between $Q_{\text{min},c}$ and $Q_{\text{max},c}$ and $P_c$ is chosen such that $E_{\text{cav}} = P_c^2/2 + \omega_c^2 Q_c^2/2$.

In the present study we generate ensembles of trajectories picked from constant energy hypersurfaces [1] to elucidate the fundamental physics. Future studies could consider differently chosen ensembles of initial states relevant to particular experimental conditions. For instance, to simulate conditions of vibrational excitation at room-temperature, energies and momenta of the molecule and cavity can be selected from a Boltzmann distribution. Alternatively, to simulate population via infrared laser pumping, only optically accessible initial states can be chosen.

4. ESTIMATING THE RABI SPLITTING

We demonstrate how to estimate the Rabi splitting induced by the cavity mode in the dipolar moment spectrum of the vibrational modes in a manner similar to Refs. 4–6. As an example, we assume that the single cavity mode $c$ is aligned along the in-plane axis through the center of the tri-atomic model to $q_3/2$, such that the only component of the permanent dipole moment $\mu$ relevant to light-matter coupling is given by $A \cos(q_3/2)(q_1 + q_2)$, where the coefficient $A$ is fitted with experimental or computational data describing the permanent dipole moment of ozone at vibrational equilibrium and we have assumed ionic dissociation with a simpler functional form. With these simplifications, we can re-write $H_F$ as

$$H_F = \frac{1}{2} \omega_c^2 Q_c^2 + \frac{1}{2} P_c^2 + \frac{1}{2} \mu^2 \lambda_c^2 - \omega_c \mu \lambda_c Q_c.$$  \hspace{1cm} (19)

The first two terms correspond to the classical total energy of the cavity mode, the third term is the dipole self-energy term more relevant in the ultrastrong coupling limit, and the last term, $H_{DF}$, is the conventional light-matter dipole-field interaction term on which we now focus our attention. To make further analytical progress, we assume that the molecule is close to its vibrational equilibrium state. By doing so, we can approximate the permanent dipole moment as $\mu \approx \mu_0 + \frac{\partial \mu}{\partial q}(q - q_0)$ where $q$ is a generalized vibrational coordinate. Whether this assumption holds depends on the degree of vibrational excitation. For instance, this assumption encounters no issues with considering solely thermal population in the tri-atomic model, where the harmonic vibrational frequencies are several times higher than $k_B T$. However, in our numerical studies, the molecules are initialized with energies larger than the dissociation energy that is itself several times larger than the vibrational frequencies, so throughout the IVR process, the vibrational mode displacements from equilibrium can be large. Nonetheless, for the purpose of providing a simple, analytic form of the Rabi splitting that can be generalized to higher orders if necessary, we plug this term into $H_{DF}$:

$$H_{LM} = - \left[ \omega_c \mu_0 \lambda_c Q_c + \frac{\partial \mu}{\partial q} \right] (q - q_0) \omega_c \lambda_c Q_c. \hspace{1cm} (20)$$

The latter term corresponds to the coupling between a vibrational transition and the cavity photon, and the Rabi splitting energy should correspond to the scaling factor of this term. We replace $Q_c$ and $q$ with quantized field operators:

$$\frac{\partial \mu}{\partial q} \bigg|_{q_0} \omega_c \lambda_c Q_c = \frac{\partial \mu}{\partial q} \bigg|_{q_0} \omega_c \sqrt{\frac{\hbar}{2M \omega_v}} \left( \hat{a}^\dagger \hat{b} + \hat{b}^\dagger \hat{a} \right) \sqrt{\frac{\hbar}{2\omega_c}} \left( \hat{a}^\dagger - \hat{a} \right),$$  \hspace{1cm} (21)

where $M$ is the effective mass of the vibration, $\omega_v$ is the frequency of the vibration, and $\hat{b}$ and $\hat{a}$ are the annihilation operators of the vibrational and cavity modes, respectively.

We collect all the non-operator terms, multiply by a factor of two, and call this term the estimated Rabi splitting energy, or the energy difference between the lower and upper polariton:

$$\hbar \Omega_{R} = \frac{\partial \mu}{\partial q} \bigg|_{q_0} \hbar \lambda_c \sqrt{\frac{\omega_c}{M \omega_v}}. \hspace{1cm} (22)$$
In our numerical studies, we have found that the cavity mode influences the unimolecular dissociation rate most strongly when the cavity is resonant with a vibrational mode dominated by the local mode vibration, such as $q_3$ when the cavity is $x$-polarized, especially for vanishing local vibrational mode-mode momentum coupling $\epsilon$. Therefore, for the cavity field along the $x$-direction we approximate $\frac{\partial \mu}{\partial q_{3}}|_{q_0}$ as

$$\frac{\partial \mu}{\partial q_{3}}|_{q_0} \approx \frac{\partial \mu}{\partial q_{3}}|_{q_3} = -A \sin (q_3^0/2)(q_1^0 + q_2^0)/2. \quad (23)$$

We estimate the Rabi splitting for typical parameters used in our numerical studies in atomic units, where $\hbar = 1$. For instance, for $A = 0.4$ a.u. so that the permanent dipole moment at equilibrium $\mu_0$ is 1 e-Bohr, $q_1^0 = q_2^0 = 2.416$ Bohr, $q_3^0 = 2.039$ rad, $M_{q_3} = 1/G_{q_3} = (2.88 \cdot 10^{-3})^{-1}$ a.u., $\omega_3 = \omega_c = 2.88 \cdot 10^{-3}$ a.u., and $\lambda_c = 0.01$ a.u., we estimate a Rabi frequency $\Omega_{\text{est}} = 4.364 \cdot 10^{-5}$ a.u. or 5.77 cm$^{-1}$. Using $\lambda_c = \sqrt{2/\omega_c} |E_c| = \sqrt{1/(\epsilon_0 V)}$ in atomic units, we estimate the mode volume as 15 nm$^3$ for $\lambda_c = 0.01$ a.u. and 0.1 nm$^3$ for $\lambda_c = 0.16$ a.u. This estimate indeed matches the splittings observed in Fourier transforms of the vibrational coordinates of the coupled molecule-cavity system under the conditions described, as in Fig. 1, where the molecule is initialized with energy $\ll \hbar \omega_1$ to prevent the appearance of overtones and combination spectra. We propagate the same initial condition for all $\lambda_c$: $\{p_1, p_2, p_3, q_1, q_2, q_3, P_c, Q_c\} = \{5, 5, -5, 2.8, 2.8, 2, 0.01, 0.01\}$ in atomic units.

5. CHARGED DISSOCIATION

Here, we study the effect of dissociation into charged, rather than neutral, species. Charged dissociation is modeled by replacing $\mathcal{F}(q_i) = q_i e^{-(q_i - q_i^0)^2/(2\sigma^2)}$ → $\mathcal{F}(q_i) = q_i$ such that the dipole moment increases monotonically with increasing inter-atomic distance after dissociation rather than asymptotically dropping to zero. In Fig. 2, we show cavity-modified chemical reactivity for charged dissociation of a single molecule in a cavity, where we note similar results except for different relative peak heights for the resonant effect.

6. ORTHOGONALLY POLARIZED CAVITY

We also explore the effect of coupling the cavity to different molecular resonances. As we show in Fig. 3(a), the
y-polarized dipolar moment spectrum for long-lived trajectories has peaks around 600 and 1000 cm\(^{-1}\), away from the resonances at 520 cm\(^{-1}\) we explore in the main text. Therefore, we can expect the light-matter coupling interaction for a y-polarized cavity to also be relatively high at these frequencies. We set a constant cavity strength \(\lambda_c = 0.05\) a.u. along the y-direction and then vary the cavity frequency \(\omega_c\) from 100 cm\(^{-1}\) to 1100 cm\(^{-1}\). Here, we observe a broader resonant effect at a different frequency of \(\sim 900\) cm\(^{-1}\), corresponding to the broader peak in the y-polarized dipolar moment spectrum, as opposed to the sharper double peak \(\sim 520\) cm\(^{-1}\) and 580 cm\(^{-1}\) in the neutral dissociation analogue in the main text where the cavity field is oriented along the x-direction.

**FIG. 3.** Dissociation in a y-polarized cavity. (a) y-polarized dipole moment spectra \(\mu_y(\omega)\) of short- and long-lived trajectories of the molecule outside the cavity. (b) Survival curves and (c) unimolecular dissociation rate for the model molecule in a y-polarized cavity. We vary cavity frequency \(\omega_c\) for cavity strength \(\lambda_c = 0.05\) a.u. and observe a broadly resonant rate slow-down around \(\sim 900\) cm\(^{-1}\).

7. RESONANCE WITH VARYING \(\lambda_c\)

Here, we investigate the change in resonance frequencies for varying cavity strength \(\lambda_c\).

8. SMALL \(\epsilon\)

To that end, we calculate the decay time of the initial reactants by varying \(\epsilon \in \{1.0, 0.3, 0.1, 0.01\}\) with fixed cavity strength \(\lambda_c\) in Fig. 5. The survival probability thresholds \(S_{th}\) differ for each \(\epsilon\) because as \(\epsilon\) decreases, the timescale of decay increases, resulting in increased computational cost. Also, we note that lower \(\epsilon\) roughly corresponds to, e.g., higher mass of the center atom relative to the other two atoms [10]. For \(\epsilon = 1.0, 0.3, \) and 0.1, the time \(t_{th}\) to reach \(S_{th}\) inside the cavity is larger, or the reaction rate decreases, whereas for \(\epsilon = 0.01\), the time to \(S(t) = 0.75\) can also decrease at a particular resonance frequency. Hence, the reaction rate can be faster. This effective increase of the reaction rate can be interpreted as follows: for large \(\epsilon\), the dynamics of energy distribution are dominated by vibrational mode-mode momentum coupling, whereas for small \(\epsilon \ll 1\), the dynamics are dominated by coupling to the cavity, which then can assist in transferring energy between vibrational modes.

The case of relatively small \(\epsilon\) can be loosely analogized to the case of intermolecular vibrational energy redistribution, since the energies of intermolecular interactions are one to three orders of magnitude lower than intramolecular ones. Alternatively, the weak mode-mode momentum couplings could represent coupling to low-frequency intramolecular vibrational modes known to serve as baths for vibrational energy [11]. Regardless of the interpretation, the results in Fig. 5 demonstrate that the cavity mode can effectively augment the coupling between vibrational modes and accelerate the reaction rate. These results may be relevant to the studies showing enhanced reaction rates when tuning the cavity into resonance with a vibrational mode of solvent molecules [12, 13] that are vibrationally weakly coupled to reactant molecules outside the cavity.

**FIG. 4.** Resonance effect for varying \(\lambda_c\). As \(\lambda_c\) increases, the higher-frequency peak corresponding to resonant tuning to a stretching mode broadens.

9. MOLECULE ENERGIES

In Fig. 6, we show qualitatively similar changes in chemical reactivity between molecule energies \(E_{mol} \in \{30, 34, 36\}\) kcal/mol with varying cavity strength \(\lambda_c\) and cavity frequency \(\omega_c\).
while at small $\epsilon$ decreases inside a resonant cavity relative to outside the cavity, larger $\epsilon$ also be increased.

(a) $E$ FIG. 6

survival probability threshold $S$

FIG. 5

trends remain consistent for varying $E$ and cavity strength $\lambda_c$ for $\epsilon = \{\text{mol}, 0.01\}$, we vary the cavity strength $\lambda_c$ for $\epsilon = 0$. For $Q_c > 0$, increasing $Q_c$ with cavity energies $E_{\text{cav}}$ from nearly 0 (red) to 5 (orange) to 25 (purple) kcal/mol results in two competing effects: the maximum amount of energy the cavity can absorb from the molecule increases while the rate at which the cavity returns the energy to the molecule also increases. The competition between these two processes results in the local maximum in $t_{S=0.01}$ for $Q_c > 0$, $Q_c < 0$ (pink) results in faster reactions than $Q_c > 0$ (orange) at the same energy because in the former, energy is initially transferred from the cavity to the molecule. The initial direction of energy transfer differs between positive and negative $Q_c$ because the sign of $Q_c$ determines the overall sign of the light-matter interaction term $\omega_c \mu \lambda_c Q_c$, which then affects the initial sign and magnitude of the time derivatives of the molecule-cavity coordinates. Overall, these results suggest that cavities even “hotter” than the “hot” molecules can appreciably affect dissociation dynamics if the state of the cavity can be controlled, potentially with coherent pumping.

10. INITIAL CAVITY STATE

To explore whether certain initial cavity states, which could potentially be preferentially generated by non-equilibrium effects such as coherent pumping, can affect dissociation dynamics differently, we explore the following different regimes in Fig. 7: $Q_c > 0$ and $P_c = 0$ (dark blue), $Q_c < 0$ and $P_c = 0$ (green), and uniformly sampled $Q_c$ and $P_c$ (light blue). Different initial signs of $Q_c$ could result in qualitatively different effects because the angle $\theta$ of the molecule orientation breaks a symmetry of the system, such that for positive (negative) $Q_c$, the light-matter interaction is negative (positive). Then, for each of these states, in Fig. 7(a) we calculate the reaction time $t_{S=0.05}$ of molecules with fixed initial energy 34 kcal/mol for varying initial cavity energy $E_{\text{cav}} = P_c^2/2 + \omega_c Q_c^2/2$. We note that while these initial conditions may not be straightforward to prepare experimentally, they illustrate critical physics of the system.

For “uniform $Q_c$” and $Q_c < 0$, as $E_{\text{cav}}$ increases, we find that the reaction rate increases and can become even faster than the reaction outside the cavity (dotted yellow). Notably, the reaction rate of the “uniform $Q_c$” case with $E_{\text{cav}} \sim 10$ kcal/mol equals the reaction rate outside the cavity, where both cases have approximately the same amount of energy per degree of freedom. In contrast, for $Q_c > 0$, the reaction rate slows down further from $E_{\text{cav}} = 0$ to $\sim 3$ kcal/mol and decreases the rate outside the cavity with further increasing $E_{\text{cav}}$ until $E_{\text{cav}}$ is as high as 25 kcal/mol.

To explain these results, in Fig. 7(b), we plot the time-dependent energy distribution for the conditions marked by the colored circles in (a). For $Q_c > 0$, increasing $Q_c$ with cavity energies $E_{\text{cav}}$ from nearly 0 (red) to 5 (orange) to 25 (purple) kcal/mol results in two competing effects: the maximum amount of energy the cavity can absorb from the molecule increases while the rate at which the cavity returns the energy to the molecule also increases. The competition between these two processes results in the local maximum in $t_{S=0.01}$ for $Q_c > 0$. $Q_c < 0$ (pink) results in faster reactions than $Q_c > 0$ (orange) at the same energy because in the former, energy is initially transferred from the cavity to the molecule. The initial direction of energy transfer differs between positive and negative $Q_c$ because the sign of $Q_c$ determines the overall sign of the light-matter interaction term $\omega_c \mu \lambda_c Q_c$, which then affects the initial sign and magnitude of the time derivatives of the molecule-cavity coordinates. Overall, these results suggest that cavities even “hotter” than the “hot” molecules can appreciably affect dissociation dynamics if the state of the cavity can be controlled, potentially with coherent pumping.
FIG. 7. Reaction rate dependence on cavity state. (a) Time $t_{S=0.05}$ for 95% of molecules to dissociate for varying cavity energy $E_{cav}$, where the cavity is initialized with $Q_c > 0$ and $P_c = 0$ (dark blue), uniformly sampled $Q_c$ and $P_c$ (“uniform $Q_c$” in light blue), and $Q_c < 0$ and $P_c = 0$ (green). In (b), we plot the time-dependent energy distribution for the colored shapes in (a). The local maximum in $t_{S=0.05}$ for $Q_c > 0$ is a result of competition between absorbing more energy from the molecule and the cavity returning it quickly. $Q_c < 0$ (pink) results in faster reactions than $Q_c > 0$ (orange) at the same $E_{cav}$ because in the former, energy is initially transferred from the cavity to the molecule. The black, dotted line marks the minimum (maximum) energy of the molecule after the first oscillation of energy transfer to (from) the cavity.

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