Supplementary Information: Driving chemical reactions with polariton condensates

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S1. DARK MODES

We use a generalization of the dark state basis introduced in [1, 2] to reduce the number of vibrational modes involved in the reaction. The bosonic operator for $D_{R,c}$, the dark mode highly localized in the c^{th} molecule when it is in electronic state $|R\rangle$ with total number of reactants N_R and products N_P is

$$\begin{aligned}\hat{a}_D^{(R,c)} =& \sqrt{\frac{g_P^2 N_P + g_R^2(N_R-1)}{g_P^2 N_P + g_R^2 N_R}}\hat{a}_{R,c} - \frac{g_R^2}{\sqrt{g_P^2 N_P + g_R^2 N_R}}\frac{1}{\sqrt{g_P^2 N_P + g_R^2(N_R-1)}}\sum_{i\neq c}^{N_R}\hat{a}_{R,i} \\ &- \frac{g_R g_P}{\sqrt{g_P^2 N_P + g_R^2 N_R}}\frac{1}{\sqrt{g_P^2 N_P + g_R^2(N_R-1)}}\sum_{j=1}^{N_P}\hat{a}_{P,j}.\end{aligned} \tag{S1}$$

Notice that, when $g_P = 0$, this dark mode will not involve vibrations in the product molecules and when $g_R = 0$, this dark mode will be the same as a vibration localized in the c^{th} molecule $\hat{a}_D^{(R,c)} = \hat{a}_{R,c}$. Similarly, the bosonic operator for $D'_{P,c}$, the dark mode highly localized in the c^{th} molecule after it has reacted and is in electronic state $|P\rangle$ with total number of reactants N_R-1 and products N_P+1 is

$$\begin{aligned}\hat{a}_D^{(P,c)\prime} =& \sqrt{\frac{g_P^2 N_P + g_R^2(N_R-1)}{g_P^2(N_P+1) + g_R^2(N_R-1)}}\hat{a}_{P,c} - \frac{g_R g_P}{\sqrt{g_P^2(N_P+1) + g_R^2(N_R-1)}}\frac{1}{\sqrt{g_P^2 N_P + g_R^2(N_R-1)}}\sum_{i=1}^{N_R-1}\hat{a}_{R,i} \\ &- \frac{g_P^2}{\sqrt{g_P^2(N_P+1) + g_R^2(N_R-1)}}\frac{1}{\sqrt{g_P^2 N_P + g_R^2(N_R-1)}}\sum_{j\neq c}^{N_P+1}\hat{a}_{P,j}.\end{aligned} \tag{S2}$$

Here, when $g_P = 0$, the dark mode in equation (S2) will be the same as a vibration localized in the c^{th} molecule $\hat{a}_D^{(P,c)\prime} = \hat{a}_{P,c}$ and when $g_R = 0$, this dark mode will not involve vibrations in the reactant molecules.

S2. POLARITON RELAXATION KINETICS

We use Boltzmann rate equations as in [3, 4] to model polariton relaxation, and solve for the steady state of $N+1$ coupled differential equations. We assume that the scattering rate W_{ij} between polariton and dark modes is the same for all dark modes, labeled by k, this gives $W_{D_k+} = W_{D+}$ and $W_{-D_k} = W_{-D}$ [5]. Since our interests lie in the distribution of energy between polariton and dark modes rather than individual dark modes, we can simplify the problem by summing over all dark-mode equations and considering only their total population $n_D = \sum_{k=2}^{N} n_D^k$. We have the following rate equations for populations in the lower n_-, upper n_+ polaritons and all dark modes n_D,

$$\begin{aligned}\frac{dn_-}{dt} &= R_{-D} + R_{-+} - \gamma_- n_- + P_-, \\ \frac{dn_D}{dt} &= -R_{-D} + R_{D+} - \gamma_D^k n_D, \\ \frac{dn_+}{dt} &= -R_{-+} - R_{D+} - \gamma_+ n_+,\end{aligned} \tag{S3}$$

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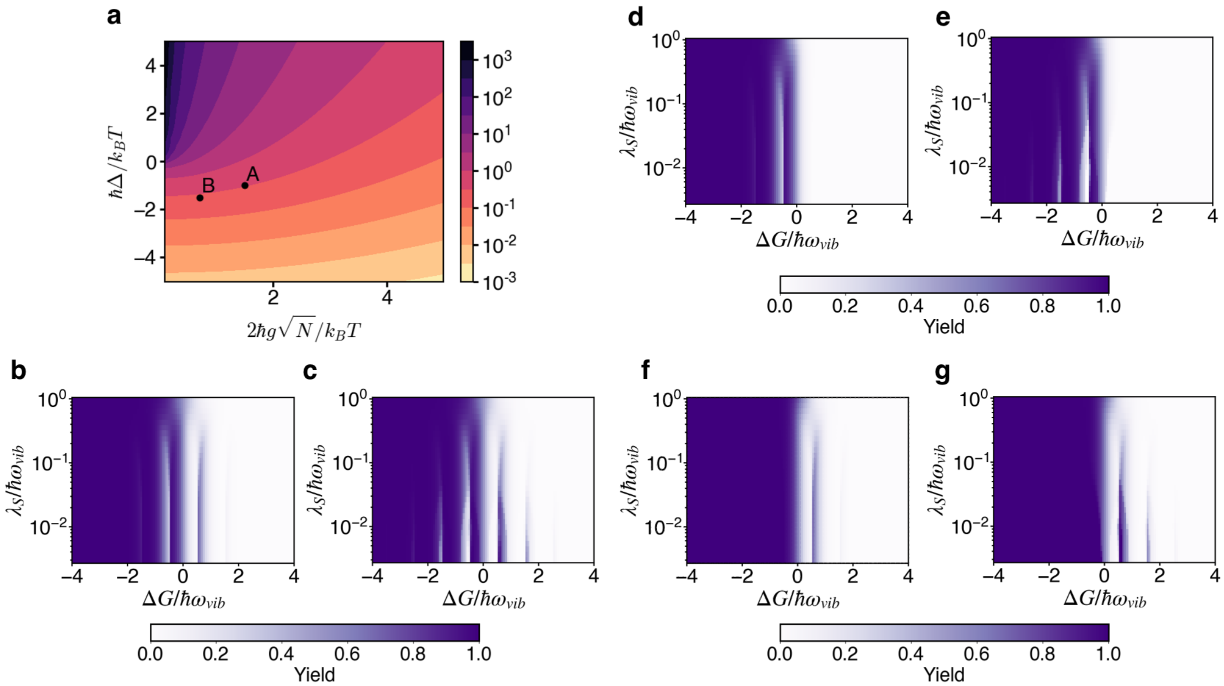

FIG. S1. **Reaction yield at room temperature.** **a**, Condensation threshold (same as Fig. 3 from the main manuscript), where point B marks a set of parameters at room temperature. **b**,**d**,**f** are results for a laser driven system without SC and **c**,**e**,**g** are for a system with SC and $P_- = 0.08N\Gamma_\downarrow$. **b**, Reaction yield N_P^{ss}/N at temperature $k_BT = 0.1408\hbar\omega_{vib}$ ($T = 300$ K when $\hbar\omega_{vib} = 185$ meV), Huang-Rhys factor $S = 3.5$, and average occupation of the intramolecular vibrational mode $\bar{n} = 0.08$. **c**, Reaction yield N_P^{ss}/N with $\Delta = -0.2113\omega_{vib}$, $2g_R\sqrt{N} = 2g_P\sqrt{N} = 0.1\omega_{vib}$, $P_- = 0.08N\Gamma_\downarrow$, $N = 10^7$, temperature and Huang-Rhys factor are the same as in **b**. **d** (**f**), The reaction yield when only the product (reactant) weakly couples with light. **e** (**g**), Analogous plots under strong coupling with $2g_P\sqrt{N} = 0.1\omega_{vib}$, $g_R = 0$ ($g_P = 0$, $2g_R\sqrt{N} = 0.1\omega_{vib}$). We assume the same scattering parameters W_{ij} and decay rates $\Gamma_\downarrow$, κ as in Fig. 2 of the main manuscript.

where

$$\begin{aligned} R_{-D} =& W_{-D_k}\Big(n_D(1+n_-) - e^{-\beta\hbar(\Omega-\Delta)/2}(N-1+n_D)n_-\Big), \\ R_{-+} =& W_{-+}\Big(n_+(1+n_-) - e^{-\beta\hbar\Omega}(1+n_+)n_-\Big), \\ R_{D+} =& W_{D_k+}\Big(n_+(N-1+n_D) - e^{-\beta\hbar(\Omega+\Delta)/2}(1+n_+)n_D\Big). \end{aligned} \tag{S4}$$

For all calculations in the main manuscript, we use $\kappa = \Gamma_\downarrow$, $(N-1)W_{D_k-} = 100\Gamma_\downarrow$, $W_{D_k+} = W_{-D_k} = W_{-+}$ and $N = 10^7$ which correspond to realistic experimental parameters $\kappa = 10^{10}$ s^{-1} ($\sim$ 100 ps), $\Gamma_\downarrow = 10^{10}$ s^{-1} ($\sim$ 100 ps), and scattering from LP to all dark modes $(N-1)W_{D_k-} = 10^{12}\ s^{-1}$ ($\sim$ 1 ps) [6].

S3. REACTION YIELD AND RATE CONSTANT

We look at the reaction yield (Fig. S1) and rate constant (Fig. S2) for point B in Fig. S1a which corresponds to room temperature $k_BT = 0.1408\hbar\omega_{vib}$ ($T = 300$ K), $\Delta = -0.2113\omega_{vib}$, $P_- = 0.08N\Gamma_\downarrow$, $2g\sqrt{N} = 0.1\omega_{vib}$ and $N = 10^7$ for intramolecular electron transfer molecules with $\hbar\omega_{vib} = 185$ meV. We observe small changes in the yield at $\Delta G/\hbar\omega_{vib} = -1.5, 1.5$ for the condensate relative to laser excitation without SC. The relative change in the rate constant is larger at low (point A in Fig. S1a) compared to room temperature (point B in Fig. S1a) since changes in activation energy are amplified at low temperature. Both show the same pattern with maximum change when $\lambda_S/\hbar\omega_{vib} \ll 1$ and $\Delta G/\hbar\omega_{vib} = n/2$ where n is an integer as seen in Fig. S2 (and Fig. 6 in the main manuscript).

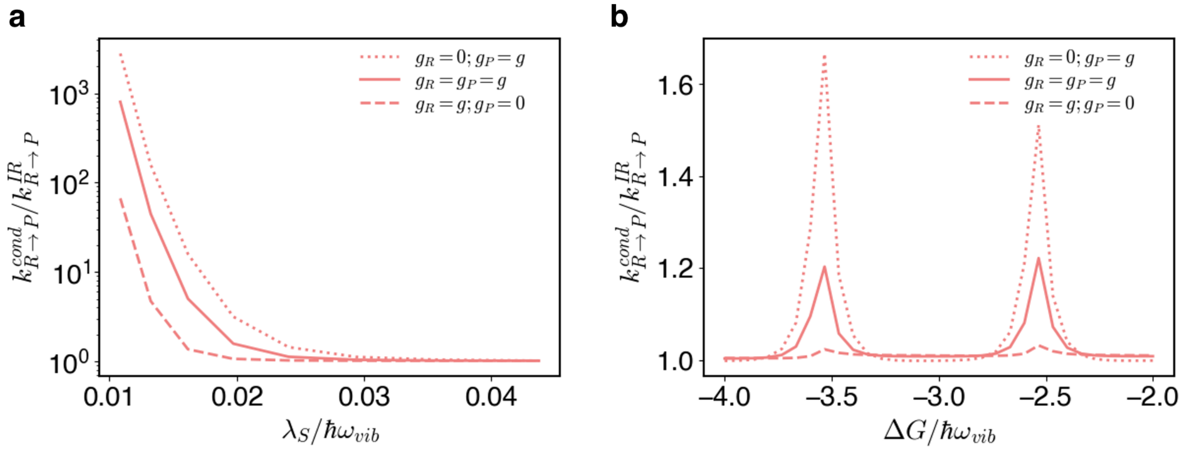

FIG. S2. **Rate constant at room temperature** Ratio of the rate constants inside $k^{cond}_{R\to P}$ and outside $k^{IR}_{R\to P}$ of the cavity under laser excitation with $k_BT = 0.1408\hbar\omega_{vib}$ ($T = 300$ K when $\hbar\omega_{vib} = 185$ meV), $\Delta = -0.2113\omega_{vib}$, $S = 3.5$, $2g\sqrt{N} = 0.1\omega_{vib}$, $P_- = 0.08N\Gamma_\downarrow$ and $N = 10^7$ for cases when only the product is coupled to the cavity $g_R = 0$; $g_P = g$ (dotted line), symmetric coupling $g_R = g_P = g$ (solid line) and only reactant is coupled to the cavity $g_R = g$; $g_P = 0$ (dashed line). **a**, Relative rate constant as a function of reorganization energy, λ_S, with $\Delta G = -3.3334\hbar\omega_{vib}$ and **b**, as a function of ΔG with $\lambda_S = 0.0437\hbar\omega_{vib}$

S4. FRANCK-CONDON FACTORS

Dependence of the FC factors on LP population is shown in Fig. S3 and they scale much better when the population in LP is large. We obtain an analytical expression for the Franck-Condon factor $|F^{f,0}_{\nu_+,\nu_-,\nu_D}|^2$,

$$F^{f,0}_{\nu_+,\nu_-,\nu_D} = \langle 0, N_-, 0 | \nu_+, \nu_-, \nu_D\rangle' \\ = \begin{cases} \sqrt{e^{-S}S^f}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}\,\tilde{w}^{-f}\left[q^{N_-}\right]\left((\tilde{x}+qx)^{\nu_+}(\tilde{y}+yq)^{\nu_-}(\tilde{z}-\tilde{z}q+zq)^{\nu_D}\frac{\exp\left(\frac{-Swq}{1-q-wq}\right)}{(1-q-wq)^{f+1}}\right) & g_P \neq 0 \\ (-1)^{\nu_D}\sqrt{\frac{N_-!}{\nu_+!\nu_-!(\nu_D-f)!}}(x+\tilde{x})^{\nu_+}(y+\tilde{y})^{\nu_-}u^{\nu_D-f}\langle(\nu_D-f)_{R,c}|(\nu_D)_{P,c}\rangle & g_P = 0 \end{cases} \quad \text{(S5)}$$

where $[q^n]G(q)$ is the coefficient of q^n when you expand $G(q)$ as a Taylor series, and

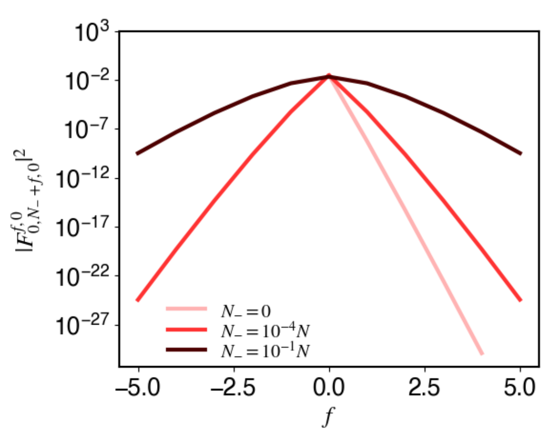

FIG. S3. **Franck-Condon (FC) factors for different channels as a function of** LP **population.** Reaction rate changes by the condensate occur due to channels featuring gain/loss f in vibrational quanta in the LP. The contribution of these channels is proportional to the corresponding FC factors and becomes more significant as the LP population N_- increases. Here, we show FC factors for $N_- = 0, 10^{-4}N, 10^{-1}N$ at resonance $\Delta = 0$ with symmetric light-matter coupling $2g_R\sqrt{N} = 2g_P\sqrt{N} = 0.1\omega_{vib}$ and Huang-Rhys factor $S = 3.5$.

$$
\begin{aligned}
u &= \left(-\cos\theta \frac{g_R}{\sqrt{g_R^2 N_R + g_P^2 N_P}} \right), \\
x &= \sin\theta \cos\theta', \\
y &= \sin\theta \sin\theta', \\
z &= \left(g_P \cos\theta \sqrt{\frac{g_R^2(N_R-1) + g_P^2 N_P}{(g_R^2(N_R-1) + g_P^2(N_P+1))(g_R^2 N_R + g_P^2 N_P)}} \right), \\
w &= \left(\frac{g_R g_P}{g_R^2(N_R-1) + g_P^2 N_P} \right), \\
\tilde{x} &= \left(\frac{-\cos\theta \sin\theta' (g_R^2(N_R-1) + g_P^2 N_P)}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right), \\
\tilde{y} &= \left(\frac{\cos\theta \cos\theta' (g_R^2(N_R-1) + g_P^2 N_P)}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right), \\
\tilde{z} &= \left(-\cos\theta \frac{g_R^2(N_R-1) + g_P^2 N_P}{g_P \sqrt{g_R^2 N_R + g_P^2 N_P}} \sqrt{\frac{g_R^2(N_R-1) + g_P^2 N_P}{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right), \\
\tilde{w} &= \left(-\cos\theta \frac{g_R^2(N_R-1) + g_P^2 N_P}{g_P \sqrt{g_R^2 N_R + g_P^2 N_P}} \right).
\end{aligned}
\tag{S6}
$$

We arrived at the expression in equation (S5) by using generating functions and the Lagrange-Bürmann formula [7]. We then recursively compute $F^{f,n}_{\nu_+,\nu_-,\nu_D}$ from $F^{f,0}_{\nu_+,\nu_-,\nu_D}$ [8]. Using

$$
\begin{bmatrix} \hat{a}_+ \\ \hat{a}_- \\ \hat{a}_D^{(R,c)} \end{bmatrix} = \begin{bmatrix} J_{11} & J_{12} & J_{13} \\ J_{21} & J_{22} & J_{23} \\ J_{31} & J_{32} & J_{33} \end{bmatrix} \begin{bmatrix} \hat{a}'_+ \\ \hat{a}'_- \\ \hat{a}_D^{(P,c)\prime} \end{bmatrix} + \begin{bmatrix} K_1 \\ K_2 \\ K_3 \end{bmatrix}
\tag{S7}
$$

where

$$
\begin{aligned}
J_{11} &= \cos\theta\cos\theta' + \sin\theta\sin\theta' \left(\frac{g_R^2(N_R-1) + g_P^2 N_P + g_R g_P}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right) \\
J_{12} &= \sin\theta'\cos\theta - \cos\theta'\sin\theta \left(\frac{g_R^2(N_R-1) + g_P^2 N_P + g_R g_P}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right) \\
J_{13} &= \sin\theta \left(\frac{(g_R - g_P)\sqrt{g_R^2(N_R-1) + g_P^2 N_P}}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right) \\
J_{21} &= \cos\theta'\sin\theta - \sin\theta'\cos\theta \left(\frac{g_R^2(N_R-1) + g_P^2 N_P + g_R g_P}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right) \\
J_{22} &= \sin\theta\sin\theta' + \cos\theta\cos\theta' \left(\frac{g_R^2(N_R-1) + g_P^2 N_P + g_R g_P}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right) \\
J_{23} &= -\cos\theta \left(\frac{(g_R - g_P)\sqrt{g_R^2(N_R-1) + g_P^2 N_P}}{\sqrt{g_R^2 N_R + g_P^2 N_P}\sqrt{g_R^2(N_R-1) + g_P^2(N_P+1)}} \right)
\end{aligned}
\tag{S8}
$$

and

$$
\begin{aligned}
J_{31} &= -\sin\theta'\left(\frac{(g_R-g_P)\sqrt{g_R^2(N_R-1)+g_P^2N_P}}{\sqrt{g_R^2N_R+g_P^2N_P}\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right)\\
J_{32} &= \cos\theta'\left(\frac{(g_R-g_P)\sqrt{g_R^2(N_R-1)+g_P^2N_P}}{\sqrt{g_R^2N_R+g_P^2N_P}\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right)\\
J_{33} &= \left(\frac{g_R^2(N_R-1)+g_P^2N_P+g_Rg_P}{\sqrt{g_R^2N_R+g_P^2N_P}\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right)\\
K_1 &= -\sin\theta\frac{g_R}{\sqrt{g_R^2N_R+g_P^2N_P}}\sqrt{S}\\
K_2 &= \cos\theta\frac{g_R}{\sqrt{g_R^2N_R+g_P^2N_P}}\sqrt{S}\\
K_3 &= -\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2N_R+g_P^2N_P}}\sqrt{S}
\end{aligned}
\tag{S9}
$$

we get the recursive formula

$$
F^{f,n+1}_{\nu_+,\nu_-,\nu_D} = \frac{1}{\sqrt{n+1}}\Big(J_{31}\sqrt{\nu_+}F^{f,n}_{\nu_+-1,\nu_-,\nu_D} + F^{f,n}_{\nu_+,\nu_--1,\nu_D}J_{32}\sqrt{\nu_-} + J_{33}\sqrt{\nu_D}F^{f,n}_{\nu_+,\nu_-,\nu_D-1} + K_3F^{f-1,n}_{\nu_+,\nu_-,\nu_D}\Big). \tag{S10}
$$

To derive equation (S5), we write the initial and final vibrational states in terms of creation/annihilation operators for the upper, lower polaritons and dark modes

$$
F^{f,0}_{\nu_+,\nu_-,\nu_D} = \left\langle 0_+0_-0_D^{(R,c)}\right| \frac{\left(\hat{a}_-\right)^{N_-}}{\sqrt{N_-!}}\frac{\left(\hat{a}'^{\dagger}_+\right)^{\nu_+}}{\sqrt{\nu_+!}}\frac{\left(\hat{a}'^{\dagger}_-\right)^{\nu_-}}{\sqrt{\nu_-!}}\frac{\left(\hat{a}_D^{(P,c)\prime\dagger}\right)^{\nu_D}}{\sqrt{\nu_D!}}\left|0'_+0'_-0_D^{(P,c)\prime}\right\rangle. \tag{S11}
$$

Writing the polariton modes as a linear combination of the photon $\hat{a}_{ph}$ and bright modes $\hat{a}_{B(N_R,N_P)}$, $\hat{a}_{B(N_R-1,N_P+1)}$,

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \frac{1}{\sqrt{N_-!\nu_+!\nu_-!\nu_D!}}\left\langle 0_{ph}0_{B(N_R,N_P)}0_D^{(R,c)}\right|\left(\sin\theta\hat{a}_{ph}-\cos\theta\hat{a}_{B(N_R,N_P)}\right)^{N_-}\left(\cos\theta'\hat{a}^{\dagger}_{ph}+\sin\theta'\hat{a}^{\dagger}_{B(N_R-1,N_P+1)}\right)^{\nu_+}\\
&\times\left(\sin\theta'\hat{a}^{\dagger}_{ph}-\cos\theta'\hat{a}^{\dagger}_{B(N_R-1,N_P+1)}\right)^{\nu_-}\left(\hat{a}_D^{(P,c)\prime\dagger}\right)^{\nu_D}\left|0_{ph}0_{B(N_R-1,N_P+1)}0_D^{(P,c)\prime}\right\rangle.
\end{aligned}
\tag{S12}
$$

Here, $\left[\hat{a}_{ph},\hat{a}_{B(N_R,N_P)}\right]=0$ and $\left[\hat{a}_{ph},\hat{a}_{B(N_R-1,N_P+1)}\right]=0$, so we can use the binomial theorem and collect these operators,

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \frac{1}{\sqrt{N_-!\nu_+!\nu_-!\nu_D!}}\sum_{l=0}^{N_-}\sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-}\binom{N_-}{l}\binom{\nu_+}{m}\binom{\nu_-}{n}\left\langle 0_{ph}0_{B(N_R,N_P)}0_D^{(R,c)}\right|\left(\sin\theta\hat{a}_{ph}\right)^{l}\\
&\times\left(-\cos\theta\hat{a}_{B(N_R,N_P)}\right)^{N_--l}\left(\cos\theta'\hat{a}^{\dagger}_{ph}\right)^{m}\left(\sin\theta'\hat{a}^{\dagger}_{B(N_R-1,N_P+1)}\right)^{\nu_+-m}\left(\sin\theta'\hat{a}^{\dagger}_{ph}\right)^{n}\\
&\times\left(-\cos\theta'\hat{a}^{\dagger}_{B(N_R-1,N_P+1)}\right)^{\nu_--n}\left(\hat{a}_D^{(P,c)\prime\dagger}\right)^{\nu_D}\left|0_{ph}0_{B(N_R-1,N_P+1)}0_D^{(P,c)\prime}\right\rangle.
\end{aligned}
\tag{S13}
$$

The only non-vanishing terms in the above summation will be those with equal number of photon creation and annihilation operators $l=m+n$, since the photon mode does not get displaced during the chemical reaction, the overlap is non-zero only when the initial and final states are exactly the same. Plugging in $l=m+n$ and $\left\langle 0_{ph}\right|(\hat{a}_{ph})^{l}(\hat{a}^{\dagger}_{ph})^{m+n}\left|0_{ph}\right\rangle=(m+n)!$

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \frac{1}{\sqrt{N_-!\nu_+!\nu_-!\nu_D!}}\sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-}\binom{N_-}{m+n}\binom{\nu_+}{m}\binom{\nu_-}{n}\left(\sin\theta\right)^{m+n}\left(\cos\theta'\right)^{m}\left(\sin\theta'\right)^{n}\\
&\times\left(-\cos\theta\right)^{N_--m-n}\left(\sin\theta'\right)^{\nu_+-m}\left(-\cos\theta'\right)^{\nu_--n}(m+n)!\\
&\times\left\langle 0_{B(N_R,N_P)}0_D^{(R,c)}\right|\left(\hat{a}_{B(N_R,N_P)}\right)^{N_--m-n}\left(\hat{a}^{\dagger}_{B(N_R-1,N_P+1)}\right)^{(\nu_++\nu_-)-(m+n)}\left(\hat{a}_D^{(P,c)\prime\dagger}\right)^{\nu_D}\left|0_{B(N_R-1,N_P+1)}0_D^{(P,c)\prime}\right\rangle
\end{aligned}
\tag{S14}
$$

Rewriting the initial bright mode $\hat{a}_{B(N_R,N_P)}$, final bright mode $\hat{a}_{B(N_R-1,N_P+1)}$, and the highly localized final dark mode $\hat{a}_D^{(P,c)\prime}$ in terms of a bright mode involving all molecules other than the reacting molecule $\hat{a}_{B(N_R-1,N_P)} = \frac{1}{\sqrt{g_R^2(N_R-1)+g_P^2 N_P}}\left[g_R \sum_{i=1}^{N_R-1} a_{R,i} + g_P \sum_{j=1}^{N_P} a_{P,j}\right]$, and vibrational modes of this molecule $\hat{a}_{P,c}$ and $\hat{a}_{R,c}$ we obtain

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \frac{1}{\sqrt{N_-!\nu_+!\nu_-!\nu_D!}} \sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-} \binom{N_-}{m+n}\binom{\nu_+}{m}\binom{\nu_-}{n}\Big(\sin\theta\Big)^{m+n}\Big(\cos\theta'\Big)^{m}\Big(\sin\theta'\Big)^{n} \\
&\times\Big(-\cos\theta\Big)^{N_--m-n}\Big(\sin\theta'\Big)^{\nu_+-m}\Big(-\cos\theta'\Big)^{\nu_--n}(m+n)! \\
&\times\left\langle 0_{B(N_R-1,N_P)}0_{R,c}\right|\left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2N_R+g_P^2N_P}}\hat{a}_{B(N_R-1,N_P)}+\frac{g_R}{\sqrt{g_R^2N_R+g_P^2N_P}}\hat{a}_{R,c}\right]^{N_--m-n} \\
&\times\left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2(N_R-1)+g_P^2(N_P+1)}}\hat{a}^\dagger_{B(N_R-1,N_P)}+\frac{g_P}{\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\hat{a}^\dagger_{P,c}\right]^{(\nu_++\nu_-)-(m+n)} \\
&\times\left[-\frac{g_P}{\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\hat{a}^\dagger_{B(N_R-1,N_P)}+\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2(N_R-1)+g_P^2(N_P+1)}}\hat{a}^\dagger_{P,c}\right]^{\nu_D}\left|0_{B(N_R-1,N_P)}0_{P,c}\right\rangle.
\end{aligned}
\tag{S15}
$$

Since $\left[\hat{a}_{B(N_R-1,N_P)},\hat{a}_{R,c}\right]=0$ and $\left[\hat{a}_{B(N_R-1,N_P)},\hat{a}_{P,c}\right]=0$, we can use the binomial expansion again

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \frac{1}{\sqrt{N_-!\nu_+!\nu_-!\nu_D!}} \sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-}\sum_{r=0}^{N_--m-n}\sum_{p=0}^{(\nu_++\nu_-)-(m+n)}\sum_{q=0}^{\nu_D} \binom{N_-}{m+n}\binom{\nu_+}{m}\binom{\nu_-}{n}\binom{N_--m-n}{r}\binom{(\nu_++\nu_-)-(m+n)}{p} \\
&\times\binom{\nu_D}{q}\Big(\sin\theta\Big)^{m+n}\Big(\cos\theta'\Big)^{m}\Big(\sin\theta'\Big)^{n}(m+n)!\Big(-\cos\theta\Big)^{N_--m-n}\Big(\sin\theta'\Big)^{\nu_+-m}\Big(-\cos\theta'\Big)^{\nu_--n}(-1)^q \\
&\times\left[\frac{g_P}{\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right]^{(\nu_++\nu_-+q)-(m+n+p)}\left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right]^{\nu_D+p-q} \\
&\times\left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2N_R+g_P^2N_P}}\right]^{r}\left[\frac{g_R}{\sqrt{g_R^2N_R+g_P^2N_P}}\right]^{N_--m-n-r}\left\langle 0_{B(N_R-1,N_P)}0_{R,c}\right|\Big(\hat{a}_{B(N_R-1,N_P)}\Big)^{r}\Big(\hat{a}_{R,c}\Big)^{N_--m-n-r} \\
&\times\Big(\hat{a}^\dagger_{B(N_R-1,N_P)}\Big)^{p+q}\Big(\hat{a}^\dagger_{P,c}\Big)^{(\nu_++\nu_-+\nu_D)-(m+n+p+q)}\left|0_{B(N_R-1,N_P)}0_{P,c}\right\rangle.
\end{aligned}
\tag{S16}
$$

The vibrational modes of all molecules other than the reacting molecule are not modified by the chemical reaction, therefore, non-zero terms in the summation satisfy $r=p+q$. Plugging in $r=p+q$ and $\left\langle 0_{B(N_R-1,N_P)}\right|(\hat{a}_{B(N_R-1,N_P)})^r(\hat{a}^\dagger_{B(N_R-1,N_P)})^{p+q}\left|0_{B(N_R-1,N_P)}\right\rangle = (p+q)!$,

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \frac{1}{\sqrt{N_-!\nu_+!\nu_-!\nu_D!}} \sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-}\sum_{p=0}^{(\nu_++\nu_-)-(m+n)}\sum_{q=0}^{\nu_D} \binom{N_-}{m+n}\binom{\nu_+}{m}\binom{\nu_-}{n}\binom{N_--(m+n)}{p+q}\binom{\nu_D}{q}\binom{(\nu_++\nu_-)-(m+n)}{p} \\
&\times\Big(\sin\theta\Big)^{m+n}\Big(\cos\theta'\Big)^{m}\Big(\sin\theta'\Big)^{n}(m+n)!(p+q)!\Big(-\cos\theta\Big)^{N_--(m+n)}\Big(\sin\theta'\Big)^{\nu_+-m}\Big(-\cos\theta'\Big)^{\nu_--n}(-1)^q \\
&\times\left[\frac{g_P}{\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right]^{(\nu_++\nu_-+q)-(m+n+p)}\left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2(N_R-1)+g_P^2(N_P+1)}}\right]^{\nu_D+p-q}\left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2N_R+g_P^2N_P}}\right]^{p+q} \\
&\times\left[\frac{g_R}{\sqrt{g_R^2N_R+g_P^2N_P}}\right]^{N_--(m+n+p+q)}\left\langle 0_{R,c}\right|\Big(\hat{a}_{R,c}\Big)^{N_--(m+n+p+q)}\Big(\hat{a}^\dagger_{P,c}\Big)^{(\nu_++\nu_-+\nu_D)-(m+n+p+q)}\left|0_{P,c}\right\rangle
\end{aligned}
\tag{S17}
$$

Changing variables from $\{m,n,q,p\}$ to $\{i,j,k,h\}$, where $i=\nu_+-m$, $j=\nu_--n$, $k=\nu_D-q$, $h=N_--m-n-p-q$ and

$f = \nu_+ + \nu_- + \nu_D - N_-,$

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \left(-\cos\theta \frac{g_R^2(N_R-1)+g_P^2 N_P}{g_P\sqrt{g_R^2 N_R + g_P^2 N_P}} \right)^{-f} \sum_{i=0}^{\nu_+}\sum_{j=0}^{\nu_-}\sum_{k=0}^{\nu_D}\sum_{h=k-f}^{i+j+k-f} \binom{\nu_+}{i}\binom{\nu_-}{j}\binom{i+j}{h+f-k}\binom{\nu_D}{k} \\
&\times \left(\frac{g_R g_P}{g_R^2(N_R-1)+g_P^2 N_P} \right)^h \left(\sin\theta\cos\theta'\right)^{\nu_+-i} \left(\frac{-\cos\theta\sin\theta'(g_R^2(N_R-1)+g_P^2N_P)}{\sqrt{g_R^2N_R+g_P^2N_P}\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}} \right)^i \left(\sin\theta\sin\theta'\right)^{\nu_--j} \\
&\times \left(\frac{\cos\theta\cos\theta'(g_R^2(N_R-1)+g_P^2N_P)}{\sqrt{g_R^2N_R+g_P^2N_P}\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}} \right)^j \left(g_P\cos\theta\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{(g_R^2(N_R-1)+g_P^2(N_P+1))(g_R^2N_R+g_P^2N_P)}} \right)^{\nu_D-k} \\
&\times \left(-\cos\theta\frac{g_R^2(N_R-1)+g_P^2N_P}{g_P\sqrt{g_R^2N_R+g_P^2N_P}}\sqrt{\frac{g_R^2(N_R-1)+g_P^2N_P}{g_R^2(N_R-1)+g_P^2(N_P+1)}} \right)^k \frac{1}{h!}\langle 0_{R,c}| \left(\hat{a}_{R,c}\right)^h \left(\hat{a}^\dagger_{P,c}\right)^{h+f} |0_{P,c}\rangle
\end{aligned}
\tag{S18}
$$

The above expression is valid only when $g_P \neq 0$. The case of $g_P = 0$ is explained in Section S4 A. Remembering the definitions of variables x, y, z, w and $\tilde{x}, \tilde{y}, \tilde{z}$ from equation (S6),

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \tilde{w}^{-f} \sum_{i=0}^{\nu_+}\sum_{j=0}^{\nu_-}\sum_{k=0}^{\nu_D}\sum_{h=k-f}^{i+j+k-f} \binom{\nu_+}{i}\binom{\nu_-}{j}\binom{i+j}{h+f-k}\binom{\nu_D}{k} x^{\nu_+-i} y^{\nu_--j} z^{\nu_D-k} \tilde{x}^i \tilde{y}^j \tilde{z}^k w^h \\
&\times \sqrt{\frac{(h+f)!}{h!}} \langle h_{R,c}|(h+f)_{P,c}\rangle
\end{aligned}
\tag{S19}
$$

This is not easy to evaluate because of the summation over h involves the term $\langle h_{R,c}|(h+f)_{P,c}\rangle$. Substituting $\langle h_{R,c}|(h+f)_{P,c}\rangle = \sqrt{\frac{(h+f)!}{h!}}\sqrt{\frac{e^{-S}}{S^f}}\hat{O}_f(S)\sum_{u=0}^{h}\binom{h}{u}\frac{(-S)^u}{u!}$,

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \tilde{w}^{-f} \sum_{i=0}^{\nu_+}\sum_{j=0}^{\nu_-}\sum_{k=0}^{\nu_D}\sum_{h=k-f}^{i+j+k-f} \binom{\nu_+}{i}\binom{\nu_-}{j}\binom{i+j}{h+f-k}\binom{\nu_D}{k} x^{\nu_+-i} y^{\nu_--j} z^{\nu_D-k} \tilde{x}^i \tilde{y}^j \tilde{z}^k w^h \\
&\times \frac{(h+f)!}{h!}\sqrt{\frac{e^{-S}}{S^f}}\hat{O}_f(S)\sum_{u=0}^{h}\binom{h}{u}\frac{(-S)^u}{u!}.
\end{aligned}
\tag{S20}
$$

Rewriting $(h+f)!w^h/h!$ as $\hat{T}_f(w)w^h$,

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \sqrt{\frac{e^{-S}}{S^f}}\hat{O}_f(S)\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \tilde{w}^{-f} \sum_{i=0}^{\nu_+}\sum_{j=0}^{\nu_-}\sum_{k=0}^{\nu_D}\sum_{h=k-f}^{i+j+k-f}\sum_{u=0}^{h} \binom{\nu_+}{i}\binom{\nu_-}{j}\binom{i+j}{h+f-k}\binom{\nu_D}{k}\binom{h}{u} \\
&\times \frac{(-S)^u}{u!} x^{\nu_+-i} y^{\nu_--j} z^{\nu_D-k} \tilde{x}^i \tilde{y}^j \tilde{z}^k \hat{T}_f(w) w^h.
\end{aligned}
\tag{S21}
$$

With the operators $\hat{O}_f(S)$ and $\hat{T}_f(w)$ defined as:

$$
\begin{aligned}
\hat{O}_f(S) &= \begin{cases} \left(\int dS\right)^f & f \geq 0 \\ \left(\frac{d}{dS}\right)^{-f} & f < 0 \end{cases} \\
\hat{T}_f(w) &= \begin{cases} \left(\frac{d}{dw}\right)^f w^f & f \geq 0 \\ \left(\int dw\right)^{-f} w^f & f < 0 \end{cases}
\end{aligned}
\tag{S22}
$$

This simplifies to

$$
\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} &= \sqrt{\frac{e^{-S}}{S^f}}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}\tilde{w}^{-f}\hat{O}_f(S)\hat{T}_f(w) \\
&\qquad \sum_{i=0}^{\nu_+}\sum_{j=0}^{\nu_-}\sum_{k=0}^{\nu_D}\sum_{h=k-f}^{i+j+k-f}\sum_{u=0}^{h}\binom{\nu_+}{i}\binom{\nu_-}{j}\binom{i+j}{h+f-k}\binom{\nu_D}{k}\binom{h}{u}\frac{(-S)^u}{u!}x^{\nu_+-i}y^{\nu_--j}z^{\nu_D-k}\tilde{x}^i\tilde{y}^j\tilde{z}^k w^h, \\
&= \sqrt{\frac{e^{-S}}{S^f}}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}\tilde{w}^{-f}\hat{O}_f(S)\hat{T}_f(w)M^f_{\nu_+,\nu_-,\nu_D}.
\end{aligned}
\tag{S23}
$$

Here we introduce $M^f_{\nu_+,\nu_-,\nu_D}$ as the part involving the summation in $F^{f,0}_{\nu_+,\nu_-,\nu_D}$ for more readability. Evaluating $M^f_{\nu_+,\nu_-,\nu_D}$,

$$
\begin{aligned}
M^f_{\nu_+,\nu_-,\nu_D} &= \sum_{i=0}^{\nu_+}\sum_{j=0}^{\nu_-}\sum_{k=0}^{\nu_D}\sum_{h=k-f}^{i+j+k-f}\sum_{u=0}^{h}\binom{\nu_+}{i}\binom{\nu_-}{j}\binom{i+j}{i+j+k-f-h}\binom{\nu_D}{k}\binom{h}{u}\frac{(-S)^u}{u!}x^{\nu_+-i}y^{\nu_--j}z^{\nu_D-k}\tilde{x}^i\tilde{y}^j\tilde{z}^k w^h \\
&= \sum_{i=0}^{\nu_+}\binom{\nu_+}{i}\tilde{x}^i x^{\nu_+-i}\sum_{j=0}^{\nu_-}\binom{\nu_-}{j}\tilde{y}^j y^{\nu_--j}\sum_{k=0}^{\nu_D}\binom{\nu_D}{k}\tilde{z}^k z^{\nu_D-k}\sum_{h=k-f}^{i+j+k-f}\binom{i+j}{i+j+k-f-h}w^h\sum_{u=0}^{h}\binom{h}{u}\frac{(-S)^u}{u!}
\end{aligned}
\tag{S24}
$$

We first focus on evaluating the summation over u. Without $u!$ in the denominator, this would have simply been a binomial expansion. The $u!$ makes it difficult to evaluate, but each term in the summation looks like the product of terms from a binomial $\binom{h}{u}$ and exponential $(-S)^u/u!$ expansion. We can use the powerful combinatorial technique of generating functions to evaluate the summation. Here, t is a dummy variable that we introduce to count the terms,

$$
M^f_{\nu_+,\nu_-,\nu_D} = \sum_{i=0}^{\nu_+}\binom{\nu_+}{i}\tilde{x}^i x^{\nu_+-i}\sum_{j=0}^{\nu_-}\binom{\nu_-}{j}\tilde{y}^j y^{\nu_--j}\sum_{k=0}^{\nu_D}\binom{\nu_D}{k}\tilde{z}^k z^{\nu_D-k}\sum_{h=k-f}^{i+j+k-f}\binom{i+j}{i+j+k-f-h}w^h([t^h](1+t)^h e^{-St})
\tag{S25}
$$

Each term in the summation over h is a product of coefficients of two generating functions,

$$
\begin{aligned}
M^f_{\nu_+,\nu_-,\nu_D} &= \sum_{i=0}^{\nu_+}\binom{\nu_+}{i}\tilde{x}^i x^{\nu_+-i}\sum_{j=0}^{\nu_-}\binom{\nu_-}{j}\tilde{y}^j y^{\nu_--j}\sum_{k=0}^{\nu_D}\binom{\nu_D}{k}\tilde{z}^k z^{\nu_D-k}w^{k-f}\sum_{h=k-f}^{i+j+k-f}\binom{i+j}{i+j+k-f-h}w^{h+f-k}([t^h](1+t)^h e^{-St}) \\
&= \sum_{i=0}^{\nu_+}\binom{\nu_+}{i}\tilde{x}^i x^{\nu_+-i}\sum_{j=0}^{\nu_-}\binom{\nu_-}{j}\tilde{y}^j y^{\nu_--j}\sum_{k=0}^{\nu_D}\binom{\nu_D}{k}\tilde{z}^k z^{\nu_D-k}w^{k-f}\sum_{h=k-f}^{i+j+k-f}([t^{i+j+k-f-h}](w+t)^{i+j})([t^h](1+t)^h e^{-St}).
\end{aligned}
\tag{S26}
$$

For notational convenience, let us define

$$
c_\alpha = [t^\alpha](w+t)^{i+j}, \qquad d_\beta = [t^\beta](1+t)^\beta e^{-St}.
\tag{S27}
$$

Since c_α is zero when $\alpha > i+j$, the lower limit of the summation over h can be shifted from $h = k-f$ to $h = 0$,

$$
\sum_{h=k-f}^{i+j+k-f} c_{i+j+k-f-h}d_h = \sum_{h=0}^{i+j+k-f} c_{i+j+k-f-h}d_h.
\tag{S28}
$$

This summation over h can be written as the coefficient of the product of two generating function

$$
\sum_{h=0}^{i+j+k-f} c_{i+j+k-f-h}d_h = [q^{i+j+k-f}]\left(\sum_{\alpha=0}^{\infty}c_\alpha q^\alpha\right)\left(\sum_{\beta=0}^{\infty}d_\beta q^\beta\right),
\tag{S29}
$$

where q is the new dummy variable. Now we will find a closed expression for the generating function

$$
C(q) = \sum_{\alpha=0}^{\infty}c_\alpha q^\alpha, \qquad D(q) = \sum_{\beta=0}^{\infty}d_\beta q^\beta.
\tag{S30}
$$

Using binomial expansion, we get the closed expression $C(q) = (w+q)^{i+j}$. However, it is much more complicated to obtain a closed expression for $D(q)$. To do so, we use the powerful Lagrange-Bürmann formula, which states that for any generating series $f(t)$ and $g(t)$ such that $f(0) \neq 0$ and a change of variable $q = t/f(t)$, we have an identity of generating functions in the dummy variable q,

$$\sum_{\beta=0}^{\infty} ([t^{\beta}]f(t)^{\beta} g(t))q^{\beta} = \frac{g(t)}{f(t)} \frac{dt}{dq}, \tag{S31}$$

where t is expressed in terms of q. In our scenario, $f(t) = (1+t)^{\beta}$ and $g(t) = e^{-St}$, hence $q = t/(1+t)$, which gives us

$$t = \frac{q}{1-q} \qquad \frac{dt}{dq} = \frac{1}{(1-q)^2} \tag{S32}$$

Writing t in terms of q we get $f(t) = \frac{1}{1-q}$ and $g(t) = e^{-Sq/(1-q)}$. Therefore we have

$$\begin{aligned} D(q) &= \frac{e^{-Sq/(1-q)}}{(1-q)^2}(1-q) \\ &= \frac{e^{-Sq/(1-q)}}{(1-q)}. \end{aligned} \tag{S33}$$

Continuing with the original summation, we now have

$$M^{f}_{\nu_+,\nu_-,\nu_D} = \sum_{i=0}^{\nu_+} \binom{\nu_+}{i} \tilde{x}^i x^{\nu_+-i} \sum_{j=0}^{\nu_-} \binom{\nu_-}{j} \tilde{y}^j y^{\nu_--j} \sum_{k=0}^{\nu_D} \binom{\nu_D}{k} \tilde{z}^k z^{\nu_D-k} w^{k-f} \left([t^{i+j+k-f}](w+t)^{i+j} \frac{e^{-St/(1-t)}}{(1-t)} \right) \tag{S34}$$

Note that in the above expression we again replaced q with t. Repeating the calculations using Lagrange-Bürmann formula three more times, for the summation over i, j and k, we get the final compressed expression of the desired summation

$$M^{f}_{\nu_+,\nu_-,\nu_D} = [q^{N_-}] \left((\tilde{x}+qx)^{\nu_+} (\tilde{y}+yq)^{\nu_-} \frac{(\tilde{z}-\tilde{z}q+zq)^{\nu_D}}{(1-q)^f} \frac{\exp\left(\frac{-Swq}{1-q-wq}\right)}{(1-q-wq)} \right). \tag{S35}$$

Applying operators $\hat{O}_f(S)$ and $\hat{T}_f(w)$ to $M^{f}_{\nu_+,\nu_-,\nu_D}$

$$\begin{aligned} F^{f,0}_{\nu_+,\nu_-,\nu_D} &= \sqrt{\frac{e^{-S}}{S^f}} \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \tilde{w}^{-f} [q^{N_-}] \left((\tilde{x}+qx)^{\nu_+} (\tilde{y}+yq)^{\nu_-} \frac{(\tilde{z}-\tilde{z}q+zq)^{\nu_D}}{(1-q)^f} \hat{O}_f(S)\hat{T}_f(w) \frac{\exp\left(\frac{-Swq}{1-q-wq}\right)}{(1-q-wq)} \right) \\ &= \sqrt{e^{-S}S^f} \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \tilde{w}^{-f} [q^{N_-}] \left((\tilde{x}+qx)^{\nu_+} (\tilde{y}+yq)^{\nu_-} (\tilde{z}-\tilde{z}q+zq)^{\nu_D} \frac{\exp\left(\frac{-Swq}{1-q-wq}\right)}{(1-q-wq)^{f+1}} \right) \end{aligned} \tag{S36}$$

A. Product not coupled

When $g_P = 0$, the expression in equation (S36) does not apply,

$$\begin{aligned} F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \sum_{m=0}^{\nu_+} \sum_{n=0}^{\nu_-} \sum_{q=0}^{\nu_D} \sum_{h=\nu_D-f-q}^{N_--m-n-q} \binom{\nu_+}{m} \binom{\nu_-}{n} \binom{(\nu_++\nu_-)-(m+n)}{h+q+f-\nu_D} \binom{\nu_D}{q} \\ & \times \Big(\sin\theta\Big)^{m+n} \Big(\cos\theta'\Big)^{m} \Big(\sin\theta'\Big)^{n} \Big(-\cos\theta\Big)^{N_--(m+n)} \Big(\sin\theta'\Big)^{\nu_+-m} \Big(-\cos\theta'\Big)^{\nu_--n} (-1)^q \\ & \times \left[\frac{g_P}{\sqrt{g_R^2(N_R-1)+g_P^2(N_P+1)}} \right]^{(f+h+2q)-\nu_D} \left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2 N_P}{g_R^2(N_R-1)+g_P^2(N_P+1)}} \right]^{\nu_D+N_--h-m-n-2q} \\ & \times \left[\sqrt{\frac{g_R^2(N_R-1)+g_P^2 N_P}{g_R^2 N_R+g_P^2 N_P}} \right]^{N_--h-m-n} \left[\frac{g_R}{\sqrt{g_R^2 N_R+g_P^2 N_P}} \right]^{h} \sqrt{\frac{(h+f)!}{h!}} \left\langle h_{R,c} | (h+f)_{P,c} \right\rangle. \end{aligned} \tag{S37}$$

Since $g_P = 0$, only terms with $f + h + 2q - \nu_D = 0$ will be non-zero,

$$F^{f,0}_{\nu_+,\nu_-,\nu_D} = \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-}\sum_{q=0}^{\nu_D} \binom{\nu_+}{m}\binom{\nu_-}{n}\binom{(\nu_+ + \nu_-) - (m+n)}{-q}\binom{\nu_D}{q}\Big(\sin\theta\Big)^{m+n}\Big(\cos\theta'\Big)^{m}$$
$$\times\Big(\sin\theta'\Big)^{n}\Big(-\cos\theta\Big)^{N_- -(m+n)} \times \Big(\sin\theta'\Big)^{\nu_+ - m}\Big(-\cos\theta'\Big)^{\nu_- - n}(-1)^q\left(\frac{1}{\sqrt{N_R}}\right)^{\nu_D - f - 2q} \tag{S38}$$
$$\times\left(\sqrt{\frac{N_R - 1}{N_R}}\right)^{N_- + f + 2q - \nu_D - m - n}\sqrt{\frac{(\nu_D - 2q)!}{(\nu_D - 2q - f)!}}\,\langle(\nu_D - 2q - f)_{R,c}|(\nu_D - 2q)_{P,c}\rangle\,.$$

From the above, we see that $q = 0$ because of the binomial coefficient involving $-q$ and

$$F^{f,0}_{\nu_+,\nu_-,\nu_D} = \sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}} \sum_{m=0}^{\nu_+}\sum_{n=0}^{\nu_-}\binom{\nu_+}{m}\binom{\nu_-}{n}\Big(\sin\theta\Big)^{m+n}\Big(\cos\theta'\Big)^{m}\Big(\sin\theta'\Big)^{n}\Big(-\cos\theta\Big)^{N_- -(m+n)}\Big(\sin\theta'\Big)^{\nu_+ - m}$$
$$\times\Big(-\cos\theta'\Big)^{\nu_- - n}\left(\frac{1}{\sqrt{N_R}}\right)^{\nu_D - f}\left(\sqrt{\frac{N_R - 1}{N_R}}\right)^{N_- + f - \nu_D - m - n}\sqrt{\frac{\nu_D!}{(\nu_D - f)!}}\,\langle(\nu_D - f)_{R,c}|(\nu_D)_{P,c}\rangle\,. \tag{S39}$$

Using the binomial expansion to collect terms, we get

$$F^{f,0}_{\nu_+,\nu_-,\nu_D} = \sqrt{\frac{N_-!}{\nu_+!\nu_-!(\nu_D - f)!}}(x + \tilde{x})^{\nu_+}(y + \tilde{y})^{\nu_-}u^{\nu_D - f}\,\langle(\nu_D - f)_{R,c}|(\nu_D)_{P,c}\rangle\,. \tag{S40}$$

B. Reactant not coupled

Starting from equation (S5) and substituting $g_R = 0$, we have $w = 0$,

$$F^{f,0}_{\nu_+,\nu_-,\nu_D} = \sqrt{e^{-S}S^f}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}\tilde{w}^{-f}\Big[q^{N_-}\Big]\left((\tilde{x} + xq)^{\nu_+}(\tilde{y} + yq)^{\nu_-}(\tilde{z} - \tilde{z}q + zq)^{\nu_D}\frac{1}{(1-q)^{f+1}}\right). \tag{S41}$$

Changing variable from q to $t = q(1+w)$

$$F^{f,0}_{\nu_+,\nu_-,\nu_D} = \sqrt{e^{-S}S^f}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}(\tilde{w}(1+w))^{-f}[t^{N_-}]\left(\Big(\tilde{x}(1+w) + xt\Big)^{\nu_+}\Big(\tilde{y}(1+w) + yt\Big)^{\nu_-}\right.$$
$$\left.\times\Big(\tilde{z}(1+w) + (z - \tilde{z})t\Big)^{\nu_D}\frac{1}{(1-t)^{f+1}}\right) \tag{S42}$$
$$= \sqrt{e^{-S}S^f}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}(\tilde{w}(1+w))^{-f}B^f_{\nu_+,\nu_-,\nu_D},$$

and we call the part of $F^{f,0}_{\nu_+,\nu_-,\nu_D}$ that involves taking the t^{N_-} coefficient

$$B^f_{\nu_+,\nu_-,\nu_D} = [t^{N_-}]\left(\frac{G_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^{f+1}}\right), \tag{S43}$$

where

$$G_{\nu_+,\nu_-,\nu_D}(t) = \Big(\tilde{x}(1+w) + xt\Big)^{\nu_+}\Big(\tilde{y}(1+w) + yt\Big)^{\nu_-}\Big(\tilde{z}(1+w) + (z - \tilde{z})t\Big)^{\nu_D}. \tag{S44}$$

When $f < 0$, then $\deg(G_{\nu_+,\nu_-,\nu_D}(t)(1-t)^{-f-1}) = N_- - 1$, therefore, $B^f_{\nu_+,\nu_-,\nu_D} = 0$. When $f = 0$, then $\deg(G_{\nu_+,\nu_-,\nu_D}(t)) = N_-$ and we have the following identity

$$[t^{N_-}]\left(\frac{G_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)}\right) = G_{\nu_+,\nu_-,\nu_D}(1). \tag{S45}$$

Using this identity, we obtain the expression for $B^f_{\nu_+,\nu_-,\nu_D}$ base case $f=0$,

$$B^0_{\nu_+,\nu_-,\nu_D} = G_{\nu_+,\nu_-,\nu_D}(1). \tag{S46}$$

Now that we have the result for $f=0$, let's derive a recursive formula for $B^f_{\nu_+,\nu_-,\nu_D}$ when $f \geq 1$. The coefficient of t^{N_-+1} in a series $\sum_n a_n t^n$ is related to the coefficient of t^{N_-} of the derivative of the same series. Using this,

$$\begin{aligned}
\left[t^{N_-}\right] \frac{d}{dt}\left(\frac{G_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^f}\right) &= (N_-+1)[t^{N_-+1}]\left(\frac{G_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^f}\right)\\
[t^{N_-}]\left(\frac{G'_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^f}\right) + f[t^{N_-}]\left(\frac{G_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^{f+1}}\right) &= (N_-+1)[t^{N_-+1}]\left(\frac{G_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^f}\right)\\
fB^f_{\nu_+,\nu_-,\nu_D} &= (N_-+1)B^{f-1}_{\nu_+,\nu_-,\nu_D} - [t^{N_-}]\left(\frac{G'_{\nu_+,\nu_-,\nu_D}(t)}{(1-t)^f}\right)
\end{aligned} \tag{S47}$$

$$B^f_{\nu_+,\nu_-,\nu_D} = \frac{1}{f}\left((N_-+1)B^{f-1}_{\nu_+,\nu_-,\nu_D} - \nu_+ x B^{f-1}_{\nu_+-1,\nu_-,\nu_D} - \nu_- y B^{f-1}_{\nu_+,\nu_--1,\nu_D} - \nu_D(z-\tilde{z})B^{f-1}_{\nu_+,\nu_-,\nu_D-1}\right) \tag{S48}$$

The expression for $B^f_{\nu_+,\nu_-,\nu_D}$ for all the different cases,

$$B^f_{\nu_+,\nu_-,\nu_D} = \begin{cases} 0 & f<0\\ G_{\nu_+,\nu_-,\nu_D}(1) & f=0\\ \frac{1}{f}\left((N_-+1)B^{f-1}_{\nu_+,\nu_-,\nu_D} - \nu_+ x B^{f-1}_{\nu_+-1,\nu_-,\nu_D} - \nu_- y B^{f-1}_{\nu_+,\nu_--1,\nu_D} - \nu_D(z-\tilde{z})B^{f-1}_{\nu_+,\nu_-,\nu_D-1}\right) & f>0 \end{cases} \tag{S49}$$

C. Product and reactant equally coupled

For the special case when $g_R = g_P$, we change variable $t = q(1+w)$ and the expression becomes

$$\begin{aligned}
F^{f,0}_{\nu_+,\nu_-,\nu_D} =& \sqrt{e^{-S}S^f}\sqrt{\frac{N_-!}{\nu_+!\nu_-!\nu_D!}}(\tilde{w}(1+w))^{-f}[t^{N_-}]\left(\left(\tilde{x}(1+w)+xt\right)^{\nu_+}\left(\tilde{y}(1+w)+yt\right)^{\nu_-}\right.\\
&\left.\times\left(\tilde{z}(1+w)+(z-\tilde{z})t\right)^{\nu_D}\frac{\exp\left(\frac{-Swt}{(1+w)(1-t)}\right)}{(1-t)^{f+1}}\right)\\
=& \sqrt{e^{-S}S^f}\sqrt{\frac{Q!}{\nu_+!\nu_-!\nu_D!}}(\tilde{w}(1+w))^{-f}A^f_{\nu_+,\nu_-,\nu_D},
\end{aligned} \tag{S50}$$

where

$$A^f_{\nu_+,\nu_-,\nu_D} = [t^{N_-}]\left(\left(\tilde{x}(1+w)+xt\right)^{\nu_+}\left(\tilde{y}(1+w)+yt\right)^{\nu_-}\left(\tilde{z}(1+w)+(z-\tilde{z})t\right)^{\nu_D}\frac{\exp\left(\frac{-Swt}{(1+w)(1-t)}\right)}{(1-t)^{f+1}}\right). \tag{S51}$$

Expanding the exponential,

$$
\begin{aligned}
A^f_{\nu_+,\nu_-,\nu_D} &= [t^Q]\left(\left(\tilde{x}(1+w)+xt\right)^{\nu_+}\left(\tilde{y}(1+w)+yt\right)^{\nu_-}\left(\tilde{z}(1+w)+(z-\tilde{z})t\right)^{\nu_D}\frac{1}{(1-t)^{f+1}}exp\left(\frac{-Swt}{(1+w)(1-t)}\right)\right)\\
&= \sum_{n=0}^{\infty}\frac{1}{n!}[t^Q]\left(\left(\tilde{x}(1+w)+xt\right)^{\nu_+}\left(\tilde{y}(1+w)+yt\right)^{\nu_-}\left(\tilde{z}(1+w)+(z-\tilde{z})t\right)^{\nu_D}\frac{1}{(1-t)^{f+1}}\left(\frac{-Swt}{(1+w)(1-t)}\right)^n\right)\\
&= \sum_{n=0}^{\infty}w^n\frac{1}{n!}\left(\frac{-S}{1+w}\right)^n[t^Q]\left(\left(\tilde{x}(1+w)+xt\right)^{\nu_+}\left(\tilde{y}(1+w)+yt\right)^{\nu_-}\left(\tilde{z}(1+w)+(z-\tilde{z})t\right)^{\nu_D}\frac{t^n}{(1-t)^{f+1+n}}\right)\\
&= \sum_{n=0}^{\infty}w^n\frac{1}{n!}\left(\frac{-S}{1+w}\right)^n[t^{Q-n}]\left(\left(\tilde{x}(1+w)+xt\right)^{\nu_+}\left(\tilde{y}(1+w)+yt\right)^{\nu_-}\left(\tilde{z}(1+w)+(z-\tilde{z})t\right)^{\nu_D}\frac{1}{(1-t)^{f+1+n}}\right)\\
&= \sum_{n=0}^{\infty}w^n\frac{1}{n!}\left(\frac{-S}{1+w}\right)^n B^{f+n}_{\nu_+,\nu_-,\nu_D}
\end{aligned}
\tag{S52}
$$

For the case when $g_R = g_P$, $w = 1/(N-1)$ is very small when a large number of molecules are coupled to the cavity. Therefore, the summation in $A^f_{\nu_+,\nu_-,\nu_D}$ converges quickly and is easy to calculate on a computer.

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