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**Sindhana Pannir-Sivajothi**

University of California San Diego

**Jorge Campos-Gonzalez-Angulo**

University of California San Diego

**Luis Martínez-Martínez**

University of California San Diego

**Shubham Sinha**

University of California San Diego

**Joel Yuen-Zhou** (✉ [joelyuen@ucsd.edu](mailto:joelyuen@ucsd.edu))

University of California San Diego

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## Article

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# Driving chemical reactions with polariton condensates

Sindhana Pannir-Sivajothi,<sup>1</sup> Jorge A. Campos-Gonzalez-Angulo,<sup>1</sup> Luis A. Martínez-Martínez,<sup>1</sup> Shubham Sinha,<sup>2</sup> and Joel Yuen-Zhou<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, USA

<sup>2</sup>Department of Mathematics, University of California San Diego, La Jolla, California 92093, USA

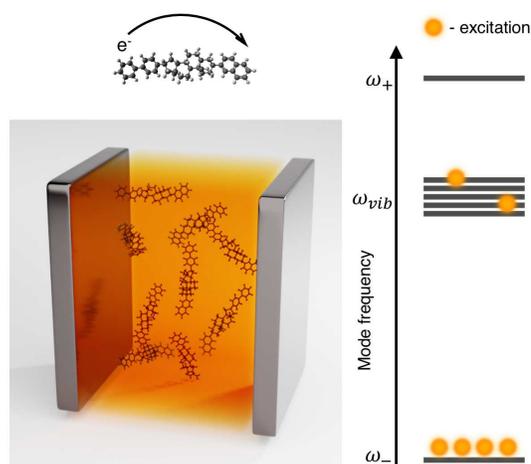
When molecular transitions strongly couple to photon modes, they form hybrid light-matter modes called polaritons. Collective vibrational strong coupling is a promising avenue for control of chemistry, but this can be deterred by the large number of quasi-degenerate dark modes. The macroscopic occupation of a single polariton mode by excitations, as observed in Bose-Einstein condensation, offers promise for overcoming this issue. Here we theoretically investigate the effect of vibrational polariton condensation on the kinetics of electron transfer processes. Compared with excitation with infrared laser sources, the condensate changes the reaction yield significantly due to additional channels with reduced activation barriers resulting from the large accumulation of energy in the lower polariton, and the many modes available for energy redistribution during the reaction. Our results offer tantalizing opportunities to use condensates for driving chemical reactions, kinetically bypassing usual constraints of fast intramolecular vibrational redistribution in condensed phase.

## I. INTRODUCTION

Light and matter couple strongly when a large number of molecules are placed within optical cavities that confine light [1–3]. As a result, hybrid light-matter excitations called polaritons form when a collective molecular transition and a photon mode coherently exchange energy faster than the individual decay from each component. Light-matter strong coupling (SC) opens up a new path to modify material properties by controlling their electromagnetic environment [4]. For instance, vibrational strong coupling (VSC), where an infrared cavity mode couples to an ensemble of localized molecular vibrations in a film or solution, influences chemical reactivity even without external pumping [5, 6]. However, the microscopic mechanism for modification of molecular processes through hybridization with light is still poorly understood [7–9], since it could be limited by the presence of a large number of quasi-degenerate dark modes that do not possess any photonic character and are likely to behave similarly to uncoupled molecules [9].

A Bose-Einstein condensate of polaritons [10] offers a solution to this problem since the macroscopic occupation of polaritonic states enhances the effects from SC. In the last decade, Bose-Einstein condensation has been demonstrated in several organic exciton-polariton systems at room temperature [11–14]. Recently, organic polariton condensates were used to build polariton transistors [15], and theoretical predictions suggest they may also modify incoherent charge transport [16]. Interestingly, the consequences of polariton condensation on chemical reactivity have not been addressed in the literature prior to the present study.

Ideas of using Bose-Einstein condensates of molecules in chemistry have been previously proposed, but they require ultracold temperatures due to the large mass of the condensing entities [17, 18]. The low effective mass that polaritons inherit from their photonic component, along with the large binding



**FIG. 1. Vibrational polariton condensate.** A large number of molecules are placed inside an optical cavity where their vibrations strongly couple to the cavity mode. The system is constantly pumped to create a polariton condensate and the right side of the figure depicts the occupation of different modes under condensation (frequencies of the upper polariton, dark modes and lower polariton are  $\omega_+$ ,  $\omega_{vib}$  and  $\omega_-$ , respectively). The rate of intramolecular electron transfer under polariton condensation is investigated.

energy of Frenkel excitons, enables room-temperature condensation [19]. The partly photonic character of polaritons also offers additional benefits such as delocalization and remote action for manipulating chemistry [20].

Here, we investigate the effect of polariton condensation on electron transfer (ET). While the reaction yield under infrared laser excitation, without SC, already differs from that under thermal equilibrium conditions [21, 22], polariton condensation amplifies this difference by changing the activation barrier for the forward and backward reactions unevenly, tilting the equilibrium towards either reactants or products.

\* joelyuen@ucsd.edu

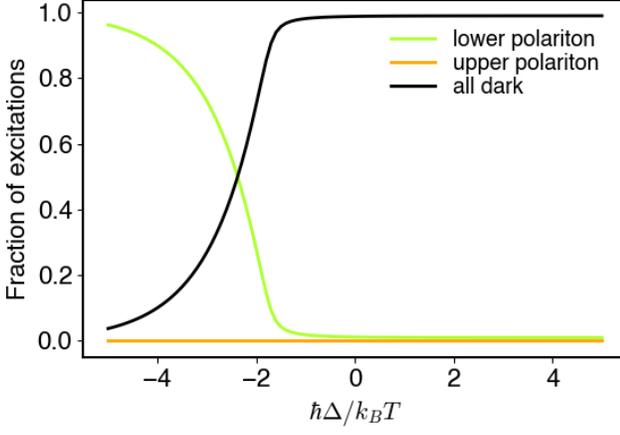


FIG. 2. **Polariton condensation transition.** Fraction of excitations in different modes as a function of cavity detuning  $\hbar\Delta = \hbar\omega_{ph} - \hbar\omega_{vib}$  while keeping the pumping rate  $P_-$  fixed. The black curve shows the excitations in all dark modes taken together. The condensation transition takes place close to  $\hbar\Delta \approx -1.5k_B T$ . Here, the lower polariton is pumped with rate  $P_- = 0.163N\Gamma_\downarrow$ , the light-matter coupling  $2g\sqrt{N} = 0.1\omega_{vib}$ , the temperature  $k_B T = 0.07\hbar\omega_{vib}$ , the cavity leakage rate  $\kappa = \Gamma_\downarrow$ , the scattering rate from the lower polariton to the  $k^{th}$  dark mode  $W_{Dk-} = 100\Gamma_\downarrow/(N-1)$ , other scattering rates  $W_{Dk+} = W_{-+} = W_{-Dk}$ .

## 52 II. BOSE-EINSTEIN CONDENSATION OF VIBRATIONAL 53 POLARITONS

54 Bose-Einstein condensation of vibrational polaritons has  
55 not been experimentally achieved yet; however, as we shall  
56 argue, there are compelling reasons to believe that they are  
57 presently within reach. Most theoretical investigations on polariton  
58 condensation with organic microcavities involve systems  
59 under electronic strong coupling (ESC) [23, 24]; polariton  
60 condensation under VSC requires a separate treatment due  
61 to the difference in energy scales and the involved relaxation  
62 pathways [25]. While typical bare exciton energies range from  
63 2-3 eV with Rabi splitting  $\sim 200$  meV under ESC, the bare  
64 frequency of vibrations is 100-300 meV with Rabi splitting  
65  $\sim 20 - 40$  meV under VSC. Since the Rabi splitting is of the  
66 order of  $k_B T$  at room temperature, thermal effects are crucial  
67 for vibrational polaritons. Under ESC, polariton relaxation  
68 is assisted by high-frequency intramolecular vibrations [26],  
69 whereas, under VSC, low-frequency solvent modes play a key  
70 role in this process [27, 28], similar to what happens in THz  
72 phonon Fröhlich condensation in biomolecules [29, 30].

73 We model the polariton system as a set of  $N$  vibrational  
74 modes ( $\hat{a}_{vib,j}$ ), with frequency  $\omega_{vib}$ , strongly coupled to a single  
75 photon mode ( $\hat{a}_{ph}$ ) with frequency  $\omega_{ph}$ . In the Hamiltonian of the system,  
76

$$\begin{aligned} \hat{H} = & \hbar\omega_{ph} \left( \hat{a}_{ph}^\dagger \hat{a}_{ph} + \frac{1}{2} \right) + \hbar\omega_{vib} \sum_{j=1}^N \left( \hat{a}_{vib,j}^\dagger \hat{a}_{vib,j} + \frac{1}{2} \right) \\ & + \sum_{j=1}^N \hbar g \left( \hat{a}_{vib,j}^\dagger \hat{a}_{ph} + \hat{a}_{ph}^\dagger \hat{a}_{vib,j} \right), \end{aligned} \quad (1)$$

77 we have applied the rotating wave approximation. Upon diagonalization of this Hamiltonian, we get normal modes: lower  
78 and upper polaritons, and  $N-1$  dark modes with frequencies  
79  $\omega_-$ ,  $\omega_+$  and  $\omega_D^k$ , respectively:

$$\begin{aligned} \omega_\pm &= \omega_{vib} + \frac{\Delta \pm \Omega}{2}, \\ \omega_D^k &= \omega_{vib} \quad 2 \leq k \leq N, \end{aligned} \quad (2)$$

81 where  $\Omega = \sqrt{\Delta^2 + 4g^2N}$  is the Rabi splitting and  $\Delta = \omega_{ph} -$   
82  $\omega_{vib}$  the detuning between cavity and molecular vibrations. To  
83 model polariton population dynamics, we use Boltzmann rate  
84 equations where the polariton system is weakly coupled to a  
85 low-frequency solvent bath, which enables scattering between  
86 modes [31, 32]. These rate equations also account for final-  
87 state stimulation,

$$\frac{dn_i}{dt} = \sum_j \left( W_{ij}n_j(1+n_i) - W_{ji}(1+n_j)n_i \right) - \gamma_i n_i + P_i, \quad (3)$$

88 where  $n_i$  is the population,  $\gamma_i$  is the decay rate and  $P_i$  is the  
89 external pumping rate of the  $i^{th}$  mode. The scattering rate  
90 from mode  $j$  to  $i$ ,  $W_{ij}$ , satisfies detailed balance:  $W_{ij}/W_{ji} =$   
91  $e^{-\beta(\varepsilon_i - \varepsilon_j)}$ . Here,  $\beta = 1/(k_B T)$ ,  $k_B$  is the Boltzmann constant,  
92  $T$  is the temperature and  $\varepsilon_i = \hbar\omega_i$  where  $\omega_i$  is the frequency of  
93 the  $i^{th}$  mode. In our calculations, only the lower polariton is  
94 pumped,  $P_- \neq 0$  while  $P_i = 0$  for all other modes. The decay  
95 from different modes is  $\gamma_i = |c_{vib}^i|^2 \Gamma_\downarrow + |c_{ph}^i|^2 \kappa$ , where  $|c_{vib}^i|^2$   
96 and  $|c_{ph}^i|^2$  are the molecular and photon fraction, respectively,  
97  $\Gamma_\downarrow$  is the decay rate of the molecular vibrations, and  $\kappa$  is the  
98 cavity leakage rate.

99 Two factors play a determinant role in the condensation  
100 threshold: (i) the rate of scattering between polariton and dark  
101 modes relative to losses from the system, *i.e.* the rate of thermalization,  
102 and (ii) the abundance of modes close in energy to the condensing mode [33].  
103 For all calculations, we assume fast thermalization with  $\sum_{k=2}^N W_{Dk-} = (N-1)W_{Dk-} = 100\Gamma_\downarrow$   
104 and  $\Gamma_\downarrow = \kappa$ . As mentioned in (ii), the presence of many modes  
105 close to the lower polariton would deter condensation by distributing  
106 the energy pumped into the system among all these  
107 modes. Thus, the energetic proximity between the dark state  
108 manifold, which has a large density of states (DOS), and the  
109 lower polariton poses one of the biggest challenges for polariton  
110 condensation under VSC.  
111

112 The distribution of excitations between the polariton and  
113 dark modes is shown in Fig. 2 for different detunings and we  
114 observe a condensation transition at  $\hbar\Delta \approx -1.5k_B T$  (see Supplementary  
115 Section S2 for details). Above the condensation  
116 threshold, a large fraction of excitations reside in the lower  
117 polariton  $\frac{\bar{n}_-}{(\sum_{k=2}^N n_D^k)} \gg \frac{1}{(N-1)e^{-\beta\hbar(\Omega-\Delta)/2}}$ .

118 The average population per molecule at the condensation  
119 threshold  $\bar{n} = P_{th}/N\Gamma_\downarrow$  is a good measure of the feasibility of  
120 vibrational polariton condensation. For instance, demanding  
121 population inversion,  $\bar{n} > 0.5$ , would be experimentally difficult  
122 to achieve in general. In Fig. 3, we plot  $\bar{n}$  for different  
123 light-matter coupling strengths,  $2\hbar g\sqrt{N}$ , and detunings,  $\hbar\Delta$ .  
124 Here, we numerically obtain  $P_{th}$  as the pumping rate when

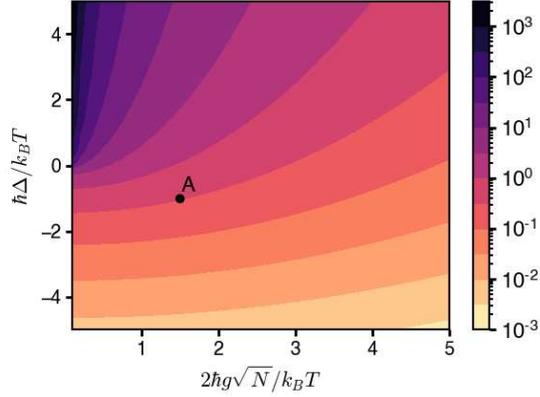


FIG. 3. **Polariton condensation threshold.** Numerically obtained average population per molecule at the condensation threshold  $\bar{n} = P_{th}/N\Gamma_{\downarrow}$  (10% of the excitations are in the lower polariton), for a range of light-matter coupling strengths  $2\hbar g\sqrt{N}$  and cavity detunings  $\hbar\Delta = \hbar\omega_{ph} - \hbar\omega_{vib}$ . In the black and purple regions of the plot ( $\Delta > 0$  and  $2\hbar g\sqrt{N}/k_B T < 2$ ), the threshold for condensation is high,  $\bar{n} \gg 1$ , and polariton condensation is difficult to achieve experimentally. The threshold for condensation is much lower,  $\bar{n} < 0.1$ , for the lighter colored (yellow, orange) regions. In our calculation, only the lower polariton is pumped and we use cavity leakage rate  $\kappa = \Gamma_{\downarrow}$ , scattering rate from the lower polariton to the  $k^{th}$  dark mode  $W_{D_k-} = 100\Gamma_{\downarrow}/(N-1)$ , other scattering rates  $W_{D_k+} = W_{-+} = W_{-D_k}$ . Calculations in Section IIIB-C are presented for the conditions in point A.

125 10% of the excitations are in the lower polariton. The thresh-  
126 old obtained this way closely corresponds with the theoretical  
127 condition for condensation

$$\bar{n}_D^k > n_{solvent} \left( \frac{\hbar(\Omega - \Delta)}{2} \right), \quad (4)$$

128 where,  $\bar{n}_D^k = \frac{1}{N-1} \sum_{k=2}^N n_D^k$  is the average occupation of a dark  
129 mode, and  $n_{solvent}(E)$  is the Bose-Einstein population of a sol-  
130 vent mode with energy  $E$  at room temperature  $T_{room}$  [33].  
131 The energy difference between the lower polariton and the  
132 dark state reservoir  $\hbar(\Omega - \Delta)/2$  determines the condensation  
133 threshold.

134 Our model does not include disorder; as a result, all dark  
135 modes are degenerate at frequency  $\omega_{vib}$ , but in experimental  
136 systems, inhomogeneous broadening of transitions can lead  
137 to non-zero density of dark states even at the bottom of the  
138 lower polariton branch [34]. This fact will affect the conden-  
139 sation threshold, and should be considered in the future while  
140 looking for experimental systems that can demonstrate vibra-  
141 tional polariton condensation. Stimulating the lower polariton  
142 directly by shining a resonant laser on it [15] or using a Ra-  
143 man scattering scheme [35] can help overcome this issue by  
144 dynamically lowering the condensation threshold.

### 145 III. CHEMICAL REACTIONS AND VIBRATIONAL 146 POLARITON CONDENSATION

147 Electron transfer has been theoretically studied under both  
148 ESC [36, 37] and VSC [38, 39]. Here, we look at how vibra-  
149 tional polariton condensation affects the rate of intramolecular  
150 nonadiabatic electron transfer using the VSC version [38] of  
151 the Marcus-Levich-Jortner (MLJ) model [40–42].

#### 152 A. Non-adiabatic electron transfer under VSC

153 Our system consists of  $N$  molecules placed inside an opti-  
154 cal cavity supporting a single photon mode with bosonic op-  
155 erator  $\hat{a}_{ph}$  and frequency  $\omega_{ph}$ . The molecules can be in the  
156 reactant  $R$  or product  $P$  electronic state; for the  $i^{th}$  molecule,  
157 these states are denoted by  $|R_i\rangle$  and  $|P_i\rangle$ , respectively. Each  
158 electronic state is dressed with a high-frequency intramolecu-  
159 lar vibrational mode with bosonic operator  $\hat{a}_{x,i}$  and frequency  
160  $\omega_{vib}$  where  $x = R, P$ ; this mode couples to the photon mode.  
161 The equilibrium geometry of this vibrational mode depends  
162 on the electronic state according to,

$$\hat{a}_{R,i} = \hat{D}_i^\dagger \hat{a}_{P,i} \hat{D}_i, \quad (5)$$

163 where  $\hat{D}_i = \exp\left(\left(\hat{a}_{P,i}^\dagger - \hat{a}_{P,i}\right)d_{vib}\right)$  is the displacement opera-  
164 tor, and  $d_{vib} = \sqrt{S}$  is a dimensionless parameter related to the  
165 Huang-Rhys factor  $S$ .

166 Apart from the intramolecular vibrations, an effective low-  
167 frequency solvent mode surrounding each molecule facilitates  
168 ET. It is treated classically, with  $\mathbf{q}_{S,i}$  and  $\mathbf{p}_{S,i}$  being its position  
169 and momentum.

170 The Hamiltonian  $\hat{H}$  for the full system is a generalization  
171 of equation (1) to account for the chemical reaction,

$$\hat{H} = \hat{H}_0 + \hat{V}_{react}, \quad (6)$$

172 and

$$\begin{aligned} \hat{H}_0 &= \hat{H}_{ph} + \sum_{i=1}^N \sum_{x=R,P} (\hat{H}_{x,i} + \hat{V}_{x,i}) |x_i\rangle \langle x_i|, \\ \hat{V}_{react} &= \sum_{i=1}^N J_{RP} \left( |R_i\rangle \langle P_i| + |P_i\rangle \langle R_i| \right). \end{aligned} \quad (7)$$

173 where  $\hat{H}_0$  describes the photon ( $\hat{H}_{ph}$ ), intramolecular vibra-  
174 tions and solvent modes of the  $i^{th}$  molecule ( $\hat{H}_{x,i}$ ), and light-  
175 matter couplings ( $\hat{V}_{x,i}$ ). The diabatic coupling  $\hat{V}_{react}$  is a per-  
176 turbation that couples  $R$  and  $P$  electronic states with coupling  
177 strength  $J_{RP}$ .

$$\begin{aligned} \hat{H}_{ph} &= \hbar\omega_{ph} \left( \hat{a}_{ph}^\dagger \hat{a}_{ph} + \frac{1}{2} \right), \\ \hat{H}_{R,i} &= \hbar\omega_{vib} \left( \hat{a}_{R,i}^\dagger \hat{a}_{R,i} + \frac{1}{2} \right) + \frac{1}{2} \hbar\omega_S \left( |\mathbf{p}_{S,i}|^2 + |\mathbf{q}_{S,i} + \mathbf{d}_S|^2 \right), \\ \hat{H}_{P,i} &= \hbar\omega_{vib} \left( \hat{a}_{P,i}^\dagger \hat{a}_{P,i} + \frac{1}{2} \right) + \frac{1}{2} \hbar\omega_S \left( |\mathbf{p}_{S,i}|^2 + |\mathbf{q}_{S,i}|^2 \right) + \Delta G, \\ \hat{V}_{x,i} &= \hbar g_x \left( \hat{a}_{x,i}^\dagger \hat{a}_{ph} + \hat{a}_{ph}^\dagger \hat{a}_{x,i} \right), \end{aligned} \quad (8)$$

178 where  $\Delta G$  is the free-energy difference of each individual 210 where  
 179 molecule reaction.

180 We construct potential energy surfaces (PES) by parametri-  
 181 cally diagonalizing  $\hat{H}_0$  as a function of the solvent coordinate  
 182  $\mathbf{q}_{S,i}$ . The operators  $\hat{N}_R = \sum_{i=1}^N |R_i\rangle \langle R_i|$  and  $\hat{N}_P = \sum_{i=1}^N |P_i\rangle \langle P_i|$   
 183 commute with  $H_0$  and correspond to the number of  $R$  and  $P$   
 184 molecules, respectively. While dynamics under  $\hat{H}_0$  conserves  
 185  $N_R, N_P$ , the effect of  $\hat{V}_{react}$  is to induce reactive transitions  
 186 that modify those quantities while keeping  $N = N_R + N_P$  con-  
 187 stant. We assign the label  $1 \leq i \leq N_R$  to  $R$  molecules, and  
 188  $N_R + 1 \leq i \leq N$  to  $P$  molecules. We also reorganize the in-  
 189 tramolecular vibrations into a single bright mode,

$$\hat{a}_{B(N_R, N_P)} = \frac{1}{\sqrt{g_R^2 N_R + g_P^2 N_P}} \left( g_R \sum_{i=1}^{N_R} \hat{a}_{R,i} + g_P \sum_{i=N_R+1}^N \hat{a}_{P,i} \right), \quad (9)$$

190 that possesses the correct symmetry to couple with light and  
 191  $N - 1$  dark modes ( $D_k$ ),

$$\hat{a}_{D(N_R, N_P)}^k = \sum_{i=1}^{N_R} c_{k,i} \hat{a}_{R,i} + \sum_{i=N_R+1}^N c_{k,i} \hat{a}_{P,i}, \quad (10)$$

192 labeled by an additional index  $2 \leq k \leq N$ , which do not cou-  
 193 ple with light. The dark modes are orthogonal to the bright  
 194 mode  $g_R \sum_{i=1}^{N_R} c_{k,i} + g_P \sum_{i=N_R+1}^N c_{k,i} = 0$ , and to each other  
 195  $\sum_{i=1}^N c_{k,i} c_{k',i}^* = \delta_{k,k'}$ . Unless mentioned otherwise, the num-  
 196 ber of  $R$  and  $P$  molecules is  $N_R$  and  $N_P$ , respectively, and for  
 197 brevity, we will drop  $(N_R, N_P)$  dependence in the subscript.  
 198 The bright and photon modes combine to form the upper pol-  
 199 ariton ( $UP$ )  $\hat{a}_+$ , and lower polariton ( $LP$ )  $\hat{a}_-$ , modes:

$$\begin{aligned} \hat{a}_+ &= \cos \theta \hat{a}_{ph} + \sin \theta \hat{a}_B, \\ \hat{a}_- &= \sin \theta \hat{a}_{ph} - \cos \theta \hat{a}_B, \end{aligned} \quad (11)$$

200 with mixing angle,

$$\theta = \tan^{-1} \left[ \frac{\Omega - \Delta}{2\sqrt{g_R^2 N_R + g_P^2 N_P}} \right], \quad (12)$$

201 where  $\Omega = \sqrt{\Delta^2 + 4(g_R^2 N_R + g_P^2 N_P)}$  is the Rabi splitting, and  
 202  $\Delta = \omega_{ph} - \omega_{vib}$  the detuning between cavity and molecular  
 203 vibrations. The eigenstates of  $\hat{H}_0$  are the dark, upper and lower  
 204 polariton modes with frequencies given in equation (2).

## 205 B. Rate constant

206 According to the MLJ theory, the rate constant for ET out-  
 207 side of an optical cavity depends on properties of the in-  
 208 tramolecular and solvent modes [40–42]. Under laser driving,  
 209 this rate constant is,

$$k_{R \rightarrow P}^{JR} = \sum_{n=0}^{\infty} P_{\bar{n}}(n) k_{R \rightarrow P}(n) \quad (13)$$

$$\begin{aligned} k_{R \rightarrow P}(n) &= \sqrt{\frac{\pi}{\lambda_S k_B T}} \frac{|J_{RP}|^2}{\hbar} \sum_{f=-n}^{\infty} |\langle n|n+f\rangle'|^2 \exp\left(-\frac{E_f^\ddagger}{k_B T}\right), \\ P_{\bar{n}}(n) &= e^{-\bar{n}} \frac{\bar{n}^n}{n!}, \\ E_f^\ddagger &= \frac{(\Delta G + \lambda_S + f\hbar\omega_{vib})^2}{4\lambda_S}, \\ \langle n|n+f\rangle' &= \langle n|\hat{D}_i|n+f\rangle. \end{aligned} \quad (14)$$

211 Here,  $P_{\bar{n}}(n)$  is the Poisson distribution with average mode pop-  
 212 ulation  $\bar{n}$ ,  $\lambda_S$  is the solvent reorganization energy,  $E_f^\ddagger$  is the ac-  
 213 tivation energy, and  $|\langle n|n+f\rangle'|^2$  is the Franck-Condon (FC)  
 214 factor, where  $|n\rangle$  and  $|n+f\rangle'$  are the intramolecular initial and  
 215 final states, respectively.  $P_{\bar{n}}(n)$  has been taken to correspond  
 216 to the ideal laser driven-damped harmonic oscillator, leading  
 217 to a coherent state in the vibrational mode. The presence  
 218 of anharmonic couplings would lead to intramolecular vibra-  
 219 tional energy redistribution (IVR) [43], reducing the value of  
 220  $P_{\bar{n}}(n)$  for high-lying Fock states. However, as we shall see be-  
 221 low, even under these ideal circumstances, the condensate can  
 222 outcompete the laser-driven situation in terms of reactivity.  
 223 We thus expect the benefits of the condensate to be enhanced  
 224 when IVR processes are taken into account.

225 Apart from vibrations within the reacting molecule, under  
 226 VSC, the ET process also depends on vibrations in all other  
 227 molecules and the photon mode, and can be represented by,

$$\sum_{k=2}^N D_k + LP + UP \rightarrow \sum_{k=2}^N D'_k + LP' + UP'. \quad (15)$$

228 Here and hereafter, the primed and unprimed quantities refer  
 229 to electronic states with  $(N_R, N_P)$  and  $(N_R - 1, N_P + 1)$   
 230 reactant-product distributions, respectively. The symmetry of  
 231 the light-matter coupling allows us to use the dark state basis  
 232 introduced in [44] and [38] to reduce the number of modes  
 233 involved in the reaction from  $N + 1$  to three,

$$D_{R,c} + LP + UP \rightarrow D'_{P,c} + LP' + UP'. \quad (16)$$

234 Here, the  $c^{th}$  molecule is reacting, while  $D_{x,c}$  and  $D'_{x,c}$  are  
 235 dark modes highly localized in it, with corresponding oper-  
 236 ators  $\hat{a}_D^{(R,c)}$  and  $\hat{a}_D^{(P,c)'} (see Supplementary Section S1).$

237 We perform all our calculations in this section using param-  
 238 eters from point A in Fig. 3, where  $\hbar\Delta = -k_B T$ ,  $2\hbar g\sqrt{N} =$   
 239  $1.5k_B T$ ,  $k_B T = 0.0667\hbar\omega_{vib}$  ( $T = 142K$  when  $\hbar\omega_{vib} = 185$   
 240 meV) and  $N = 10^7$ ; we choose pumping rate  $P_- = 0.08N\Gamma_\downarrow$ ,  
 241 which leads to average mode populations  $N_+ = 0.052$ ,  $N_- =$   
 242  $1.04 \times 10^4$  and  $N_D = 0.079$  under symmetric coupling  $g_R =$   
 243  $g_P = g$ . Here, 1.3% of all excitations reside in the lower pol-  
 244 ariton. To compare the reaction rates under polariton con-  
 245 densation and outside the cavity under pumping, we take  
 246  $\bar{n} = 0.08$  in equation (13). Under condensation, the ini-  
 247 tial vibrational state of the system can be described by  
 248  $\rho = \sum_{n_+, n_-, n_D} P(n_+, n_-, n_D) |n_+, n_-, n_D\rangle \langle n_+, n_-, n_D|$ , where  
 249 the entries in  $|n_+, n_-, n_D\rangle$  label number of quanta in the  $UP$ ,  
 250  $LP$  and  $D_{R,c}$  modes, respectively. The results from Section II

251 provide us only with the average steady-state mode popula- 286 where  
 252 tions,  $N_+$ ,  $N_-$  and  $N_D$ , and not the distribution  $P(n_+, n_-, n_D)$ .  
 253 For simplicity, we assume the semiclassical approximation  
 254  $P(n_+, n_-, n_D) \approx \delta_{n_+, 0} P_{N_D}^{th}(n_D) \delta_{n_-, N_-}$ , where  $P_{N_D}^{th}(n)$  is the  
 255 thermal distribution with average population  $N_D$ . This approx-  
 256 imation is reasonable for populations  $N_+ < N_D \ll 1 \ll N_-$ ,

$$\rho = \sum_{n_D} P_{N_D}^{th}(n_D) |0, N_-, n_D\rangle \langle 0, N_-, n_D|. \quad (17)$$

257 The product vibrational states are  $|v_+, v_-, v_D\rangle'$ .

258 We assume that cavity leakage and rate of scattering be-  
 259 tween modes is much faster than the rate of the chemical reac-  
 260 tion. For a cavity with  $\sim 100$  ps lifetime and ET reactions with  
 261  $1/k_{R \rightarrow P} \sim 10^6 - 10^2$  ps [45], this assumption is valid. There-  
 262 fore, if the populations of polariton modes change during the  
 263 course of reaction, they quickly reach a steady state before the  
 264 next molecule reacts. Similarly, we also assume that the pol-  
 265 ariton and dark mode populations reach a steady state before  
 266 the backward reaction takes place while computing the rate  
 267 constant  $k_{P \rightarrow R}^{cond}$ . Generalizing the cavity MLJ theory presented  
 268 in [38], we calculate the rate constant

$$k_{R \rightarrow P}^{cond} = \sum_{n=0}^{\infty} P_{N_D}^{th}(n) k_{R \rightarrow P}^{cond}(n) \quad (18)$$

269 for the forward reaction under polariton condensation, where

$$k_{R \rightarrow P}^{cond}(n) = \sqrt{\frac{\pi}{\lambda_S k_B T}} \frac{|J_{RP}|^2}{\hbar} \sum_{v_+=0}^{\infty} \sum_{v_-=0}^{\infty} \sum_{v_D=0}^{\infty} W_{v_+, v_-, v_D}^{f, n}, \quad (19)$$

$$W_{v_+, v_-, v_D}^{f, n} = |F_{v_+, v_-, v_D}^{f, n}|^2 \times \exp\left(-\frac{E_{v_+, v_-, v_D}^{f, n \ddagger}}{k_B T}\right).$$

270 The FC factor  $|F_{v_+, v_-, v_D}^{f, n}|^2 = |\langle 0, N_-, n | v_+, v_-, v_D \rangle'|^2$ , and ac-  
 271 tivation energy  $E_{v_+, v_-, v_D}^{f, n \ddagger}$  play an important role in determin- 310  
 272 ing the rate constant.

273 While many methods have been developed for computing 311  
 274 multimode FC factors [46–48], the focus has been on in-  
 275 creasing the number of modes while keeping their occupation  
 276 small. The current problem, however, offers a new technical  
 277 challenge: the large occupation of  $LP$  makes the aforemen-  
 278 tioned methods computationally expensive. Instead, we draw  
 279 inspiration from previous work that employs generating func-  
 280 tions [47] and combine those techniques with the powerful  
 281 Lagrange-Bürmann formula [49] to obtain analytical expres-  
 282 sions for the required three-dimensional FC factors (see de-  
 283 tails in Supplementary Section S4).

284 The activation energies for the various channels of reactiv-  
 285 ity are,

$$E_{v_+, v_-, v_D}^{f, n \ddagger} = \frac{(E_P^{v_+, v_-, v_D} - E_R^{0, N_-, n} + \lambda_S)^2}{4\lambda_S}, \quad (20)$$

$$E_P^{v_+, v_-, v_D} = \Delta G + \hbar \left[ \omega'_+ \left( v_+ + \frac{1}{2} \right) + \omega'_- \left( v_- + \frac{1}{2} \right) + \omega_{vib} \left( v_D + \frac{1}{2} \right) \right], \quad (21)$$

$$E_R^{0, N_-, n} = \hbar \left[ \omega_+ \frac{1}{2} + \omega_- \left( N_- + \frac{1}{2} \right) + \omega_{vib} \left( n + \frac{1}{2} \right) \right].$$

287 When condensation takes place, the number of quanta in  
 288 the lower polariton  $N_- \sim 10^5$  is so large that the summation in  
 289  $k_{R \rightarrow P}^{cond}(n)$  becomes difficult to estimate. To simplify the com-  
 290 putation and gain intuition, we group channels into sets with  
 291 same change in total number of intramolecular vibrational  
 292 quanta  $f = v_+ + v_- + v_D - N_- - n$  upon ET. The closeness  
 293 in energy between PES with same  $f$ , and hence similar ac-  
 294 tivation barriers, is the rationale for this grouping.  $k_{R \rightarrow P}^{cond}(n)$   
 295 then goes from a free summation over three indices  $v_+$ ,  $v_-$   
 296 and  $v_D$  into a summation over four indices  $f$ ,  $v_+$ ,  $v_-$  and  $v_D$   
 297 with the constraint  $v_+ + v_- + v_D = N_- + n + f$ ,

$$k_{R \rightarrow P}^{cond}(n) = \sqrt{\frac{\pi}{\lambda_S k_B T}} \frac{|J_{RP}|^2}{\hbar} \sum_{f=-N_- - n}^{\infty} \sum_{v_+, v_-, v_D}^{v_+ + v_- + v_D = N_- + n + f} W_{v_+, v_-, v_D}^{f, n}. \quad (22)$$

298 To understand the qualitative difference between reactions  
 299 under polariton condensation and external pumping without  
 300 SC, in Fig 4a-b we plot the PESs (not to scale) showing the  
 301 forward reaction under symmetric light-matter coupling and  
 302 zero detuning. The yellow (black) parabolas in Fig. 4a-b  
 303 represent PESs for a molecule in electronic state  $|R\rangle$  ( $|P\rangle$ )  
 304 and vibrational state  $|2\rangle$  ( $|2+f\rangle'$ ) in Fig. 4a and  $|0, N_-, 2\rangle$   
 305 and  $|0, N_-, 2+f\rangle'$  in Fig. 4b. The red parabolas in Fig. 4b are  
 306 additional final PESs provided by the condensate that account  
 307 for all other final vibrational states  $|v_+, v_-, v_D\rangle'$ .  
 308  
 309

### 310 C. Modified yield under condensation

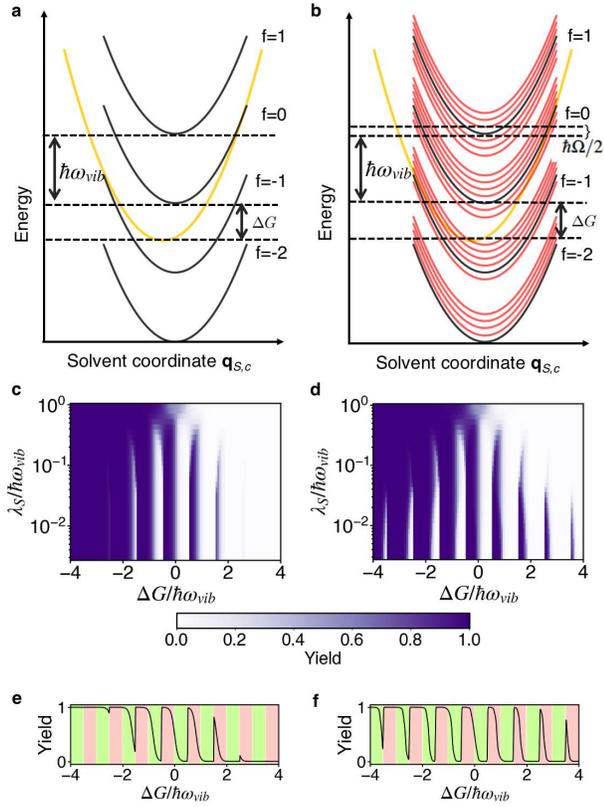
311 The net rate of ET is,

$$\frac{dN_R}{dt} = -k_{R \rightarrow P}^z N_R + k_{P \rightarrow R}^z N_P, \quad (23)$$

312 where  $k_{R \rightarrow P}^z$  and  $k_{P \rightarrow R}^z$  ( $z = IR, cond$ ) are the rate constants for  
 313 the forward and backward reactions, respectively, which are  
 314 themselves functions of  $N_R$  and  $N_P$  when  $g_R \neq g_P$ . We find  
 315 the steady state solution  $N_R^{SS}$  from this equation and compute  
 316 the reaction yield  $N_P^{SS}/N$ .

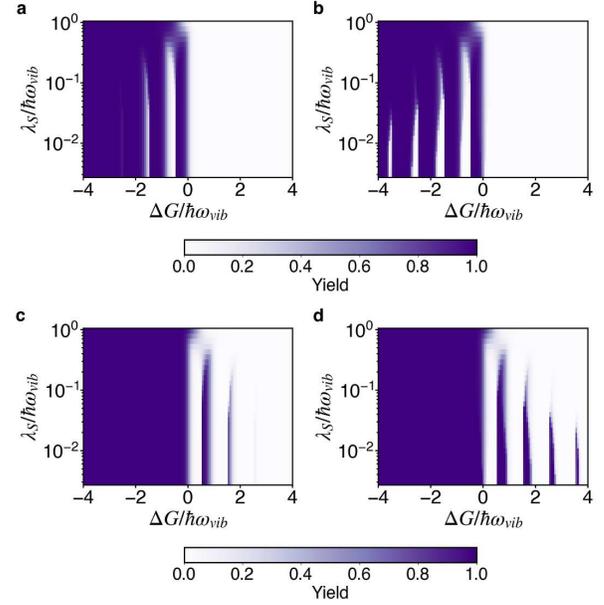
317 The difference in yield between the condensate and bare  
 318 case is particularly large when  $\lambda_S \ll \hbar\omega_{vib} < |\Delta G|$  (see Fig.  
 319 4c-d for symmetric coupling  $g_R = g_P$ ). To understand the un-  
 320 derlying reason, we define the dominant channel  $f_{min}$  as the  
 321 one with minimum activation barrier outside of the cavity.

$$\frac{1}{k_B T} \frac{dE_f^\ddagger}{df} = \frac{\hbar\omega_{vib}}{k_B T} \left( \frac{\Delta G + \lambda_S + f\hbar\omega_{vib}}{2\lambda_S} \right) \quad (24)$$



**FIG. 4. Potential energy surfaces (not to scale) and reaction yield.** **a,c,e** are results for a laser driven system without SC and **b,d,f** are for the same system under SC and 1.3% of the population in the lower polariton (condensation). All these plots are for symmetric light-matter coupling  $g_R = g_P$ . **a,b**, For a clearer qualitative picture, we plot the PESs under zero detuning  $\Delta = 0$ . Initial (yellow) and final (black) PESs for a molecule undergoing the forward reaction with solvent coordinate  $\mathbf{q}_{S,C}$ . While the energy separation between black PESs is  $\hbar\omega_{vib}$ , the condensate provides many additional final PESs (red, separated by  $\hbar\Omega/2$  at resonance). **c**, Reaction yield  $N_P^{SS}/N$  at temperature  $k_B T = 0.0667\hbar\omega_{vib}$  ( $T = 142K$  when  $\hbar\omega_{vib} = 185$  meV), Huang-Rhys factor  $S = 3.5$ , and average occupation of the intramolecular vibrational mode  $\bar{n} = 0.08$ . **d**, Reaction yield  $N_P^S/N$  with  $\Delta = -0.0667\omega_{vib}$ ,  $2g_R\sqrt{N} = 2g_P\sqrt{N} = 0.1\omega_{vib}$ ,  $P_- = 0.08N\Gamma_\downarrow$ ,  $N = 10^7$ , temperature and Huang-Rhys factor are the same as **c**. The contributions of the red PESs through the condensate provide a broader tunability of reaction yields with respect to  $\Delta G$  than under laser driving without SC. Notice that originally endergonic (exergonic) reactions in the absence of optical pumping can become exergonic (endergonic) under the featured nonequilibrium conditions. **e,f**, A cross-section of plot (**c-d**) when  $\lambda_S = 10^{-2}\hbar\omega_{vib}$ . The pink shaded regions correspond to cases where the dominant forward (backward) channel is in the inverted (normal) regime; the opposite is true for the green shaded regions. The condensate amplifies the forward (backward) reaction in the pink (green) shaded regions.

Setting the derivative in equation (24) equal to zero and taking into account the discrete nature of  $f$ , we find the dominant channel,  $f_{min} = \left\lfloor \frac{-\Delta G - \lambda_S}{\hbar\omega_{vib}} \right\rfloor$  or  $\left\lceil \frac{-\Delta G - \lambda_S}{\hbar\omega_{vib}} \right\rceil$ . When  $\lambda_S \ll \hbar\omega_{vib}, |\Delta G|$ , this channel contributes most to the rate constant



**FIG. 5. Reaction yield for asymmetric light-matter coupling.** **a** (**c**), The yield of the reaction when only the product (reactant) weakly couples with light. **b** (**d**), Analogous plots under strong coupling  $2g_P\sqrt{N} = 0.1\omega_{vib}$ ,  $g_R = 0$  ( $g_P = 0$ ,  $2g_R\sqrt{N} = 0.1\omega_{vib}$ ). We use parameters  $\Delta = -0.0667\omega_{vib}$ ,  $k_B T = 0.0667\hbar\omega_{vib}$  ( $T = 142K$  when  $\hbar\omega_{vib} = 185$  meV),  $S = 3.5$ ,  $P_- = 0.08N\Gamma_\downarrow$  and  $N = 10^7$ . We assume the same scattering parameters  $W_{ij}$  and decay rates  $\Gamma_\downarrow$ ,  $\kappa$  as in Fig. 2.

because  $\frac{1}{k_B T} \left| \frac{dE_f^\ddagger}{df} \right| \gg 1$ . We define Marcus normal  $\left. \frac{dE_f^\ddagger}{df} \right|_{f_{min}} > 0$  and inverted  $\left. \frac{dE_f^\ddagger}{df} \right|_{f_{min}} < 0$  regimes with respect to the dominant channel. If the dominant forward channel is in the inverted regime, the dominant backward channel (which can be found by replacing  $\Delta G \rightarrow -\Delta G$  in equation (24)) will be in the normal regime when  $\lambda_S \ll \hbar\omega_{vib}, |\Delta G|$ . Condensation provides many additional channels for the forward and backward reactions (separated by  $\sim \hbar\Omega/2$ , see red curves in Fig. 4b, showing only the forward channels at resonance  $\Delta = 0$ ) due to the transfer of quanta from  $LP$  to  $D'_{P,C}$  or  $UP'$  during the reaction. Importantly, when the dominant channel is in the inverted regime, the higher-energy additional channels catalyze the corresponding reaction, as in the original MLJ mechanism. Therefore, when  $\lambda_S \ll \hbar\omega_{vib}, |\Delta G|$ , depending on whether the dominant forward or backward channel is in the inverted regime, the yield is enhanced or suppressed (see Fig. 4f). This modification is periodic in  $\Delta G$  with period  $\sim \hbar\omega_{vib}$ , and decays for large  $\Delta G/\hbar\omega_{vib}$  due to concomitant decline in FC factor for large changes in the number of vibrational quanta between the initial and final states. Apart from reduced activation energy, the additional channels provided by the condensate also have large enough FC factors to affect the rate constant. Changes in the rate constant as a function of  $\lambda_S$  (Fig. 6a) and  $\Delta G$  (Fig. 6b) are large for small  $\lambda_S/\hbar\omega_{vib}$  and when  $\Delta G/\hbar\omega_{vib} = n/2$  where  $n$  is an

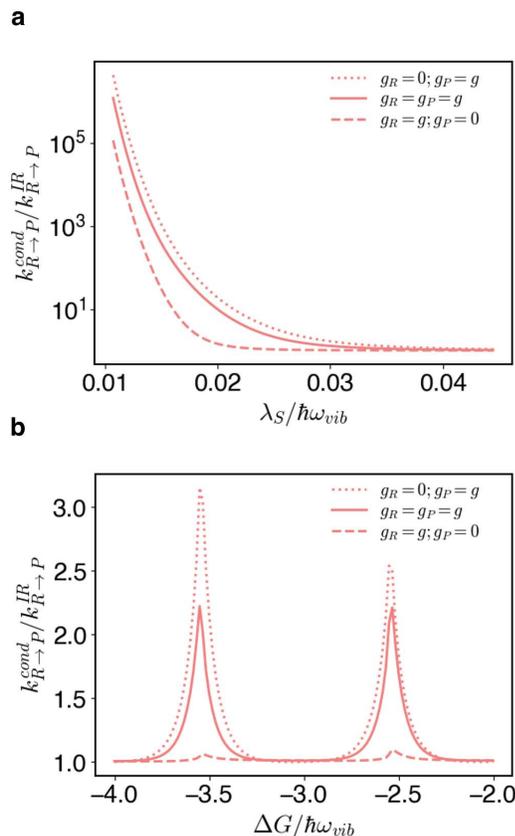


FIG. 6. **Rate constant.** Ratio of the rate constants inside  $k_{R \rightarrow P}^{cond}$  and outside  $k_{R \rightarrow P}^{LR}$  of the cavity under laser excitation with  $\Delta = -0.0667\hbar\omega_{vib}$ ,  $k_B T = 0.0667\hbar\omega_{vib}$  ( $T = 142K$  when  $\hbar\omega_{vib} = 185$  meV),  $S = 3.5$ ,  $2g\sqrt{N} = 0.1\omega_{vib}$ ,  $P_- = 0.08N\Gamma_{\downarrow}$  and  $N = 10^7$  for cases when only the product is coupled to the cavity  $g_R = 0$ ;  $g_P = g$  (dotted line) and  $N_R = N_P$ , 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) and  $N_R = N_P$ . **a**, Relative rate constant as a function of reorganization energy,  $\lambda_S$ , with  $\Delta G = -3.3334\hbar\omega_{vib}$  and **b**, as a function of  $\Delta G$  with  $\lambda_S = 0.0437\hbar\omega_{vib}$ .

teger since activation energy effects are large for these set of parameters. These plots are at 142 K; changes in rate constant and yield at room temperature are more modest since higher temperatures reduce the effect of changes in activation energy (see Supplementary Section S3).

#### IV. DISCUSSION

Our result is a first step towards understanding the effect of Bose-Einstein condensation of polaritons on chemical reactivity. We demonstrate this effect using a simple electron transfer model (MLJ) with molecular vibrations strongly coupled to light. In particular, we show that one can counteract the massive degeneracy of dark modes and enhance polaritonic effects by having a macroscopic occupation of the lower polariton mode *i.e.*, Bose-Einstein condensation. Our results indicate that the latter is feasible for experimentally realizable pump

powers and Rabi splittings, despite the close proximity in energy of the dark state manifold with  $\hbar\Omega \sim k_B T$ . These results can guide the choice of suitable materials for condensation under VSC. While laser driving without SC modifies the reaction yield, this change is amplified by the condensate, due to the availability of many additional reactive channels that differ in energy by  $\sim \hbar\Omega/2$  rather than  $\sim \hbar\omega_{vib}$ . For a wide range of parameters, we find that this leads to a periodic dependence of reaction yield as a function of  $\Delta G$  (with period  $\sim \hbar\omega_{vib}$ ), rendering a set of originally endergonic reactions exergonic, and vice versa. These effects are substantially weaker under laser driving, and highlight both the energetic (availability of additional channels with lower activation energy) and entropic (redistribution of vibrational energy from the condensate into the polariton and dark modes upon reaction) advantages of exploiting polariton condensates for reactivity. To summarize, vibrational polariton condensation offers a novel strategy to accumulate energy into a well defined normal mode, a holy-grail in the field of vibrational dynamics that has been historically hindered by IVR. Its successful demonstration could revive hopes of "mode selective chemistry" [50], beyond electron transfer processes. In future work, it will be interesting to explore how the studied phenomena generalize to molecular polariton condensates in different spectral ranges.

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#### Author contributions

S.P.S. developed model, calculations, and interpretation of the results in the manuscript. L.A.M.M. provided guidance in the development of the initial model. J.A.C.G.A. developed the optimal basis to carry out the calculations for the electron transfer reaction under condensation and provided guidance on the interpretation of phenomenology. S.S. assisted on the calculation of multidimensional Franck-Condon factors. J.Y.Z. conceived the original version of the project and supervised the work throughout.

#### Code availability

Computational scripts used to generate the plots in the present article are available by email upon request to the au-

415 thors.

416

### Competing interests

417 The authors declare no competing interests.

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