

# A macroscopic condensation theory for vibrational strong coupling effects

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Recent experiments demonstrated the possibilities of modifying ground-state chemical reaction rates by placing an ensemble of molecules in an optical microcavity. This regime is commonly referred to as Vibrational Strong Coupling (VSC), and typically operates in the absence of any light source (in the dark). VSC causes reaction rate constant modifications, exhibits phase-transition type of behavior for equilibrium constant modifications, and the effect starts only when the collective Rabi splitting surpasses a threshold. Existing theoretical work often focuses on the single excitation pictures, centered around the idea of vibrational polaritons and dark states. We find that due to the many-body nature of VSC, most of the VSC effects can be potentially explained by forming a macroscopic condensation of vibrations. We theoretically demonstrate that by surpassing a critical Rabi splitting, the VSC system starts to macroscopically occupy one condensate state, which we believe could be the common explanation for VSC-induced effects.

Collective coupling between matter excitations with photonic excitations inside an optical cavity forms polaritons<sup>1</sup>, a quasi-particle that is a superposition of both types of excitations. This field is often referred to as cavity quantum electrodynamics (QED)<sup>2–4</sup>, with the focus on investigating the fundamental properties of polaritons and how to control them. Historically, the field has focused on exciton-polaritons<sup>5–7</sup> by coupling optical transitions of materials to cavity photonic excitations, including atoms<sup>4</sup>, molecules<sup>5–10</sup>, solid-state and nano materials<sup>11,12</sup>. Very recently (since 2015), Ebbesen<sup>13,14</sup> and Simpkins<sup>15</sup> have independently achieved the vibrational strong coupling (VSC) condition in cavity QED, by coupling the vibrational transition to an IR cavity mode, forming vibrational polaritons. Since then, there are a lot of intriguing phenomena reported under VSC, most of them operate without any optical pumping (under the dark<sup>16</sup>), and exhibit change of ground state chemical reaction rate constants, suppression<sup>17–21</sup> or enhancement<sup>22–25</sup>, typically by 4–5 times. Note that these experiments are fundamentally different than those that use external lasers to probe the vibrational polaritons and single-excitation subspace<sup>26–28</sup>, which can be theoretically explained<sup>27,29–31</sup>. VSC effect under the dark has been used to selectively slow down one reaction

out of two competing reactions<sup>32</sup>, thus imposing the selectivities towards one of them<sup>33</sup>. VSC has been shown to change the equilibrium constant for charge transfer complexation reaction<sup>34</sup>, for conformational changes of chemical complex<sup>35</sup>, and exhibit a phase transition type of behavior for the equilibrium constant upon changing the molecular concentration<sup>34,35</sup>. Similar phase transition-type behavior is also observed in the VSC-induced polymerization experiments<sup>25,36–38</sup>. It was speculated that the vibrational point group symmetry played a crucial role in the system to exhibit the VSC effect<sup>39</sup>. VSC has also been shown to significantly enhance the electrical conductance through originally non-conducting polymers<sup>40</sup>, and alter the glass transition temperature in polymer films<sup>41</sup>. Since there is no external pumping in these VSC experiments, it was speculated that the zero-point-vacuum field fluctuation must be responsible for the observed effects<sup>17</sup>.

While the experimental mysteries keep piling up, there is no well-accepted theoretical explanation<sup>42,43</sup> for all of the above-mentioned VSC effects, despite progress on the VSC-induced rate constant modification theories for a few-molecules coupled to the cavity<sup>44–58</sup>, on VSC-influenced electron transfer reactions<sup>59,60</sup>, or for a special model of collective coupling between cavity mode, solvent, and reaction

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coordinate<sup>61–63</sup>. The most challenging effect to explain is indeed the collective coupling effect: how does weak light-matter coupling per vibration even modify chemical reactivities and properties? So far, neither classical Transition State Theory<sup>44,64–67</sup> (or beyond classical rate theory<sup>68</sup>) nor quantum dynamics simulations<sup>54</sup> (under the mean field limit<sup>69</sup>) could explain this effect, but there are several hypotheses to demonstrate the collectiveness in VSC<sup>21,29,31,46,54,59,61–63,70–81</sup>, typically for  $N \approx 2 - 10^3$  vibrations collectively coupled to the cavity.

The key challenge for any theory to explain the VSC effect (without any external laser pumping) is that the light-matter coupling strength  $g_c$  is very weak, and only the collective light-matter coupling is large, which is often reported by the Rabi splitting  $\Omega_R = 2\sqrt{N}g_c$  measured from linear optical spectra. Typically<sup>82</sup>,  $N \approx 10^6 - 10^{12}$ , and  $\Omega_R \approx 100 \text{ cm}^{-1}$ , hence  $g_c \approx 5 \times 10^{-5} - 5 \times 10^{-2} \text{ cm}^{-1}$ . As a reference, room temperature thermal energy is  $k_B T \approx 208 \text{ cm}^{-1} \approx 26 \text{ meV}$ . How can such a collective, delocalized light-matter coupling influence local chemical bond breaking, while the local light-matter coupling strength  $g_c$  is so weak? Another theoretical challenge to understand the VSC effect is that if one uses the single excitation picture mentioned above, then the  $N-1$  dense manifold of dark vibrational polariton states should dominate and diminish all of the VSC kinetics effects from the polariton states. The energy gap between  $|\pm\rangle$  and dark states is only  $\Omega_R/2 \approx 50 \text{ cm}^{-1}$ , and the effective free energy for the dark states is lowered due to the entropic contribution from the dark state degeneracy, which is  $k_B T \ln(N-1) \approx 2760 - 5520 \text{ cm}^{-1}$  (for  $N = 10^6 - 10^{12}$ ), making the dark states the most stable configuration in terms of free energy<sup>83</sup>. So one should expect that the dark state becomes the dominant manifold of states, and the chemical properties, including the reactivities and rate constant, should be identical to the outside cavity case.

The above-mentioned single excitation subspace pictures are largely borrowed from the excitonic/electronic strong coupling (ESC) case, and the mechanistic discussions are largely centered around the vibrational polaritons and dark states. However, we realize that ESC and VSC systems have very different energy scales compared to  $k_B T$ . The key difference is the emitter frequency. For ESC, optical transition has a typical value of  $\hbar\omega_0 \sim 2 \text{ eV}$ , and for VSC,  $\hbar\omega_0 \approx 1000 \text{ cm}^{-1} \approx 124 \text{ meV}$ . This means that under room temperature, the Boltzmann probability for the excitonic system to be in the excited state is  $\bar{n}/N = e^{-\beta\hbar\omega_0} \approx e^{-77} \approx 10^{-34}$ , and for the range of  $N$  effectively coupled to each radiation mode in cavity QED, no molecules are in the excited states unless there is a laser excitation, and the single excitation/few excitation picture (polariton and dark states) is indeed a good mechanistic picture. On the other hand, for VSC, the Boltzmann probability for the vibrational DOF to be in the excited state is  $\bar{n}/N = e^{-\beta\hbar\omega_0} \approx e^{-5} \approx 6.7 \times 10^{-3}$ , so as large as 1/1000. For  $N = 10^6$  molecules, that means  $\bar{n} \approx 10^3$  of them are already in the excited states, due to the thermal distribution. As such, using the single/few excitation subspace picture in VSC is not appropriate. Upon coupling  $N = 10^{12}$  molecular vibrations to the cavity, one, in principle, needs to consider at least up to the billionth excitation subspace!

The above discussions made us realize that the key to unraveling the VSC mysteries lies in describing the many-body physics of it, not in the superposition of a one-excitation (one-body) picture described in Eq. (3). The condensed matter physics community has already provided well-established theories to understand intriguing phenomena, such as superfluidity and superconductivity. Weakly interacting bosonic particles can condense into one macroscopic state (bosonic Coherent state)<sup>84</sup>, which eventually explains superfluidity<sup>85</sup>. Weak interactions between pairs of electrons mediated through lattice phonon vibrations cause Cooper pairs to condense into a macroscopic state (Cooper pair Coherent state), through the Bardeen-Cooper-Schrieffer (BCS) mechanism<sup>86,87</sup>, which eventually explained superconductivity (the phonon-mediated kind). In the context of VSC, it is

possible that weak light-matter couplings between the cavity mode and vibrations lead to effective interactions between two vibrations (phonons), and these many-body interactions lead to a new macroscopic state (just like the Coherent states in BCS or BEC), such that the VSC cavity QED system is dominated by that one macroscopic state at room temperature. We thus conjecture that in VSC, vibrations (described by hard-core bosons) condensed into one macroscopic state (under certain critical conditions) that dominates the behavior of the VSC systems and causes the mysterious effects observed experimentally<sup>17,35</sup>. As such, we believe that vibrational polaritons do not give the correct mechanistic picture to understand VSC-induced effects when there is no external laser pumping; rather, the macroscopic condensation into one state does.

In this work, we theoretically demonstrate that the weak interaction of vibrations and the cavity mode causes effective interactions among all vibrational DOFs that occur inside the cavity, using the Schrieffer-Wolff transform<sup>88</sup>. The resulting effective Hamiltonian (Eq. (14)) is mathematically isomorphic to the BCS-type effective Hamiltonian<sup>86,89</sup>. This suggests that we can use the standard BCS variational procedure to find the macroscopic ground state (for condensate), which we refer to as  $|\tilde{0}\rangle$  (Eq. (18)). This macroscopic state is a true many-body state, in stark contrast to the superposition of  $N$ -single-particle states in the single excitation subspace (Eq. (3)).

We further show that the macroscopic state  $|\tilde{0}\rangle$  is stable compared to the normal thermodynamic state (which contains many microscopic states), in terms of free energy (when considering the dense manifold of vibrational excitations in the system). This  $|\tilde{0}\rangle$  is also stable compared to the vacuum states of vibrations outside the cavity, in terms of both energy and free energy. In ref. 35, it was speculated that strong coupling of a significant fraction of the molecules at the onset of VSC appears to pull nearly all the molecules into one phase by dipolar interactions due to the zero-point field oscillations of the optical mode. Our theoretical analysis suggests that this phase transition corresponds to the normal phase to macroscopic coherent state transition. Our work thus provides a concrete theoretical foundation to support the early hypothesis in ref. 35. Despite the early theoretical work that hypothesizes a phase transition behavior in VSC<sup>74,76</sup> or laser pumping-induced polariton condensation onto lower polariton state<sup>90</sup> (similar to the exciton polariton condensation upon laser driving), none of them suggest that the key mechanism of VSC is due to a macroscopic condensation due to the many-body interactions among vibrations mediated by cavity without laser pumping.

We further derived a simplified, analytic gap equation with approximations, giving rise to the condition (Eq. (40)) under which the condensation state is more stable in terms of free energy. Using detailed parameters from the Ebbesen NMR experiments, our theory provides a reasonable estimate of the critical Rabi splitting required to achieve the condensate phase, in agreement with the experimental values. Our theory predicts that the critical value of the Rabi splitting scales as  $\Omega_R \propto \sqrt{\hbar\omega_0 + k_B T}$ , meaning that with lower vibrational frequency  $\omega_0$  and lower  $T$ , it requires a smaller Rabi splitting to achieve the condensation. This prediction can be tested using the same Ebbesen NMR experimental setup, with isotope effects (replacing C-H vibrations to C-D vibrations) or substitutions (replacing C-H vibrations to C-F vibrations, which also have NMR signatures). Due to the macroscopic condensation, there is an additional energy penalty  $\Delta_n$  (the gap equation) for each DOF to overcome it in order to get excited from  $|\tilde{0}\rangle$ . We further use the gap equation to derive the reaction rate constant suppression factor  $k/k_0$ , and found that it gives a quantitative agreement with the experimental data reported in refs. 17,18. We believe that macroscopic condensation could be the common origin of all VSC-induced rate constant and equilibrium constant modifications, phase transitions, and beyond.

## Results and discussions

### Effective Hamiltonian

Collective light-matter couplings are commonly described by the Tavis-Cummings Hamiltonian<sup>91</sup> as follows

$$\hat{H} = \sum_{n=1}^N \hbar \omega_n \hat{\sigma}_n^\dagger \hat{\sigma}_n + \hbar \omega_c \hat{a}^\dagger \hat{a} + \sum_{n=1}^N \hbar g_n [\hat{\sigma}_n^\dagger \hat{a} + \hat{a}^\dagger \hat{\sigma}_n], \quad (1)$$

where  $N$  emitters are collectively coupled to a cavity mode described by  $\{\hat{a}^\dagger, \hat{a}\}$  under the rotating wave approximation. For the emitter, one often approximate them as a two-level system,  $\{|g_n\rangle, |e_n\rangle\}$ , with  $\hat{\sigma}_n^\dagger = |e_n\rangle\langle g_n|$ , and  $\hat{\sigma}_n = |g_n\rangle\langle e_n|$ . Further,  $\omega_n$  is the emitter frequency of the emitter  $n$  and  $g_n$  is the light-matter coupling strength between this emitter and the cavity mode. More commonly, one assumes that  $\omega_n = \omega_0$ , and  $g_n = g_c$  without any disorders in emitter frequency and in light-matter coupling strength<sup>91</sup>. In the single excitation subspace, one has

$$\hat{a}^\dagger |0\rangle \equiv |g\rangle \otimes |1_{\text{ph}}\rangle, \quad \hat{\sigma}_n^\dagger |0\rangle = |e_n\rangle \otimes |0_{\text{ph}}\rangle, \quad (2)$$

where  $|0\rangle$  is the TC vacuum state without any excitations, and  $|0_{\text{ph}}\rangle$  is the zero photon state. With symmetry  $\omega_n = \omega_0$  and  $g_n = g_c$  (no disorders), and under the resonance condition  $\omega_c = \omega_0$ , there are two optically bright polariton states

$$|\pm\rangle = \frac{1}{\sqrt{2}} \left[ \hat{a}^\dagger \otimes \hat{I}_\sigma \pm \frac{1}{\sqrt{N}} \sum_{n=1}^N \hat{\sigma}_n^\dagger \otimes \hat{I}_a \right] |0\rangle, \quad (3)$$

where  $\hat{I}_\sigma$  and  $\hat{I}_a$  are identities in the matter and photonic subspace, respectively. The eigenenergies associated with  $|\pm\rangle$  are  $E_\pm = \hbar\omega_0 \pm \hbar\sqrt{N}g_c$ , and there is an energy splitting, commonly referred to as the Rabi splitting  $\Omega_R$ , expressed as

$$\Omega_R = 2\sqrt{N}g_c, \quad (4)$$

and a  $N-1$  degenerated, optically dark (zero transition dipole from the ground state) states with the original energy of emitter  $E_D = \hbar\omega_0$ . The system achieves strong coupling condition<sup>43</sup> when

$$\Omega_R > (\gamma_0 + \gamma_c)/2, \quad (5)$$

with  $\gamma_0$  as the matter line width and  $\gamma_c$  as the cavity line width. This means that one will be able to observe the splitting of the original one peak as two peaks in linear spectra<sup>92</sup>.

With the TC Hamiltonian in Eq. (1), we assume that the molecular vibration will have a normalized line shape function as

$$\mathcal{A}_\nu(\omega - \omega_0) = \frac{1}{N} \sum_n \delta(\omega - \omega_n), \quad (6)$$

such that  $\int d\omega \mathcal{A}_\nu(\omega - \omega_0) = 1$ . We define the mean frequency as

$$\omega_0 = \frac{1}{N} \sum_n \omega_n, \quad (7)$$

The line shape function  $\mathcal{A}_\nu$  usually peaks at the mean frequency  $\omega_0$  (peak frequency), with a Gaussian shape or Lorentzian shape (or the Voigt convolution between them). These frequency disorders are caused by the coupling between the vibrational modes with their local environment, such as other spectator modes in the molecules or from the solvent, causing a frequency broadening away from  $\omega_0$ . This type of disorder is often referred to as the static disorder, causing inhomogeneous broadening of the spectra. We will further consider the effect of dynamical disorders (homogeneous broadening) and their impact in the “Methods” Section (Eq. (78)).

With the Gaussian line shape,

$$\mathcal{A}_\nu(\omega - \omega_0) = \frac{1}{\sqrt{2\pi}\sigma^2} \exp\left[-\frac{(\omega - \omega_0)^2}{2\sigma^2}\right]. \quad (8)$$

The light-matter detuning with each individual frequency is expressed as

$$\delta_n = \omega_n - \omega_c. \quad (9)$$

Further, the light-matter coupling strength exhibits disorders<sup>61,62,66,92</sup> due to the orientational disorders of the transition dipole vector with respect to the cavity field polarization direction

$$g_n = g_c \cos \phi_n, \quad (10)$$

where  $\phi_n$  is the angle between the transition dipole vector of the  $n_{\text{th}}$  molecule relative to the field polarization direction, and it is believed to be isotropic in 3D, such that  $\langle \cos \phi_n \cdot \cos \phi_m \rangle = \delta_{nm}/3$ . With disorders<sup>92</sup>, the composition and energy of these states will change<sup>71,93</sup> and will impact the optical spectra of polaritons<sup>92,93</sup> and Rabi splitting<sup>94,95</sup>. For example, with isotropic dipole angular disorder, the experimentally observed Rabi splitting is<sup>92,95</sup>  $\Omega_R^{\text{exp}} = 2\sqrt{N}g_c/\sqrt{3}$ . Frequency disorder, on the other hand, could potentially enlarge Rabi splitting<sup>94,95</sup>. One thus has to be careful when using  $\Omega_R^{\text{exp}}$  to extract  $\Omega_R = 2\sqrt{N}g_c$ .

Further,  $\hat{\sigma}_n^\dagger$  and  $\hat{\sigma}_n$  in Eq. (1) satisfy the Pauli-matrix commutation relations

$$[\hat{\sigma}_n^\dagger, \hat{\sigma}_n] = \hat{\sigma}_n^z, \quad [\hat{\sigma}_n^\dagger, \hat{\sigma}_m]_+ = \hat{I}_n \quad (11)$$

$$[\hat{\sigma}_n^\dagger, \hat{\sigma}_m] = 0, \quad [\hat{\sigma}_m^\dagger, \hat{\sigma}_n]_+ = 0. \quad (12)$$

These commutation relations (for hardcore bosons) are identical to those of Cooper pairs in the BCS theory when only considering the single excitation subspace. Here, we only consider the lowest two vibrational quantum states  $|g_n\rangle, |e_n\rangle$ , and their energy difference gives rise to the optical transition frequency  $\omega_n$ . The higher vibrational levels are not included, nor do we consider a perfect harmonic case for the vibrations and treat them using bosonic operators. In this sense, using the hard-core boson ( $SU(2)$  symmetry) partially considers the unharmonic nature of the vibration, and the full consideration, which should include all vibrational levels (for example, on a Morse potential<sup>63</sup>), is beyond the current scope of the work.

To adiabatically integrate out the photonic DOF,  $\hat{a}^\dagger$  and  $\hat{a}$ , we apply Schrieffer-Wolff (SW) transform<sup>88,96</sup> on the TC Hamiltonian (Eq. (1)), effectively performing 2nd order perturbative expansion in  $\lambda_n = g_n/\delta_n$ . Indeed, for VSC,  $g_c \approx 5 \times 10^{-5} - 5 \times 10^{-2} \text{ cm}^{-1}$  (for  $N = 10^6 - 10^{12}$  and  $\Omega_R = 100 \text{ cm}^{-1}$ ), and  $|\lambda_n| \ll 1$  for  $\delta_n > 1 \text{ cm}^{-1}$ . We choose the generator  $\hat{S} = \sum_{n=1}^N \lambda_n (\hat{\sigma}_n^\dagger \hat{a} - \hat{\sigma}_n \hat{a}^\dagger)$ , and the Hamiltonian in Eq. (1) can be transformed as

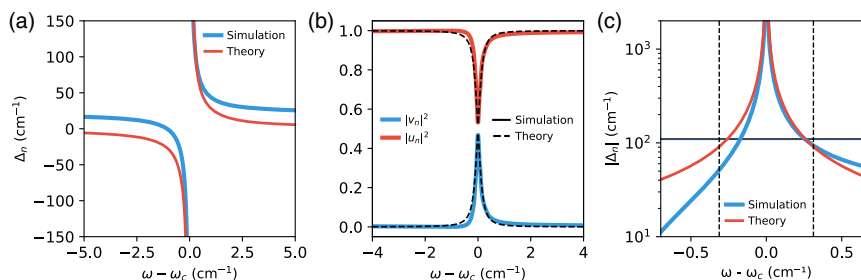
$$e^{\hat{S}} \hat{H} e^{-\hat{S}} = \hat{\mathcal{H}} + \mathcal{O}(\lambda^3), \quad (13)$$

with  $\lambda_n$  chosen to satisfy the SW transform criteria (see details in the Supplementary Note 1A). The resulting effective Hamiltonian is expressed as

$$\hat{\mathcal{H}} = \sum_{n=1}^N \hbar \tilde{\omega}_n \hat{\sigma}_n^\dagger \hat{\sigma}_n + \sum_{n \neq m} G_{nm} \hat{\sigma}_n^\dagger \hat{\sigma}_m, \quad (14)$$

and the re-normalized vibrational frequency is

$$\tilde{\omega}_n = \omega_n + g_n^2/\delta_n. \quad (15)$$



**Fig. 1 | Numerical Simulation compared to the Analytic theory.** Here, we consider a system with  $\omega_0 = 1000 \text{ cm}^{-1}$ ,  $\Omega_R = 50 \text{ cm}^{-1}$ ,  $\omega_0 - \omega_c = 1 \text{ cm}^{-1}$ ,  $N = 10^7$ , and  $\sigma = 20 \text{ cm}^{-1}$ . **a** The numerical gap  $\Delta_n$  (blue) and the analytic expression  $\Delta(\omega)$  in Eq. (68) (red). Note that the energy contribution will be  $-\Delta_n u_n v_n$ , so the changing sign of  $\Delta_n$  will be compensated by the changing sign of  $u_n v_n$ , such that the  $|\tilde{0}\rangle$  state's energy will be lowered. **b** The expansion coefficients  $|u_n|^2$  (red) and  $|v_n|^2$  (blue), as a

function of the detuning, obtained from numerical simulation (solid line) and analytic expression (black dashed) using Eqs. (30) and (31). **c** The absolute value of gap,  $|\Delta_n|$  obtained numerically (blue) and using Eq. (68) (red), with the black horizontal line indicating the value of  $\sqrt{e^{-\beta\hbar\omega_0}(\hbar\omega_0 + k_B T)}$ . Above the blackline is the gap that satisfies the condition in Eq. (39). Two vertical dashed lines indicate the critical frequency  $\omega_c^-$  and  $\omega_c^+$  based on Eq. (41).

The effective interactions between two vibrational excitations are

$$G_{nm} = \frac{\hbar}{2} g_n g_m \left( \frac{1}{\delta_n} + \frac{1}{\delta_m} \right). \quad (16)$$

Note that  $G_{nm}$  is the effective interaction between  $\hat{\sigma}_n^\dagger$  and  $\hat{\sigma}_m$  due to their coupling to  $\hat{a}$ . The physical picture of such effective all-to-all interaction is also crystal clear: due to the light-matter coupling term,  $\hat{\sigma}_n^\dagger|0\rangle \rightarrow \hat{a}^\dagger|0\rangle$  through the  $g_n \hat{a}^\dagger \hat{\sigma}_n$  term, and  $\hat{a}^\dagger|0\rangle \rightarrow \hat{\sigma}_m^\dagger|0\rangle$  through the  $g_m \hat{\sigma}_m^\dagger \hat{a}$  term, thus effectively create a coupling term between  $n$  and  $m$ , with coupling strength expressed at the 2nd order perturbation level. Note that a similar analysis of cavity-mediated vibrational excitation energy transfer between vibrational modes has also been investigated in the case of a single molecule<sup>45</sup> strongly coupled to the cavity. Our above-mentioned perturbative analysis is valid when the perturbative parameter  $|\lambda_n| = |g_n/\delta_n| \ll 1$ , and will break down when  $\delta_n = 0$ . The effective magnitude  $|G_{nm}|$  will become larger when the detuning  $\delta_n$  and  $\delta_m$  are reduced. This might be the key to explaining the VSC resonance condition, which often requires very sensitive matching of the cavity frequency with vibrational frequency  $\omega_c \approx \omega_0$ . In the experiments, due to the mirror fluctuations<sup>97,98</sup>, the best one could say is  $\delta_n \approx 10^{-1} - 1 \text{ cm}^{-1}$ , even for the “perfect” detuning at  $\omega_c \approx \omega_0 - 10^3 \text{ cm}^{-1}$ . As such,  $\lambda_n$  is a valid perturbative parameter per site  $n$ . Under the rotating-wave approximation, the effective Hamiltonian can be viewed as a special case of the effective BCS Hamiltonian<sup>99–101</sup>. In addition, the effective Hamiltonian could also be viewed as a long-range random bond  $X$ - $Y$  model with random  $Z$ -field<sup>102–105</sup>, the Lipkin–Meshkov–Glick Hamiltonian<sup>103,106–108</sup>, or a spin-glass type of Hamiltonian<sup>76,109–112</sup>.

### Macroscopic condensate state

We conjecture that the true ground state of  $\hat{\mathcal{H}}$  is a many-particle, macroscopic state, which we denote as  $|\tilde{0}\rangle$ . Because  $\hat{\mathcal{H}}$  is mathematically isomorphic to the BCS effective Hamiltonian, we hypothesize that this should be the coherent state of many hard-core Bosons that has the same form as the Schrieffer ansatz in the BCS theory<sup>86,87</sup>. We thus follow the standard procedure in the BCS theory<sup>89</sup> closely. The coherent state for our hard-core Bosons is

$$|\tilde{0}\rangle = \prod_{n=1}^N e^{\alpha_n \hat{\sigma}_n^\dagger} |0\rangle, \quad (17)$$

and using the hard-core boson's commutation relation in Eqs. (11) and (12), the many-body coherent state is expressed as

$$|\tilde{0}\rangle = \prod_{n=1}^N (u_n + v_n \hat{\sigma}_n^\dagger) |0\rangle = \bigotimes_{n=1}^N |\phi_n\rangle. \quad (18)$$

with the expansion coefficients

$$u_n = \frac{1}{1 + \alpha_n^2}, \quad v_n = \frac{\alpha_n}{1 + \alpha_n^2}. \quad (19)$$

Eq. (18) is identical to the Schrieffer ansatz for BCS-type ground state with Cooper pairs<sup>87</sup>, with detailed derivations provided in the Supplementary Note II. Here,  $|\phi_n\rangle = u_n |g_n\rangle + v_n |e_n\rangle$ , and  $|0\rangle \equiv |g_1\rangle \otimes |g_2\rangle \otimes \dots \otimes |g_N\rangle$  is the zero-particle state for the effective Hamiltonian in Eq. (14) (without the photonic DOF, so it is different than what is expressed in Eq. (2)), where  $u_n$  and  $v_n$  are variational parameters, satisfying  $u_n^2 + v_n^2 = 1$  for all  $n \in [1, N]$ , which can be determined by the BCS variational procedure (or equivalently, through the Bogoliubov canonical transform, Eq. (65)). Note that  $|\tilde{0}\rangle$  in Eq. (18) is a true many-body state that is in stark contrast to the single excitation state  $|\pm\rangle$  in Eq. (3). The condensate state can be solved using variational principle calculations, or effectively, the Bogoliubov transform, with details provided in the “Methods” section.

This leads to the following coupled equations

$$\begin{pmatrix} \hbar\tilde{\omega}_n - \mu & \Delta_n \\ \Delta_n^* & -(\hbar\tilde{\omega}_n - \mu) \end{pmatrix} \begin{pmatrix} u_n^* \\ v_n^* \end{pmatrix} = E_n \begin{pmatrix} u_n^* \\ v_n^* \end{pmatrix} \quad (20)$$

where we have defined the gap  $\Delta_n$  (for  $n \neq m$ ) as

$$\Delta_n \equiv \sum_{m \neq n} G_{nm} u_m v_m. \quad (21)$$

The matrix equation in Eq. (20) has two eigenvalues  $\pm E_n$ , with  $E_n$  expressed as

$$E_n = \sqrt{(\hbar\tilde{\omega}_n - \mu)^2 + |\Delta_n|^2}, \quad (22)$$

which describes the dispersion relation of Bogolons, with eigenvectors

$$u_n = \cos \theta_n, \quad v_n = \sin \theta_n. \quad (23)$$

Note that  $\Delta_n \propto N$ , which is due to the sum of all other  $m$ . Details of the derivations are provided in Supplementary Note IIB. Even though Eq. (20) looks formally like a single particle equation with two states, the coupling term  $\Delta_n$  (see Eq. (21)) contains all coefficients  $\{u_m, v_m\}$  such that these equations (for different  $n$ ) are coupled to each other, describing the many-body physics. This was the true genius of the BCS theory. Further,  $\Delta_n$  coupling term opens up an energy gap for the single particle state.

We want to obtain an explicit expression for the gap equation. Notice that

$$u_n^* v_n = \cos \theta_n \sin \theta_n = \frac{1}{2} \sin 2\theta_n = \frac{\Delta_n}{2E_n}, \quad (24)$$

together with the definition of  $\Delta_n$  in Eq. (21), one can derive the well-known BCS-type gap equation as follows

$$\Delta_n = \sum_{m \neq n} G_{nm} \cdot \frac{\Delta_m}{2E_m} = \sum_{m \neq n} \frac{G_{nm} \Delta_m}{2\sqrt{(\hbar\tilde{\omega}_m - \mu)^2 + |\Delta_m|^2}}. \quad (25)$$

The energy gap is the energy needed to create collective excitation of the Bogoliubov quasiparticle, Bogolons. See Eq. (65) in the “Methods” Section for details.

Further, we have a second complementary equation

$$\bar{n} = \sum_n v_n^2 = \sum_{n=1}^N \frac{1}{2} \left[ 1 - \frac{\hbar\tilde{\omega}_n - \mu}{\sqrt{(\hbar\tilde{\omega}_n - \mu)^2 + |\Delta_n|^2}} \right]. \quad (26)$$

For a given VSC system,  $T$ ,  $N$  are fixed, and  $\bar{n}$  should also be fixed (through Eq. (57)). As such, one can numerically solve (thanks to more advanced computing powers nowadays compared to the BCS<sup>86,87</sup> era in 1957) for  $\mu$  and  $\Delta_n$  from Eqs. (25) and (26), which allows one to determine all  $\{u_n, v_n\}$  in Eqs. (30) and (31) and thus the new ground state  $|\tilde{0}\rangle$  in Eq. (18). Detailed algorithms are provided in the “Methods” section and in Supplementary Note V.

Figure 1 presents our numerical simulation to solve Eqs. (25) and (26). We consider a model system with  $\omega_0 = 1000 \text{ cm}^{-1}$ ,  $\Omega_R = 50 \text{ cm}^{-1}$ ,  $\omega_0 - \omega_c = 1 \text{ cm}^{-1}$ ,  $N = 10^7$ , and  $\sigma = 20 \text{ cm}^{-1}$ . Figure 1a presents the numerically computed gap  $\Delta_n$  as a function of  $\omega_n - \omega_c$  (blue curve), indicating the peaking behavior of the gap at the frequency close to  $\omega_c$ . Figure 1b presents the numerically obtained  $|u_n|^2$  (red) and  $|v_n|^2$  (blue), and indeed, when  $\omega_n$  is close to the  $\omega_c$ , these probability significantly deviate from the original Boltzmann probabilities. Note that these “hot spots” are in the frequency domain, not necessarily in real space. The overall statistics for  $N$  molecules satisfied the Boltzmann distribution (Eq. (57)), as the constraint (the  $-\mu\bar{n}$  part in Eq. (59)) is explicitly enforced in our calculation.

### The gap equation

To solve Eqs. (25) and (26) analytically (with approximations), one may replace the sum by integrals:  $\frac{1}{N} \sum_n f(\tilde{\omega}_n) \rightarrow \int d\omega \mathcal{A}_\nu(\omega - \omega_0) f(\omega)$ , using the normalized lineshape function (Eq. (6)) as the vibrational frequency distribution function. For  $g_n = g_m = g_c$  special case, we have

$$\Delta(\omega) = N \int d\omega' \mathcal{A}_\nu(\omega') \left( \frac{1}{\omega - \omega_c} + \frac{1}{\omega' - \omega_c} \right) \times \frac{\hbar}{4} \frac{g_c^2 \Delta(\omega')}{\sqrt{(\hbar\omega' - \mu)^2 + |\Delta(\omega')|^2}}, \quad (27)$$

which is a nonlinear integral equation. A key feature of this equation is that it contains the resonance behavior of the VSC experiments, which often observe that the rate changes at  $\omega_c \approx \omega_0$ . Here, the energy gap equation exhibits this behavior due to the convolution between the line shape function  $\mathcal{A}_\nu(\omega' - \omega_0)$  and the detuning function  $1/[(\omega - \omega_c)(\omega' - \omega_c)]$ . This might also explain why some VSC experiments<sup>22,24,113,114</sup> have reproducibility challenges<sup>113</sup>, likely due to the non-perfect matching between  $\omega_c$  and  $\omega_0$  (either through the non-zero detuning due to the limitations of experimental conditions, or caused by the mirror fluctuations of the FP cavity<sup>97</sup>).

Similarly, Eq. (26) can also be replaced by integral form

$$\bar{n} = N \int d\omega \mathcal{A}_\nu(\omega - \omega_0) \frac{1}{2} \left[ 1 - \frac{\hbar\omega - \mu}{\sqrt{(\hbar\omega - \mu)^2 + |\Delta(\omega)|^2}} \right] \quad (28)$$

One can solve the integral in Eq. (28) and obtain  $\mu = \mu(\Omega_R)$ , then plugging into Eq. (27) solve the analytic expression of the gap. With detailed expressions of  $\mathcal{A}_\nu$  (such as Eq. (8)), one should be able to work it out.

For a simple special case, when there is no disorder in frequency,  $\omega_n = \omega_0$ , using Eq. (28) by setting  $\mathcal{A}_\nu(\omega - \omega_0) \rightarrow \delta(\omega - \omega_0)$ , we can solve

$$\mu = \hbar\omega_0 - \sqrt{\frac{1}{1 - \alpha^2}} \cdot \alpha |\Delta(\omega_0)|, \quad \alpha = \frac{N - 2\bar{n}}{N} \quad (29)$$

For  $N \gg \bar{n}$ ,  $\alpha \approx 1$ ,  $1 - \alpha^2 \approx 4\bar{n}/N$ , thus  $\mu \approx \hbar\omega_0 - \sqrt{N/\bar{n}} \cdot |\Delta|/2$ . This  $\mu$  can be used as the initial guess and plugged into Eq. (27) to solve the  $\Delta(\omega)$ . The obtained  $\Delta(\omega)$  can then be used and plugged into Eq. (28) to solve a refined expression of  $\mu$ , and this procedure can be done iteratively, such that there is an analytic version of the Self-Consistent Field (SCF) procedure. In this work, we decided to keep it simple and stop at the no-disorder limit of  $\mu$  in Eq. (29), and plug it into Eq. (27) only once, to obtain an approximate expression of  $\Delta(\omega)$ , discussed in the “Methods” Sections, with detailed expressions in Eq. (68), as well as approximate forms in Eqs. (69)–(70).

Further, using  $\mu$  expressed in Eq. (29), and the  $\Delta(\omega)$  expression in Eq. (68) (or Eq. (70) for the small detuning case), we have analytic expressions for the expansion coefficients

$$u^2(\omega) = \frac{1}{2} \left[ 1 + \frac{\hbar\omega - \mu}{\sqrt{(\hbar\omega - \mu)^2 + |\Delta(\omega)|^2}} \right] \quad (30)$$

$$v^2(\omega) = \frac{1}{2} \left[ 1 - \frac{\hbar\omega - \mu}{\sqrt{(\hbar\omega - \mu)^2 + |\Delta(\omega)|^2}} \right] \quad (31)$$

For the VSC system that exhibits angular disorders, one needs to solve Eqs. (25) and (26) numerically, and detailed discussions are provided in Supplementary Note III.

For the pure-homogeneous case, one can drastically simplify the analysis, with  $\omega_n = \omega_0$  for all  $n \in [1, N]$ . In this case, all  $v_n^2$  are identical due to symmetry, and from Eq. (56),  $v_n^2 = e^{-\beta\hbar\omega_0}$ , and  $u_n^2 = 1 - e^{-\beta\hbar\omega_0}$ . The gap  $\Delta_n$  in Eq. (21) (for all  $n \in [1, N]$ ) becomes

$$|\Delta_n| = \left| G \sum_{m \neq n} u_m^* v_m \right| \approx (N-1) |G| \sqrt{e^{-\beta\hbar\omega_0} (1 - e^{-\beta\hbar\omega_0})} \approx N |G| \sqrt{e^{-\beta\hbar\omega_0}} \approx \frac{N \hbar g_c^2}{|\omega_0 - \omega_c|} \sqrt{e^{-\beta\hbar\omega_0}}, \quad (32)$$

where we have used  $N-1 \approx N$ .

We are confident that there must be better versions of the gap equation for Eq. (27) with an analytic form (or for other lineshapes, such as for Lorentzian lineshapes), just like many available gap equations for the BCS theory. Nevertheless, it is good to pause here and return to some simple physical pictures before continuing to search for those expressions. The typical values for the VSC experiments to achieve effects are  $\Omega_R^{\text{exp}} \approx 100 \text{ cm}^{-1}$  when the sample has isotropic orientational disorders, and thus  $\sqrt{N} g_c \approx \sqrt{3} \Omega_R^{\text{exp}} / 2$ ,  $\omega_0 \approx 1000 \text{ cm}^{-1}$ ,  $e^{-\beta\hbar\omega_0} \approx 8.2 \times 10^{-3}$ . As such, for a detuning with  $|\omega_0 - \omega_c| \approx 1 \text{ cm}^{-1}$ , the estimated gap per quasi-particle (Bogolons) using Eq. (32) is

$|\Delta_n| \approx 677.8 \text{ cm}^{-1}$ , already surpassing room temperature thermal fluctuations  $k_B T \approx 208 \text{ cm}^{-1}$ . The many-body picture seems to resolve the conceptual challenge faced in the single-excitation picture in VSC. In a single excitation picture, the energy gap between  $|\pm\rangle$  and  $\{|D_j\rangle\}$  is  $\Omega_R/2 = \sqrt{N}g_c \approx \sqrt{3}\Omega_R^{\text{exp}}/2 \approx 86.6 \text{ cm}^{-1}$  (for zero detuning  $\omega_c - \omega_0 = 0$  and for  $\Omega_R^{\text{exp}} \approx 100 \text{ cm}^{-1}$ ), and typically,  $\sqrt{N}g_c < k_B T$ , and the dark states also have a large effective entropic contribution to the free energy  $-k_B \ln(N-1)$ , making it difficult to understand why polariton states are playing a special role in terms of VSC. In the many-body picture, the vibrations (here, the hard core bosons) condense into one macroscopic state  $|\tilde{0}\rangle$ , opening up an energy gap per Bogolon with  $\Delta_n \approx \frac{1}{4}\hbar\Omega_R^2\sqrt{e^{-\beta\hbar\omega_0}}/|\omega_0 - \omega_c| \gg k_B T$ , making  $|\tilde{0}\rangle$  the special dominant state in VSC.

### Condition to achieve macroscopic condensation

Due to the more stable new ground state  $|\tilde{0}\rangle$ , the system condenses to this single macroscopic state. This opens up a gap between  $|\tilde{0}\rangle$  and the normal thermodynamic states of  $N$  vibrations at temperature  $T$ . For the normal thermodynamic states, their energy is

$$\mathcal{E}_0 = N \cdot \frac{e^{-\beta\hbar\omega_0}}{1 + e^{-\beta\hbar\omega_0}} \cdot \hbar\omega_0 \approx N e^{-\beta\hbar\omega_0} \cdot \hbar\omega_0. \quad (33)$$

There is a dense manifold of microscopic states with an entropy of  $S = \ln[N!/(n! \cdot (N - n)!)]$ . The entropy for the normal state can also be evaluated using the Gibbs formula (equivalently through the Stirling approximation of the Boltzmann entropy) as  $S = -Nk_B(p_g \ln p_g + p_e \ln p_e)$  (where  $p_e = e^{-\beta\hbar\omega_0}/(1 + e^{-\beta\hbar\omega_0})$  and  $p_g = 1/(1 + e^{-\beta\hbar\omega_0})$ ). As such, the dense manifold of the normal excited states has a free energy that is lowered due to the entropic contribution

$$\begin{aligned} \mathcal{F}_0 &= \mathcal{E}_0 - TS = \mathcal{E}_0 - [\mathcal{E}_0 + Nk_B T \ln(1 + e^{-\beta\hbar\omega_0})] \\ &= -Nk_B T \ln(1 + e^{-\beta\hbar\omega_0}) \approx -Nk_B T e^{-\beta\hbar\omega_0}. \end{aligned} \quad (34)$$

Further, the vacuum state  $|0\rangle$  (outside the cavity) has a free energy of  $\mathcal{F}_g = 0 \cdot N - T \ln 1 = 0$ , and the normal manifold of states (thermodynamic state) has a lower free energy than  $|0\rangle$ , thus it is more probable to be seen at  $T$ .

For the macroscopic state  $|\tilde{0}\rangle$ , the free energy associated with this single macroscopic state is  $\tilde{\mathcal{F}}_0 = \tilde{\mathcal{H}} - k_B T \ln 1 = \tilde{\mathcal{H}}$ , which is the same as the new ground state's energy, where  $\Delta_n$  is the gap for each of the vibrational DOF (c.f. Eq. (20)). Thus, as long as the gap surpasses the Entropic contribution of the normal states, the macroscopic BCS-type  $|\tilde{0}\rangle$  is a more favorable state for the system.

The gap for the entire  $N$  particle system is

$$\sum_{n=1}^N \Delta_n u_n v_n \approx N \Delta_n \sqrt{e^{-\beta\hbar\omega_0}} \approx \frac{N^2 \hbar g_c^2}{|\delta_0|} e^{-\beta\hbar\omega_0}, \quad (35)$$

where  $\Delta_n$  is expressed in Eqs. (32) and (35) scales as  $\propto N^2 g_c^2$ . As such, the estimated free energy for  $|\tilde{0}\rangle$  (c.f. Eq. (55)) is

$$\begin{aligned} \tilde{\mathcal{F}}_0 &= \tilde{\mathcal{E}} = \sum_n \hbar \tilde{\omega}_n |v_n|^2 - \sum_n \Delta_n u_n v_n \\ &\approx N \hbar \omega_0 e^{-\beta\hbar\omega_0} - N^2 \frac{\hbar g_c^2}{|\omega_0 - \omega_c|} e^{-\beta\hbar\omega_0} \end{aligned} \quad (36)$$

where  $\tilde{\mathcal{E}}$  is the expectation value of energy for the new ground state, with details provided in Supplementary Note IID.

The interesting observation is that for the condensate phase, free energy depends on  $N$  quadratically, as

$$\tilde{\mathcal{F}}_0 \approx -a \cdot N^2 + b \cdot N = -a(N - b/2a)^2 + b^2/4a, \quad (37)$$

with  $a = \hbar g_c^2 e^{-\beta\hbar\omega_0}/|\omega_0 - \omega_c|$  and  $b = \hbar \omega_0 e^{-\beta\hbar\omega_0}$ , whereas for the normal phase,  $\mathcal{F}_0 = -c \cdot N$  with  $c = k_B T e^{-\beta\hbar\omega_0}$ , which is linearly depending

on  $N$ . For large enough  $N$  at a given  $T$ , the condensate phase will have a lower free energy than the normal phase. Another way to look into this problem is that by defining order parameter  $\varphi = \sqrt{N} \propto \Omega_R$ , then  $\tilde{\mathcal{F}}_0 \approx -a \cdot \varphi^4 + b \cdot \varphi^2$ , and  $\mathcal{F}_0 = -c \cdot \varphi^2$ , which is the seminal Landau model for phase transition, with the difference that the leading order terms are negative. The quadratic dependence of  $N$  for  $\tilde{\mathcal{F}}_0$  suggests a super-extensive behavior (has a higher power dependence of  $N$  compared to the normal phase  $\mathcal{F}_0$ , which depends on  $N$  linearly and extensive). This is due to the all-to-all couplings in  $\tilde{\mathcal{H}}$  (Eq. (14)) and also commonly encountered in the spin-magnetization physics.

To discover the conditions under which the new ground state  $|\tilde{0}\rangle$  has even a lower free energy than the normal state (and thus, lower than the vacuum state  $|0\rangle$ ), one has the condition  $\tilde{\mathcal{F}}_0 = \tilde{\mathcal{H}} < \mathcal{F}_0$ :

$$N \hbar \omega_0 e^{-\beta\hbar\omega_0} - \sum_n \Delta_n u_n v_n < -N k_B T e^{-\beta\hbar\omega_0}. \quad (38)$$

Assuming that  $u_n v_n \approx \sqrt{e^{-\beta\hbar\omega_0}}$ , or equivalently, using  $\mu$  in Eq. (29), one has

$$|\Delta_n| > \sqrt{e^{-\beta\hbar\omega_0}} \cdot (\hbar\omega_0 + k_B T), \quad (39)$$

which is the condition that the Bogolon with frequency  $\omega_n$  and a gap  $|\Delta_n|$  shall be more stable than the normal thermodynamic phase. For the no-disordered case, using  $|\Delta_n|$  expression in Eq. (32), we have

$$\hbar \Omega_R^2 > 4|\omega_0 - \omega_c| \cdot (\hbar\omega_0 + k_B T). \quad (40)$$

Upon achieving the above condition for the no-frequency disorder case, all DOFs (for  $n \in [1, M]$ ) participate in the macroscopic state  $|\tilde{0}\rangle$ .

With frequency disorders, the above picture, where all  $N$  DOFs participate in the macroscopic state, will change. This is because for a range of  $\omega_n$ , the gap  $\Delta(\omega_n)$  will be very different, having a very large value for  $\omega_n \approx \omega_c$ , and small when the detuning is large. For a system with frequency disorders, one should expect that only for those Bogolons with frequency close to  $\omega_c$  would open up a large enough gap. As such, only a fraction of molecules out of  $N$  participate in the condensate state  $|\tilde{0}\rangle$ . Using the approximate expression of  $\Delta(\omega)$  in Eq. (70), we have the frequency range within which the Bogolon has a large enough gap to make it more stable than the normal thermodynamics phase. This leads to the *critical frequency* expressed as follows:

$$\omega_c^\pm = \omega_c \pm \frac{\hbar N g_c^2}{2(\hbar\omega_0 + k_B T) - \hbar N g_c^2 \cdot \Xi(\delta_0, \sigma)}, \quad (41)$$

where  $\Xi(\delta_0, \sigma)$  is

$$\Xi(\delta_0, \sigma) \equiv \left| \frac{\sqrt{\pi}}{\sqrt{2}\sigma} e^{-\delta_0^2/2\sigma^2} \operatorname{erfi}\left(\frac{\delta_0}{\sqrt{2}\sigma}\right) \right|. \quad (42)$$

Eq. (41) means that for  $\omega_n \in [\omega_c^-, \omega_c^+]$ , these Bogolons are more stable than the normal thermodynamical phase, whereas for  $\omega_n < \omega_c^-$  and  $\omega_n > \omega_c^+$ , the Bogolons can be excited to normal phase due to their small energy gap. The numerical test of the critical frequency is provided in Fig. 1c. Note that Eq. (41) has a further approximation when we derived it, so it slightly deviates from the true intercepts between the red curve of  $|\Delta(\omega)|$  and the black line  $\sqrt{e^{-\beta\hbar\omega_0}}(\hbar\omega_0 + k_B T)$ .

The fraction of the participating vibrations in this condensate phase (out of a total  $N$ ) is thus

$$\rho = \int_{\omega_c^-}^{\omega_c^+} d\omega A_\nu(\omega - \omega_0) = \int_{\omega_c^-}^{\omega_c^+} \frac{d\omega}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(\omega - \omega_0)^2}{2\sigma^2}\right]. \quad (43)$$

Note that in either case,  $|\tilde{0}\rangle$  has a lower free energy than the normal state, as well as the vacuum state  $|0\rangle$ . Equations (40) and (41)–(43) are

the key results of this work, which predicts the critical condition that the Condensation in VSC cavity QED will occur with a reasonably large  $\Omega_R$ , a reasonably small light-matter detuning  $|\omega_0 - \omega_c|$ , and a reasonably low vibrational frequency  $\omega_0$ , and could even occur at room temperature, as most of the VSC experiments were operating<sup>17,21,34,35,38</sup>.

### Estimation based on the experiments

As shown in the previous work<sup>94,95</sup>, one needs to be careful with the experimentally measured Rabi splitting, because frequency disorder also contributes to it<sup>94,95</sup>. Following ref. 94, and considering the angular disorder which reduces the effective Rabi splitting by refs. 61,92,95  $1/\sqrt{(\sum_n \cos^2 \theta)/N} = 1/\sqrt{3}$  times. The dipole angular control has been experimentally accomplished for VSC and verified<sup>115,116</sup> using voltage-controlled switching<sup>115</sup> or temperature-controlled switching<sup>116</sup> of liquid crystal molecules in different alignments (e.g., Fig. 3a in ref. 116). Combining this angular disorder with the broadening of cavity line width and molecular line width, we have

$$\Omega_R^{\text{exp}} = \frac{2}{\sqrt{3}} \left( N g_c^2 \sqrt{1 + \frac{\gamma(\kappa + \gamma)}{2N g_c^2}} - \frac{\gamma^2}{4} \right)^{1/2}, \quad (44)$$

where with  $\gamma$  as the vibrational line width ( $\gamma = 2\sigma$ ) and  $\kappa$  as the cavity line width, if both lineshapes are Lorentzian<sup>94</sup>. Using the above, the actual Rabi Splitting (that reports the actual light-matter coupling strength)  $\Omega_R = 2\sqrt{N}g_c$  is expressed

$$\Omega_R = \left[ \frac{[\gamma^2(\kappa + \gamma)^2 + 4(3(\Omega_R^{\text{exp}})^2 + \gamma^2)]^{1/2} - \gamma(\kappa + \gamma)}{2} \right]^{1/2}. \quad (45)$$

Numerically, we found that the detailed value of  $\gamma$  and  $\kappa$  in most of the experiments has a limited impact on  $\Omega_R$ , whereas the majority impact from the  $1/\sqrt{3}$  factor due to the angular disorder, such that  $\Omega_R \approx \sqrt{3}\Omega_R^{\text{exp}}$ . It is thus important to emphasize that the experimentally reported Rabi splitting from linear spectra  $\Omega_R^{\text{exp}}$  would be only  $1/\sqrt{3}$  of the  $2\sqrt{N}g_c$ , when one needs to compare theory and experiments quantitatively.

In ref. 35 for the VSC-NMR experiment, under the concentration of 1M, the experimentally observed Rabi splitting is  $\Omega_R^{\text{exp}} \approx 83 \text{ cm}^{-1}$ , with cavity line width  $\kappa = 70 \text{ cm}^{-1}$  and vibrational line width  $\gamma = 2\sigma = 18 \text{ cm}^{-1}$ , leading to  $\Omega_R = 2\sqrt{N}g_c \approx 142.2 \text{ cm}^{-1}$ . For the critical concentration at 0.5M,  $\Omega_R$  should be reduced by  $\sqrt{2}$  because  $N$  is effectively reduced by 2 (c.f. Eq. (4)), leading to the experimentally observed critical  $\Omega_R \approx 142.2/\sqrt{2} \approx 100.5 \text{ cm}^{-1}$ , or equivalently,  $\Omega_R^{\text{exp}} \approx 58.6 \text{ cm}^{-1}$  at the critical concentration of 0.5M. For the no-disordered limit, the critical condition requires the detuning at an order of  $|\omega_0 - \omega_c| \approx 0.79 \text{ cm}^{-1}$ , and Eq. (40) predicts the same critical Rabi splitting ( $\Omega_R^{\text{exp}} \approx 58.6 \text{ cm}^{-1}$ ) to see VSC modification. For the reaction reported in refs. 17,18, where the rate constant suppression by up to 4.5 times is achieved when coupling the cavity to Si-C vibrations. From Fig. 3D in ref. 18, it seems that this modification only start to occur when  $\Omega_R^{\text{exp}} > 55 \text{ cm}^{-1}$ , with no data point reported for a smaller  $\Omega_R^{\text{exp}}$ . In this setup,  $\hbar\omega_0 = 860 \text{ cm}^{-1}$ ,  $\Omega_R^{\text{exp}} \approx 55 \text{ cm}^{-1}$ ,  $\kappa = 24.1 \text{ cm}^{-1}$ ,  $\gamma = 40 \text{ cm}^{-1}$ . As such,  $\Omega_R \approx 98.3 \text{ cm}^{-1}$ , that means  $\delta_0 \approx 2.3 \text{ cm}^{-1}$  for this system when using Eq. (40) (and assuming no frequency disorders). That means  $\Omega_R^{\text{exp}} < 50 \text{ cm}^{-1}$  there will be no condensate.

Of course, the above estimation should be viewed, to the best, as an averaged, simplified estimation, because the expression itself does not consider any frequency and angular disorders. The real experimental systems do have frequency and dipole angular disorders. The real system in ref. 35 has an estimated detuning of  $|\delta_0| = |\omega_c - \omega_0| \approx 1 \text{ cm}^{-1}$ . Together with  $\omega_0 = 2970 \text{ cm}^{-1}$ ,  $k_B T = 200 \text{ cm}^{-1}$ , and the experimental critical  $\Omega_R^{\text{exp}} \approx 54.8 \text{ cm}^{-1}$ , Eq. (41) indicates that

$|\omega_c^\pm - \omega_c| \approx 0.25 \text{ cm}^{-1}$ , meaning that only the vibrations in the frequency window of  $0.5 \text{ cm}^{-1}$  centered around  $\omega_c$  participate in the condensate. Further, Eq. (43) suggests that in this window of frequency,  $\rho \approx 1.1\%$ , 1 out of 100 vibrations participates in the macroscopic state  $|\bar{0}\rangle$ . For  $N = 10^6$  molecules, this means  $10^4$  participate in the condensate in the Ebbesen NMR system. In ref. 35, it was speculated that there would be such a phase transition. Our theory on VSC-induced Condensation provides a concrete theoretical explanation for this phase transition behavior. For VSC rate constant measurements, there are also extensive data points provided in ref. 21.

Equation (40) predicts that the critical Rabi splitting to achieve the condensation in VSC scales with  $\sqrt{|\omega_0 - \omega_c|}$ , and  $\sqrt{\hbar\omega_0 + k_B T} \propto \sqrt{T}$  as well as  $\sqrt{\hbar\omega_0 + k_B T} \propto \sqrt{\hbar\omega_0}$ . These conditions and scalings could be experimentally tested in the VSC effects, and our theory predicts that the critical  $\Omega_R$  to achieve the VSC condensation should have a  $\sqrt{T}$  dependence with Temperature, as well as have a  $\sqrt{\omega_0}$  dependence that could be checked with isotopic/element-substitution effects.

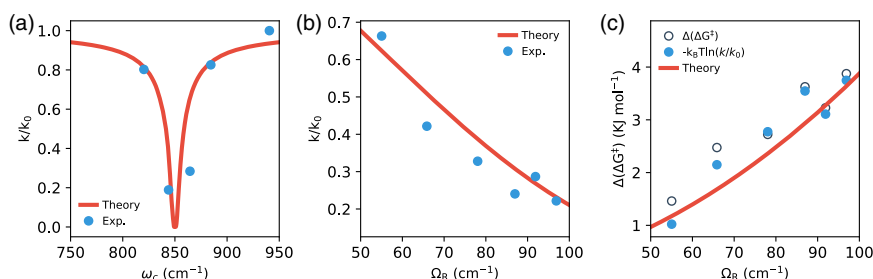
In principle, the Moran-Ebbesen NMR experiment<sup>35</sup> is ideal for this test, by varying temperature and using isotopes/substitutions to change  $\omega_0$ . The potential challenge to see a  $T$ -dependence of critical  $\Omega_R$  change is that it also depends on the vibrational frequency  $\omega_0$ . On the other hand, it will be easier to see the isotope effect when changing C-H vibrations to C-D, which will typically reduce the frequency to  $\omega_0 \approx 2100 \text{ cm}^{-1}$ , or even substitute the C-H vibrations to C-<sup>19</sup>F, which has a much lower frequency of  $\omega_0 \approx 1000\text{--}1400 \text{ cm}^{-1}$  and even larger vibrational transition dipole. Using Eq. (40), this suggests that the C-D system ( $\omega_0 \approx 2100 \text{ cm}^{-1}$ ) will have  $\Omega_R^{\text{exp}} \approx 50 \text{ cm}^{-1}$  as a critical condition, and the C-F system ( $\omega_0 \approx 1400 \text{ cm}^{-1}$ ) will have  $\Omega_R^{\text{exp}} \approx 41.5 \text{ cm}^{-1}$  as a critical condition. For the C-F vibrations within the same Moran-Ebbesen NMR molecule, if we take  $\omega_0 \approx 1400 \text{ cm}^{-1}$ , the current theory predicts that, if one still wants to keep  $\rho = 1.1\%$ , then for C-F frequency  $\omega_0 \approx 1400 \text{ cm}^{-1}$ , and still assuming  $\kappa = 70 \text{ cm}^{-1}$  and  $\gamma = 2\sigma = 18 \text{ cm}^{-1}$ , the critical Rabi splitting will reduce to  $\Omega_R = 57 \text{ cm}^{-1}$  and  $\Omega_R^{\text{exp}} = 34 \text{ cm}^{-1}$ . This could be tested by future experiments.

The other possible experiments are the charge-transfer complexation reaction under VSC<sup>34</sup>, where the equilibrium constant  $K$  should also exhibit the same phase transition behavior if one can lower the  $\omega_0$  coupled to the cavity. Another prediction of Eq. (40) is that, when  $\hbar\omega_0 \ll k_B T$ , satisfying only the standard strong-coupling criterion (Eq. (5)) is insufficient to produce condensation. There are recent experiment<sup>117</sup> that strongly couple the intermolecular vibrations at terahertz frequencies ( $\nu = 0.5 \text{ THz}$ , or  $\omega_0 = 16.7 \text{ cm}^{-1}$ ) with the cavity. The current theory (Eq. (39)) predicts that unless  $\Omega_R \sim \sqrt{k_B T} \approx 14 \text{ cm}^{-1}$ , there will be no VSC-induced condensation and associated effect in these THz-VSC strong coupling systems. Similar analysis for the disordered case can be performed using Eqs. (41)–(43) and give valuable predictions.

### How VSC impacts chemical kinetics?

We denote  $k_0$  as the rate constant outside the cavity, and  $k$  as the rate constant inside the cavity. Most of the experiments report  $k/k_0$  as a function of  $\omega_c - \omega_0$ , which is commonly referred to as the action spectrum, and often found 4–5 times of rate constant reduction<sup>17,19,21</sup> or enhancement<sup>22,23,118,119</sup>. Due to the macroscopic occupation of the  $|\bar{0}\rangle$  state, the system has to react from the  $|\bar{0}\rangle$  state to the possible product states. There is an additional energy penalty  $\Delta_n$  for it in order to get excited from  $|\bar{0}\rangle$ , then react. Note that this mechanism of rate constant suppression does not depend on the details of reaction mechanisms. As such, if we assume this is the main mechanism for the rate constant modification, we have

$$\frac{k}{k_0} = e^{-|\Delta_n|/k_B T} = \exp \left[ -\frac{3\hbar \cdot [\Omega_R^{\text{exp}}]^2}{4k_B T |\omega_0 - \omega_c|} \cdot \sqrt{e^{-\beta\hbar\omega_0}} \right], \quad (46)$$



**Fig. 2 | Theory and the experimental data for the rate constant modification.** A comparison of theory in Eq. (46) (red curve) with the experimentally reported data (blue dots) reproduced from ref. 18 for the desilylation reaction of 1-phenyl-2-trimethylsilylacetylene<sup>17</sup>. **a** The action spectrum of  $k/k_0$  as a function of  $\omega_c$ . **b**  $k/k_0$  as a function of  $\Omega_R^{\text{exp}}$  at  $|\omega_0 - \omega_c| \approx 3$  cm<sup>-1</sup>. **c** Effective  $\Delta(\Delta G^\ddagger)$  obtained from theory in

Eq. (49), from experimental rate constant data using  $-k_B T \ln(k/k_0)$  with the experimental  $k/k_0$  (blue solid dots) as well as the  $\Delta(\Delta G^\ddagger)$  reported in ref. 18 using a Eyring-type plot for both inside and outside cavity cases (which is a different procedure than taking  $-k_B T \ln(k/k_0)$  with the experimental  $k/k_0$ ).

regardless of the detailed reaction mechanism outside the cavity. Further, Eq. (46) can be approximated through Taylor expansion

$$\frac{k}{k_0} \approx 1 - \frac{3\hbar [\Omega_R^{\text{exp}}]^2}{4k_B T |\omega_0 - \omega_c|} \cdot \sqrt{e^{-\beta\hbar\omega_0}}. \quad (47)$$

We believe that this is the first time that Eqs. (46) and (47) are presented in the literature. The above expression suggests that the rate constant suppression scales as  $k/k_0 \propto [\Omega_R^{\text{exp}}]^2$ , which was empirically observed in the Ebbesen VSC experiments (Fig. 3A in ref. 17 or Fig. 3D in ref. 18). We originally thought that this quadratic scaling ought to be related to Fermi's Golden Rule<sup>56–58,62</sup>, which is also quadratic in coupling strength. However, those FGR faces challenges in explaining the collective effect and requires per-vibrational light-matter coupling to be as large as  $\Omega_R^{\text{exp}}$ . The current theory, on the other hand, explains such quadratic scaling from a different perspective. It is because the coherent coupling among vibrations (hardcore bosons) leads to an energy gap per DOF, which scales as  $[\Omega_R^{\text{exp}}]^2$ . Further, Eq. (47) also suggests that  $k/k_0 \propto |\omega_0 - \omega_c|^{-1}$ , with the width of the peak as  $3\hbar[\Omega_R^{\text{exp}}]^2 \sqrt{e^{-\beta\hbar\omega_0}}/4k_B T$ . This explains why the rate constant modification is sensitive to the resonance condition  $\omega_c \approx \omega_0$ , which is completely different than what we thought before (as photonic and vibrational energy transfer that matches lineshape relation<sup>58</sup>).

In experimental reports<sup>17–19</sup>, people often assume that the rate constant still follows the Eyring-type equation, such that<sup>18</sup>

$$\Delta(\Delta G^\ddagger) \equiv \Delta G^\ddagger - \Delta G_0^\ddagger = -k_B T \ln(k/k_0). \quad (48)$$

where  $\Delta G^\ddagger$  is the free energy barrier of the reaction inside the cavity, and  $\Delta G_0^\ddagger$  is for outside the cavity (and please do not confuse the  $\Delta$  here with our gap expressions). Note that this is not an actual change in the free energy barrier, but rather an effective measure of the purely kinetic effect. In fact, based on Eq. (46),  $\Delta(\Delta G^\ddagger) = |\Delta_n|$ , and this effective free energy change measured from the rate constant change directly corresponds to the gap for exciting Bogolon. Our current theory suggests that

$$\Delta(\Delta G^\ddagger) \approx -k_B T \ln \left( 1 - \frac{3\hbar \cdot [\Omega_R^{\text{exp}}]^2}{4k_B T |\omega_0 - \omega_c|} \cdot \sqrt{e^{-\beta\hbar\omega_0}} \right). \quad (49)$$

One can see a non-linear relation of  $\Delta(\Delta G^\ddagger)$  with  $\Omega_R^{\text{exp}}$ , which has been observed experimentally<sup>18,20</sup>. If one hypothesizes that an unknown mechanism forces the upper or lower vibrational polariton states to be a gateway of VSC polaritonic chemical reactions<sup>64,67</sup>, then the

activation free energy change should change linearly<sup>67</sup> with  $\Omega_R$ . Furthermore, in ref. 20, it was pointed out that a very small Rabi splitting observed in optical spectra can lead to much larger changes in activation free energy, such that  $\Delta(\Delta G^\ddagger) > \Omega_R$ , which seems to be a general trend in most VSC experiments<sup>17–19</sup> and requires a theoretical explanation. Our current theory indicates that the nonlinear increase of effective  $\Delta(\Delta G^\ddagger)$  when increasing  $\Omega_R^{\text{exp}}$ , and this is due to the gap  $\Delta_n$  the system needs to overcome in order to excite the Bogolon, expressed as Eq. (49).

Figure 2 presents a comparison of theory (Eq. (46), red curve) with the experimentally reported data (blue dots) reproduced from ref. 18 for the desilylation reaction of 1-phenyl-2-trimethylsilylacetylene<sup>17</sup>. Figure 2a presents the action spectrum of  $k/k_0$ , as a function of changing  $\omega_c$ . Here, we use a model parameter of  $\omega_0 \approx 850$  cm<sup>-1</sup>, as opposed to the original work, where there is a double peak for the vibrational transmission spectra<sup>17,120</sup>. Figure 2b presents the  $k/k_0$  as a function of  $\Omega_R^{\text{exp}}$ , using the theory in Fig. 2b and assuming a  $|\omega_0 - \omega_c| \approx 3$  cm<sup>-1</sup> detuning. The deviation of the experimental data from the theoretical quadratic curve is likely due to the difficulty in experimentally controlling detuning  $|\omega_0 - \omega_c|$  when changing the concentration of the reactant (thus changing  $\Omega_R^{\text{exp}}$ ), and each experimental data point corresponds to a slightly different  $|\omega_0 - \omega_c|$ . Figure 2c presents the effective  $\Delta(\Delta G^\ddagger)$  obtained from theory using Eq. (48) (red curve), the experimental data converted from  $-k_B T \ln(k/k_0)$  by using experimental value of  $k/k_0$  (blue open circles), and the experimentally reported value of  $\Delta(\Delta G^\ddagger)$  by using Eyring-type equation and analysis (blue dots). The theory provides a semi-quantitative agreement with the experimental data<sup>18</sup>.

When frequency disorders are explicitly considered, Eq. (46) should be modified as

$$\frac{k}{k_0} = \frac{1}{N} \sum_n e^{-|\Delta_n|/k_B T} \approx \int d\omega \mathcal{A}_\nu(\omega - \omega_0) e^{-\Delta(\omega)/k_B T}, \quad (50)$$

where  $\Delta(\omega)$  is approximated using Eq. (68). Since a closed-form expression for the above integral was not available, we evaluated it numerically by using the trapezoidal rule. In addition, we used numerical simulations to directly evaluate  $e^{-|\Delta_n|/k_B T}$ . The results are presented in Supplementary Fig. 1. Alternatively, when assuming Eq. (46) that condensate forms at  $\omega_c \approx \omega$ , and the vibrational frequency  $\omega$  follows a lineshape  $\mathcal{A}_\nu(\omega - \omega_0)$  that centered around  $\omega_0$ , then the rate constant modification should be expressed by the following convolution<sup>56,58</sup>

$$\frac{k}{k_0} = \int d\omega \mathcal{A}_\nu(\omega - \omega_0) \cdot \exp \left[ -\frac{3\hbar [\Omega_R^{\text{exp}}]^2}{4k_B T |\omega - \omega_c|} \cdot \sqrt{e^{-\beta\hbar\omega}} \right], \quad (51)$$

**Table 1 | Experimental results and theoretical predictions for the Simpkins VSC experiments<sup>21</sup>, for three vibrations**

| Vibration | $\omega_0$ | $\hbar\Omega_R^{\text{exp}}$ | $\sigma$ | $\kappa$ | $\rho$ | $\hbar\Omega_{\text{crt}}^{\text{exp}}$ | $\hbar\Omega_{\text{crt}}$ |
|-----------|------------|------------------------------|----------|----------|--------|-----------------------------------------|----------------------------|
| OH        | 2900       | 188                          | 78.5     | 154      | 4.4%   | 77.7                                    | 157.6                      |
| NCO       | 2260       | 112                          | 20.5     | 38       | 7.4%   | 41.6                                    | 73.7                       |
| CO        | 1730       | 38                           | 9.5      | 17       | 2.3%   | 24.6                                    | 43.2                       |

All of the energies/frequencies are reported in the unit of  $\text{cm}^{-1}$ . Here,  $\omega_0$  is the vibrational frequency,  $\hbar\Omega_R^{\text{exp}}$  is the experimentally measured Rabi splitting,  $\sigma$  and  $\kappa$  are the molecular and the cavity line width, respectively.  $\rho$  corresponds to the fraction of vibrations actively participating in the condensate formation predicted by Eq. (43).  $\hbar\Omega_{\text{crt}}^{\text{exp}}$  and  $\hbar\Omega_{\text{crt}}$  correspond to the predicted experimental and homogenous (no orientational disorder) Rabi splitting (in  $\text{cm}^{-1}$ ) if the system reaches  $\rho = 1\%$  for the condensate. For all  $\rho$  calculations, we use the detuning  $\delta_0 = 3 \text{ cm}^{-1}$ .

which removes the singularity at  $\omega \approx \omega_c$ , and avoid the artifacts of  $k/k_0 \rightarrow 0$ . Both Eqs. (50) and (51) suggest that the width of the action spectrum could be impacted by the lineshape<sup>58</sup>  $A_\nu(\omega - \omega_0)$ , as many experiments suggest that rate constant modifications closely follow the lineshape<sup>17,21</sup>.

The current theory also indicates that there should be a critical  $\Omega_R$  (such as Eq. (40)), upon passing it, the system starts to exhibit condensation into  $|\bar{0}\rangle$  and rate constant modifications. Note that the precondition to use Eq. (46) is to achieve the condensate. As such, in principle,  $k/k_0$  in Eq. (46) should be modified as

$$\frac{k}{k_0} = \Theta(\Delta\mathcal{F}) \cdot \exp\left[-\frac{3\hbar[\Omega_R^{\text{exp}}]^2}{4k_B T|\omega_0 - \omega_c|} \cdot \sqrt{e^{-\beta\hbar\omega_0}}\right] \quad (52)$$

where  $\Theta$  is the Heaviside step function, characterizing the condition to achieve the condensate, and  $\Delta\mathcal{F} = \frac{3}{4}\hbar[\Omega_R^{\text{exp}}]^2 - |\omega_0 - \omega_c| \cdot (\hbar\omega_0 + k_B T)$  characterize the free energy difference. For  $\Delta\mathcal{F} < 0$ , there should not be any modifications on the rate constant, and thus  $k/k_0 = 1$ . This threshold, phase-transition type behavior has been observed in the charge transfer complexation reaction for equilibrium constant modification (see Eq. (54)), which could also be interpreted by modifying the forward rate constant. However, it has not been explicitly mentioned in the published work of VSC rate constant modifications<sup>17,18,21</sup>. Nonetheless, the reported rate constant modification always starts from a certain value of  $\Omega_R^{\text{exp}} > 55 \text{ cm}^{-1}$ , e.g., in ref. 18, which agrees with what we estimated from the current theory. Further, we examine the experimental data reported in ref. 21 by Simpkins. In that work, the cavity is coupled to three different vibrational modes, all of which lead to rate constant suppressions. The three vibrational frequencies,  $\omega_0$ , and their corresponding vibrational line width  $\sigma$ , the cavity line width  $\kappa$ , and the experimentally measured Rabi splitting  $\Omega_R^{\text{exp}}$  are listed in Table 1. Based on Eq. (43), we estimate that the fraction of vibrational modes participating in the condensate state is  $\rho \sim 2\text{--}7\%$ . If one uses  $\rho \approx 1\%$  as criteria for VSC modification (from the Ebbesen NMR experiments), then one can estimate the critical value of the Rabi splitting  $\hbar\Omega_{\text{crt}} = 2\sqrt{N}g_c$ , or converting it to the critical Rabi splitting from the linear spectra based on Eq. (44), which we denote as  $\hbar\Omega_{\text{crt}}^{\text{exp}}$  in Table 1. This means that, for the NCO vibration coupling, for example, if one reduces the Rabi splitting to  $\hbar\Omega_{\text{crt}}^{\text{exp}} \approx 41.6 \text{ cm}^{-1}$  (see row two in Table 1), one should stop seeing any rate constant suppression. Below this critical Rabi splitting, coupling NCO to the cavity will no longer result in any suppression of the rate constant. This is where the phase transition type behavior should occur for the NCO vibrations.

Note that Eq. (46) always leads to the rate constant suppression. Rate constant enhancement<sup>22,23,119</sup> would likely depend on the details of the reaction mechanism, such that the modification of  $\{|u_n^2|, |\nu_n^2|\}$  in the frequency window  $\omega \in [\omega_c^-, \omega_c^+]$  (see Fig. 1b) dictates the overall apparent rate constant. We provide a qualitative model in the

Supplementary Note VI, but quantitative analysis is beyond the scope of the current work and will be our focus in the near future.

### Why cooperative VSC even works?

We should note that our above discussions on rate constant modifications are formulated in the context of a cavity directly coupled to vibrations of the reactant<sup>17,19,21</sup>, either the reaction coordinate-related normal modes<sup>17</sup> or the non-reactive normal modes (spectator modes)<sup>45,55</sup>. There are other types of the cooperative VSC experiments<sup>22,23,118,119</sup> that couple the cavity mode to the solvent vibrations (with frequency  $\omega_0$ ), and the solvent frequency closely matches a reactive vibrational frequency  $\omega_R$  in reactant molecules. Due to the low concentrations of the reactant, the strong coupling and Rabi splitting are mainly caused by cavity coupling to solvent vibrations<sup>22</sup>.

In those cooperative coupling VSC experiments<sup>22,23,118,119</sup>, it was found that the cooperative resonant condition  $\omega_c \approx \omega_0 \approx \omega_R$  is required to achieve rate constant modifications. The isotope control experiments<sup>22,23</sup> could set  $\omega_c \approx \omega_0 \neq \omega_R$ , and there will be no obvious VSC rate constant modifications, even though a strong coupling condition between cavity and solvent is still satisfied<sup>22,23</sup>. These cooperative couplings through solvent DOF have shown either rate constant suppression<sup>118</sup> or enhancement<sup>22,23,119</sup>. In the past, we have developed a theoretical model<sup>61</sup> and rate constant theory<sup>62</sup> based on FGR to explain this phenomenon (through a mechanism of cavity-solvent strong coupling that removes the thermal vibrational excitations away from the reactant), but that theory<sup>62</sup> is still in the effective single excitation subspace mechanistic picture (Eq. (3)). We should also note that the reaction reported in ref. 22 was under debate, as ref. 113 claims that there is no obvious VSC effect when trying to reproduce it, but later experimental works<sup>24,121</sup> suggest that there are cooperative VSC modifications of the rate constant in different types of cavities.

With the current theory, we hypothesize that the new macroscopic state  $|\bar{0}\rangle$  now contains both solvent vibrations and the reactant vibrations. For example, we consider a total of  $N$  solvent DOF, and a total of  $\mathcal{M}$  reactant molecules (and  $\mathcal{M} \ll N$  for these cooperative coupling experiments<sup>22-24,114,118,119,121</sup>). Through the same procedure,

$$|\bar{0}\rangle = \prod_{n=1}^N (u_n + \nu_n \hat{\sigma}_n^\dagger) \otimes \prod_{m=1}^{\mathcal{M}} (u_m + \nu_m \hat{\sigma}_m^\dagger) |0\rangle, \quad (53)$$

the macroscopic quantum state is now a many-body state that involves both solvent and reactant molecules, a co-condensate of their vibrational DOFs. The rate constant modification requires that the detuning is small, and thus the resonance condition  $\omega_c \approx \omega_0 \approx \omega_R$ . The current theory provides a possible explanation for this cooperative coupling effect as the co-condensation among the solvent and solute vibrational DOFs. Upon isotope substitution in the solvent, which makes  $\omega_0 \neq \omega_R$ , even though the strong coupling condition is still achieved between cavity and solvent<sup>22,23</sup> at  $\omega_c \approx \omega_0$ , the vibrations in the reactant molecules no longer participate in forming the macroscopic state  $|\bar{0}\rangle$  (described by Eq. (18), as opposed to Eq. (53)), and thus there is no VSC-induced rate constant modifications. The current theory explains why the cooperative strong coupling is very sensitive to the frequency matching for the cavity, solvent, and reactant. Further numerical studies and detailed model investigations are still required.

### How VSC impacts equilibrium constant?

In the VSC NMR experiment<sup>35</sup>, Moran and Ebbesen discovered that VSC can modify the equilibrium constant  $\mathcal{K}$  of the conformation change of a molecule between the unfolded configuration and a folded configuration (see Fig. 4d in ref. 35). Further, the equilibrium constant modification has also been shown in a charge transfer complexation reaction<sup>34</sup>, which also exhibits a phase transition type of behavior (see

Fig. 2a in ref. 34). These modifications on the equilibrium constant  $\mathcal{K}$  were previously thought to be theoretically impossible when considering classical statistical mechanics<sup>44,67,78,122</sup>. Explaining the VSC-induced significant change of  $\mathcal{K}$ , which exhibits a phase transition type of behavior<sup>34,35</sup> upon a critical value of  $\Omega_R$ , is another challenging task in theoretical chemistry<sup>67,78,122</sup>.

Our current theory provides a possible explanation for the change of  $\mathcal{K}$ . Let us consider a simple model for two species (diabatic electronic states)  $|\mathcal{R}_n\rangle$  for the reactant, which couples to the vibrational DOF ( $\hat{\sigma}_n^\dagger, \hat{\sigma}_n$ ), and  $|\mathcal{P}_n\rangle$  for the product.  $|\mathcal{R}_n\rangle$  and  $|\mathcal{P}_n\rangle$  can couple to each other through electronic coupling  $\langle \mathcal{R}_n | \hat{V} | \mathcal{P}_n \rangle = \mathcal{V}$ , giving two adiabatic states, with the lower energy one as the ground state that exhibit two minimum. The equilibrium constant (assuming detailed balance) can be written as

$$\mathcal{K} = \frac{[\mathcal{P}]}{[\mathcal{R}]} = \frac{k_1}{k_2}, \quad (54)$$

where  $k_1$  describes the rate constant for the forward process and  $k_2$  for the backward process. If the cavity only has VSC coupling to the vibrational DOFs in  $|\mathcal{R}_n\rangle$ , then due to the macroscopic occupation in  $|\tilde{0}\rangle$  for the vibrations on the reactant side,  $k_1$  could be modified. If the cavity couples to both vibrational modes associated with the  $|\mathcal{R}_n\rangle$  and  $|\mathcal{P}_n\rangle$  states, it is also possible that  $k_1$  and  $k_2$  get modified in different way (or in same way but in different magnitude), causing  $\mathcal{K}$  changes. After all,  $\mathcal{K}$  is nothing but the ratio of two rate constants, and VSC can change rate constants.

In this work, we used a many-body physics approach, akin to the BCS theory, to analyze the many-body macroscopic ground state (Eq. (62)) in VSC Cavity QED. We derived the Gap equation (Eqs. (25), (27), and (68)) that characterizes energy stabilization of the condensate state compared to the normal thermodynamic state (Eq. (40)). We found that upon collective light-matter coupling, vibrations (described by hard-core bosons) could condense into one macroscopic state  $|\tilde{0}\rangle$  (see Eq. (62)), as long as one can achieve a critical value of  $\Omega_R$  (see Eq. (40)). Our theory provides potential explanations for many recently observed VSC mysteries. The Moran-Ebbesen NMR experiment<sup>35</sup> and charge-transfer complex experiment<sup>34</sup> could provide direct evidence to see such a normal phase to the condensation phase. Our current theory provides a good agreement on the critical value of  $\Omega_R$  to achieve the observed new phase, which agrees with the experiment<sup>35</sup>.

The current theory has several predictions that could be experimentally verified. One of the most important predictions is the condition to achieve the condensation phase, which requires a critical  $\Omega_R$  (Eq. (40)). This phase transition type of behavior has already been observed in the NMR experiment<sup>35</sup>, the charge-transfer complexation reaction experiments<sup>34</sup>, and should also be observed in the VSC-modification of rate constants<sup>18,21</sup>. One possibility is to use the recently reported reactions in ref. 21, and gradually reduce the  $\Omega_R$ , one should observe a sudden jump of the  $k/k_0$  value back to 1, exhibiting a similar phase transition type behavior. Our theory provides quantitative predictions for the critical  $\Omega_R$  required to achieve the condensate and thus VSC-induced modifications. More generally, the critical condition is  $\Omega_R \propto \sqrt{\hbar\omega_0 + k_B T}$ , which could be checked by multiple known VSC experiments<sup>17–19</sup>. Further, the current theory (Eq. (40)) also predicts that the condensation condition is very sensitive to the cavity-vibration frequency detuning  $|\omega_c - \omega_0|$ , which likely explains why some VSC experiments<sup>22,24,113,114,121</sup> have issues on the reproducibility<sup>113</sup> due to the non-perfect matching between  $\omega_c$  and  $\omega_0$  (either through the non-zero detuning, or caused by the mirror fluctuations of the FP cavity<sup>97</sup>).

Our theory also provides possible explanations for modifications in the VSC rate constant, as the system needs additional thermal energy to excite Bogolons. This leads to our rate constant theory in Eq. (46) or Eq. (47), which predicts the quadratic dependence

$k/k_0 \propto [\Omega_R^{\text{exp}}]^2$ . As a corollary, the effective  $\Delta(\Delta G^\ddagger) = -k_B T \ln(k/k_0)$  scales non-linearly with  $\Omega_R^{\text{exp}}$ . The rate constant modification also scales as Eq. (47) which suggests that  $k/k_0 \propto |\omega_0 - \omega_c|^{-1}$ , with the width of the peak as  $3\hbar[\Omega_R^{\text{exp}}]^2 \sqrt{e^{-\beta\hbar\omega_0}}/4k_B T$ . Comparing with the experimental data reported in ref. 18, our theory seems to provide a reasonable semi-quantitative agreement with all trends, with nearly no free parameter ( $|\omega_0 - \omega_c|$  is viewed as a free parameter, which is difficult to read out and control from the experiments). This also means the future experimental platform could focus on cavity structures that provide stable light-matter detuning  $|\omega_0 - \omega_c|$ , which is the key for  $k/k_0$  reproducibility and data consistency, as suggested by the current theory (Eq. (47)). The recent experimental work on using the non-local meta-surfaces plasmonic structure<sup>24</sup>, or fixed-width Fabry–Pérot cavity<sup>123</sup> could be a good starting point.

Similarly, one can qualitatively understand the cooperative VSC rate constant effects and the change of equilibrium constant from the condensation picture, although detailed reaction models are required to construct a quantitative argument. Assuming that the VSC-induced effects originate from a single macroscopic state could also pave the way for understanding other mysterious effects. For example, why could vibrational symmetry also have a significant impact on the VSC effect<sup>39</sup>? This could be explained by the fact that the macroscopic state that dominates the VSC system's behavior should be sensitive to the vibrational symmetry of each single-particle state, which are the building blocks of this macroscopic state. Why VSC can significantly enhance the conductivities<sup>40</sup> could also be potentially explained by the macroscopic occupation of the condensation that impacts how electrons are transported through the phonon environments. The phase transition type of behavior in VSC-impacted polymerizations could also be explained by the macroscopic occupation of the  $|\tilde{0}\rangle$ .

Our theoretical analysis leads to the conclusion that the mystery of VSC modifications observed in experiments could arise from a many-body quantum mechanical effect: the condensation into a single macroscopic coherent state, or the macroscopic occupation of the state  $|\tilde{0}\rangle$ . This state is non-local and macroscopic. This is why the previous theoretical effects<sup>44,66</sup>, including our own<sup>56–58</sup>, cannot explain the collective effect, because this macroscopic state cannot be obtained perturbatively from a few-body solution<sup>86</sup>. A clear mechanistic understanding of VSC could elevate our knowledge of chemistry to a new era that goes beyond the traditional intuitive paradigm, which often involves only the local barrier crossing at the individual molecular scale. Similarly, this work brings the many-body physics picture into the cavity QED and quantum optics community, which traditionally focuses on few-body excitations (Eq. (3), due to the use of the exciton-polariton system).

We hope that we have provided the first promising candidate of a universal theory to explain nearly all VSC Cavity QED effects and offer valuable insights. If eventually verified by experiments (e.g., our theoretical predictions on critical  $\Omega_R \propto \sqrt{\omega_0}$  through isotope/substitution experiments, or the rate constant scalings with different factors), our theory suggests that VSC Cavity QED is an experimental platform that actually generates yet another type of macroscopic condensation and macroscopic coherent state, in addition to the well-known Bose-Einstein (BEC) condensates, superfluidity, and the Cooper-Pairs condensation in the BCS-type superconductivity<sup>86,87</sup>. Unlike those other condensates and macroscopic states, which often require very low temperatures, VSC condensations occur at room temperature.

## Methods

The expectation value of  $\hat{\mathcal{H}}$  under  $|\tilde{0}\rangle$  is expressed as

$$\bar{\mathcal{E}} \equiv \langle \tilde{0} | \hat{\mathcal{H}} | \tilde{0} \rangle = \sum_n \hbar \tilde{\omega}_n |v_n|^2 - \sum_{n \neq m} G_{nm} \cdot (u_n v_m^\dagger u_m^\dagger v_n). \quad (55)$$

The expectation value for the phonon excitations is

$$\bar{n} \equiv \langle \tilde{0} | \sum_n \hat{\sigma}_n^\dagger \hat{\sigma}_n | \tilde{0} \rangle = \sum_n |\nu_n|^2 = \sum_n \frac{e^{-\beta \hbar \omega_n}}{1 + e^{-\beta \hbar \omega_n}} \quad (56)$$

$$\approx N \int d\omega \mathcal{A}_\nu(\omega - \omega_0) e^{-\beta \hbar \omega} \approx N \cdot e^{-\beta \hbar \omega_0},$$

where  $\bar{n}$  is the excitation expectation value (number of phonon excitations) at  $T$  and at a given  $N$ . When counting the total system with  $N$  vibrational DOF, we expect that overall they still satisfy the Boltzmann statistics

$$\sum_n |\nu_n|^2 = \sum_n \frac{e^{-\beta \hbar \omega_n}}{1 + e^{-\beta \hbar \omega_n}}. \quad (57)$$

But for the individual site  $n$  in the new BCS-state  $|\tilde{0}\rangle$ , very likely

$$|\nu_n|^2 \neq \frac{e^{-\beta \hbar \omega_n}}{1 + e^{-\beta \hbar \omega_n}}, \quad (58)$$

especially when  $\omega_n \rightarrow \omega_c$  due to the large effective coupling  $G_{nm}$  (c.f. Eq. (16)). We shall see later that this is indeed the case for systems with vibrational frequency disorders (such that  $\omega_n \neq \omega_0$ , see Fig. 1b).

As Schrieffer noticed<sup>87</sup>, the trial ansatz described in Eq. (18) does not have a fixed excitation number  $\bar{n}$ . Further, one needs to satisfy the normalization  $|u_n|^2 + |\nu_n|^2 = 1$  for all  $n$ . As such, one needs to perform the conditional minimization using the Lagrange multiplier method. With  $\bar{\mathcal{H}}$  and  $\bar{n}$  expressions, and following the standard<sup>89</sup> Schrieffer variational procedure<sup>86,87</sup> and performing the conditional minimization using the Lagrange multiplier method<sup>89</sup>, we variationally minimize the following function

$$\bar{\mathcal{H}} \equiv \bar{\mathcal{E}} - \mu \bar{n} + \sum_n E_n (|u_n|^2 + |\nu_n|^2 - 1), \quad (59)$$

where the  $\mu$  is the chemical potential of the vibrational excitations, and  $E_n$  is effectively the energy level for particle  $n$ , both are Lagrange multipliers. Setting the variational condition  $\delta \bar{\mathcal{H}} = 0$  requires that

$$\frac{\partial \bar{\mathcal{H}}}{\partial u_n} = 0, \quad \frac{\partial \bar{\mathcal{H}}}{\partial \nu_n} = 0, \quad (60)$$

for all possible  $n \in [1, N]$ . This leads to the effective eigenvalue equation in Eq. (20), with Eigenvalue expressed in Eq. (22) and eigenvector in Eq. (23). The mixing angle in Eq. (23) is

$$\cos 2\theta_n = (\hbar \tilde{\omega}_n - \mu)/E_n, \quad \sin 2\theta_n = \Delta_n/E_n. \quad (61)$$

The macroscopic ground state in Eq. (18) can also be expressed as

$$|\tilde{0}\rangle = \prod_{n=1}^N (\cos \theta_n + \sin \theta_n \hat{\sigma}_n^\dagger) |0\rangle. \quad (62)$$

Equivalently, the coefficients in Eq. (23) can be expressed as

$$u_n^2 = \frac{1}{2} \left[ 1 + \frac{\hbar \tilde{\omega}_n - \mu}{E_n} \right] = \frac{1}{2} \left[ 1 + \frac{\hbar \tilde{\omega}_n - \mu}{\sqrt{(\hbar \tilde{\omega}_n - \mu)^2 + |\Delta_n|^2}} \right] \quad (63)$$

$$\nu_n^2 = \frac{1}{2} \left[ 1 - \frac{\hbar \tilde{\omega}_n - \mu}{E_n} \right] = \frac{1}{2} \left[ 1 - \frac{\hbar \tilde{\omega}_n - \mu}{\sqrt{(\hbar \tilde{\omega}_n - \mu)^2 + |\Delta_n|^2}} \right]. \quad (64)$$

Similar to the BCS-ground state, this  $|\tilde{0}\rangle$  should also be a broken symmetry state that breaks the local  $U(1)$  symmetry, caused by the

Higgs-type mechanism (when the gauge field consumes the Goldstone boson)<sup>89</sup>.

We note that the same eigenequation (Eq. (20)) and eigenvalue (Eq. (22)) can also be obtained from the Bogoliubov transform<sup>84,89</sup>,

$$\begin{pmatrix} \hat{b}_n \\ \hat{b}_n^\dagger \end{pmatrix} = \begin{pmatrix} u_n & \nu_n \\ \nu_n^* & u_n^* \end{pmatrix} \begin{pmatrix} \hat{\sigma}_n \\ \hat{\sigma}_n^\dagger \end{pmatrix}. \quad (65)$$

The above transform preserves the commutation relation of the hard-core bosons (Eqs. (11) and (12)), hence it is a canonical Bogoliubov transform, with details provided in the Supplementary Note IIC.

These  $(\hat{b}_n^\dagger, \hat{b}_n)$  are the creation and annihilation operators of Bogolons, Bogoliubov quasiparticles. Note that Bogolons are collective excitations of the system, because  $(u_n, \nu_n)$  depends on  $\Delta_n$  (c.f. Eq. (21)), which depends on all other particle states  $(u_m, \nu_m)$ . Under the Bogolon picture,  $\hat{\mathcal{H}}$  is diagonalized as

$$\hat{\mathcal{H}} = \sum_n \begin{pmatrix} \hat{b}_n^\dagger & \hat{b}_n \end{pmatrix} \begin{pmatrix} E_n & 0 \\ 0 & -E_n \end{pmatrix} \begin{pmatrix} \hat{b}_n \\ \hat{b}_n^\dagger \end{pmatrix} \quad (66)$$

with the diagonal energy  $\pm E_n$  (c.f. Eq. (22), i.e., the Bogolon dispersion). The Bogoliubov canonical transform yields an equivalent result to the Schrieffer variational procedure in Eq. (60), which is a well-known result in the BCS literature.

To numerically solve the coupled equations Eqs. (25) and (26), one could focus on solving the coupled eigenequations in Eq. (20). Note that for diagonalizing the eigenequation (Eq. (20)) associated with  $n$ , it requires the knowledge of other  $\{u_m, \nu_m\}$  to compute  $\Delta_n$  (see Eq. (25)), and Eq. (20) thus needs a SCF solution, very similar to the case of Hartree-Fock theory in electronic structure. One could, in principle, provide the initial guess  $\{u_n, \nu_n\}$ , which could simply be the Boltzmann probability, then compute all  $\Delta_n$  using Eq. (21), then solve Eq. (20) again, iteratively (with the constrains in Eq. (59)), until a certain threshold (say the changes in  $\{|u_n|^2, |\nu_n|^2\}$  between two adjacent iterations is smaller than a threshold) is reached. Many useful techniques in the field of electronic structure that employ similar SCF procedures can be borrowed to solve these equations. Here, we perform minimization by iterating a fixed-point map<sup>124</sup> on the global  $g_m u_m \nu_m$  parameters, enforcing the expectation value for the phonon excitation number to be constrained at the Boltzmann distribution value (Eq. (56)) at each step via monotone bisection for  $\mu$  with linear mixing and small-detuning regularization for robustness, see Supplementary Note V.

## Gap equation expressions

Using  $\mu$  in Eq. (29) as an approximate expression, plugging it into Eq. (27), and assuming that the majority of the frequency-dependent contribution comes from the line shape and detuning functions inside the integral, one has

$$\Delta(\omega) = N \sqrt{1 - \alpha^2} \frac{\hbar}{4} g_c^2 \int d\omega' \mathcal{A}_\nu(\omega') \left( \frac{1}{\omega - \omega_c} + \frac{1}{\omega' - \omega_c} \right) \quad (67)$$

$$\approx N \sqrt{e^{-\beta \hbar \omega_0}} \frac{\hbar}{2} g_c^2 \int d\omega' \mathcal{A}_\nu(\omega') \left( \frac{1}{\omega - \omega_c} + \frac{1}{\omega' - \omega_c} \right)$$

where we have used the fact that  $N \sqrt{1 - \alpha^2} \approx N \sqrt{4\bar{n}/N} \approx 2N \sqrt{e^{-\beta \hbar \omega_0}}$ . Assuming  $\mathcal{A}_\nu$  has a Gaussian line shape (Eq. (8)), one can get analytic and approximate expressions for the gap (through the Dawson function type integral), resulting in the following expression with error function

$$\Delta(\omega) \approx \frac{1}{2} \hbar N g_c^2 \sqrt{e^{-\beta \hbar \omega_0}} \left[ \frac{1}{\delta_\omega} + \frac{\sqrt{\pi}}{\sqrt{2\sigma}} e^{-\delta_\omega^2/2\sigma^2} \operatorname{erfi} \left( \frac{\delta_\omega}{\sqrt{2\sigma}} \right) \right], \quad (68)$$

where  $\text{erfi}(x) = -i \text{erf}(ix)$  is the imaginary error function, and we have defined  $\delta_\omega = \omega - \omega_c$  and  $\delta_0 = \omega_0 - \omega_c$ . In the limit of small frequency disorders, i.e.,  $|\delta_0| \gg \sqrt{2}\sigma$ , the above expression in Eq. (68) can be Taylor expanded as

$$\Delta(\omega) \approx N \sqrt{e^{-\beta \hbar \omega_0}} \frac{\hbar}{2} g_c^2 \left( \frac{1}{\delta_\omega} + \frac{1}{\delta_0} + \frac{\sigma^2}{\sqrt{2}\delta_0^3} \right) + \mathcal{O}\left(\frac{3\sigma^4}{\delta_0^5}\right). \quad (69)$$

In the regime  $|\delta_0| \ll \sqrt{2}\sigma$ , the gap function can be expanded as

$$\Delta(\omega) \approx \hbar N g_c^2 \sqrt{e^{-\beta \hbar \omega_0}} \left( \frac{1}{\delta_\omega} + \frac{\delta_0}{\sigma^2} \right) + \mathcal{O}\left(\frac{\delta_0^3}{3\sigma^4}\right). \quad (70)$$

The above expression will be useful when  $\omega$  is very close to  $\omega_c$ , which we believe will be a macroscopic condensation and VSC effect. Detailed derivations of Eq. (68) is provided in the Supplementary Note IV, in Eqs. S52–S77.

When considering  $\omega = \omega_0$  case of Eq. (69),  $\Delta(\omega_0)$  is expressed as

$$|\Delta(\omega_0)| \approx \hbar N g_c^2 \sqrt{e^{-\beta \hbar \omega_0}} \left( \frac{1}{|\delta_0|} + \frac{1}{\sqrt{2}} \frac{\sigma^2}{|\delta_0|^3} \right), \quad (71)$$

and the no frequency disorder limit of ( $\omega_n = \omega_0$ ) result in Eq. (32) as a special case of Eq. (71) when  $\sigma \rightarrow 0$ .

One can further obtain more accurate expressions for the gap equation (without assuming Eq. (29)) as follows

$$\mu = \hbar \omega_0 - \frac{\Omega_R^2}{8} \left( K + \frac{1}{\delta_0} \right) \left( 1 - \frac{2\bar{n}}{N} \right) \quad (72)$$

$$\Delta(\omega) = \frac{\Omega_R^2}{4} \left( K + \frac{1}{\omega - \omega_c} \right) \sqrt{\frac{\bar{n}}{N} \left( 1 - \frac{\bar{n}}{N} \right)} \quad (73)$$

$$K = \frac{1}{\sqrt{2\pi}\sigma} \text{PV} \left( \int_{-\infty}^{\infty} \frac{e^{-s^2}}{s + \delta_0/\sqrt{2}\sigma^2} ds \right) \equiv \frac{\sqrt{2}}{\sigma} \mathcal{D}(\delta_0/\sqrt{2}\sigma^2), \quad (74)$$

where  $\sigma$  is the width of the line shape, PV represents the principal value of the integral, and  $\mathcal{D}(\delta_0/\sqrt{2}\sigma^2)$  is the Dawson function. The detailed derivations are provided in Supplementary Note IV.

### Local dissipative bath to the vibrations

Here, we further consider the effects of homogeneous broadening (dynamical disorders) on the vibrations. These effects are commonly modeled by local bath terms coupled to the vibrational modes, with the origin of interactions between those VSC modes and non-reactive spectator vibrational modes in the molecules or from the solvent DOFs<sup>48,54,62</sup>. Here, we consider two separate cases. One is the Holstein–Tavis–Cummings model (HTC) model<sup>43,125,126</sup>, expressed as

$$\hat{H} = \sum_{n=1}^N \hbar \omega_n \hat{\sigma}_n^\dagger \hat{\sigma}_n + \hbar \omega_c \hat{a}^\dagger \hat{a} + \sum_{n=1}^N \hbar g_n [\hat{\sigma}_n^\dagger \hat{a} + \hat{a}^\dagger \hat{\sigma}_n] + \sum_{n=1}^N \sum_{\nu} c_{\nu,n} \hat{\sigma}_n^\dagger \hat{\sigma}_n \otimes (\hat{b}_{\nu,n}^\dagger + \hat{b}_{\nu,n}) + \hbar \omega_{\nu,n} \hat{b}_{\nu,n}^\dagger \hat{b}_{\nu,n} \quad (75)$$

where the local phonon bath DOF  $\{\hat{b}_{\nu,n}^\dagger, \hat{b}_{\nu,n}\}$  couple to the vibrational excited states  $|e_n\rangle$  of the  $n$ th molecule, and  $\omega_{\nu}$  is the frequency of the phonon bath mode. The coupling strength  $c_{\nu}$  is described by the spectral density

$$J_n(\omega) = \sum_{\nu} c_{\nu,n}^2 \delta(\omega - \omega_{\nu,n}), \quad (76)$$

and the reorganization energy is

$$\lambda_n = \int_0^\infty d\omega \frac{J_n(\omega)}{\hbar \omega} = \sum_{\nu} \frac{c_{\nu,n}^2}{\hbar \omega_{\nu,n}}. \quad (77)$$

Performing a polaron transform<sup>127,128</sup> of the above Hamiltonian with respect to the bath coordinates gives

$$\hat{H} = \sum_{n=1}^N (\hbar \omega_n - \lambda_n) \hat{\sigma}_n^\dagger \hat{\sigma}_n + \sum_{n,\nu} \hbar \omega_{\nu,n} \hat{b}_{\nu,n}^\dagger \hat{b}_{\nu,n} + \hbar \omega_c \hat{a}^\dagger \hat{a} + \sum_{n=1}^N \hbar g_n (\hat{\sigma}_n^\dagger \hat{a} \hat{X}_n + \hat{\sigma}_n \hat{a}^\dagger \hat{X}_n) \quad (78)$$

where the bath displacement operator for the  $n$ th vibration mode is expressed as

$$\hat{X}_n = \exp \left[ - \sum_{\nu} \frac{c_{\nu,n}}{\hbar \omega_{\nu,n}} (\hat{b}_{\nu,n}^\dagger - \hat{b}_{\nu,n}) \right] \quad (79)$$

Integrating the bath modes by taking a quantum thermal average of  $\hat{X}_n$ , we obtain

$$\kappa_n = \langle \hat{X}_n \rangle_T = \exp \left[ - \frac{1}{2} \sum_{\nu} \frac{c_{\nu,n}^2}{\hbar^2 \omega_{\nu,n}^2} \coth \left( \frac{\hbar \omega_{\nu,n}}{2k_B T} \right) \right]. \quad (80)$$

Details of the derivations are provided in Supplementary Note IX. Thus, we can rewrite the effective thermal averaged (over bath modes) Hamiltonian as

$$\hat{H}_T = \sum_{n=1}^N (\hbar \omega_n - \lambda_n) \hat{\sigma}_n^\dagger \hat{\sigma}_n + \hbar \omega_c \hat{a}^\dagger \hat{a} + \sum_{n=1}^N \hbar g_n \kappa_n (\hat{\sigma}_n^\dagger \hat{a} + \hat{\sigma}_n \hat{a}^\dagger) \quad (81)$$

As one can see, the thermodynamic effect of the local bath mainly arises from a reduction in the effective light-matter interaction strength, since  $0 < \kappa_n \leq 1$ . We will then use Eq. (81) as the starting point to perform the Schrieffer–Wolff transform and variational calculations to obtain the condensate state, with a reduced light-matter coupling strength  $g_n \kappa_n$ . All the conclusions we obtained remain the same, except now with a substitution  $g_n \rightarrow g_n \kappa_n$ . Note that for the very low frequency phonon  $\omega_{\nu} \ll k_B T$ ,  $\kappa \rightarrow 0$ , and one should treat those modes as static disorder (see Eq. (6)) because the thermal average of the polaron coupling operator does not give the accurate physics. One can use the variational polaron transform<sup>129–131</sup> to naturally determine different frequencies. To estimate  $\kappa_n$ , using typical vibrational parameters in VSC<sup>28</sup>, with  $\lambda = c_{\nu}^2/\omega_{\nu} \approx 10 \text{ cm}^{-1}$ , and a characteristic phonon frequency  $\omega_{\nu} = 200 \text{ cm}^{-1}$ , we estimated  $\kappa \approx 0.95$  at  $T = 300 \text{ K}$ . Additional results of scanning a range of parameters are provided in Supplementary Note IX. All of these results suggest that for the typical  $\lambda \approx 10 \text{ cm}^{-1}$  in VSC, the formation of condensation is not significantly impacted.

The other type of commonly used spectator mode-vibrational mode coupling Hamiltonian<sup>48,56,62</sup> assumes the bi-linear coupling between a hard-core boson and the bath as follows

$$\hat{H} = \sum_{n=1}^N \hbar \omega_n \hat{\sigma}_n^\dagger \hat{\sigma}_n + \hbar \omega_c \hat{a}^\dagger \hat{a} + \sum_{n=1}^N \hbar g_n [\hat{\sigma}_n^\dagger \hat{a} + \hat{a}^\dagger \hat{\sigma}_n] + \sum_{n=1}^N \sum_{\nu} c_{\nu,n} (\hat{\sigma}_n^\dagger + \hat{\sigma}_n) \otimes (\hat{b}_{\nu,n}^\dagger + \hat{b}_{\nu,n}) + \hbar \omega_{\nu,n} \hat{b}_{\nu,n}^\dagger \hat{b}_{\nu,n}. \quad (82)$$

Using the polaron transform (see Supplementary Note IX) and performing a thermal average of the polaron coupling term (keep only rotating wave terms), Eq. (82) becomes

$$\hat{\mathcal{H}}_T = \sum_{n=1}^N \frac{\hbar\omega_n}{2} (1 + \kappa_n^4) \hat{\sigma}_n^\dagger \hat{\sigma}_n + \hbar\omega_c \hat{a}^\dagger \hat{a} + \sum_{n=1}^N \frac{\hbar g_n}{2} (1 + \kappa_n^4) (\hat{\sigma}_n^\dagger \hat{a} + \hat{\sigma}_n \hat{a}^\dagger), \quad (83)$$

where  $\kappa_n^4 = \exp[-2\sum_{\nu} \frac{C_{\nu,n}^2}{\hbar^2 \omega_{\nu,n}^2} \coth(\frac{\hbar\omega_{\nu,n}}{2k_B T})]$  (c.f. Eq. (80)). One can see that the effective light-matter coupling term for the rotating wave terms is rescaled as  $g_n \rightarrow g_n(1 + \kappa_n^4)/2$ , and thus even puts a lower bound on the coupling strength to be not smaller than 1/2 of its original value and not significantly impact the light-matter coupling strength nor the stability of condensate. Details of the derivations are provided in Supplementary Note IX.

We want to emphasize that a finite reduction of  $g_n$  (in either Eq. (81) or Eq. (83)) will not impact the formation of the condensation. As Schrieffer pointed out<sup>86,87</sup>, the many-body interactions lead to the formation of a macroscopic coherent state (giving rise to  $|\Delta_n| \propto N$ , see Eq. (32)), and no matter how weak the  $g_n \kappa_n$  is, as long as  $N$  is large enough and surpasses the threshold

$$\hbar\Omega_R^2 > 4\kappa_n^{-2} \cdot |\omega_0 - \omega_c| \cdot (\hbar\omega_0 + k_B T), \quad (84)$$

when considering the  $\kappa_n$  effect in Eq. (81) (c.f. Eq. (40)), the formation of the condensation will happen, and it is inevitable. On the other hand, the detailed value of  $\lambda_n$  and  $\kappa_n$  will impact the specific condition when the condensate is achieved (the critical concentration or critical  $\Omega_R$ ).

## Data availability

The data generated in this study have been deposited in [https://github.com/Smontillo/BCS\\_VSC.git](https://github.com/Smontillo/BCS_VSC.git).

## Code availability

The source code for minimizing the BCS equations used in this work, and the code for producing all the figures in the main text and the supplementary notes, are available at [https://github.com/Smontillo/BCS\\_VSC.git](https://github.com/Smontillo/BCS_VSC.git).

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## Author contributions

M.E.M. and S.M.V. contributed equally to this work. P.H. designed the research and developed the mechanism. P.H. and M.E.M. conducted theoretical derivations. S.M.V. and M.E.M. performed numerical evaluations of the theoretical expressions. P.H. wrote the initial manuscript, and all authors revised it.

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## Competing interests

The authors declare no competing interests.

## Additional information

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