Theory of vibronic assistance in the nonequilibrium condensation of exciton polaritons in optically-pumped organic single crystal microcavities

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We present a reaction/diffusion model for the formation of a lower polariton condensate in a microcavity containing an organic semiconducting molecular crystalline film. Our model—based upon an anthracene film sandwiched between two reflecting dielectric mirrors—consists of three coupled fields corresponding to a gas of excitons created by an external driving pulse, a reservoir of vibron states formed by the coupling between a ground-state vibrational model and a cavity photon, and a lower polariton condensate. We show that at finite temperature, the presence of the vibron reservoir can augment the exciton population such that a lower critical pumping threshold is required to achieve condensation.

I. INTRODUCTION

Over the past few years, there has been considerable excitement regarding the formation of polariton Bose condensates in quantum dot microcavities. This has spurred a parallel effort to observe similar effects in microcavity systems involving organic semiconducting films. While organic semiconducting systems share many of the features as their inorganic counterparts, they differ in that excitons tend to be more local to the individual molecular sites, phonons play a central role, and the dielectric constant is considerably smaller. As a result, organic systems present both a challenge and opportunity for observing optical/electronic processes.

In this paper we consider the formation of polariton condensates under non-equilibrium conditions. While Bose condensation in atomic gases can be understood as an equilibrium phenomena since one can impose the condition that the average number of atoms in the gas is conserved, polaritons form due to the strong coupling between a photon field and an optical transition. They are transient quasi-particles that can exist only so long as the system is continuously resupplied with photons. Bose condensation occurs once the density of excitons reaches a critical threshold such that the condensate density grows exponentially in time.

For the cases in consideration here, we assume that excitons and photons within the cavity couple to give rise to at least two incoherently coupled populations: free excitons and lower polaritons. We can also add to this picture quantized vibrational modes of the molecular electronic ground. Let us denote the vibronic states as $|n_v⟩$ where $n$ denotes electronic excitation and $v$ denotes vibrational excitations. In the weak coupling limit, optical transitions occur predominantly from the lowest vibrational state of the electronic ground state to various vibrational states in the excited electronic state, with probability weighted by the Franck-Condon factors. However, in the limit of strong coupling to the photon field, which is appropriate for discussing polaritons, the lower electronic state is dressed by the photon field and vibrational states in the electronic ground come into resonance with the states in the upper electronic state. Here we consider a three-state system in which the ground state, $|0⟩$, and a single quantized mode of the ground state, $|1⟩$, are dressed by the photon field and are strongly coupled to the $|1_0⟩$ state in the upper electronic state. Thus, the

![FIG. 1: Dispersion curves for a system with an exciton (with frequency $ω_x$) and vibrational mode (with frequency $ω_v$) is coupled to a 2D photon cavity. The curves are labels to reflect the dispersion of the lower polariton (LP) and two upper polariton (UP1 and UP2) branches. Here the cavity off-set, $Δ$, is such that $ω_{LP} = Δ + ω_v$ and the dashed line indicates the bare exciton energy.](image-url)
dressed states include the photon field in the sense that

\[
\langle 0_o, n_k + 1 | H | 0_o, n_k + 1 \rangle = \hbar \omega_c(k) \tag{1}
\]

\[
\langle 1_o, n_k + 1 | H | 0_o, n_k + 1 \rangle = \hbar \omega_x + \omega_c(k) \tag{2}
\]

\[
\langle 1_o, n_k | H | 1_o, n_k \rangle = \hbar \omega_x, \tag{3}
\]

where \( \omega_c(k) \approx k^2 / 2m + \Delta \) is the dispersion relation for a microcavity with cut-off frequency \( \Delta = 2 \pi c / L \eta \) and effective mass \( m = 2 \pi \eta / cL \). Here, \( \eta \) is the refractive index of the material in the cavity and \( L \) is the spacing between reflective mirrors. For example, a \( L = 2300 \) Å cavity containing anthracene \( (\eta = 1.70) \), one obtains \( \hbar \Delta = 3.11 \) eV and an effective mass of \( m = 1.8 \times 10^{-5} m_e \). A cavity with this geometry would be in resonance with the \( S_0 \rightarrow S_1 \) electronic transition of anthracene. This amounts to a “shift” in the lower energy levels by \( \Delta \). In other words, the presence of a photon in the cavity can bring any of the vibrational states into resonance with the exciton when the cavity itself is not in resonance with the excitons.

The coupling between the exciton state and the cavity states is given by the Rabi frequencies

\[
\hbar \Omega_1 = \langle 1_o, n_k | H | 0_o, n_k + 1 \rangle
\]

and

\[
\hbar \Omega_2 = \langle 1_o, n_k | H | 0_o, n_k + 1 \rangle
\]

as given by the transition moment between the \( | 1_o \rangle \) exciton state and the two vibrational states in the ground electronic state, \( | 0_o \rangle \) and \( | 0_1 \rangle \). In general, the Rabi frequency for an on-resonance excitation can be expressed in terms of the electric field amplitude of the cavity mode and the transition dipole moment viz.

\[
\Omega = \mu_{fi} E / \hbar \tag{4}
\]

If we invoke the Franck-Condon principle and assume that the transition occurs in a fixed frame of the nuclear motion, then

\[
\mu_{fi} = \mu_{10} f_{0-v} \tag{5}
\]

where \( f_{0-v} \leq 1 \) is the overlap integral between displaced harmonic oscillator states and \( \mu_{10} \) is the exciton transition moment. Thus, knowing the Rabi frequency, \( \Omega_1 \) for the exciton in the cavity we can reliably estimate

\[
\Omega_2 = f_{0-1} \Omega_1 = f_{0-1}(f_{0-0} \mu_{10} E / \hbar). \tag{6}
\]

The overlap is determined by the Huang-Rhys factor, \( S \) with \( f_{0-v} = \sqrt{S^v / \eta} \exp(-S) \). For polyacene systems such as anthracene, the Huang-Rhys factor for the high-frequency C=C modes between the \( v = 0 \) vibrational state of the exciton and the \( v = 1 \) vibrational state of the ground electronic state is approximately \( S = 1 \) for the lowest excited state as determined by comparing the \( (0-0) \) and \( (0-1) \) spectral areas. This implies that \( \Omega_2 \approx 0.36 \times \Omega_1 \).

Diagonalizing \( H \) in the dressed basis, one obtains polariton dispersions similar to what is shown in Fig. 1.

Here, we have taken the exciton energy at 3.11 eV, which is the \( S_0 \rightarrow S_1 \) transition in anthracene, included a single vibrational mode at 0.2 eV, and set the cavity cut-off at 2.9 eV so that \( \Delta = \omega_c - \omega_x \). The resulting polariton states are superpositions of a cavity photon mode with the molecular exciton and ground-state vibrational mode (which we’ll refer to as a “vibron” mode). The lower polariton (LP) branch, which is predominantly “photon” in character undergoes avoided crossings with the upper polariton branches which are predominantly vibronic or excitonic in character.

A multi-state model involving the mixing between the cavity and the vibronic sub levels was used recently by Kéna-Cohen and Forrest\(^ {21,22} \) to describe the multiple resonances observed in anthracene microcavites. In this case, the vibronic sublevels are those of the electronic excited state and not the ground state, which we assume. At thermal equilibrium, all of the population is in the \( | 0_o \rangle \) state and the vibrationally excited states would have essentially no population and would not ordinarily come into play in the optical response of the system. However, in a driven system and one in which the \( | 1_o \rangle \) exciton state does carry oscillator strength to the \( | 0_o \rangle \) states via the Franck-Condon principle, one should be able to create a nonthermal population inversion in these states which can act as a reservoir.

In this paper, we consider the role that vibrational cooling may have on the formation of a polariton condensate in the incoherent pumping regime. In a recent set of experiments by Lidzey’s group, it was apparent that vibrational modes can contribute to the LP polariton population and may serve as an important cooling mechanism for UP and free excitons.\(^ {12,16} \) Our model consists of a reaction/diffusion equation whereby a population of free excitons is coupled to a population of vibrational modes and can serve as a reservoir for the formation of a LP Bose condensate. Our model assumes that condensation occurs when fluctuations about a steady state condensate with zero initial amplitude begin to grow exponentially in time once a threshold population of excitons has been achieved. The model results in a series of phase-diagram of exciton pumping rate vs. lattice temperature and cavity cut-off. We show that when the cavity cut-off resonance from the exciton mode, thermalized vibrons can enhance the exciton population and lead to lower critical pumping rates as the lattice temperature is increased. This seems counterintuitive since one expects condensates to form as the temperature is lowered. However, as we discuss next, the symmetry breaking transition in a driven system comes about due to the external driving force rather than through internal interactions or density of states.
II. THEORETICAL REACTION/DIFFUSION MODEL

We begin with the requirement that the condensate density obey a continuity equation with sink and source terms representing the temporal decay of the condensate with effective mass $m_{LP}$ due to cavity loss (with rate $\gamma$) and creation of new condensate due to the presence of a singlet exciton reservoir, $S$. Thus, we write using the hydrodynamic form\cite{23}

$$\partial_t \rho = -\nabla \cdot (\rho \nabla s)/m_{LP} + (r \cdot u - \gamma) \rho,$$

where the action, $s$ satisfies a quantum Hamilton-Jacobi equation of the form:

$$\partial_t s + \frac{1}{2m} (\nabla s)^2 - \frac{\hbar^2}{2m} \frac{1}{\sqrt{\rho}} \nabla^2 \sqrt{\rho} + g \rho = 0,$$

and that the current $J = \rho \nabla s/m$. Using $\phi = \sqrt{\rho} \exp(i s/\hbar)$ as the condensate amplitude, one obtains a Gross-Pitaevskii (GP) equation that properly incorporates the source and sink terms as an optical potential.

$$\partial_t \phi = -\eta \nabla^2 \phi + \left( g|\phi|^2 + \frac{i}{2} (r \cdot S - \gamma) \right) \phi,$$

where $\eta = \hbar/2m_{LP}$ is the LP diffusion constant and $g$, $r$, and $\gamma$ are rates. If we take the exciton reservoir to be constant (in both time and space), then we can begin to see the conditions necessary for establishing a condensate in a driven, non-equilibrium system. The trivial solution is given by $\phi = 0$ in which no condensate will forms at any time. This provides us with the trivial steady-state solution of $\phi_{ss}(x,t) = 0$.

However, if we introduce non-trivial fluctuations about the steady state, $\phi(x,t) = \phi_{ss}(x,t) + \delta \phi(x,t)$ and ask whether or not such amplitude fluctuations will grow or decay in time, one sees that if the optical potential term $(r \cdot S - \gamma) < 0$, then any fluctuation in the polariton component will decay exponentially in time and no long-lived condensate will form. On the other hand, if the exciton density is sufficiently large that $(r \cdot S - \gamma) > 0$, then the condensate amplitude will grow exponentially with a rate $(r \cdot S - \gamma)$. Thus we conclude there exists a critical exciton density, $S_0$, whereby the polariton decay due to cavity leakage is exactly counterbalanced by re-population from a free exciton reservoir. Once a critical density of excitons has been achieved in a given region, the LP condensate population in that region experiences exponential growth. Thus, one expects that once $S_0 = \gamma/r$. Taking the exciton density to be proportional to the exciton pumping rate, $p_0$, then one expects $p_0, \text{crit} \propto 1/r$. The presence of a threshold exciton population for the formation of a condensate at long time is the hallmark of a quantum phase transition in a non-equilibrium system.\cite{24,25} The principle result of the work presented here is that the inclusion of dressed ground state vibrational modes

As discussed in the Introduction, local vibrational modes play very important roles in the electronic spectroscopy of most molecular semiconductors and in microcavity system, may serve as a viable cooling mechanism for excitons. With this in mind, we adopt a continuum model where we write the singlet exciton density, $S(x,t)$, and vibron density, $v(x,t)$, as a solutions to the following reaction/diffusion equations which, in turn, are coupled to the GP equation for the condensate amplitude,

$$\partial_t S = D_s \nabla^2 S - r \cdot S |\phi(x,t)|^2 + p(x,t) - \gamma S + (k_1 v(x,t) - k_S)$$

$$\partial_t v = D_v \nabla^2 v - k_1 v(x,t) + k_S$$

where $rS|\phi|^2$ corresponds loss of exciton density in a given spatial region due to the formation of the condensate, $\gamma S$ is the singlet exciton radiative rate, and $p(x,t)$ is the rate that excitons are pumped into the system by some external source. We imagine a experimental situation where excitons in a thin-film within a microcavity are created in a given region illuminated by a steady laser spot, the excitons diffuse incoherently through through the sample as UP polaritons and are either rapidly thermalized with UP vibrons or decay through radiative process. Taking $A = \pi a$ as the area illuminated by the pumping pulse we can relate the pumping rate to an irradiance via $E_p = p_0 \omega c/A \approx 0.32 p_0 W/m^2$ taking $\sigma = 500 m^2$ and $p_0$ is given in $\text{nm}^{-1}$. Thus a $p_0 = 4000 \text{nm}^{-1}$ would correspond to an irradiance of 1.3 kW/m$^2$ which is comparable to the average solar irradiance on the Earth’s surface.

Putting aside any decay channels for the moment, let us assume that the exciton and vibron populations are rapidly thermalized so that we can write

$$k_1 = e^{-\beta \delta k},$$

where $\delta = \omega_x - (\omega_v + \Delta)$ is the energy gap between the exciton and vibrons. This provides a useful means for incorporating the geometry of the cavity and the temperature of the lattice itself into our equations of motion. We also have assumed that the energy difference between the free exciton reservoir and LP polariton condensate is much greater than $k_B T$ so that any exciton population removed by condensate formation does not escape to re-populate the free exciton reservoir. A final assumption we make is that the diffusion constant appearing in Eq.\cite{11} can be effectively set to zero since we can assume that molecular vibrational excitations are local to the molecular sites in the system.

III. NUMERICAL RESULTS

We next consider the numerical integration of the equations of motion given above. For this, we use the method of lines approach as implemented in the NDSolve[] routine in Mathematica.\cite{26} For numerical purposes, we use
the exciton decay rate, $\gamma_S$ and the singlet exciton diffusion constant to set the time and length-scales of our model. The exciton decay rate, $\gamma_S$ includes all radiative and non-radiative processes that diminish the exciton population that do not contribute to the formation of either lower polaritons or $|0, n+1\rangle$ vibrons. Since the singlet exciton radiative lifetime is at least 1 ns, setting $\gamma_S = 1\text{ns}^{-1}$ is a reasonable estimate. From transient singlet diffusion constant for excitons in anthracene is $D_S = 0.13\mu\text{m}^2/\text{ns}$ at 10K. This produces a length-scale $\ell = \sqrt{D_S/\gamma_S} = 1.14\mu\text{m}$. From Eq. 12 excitons are pumped into the system in an area $A \propto \pi \sigma = 100\pi \ell^2$, so that $p_o/A$ gives the number of excitons that are created in the system per unit time per unit area.

Below, we consider two possible regimes. One in which lifetime of the exciton gas is short relative to that of the polariton condensate and the other in which the exciton gas is long-lived. In each case, we “seed” the condensate with a small amplitude about the center of our grid and determine whether or not this “seed” fluctuation grows or decays as the temperature and pumping strength are varied.

### A. Slow interconversion regime

Let us first consider the case where the conversion from the exciton gas to the LP condensate is slow compared to the exciton to vibron conversion. We shall refer to this as a slow conversion regime and take $r \ll k$ in our equations of motion. We would expect this limit to be valid when the energy difference between the vibron state and the free exciton is on the order of $kT$ and the Rabi splitting between the exciton and cavity modes to be small. Taking the pumping rate to be a gaussian that grows exponentially to some maximum value

$$p(x, t) = p_o e^{-x^2/2\sigma}(1 - e^{-t/\tau})$$

In Fig. 2 we show the results of a representative numerical simulation using a pumping rate of $p_o = 4,000\text{ns}^{-1}$, which corresponds to an irradiance of $\approx 1.1kW/m^2$, which is above the threshold for forming the LP condensate. As point of reference, solar irradiance of the earth...
is on the order of 1 kW/m$^2$. The three panels in Fig. 2(a-c) are the time-dependent densities for the free exciton gas, the vibron reservoir, and the condensate at a lattice temperature of 10K. As seen in Fig. 2, the exciton gas forms and begins populating the vibron reservoir. As the population in the vibron reservoir increases, it augments the exciton density such that a critical population can be established for forming a stable condensate.

In Figs. 2d-f we show the formation of the condensate when the lattice temperature is considerably warmer at 200K. Here the vibron reservoir rapidly augments the exciton population and the condensate forms at a much earlier time than in the previous example at 10K. Also, one notes that the condensation is far more abrupt and produces a rapidly evolving condensate wave packet. The system does, however, reach a steady state at long time.

Once the condensate forms, it depletes the exciton density and at long times, the system (exciton gas, vibron reservoir, and condensate) approaches a steady state. This is evidenced in Fig. 2(a-c) were we show the condensate density at $x = 0$ (center of the grid) versus time for various cavities at different temperature. In each case, the exciton pumping rate is above the critical threshold.

In Fig. 2h and b, the vibron state (at $\Delta + \omega_c$) is lower in energy than the exciton energy. In both cases, the condensate forms about 1 ns after the pumping is initialized. In all cases, the initial rapid buildup of polariton density drops almost immediately due to the ballistic spread of the polariton wave packet away from the pumping region. After one or two “bounces” the polariton density relaxes to a steady state population.

In Fig. 2h, the cavity off-set at $\Delta = 2.85$eV is such that the vibron level is considerably lower than the exciton level. In this case, the initial formation time of the polariton condensate shows a weak dependency on the temperature, but the steady-state population is clearly dependent upon the temperature with warmer systems leading to a greater steady state polariton density at long times. In the intermediate case at $\Delta = 2.88$eV, the polariton steady state is reached much sooner. While the rate at which the polariton population approaches the steady state does depend upon the temperature, the final steady-state population shows very little dependency.

Lastly in Fig. 2h we consider a case in which the vibron level is well above the exciton level and plays no significant role in the formation of the polariton condensate at any temperature. Here, we can again see a series of beats as the polariton condensate forms, decays, and reforms until a steady-state population is achieved. These beats are not due to quantum coherences between the exciton and polariton since we are treating the exciton gas as a classical reservoir. The beats are are due to population depletion and replenishment from both the vibron reservoir and the pumping field.

In examining the final steady state populations, we note that steady-state condensate population is enhanced by at least a factor of 3 to 5 by the presence of the vibron reservoir. This implies that cavities which can take advantage of the lower-lying vibron levels can produce a higher density condensate which translates into a more intense steady-state optical signal.

In Fig. 3 we show how the condensation delay times depend upon both the lattice temperature and the exciton pumping rate for a cavity with $\Delta = 2.88$eV. The model does give a critical pumping rate of $p_c = 3800$ns$^{-1}$, corresponding to an irradiance of 1.2 kW/m$^2$, below which long-lived polariton condensates will not form at any temperature. Close to this threshold, the delay time is very sensitive to the lattice temperature to the extent that for a very cold lattice the condensation delay time can be $\approx 6 \times$ longer than that of a warmer lattice. It is important to point that an irradiance of 1.2 kW/m$^2$ is essentially the intensity of bright sunlight which implies that the critical pumping rates given by our model are not unreasonably intense and can easily be achieved. However, this is the irradiance within the cavity itself and we have not taken into account the fact that the pumping laser needs to penetrate through the DBR to the cavity.

On first thought it seems counterintuitive that a warmer system would have an easier time forming a stable polariton condensate since we expect condensation to occur as the temperature is lowered past some critical temperature. However, the symmetry breaking mechanism in this case is the density of excitons in a given region which are introduced into the system via the external pumping source. By populating the vibron mode, which does not contribute directly to the lower polariton population, and allowing this mode to equilibrate and populate the exciton mode, it effectively augments the local exciton density such that the critical density can be reached at lower exciton pumping rates. Increasing the temperature, causes as shift in the steady state populations of vibrons and excitons towards more population in the higher-energy species.

**B. Rapid interconversion regime**

Central to our theory is the rate that free excitons are converted to lower polaritons. To estimate this rate, let us assume that the “golden rule” is valid, such that the maximum value of the rate is given by

$$r_{max} = \frac{2\pi}{\hbar} |\Omega|^2 \rho(k_{ex} = k_{cav})$$  \hspace{1cm} (13)

where $\rho(k_{ex} = k_{cav})$ is the density of cavity states evaluated at the avoided crossing. Since the cavity contains a two-dimensional gas of photons with dispersion $E_k = \Delta + \hbar \eta k^2$, the density of states is constant with

$$\rho(k_{ex} = k_{cav}) = \frac{\pi}{\hbar \eta}$$  \hspace{1cm} (14)

Using the numerical values for our model cavity and setting $\Omega = 0.05$eV, one obtains $r_{max} = 1.9 \times 10^7$ns$^{-1}$.

We can follow a similar line of reasoning for the coupling between the exciton and vibron reservoirs. The vibron reservoir in our model corresponds to an ensemble
of UP polaritons formed by mixing a cavity mode with a ground-electronic state vibrational mode of the molecules in the cavity. If we assume that the golden rule holds, then we can estimate the exciton to vibron conversion rate by multiplying Eq. 13 a Franck-Condon factor. i.e. \( k = f_0^2 \times r_{\text{max}} \). Based upon arguments above, the exciton to vibron conversion rate is at least an order of magnitude slower than the exciton to LP conversion.

For the LP decay, let us assume that the cavity has a quality factor, \( Q = 6000 \), that corresponds to the number of times a photon will traverse the cavity before escaping. Taking the cavity width to be \( \approx 250 \text{ nm} \), one obtains an LP decay rate of \( \gamma = 120 \text{ ns}^{-1} \).

Since the conversion rates in this regime are far greater than in the slow conversion regime we just examined, the critical pumping strengths will be considerably lower. However, the life times and dynamics will be considerably faster. In thinking about possible experimental situations, we consider the effect of a single 30 fs gaussian shaped pulse that drives the creation of an exciton gas. The density of excitons created will depend upon the intensity (and duration) of the pulse. Prior to the arrival of the pulse, we seed the condensate with a very small amplitude fluctuation at \( x = 0 \) which will have decayed somewhat by the time the pulse arrives.

In Fig. 5 we show how the condensate population at the center of the simulation cell varies in time for a non-resonant cavity system with \( \Delta = 2.88 \text{ eV} \) and at a fixed pumping strength of \( p_0 = 60 \text{ ns}^{-1} \). At \( t = 0 \text{ fs} \), a condensate density \( |\phi(t)|^2 \) at \( x = 0 \) for different cavities for \( p_0 \) above the critical pumping threshold.
condensate fluctuation is introduced and at \( t = 60\text{fs} \) the 30 fs excitation pulse reaches its maximum intensity and creates a population of excitons, which go on to produce more condensate as well as vibrons. After 100 fs, the system evolves without further pumping and the population in the condensate will either decay due to cavity loss, or continue to grow as excitons are converted to LP condensate. The various curves shown here correspond to different lattice temperatures. For the case at hand, when the lattice temperature is above 45K, the condensate population continues to grow following the initial pulse. This indicates that sufficient exciton density is present to spawn the formation of a long-lived polariton condensate. Below this temperature, the LP population simply decays.

Fig. 6 shows a phase diagram for the off-resonant cavity in terms of the threshold temperature needed to produce a long-lived condensate at a given pumping strength. As temperature is decreased, the role of the vibronic reservoir is diminished and higher pumping strengths are required to form a long-lived condensate.

In Fig. 7 we considered what happens if there is a special off-set between the pumping pulse and the initial condensate "seed" fluctuation. We initialized the condensate with a small gaussian centered off-center at 50\( \mu \text{m} \) and created exciton density centered about \( x = 0 \) at 60 fs later. In this case, the condensate appears to migrate before decaying and there are a number of "beats" in the density itself. The beats occur even when the seed fluctuation is located at \( x = 0 \) and are due to cyclic growth/decay kinetics between the condensate and exciton densities, much like what is observed in predator/prey and disease models rather than to coherent motion of the condensate itself. At long times following the pulse, the condensate eventually decays due to cavity loss. It should be pointed out, however, that while the requisite pumping intensity in this model is lower than in the "slow conversion" case, the integrated density of the condensate wave function is considerably less. However, this density can be used to further seed the production of additional condensate if subsequent pulses are introduced.

In Fig. 8 we show the real (line) and imaginary (+) components of the quasiparticle excitation spectrum for in the slow (a: \( \gamma' \gg \gamma \)) and rapid (b: \( \gamma' \ll \gamma \)) conversion models. Dashed curves are the Bogoliubov quasi-particle spectra for the equilibrium Bose condensate. Unless otherwise specified, we have set, \( g = 1 \), \( m_{LP} = 10^{-5} m_e \), \( \phi_o = 1 \) and \( rS_o = 3 \).
IV. STABILITY ANALYSIS

We can introduce a time-dependent fluctuation about the steady-state \( \Psi_o = \{ \phi_o, \psi_o, S_o, v_o \} \) by writing the solution to Eqs. 9 and 10 as \( \Psi(t) = \Psi_o + \delta \Psi(t) \).

Let us consider the time evolution of Eqs. 9 and 10 by writing \( \Psi(t) = \{ \phi(t), \psi(t), S(t), v(t) \} \) and introducing a fluctuation about its steady state such that \( \Psi(t) = \Psi_o + \delta \Psi(t) \). Introducing this into Eq. 9. and 10, keeping only terms linear in \( \delta \Psi \), and transforming from real to k-space, produces a set of coupled equations for the fluctuations:

\[
\frac{i}{\hbar} \begin{pmatrix} \delta \phi_k \\ \delta \phi'_k \\ \delta S_k \\ \delta v_k \end{pmatrix} = M(k) \begin{pmatrix} \delta \phi_k \\ \delta \phi'_k \\ \delta S_k \\ \delta v_k \end{pmatrix},
\]

where the stability matrix is given by

\[
M(k) = \begin{bmatrix}
\eta k^2 + (g|\phi_o|^2 + \frac{1}{2}(rS_o - \gamma)) & -g|\phi_o|^2 & -i\phi_oS_o & 0 \\
-g|\phi_o|^2 & \eta k^2 - (g|\phi_o|^2 - \frac{1}{2}(rS_o - \gamma)) & -i\phi_oS_o & 0 \\
-i\phi_oS_o & -i\phi_oS_o & \frac{1}{2}r|\phi_o|^2 & 0 \\
0 & 0 & 0 & -ik' \\
\end{bmatrix}.
\]

In writing this, we assume the steady-state solutions are homogeneous and that wave-vector, \( k \), remains a constant of the motion. We have also used \( \mu = g|\phi_o|^2 \) as the chemical potential of the condensate. (Note that the \( k \) and \( k' \) appearing in the matrix elements coupling the reservoirs are rate constants and not wave-vectors.) The stability matrix, \( M \), given above is similar to the equations of motion reported by Wouters and Carusotto[20] and by Byrnes et al.[30] In the absence of the reservoir, the eigenvalues of the upper 2 \times 2 block of \( M(k) \) are the Bogoliubov modes corresponding to excitations of the condensate. These modes vanish at \( k = 0 \) corresponding to a Goldstone brach that can be understood as a slow rotation of the condensate across the sample[25] and the linear dispersion about \( k = 0 \) is characteristic of a superfluid state.

Let us consider the stability of the polariton/exciton/vibron equations in the steady-state limit by first assuming that the exciton and vibron reservoirs are equilibrated rapidly. This allows us to write an effective exciton decay constant, \( \gamma_S \), that will depend both upon the lattice temperature and the cavity offset. Including the coupling to the reservoir, two regimes can be identified. First, in the limit where \( \gamma'_S \gg \gamma \) in which the reservoir relaxation is very rapid compared to the polariton relaxation rate, the dispersion around \( k = 0 \) is flat corresponding to a diffusive Goldstone mode which is in stark contrast to the linear dispersion of the sound-mode in an equilibrium Bose condensate. For a Bose condensate, the gap at \( k = 0 \) necessarily vanishes and the dispersion about \( k = 0 \) is linear corresponding to the formation of a superfluid with the slope proportional to the sound velocity.

In the non-equilibrium case, the sound velocity vanishes as well as seen in Fig. [8], which corresponds to our “slow” regime in which the exciton gas decays rapidly compared to the polariton condensate.

On the other hand, if \( \gamma \gg \gamma'_S \) a gap opens at \( k = 0 \) and the polaritons again take on an effective mass. The gap and the flattening of the spectrum is akin to the blue-shift observed by Kasprzak for a polariton condensate driven well above the condensation threshold[32,33]. It was speculated that the flattening could be due to either polariton localization in real-space or to pump and decay processes. Here, as in Refs. [24,36] the flattening and gap is entirely due to competing decay processes between the exciton reservoir and the polariton gas.

V. DISCUSSION

In this paper we have focused upon the role that molecular vibrational excitations may play in the formation of a LP condensate in a microcavity containing a thin-film organic semiconductor, such as anthracene. In our model, molecular vibrational excitations coupled to the photon field serve as a secondary thermal reservoir for free excitons. Thermal fluctuations from the vibron reservoir can augment the exciton density such that at finite lattice temperature polariton condensation can be achieved at lower exciton pumping rates. We assumed that the vibron reservoir involved only a single vibrational model per molecule. In a realistic system, there will be multiple vibrational modes as evidenced by the various Franck-Condon peaks in the emission spectrum of many organic semiconductors. Assuming the mechanism presented here holds true in the multi-mode case, these Franck-Condon modes should provide a reservoir for the exciton gas and greatly facilitate the formation of a stable LP condensate.

We explored two limits of the model. In the “slow conversion” model, we assumed that the rate of conversion between continuously driven and replenished gas of free excitons and a vibronic reservoir level was comparable to the rate of conversion between the exciton and a lower polariton condensate. In this limit, the tempera-
tecture of the molecular crystal lattice plays an important role in providing a sufficient exciton density to spawn the growth of fluctuations about the condensate vacuum. At long times, this model produces steady state solutions with populations in both condensate and non-condensate channels. In the “rapid conversion” limit, we assumed that the conversion of the exciton gas to LP condensate could be estimated from the Rabi splitting between the upper and lower polariton branches and the density of states of photons in a two-dimensional cavity. In this model, the exciton gas is pumped impulsively via a single 30 fs pulse. Here, too, the growth or decay of condensate fluctuations hinges upon the pumping being above a threshold intensity and shows a pronounced sensitivity to the temperature of the lattice when the cavity is off-resonance with the exciton. In both models, it is highly encouraging that the threshold intensities are well within the margins of current experimental capabilities.

Lastly, along a similar vein, one can model an electrically pumped system in which electrons and holes are injected onto a microcavity device and recombine to form singlet and triplet excitons. We suspect that both the triplet excitons and bound charge-transfer contact pairs may serve a similar role as the vibronic reservoir in the present model. We are currently exploring this possibility.

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