Microscopic Theory of Polariton Lasing via Vibronically Assisted Scattering

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Polariton lasing has recently been observed in strongly coupled crystalline anthracene microcavities. A simple model is developed describing the onset of the non-linear threshold based on a master equation including the relevant relaxation processes and employing realistic material parameters. The mechanism governing the build-up of the polariton population - namely bosonic stimulated scattering from the exciton reservoir via a vibronically assisted process - is characterized and its efficiency calculated on the basis of a microscopic theory. The role of polariton-polariton bimolecular quenching is identified and temperature dependent effects are discussed.

I. INTRODUCTION

In strongly coupled semiconductor microcavities, the cavity mode and the excitonic resonance mix and form new bosonic quasiparticles, the polaritons. Their properties differ significantly from those of the bare uncoupled excitations, though they originate from them. The lower polariton (LP) has a peculiar dispersion law with a deep minimum at small wavevectors, characterized by a tiny mass. At high densities, the build-up of a large population at the bottom of this branch is favoured by bosonic final-state stimulation as soon as the occupation per mode of the lower polariton states exceeds unity. Coherent light-emission, called polariton lasing, results from this macroscopic population due to the finite lifetime of the polaritons which leak out of the cavity via their photonic component. This is only one of the many outstanding phenomena that have attracted more and more attention to the field of polaritonics in inorganic semiconductor microcavities since the pioneering observation of the strong coupling regime.

The weak binding energy and oscillator strength of Wannier-Mott excitons characteristic of inorganic semiconductors are limitations that can be overcome employing organic semiconductors having strongly bound Frenkel excitons with a large oscillator strength. The strong coupling regime in an organic based microcavity was first observed at room temperature using a porphyrine molecule (4TBPPZn) dispersed in a polystyrene film as optically resonant material at room temperature and later in a variety of organic materials including polycene molecular crystals. The latter are also characterized by the presence of well developed vibronic replicas that participate in polariton formation and affect their luminescence. In contrast to the case of inorganic microcavities, manifestations of bosonic stimulation using organic cavity polaritones have been quite elusive. Recently, however, several non-linear phenomena were reported: room temperature polariton lasing in an anthracene single crystal microcavity and nonlinear emission in polymer-based microcavities. In anthracene, the observation of a threshold for nonlinear emission was accompanied by a significant line narrowing and by a collapse of the emission lifetime. In that case, a comparison with the best-case estimate of the threshold for conventional lasing inferred from amplified stimulated emission measurements shows that the lasing threshold observed in the strongly coupled microcavity is slightly lower than that anticipated for a conventional laser. The temperature dependence of the polariton lasing threshold has also been investigated and shows an order of magnitude decrease from room temperature to low temperatures. These experiments demonstrate the high excitation density regime of polariton bosonic stimulation, which could pave the way to the observation in organic based microcavities of other phenomena related to polariton fluids where weak polariton-polariton interactions may also manifest.

In the present work, we develop a semiclassical kinetic model to describe the onset of the non-linear threshold for polariton lasing in anthracene-based microcavities. We show, in particular, that the mechanism providing the bosonic final-state stimulated formation of the ensemble of lower cavity polaritons is the vibrationally assisted radiative decay of incoherent excitons, previously populated by non-resonant pumping. In Section III we set up a minimal master equation to describe the polariton population dynamics, we make a realistic choice of material parameters and we fit the experimental data on the pump dependence of the polariton emission, pointing out the relevance of bimolecular quenching processes. In Section IV we calculate microscopically the efficiency of the relevant scattering process justifying the value obtained from the fit. In Section V we consider within our model the dependence of the polariton lasing threshold on temperature. Finally, in Section VI we present our conclusions.
II. TWO-LEVEL MODEL

We model the dynamics of the lasing process using a minimal rate-equation approach. In this section, we estimate the typical time-scale of the mechanism which selectively transfers excitations from the reservoir to the bottom of the polariton branch, without any assumptions regarding its microscopic nature.

A. The Master Equation

The anthracene crystal has two molecules per unit cell and strongly anisotropic optical properties.\textsuperscript{9,16} Excitations in this material are well-described within the Frenkel-exciton framework, which is based on the intramolecular promotion of an electron from the highest occupied molecular orbital to the lowest unoccupied one. Because of molecular dipole-dipole interaction, the excitation can propagate, resulting in two orthogonal transition dipole moments, $\hat{\mu}_{a,b}$, directed along the in-plane $a$ and $b$ axes. When a thin anthracene crystal is placed between two mirrors, light couples to both $a$- and $b$-polarized excitons and creates two orthogonally-polarized lower polariton branches. Measurements are usually reported for light polarized along $a$ and $b$ in these cases the $s$- and $c$-in-cavity light polarizations separately couple to the dipole moments $\hat{\mu}_{a,b}$ and no mixing effect is present.

We focus only on $b$-polarized excitons,\textsuperscript{16} i.e. those with largest oscillator strength, for which lasing has been reported\textsuperscript{12} and neglect other polaritonic and excitonic states. The initial relaxation of the pump excitations is also neglected, and the presence of an effective excitonic reservoir at a fixed energy independent on the cavity properties is considered.\textsuperscript{17} We note that the experimental photoluminescence (PL) from anthracene micro-cavities shows always a clear maximum at energy $\sim 2.94$ eV regardless of the cavity thickness.\textsuperscript{12,16} and indeed lasing has been achieved in a cavity where the minimum of the LP is exactly at 2.94 eV. This is a signature that the microscopic dynamics resulting in the lasing phenomenon is that of a two-level process rather than that of the well-known polariton bottleneck. We thus develop a two-level master equation for $\nu_e(t)$ and $\nu_p(t)$, the surface density of reservoir excitons and of lasing polaritons located near $k = 0$, respectively.

We denote with $A_0$ the subregion of the Brillouin zone located around $k = 0$ which is occupied by the lasing polaritons. Because states at the bottom of the LP branch do not have a well-defined wavevector $k$, we consider all of the localized wavepackets with energy $\sim E_{\text{LP}}(k = 0)$ as equally contributing to the lasing process. $N_{\text{pol}}$ is the number of such polaritonic states, while $N_{\text{exc}}$ is the number of excitonic states. The polariton and exciton decay rates are $\Gamma_p = |c_p^e|^2/\tau_e + |c_p^e|^2/\tau_p$ and $\Gamma_e = 1/\tau_e$, respectively, where $\tau_p$ ($\tau_e$) is the bare photon (exciton) life-time and $c_p^e$ ($c_p^e$) is the photonic (excitonic) Hopfield coefficient for the lasing polaritons.

The parameter $Z^{c^+}$ is the decay rate via other channels, such as phonons, lower polaritons outside the $A_0$ region and leaky modes, whereas bimolecular quenching processes are treated separately, with a rate $\gamma'$. A standard pump term proportional to $P'(t)$ is included; in order to take into account possible saturation effects the term $(1 - \nu_e/\bar{\nu}_e)$ has been considered ($\bar{\nu}_e = N_{\text{exc}}/A$ is the surface-density of excitonic states and $A$ is the area of the sample).

The rate of resonant excitation transfer from the reservoir to the lasing polaritons is $W^{e \rightarrow p}$. We retain the bosonic enhancement term $(1 + \nu_p/\bar{\nu}_p)$ responsible for lasing effects, where $\bar{\nu}_p = N_{\text{pol}}/A$ is the surface-density of polaritonic states.

The master equation for $\nu_e(t)$ and $\nu_p(t)$, whose physics is sketched in Fig. 1 reads:

$$
\dot{\nu}_e = -\Gamma_e \nu_e - W^{e \rightarrow p} \nu_e \left( 1 + \frac{\nu_p}{\bar{\nu}_p} \right) - Z^{c^+} \nu_e + \gamma' \left( \nu_e + |c_p^e|^2 \nu_p \right) \nu_e + \left( 1 - \frac{\nu_p}{\bar{\nu}_p} \right) P'(t) \\
\dot{\nu}_p = -\Gamma_p \nu_p + W^{e \rightarrow p} \nu_e \left( 1 + \frac{\nu_p}{\bar{\nu}_p} \right) + \gamma' \left( \nu_e + |c_p^e|^2 \nu_p \right) |c_p^e|^2 \nu_p
$$

The full derivation is given in appendix A. Note that the resulting equations are completely analogous to those describing conventional lasing\textsuperscript{10} with the important difference that the lasing state is a polariton and thus retains an excitonic component.

B. Parameters

We relate Eq. (1) to the experimental system in Ref. \textsuperscript{12} using the following parameters.
Simulation Parameters

| Parameter  | Value                  |
|------------|------------------------|
| $\rho_0$   | $4.2 \times 10^{21}$ cm$^{-3}$ |
| $v_c$      | $5.4 \times 10^{-16}$ cm$^{-2}$ |
| $\tau_p$   | $85$ fs $\sim 1$ ps |
| $\tau_e$   | $2$ ns |
| $c_p^{(e)}$| $0.92$ |
| $c_p^{(c)}$| $0.39$ |

Fit Parameters

| Parameter  | Value                  |
|------------|------------------------|
| $\tau_p$   | $85$ fs $4 \times 10^9$ s$^{-1}$ |
| $W^{(e)}$  | $1.5 \times 10^{-6}$ cm$^2$s$^{-1}$ |
| $\gamma$   | $1 \times 10^{-6}$ |

TABLE I. Parameters for the numerical simulations. (top) List of the most important simulation parameters used in the numerical simulations. (bottom) Results of the fit reported in Fig. 2.

FIG. 2. Time-integrated surface density of polaritons $\int \nu_p(\tau) d\tau$ calculated from solution of Eq. (1) (lines) and from experimental data (squares). The bimolecular quenching rate is taken from the measured 3D bulk value: $\gamma' = \gamma_{3D}/L_z$.

The calculation parameters are: (dashed line) $\tau_p = 85$ fs, $W^{(p)} = 7 \times 10^7$ cm$^{-1}$; (solid line) $\tau_p = 1$ ps, $W^{(p)} = 7 \times 10^4$ cm$^{-1}$. Because the experimental data is in arbitrary units, here and in the following fits the experimental data is normalized so that the first experimental and theoretical points coincide.

a. Anthracene Crystal. The experimental microcavity embeds a crystal of anthracene with thickness $L_z = 120$ nm; the molecular density is $\rho_0 = 4.2 \times 10^{21}$ cm$^{-3}$; we ignore the monolclinic structure of the unit cell and instead estimate its linear size as $a = (\rho_0/2)^{-1/3} = 7.8 \times 10^{-8}$ cm, including the presence of two molecules per unit cell. The number of layers is estimated as $N = L_z/a \approx 153$. The absorption maximum of the anthracene crystal is at energy $E_0 = 3.17$ eV. The exciton measured lifetime is of the order of $\tau_e \sim 1-3$ ns and in the next simulations we take the intermediate value $\tau_e = 2$ ns. The contribution of $Z^{e-p}$ is neglected because it can be included into $\tau_e$ without any substantial difference as long as $\tau_e < 1/Z^{e-p}$, which can be safely assumed.

b. Microcavity and Polaritons. If we assume homogeneous broadening, the cavity lifetime can be estimated from the polariton linewidth at $k = 0$, where it is mostly photon-like. Using this approach, we obtain a lower bound $\tau_p = 85$ fs. An exact calculation assuming perfect interfaces for the mirrors results in an upper bound $\tau_p = 1$ ps. We will estimate $W^{e-p}$ corresponding to both extrema. The Hopfield coefficients of the LP branch are $c_p^{(p)} = 0.92$ and $c_p^{(c)} = 0.39$.

For small $|k|$, the $A_0$ region has cylindrical symmetry. Its radius, $q_0$, can be estimated using $E_{LP}(q_0) - E_{LP}(k = 0) = \Gamma_0/2$, where $\Gamma_0 = 15$ meV is the linewidth of polaritons at $k = 0$ below threshold. We obtain $q_0 = 2.2 \times 10^4$ cm$^{-1}$.

c. Pump. The pump density is:

$$P'(t) = P'_0 \exp \left[ -\frac{t^2}{2\sigma^2} \right], \quad \sigma = \frac{150}{2\sqrt{2} \ln 2} \text{ fs} \approx 64 \text{ fs},$$

with $P'_0 = P_0/(\pi \tau_0^2 \hbar \omega_{\text{pump}})$ where $\tau_0 = 110$ $\mu$m is the radius of the pump spot and $\hbar \omega_{\text{pump}} = 3.45$ eV is the energy of the pump photons. Because $E_{tot} = \int P(t) dt = \sqrt{2\pi} \rho_0 \sigma$ and because $E_{tot}$, the total absorbed energy, and $\sigma$ are experimentally known, $P_0$ is also known.

d. Bimolecular Quenching Rate. To the best of our knowledge there are no measurements of the bimolecular quenching rate, $\gamma'$, for two-dimensional anthracene crystals. According to the standard theory for bimolecular quenching, $\gamma' = \gamma_{3D}/L_z$, where $R$ is the Förster radius of the exciton and sets the volume around the exciton in which annihilation happens, while $D$ is the diffusion coefficient of excitons. Measurements for three-dimensional anthracene crystals have yielded values of $\gamma' = 8 \pi RD = 10^{-8}$ cm$^{-3}$ s$^{-1}$ and $D \sim 1 - 10 \times 10^{-3}$ cm$^2$ s$^{-1}$. The corresponding diffusion length $\ell = (\tau_e D)^{1/2} \sim 1 - 3 \times 10^{-6}$ cm is smaller than $L_z = 1.2 \times 10^{-5}$ cm and suggests that excitons can be treated as diffusing in a three-dimensional environment. As a result, we initially fix $\gamma' = \gamma_{3D}/L_z = 7 \times 10^{-4}$ cm$^2$ s$^{-1}$.

Parameters used in the numerical simulations are briefly summarized in Table I.

C. Results

Since all other parameters are known, we leave only $W^{e-p}$ as a fit parameter. We numerically integrate equations (1a) and (1b) and once the complete time-dependent functions $\nu_{e,p}(t)$ are known we compute the integral $\int \nu_{e,p}(\tau) d\tau$ and compare it with the experimental values.

In Fig. 2 the fits obtained for the extreme values of $\tau_p = 85$ fs and $1$ ps are shown. The value of $W^{e-p}$ has been fit to the experimentally observed threshold value. In both cases, $W^{e-p}$ is of the order $10^5$ s$^{-1}$. The agreement with the experiment is poor and it is apparent that the chosen value of $\gamma'$ does not properly describe the transition between linear and sublinear region below threshold. Note that the exciton lifetime $\tau_e \sim 2$ ns is shorter than the reported bulk values $\tau_{e,bulk} \sim 10$ ns; surface interactions or defects within the layers could explain this discrepancy. In this situation, the excitonic diffusion coefficient can be smaller, resulting in a reduced possibility...
The resulting values for $W_{\nu}$. Assuming that at threshold $\gamma$ value is two orders of magnitude smaller than of excitons at threshold via $\Gamma$ densities. We can roughly estimate the surface density lead to observable effects in presence of high excitonic compared to the exciton and polariton lifetimes, it can the scattering process acts on a sensibly longer timescale at lower excitation density.

Above threshold seems to be in better agreement with reaction of the annihilation process. Indeed, our calculation few percent of the total molecular density. Such high densities, that at threshold the exciton density reaches a peak of the normalized surface exciton and polariton in Fig. 4 and Fig. 5, which shows the time dependence of the normalized surface density of polaritons $\nu_p(t)$ (squares) and of lasing photons $\nu_e(t)$ (circles). See Fig. 3 for the parameters; $\tau_p = 85$ fs.

In conclusion, using our simple two-level model we have extracted an estimate for the scattering process $W_{\nu} \sim 0.01$ relevant to polariton lasing in anthracene. Furthermore, we believe that the strongly reduced rate of bimolecular annihilation observed should motivate further experimental and theoretical studies of this process.

III. THE SCATTERING MECHANISM

In this section we focus on the microscopic origin of the excitation transfer of Sec. III. In particular, we propose as the relevant mechanism the radiative recombination of a molecular exciton assisted by the emission of a vibrational quantum of the electronic ground state. We show that the resulting scattering rate is in good agreement with that obtained in the previous Section. Finally, we also consider an alternative and possibly coexisting
model based on the non-radiative emission of an optical phonon.\textsuperscript{26}

A. Radiative Transition

The absorption and PL spectra of anthracene show several vibronic resonances.\textsuperscript{22} The resonances observed in absorption correspond to the molecular vibrations of the first electronically excited state, and those in PL to the vibrations of the electronic ground state.\textsuperscript{19} Strong light-matter coupling has only been demonstrated for the former since the fraction of vibrationally excited ground-state molecules is negligible at room temperature. However, as shown schematically in Fig. 6 the transitions responsible for the vibronic structure in PL result in the scattering of excitons to lower energy polaritons, where the missing energy exactly corresponds to that of the vibrational quantum, $E_{01} \approx 173$ meV.\textsuperscript{11}

In appendix B we discuss the approximations needed to apply the known microscopic theory\textsuperscript{11,20} to the present system.\textsuperscript{8} For instance, the microscopic model considers a thin organic material comprising $N \approx O(1)$ layers and placed in the middle of the microcavity\textsuperscript{20,28} whereas the experimental sample embeds an organic material which fills the whole region between the two mirrors ($N \approx O(10^2)$) and has no planar translational invariance.\textsuperscript{12} Moreover, the theory assumes the presence of perfect mirrors, whereas in experiment $\tau_p$ is always finite.

In equation (2) the scattering rate $W^{c\rightarrow p}$ from one molecular exciton (labelled by $j$) to a lasing polariton (labelled by $k$) is related to the parameters of a anthracene microcavity. As discussed in appendix A the scattering rate appearing in the master equation is $W^{c\rightarrow p} = \sum_{k \in A_0} W^{j\rightarrow k}$. Working in the energy space and defining the spectral region of lasing polaritons $E \in [E_{inf}^{A_0}, E_{sup}^{A_0}]$ and the polariton density of states $D(E)$, we get:

$$W^{c\rightarrow p} = \int_{E_{inf}^{A_0}}^{E_{sup}^{A_0}} \frac{\pi^2 |c_p|^{2}}{\hbar} \frac{2}{2MN} f(E_0 - E) D(E) \, dE$$

where $E$ is the energy of the exciton-phonon coupling, $M$ the number of unit cells in the two-dimensional quantization surface and $V_1$ is the fit light-matter coupling. $S$ is the Huang-Rhys parameter, which is approximately $\sim 1.2^6$. See appendix B for more details. The 2D density of states is

$$D(E) = \frac{mM a^2}{2\pi \hbar^2} \theta \left( E - E_{LP}(k = 0) \right),$$

where the effective mass $m$ can be obtained from the fits of the dispersion relations: $m \sim 1.7 \times 10^{-5} m_e$; moreover, $\bar{\nu}_c = 2N/a^2$. The normalized linewidth of (0-1) photoluminescence $f(E)$ is a Lorentzian centered in zero with $FWHM \Gamma = 100$ meV; we also assume $E_{inf}^{A_0} = E_0 - E_{01} = E_{LP}(k = 0)$ whereas $E_{sup}^{A_0} = E_{inf}^{A_0} + 7.5$ meV (see Sec. I). We obtain:

$$W^{c\rightarrow p} = \frac{\pi S |c_p|^{2}}{2} \frac{m V_1^2}{\bar{\nu}_c \hbar^3} \int_{E_{inf}^{A_0}}^{E_{sup}^{A_0}} f(E_{inf}^{A_0} - E) \, dE.$$  (3)

The rate before the integral is equal to $\approx 1.0 \times 10^7$ s$^{-1}$, while the contribution from the integral, which comes from the lineshape, is $\approx 0.047$. Thus, the theoretical microscopic mechanism is $W^{c\rightarrow p} \approx 5 \times 10^6$ s$^{-1}$.

Because the theoretical model neglects effects which can possibly lower the efficiency of the resonant scattering, we consider our estimate to be in good agreement with the values estimated from data in Sec. II.

B. Non-radiative transition

We now consider an alternative and possibly coexisting relaxation channel, which is non-radiative.\textsuperscript{26} An exciton is scattered from the reservoir to one polariton state by the emission of a molecular vibration of the electronic excited state. This is due to the intramolecular exciton-phonon coupling\textsuperscript{26} which has been demonstrated to play a key role in the modeling of the PL of J-aggregates microcavities.\textsuperscript{31,32}

Note that in this case the considered phonon belongs to the electronic excited state, whereas in the radiative case it was related to the electronic ground state. Moreover, the resulting scattering element $W^{c\rightarrow k}$ includes the excitonic content of the outcoming polariton, whereas Eq. (3) is weighted by the photonic Hopfield coefficient.

The scattering rate from one molecular exciton (labelled by $j$) to one lasing polariton (labelled by $k$) is given by\textsuperscript{26}

$$W^{j\rightarrow k} = \frac{2\pi g^2}{\hbar} E_{11}^{\text{rel}} |c_p|^{2} \frac{\pi^2}{2NM} \delta(E_0 - E_{LP}(k) - E_{11}).$$  (4)

where $g = \sqrt{S} \sim 1$ is the strength of the exciton-phonon coupling\textsuperscript{26} $E_{11}$ is the energy quantum of a vibration of the excited state. Even if the Franck-Condon model which we are using prescribes $E_{11} = E_{01}$, this is not necessarily true in general. The factor $|c_p|^{2} / (2NM)$ is the
Hopfield coefficient for the exciton of the molecule $j$ relative to the polariton $k$. Because $c_j^{(e)} = c_k^{(e)} = \sum_j c_j^{(e)} \forall k$, we are assuming that the exciton is equally distributed among all the molecules. This is consistent with the assumptions used in the derivation of the master equation (see appendix A).

The comparison of Eq. (4) with Eq. (B5) for the radiative case shows that the two processes have a similar efficiency. Indeed, using Eq. (B3):

$$\frac{W_{j \rightarrow k}^{\text{RAD}}}{W_{j \rightarrow k}^{\text{NON-RAD}}} = \frac{\pi V_1^2}{2E_1^2} \frac{|c_p^{(p)}|^2}{|c_p^{(e)}|^2},$$

because both $V_1$ and $E_{11}$ are of the same order of magnitude, 100 meV, the efficiency ratio mainly depends on the Hopfield coefficients of the bottom polaritons. Thus, as in our case $|c_p^{(p)}|^2/|c_p^{(e)}|^2 \approx 5$, we expect the radiative mechanism to be the main origin of the excitation transfer which results in lasing, even if to understand the importance of the non-radiative transfer a more detailed analysis is necessary.

In conclusion, we have studied two physical mechanisms which can possibly induce the excitation transfer studied in Sec. II. Using simple models, we have obtained estimates which are in good agreement with those from the data. The photonic and excitonic components of the bottom polaritons are crucial for determining the importance of the two mechanisms. We thus expect that in materials requiring different cavity detunings to match the condition $E_0 - E_{\inf} = E_{\text{lasing}}(k = 0)$, the relevance of the two processes could be reversed. An experimental analysis exploring several organic crystals would thus be of the greatest interest.

IV. TEMPERATURE

Reported data for anthracene microcavities show a reduction of the lasing threshold of slightly less than an order of magnitude once temperature is lowered from 300 K to 12 K. In this section we discuss temperature effects within the framework of the developed model, and the related consequences on the lasing properties.

Experimental studies on the PL from bulk anthracene crystals have shown a strong temperature dependence characterized by spectral narrowing. The temperature dependence obtained using thin crystals grown from solution is shown in Fig. 7. Here, the crystals were grown on silicon substrates to ensure good thermal contact to the cryostat cold finger and were excited using 1 ns-long pulses at $\lambda = 337$ nm. A composite vibronic structure emerges, which can be understood in terms of a high-energy phonon (considered in this work) and of a low-energy phonon, which is not resolved at room temperature because of thermal broadening. Such a system requires the use of two-phonon states in order to exactly reproduce the spectrum, however, we ignore this complication because we are only interested in the phenomenological properties of the line which is responsible for lasing.

The scattering rate $W^{\text{e-\text{ph}}}$ in Eq. (3) depends on temperature via $f(E)$. On the one hand, at low temperature the Lorentzian is narrower, and thus a smaller fraction of the oscillator strength is dispersed into non-lasing modes. On the other hand, only a fraction of the oscillator strength of the (0-1) transition contributes to lasing, because the other lines are far detuned. Additionally, both the quantum yield, estimated at room temperature to be 0.5, and the exciton lifetime $\tau_e$ are expected to increase at low temperature.

In Fig. 7 we compute the dependence of the integral appearing in Eq. (3):

$$I \approx \int_{E_{\inf}^{\text{a}}}^{E_{\sup}^{\text{a}}} f(E_{\inf}^{\text{a}} - E) \, dE$$

on the width of the Lorentzian function $f(E)$ which represents the normalized spectrum of the (0-1) PL emission. Whereas at room temperature the FWHM is $\approx 0.1$ eV, at 12 K it is $\approx 0.01 - 0.02$ eV, and thus $W^{\text{e-\text{ph}}}$ increases of at least a factor of 5.

Roughly speaking, the observed thermal reduction of the threshold is of less than one order of magnitude, and thus similar to the numbers of our estimates. This points out a possible connection between the temperature dependence of the laser threshold and of the PL of anthracene crystals. A more systematic analysis, both theoretical and experimental, goes beyond the scope of this work, and will be the focus of future investigations. As long as the thermal linewidth narrowing is considered, we observe that when the radiative transition is not perfectly resonant with the lasing polaritons it could even result in the opposite effect.

For the sake of completeness, in appendix C we include the thermal population of the vibrations of the molecu-
lar ground state in the master equation (1a) and demonstrate that it can be safely neglected.

V. CONCLUSIONS

In this work, a minimal model to describe the polariton lasing observed in crystalline anthracene microcavities has been developed. Only the essential features of the physical processes involved have been included: the incoherently pumped exciton reservoir, the vibronically assisted radiative scattering from the reservoir to the bottom of the lower polariton branch, the onset of bosonic stimulation and the build-up of the polariton population with increasing pump intensity, the polariton losses through the mirrors and bimolecular quenching processes. All the relevant material parameters, except from the bimolecular quenching rate, have been determined independently from the experimental data on the pump dependence of the polariton emission. In particular, the efficiency of the scattering mechanism here considered - which takes into account the prominent role of vibronic replicas in the photophysics of anthracene microcavities - has been calculated microscopically. The numerical simulations obtained are in good agreement with the data and describe well the onset of the non-linear threshold for polariton lasing. A possible reason for the observed temperature dependence of the threshold has also been discussed. The present model could be extended to include further ingredients, in particular polariton-polariton scattering, and be applied to other microcavity systems exhibiting pronounced vibronic replicas.

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Appendix A: Derivation of the Master Equations

We present the derivation of the master-equation (1). We focus on the exciton reservoir (excitons are labeled by \( j \)) and on the polaritons in the \( A_0 \) region, which are resonantly populated by the reservoir (labeled by \( k \)). The dynamics of the system is described by \( N_{\text{exc}} + N_{\text{pol}} \) coupled differential equations:

\[
\begin{align*}
\dot{n}_j &= - \Gamma_j n_j - \sum_{k \in A_0} W_{j \rightarrow k} n_j (1 + n_k) - \sum_{k \notin A_0} W_{j \rightarrow k} n_j + \\
&\quad - \gamma \left( \sum_{j'} n_{j'} + \sum_{k'} |c_{k'}^{(e)}|^2 n_{k'} \right) n_j (1 - n_j) P(t); \\
\dot{n}_k &= - \Gamma_k n_k + \sum_j W_{j \rightarrow k} n_j (1 + n_k) + \\
&\quad - \gamma \left( \sum_{j'} n_{j'} + \sum_{k'} |c_{k'}^{(e)}|^2 n_{k'} \right) |c_k^{(e)}|^2 n_k.
\end{align*}
\]

The term \( \sum_{k \notin A_0} W_{j \rightarrow k} n_j \) describes excitons scattered to other polariton states via other decay mechanism, as for example, lattice phonons and luminescence. We don’t include a similar term \( \sum_{k' \notin A_0} W_{k' \rightarrow k} n_{k'} (1 + n_k) \) in equation (1b) because negligible compared to the efficient direct scattering from the reservoir. The probability of annihilating an exciton (or polariton) because of bimolecular quenching is proportional to the total number of excitons \( \sum_{j'} n_{j'} + \sum_{k' \in A_0} |c_{k'}^{(e)}|^2 n_{k'} \) (we neglect the minor contribution of polaritons \( k' \notin A_0 \)).

In order to derive the master equation for the surface density of excitations \( \nu_e(t) = \sum_{j} n_{j}(t)/A \) and \( \nu_p(t) = \sum_{k} n_{k}(t)/A \) we have to make the following assumptions. We take \( W_{j \rightarrow k} \) to be independent from \( j \) and \( k \in A_0 \), renamed \( W \); the same holds for \( \Gamma_j \), substituted by \( \Gamma_e \) for \( \Gamma_k \), renamed \( \Gamma_p \), and for \( c_{k'}^{(e)} \), renamed \( c_{p}^{(e)} \). We introduce the quantities \( \tilde{W}^e = \sum_{k \in A_0} W \) and \( \tilde{Z}^e = \sum_{k \notin A_0} W_{j \rightarrow k} \). Finally, \( n_j \) and \( n_k \) are not expected to have a significant dependence on \( j \) and \( k \). Clearly, this approach is more justified the more the \( A_0 \)
region is small. We sum the equations (A1a) and (A1b):

\[
\sum_j \dot{n}_j = -\sum_j \left( \Gamma_j n_j - \sum_{k \not\in A_0} W_{j \rightarrow k} n_j (1 + n_k) + \sum_{k \not\in A_0} W_{k \rightarrow j} n_k + \right.
\]

\[
- \gamma \left( \sum_{j'} n_{j'} + \sum_{k'} |c_{k'}^{(e)}|^2 n_{k'} \right) \sum_j n_j + \left. \sum_j (1 - n_j) P(t) \right) \quad (A2a)
\]

\[
\sum_k \dot{n}_k = -\sum_k \Gamma_k n_k + \sum_j \left( \sum_{k} W_{j \rightarrow k} n_j (1 + n_k) + \right.
\]

\[
- \gamma \left( \sum_{j'} n_{j'} + \sum_{k'} |c_{k'}^{(e)}|^2 n_{k'} \right) \sum_k |c_{k}^{(e)}|^2 n_k \quad (A2b)
\]

Using the listed assumptions, we obtain:

\[
\nu_e = -\Gamma_e \nu_e - W_{e \rightarrow p} \nu_e \left( 1 + \frac{\nu_p}{\nu_p} \right) - Z_{e \rightarrow p} \nu_e + \gamma' (\nu_e + |c_p^{(e)}|^2 \nu_p) \nu_e + \left( 1 - \frac{\nu_e}{\nu_p} \right) P'(t) \quad (A3a)
\]

\[
\nu_p = -\Gamma_p \nu_p + W_{p \rightarrow e} \nu_p \left( 1 + \frac{\nu_p}{\nu_p} \right) + \gamma' (\nu_e + |c_p^{(e)}|^2 \nu_p) |c_p^{(e)}|^2 \nu_p \quad (A3b)
\]

which is written in terms of the surface density of excitonic states \(\nu_e = N_{exc}/A = L \epsilon \rho\) and of polaritonic states \(\nu_p = N_{pol}/A\), of the pump rate density \(P'(t) = \nu_p P(t)\) and of the quenching parameter \(\gamma' = \gamma A\).

**Appendix B: Scattering Rate Due to Radiative Transition**

We compute the scattering rate of a molecular exciton to a lasing polariton state via radiative emission assisted by the emission of a vibration (see Sec. [III]).

Linear optical properties of strongly-coupled microcavities can be quantitatively described with a simple model for the light-matter interaction which conserves the in-plane momentum:

\[
H_k = \begin{pmatrix}
\hbar \omega_k & V_1 & V_2 & V_3 \\
V_1^* & E_{10} & 0 & 0 \\
V_2^* & 0 & E_{11} & 0 \\
V_3^* & 0 & 0 & E_{12}
\end{pmatrix}.
\]

The energy of the cavity photon, \(\hbar \omega_k = (c/n_{eff}) \sqrt{|k|^2 + \pi^2/L^2}\) and the energy of the exciton accompanied by \(i\) vibronic replicas, \(E_{1i}\), are measurable quantities. The couplings \(V_i\) can be fit from the measured polariton dispersion relations which are the eigenvalues of (B1).

We focus on the \(b\) exciton and on light polarized along \(b\); the microscopic expression of their coupling is:

\[
V^m_1(k) = \frac{\mu e^{-S/2}}{n_{eff}} \sqrt{\frac{8\pi \hbar \omega_k}{La^2}} \sqrt{\frac{2(N + 1)}{\pi}} \sqrt{1 - \frac{|k|^2}{L^2} + |k|^2}
\]

(B2)

where \(S\) is the Huang-Rhys parameter, \(\mu\) is the dipole moments of the \(b\) Davydov branch, \(n_{eff}\) is the effective refractive index, \(\hbar \omega_k\) is the photon energy, \(L\) is the effective length of the cavity, \(a\) is the spacing between molecules, \(N\) is the number of monolayer comprising the organic material. Neglecting the dependence on \(k\), we identify the fit parameter \(V_1\) of equation (B1) with the following microscopic expression:

\[
V_1 = V^m_1(k = 0) = 4\mu e^{-S/2} \frac{(\pi c h)^{1/2}}{La n_{eff}^{3/2}} (N + 1)^{1/2}.
\]

(B3)

As a simple consistency check of (B3), we take \(n_{eff} = 1.74\) and \(L = 120\) nm and \(\mu \sim 1\) D: we obtain \(V_1 \sim 74\) meV, whose order of magnitude is compatible with the fit value of 108 meV. Thus, even if the theoretical estimate is based on the assumption of a perfect cavity without losses, whereas the fit value refers to a realistic imperfect system, the error is under control.

Let’s focus on the light-matter interaction responsible of the exciton radiative recombination assisted by the emission of one molecular vibration:

\[
\dot{V}_n = -\mu \left( -\sqrt{S e^{-\frac{S}{2}}} \right) \hat{v}_n^1 \hat{B}_n + \gamma' \sum_k \left( \frac{4\pi \hbar \omega_k}{La^2 M n_{eff}^2} \frac{\omega_k - \omega_{k} \epsilon}{\omega_k} \hat{a}_{kp}^\dagger \right) + H.c.
\]

where \(M\) is the number of unit cells included in the two-dimensional quantization area, \(\hat{v}_n^1\) is the operator creating a vibronic replica at the ground state of the molecule placed at \(n\), \(B_n\) is the operator destroying an electronic excitation, \(\hat{a}_{kp}\) is the photon field operator with \(p\) polarization.

We are interested in the scattering of the molecular exciton at \(n\) into the lasing polariton region \(A_0\). Using the Fermi Golden Rule, the scattering rate from one molecular exciton (labelled by \(j\)) and a lasing polariton (labelled by \(k\)) is (see also appendix [A]):

\[
W_{j \rightarrow k} = \frac{2\pi \mu S}{\hbar} \frac{e^{-S/2}}{4} \frac{\pi c h}{La^2 n_{eff}^2} \frac{1}{M} |c_p| |d(E_0 - E_{LP}(k) - E_{01})|^2
\]

(B5)

We are assuming that the scattering process only depends on the energy of the final state accordingly with the picture of bottom polaritons as states with a non-defined wavevector and with similar optical properties.

We can make the previous equation more realistic by substituting the delta function \(d(E)\) with the normalized lineshape of the (0-1) photoluminescence, dubbed here \(f(E)\). In this work, we consider a Lorentzian linewidth
FIG. 9. Time-integrated surface density of polaritons \( \int \nu_p(\tau) d\tau \) calculated from solution of Eq. (C5) (lines) and from experimental data (squares). The calculation parameters are: (dashed line) \( \tau_p = 85 \) fs; (solid line) 1 ps. The fit parameters are as in Fig. 4.

\[
f(E) = \Gamma/(2\pi(E^2 - (\Gamma/2)^2)).
\]
Comparing this last expression to (B3) we get \((N + 1 \approx N)\):

\[
W^{j \rightarrow k} \approx \frac{V^2 \pi^2 S|c_p|^2}{2} \frac{1}{MN} f(E_0 - E_{LP}(k) - E_{01})
\]

This expression links the scattering rate assisted by the emission of one molecular vibration to known parameters.

Appendix C: Thermal Population of Vibronic Replicas

Up to now the scattering of one polariton to the exciton reservoir assisted by the absorption of a replica of the ground state has been neglected. However, at room temperature, a fraction of the molecules quantified by the Bose-Einstein distribution is in a vibrationally excited state; taking \( E_{01} \approx 173 \) meV and room temperature \((k_BT \approx 25.6 \) meV\) the 2D density of such molecules is:

\[
\tilde{\nu}_e = \frac{1}{e^{E_{01}/k_BT} - 1} \approx 5 \times 10^{16} \text{ cm}^{-2} \times 10^{-3} \approx 5 \times 10^{13} \text{ cm}^{-2}.
\]

Even if \( 10^{-3} \) is a small fraction in absolute terms, the density of phonon-excited molecules is comparable to the density of excitons of the previous simulations (see e.g. Fig. 5). Thus, polariton depletion because of back-scattering into the exciton reservoir can affect the gain of the lasing process.

In order to study the effect of this process, we include in the right-hand side of equation (A14) the term:

\[
- \sum_j W^{j \rightarrow k} m_j n_k
\]

where the sum is over all the molecules and \( m_j \) is the population of the phonon state of the \( j \)-th molecule. We do not consider \( m_j \) as a dynamical variable but rather consider the thermal equilibrium population: \( m_j \approx (e^{E_{01}/k_BT} - 1)^{-1} \). Consequently, Eq. (A3) includes the term:

\[
- \frac{1}{A} \sum_{k \in A_0} \sum_j W^{j \rightarrow k} m_j n_k = -W^{e \rightarrow p} \frac{\tilde{\nu}_e}{e^{E_{01}/k_BT} - 1} \frac{\nu_p(t)}{\tilde{\nu}_p}.
\]

The depletion rate is estimated as:

\[
-W^{e \rightarrow p} \frac{\tilde{\nu}_e}{e^{E_{01}/k_BT} - 1} \frac{\nu_p(t)}{\tilde{\nu}_p} \approx -10^{-5} \times 10^{-9} \times 10^{-3} \text{ s}^{-1} \times \nu_p(t).
\]

We compare it to the polariton decay rate, \( \Gamma_p > 10^{12} \text{ s}^{-1} \), and conclude that it is not the dominant polariton depletion mechanism. This would be the case for microcavities with larger Q factors, which thus would benefit from lower temperatures freezing the main polariton decay channel. The contribution of this process on the reservoir population is also negligible, because polaritonic states \( N_{\text{pol}} \) are a negligible fraction of the excitonic states \( N_{\text{exc}} \).

We now take into account the population of phonon-excited molecules \( \nu_v(t) \approx \sum_j m_j(t)/A \) dynamically. We consider the following master equation (the derivation is a generalization of the previous discussion):

\[
\dot{\nu}_e = - (\Gamma_e + Z^{e \rightarrow}) \nu_e - W^{e \rightarrow p} \nu_e \left( 1 + \frac{\nu_p}{\tilde{\nu}_p} \right) + W^{e \rightarrow p} \frac{\nu_p}{\tilde{\nu}_p} \nu_v +
\]

\[
- \gamma' \left( |c_p|^2 \nu_p \right) \nu_e + \left( 1 - \frac{\nu_e}{\tilde{\nu}_e} \right) P'(t)
\]

\[
\dot{\nu}_p = -\Gamma_p \nu_p + W^{e \rightarrow p} \nu_e \left( 1 + \frac{\nu_p}{\tilde{\nu}_p} \right) - W^{e \rightarrow p} \frac{\nu_p}{\tilde{\nu}_p} \nu_v +
\]

\[
- \gamma' \left( |c_p|^2 \nu_p \right) \left( |c_p|^2 \nu_p \right) \nu_p
\]

\[
\dot{\nu}_v = -\Gamma_v \left( \nu_v - \frac{\nu_e}{e^{E_{01}/k_BT} - 1} \right) - W^{e \rightarrow p} \frac{\nu_p}{\tilde{\nu}_p} \nu_v +
\]

\[
+ W^{e \rightarrow p} \frac{\nu_p}{\tilde{\nu}_p} \left( 1 + \frac{\nu_p}{\tilde{\nu}_p} \right)
\]

\( \Gamma_v \) models the relaxation to the vibrational ground state, and the presence of an equilibrium population is taken into account; we set \( \Gamma_v = 10 \) ps. The other two terms of equation (C5a) are due to polariton back-scattering to the exciton reservoir and to the exciton radiative recombination respectively.

In Fig. 4 we show the results, which are obtained with the same parameters used in the main text. No qualitative difference with Fig. 3 is observable and this refinement can not take fix the above-threshold discrepancy. For \( \tau_p = 1 \) ps (solid line), the situation in which the back-scattering efficiency is most comparable to the polariton PL rate, a slight shift of the threshold towards higher pump fluences is observable.

Direct inspection of the time dependence of \( \nu_v(t) \) shows that at threshold the system is driven out of equilibrium on the time-scale of \( 5 \sim 50 \) ps (Fig. 10). However, even
FIG. 10. Time-dependence of the relative surface density of exciton $\nu_e(t)/\nu_0$ (dash-dotted lines), of lasing polaritons $\nu_p(t)/\nu_0$ (dotted lines) and of vibrationally excited molecules $\nu_v(t)/\nu_0$ (dashed lines) at threshold ($E_{\text{th}} = 300 \text{ nJ}$, $\tau_0 = 85 \text{ fs}$). Top: $\nu_v(t)$ is a dynamical quantity; bottom: $\nu_e(t) = \nu_c/(e^\beta E_{\text{th}} - 1)$ is static.

when $\nu_e(t)$ is consistently driven out of equilibrium, no significant difference in the population of excitons and of polaritons is observable. Polaritons are so few that only massive back-scattering to exciton states can affect the reservoir population. On the other hand, the polariton escape through the mirrors remains the dominant timescale for the polariton depletion.

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