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2014 EPL 105 47009

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A Letters Journal Exploring the Frontiers of Physics

Made open access 29 December 2014

February 2014

EPL, **105** (2014) 47009
doi: 10.1209/0295-5075/105/47009

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Polariton condensation with saturable molecules dressed by vibrational modes

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received 31 October 2013; accepted in final form 6 February 2014
published online 3 March 2014

PACS `71.36.+c` – Polaritons (including photon-phonon and photon-magnon interactions)
PACS `03.75.Kk` – Dynamic properties of condensates; collective and hydrodynamic excitations, superfluid flow
PACS `78.66.Qn` – Polymers; organic compounds

Abstract – Polaritons, mixed light-matter quasiparticles, undergo a transition to a condensed, macroscopically coherent state at low temperatures or high densities. Recent experiments show that coupling light to organic molecules inside a microcavity allows condensation at room temperature. The molecules act as saturable absorbers with transitions dressed by molecular vibrational modes. Motivated by this, we calculate the phase diagram and spectrum of a modified Tavis-Cummings model, describing vibrationally dressed two-level systems, coupled to a cavity mode. Coupling to vibrational modes can induce re-entrance, *i.e.* a normal-condensed-normal sequence with decreasing temperature and can drive the transition first-order.

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Introduction. – Microcavity polaritons (superpositions of photons and excitons) are bosonic quasiparticles which can form a Bose-Einstein condensate (BEC) [1,2]. Experimentally, above a critical density or below a critical temperature polaritons accumulate in low-energy modes, accompanied by enhanced spatial and temporal coherence. Such coherence naturally relates to lasing, but differs in that the occupied states are polaritons, not cavity photons, and the coherence results from stimulated scattering, not stimulated emission [3,4]. At low densities the critical temperature for condensation goes as $k_B T_c \sim \hbar^2 \rho/m$ with ρ and m the density and the mass of polaritons, respectively. At higher densities, when $k_B T_c$ reaches the scale of the light-matter coupling, there is a crossover to an almost density-independent form [5]. Consequently, in order to reach temperatures higher than the 20–100 K attained in CdTe [1] and GaAs [2], one requires materials with larger light-matter coupling, such as GaN and ZnO [6–8]. Alternatively, one may replace the Wannier excitons in inorganic semiconductors with electronic excitations in organic molecules, which may have large oscillator strengths, allowing room temperature condensation.

Recent experiments on organic-based microcavity polaritons have explored a wide variety of organic materials. These include molecular crystals of anthracene [9,10], molecular aggregates coupled by Förster transfer, *e.g.* J-aggregates of cyanine dyes [11,12] and amorphous molecular structures of conjugated polymers [13]. Several of these systems have shown condensation or lasing of polaritons at room temperature: Polariton lasing has been reported with molecular crystals of anthracene [10], and polariton lasing using J-aggregates, where a separate organic dye acts as a gain medium has been seen [14]. Very recently, experiments on amorphous materials have shown interacting polariton condensates [15], and the formation of a thermalised and an interacting polariton BEC [13].

The materials used in these experiments differ in their structure, and especially in the mechanisms for electronic excitation transfer between and within molecules. However, as discussed below, these differences have a reduced significance in the presence of strong light-matter coupling. As well as the obvious significance of room temperature BEC, understanding polariton condensation in these organic materials may facilitate lower lasing thresholds

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enabling electrically pumped organic lasers [16]. The theory of excitons and polaritons in molecular crystals has a long history [17–19]. Recent theoretical work on polariton condensation has generally modelled the system as a weakly interacting gas of polaritons derived from a model of saturable absorbers [20]. Rate equations based on such models have been used to calculate the luminescence spectrum [21,22] and relaxation processes [23,24]. The effects of disorder on the spectrum [25,26] have also been considered. Such theories well describe the very low density regime. The approach we will describe below, starting from two-level systems, encompasses also higher densities.

We focus on molecular crystals, consisting of many separate saturable optical absorbers. In the absence of an optical cavity, hopping of excitations between molecules is crucial in determining the band structure and polarisation properties of Frenkel excitons [17–19]. However, when strongly coupled to an optical cavity, the rate of hopping between molecules is dwarfed by cavity-photon–mediated transport. The effective exciton mass due to the exciton hopping is four orders of magnitude larger than the photon mass, and the polariton splitting is at least an order of magnitude larger than exciton bandwidth. Consequently, exciton hopping can generally be neglected when considering the thermodynamics of polaritons.

Following these considerations, we study a model of two-level systems, describing localised electronic excitations of the molecules, coupled to a common photon mode. This is a variant of the Dicke [27] or Tavis-Cummings [28] model. Hepp and Lieb [29] showed that in the canonical ensemble above a critical light-matter coupling strength, the system undergoes a continuous phase transition from a normal to superradiant state. The critical temperature of this transition can be suppressed to $T = 0$, producing the quantum phase transition much discussed for cavity and circuit QED [30–32]. It has, though, long been thought that the phase transition of this model in the canonical ensemble is forbidden [33]. Recently, however, this debate has been re-opened [32,34,35] suggesting that the transition in the canonical ensemble may in fact be possible [36]. In this paper we focus on the grand canonical ensemble where this issue does not arise [37]. In this ensemble the phase transition is identical to the BEC transition [5,37,38], with the superradiant state corresponding to the condensate.

Work on kinetics of polariton relaxation [23,24] has shown the crucial role of the local vibrational modes in energy relaxation: Polariton relaxation is most efficient when the polariton splitting is resonant with the vibrational frequency. The importance of strong coupling to vibrational modes has also been recognised in contexts such as energy transfer in light harvesting complexes [39,40]. In particular, these works show that such vibrational modes cannot simply be regarded as Markovian baths leading to dephasing or dissipation. In order to consider such effects within the context of saturable optical absorbers, we need to augment the Tavis-Cummings model by introducing an additional feature: Coupling between electronic excitations and local vibrational modes of the molecules.

In this letter, we consider the effects of coupling between the two-level systems and local vibrational modes on collective behaviour within the Tavis-Cummings model. Current experiments are far from equilibrium due to the combination of loss of photons, external incoherent pumping and the dephasing of vibrational modes caused by coupling to other molecules. Coupling between electronic excitations and vibrational modes can act as a route to relaxation and thermalisation, but as we will show, this is not its only rôle. The driven-dissipative Tavis-Cummings model has been used to explore the crossover between polariton condensation and "textbook" lasing [41,42], and so the model we present provides a basis to address similar questions in the presence of vibrational modes. However, in this letter we focus on first providing a firm foundation in thermal equilibrium, as a reference to which the out-of-equilibrium physics can be compared. We show how coupling to vibrational modes modifies the phase diagram; such modifications are greatest when there is strong coupling to soft vibrational modes, so we focus on such a regime. To explain this behaviour we consider the excitation spectrum and discuss how the typical BEC scenario of condensation when the chemical potential hits the polariton spectrum is modified by the presence of multiple vibrational sidebands. Finally, we consider the limit of very large coupling to vibrational modes, and explain how this can drive the phase transition first order.

Model. – The model we study generalises the Tavis-Cummings model [28], which describes N two-level systems (electronic states of molecules) coupled to a single-photon mode in the microcavity. To this we add a coupling between two-level systems and vibrational modes of the molecules. We thus have (setting $\hbar = 1$ throughout)

$$\hat{H} - \mu\hat{L} = \tilde{\omega}_c\hat{\psi}^\dagger\hat{\psi} + \sum_{n=1}^{N}\Bigg[\frac{\tilde{\epsilon}}{2}\sigma_n^z + g\left(\sigma_n^+\hat{\psi} + \hat{\psi}^\dagger\sigma_n^-\right) + \Omega\hat{a}_n^\dagger\hat{a}_n + \frac{\Omega\sqrt{S}}{2}\sigma_n^z\left(\hat{a}_n + \hat{a}_n^\dagger\right)\Bigg]. \tag{1}$$

Here $\hat{L} = \hat{\psi}^\dagger\hat{\psi} + \sum_n \sigma_n^z/2$ is the total number operator, $\hat{\psi}^\dagger$ is the creation operator for a cavity photon, $\tilde{\omega}_c = \omega_c - \mu$, where ω_c is the photon frequency. Two-level systems are described by the Pauli matrices σ_n^i, $\tilde{\epsilon} = \epsilon - \mu$, where ϵ is the bare optical transition frequency of the molecules, and the bare molecule-photon coupling strength is denoted g. Vibrational excitations of a molecule, with frequency Ω, are created by the operators $\hat{a}_n^\dagger$. The coupling of these excitations to the electronic state of the molecule is $\Omega\sqrt{S}$, where the Huang-Rhys parameter S quantifies the average number of vibrational excitations emitted or absorbed in an electronic transition. The characteristic polariton splitting is determined by $g\sqrt{N}$. (NB, as discussed later, $g\sqrt{N}$ is only *equal* to the polariton splitting in the absence of coupling to vibrational modes.) The chemical potential μ controls the total excitation density, $\langle L \rangle$. Equation (1) describes a cavity single mode, while a planar microcavity supports multiple transverse cavity modes with different in-plane momenta. Neglecting these other modes is equivalent to neglecting the depletion of the condensate by long wavelength fluctuations, *i.e.* considering the mean-field (MF) theory. In [5] it was shown that these fluctuations are only relevant at extremely low densities and that MF theory, as we consider in this manuscript, is otherwise accurate.

We next discuss the parameters we use when presenting numerical results. In the following we measure energies in units of a characteristic scale $g_0\sqrt{N}$, corresponding to a typical polariton splitting. In some cases it is useful to show evolution of phase boundaries with g, in which case we plot as a function of g/g_0. For the energies ω_c, ϵ, the physically important quantity is the photon-exciton detuning, $\Delta = \omega_c - \epsilon$. We consider a case where the cavity frequency is detuned above the molecular transition and we choose $\Delta = 2g_0\sqrt{N}$. We choose this detuning for two reasons. Firstly, a thermal equilibrium BEC of polaritons in inorganic materials [1] required $\Delta > 0$, as this increases the excitonic fraction, and hence the scattering and thermalisation rate of the polaritons [43,44]. Secondly, the Tavis-Cummings model can show multiple normal-superradiant phase transitions [38] when $\Delta > 0$. This is linked [45] to the “Mott lobes” in the Jaynes-Cummings-Hubbard model [46]. We explore whether such Mott lobes survive coupling to vibrational modes.

The parameters S and $\Omega/g_0\sqrt{N}$ control the effects of the vibrational modes. To clearly observe the effects of vibrational dressing it is necessary to consider relatively large Huang-Rhys factors, corresponding to “ultrastrong” coupling to vibrational modes. We present results for both $S = 2$ and $S = 6$. While these values are quite large for organic emitters (for anthracene [47] $S = 0.182$), values such as $S = 3.3$ have been seen for LO phonons in carbon nanotubes [48]. Some features of vibrational dressing do survive for small S, though in a subdued manner, particularly the behaviour of the excitation spectrum. Regarding Ω, distinct behaviour occurs for soft modes, $\Omega \ll g_0\sqrt{N}$, *vs.* stiff modes, $\Omega \sim g_0\sqrt{N}$. We show that a soft mode is required for a re-entrant phase boundary, while the first-order transition requires a stiffer vibrational mode. We thus present results for $\Omega/g_0\sqrt{N} = 0.05, 0.5$. The latter value is comparable to that for anthracene [47] $\Omega = 42\,\text{meV}$ measured in units of the polariton splitting of ref. [9]. Such stiff modes arise due to the π-bonded carbon rings.

Phase diagrams and re-entrance. – The Hamiltonian (1), supports two distinct phases: normal and condensed. The order parameter distinguishing these phases is the expectation of the photon field $\langle \hat{\psi} \rangle$. In the following, we shall define a rescaled order parameter $\lambda = \langle \hat{\psi} \rangle / \sqrt{N}$. In the normal phase $\lambda = 0$, whereas in the condensed phase there is a macroscopic expectation of the photon field so $\lambda \neq 0$. In the various phase diagrams, we plot a colour map of the rescaled order parameter, λ.

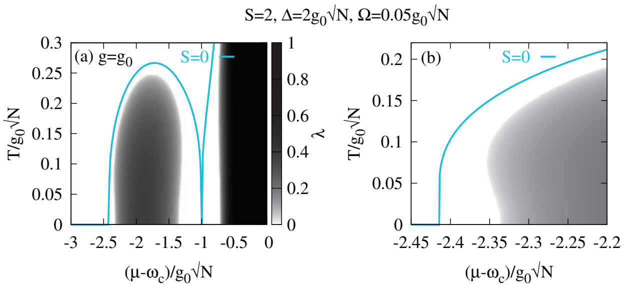

Fig. 1: (Colour on-line) (a) Grayscale map of order parameter *vs.* temperature and μ, both measured in units of $g_0\sqrt{N}$. The solid line shows the phase boundary with $S = 0$ for comparison. (b) A close-up of the re-entrance, shown for clarity. Parameters: $\Delta = \omega_c - \epsilon = 2g_0\sqrt{N}$, $S = 2$, $\Omega = 0.05g_0\sqrt{N}$.

The equilibrium phase diagram can be calculated within a MF treatment of the photon field, known to be exact [38] in the thermodynamic limit $N \to \infty$, $g\sqrt{N} \to$ const. The MF theory yields the self-consistency condition $\tilde{\omega}_c \lambda = -g\sqrt{N}\langle \sigma^- \rangle$, where the polarisation $\langle \sigma^- \rangle$ is found by exactly diagonalising the on-site problem

$$h = \left[\tilde{\epsilon} + \Omega\sqrt{S}\left(\hat{a} + \hat{a}^\dagger\right)\right]\frac{\sigma^z}{2} + g\sqrt{N}\left(\lambda\sigma^+ + \text{H.c.}\right) + \Omega\hat{a}^\dagger\hat{a} \tag{2}$$

numerically, whilst truncating the maximum number of vibrational excitations, n_{max}, at $n_{max} \gg S$, and thermally populating the resulting eigenstates. Anticipating possible first-order transitions, one must also compare the free energies of the normal ($\lambda = 0$) and condensed ($\lambda \neq 0$) solutions to determine the global minimum free energy.

Figure 1 shows a phase diagram: Critical temperature as a function of chemical potential. The gross structure of the phase diagram seen in fig. 1(a) (grayscale) is similar to that seen for $S = 0$ (solid blue line) [38,45], having two separate condensed regions. Coupling to vibrational modes changes some features. Firstly, the condensed region shrinks. This is because the *effective* coupling strength to light is suppressed by the dressing of vibrations. Secondly, re-entrant behaviour as a function of temperature is introduced, fig. 1(b), *i.e.* on decreasing temperature near the edge of the lobe, there is a sequence of transitions from normal to condensed and back to normal. The re-entrance can be explained by the effect of vibrational sidebands. Generally, condensation occurs when the chemical potential reaches a polariton mode, leading to a macroscopic occupation of that mode. If there is a sideband below the bare polariton, then condensation will occur at a smaller chemical potential. Such sidebands are associated with transitions from a vibrationally excited electronic ground state to an electronic excited state with fewer vibrational excitations, and as such they only occur when vibrational modes are thermally occupied, *i.e.* for, $k_B T > \Omega$. Since the characteristic temperature required for the condensed phase (except at $\mu \to \omega_c$) is $k_B T \sim g\sqrt{N}$, re-entrance is only visible if $\Omega \ll g\sqrt{N}$.

Photoluminescence spectrum. – Further understanding of the origin of the re-entrance can be found by looking at the nature of the mode which condenses. For a second-order phase transition, the mechanism is as described earlier: When the chemical potential reaches a bosonic mode, which cannot be saturated, it will become macroscopically occupied. However, this presents an apparent paradox for a system with vibrational sidebands. The luminescence spectrum formally has an infinite number of sidebands both above the bare polariton mode, associated with creating additional vibrational excitations upon a transition and, at $T > 0$, below the bare polariton, associated with destroying existing thermally populated vibrational excitations. Thus, at any non-zero temperature, there are an infinite number of modes below the bare polariton, which one would expect to become macroscopically occupied, and so condensation would appear to be possible at arbitrarily negative chemical potentials. This is not observed, as shown in fig. 1(a).

The resolution of this apparent paradox lies in the changing nature of the normal modes as one varies the chemical potential. The normal modes arises from the hybridisation of the photon with the various vibrational sidebands of the molecular transition. The photon, being bosonic in nature, has an unbounded occupation. The molecular excitation, on the other hand, is a hard-core boson with occupation zero or one, and so cannot be macroscopically occupied. In general, polariton modes are superpositions of the bosonic cavity field and the hard-core bosonic molecular excitations. As such, because the nature of the mixture varies, there are points where the mode can be purely excitonic, *i.e.* has a vanishing photon component. Condensation can only occur if the chemical potential hits a mode which has some photon component (measured by the spectral weight). The crossing of a purely excitonic point would lead to the inversion of two-level systems, but no condensation.

Figure 2(a) shows the photon spectral weight of the normal modes along with the chemical potential. The spectral weight of the sidebands is increasingly small as one goes to transitions involving larger differences of numbers of vibrational excitations, but as long as the spectral weight is not exactly zero, these modes appear susceptible to becoming macroscopically occupied. There are many places where the chemical potential appears to cross the vibrational sidebands, but crucially, all these crossings are avoided because the photon spectral weight of the sideband vanishes at these specific points, *i.e.* the mode becomes purely excitonic. After such an avoided crossing, the spectral weight of the mode becomes negative. The Bose occupation function, $n_B(\omega) = \left[e^{\beta(\omega-\mu)} - 1\right]^{-1}$, is negative for energies below the chemical potential. When a negative spectral weight is combined with a negative occupation, they give a meaningful positive luminescence spectrum [49] $P(\omega) = -n_B(\omega)\Im\left[\pi\mathcal{D}(i\omega_n = \omega - \mu + i0)\right]$. Technical details of the calculation of the Green's function, $\mathcal{D}$, are given in [50].

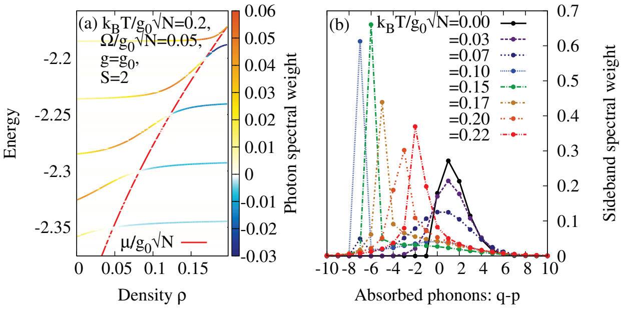

Fig. 2: (Colour on-line) (a) Spectral weight of normal modes *vs.* density of excitations ρ (number of excitons per molecule). Lines are coloured according to their spectral weight (white corresponding to zero weight). The solid (red) line shows the chemical potential. (b) Spectral composition of the mode which acquires a macroscopic occupation for various temperatures. Each line shows the discrete probability distribution for the number of phonons absorbed in the associated mode. Parameters: $S = 2, k_B T = 0.2 g_0\sqrt{N}, \Delta = 2g_0\sqrt{N}, \Omega = 0.05 g_0\sqrt{N}$.

Figure 2(b) shows the composition of the mode which acquires a macroscopic occupation, exactly at the critical point, for various temperatures (see [50] for how this is calculated). At low temperature the number of vibrational quanta can only increase; there are no vibrational excitations in the ground state. At high enough temperature, $k_B T > \Omega$, the vibrational mode of the electronic ground state is thermally populated. As a consequence, the re-entrant behaviour as a function of T appears in fig. 1(a). This corresponds to the emission of vibrational quanta in the electronic transition at the critical point, *i.e.* sideband spectral weight occurs at negative $q - p$, as clearly illustrated in fig. 2(b).

First-order transition in large-S limit and variational polaron transform. – We now turn to consider the behaviour when $S \gg 1$. Such values, which correspond to ultrastrong coupling to vibrational modes, are interesting because, as seen in fig. 3 for $S = 6$, they can lead to first-order transitions into the superradiant state. At small T the strength of the first-order jump is largest at points near to, but not exactly at, $\mu = \epsilon$. For yet larger S (not shown) a first-order jump can also occur within the condensed phase. If viewed as a dynamical system, the first-order jump in the field could be potentially regarded as an optical switch. The size of jump of λ can be controlled by varying the ratio $\Omega/g\sqrt{N}$. First-order transitions have also recently been noted within other variants of the Tavis-Cummings model [51].

The existence of a first-order phase transition can be understood by considering the extent of polaron formation at large S, *i.e.* the extent of entanglement of the vibrational and electronic states of the molecule. Since we always consider MF theory for the photon mode, there is

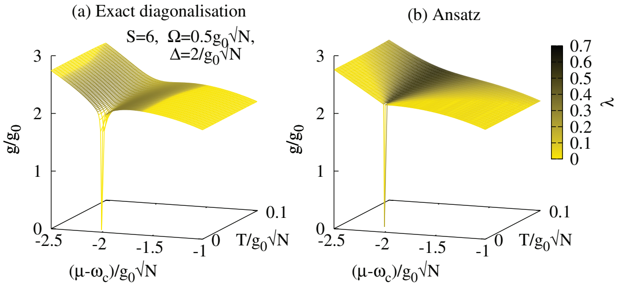

Fig. 3: (Colour on-line) Critical g/g_0 *vs.* chemical potential and temperature for $S = 6$. Calculated by exact diagonalisation of eq. (2) (a), vibrational MF ansatz (b). The colour scale shows $\lambda = \langle\psi\rangle/\sqrt{N}$ at the phase boundary: Light (yellow) colours imply a 2nd-order transition, whereas dark (black) ones indicate a strongly 1st-order transition. Around resonance the transition is always (weakly) 1st order. Parameters: $\Omega = 0.5g_0\sqrt{N}, \Delta = 2g_0\sqrt{N}$.

never entanglement between the photon mode and other modes. The entanglement we consider corresponds to conditional displacement of the vibrational mode, dependent on the state of the two-level system. Such entanglement reduces the overlap between the electronic ground and excited states, and so reduces the coupling to light. Such entanglement also lowers the vibrational energy. This is favoured in the normal state. In the condensed state, it is instead favourable to increase the optical polarisation by suppressing the entanglement, and having similar vibrational configurations for both electronic states. As a result, at a given value of g it is possible to sustain a self-consistent solution both for the normal state and the condensed state. A first-order transition arises due to switching between these states.

To further elucidate this first-order transition, we introduce a variational ansatz which captures the behaviour at large S. This ansatz can be framed as an additional MF approximation for the vibrational modes. However, to allow for the entanglement between vibrational modes and the electronic states discussed above, we first make a variational polaron transform [52,53] $\hat{H} \to \hat{H}' = e^{\hat{K}}\hat{H}e^{-\hat{K}}$, where $\hat{K} = \frac{\eta}{2}\sqrt{S}\sigma^z(\hat{a}^\dagger - \hat{a})$. This transform conditionally displaces the vibrational mode dependent on the state of the two-level system. This will therefore transform a product state to an entangled state. By using such a displacement followed by a MF theory, *i.e.* a product state, we obtain a state which is effectively entangled in the original basis, with the entanglement depending on η. Thus, this transform followed by the MF approximation $\hat{a} \to \alpha$, corresponds to a variational approach with η, α, and λ as variational parameters. This ansatz is valid if the vibrational states are approximately coherent states, which requires $S \gg 1$. The free energy of this vibrational MF theory can be written as

$$\frac{F}{N} = \tilde{\omega}_c\lambda^2 + \Omega\alpha^2 - \frac{\Omega S}{4}\eta\left(2-\eta\right) - \frac{1}{\beta}\ln\left(2\cosh(\beta\zeta)\right), \quad (3)$$

where $\zeta = \sqrt{\delta^2 + (\tilde{g}\lambda)^2}$ is written in terms of the effective molecular transition frequency δ and vibrationally dressed optical coupling $\tilde{g}$, given by

$$\delta = \frac{\tilde{\epsilon} + 2\Omega\sqrt{S}(1-\eta)\alpha}{2}, \qquad \tilde{g} = g\sqrt{N}e^{-S\eta^2/2}. \quad (4)$$

Minimising this free energy with respect to the variational parameters λ, α and η we obtain the gap equation $\tilde{\omega}_c\lambda = \tilde{g}^2\lambda\tanh(\beta\zeta)/2\zeta$. Defining $\kappa = \tilde{g}^2\lambda^2\tanh(\beta\zeta)/[\zeta^2 - (\delta\tanh(\beta\zeta))^2]$ we may write the equations for α, η as

$$\alpha = \frac{\delta\sqrt{S}\kappa\tanh(\beta\zeta)}{2\zeta\kappa + \Omega}, \qquad \eta = \frac{\Omega}{2\zeta\kappa + \Omega}. \quad (5)$$

The equation for η, describing the extent of polaron formation, is instructive. At small λ or large Ω, $\eta \to 1$, and one has fully developed polarons (fully entangled vibrational and electronic states). If, on the other hand, λ is large, *i.e.* the drive is strong, then $\eta \to 0$ and the polaron formation is suppressed [52,53]. In addition to this behaviour, typical of a variational polaron transform, there is an extra level of self-consistency here: The photon field λ depends on the polarisation of the molecules, and hence the effective coupling strength $\tilde{g}$. When the bare coupling g is small, the photon field is small, and polarons are well developed, further suppressing the effective coupling $\tilde{g}$. At larger g, polaron formation is suppressed, producing a stronger effective coupling $\tilde{g}$. At zero temperature, this leads to a jump within the condensed phase, between a weakly and strongly polarised phase. Within the variational approach, such a jump occurs near $\epsilon = \mu$ if $S > 27/8$. At non-zero temperature the same effect leads to a first-order normal to condensed phase transition.

Figure 3 shows the close match between the variational polaron transform and the exact diagonalisation of eq. (2) in the large-S limit. In this limit, one expects that the vibrational state can be approximately described as a coherent state. For smaller S, the vibrational MF theory predicts more strongly first-order transitions than the exact diagonalisation. Exact diagonalisation shows that the first-order jump reduces and the transition becomes second-order as $S \to 0$ for all values of μ. Note that in the limit $S \to 0$, the vibrational modes are irrelevant, and both the vibrational MF theory and the numerical diagonalisation reduce to the Tavis-Cummings model.

Conclusion. – In conclusion, we have studied the Tavis-Cummings model dressed by local vibrational modes. Coupling to vibrational modes suppresses the critical temperature for the superradiant phase and can induce re-entrance, *i.e.* a sequence of normal-condensed-normal transitions as a temperature decreases. For sufficiently strong coupling to vibrational modes, the phase transition can become first-order, which can be understood within a variational polaron ansatz. We also resolved an apparent paradox raised by the existence of vibrational sidebands in the luminescence spectrum: Although vibrational sidebands exist below the bare polariton frequency, condensation at most of these sidebands is avoided as the photon spectral weight vanishes when the chemical potential crosses such modes. Nonetheless, at large coupling to vibrational modes, the polariton mode which does condense contains a strong admixture of different vibrational sidebands. These results illustrate the rich possibilities arising from collective effects when coupling electronic systems to both radiation and vibrational modes.

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We acknowledge discussions with S. Yarlagadda, B. Lovett and R. Gomez-Bombarelli. JAC acknowledges support from EPSRC, SR from the Cambridge Commonwealth trust, JK from EPSRC program "TOPNES" (EP/I031014/1) and EPSRC (EP/G004714/2). Argonne National Laboratory's work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contract No. DE-AC02-06CH11357. JAC performed the numerical calculations, and SR performed the variational calculations. All authors contributed to the conception of the project, and the preparation of the manuscript.

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