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Nonequilibrium polariton dynamics in organic microcavities

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Microcavities containing a *J*-aggregate forming organic dye were prepared in the strong-coupling regime. Changing the position of the neat organic films within the microcavity allows a tuning of the giant Rabi splitting observed. We set the Rabi splitting to 25 meV and study the thermal activation of the higher-energy polariton emission under excitation off resonance. This is found to exhibit an Arrhenius activation with an energy corresponding to the polariton branch splitting. A constant offset to the upper polariton is observed at low temperature. Microsecond gated spectroscopy reveals that thermalization of the system occurs on the time scale of milliseconds, which contrasts with the polariton lifetime in the range of picoseconds. Bulk sample heating cannot fully account for the slow polariton thermalization observed in steady-state experiments, suggesting that long-lived macroscopic polariton coherence influences the polariton relaxation.

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The control of light-matter interactions in optical microcavities is presently leading to an improved generation of photonic devices and has given rise to a range of interesting physical concepts.[1–9] Whereas weak exciton-photon coupling leads to spectrally pure emission at the energy of the cavity photon mode and a spatially directed emission along the main cavity axis, strong coupling results in the creation of quasiparticles from a quantum-mechanical superposition of exciton and photon states. These optical polaritons have recently attracted considerable attention due to the demonstration of Bose-Einstein-like massive condensates[9] and stimulated scattering exhibiting laserlike amplification without the need of inversion.[6–8] The splitting between the two polariton branches is referred to as Rabi splitting and is governed by the strength of the light-matter interaction, which in turn depends on the oscillator strength of the optically active material. Most studies to date have focused on atomic systems or inorganic quantum wells. However, organic semiconductors are known to have extremely large oscillator strengths and are therefore ideal candidates as optically active materials in microcavities. Giant Rabi splitting, up to an order of magnitude larger than that observed with conventional inorganic materials, has been demonstrated in organic materials embedded in a polymer matrix inside a microcavity.[4,10,11] This allows the strong-coupling regime to be studied at room temperature. Room-temperature polariton emission has also been observed, although rapid thermalization was found to inhibit emission from the upper polariton branch.[10] We have recently demonstrated a *J*-aggregate system suitable for microcavities, which can be prepared in neat films without the need of a host polymer matrix.[12,13] This has allowed us to move the position of the optically active layer inside the cavity and thereby tune the strength of the light-matter interaction, i.e., the Rabi splitting.[14] By tuning to a suitable splitting of 25 meV we are able to observe the expected Boltzmann-type activation of the upper polariton as well as the thermalization of the sample, which occurs on a time scale of milliseconds.

λ/2 microcavities were prepared by spin coating a saturated solution of the specific dye salt 1,1′-diethyl-2,2′-cyanine decahydro-closo-decaborate $[(PIC^+)_2+B_{10}H_{10}^{2}]$ in a 2:1 mixture (weight ratio) of acetonitrile and ethylene dichloride, which forms *J* aggregates in thin solid films. Details of the synthesis and characterization of PIC have been published elsewhere.[15] PIC layers were sandwiched in between a dielectric and a silver mirror with a SiO_2 layer inserted between the metal mirror and the organic layer to prevent luminescence quenching. A detailed description of these cavities and the fabrication procedure can be found in our previous work.[12,14] By including SiO_2 spacer layers between the two mirrors and the dye, we have previously demonstrated a tuneability of the Rabi-splitting energy.[14] Emission spectra were measured with a charge-coupled device camera coupled to a 0.3-m monochromator employing a 1200-lines/mm grating. The photoluminescence (PL) was excited using a frequency-doubled diode laser operating at 532 nm. All measurements were performed in a helium atmosphere in a static flow helium cryostat. Figure 1 shows the absorption and emission spectra of a PIC layer at 4.2 K. The absorption shows the characteristics of a *J* aggregate with a narrow absorption band at 2.179 eV and a full width at half maximum of 41 meV. This is assigned to the exciton of the *J* aggregate. Additional absorption bands are observed at higher energy, which are in agreement with absorption spec-

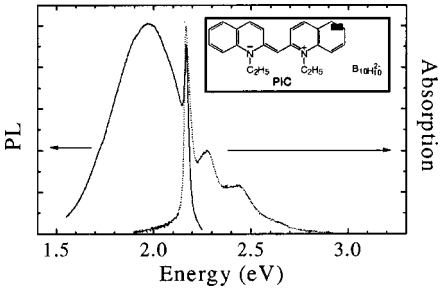

FIG. 1. Absorption (dotted line) and PL spectrum (solid line) of a thin film of the 1,1′-diethyl-2,2′-cyanine decahydro-closo-decaborate dye (PIC) at 4.2 K. Inset: molecular structure of PIC in its specific salt.

tra of different PIC salts (PIC-I, PIC-Cl, PIC-Br) dispersed in various polymer matrices.[16–18] A slight shift of 4 nm of the exciton band to higher energies as well as spectral narrowing is observed with decreasing temperature. The PL spectrum exhibits a narrow exciton peak, offset from the absorption by a Stokes shift of 10 meV. A further broad emission band centered at 1.979 eV is observed, which is thought to originate from a structural defect state.[18] The lifetime of the exciton at 2.179 eV could be estimated using a streak camera setup and was found to be below 4 ps,[19] which is extremely short compared to organic dyes and polymers.

In the weak-coupling regime the density of photon modes inside a cavity is strongly modified compared to the situation in vacuum. Only a few photon modes are allowed due to the restricted geometry, whereas all other photon modes are suppressed. Consequentially, photons can only be emitted into these allowed modes. A broad emission spectrum of an optically active material in vacuum is reduced to the small spectral width of the allowed photon modes. In the strong-coupling regime, however, the situation is different. In this case the simplest picture of the two coupled modes resulting from the photon and exciton is a photon, which creates an exciton, which in turn decays to emit a photon. This process cycles rapidly until the photon leaves the cavity through a leaky mode.[20] Figure 2 shows the low-temperature PL spectra as a function of the detuning between the exciton energy and the cavity photon mode. The exciton energy of the *J* aggregate is defined as 0 meV, and the photon mode can be tuned by varying the angle between the wave vector of the emitted photon and the cavity normal. The PL shows the expected behavior of an optical microcavity in the strong-coupling regime,[21] which is manifested by two polariton emission peaks to the left and right of the exciton. Replotting the peak position of the microcavity PL as a function of the detuning energy in the inset of Fig. 2 yields the typical anticrossing behavior of the two polariton branches. We note that in previous experiments on organic microcavities in the strong-coupling regime, the Rabi splitting has been too large to observe the upper polariton branch in emission at room temperature.[10] The dispersion curve is identical to that obtained from transmission measurements of the cavity.[21] The smallest distance between the two branches of 25 meV, the so-called vacuum Rabi-splitting energy, is achieved at 0 meV detuning. We note that the broad defect band in the PL in

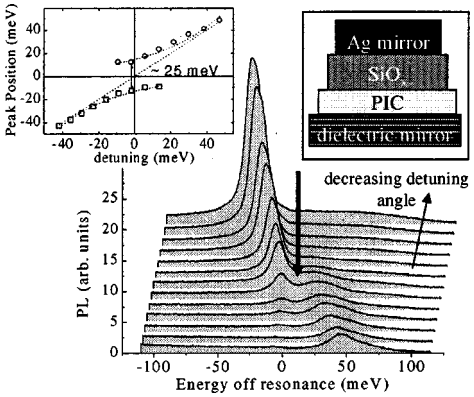

FIG. 2. PL spectra of the microcavity at different angles between the cavity normal and the measurement direction corresponding to different cavity detunings. The bold arrow indicates 0 meV detuning between 29° and 30°. Left inset: Peak position of the high-energy (○) and low-energy (□) bands of the PL spectra as a function of cavity detuning. The dotted lines are a guide to the eye. Right inset: Structure of the microcavity used in this study.

Fig. 1 increases with temperature.[18,19] Although our cavities show clear strong-coupling behavior in transmission at room temperature,[12] a rise in nonradiative PL decay makes PL measurements increasingly difficult at elevated temperatures.

As both polariton branches are observed in the PL of our optical organic microcavity we are able to study the dependence of the relative intensity of the two branches on temperature. Figure 3 shows the PL spectra of the cavity at a fixed detuning angle for different temperatures, normalized to the value of the PL at −12.5 meV. Two effects are clearly seen. First, the ratio of the emission intensities of the high- and low-energy bands increases with increasing temperature. Second, the energetic distance between the two polariton branches increases slightly with increasing temperature. These observations reflect the fact that the energetic position of the exciton of the *J* aggregate shifts with temperature, as does the resonance wavelength of the cavity due to a minor temperature dependence of the refractive index. Both shifts lead to the small change in detuning between the exciton and the cavity photon mode energy. In comparison to inorganic

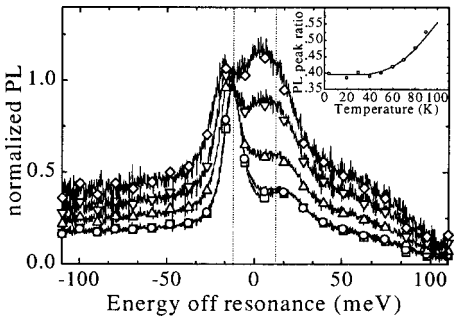

FIG. 3. Temperature dependence of the normalized microcavity PL spectra at fixed detuning: 4.2 K (□), 50 K (○), 100 K (▽), 150 K (△), 190 K (◇). Inset: PL values at +12.5 meV as a function of temperature. The line corresponds to a Boltzmann-type fit with a constant offset and an activation energy of 25 meV.

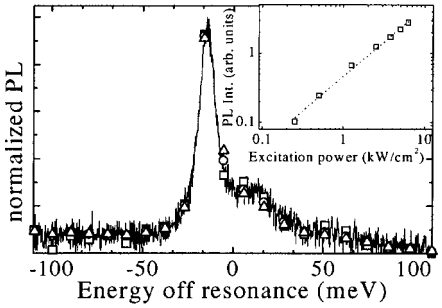

FIG. 4. Normalized polariton PL spectra measured at 4.2 K with different excitation intensities: 0.5 kW/cm^2 (□), 2.5 kW/cm^2 (○), 6.25 kW/cm^2 (▽). The inset shows the integrated PL as a function of laser intensity.

semiconductors, however, the temperature dependence of the PIC exciton is relatively weak, and does not change at all between 4.2 and 90 K. For this reason we consider only the thermal activation of the upper branch in the 4.2–90 K range. The inset in Fig. 3 shows the ratio of the PL of the high-energy peak at 12.5 meV to the PL of the low-energy peak at −12.5 meV as a function of temperature. The line indicates that the data are well described by a Boltzmann-type function of the form $PL(T)=PL_0+A^*e^{-\Delta E/kT}$, with a constant offset PL_0, a preexponential factor A, and the energetic splitting between the two peaks, $\Delta E=25$ meV.

Theoretical studies[22–24] dealing with the temperature dependence of an optical inorganic semiconductor microcavity predict that the PL spectrum can be described in terms of the absorption spectrum weighted by a Boltzmann distribution. The relaxation of the nonresonant excitons via scattering processes ends in a bottleneck state.[22,23] The two radiative polariton states of the strong-coupling regime should subsequently be populated by the absorption and emission of acoustic phonons from a thermally populated phonon reservoir. The interaction with this thermally populated phonon reservoir should lead to a Boltzmann-like activation behavior of the PL. Deviations from the pure Boltzmann law have previously been observed in inorganic microcavities,[25] and have been attributed to exciton trapping effects or elevated electronic temperatures.

From the present experiments a number of possible reasons for the observed nonvanishing upper polariton emission at low temperatures can be safely excluded. A simple explanation would be the saturation of the lower-energy band. As can be seen in Fig. 4, however, PL spectra taken at 4.2 K exhibit no change upon changing excitation intensity. If the lower energy level were to saturate, the higher-energy level should exhibit an increasing population with increasing excitation intensity. From the PL dependence on excitation density we can also exclude temperature-independent exciton-exciton scattering during relaxation[22] as a population pathway of the upper branch, as this should exhibit a square dependence on excitation intensity. The inset in Fig. 4 shows that the sum of the emission of both PL bands increases linearly with excitation intensity, which excludes any bimolecular interaction process as a population pathway. We also note that the local temperature of the organic film could exceed 4.2 K, allowing thermal population of the upper polariton level. If this were the case, however, a strong dependence of the PL spectrum on excitation intensity, which ranges from 0.5–6.25 kW/cm^2, should be observed, as the local film temperature should be a function of the ambient temperature, the interfacial thermal conductivities and heat capacities, and the incident laser power. As seen in Fig. 4, no change in spectrum is observed with a change in excitation intensity, although the spectrum itself depends strongly on temperature. The same result was obtained by modulating the average excitation intensity by chopping the laser beam at different frequencies.

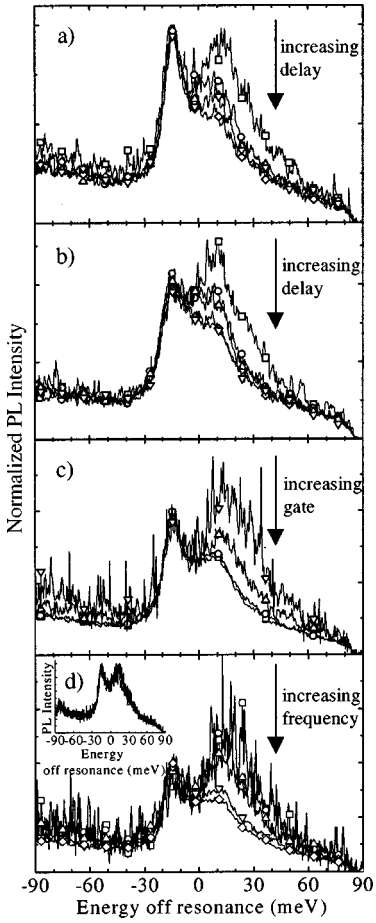

FIG. 5. Gated PL spectra detected after opening of the laser beam normalized to the lower polariton peak. (a) 4.2 K, 10 Hz chop rate, 0.5 ms detection time windows delayed by 0 ms (□), 0.5 ms (○), 2 ms (△), 5 ms (▽), cw (◇). (b) 80 K, 10 Hz chop rate, 0.5 ms detection time windows delayed by 0 ms (□), 0.5 ms (○), 2 ms (△), 5 ms (▽), cw (◇). (c) 4.2 K, 50 Hz chop rate, 0 ms delay, detection time windows of 500 μs (□), 250 μs (○), 100 μs (△), 50 μs (▽). (d) 4.2 K, 0 ms delay, 0.5 ms detection time window at chop rates of 2 Hz (□), 5 Hz (○), 10 Hz (△), 20 Hz (▽), 50 Hz (◇). The inset shows three normalized spectra measured at different excitation intensities (0.75, 1.125, and 1.5 kW/cm^2) (0 ms delay, 0.5 ms gate, 10 Hz chop rate).

Remarkably, however, a small spectral change is observed within 20 ms of opening the laser beam shutter. In order to investigate this further, we performed time gated PL measurements using a mechanical chopper and an intensified gated diode array coupled to a 0.3-m monochromator employing a 1200-lines/mm grating. Figure 5(a) shows the

relative change in PL spectrum at 4.2 K normalized to the lower polariton band for a chop frequency of 10 Hz and an average power of 30 mW detected in 0.5 ms time windows at different delay times. Surprisingly, a slow thermalization of the system is observed on the scale of a few milliseconds, which contrasts with the expected polariton lifetime on the scale of picoseconds. A similarly slow relaxation is also observed at a substantially higher lattice temperature of 80 K, as seen in Fig. 5(b). In this case the decay of the upper polariton emission converges at a higher level than at 4.2 K. A further increase in the high-energy emission band is observed by reducing the width of the detection window immediately after opening the laser beam (0 ms delay), as can be seen in Fig. 5(c). Although the gated spectra of the nonthermalized emission do not depend on the excitation intensity of the laser as seen in the inset of Fig. 5(d), they do depend on the ratio between the on and off periods of the chopper. This is probed in Fig. 5(b) by varying the chopper frequency and detecting immediately after the opening of the chopper in a time window of 0.5 ms. As the frequency is increased, the upper polariton emission decreases.

The observed dependence of the gated spectra on delay time and frequency suggest that a macroscopic thermalization of the sample with the environment is taking place. Upon opening the laser shutter the organic layer heats up rapidly due to thermal irradiation, but heat dissipation by thermal transport through the glass contact layers as well as thermal convection to the helium environment are expected to be rather slow processes. It is instructive, however, to compare Figs. 5(a) and 3. As seen in Fig. 3, the upper polariton emission increases with increasing temperature, but at the same time the lower branch broadens and shifts to lower energy. In Fig. 5(a) a range of relative intensities of the polariton branches comparable to that in Fig. 3 is observed, however, no change in the shape and position of the lower branch occurs. This observation strongly suggests that the measured slow thermalization process *is not* due to a macroscopic heating effect, in agreement with the steady-state PL measurements as a function of excitation intensity.

Macroscopic polariton coherence, described in terms of dynamic Boson condensation, has been observed in inorganic microcavities over time scales of up to 1 ns,[5] three orders of magnitude longer than the polariton lifetime. In the present case, collective polariton relaxation is observed on time scales nine orders of magnitude larger than the polariton lifetime, which seems physically implausible. The lattice temperature in the measurements in Fig. 5 remains unchanged as manifested by the absence of a change of the lower polariton peak, so a tentative explanation of the observed dynamics may be based on energy accumulation in a dynamic state on the upper polariton level with extremely slow dissipation to the lower polariton level. We note, however, that the upper polariton peak population clearly also depends on the ambient temperature. A similar cavity with a Rabi splitting of 50 meV, which only exhibits emission from the lower polariton at 4.2 K, showed no trace of the upper polariton emission under gated detection.

Our results suggest that there is a wide range of surprising physics to be found in optical organic semiconductor microcavities exhibiting giant Rabi splitting. Thermalization of polaritons does not necessarily only depend on the lattice temperature, but rather on long-lived interactions between dynamic polariton states. This observation could be of importance for the design of optical switching devices, working on rapid nonthermal population. Further experiments, such as time-resolved polariton detection and site selective excitation, are evidently required to understand the precise origin of our surprising results.

In summary we have presented temperature-dependent and time-resolved PL from organic microcavities in the strong-coupling regime. Ultraslow thermalization results in a finite population of the upper polariton branch at low temperature and a deviation from the expected Boltzmann-type activation, suggesting that long-lived collective effects dominate polariton relaxation.

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[1] S. Haroche *et al.*, Phys. Today **42** (1), 24 (1989).
[2] C. Weisbuch *et al.*, Phys. Rev. Lett. **69**, 3314 (1992).
[3] R. Houndre *et al.*, Phys. Rev. Lett. **73**, 2043 (1994).
[4] D. G. Lidzey *et al.*, Nature (London) **395**, 53 (1998).
[5] J. J. Baumberg, Phys. World **15** (3), 37 (2002).
[6] R. M. Stevenson *et al.*, Phys. Rev. Lett. **85**, 3680 (2000).
[7] R. Houdré *et al.*, Phys. Rev. Lett. **85**, 2793 (2000).
[8] M. Saba *et al.*, Nature (London) **414**, 731 (2001).
[9] J. J. Baumberg *et al.*, Phys. Rev. B **62**, 16 247 (2000).
[10] D. G. Lidzey *et al.*, Phys. Rev. Lett. **82**, 3316 (1999).
[11] D. G. Lidzey *et al.*, Science **288**, 1620 (2000).
[12] P. Schouwink *et al.*, Chem. Phys. Lett. **344**, 352 (2001).
[13] H. v. Berlepsch *et al.*, J. Phys. Chem. B **106**, 5689 (2001).
[14] P. Schouwink *et al.*, Chem. Phys. (to be published).
[15] T. N. Gerasimova, Chem. Sustainable Dev. **8**, 109 (2000).
[16] D. A. Higgins *et al.*, J. Am. Chem. Soc. **118**, 4049 (1996).
[17] T. Kobayashi *et al.*, J. Lumin. **72-74**, 38 (1997).
[18] M. Vacha *et al.*, J. Phys. Chem. B **102**, 1916 (1998).
[19] P. Schouwink, Ph.D. thesis, University of Mainz, 2002.
[20] V. Savona *et al.*, Solid State Commun. **93**, 733 (1995).
[21] P. Schouwink *et al.*, J. Lumin. **94-95**, 821 (2001).
[22] V. Savona, in *Confined Photon Systems: Fundamentals and Applications*, edited by H. Benisty *et al.* (Springer, New York, 1999).
[23] F. Tassone *et al.*, Phys. Rev. B **56**, 7554 (1996).
[24] F. Tassone *et al.*, Phys. Rev. B **53**, 7642 (1996).
[25] J. Wainstain *et al.*, Solid State Commun. **99**, 317 (1996).