

DOI: 10.1002/cphc.201200734

VIP

Polariton Dynamics under Strong Light–Molecule Coupling

Tal Schwartz,^[a] James A. Hutchison,^[a] Jérémie Léonard,^[b] Cyriaque Genet,^[a] Stefan Haacke,^[b] and Thomas W. Ebbesen^{*[a]}

We present a comprehensive experimental study of the photo-physical properties of a molecule–cavity system under strong coupling conditions, using steady-state and femtosecond time-resolved emission and absorption techniques to selectively

excite the lower and upper polaritons as well as the reservoir of uncoupled molecules. Our results demonstrate the complex decay routes in such hybrid systems and that, contrary to expectations, the lower polariton is intrinsically long-lived.

1. Introduction

Since the observation of strong coupling of light and molecules by the Sheffield group,^[1] optical cavities with organic molecules have been extensively studied,^[2–13] as they provide a new platform to study strong coupling effects at room temperature, with Rabi-splitting values of up to hundreds of meV. In the recent years, several applications of molecular optical cavities were demonstrated, including electrically pumped polariton LEDs^[7] and low-threshold polariton lasing,^[8] and it is believed that condensation of polaritons^[14] should be possible in such cavities at room temperature, due to the extremely large Rabi-splitting and the high binding energy of excitons in molecular dyes. Moreover, these systems offer a unique combination of quantum electrodynamics and functional molecular properties,^[12] and we have recently demonstrated that the hybridization of photonic and molecular states can even result in the modification of a chemical reaction.^[13] Alternatively, strong coupling of molecules with surface plasmons^[15–19] or localized plasmons^[20–22] provides a complementary approach with similar physics and which offers greater tunability and potential for nano-scale integration.

It is already well established that strong coupling with molecules exhibits many different features compared to inorganic semiconductors, and that it cannot be viewed as the coupling of a simple two-level system to the electromagnetic field. The existence of a large manifold of vibrational sublevels and the so-called incoherent (or uncoupled) states,^[9,10] alters the dynamics of the system and results in new underlying physical processes which are currently the subject of much interest. In this context, the two representations of strong coupling shown in Figure 1 will be useful for presenting and discussing

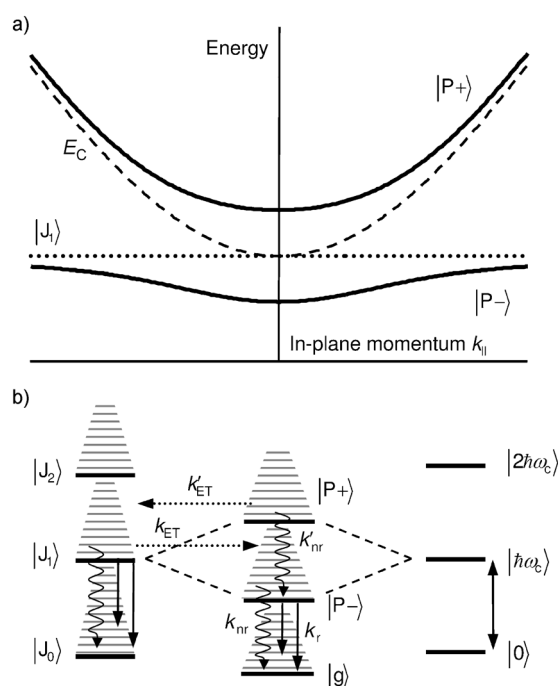


Figure 1. a) Dispersion diagram of a strongly coupled system: The angle-dependent cavity resonance with an energy E_C is coupled to the molecular level J_1 , forming the two polariton branches $|P+\rangle$ and $|P-\rangle$. b) Jablonski molecular state diagram of the same system in interaction with the reservoir of uncoupled J-aggregates.

the results of this study. Since a localized molecular excitation is coupled to a propagating photon in the cavity, the coupled system has the typical dispersion features shown in Figure 1a with an anti-crossing at resonance. On the other hand, in a Jablonski-type molecular state diagram including vibronic manifolds, the various relaxation pathways of the system are easily visualized (Figure 1b). The relative contribution of these pathways as well as the nature of the incoherent states (uncoupled molecules) and their contribution to the polariton dynamics are still not fully understood and require further study. Although there have been considerable advances in the theoretical study of strong coupling with molecules, experiments on the dynamics of such systems are still relatively scarce.^[13,17,22–25]

[a] Dr. T. Schwartz,^{*} Dr. J. A. Hutchison, Dr. C. Genet, Prof. T. W. Ebbesen
ISIS & icFRC, Université de Strasbourg and CNRS (UMR 7006)
8 allée Gaspard Monge, 67000, Strasbourg (France)
E-mail: ebbesen@isis-ulp.org

[b] Dr. J. Léonard, Prof. S. Haacke
Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Université de Strasbourg, CNRS, IPCMS-DON
23, rue du Loess, 67034 Strasbourg (France)

[*] Current address
School of Chemistry, Tel Aviv University, Israel

Here we report a comprehensive spectroscopic study of polariton dynamics in a prototypical molecular system involving J-aggregate cyanine molecules. This model system is studied using both steady-state and time-resolved spectroscopic methods. With wavelength selective excitation of the upper and lower polaritons and the uncoupled reservoir of molecules, the complex relaxation pathways of the coupled system, and its interaction with the uncoupled states is revealed, complementing and clarifying earlier studies.^[15,25]

2. Results and Discussion

The system which we study is a cavity made by J-aggregate molecules embedded in a metallic planar cavity (see Experimental Section). First, the organic cavity system was characterized by measuring its transmission (T) and reflection (R) spectra, extracting the absorption spectrum as $\bar{A} = 1 - T - R$ (as opposed to the absorbance given by $A = -\log T$), which is compared in Figure 2a to the absorption of a bare polymer/dye film prepared using the same parameters. A Rabi splitting of 320 meV is clearly visible between the two cavity absorption peaks due to the formation of the hybrid light/exciton coupled states. We note that since the splitting appears in the cavity absorption spectrum, it unequivocally proves that our system is indeed in the strong coupling regime.^[28]

Static Measurements

In the same Figure 2a, the fluorescence spectrum of the bare and the dressed molecules upon UV excitation is shown. For the coupled system, there are two emission peaks. The one around 595 nm corresponds to the presence of uncoupled molecules while the peak at 640 nm is associated with the lower polariton $|P-\rangle$. Indeed, by taking the ratio of the absorbance at 590 nm before and after coupling, assuming that the absorption cross section of uncoupled molecules is the same as bare molecules, one can estimate that the fraction of uncoupled molecules is less than 5%. This assumption is supported by the fact that the fluorescence decay of uncoupled molecules is basically unchanged by the cavity, as demonstrated

below. Our observation that the system is dominated by the coupled states stands in contradiction to theoretical models,^[9] which evaluate the fraction of coupled states as $\sim 30\%$ for parameters similar to those of our experiments. That model, however, assumes a perfect cavity with a cavity mode existing for any energy value and a negligible cavity linewidth, which cannot be assumed for our metallic cavity. It should be noted that one cannot extrapolate the ratio of uncoupled to coupled molecules in the cavity from the ratio of their fluorescence intensities (at 595 and 640 nm) since this requires knowledge of the absolute quantum yields. In Figure 2b the dispersion diagram is shown as recorded by angle resolved transmission (white circles) and emission (color map). As expected, the uncoupled molecule emission is dispersionless while that of $|P-\rangle$ follows the transmission dispersion. Surprisingly, the fluorescence is slightly blue shifted by about 10 nm relative to the absorption peak (excitation at 380 nm). This might partially originate from some residual emission of uncoupled molecules at those wavelengths (see minor emission peak of bare film between 600 and 650 nm). The upper polariton $|P+\rangle$ does not emit at room temperature as has been reported previously^[15,26] due to a very rapid non-radiative decay as will be seen further down.

The simplest way to explore the pathways leading to the $|P-\rangle$ fluorescence is to measure the excitation (also called action) spectrum as shown in Figure 3a. The graph gives the emission intensity at 630 nm as a function of the excitation wavelength. As expected, the excitation spectrum closely resembles the absorption with two contributions: a major pathway via $|P+\rangle$ which is angle-dependent (Figure 3a), and a smaller contribution via the uncoupled molecules (shoulder at 590 nm, angle insensitive). The latter can be both the result of direct emission from the uncoupled molecules and/or the consequence of energy transfer from J_1 to $|P-\rangle$. To try to answer this question, the excitation spectrum were recorded at different emission wavelengths every 5 nm between 595 and 650 nm as shown in Figure 3b. The increasing intensity in the excitation spectra at 550 nm (where $|P+\rangle$ absorbs) on going from emission wavelengths 610 to 595 nm (where the J_1 emission dominates) reveals that energy transfer is occurring

between $|P+\rangle$ and J_1 . The intensity variation in the excitation spectra recorded for emission wavelengths between 610 and 650 nm (where $|P-\rangle$ emission dominates), however, does not allow one to infer energy transfer from J_1 to $|P-\rangle$. The evidence for the latter process is found in the transient absorption data presented below. The ratio of the area under the curve of two $|P-\rangle$ peaks in the excitation spectra gives the relative quantum efficiencies (after correction for absorption) of the pathways and confirms that the

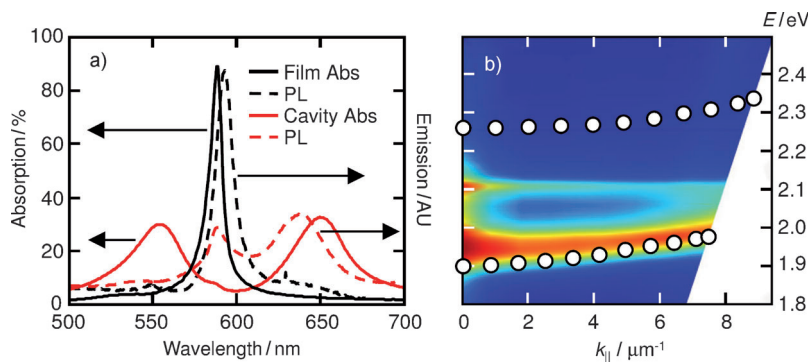


Figure 2. a) Absorption (—) and emission (----) of the bare molecules and the coupled system upon excitation at 400 nm. b) Dispersion diagram of the coupled system, measured by transmission (white circles) and emission (color) under nonresonant excitation.

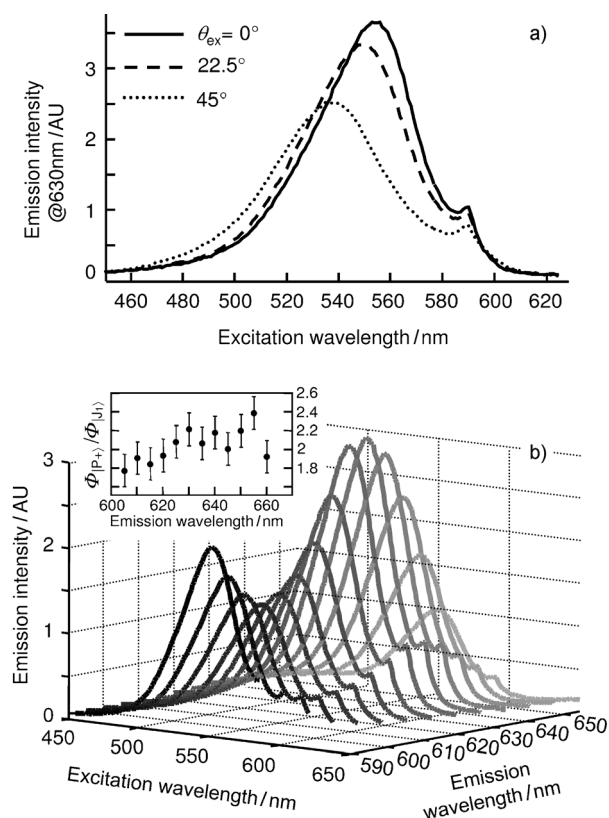


Figure 3. a) Excitation spectra of the emission at 630 nm of the coupled system for three different excitation angles. b) Excitation spectra measured for emission wavelengths every 5 nm between 595 and 650 nm. Inset: ratio of emission of $|P-\rangle$ to J_1 emission, determined from the area under the curves. The inset shows the ratio between the area of the $|P+\rangle$ peak and the area of the J_1 peak, normalized by the ratio of absorption at the same wavelength. This ratio corresponds to the ratio of the quantum efficiencies of the two paths leading to $|P-\rangle$ emission.

emission from $|P-\rangle$ by direct excitation of the coupled molecules dominates by a factor of about two under these conditions.

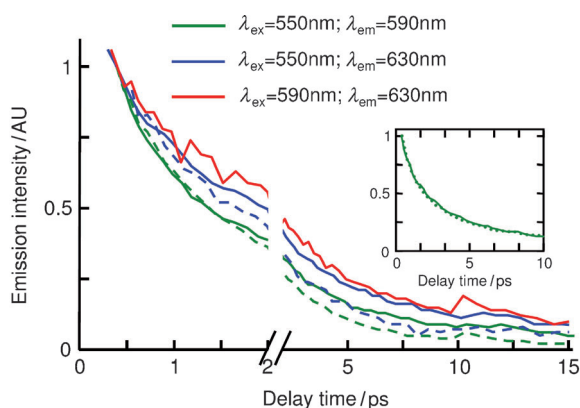


Figure 4. Time-resolved fluorescence measurements for the cavity (—) and a bare molecular film (----) following a pulsed excitation. The curves are normalized at a delay time of $t=0.4$ ps. The inset shows the $|P-\rangle$ emission decay with different pump intensities—20 (.....) and 350 $\mu\text{J cm}^{-2}$ (—) per pulse.

Time-Resolved Analysis

To gain further insight, the dynamics of the system was analyzed with femtosecond time resolution by both fluorescence up-conversion and tunable pump-probe differential absorption spectroscopy. Figure 4 compares the fluorescence lifetime of the J -aggregate outside the cavity (----) with that of the coupled system (—). The decays are not mono-exponential but as the first half-lives indicate, the emission decay from $|P-\rangle$ with $\tau_{1/2} \sim 2$ ps is twice as slow as that from J_1 ($\tau_{1/2} \sim 1$ ps whether in the cavity or not). The $|P-\rangle$ fluorescence decay is the same whether exciting at 550 or 590 nm. Moreover, we verify that the fluorescence decay time is independent of the excitation intensity used (as shown in the inset of Figure 4),

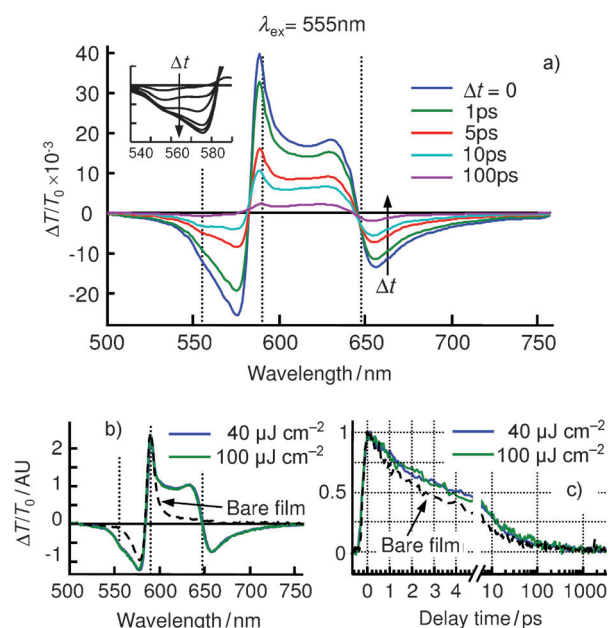


Figure 5. a) Evolution of transient differential absorbance spectra after excitation at 555 nm into the upper polariton. Inset: rapid growth of the spectrum between 540 and 580 nm within the 150 fs pulse width. b) Comparison of the transient spectra of the cavity at two different pump powers at 555 nm (—) compared to the transient spectrum of the bare film (----). c) Decay kinetics (normalized at $\Delta t=0$) for conditions as in (b), represented by the trace of the most significant term of a singular value decomposition of the raw data.^[29]

demonstrating that there are no exciton-exciton interactions within the intensity range used in our experiment. We observed a small spectral red shift at very early times (<1 ps), which is most likely due to vibrational relaxation, typical of such J -aggregates.^[29]

Transient absorbance spectra were recorded after exciting or pumping with different wavelengths to selectively reach $|P+\rangle$, J_1 or $|P-\rangle$. Figure 5 gives the transient spectrum immediately after exciting directly to $|P+\rangle$ (150 fs pulse at 555 nm) and its evolution as a function of time. The inset shows a detail of the spectrum which evolves over a timescale of the duration of the pulse (~ 200 fs) and which is attributed to fast vibration relaxation. Otherwise the spectral shape does not change during

the subsequent decay. It was verified that the spectral shape of the transient signal and its normalized decay kinetics are invariant with pump intensity, as can be seen in Figures 5b and c where it is also compared to the transients of the bare molecules. The decay kinetics are multi-exponential with a first-half life of about 4 ps. Notice also the long decay tail at 100 ps and beyond. These dynamic features can be understood by the heterogeneity of the J-aggregate assemblies formed by the cyanine molecules in any given sample. For the same reason, the decay kinetics are similar but not identical to those measured by fluorescence, as the latter favors a subset of the excited population that gives rise to the strongest fluorescence.

The transient spectra in Figure 5, in good agreement with published data,^[25] were measured as the relative change in transmission upon excitation, that is, $\Delta T/T_0$, where $\Delta T = T^* - T_0$, and T_0 and T^* are the transmission spectra before pumping (ground state) and at a time delay Δt after excitation, respectively. In standard pump-probe spectroscopy of molecular systems, this quantity is directly related to the differential absorbance by the Beer-Lambert law [Eq. (1)]:

$$\Delta A(\lambda) = -\log_{10}\left(1 + \frac{\Delta T}{T_0}\right) = [\sigma^*(\lambda) - \sigma_0(\lambda) - \sigma_{SE}(\lambda)]\kappa d[M^*] \quad (1)$$

where $\sigma^*(\lambda)$ is the excited-state absorption cross-section in cm^{-2} , $\sigma_0(\lambda)$ the ground-state absorption cross-section, $\sigma_{SE}(\lambda)$ the stimulated emission cross-section of the excited state, κ the constant that relates the molar extinction coefficient to the cross-section ($2.63 \times 10^{20} \text{ M}^{-1} \text{ cm}$), d (cm) the path length or thickness of the film, and $[M^*]$ the concentration of excited species. Moreover, for small transmission changes, $\Delta T \ll T_0$, the relation in Equation (1) can be approximated by $\Delta A = -\ln(10)\Delta T/T_0$, as presented in Figure 5.

However, in the case of the Fabry-Perot cavity, where the transmission is determined by the interference of multiple reflections, the information contained in the reflection R cannot be ignored in the estimation of the transient absorption. Since the total absorption of the cavity is $\bar{A} = 1 - T - R$, it is straightforward to plot the transient absorption change of the cavity system by summing up the absolute changes in transmission ΔT and reflection ΔR , that is, $\Delta \bar{A} = -(\Delta T + \Delta R)$.

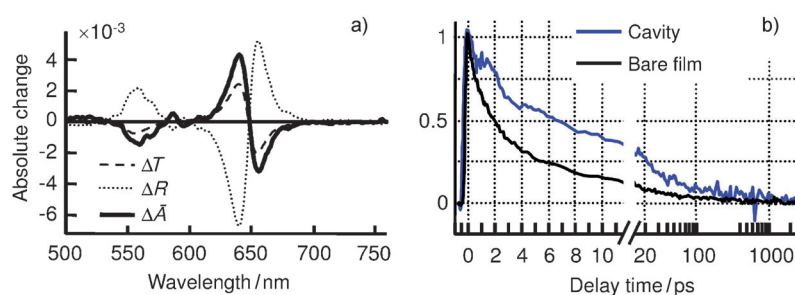


Figure 6. a) Spectrum and b) temporal evolution of the total change in absorption at $\Delta t = 0$ (—) determined from the sum of the absolute changes in transmission and reflection, under the same conditions as in Figure 5 (see text).

Figure 6 shows the resulting spectrum (bold line) which has the expected features when considering the ground state spectrum of the coupled system, in particular the negative dips at the two absorption peaks (see Figure 2) of the polaritons states, a consequence of the depopulation of $|g\rangle$. The other positive features can only be associated with absorption towards higher states. Notice that the large negative dip at 590 nm seen in Figure 5a disappears. The latter looks, at first sight, as due to the depopulation of the ground state J_0 of the uncoupled molecules, combined with the fact that the cross-section of the ground state is much greater than that of the excited state at that wavelength [Eq. (1)]. However, such a large dip is surprising considering that less than 5% of the molecules are uncoupled. In fact, closer analysis indicates that this feature is exaggerated in Figure 5a only because T_0 is very small at 590 nm, thereby boosting $\Delta T/T_0$. Hence, it is clear that using $\Delta T/T_0$ alone to estimate the transient response (as done by us and others in the past) is not suitable for structures such as Fabry-Perot cavities. The kinetics of the absorption also shows a somewhat slower decay compared to the trace of Figure 5c, with its half-life time increasing to ~ 6 ps. This can be understood by the fact that the slower decay of the signal at wavelengths around $|P-\rangle$ is obscured in the $\Delta T/T_0$ spectrum due to the exaggerated contribution of J_1 .

When exciting at 590 nm, where the residual absorption to J_1 is the strongest, the transient spectrum and its decay kinetics (Figure 7) remain the same. In contrast, upon pumping at 645 nm directly into the $|P-\rangle$, the transient spectrum and its

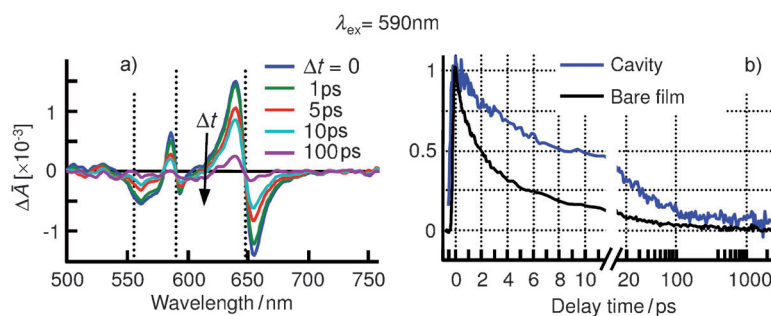


Figure 7. Evolution of the transient absorption spectrum after excitation at 590 nm, corresponding to the absorption peak of the uncoupled reservoir, and b) its corresponding decay kinetics.

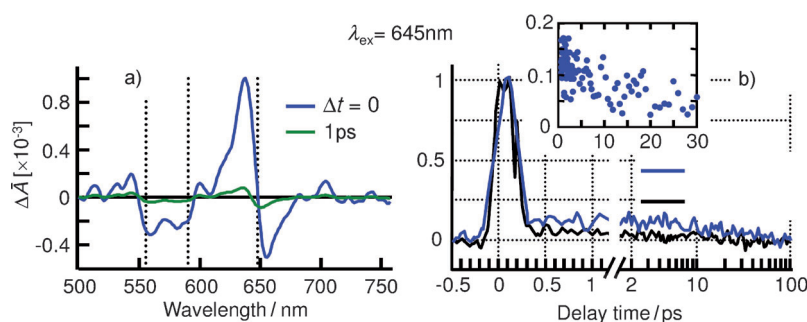


Figure 8. a) Evolution of the transient absorption spectrum after excitation at 645 nm into the lower polariton, and b) its corresponding decay kinetics. The inset shows the detailed long-term decay following the fast spike.

evolution are more complex (Figure 8). There is a short component which decays very fast over the timescale of the 150 fs pulse followed by a very long component with similar spectrum and kinetics as that observed when exciting into $|P+\rangle$ and J_1 . One could be tempted to attribute the fast component to the very short radiative lifetime of our low Q -factor cavity (ca. 25 fs). Nevertheless, when the bare film (without cavity) is excited under the same conditions, the same fast signal is detected. Moreover, it varies with probe light intensity, unlike the other transient data, indicating some multi-photon process.^[30] Note that in all three cases there is a negative signal close to the $|P+\rangle$ wavelength. One should emphasize that the origin for this signal is not the excited $|P+\rangle$ population (besides the first ~ 200 fs in Figure 5), but rather the ground-state bleaching. This is evident by the fact that it evolves at the slow rate of the $|P-\rangle$ decay.

In summary, all the pump-probe data give the same result whether exciting into $|P+\rangle$, J_1 or $|P-\rangle$, revealing that the observed transient spectrum is the difference spectrum of the ground state and $|P-\rangle$. This implies that no matter how the system is excited, it will quickly evolve to populate the lower polariton state, after which it will relax back to the ground state over a timescale of several ps. The kinetics are also in agreement with the fluorescence decay measured from the lower polariton. Such data provides a relatively simple picture of the internal dynamics of the coupled molecules and their interaction with the uncoupled ones, but raises some fundamental questions as discussed below.

Cavity polaritons are a mixture of the material excitation and the cavity photon, and their lifetime is expected to be governed by the dynamics of the shorter of the two components. For instance, in the case of a single emitter in a low Q -factor cavity such as the one in the present experiments, the polariton is expected to have a lifetime twice the radiative decay of the photon in the cavity (ca. 50 fs) as the rates of exchange in both directions between the cavity and the excited state are assumed equal. The observation of polariton lifetimes longer than expected from such considerations, as reported here, has been explained by energy transfer from the reservoir of uncoupled molecules such that the emission from the lower polariton is governed by the kinetics of the uncoupled molecules.^[9,10,25] While this energy-transfer process does occur, as seen from the fluorescence excitation spectra, our results indi-

cate that such a mechanism is not responsible for the observed long $|P-\rangle$ lifetime. First of all, and most importantly, $|P-\rangle$ has a slower decay than the molecules of the uncoupled reservoir. Secondly, the transient absorption spectrum is always that of the coupled system while if the reservoir was responsible for the dynamics, the transient spectrum would be dominated by that of the uncoupled molecules. Similar observations of slowly decaying lower polariton have been made

for very different groups of molecules strongly coupled to either cavities or plasmonic resonances with similar low Q -factors.^[13,17,22–24] In all of these cases, including the present one, the lower polariton lifetime resembles that of the excited state of the bare molecule. One possible reason could be the fact that the splitting is much larger than $k_B T$ in these strongly coupled molecular system, such that once the system has relaxed to $|P-\rangle$ it is in a potential-minima well below the energy of the non-interacting photon or excitons that compose the polariton. In other words, $|P-\rangle$ can be thought of as a quasi-bound state, much like a molecular bonding orbital formed by atomic states, and the corresponding binding energy is much larger than $k_B T$. Another possible reason for the long-lived $|P-\rangle$ could be due to the high density of molecules ($\sim 10^{20}$ cm⁻³) involved in the strong coupling in these experiments and its consequences for the coupling exchange rates in the cavity. In essence, in the process of exchanging photons between the cavity and the molecules, the rate of absorption by the molecules should be faster than the reverse process by a factor corresponding to the number of molecules (ca. 10^5) in the effective mode volume of the cavity. Further theoretical analysis, beyond the scope of this paper, will be necessary in order to verify and understand the long-lived polaritons, as this is an issue of fundamental importance.

Looking again at Figure 1a, one is now in a position to put some numbers on the various relaxation rate constants in the system. The Förster-type energy transfer between the coupled and uncoupled molecules occurs within the pulse duration (i.e. k_{ET} and $k'_{ET} > 10^{13}$ s⁻¹), which is not surprising considering the high molecular concentration which enables efficient dipole-dipole coupling between the molecules. The energy transfer is in competition with the decay of J_1 ($\leq 10^{12}$ s⁻¹) and $|P+\rangle$ ($k'_{nr} > 10^{13}$ s⁻¹). Finally, the longest lived species $|P-\rangle$ decays relatively slowly, as discussed above, with $k_r + k_{nr} \leq 10^{12}$ s⁻¹ $< k(J_1)$. The non-exponential decay of $|P-\rangle$ (as well as J_1) and long residual signal at 100 ps is explained by the heterogeneity of the J -aggregates.

The fact that the lower polariton is the only emitting state in the coupled system is typical of many aromatic molecules, where only the lowest excited state emits, which is known as Kasha's rule. This is because the non-radiative decay of the higher states dominates at room temperature. Upon lowering

the temperature, emission from the upper polariton has been observed.^[26] An interesting feature of the coupled systems is the blue shifted emission of $|P-\rangle$ (Figure 2). Unlike other reports of blue-shifted $|P-\rangle$ emission under high-intensity pumping,^[31,32] the shift observed here occurs even at a very low excitation power, and does not depend on the excitation intensity. Such anti-Stokes behavior is observed in certain inorganic pigments where the extra energy comes from the surrounding crystal which here could be provided by the J-aggregate lattice. In any case, energy transfer in an inhomogeneous population of J-aggregates could already shift the emission within a range defined by $k_B T$. The simplest explanation, discussed earlier, is that fluorescence measurement samples the sub-set of J-aggregates that fluoresce most strongly.

Just as the ground-state spectrum of the coupled system can be calculated using a semi-classical approach,^[33,34] we have found that the differential transient spectrum can also be predicted using a "quasi-static" solution of Maxwell's equations, as illustrated in Figure 9. Normally, the ground-state absorption of the bare film is first measured and using the Kramers–Kronig relations, the full complex refractive index $n_0 = n'_0 + in''_0$ is ob-

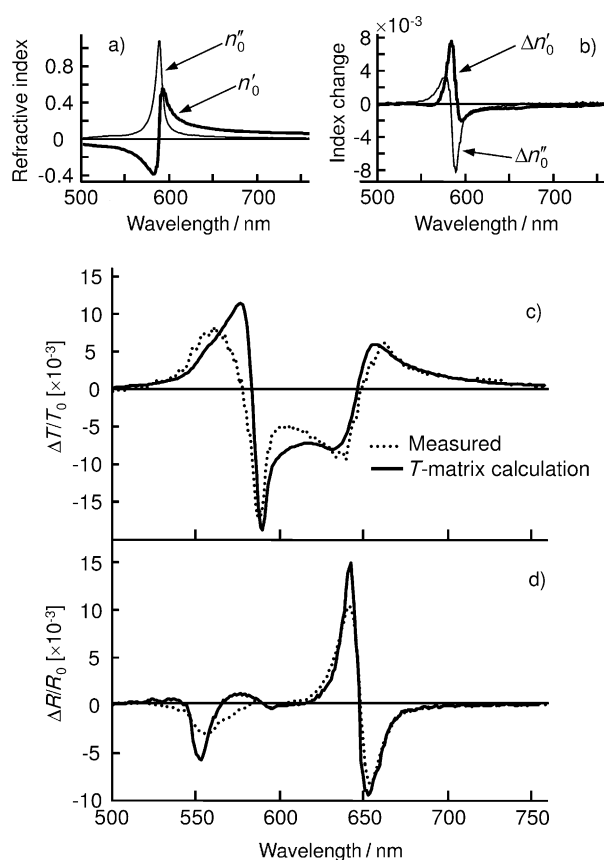


Figure 9. a) Real (n'_0) and imaginary (n''_0) parts of the complex refractive index of a bare molecular film obtained with the Kramers–Kronig relation from the measured absorbance. b) Differential real ($\Delta n'$) and imaginary ($\Delta n''$) parts of the complex refractive index obtained from the transient absorption of the same bare molecular film. c,d) Comparison of the calculated differential spectra for the strongly coupled cavity system, using the information of (a) and (b) (—, see text), and the experimentally measured transient transmission (c) and reflection (d) spectra (.....).

tained (Figure 9a) and inserted into Maxwell's equations to calculate either the reflection R_0 or transmission T_0 of the composite cavity. In the same way, the real ($\Delta n'$) and imaginary ($\Delta n''$) parts of the refractive-index change induced upon excitation are also connected by the Kramers–Kronig relations. By measuring the transient absorption of the bare film and calculating the associated refractive index change, we can recalculate the excited-state transmission T^* of the cavity from which the differential absorbance (T^*/T_0) can be determined as a function of the wavelength. As seen in Figure 9c, it compares extremely well with the experimental spectrum. The same can be done for the transient reflection data, as shown in Figure 9d. The fact that one can easily predict the transient absorption spectrum, as just shown, should not mislead one into concluding that new discrete states are not formed by the strong coupling process. As our results and others show, the polaritonic states have a discrete emission with long-range coherence, as demonstrated recently by the Lyon group.^[19] Furthermore, these states have their own distinct dynamics, which can be very different from those of the bare molecules and may even result in modification of the chemical reaction rates.^[13]

3. Conclusions

In summary, by using the wavelength-selective transient absorption technique and fluorescence measurements, we have been able to further clarify the dynamics of the strongly coupled J-aggregate–cavity system. In particular, we have demonstrated unequivocally that the intrinsic lifetime of the lower polariton can be much longer than the radiative lifetime of the cavity, and that this cannot be explained by energy transfer from the uncoupled reservoir. This is of fundamental importance and also has implications in the use of polaritons for technological purposes.

Experimental Section

Cavity Preparation

A 30 nm-thick Ag layer was sputtered on a quartz substrate. Then, a polymer film doped with the J-aggregate molecules (TDBC) (5,6-dichloro-2-[[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)benzimidazol-2-ylidene]propenyl]-1-ethyl-3-(4-sulphobutyl) benzimidazolium hydroxide, inner salt, sodium salt, Few Chemicals) was deposited by spin-casting (1550 rpm) to form a layer of ~ 145 nm, tuned to overlap the normal-incidence cavity resonance with the peak wavelength of the dye absorption (588 nm). This type of molecule was used previously in strong-coupling studies,^[7,15,19] due to its narrow absorption linewidth (30 meV) and relatively high fluorescence quantum yield in the uncoupled state. The polymer/dye solution was prepared by dissolving polyvinyl alcohol (molar weight 205 000) in water (5 wt%) at 90 °C for several hours, cooling to room temperature and mixing with an equal amount of 0.5 wt% water solution of TDBC. Prior to spin-casting, the mixture was filtered using a 0.2 micron nylon membrane filter. Finally, the cavity was formed by sputtering a second layer of Ag (30 nm), which gives an empty cavity Q-factor of ~ 30 .^[12]

Time-Resolved Measurements

A pump-probe system (Helios, Newport) pumped by a tunable optical parametric amplifier (OPA) with a 150 fs pulse width was used for the transient absorption spectroscopy. The fluorescence lifetimes were measured by type-II frequency mixing of the fluorescence signal with a 40 fs, 800 nm gate pulse in a 200 μm -thick β -barium borate (BBO) crystal. The same setup as described elsewhere^[27] is used here for up-conversion of the visible fluorescence of the J-aggregates, and detection of the UV, time-gated signal resulting from the sum frequency generation (SFG). Photoexcitation is done with a tunable, sub 50 fs VIS pulse from a home-made non-collinear optical parametric amplifier (NOPA).

Acknowledgements

This work was supported in part by the ERC (grant 227577) and the icFRC (International Center for Frontier Research in Chemistry). We thank Astrid Lambrecht and Serge Reynaud for fruitful discussions.

Keywords: cavity · J-aggregates · polariton · strong coupling · time-resolved spectroscopy

- [1] D. G. Lidzey, D. D. C. Bradley, M. S. Skolnick, T. Virgili, S. Walker, D. M. Whittaker, *Nature* **1998**, 395, 53–55.
- [2] D. G. Lidzey, D. D. C. Bradley, A. Armitage, S. Walker, M. S. Skolnick, *Science* **2000**, 288, 1620–1623.
- [3] P. Schouwink, H. V. Berlepsch, L. Dahne, R. F. Mahrt, *Chem. Phys. Lett.* **2001**, 344, 352–356.
- [4] P. A. Hobson, W. L. Barnes, D. G. Lidzey, G. A. Gehring, D. M. Whittaker, M. S. Skolnick, S. Walker, *Appl. Phys. Lett.* **2002**, 81, 3519–3521.
- [5] N. Takada, T. Kamata, D. D. C. Bradley, *Appl. Phys. Lett.* **2003**, 82, 1812–1814.
- [6] R. J. Holmes, S. R. Forrest, *Phys. Rev. Lett.* **2004**, 93, 186404.
- [7] J. R. Tischler, M. S. Bradley, V. Bulović, J. H. Song, A. Nurmikko, *Phys. Rev. Lett.* **2005**, 95, 036401.
- [8] S. Kéna-Cohen, S. R. Forrest, *Nat. Photonics* **2010**, 4, 371–375.
- [9] V. M. Agranovich, M. Litinskaia, D. G. Lidzey, *Phys. Rev. B* **2003**, 67, 085311.
- [10] M. Litinskaya, P. Reineker, V. M. Agranovich, *J. Lumin.* **2004**, 110, 364–372.
- [11] P. Michetti, G. C. La Rocca, *Phys. Rev. B* **2005**, 71, 115320.
- [12] T. Schwartz, J. A. Hutchison, C. Genet, T. W. Ebbesen, *Phys. Rev. Lett.* **2011**, 106, 196405.
- [13] J. A. Hutchison, T. Schwartz, C. Genet, E. Devaux, T. W. Ebbesen, *Angew. Chem.* **2012**, 124, 1624–1628; *Angew. Chem. Int. Ed.* **2012**, 51, 1592–1596.
- [14] J. Keeling, N. G. Berloff, *Contemp. Phys.* **2011**, 52, 131–151.
- [15] J. Bellessa, C. Bonnand, J. C. Plenet, J. Mugnier, *Phys. Rev. Lett.* **2004**, 93, 036404.
- [16] J. Dintinger, S. Klein, F. Bustos, W. L. Barnes, T. W. Ebbesen, *Phys. Rev. B* **2005**, 71, 035424.
- [17] A. Salomon, C. Genet, T. W. Ebbesen, *Angew. Chem.* **2009**, 121, 8904–8907; *Angew. Chem. Int. Ed.* **2009**, 48, 8748–8751.
- [18] T. K. Hakala, J. J. Toppari, A. Kuzyk, M. Pettersson, H. Tikkanen, H. Kunttu, P. Törmä, *Phys. Rev. Lett.* **2009**, 103, 053602.
- [19] S. A. Guebrou, C. Symonds, E. Homeyer, J. C. Plenet, Y. N. Gartstein, V. M. Agranovich, J. Bellessa, *Phys. Rev. Lett.* **2012**, 108, 066401.
- [20] Y. Sugawara, T. A. Kelf, J. J. Baumberg, M. E. Abdelsalam, P. N. Bartlett, *Phys. Rev. Lett.* **2006**, 97, 266808.
- [21] T. Ambjörnsson, G. Mukhopadhyay, P. S. Apel, M. Käll, *Phys. Rev. B* **2006**, 73, 085412.
- [22] Y. W. Hao, H. Y. Wang, Y. Jiang, Q. D. Chen, K. Ueno, W. Q. Wang, H. Misawa, H. B. Sun, *Angew. Chem.* **2011**, 123, 7970–7974; *Angew. Chem. Int. Ed.* **2011**, 50, 7824–7828.
- [23] J. H. Song, Y. He, A. V. Nurmikko, J. Tischler, V. Bulovic, *Phys. Rev. B* **2004**, 69, 235330.
- [24] P. Vasa, R. Pomraenke, G. Cirmi, E. De Re, W. Wang, S. Schwieger, D. Leipold, E. Runge, G. Cerullo, C. Lienau, *ACS Nano* **2010**, 4, 7559–7565.
- [25] T. Virgili, D. Coles, A. M. Adawi, C. Clark, P. Michetti, S. K. Rajendran, D. Brida, D. Polli, G. Cerullo, D. G. Lidzey, *Phys. Rev. B* **2011**, 83, 245309.
- [26] D. M. Coles, P. Michetti, C. Clark, A. M. Adawi, D. G. Lidzey, *Phys. Rev. B* **2011**, 84, 205214.
- [27] J. Léonard, T. Gelot, K. Torgasin, S. Haacke, *J. Phys. Conf. Ser.* **2011**, 277, 012017.
- [28] R. Houdré, *Phys. Status Solidi B* **2005**, 242, 2167–2196.
- [29] H. Kano, T. Kobayashi, *J. Chem. Phys.* **2002**, 116, 184–195.
- [30] M. Furuki, M. Tian, Y. Sato, L. S. Pu, H. Kawashima, S. Tatsuura, O. Wada, *Appl. Phys. Lett.* **2001**, 78, 2634–2636.
- [31] R. Houdré, J. L. Gibernon, P. Pellandini, R. P. Stanley, U. Oesterle, C. Weisbuch, J. O’Gorman, B. Roycroft, M. Ilegems, *Phys. Rev. B* **1995**, 52, 7810–7813.
- [32] C. Ciuti, P. Schwendimann, B. Deveaud, A. Quattropani, *Phys. Rev. B* **2000**, 62, R4825.
- [33] Y. Zhu, D. J. Gauthier, S. E. Morin, Q. Wu, H. J. Carmichael, T. W. Mossberg, *Phys. Rev. Lett.* **1990**, 64, 2499–2502.
- [34] M. S. Bradley, J. R. Tischler, Y. Shirasaki, V. Bulović, *Phys. Rev. B* **2008**, 78, 193305.

Received: September 8, 2012

Published online on December 11, 2012