Strong exciton–photon coupling at room temperature in microcavities containing two-dimensional layered perovskite compounds

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Abstract. We have realized Perot–Fabry microcavities containing a two-dimensional layered perovskite-type semiconductor: \((\text{C}_6\text{H}_5\text{C}_2\text{H}_4–\text{NH}_3)_2\text{PbI}_4\) between a dielectric mirror and a metallic mirror. A strong coupling regime between the perovskite exciton and the confined photon mode has been evidenced at room temperature from angular-resolved reflectivity experiments, anticrossings as large as 190 meV are observed between the excitonic and cavity modes. We have shown that the design of the microcavity can be varied at will, so that the detuning or the Rabi splitting can be precisely chosen. The emission of the polaritonic low energy branch has been observed.

Light–matter interactions inside a planar microcavity modify the emission of light. In the weak coupling regime, spontaneous emission can be dramatically enhanced or reduced, and this regime is employed in applications such as vertical cavity surface emitting lasers [1] or resonant cavity light emitting diodes [2]. In the strong coupling regime, the cavity photon mode and the exciton are no longer eigenmodes of the system, the new eigenmodes are a linear and coherent superposition of the exciton and photon states, called cavity polaritons [3], the anticrossing between the exciton and photon modes is the Rabi splitting. Since the first experimental evidence of strong coupling in a semiconductor microcavity over a decade ago [3], this field has been intensively studied due to the interest in coherent and stimulated effects in such systems

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which can lead to new optical devices [4]. In particular, the properties of polaritons to form a Bose–Einstein condensate may lead to the realization of low threshold polariton lasers [5].

The field has been recently expanded to one-dimensional microcavities containing thin layers of organic materials [6]–[10] or hybrid organic–inorganic materials [11, 12] in which the strong coupling regime has been observed. Because of the relatively large oscillator strengths of the exciton in these materials, Rabi splittings around 150 meV for zinc porphyrin [6], J-aggregates of cyanine dyes [7]–[9] or perovskites [11, 12], and even as large as 430 meV for a sigma-conjugated polysilane [10], have been reported at room temperature. Because of the increased interaction strength between the organic excitons and photons, strong coupling can occur in organic microcavities having $Q$ factors as low as 10 [13]. The large Rabi-splittings obtained in organic microcavities are of particular significance for current efforts to achieve polariton lasing in microcavities at room temperature because it will be possible to maintain the strong coupling at 300 K.

We report here the realization of Perot–Fabry microcavities containing a two-dimensional layered perovskite-type semiconductor: $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4–\text{NH}_3)_2\text{PbI}_4$, showing the strong-coupling regime at room temperature. Compared to the state of the art of the technology regarding semiconductor-based microcavities, it is often thought that technological difficulties reduce the control of the design in microcavities containing molecules. We show here that the design of the microcavity can be varied at will, so that the detuning between the photon and excitonic modes or the Rabi splitting can be precisely chosen.

Two-dimensional layered perovskite compounds such as $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4–\text{NH}_3)_2\text{PbI}_4$ [bis-(phenethylammonium) tetraiodoplumbate], have been shown to have a self-organized multiple quantum well structure when the organic solution is deposited by spin-coating on a substrate [14]. The spatial structure of this bidimensional structure is shown in figure 1. Because the bandgap of PbI$_4$ layers is smaller than that of organic layers, the lowest exciton is confined in the PbI$_4$ layer, so that the quantum wells consist of PbI$_4$ inorganic monolayers (thickness around 0.5 nm) and the barriers consist of the organic alkylammonium layers (thickness around 1 nm). By virtue of the high contrast in dielectric constants between the organic layers and the PbI$_4$ layers, the Coulomb interaction in the well layer is hardly screened by the presence of the barrier layers, so the interaction between an electron and a hole in an exciton is strengthened resulting in very large exciton binding energies of a few hundred milli-electron-volt and huge oscillator strengths. The absorption and corresponding photoluminescence spectra of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ are shown in figure 2.

The general structure of the Perot–Fabry microcavities used in this work is shown in figure 3: it consists of a thin perovskite layer (thickness $d$) inserted between two polymethylmethacrylate (PMMA) layers (thicknesses $d_1$ and $d_2$), this whole superposition being embedded between two mirrors. The bottom mirror is a commercial dielectric mirror, centered at 2.41 eV at normal incidence, the reflectivity at 2.41 eV is 98%, the stop-band extends from 1.98 eV to 2.95 eV. The top mirror of the microcavity is produced by thermal evaporation of silver (thickness between 30 and 40 nm) on the $d_2$ thick PMMA layer. The active layer of the structure is the thin film of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4–\text{NH}_3)_2\text{PbI}_4$ perovskite, deposited by spin-coating a 10 wt.% solution of $\text{C}_6\text{H}_5\text{C}_2\text{H}_4–\text{NH}_3\text{I}$ and PbI$_2$ dissolved in stoichiometric amounts in N,N-dimethylformamide (DMF) on top of the $d_1$ thick PMMA layer. Stoichiometric atomic force microscopy (AFM) measurements show that a high-quality polycrystalline film is obtained, the surface rugosity is evaluated to be very small: 2 nm. Spin-coated PMMA layers, optically inactive, act as spacer layers. The thicknesses of the PMMA layers and the perovskite layers...
Figure 1. Bidimensional structure of the perovskite layers deposited by spin-coating. PEA = phenylethylamine. The x-axis is perpendicular to the substrate.

Figure 2. Absorption spectrum and photoluminescence spectrum (excitation wavelength: 405 nm) of a 50 nm thick \((C_6H_5C_2H_4NH_3)_2PbI_4\) layer deposited by spin-coating on a glass substrate.

have been calibrated very precisely from AFM measurements as a function of the spin-coating parameters and of the solution concentrations, the thicknesses can be controlled to within less than 10 nm. As a consequence of this very good technological control, \(d_1, d_2\) and \(d\) can be very
small: typically several 10 nm. Knowing the refractive indexes of the PMMA and perovskite layers: $n_{\text{PPMA}} = 1.5$ and $n_{\text{Pero}} = 1.8$, measured with a spectroscopic ellipsometer (Sopra model GESP5), we conclude that we are able to realize $\lambda/2$-cavities. Additionally, it is possible to change the design of the microcavity: table 1 describes the design of four microcavities we have realized. As an example, for a fixed value of the thickness $d$ of the perovskite film, varying the total thickness of the spacer layers ($d_1 + d_2$) allows the varying of the detuning between the cavity photon mode and the perovskite layer exciton wavelength, because the energy of the photon mode depends on the optical length of the cavity: $n_{\text{PPMA}}(d_1 + d_2) + n_{\text{Pero}}d$. As another example, for fixed values of $d$ and $d + d_1 + d_2$, varying $d_1$ relative to $d_2$ allows the spatial position of the perovskite thin film to be shifted relative to the spatial position of the nodes and antinodes of the electrical field in the cavity: see figure 4, where the electrical field is calculated from a transfer matrix method for two different values of $d_1$.

Angle-resolved reflectivity ($R$) measurements of the microcavities are performed using a xenon lamp as the excitation source, between angles of incidence of $0^\circ$ and $80^\circ$, at room temperature. Because of the high reflectivity of the dielectric mirror, transmission ($T$) measurements were not possible. Therefore, it can be considered that $R \gg T$ and then $1 - R \approx A$, where $A$ is the absorption, which is the relevant parameter to study the strong coupling. The total thickness $d + d_1 + d_2$ being constant along the sample (no optical wedge) because of the deposition method of the layers (spin-coating), varying the angle of incidence $\theta$ relative to the surface normal is a method to tune the relative energy separation between the perovskite exciton energy (which is dispersionless, and so angle-independent) and the cavity photon mode energy, which is related to $\theta$ by [15]:

$$E_{\text{ph}}(\theta) = \frac{E_0}{\cos(\theta_{\text{int}})},$$

(1)
Figure 4. Profile of the electric field for the cavity mode energy 2.4 eV, corresponding to an incident angle equal to 45°, (a) in microcavity MC1, (b) in microcavity MC2.

Figure 5. Reflectivity spectra of microcavity MC1 for several incidence angles at room temperature. The dashed lines are guides to the eyes.

where $E_0$ is the photon mode energy at normal incidence ($\theta = 0$) and

$$\cos(\theta_{int}) = \sqrt{1 - \frac{\sin^2 \theta}{n_{eff}^2}},$$

(2)

where $n_{eff}$ is the effective refractive index of the entire cavity.

Figure 5 shows a series of reflectivity spectra at room temperature for microcavity MC1 where $d_1 = d = d_2 = 50$ nm. Two dips, whose energy position, intensity and linewidth are angle-dependant, can be seen. A clear anti-crossing between the two transitions can be seen. For low incidence angles, the lower energy minimum is the stronger one. As the angle increases, the intensity of the low energy minimum progressively decreases whereas the intensity of the high energy one increases. At 40°, both transitions have the same intensity with an energy separation of 190 meV. For angles superior to 40°, the upper energy minimum becomes the stronger one, and the lower energy minimum intensity decreases. Above 60°, the intensity of the low energy
The anticrossing is the signature of the strong coupling between the perovskite exciton and the cavity mode. The energies of the two minima observed in figure 5, which correspond to the upper polariton branch (UPB) and the lower poalriton branch (LPB), are reported as a function of the angle of incidence $\theta$ in figure 6. The experimental results are fitted to the dispersion using a standard two-level model [17] (solid lines in figure 6):

$$E_{\text{UPB,LPB}} = \frac{E_{\text{ph}}(\theta) + E_{\text{per}}}{2} \pm \sqrt{V^2 + \left(\frac{E_{\text{ph}}(\theta) - E_{\text{per}}}{2}\right)^2}.$$

This relation is the same as the relation obtained for two coupled oscillators with a coupling energy of $V$. $V$ is a fitting parameter, assumed to be constant at all angles. The horizontal dashed-dotted line at $E_{\text{per}} = 2.433$ eV corresponds to the perovskite exciton transition energy. The dashed line represents the angular dispersion of the photon mode $E_{\text{ph}}(\theta)$, from formula (1), where $E_0$ and $n_{\text{eff}}$ are fitting parameters ($E_0 = 2.210$ eV and $n_{\text{eff}} = 1.77$). The very good agreement between the experimental and calculated results shows unambiguously that strong coupling leads to a Rabi splitting equal to $2V = 190$ meV.

The strong coupling occurs when the anti-crossing is larger than the homogeneous and inhomogeneous linewidth of the cavity photon mode and the excitons. Far from resonance, the LPB branch has a strong cavity photon mode character: the cavity mode linewidth is around 100 meV, leading to a typical quality factor at 2.41 eV of about 25. From the absorption spectrum of a perovskite in figure 2, the linewidth of the perovskite exciton is deduced to be 80 meV, which is satisfactory as compared to an anti-crossing of 190 meV.

Compared to the state of the art of the technology regarding semiconductor-based microcavities, it is thought that technological difficulties regarding the control of the design remain in microcavities containing molecules. In order to evaluate this control of the
Figure 7. Dispersion of the UPB and LPB for (a) microcavity MC2, (b) microcavity MC3. The squares are experimental data. The solid lines are fits from two level system resolution, the fitting parameters are (a) $n_{\text{eff}} = 1.85$, $E_0 = 2.244$ eV, $V = 75$ meV, (b) $n_{\text{eff}} = 1.88$, $E_0 = 2.277$ eV, $V = 68$ meV. The dotted line represents the energy of the uncoupled perovskite exciton. The dashed line represents the dispersion of the uncoupled photon cavity mode.

microcavity design, we have realized several $\lambda/2$-microcavities, varying the parameters $d$, $d_1$ and $d_2$ (see table 1). The experimental energies of the UPBs and LPBs are reported in figure 7 as a function of the incident angle, for microcavities MC2 and MC3. In the microcavity MC2, the perovskite layer lies near a node of the electric field, while in the microcavity MC1, the perovskite layer lies at an anti-node of the electric field (see figure 4). So it is expected that the interaction between the excitonic and the photon modes is weaker in MC2 than in MC1. In fact, it is seen in figure 7(a) that the Rabi splitting is 150 meV for MC2, compared to 190 meV in MC1. In the microcavity MC3, the perovskite excitons are localized near a node of the electric field like in MC2: the value of the Rabi splitting is then almost the same in MC2 and MC3. But the cavity photon energy mode at $\theta = 0$ is higher in MC3 than in MC2, so that the detuning at $\theta = 0$ is smaller in MC3 than in MC2: it can be seen in figure 7(b), that the anti-crossing occurs at smaller angles for MC3. These different experiments show that the realization of $\lambda/2$ cavities containing perovskite thin layers is highly controlled and reproducible.

The high value of the Rabi splitting is due to the increased interaction strength between perovskite excitons and photons. We evaluate the oscillator strength from the spectroscopic ellipsometry measurement of the complex refraction index of a 210 nm thick layer of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ deposited on a glass substrate. The fit of this measurement with a Lorentzian oscillator provides an oscillator strength of $5 \times 10^{15}$ cm$^{-2}$. This value compares to the oscillator strength of J-aggregates [7, 8]. As our perovskite layer has a two-dimensional structure, it is possible to define an oscillator strength per quantum well: $f_{\text{QW}}$. Knowing the thickness of the PbI$_4$ layer: 0.6 nm and the thickness of the alkyl chain: 1.0 nm from the crystalline structure [18], we evaluate $f_{\text{QW}} = 3.6 \times 10^{13}$ cm$^{-2}$. It is remarkable that this value is considerably larger than in an InGaAs structure [19]: $4.2 \times 10^{12}$ cm$^{-2}$ per quantum well. Figure 8 shows the experimental energies of the UPB and LPB as a function of the incident angle for a $\lambda/2$-microcavity MC4 containing a perovskite layer of thickness $d = 100$ nm, in which $d_1 = 0$ and $d_2 = 50$ nm. It can be seen that the Rabi splitting is larger in MC4 ($2V = 184$ meV)
than in MC2 ($2V = 150$ meV) or MC3 ($2V = 136$ meV), which is coherent with an increased total oscillator strength in the microcavity containing a larger number of quantum wells.

To demonstrate the strong coupling unambiguously, photoluminescence experiments have to be performed in addition to the reflectivity experiments. In order to observe the emission of the polaritonic mixed states, angle-resolved photoluminescence experiments have been performed at room temperature. A 405 nm diode laser beam is focused on the microcavities through the dielectric mirror, at normal incidence, and the photoluminescence spectra are recorded for various detection angles. Figure 9 shows the photoluminescence spectra obtained for MC1 for different angles of detection, ranging from 5° to 60°. For the lower angles, two peaks are present in the spectra. The position of the high energy peak is independent of the detection angle, whereas the position of the lower energy peak varies as the detection angle is tuned. For the higher angles, the lower energy peak becomes more and more intense, suggesting a bottleneck effect. Further experiments are needed to study this effect quantitatively.

The energy positions of the luminescence peaks of MC1 have been reported as circles in figure 10, superimposed to the fitted dispersion curves of the UPB and LPB. The dispersionless data correspond to the non-coupled part of the perovskite exciton, since the energy position of this peak corresponds to that of the photoluminescence spectrum of the perovskite layer. The variation of the low energy photoluminescence peak as a function of the detection angle coincides with the dispersion relation of the low energy polaritonic branch. This clearly indicates that this photoluminescence arises from the polaritonic emission and confirms the demonstration of the strong coupling regime in the microcavities containing perovskite thin layers. The emission of the UPB has not been observed. If we assume that thermodynamical equilibrium exists for all polariton states in a microcavity, we note that the occupation rate of this branch is $\exp(2V/k_B T)$ times smaller (with $2V \gg k_B T$ at room temperature) than the occupation rate of the lower energy branch [15]. Nevertheless, the lifetime of the cavity polaritons is probably too small to reach the thermodynamical equilibrium. Other explanations
Figure 9. (a) Photoluminescence spectrum of the structure before the evaporation of the top mirror, (b) Photoluminescence spectra of MC1 recorded for detection angles varying from $5^\circ$ to $60^\circ$.

Figure 10. Calculated dispersion of the UPB and LPB branches from two level system resolution (the fitting parameters are $n_{\text{eff}} = 1.72$, $E_0 = 2.282$ eV and $V = 96$ meV). The full circles are the experimental data from the photoluminescence spectra.

can be proposed: it has been suggested that the absence of the UPB emission could be due to the relaxation towards uncoupled excitonic states [20] or could be explained by fast emission of optical phonons between the UPB and LBP [17].

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In summary, we have demonstrated the strong coupling regime between the two-dimensional perovskite exciton and the confined photon modes in a Perot–Fabry microcavity at room temperature and we have observed the emission of the low energy polariton. We have shown that our technological developments allow the realization of reproducible $\lambda/2$ microcavities whose different parameters are very well controlled. This work opens the way to more complex structures where the perovskite excitons can be coupled via the cavity photon [8] to different excitons: strong coupling regime has been demonstrated at room temperature in hybrid microcavities containing perovskite molecules and organic dye molecules [12]. In particular, following the theoretical work of Agranovich et al [21], the possibility of coupling perovskite exciton and an inorganic semiconductor exciton in the same Perot–Fabry microcavity will be explored. Perovskites (R–NH$_3$)$_2$MX$_4$ (R: organic molecule, M: metal, X: halogen) are good candidates for this challenge because their absorption wavelength can be easily tuned by varying the nature of R, M, or X [22, 23], and can thus be chosen in resonance with the inorganic exciton energy.

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