Strong Coupling

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Thermodynamics of Molecules Strongly Coupled to the Vacuum Field**

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Light-matter interactions can be classified into two very different regimes based on the strength of the interactions. In the weak regime, the energy levels of the material remain essentially unchanged, such as upon excitation of molecules and subsequent fluorescence. In the so-called strong coupling regime, the interactions become so strong that new hybrid light-matter states are formed by very rapid photon exchange. Atoms and semiconductors have been studied in this regime owing to the unique properties of the hybrid states and the potential they offer in physics.[1–14] Molecules can also be strongly coupled to the electromagnetic environment,[15–35] which opens fascinating possibilities for molecular and material science that remain largely unexplored. To achieve this regime, the molecules are typically placed in an optical cavity, such as two parallel mirrors, that is resonant with a transition in the molecule (Figure 1a). Upon strong coupling, the excited state is split into two new hybrid states (P−, P+), also known as polaritons, resulting in two new peaks in the ground state absorption spectrum. In this condition, the molecules can be thought as dressed by the electromagnetic field, in analogy to the terminology proposed for atoms by Cohen–Tannoudji and Haroche.[3] The energy separating P− and P+ is known as the Rabi splitting. In the experiments presented herein, the Rabi splitting $\hbar\Omega_{RV}$is due to the vacuum electromagnetic field, which is always present in the cavity even in the absence of light.[36] For dye molecules, $\hbar\Omega_{RV}$ can be very large, on the order of 0.1 to 1 eV, owing to their high transition dipole moments (that is, large absorption extinction coefficients). Furthermore, $\hbar\Omega_{RV}$ is itself proportional to the square root of the concentration of coupled molecules in the cavity, that is $\sqrt{C}$, which enables the Rabi splitting and therefore the properties of the dressed molecules to be modulated.

This concentration dependence implies that the energies of P+ and P− are determined collectively by the number of dressed molecules involved. In fact, it is known that the P+ and P− are so-called Dicke states,[37] and their collective nature can be observed, for instance, in the fluorescence of P−, which is coherent for molecules micrometers apart.[28] In other words, many molecules are dressed together by the same electromagnetic field (or mode) (Figure 1b). In our experiments, the number of molecules in the volume of the mode of the cavity is about 10^5. It should be noted that other Dicke states are also formed, which are located between P+ and P-, so-called dark states as the transition dipole moment to these states is zero and therefore they are not visible in the absorption spectrum of the coupled molecules.[6]

As can be noticed in the absorption spectrum (Figure 1a), a small residual absorbance peak (circled) remains between

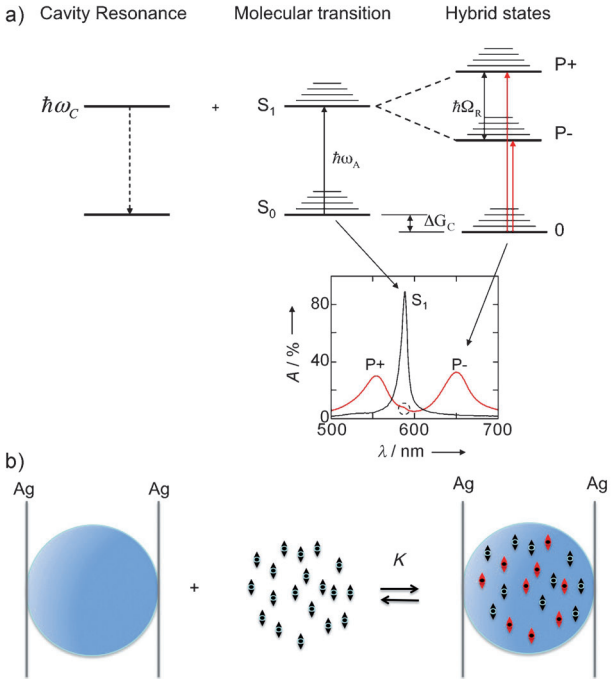

Figure 1. a) The strong coupling between molecules resonant with a cavity mode $\hbar\omega_C$, leading to the formation of two new eigen hybrid light-matter states P+ and P− separated by the Rabi splitting energy $\hbar\Omega_R$. The ground-state energy of the coupled or dressed molecules is modified as compare to the bare molecules by the standard Gibbs free energy $\Delta G_C^{\ominus}$. An example of the absorption spectra of the bare and dressed molecules (J-aggregates of TDBC) is also shown.[24] The dashed circle shows a small bump in the spectrum indicating that not all the molecules are dressed in a coupled system. b) Illustration of how one cavity mode interacts with many molecules to form the dressed molecules and the collective Dicke states states P+ and P−. *K* is the equilibrium constant. Here the fraction of molecules that are coupled to the mode are indicated in red.

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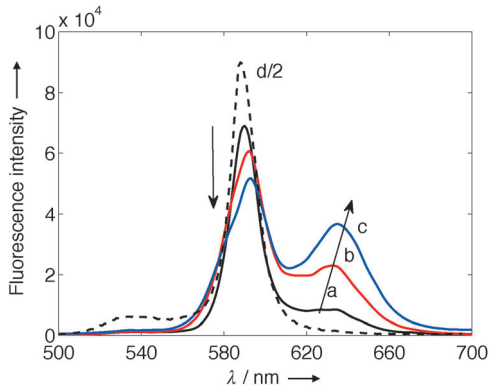

Figure 2. Fluorescence spectra of cavities with different concentrations of TDBC in polyvinylalcohol, with the fluorescence intensity I_F recorded normal to the surface with the excitation wavelength at 450 nm (a: 0.045 M, b: 0.06 M, c: 0.07 M, d: 0.0135 M).

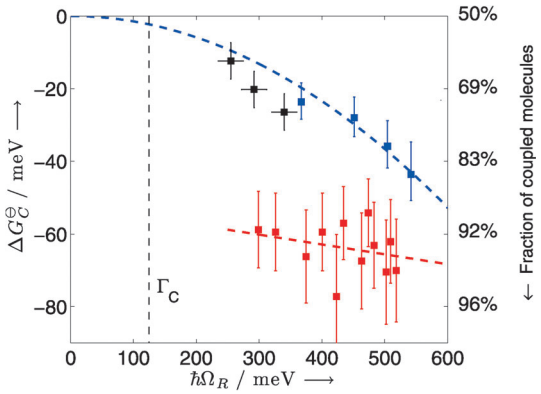

Figure 3. Standard Gibb's free energy $\Delta G_C^{\ominus}$ as a function of the Rabi splitting. Black points are TDBC fluorescence data (see text). The blue and red points represent the data after deconvolution for BDAB and merocyanine, respectively. The curves are linear or quadratic fits of the data points. The correspondence with the proportion of coupled molecules is given on the right side.

the polariton peaks, which indicates that some of the molecules (in the form of J-aggregates of TDBC, see the Supporting Information) are not dressed, or in other words not coupled. In fact this is a general feature of such systems. In Figure 2, we show the fluorescence of the TDBC J-aggregates inside the cavity at different concentrations. In the cavity there are two fluorescence peaks: one that is due to the uncoupled molecules at 590 nm and one at longer wavelengths associated with P−. Two trends can be noticed. First with concentration, the two peaks separate as the coupling strength or Rabi splitting increases. At the same time, the fluorescence of the bare J-aggregates decreases relative to P−. In other words, the fraction of coupled molecules to the uncoupled ones increases with the Rabi splitting $\hbar\Omega_{RV}$. This is very reminiscent of molecular complexation, where the equilibrium is shifted towards complexed state as the equilibrium constant K increases.

If this analogy is pertinent then one can view the uncoupled (U) and the coupled molecules (C) as linked by an equilibrium (Figure 1 b):

$$\mathrm{U} \overset{K}{\rightleftarrows} \mathrm{C}$$

$$\text{with an equilibrium constant } K = \frac{[\mathrm{C}]}{[\mathrm{U}]} = \exp\left(\frac{-\Delta G_C^{\ominus}}{k_B T}\right) \qquad (1)$$

where $\Delta G_C^{\ominus}$ is the standard Gibbs free energy difference between ground states of the uncoupled and coupled molecules (as in Figure 1 a), $[\mathrm{U}]+[\mathrm{C}]=[\mathrm{N}]$, the total concentration of molecules in the system, and k_B is Boltzmann's constant. Note the thermodynamic quantities quoted here will all be given in molecular energies and in eV. The standard Gibbs free energy is the appropriate thermodynamic quantity in this context, as the experiments are done at constant pressure and not at constant volume. The thermal bath is provided by the matrix in which the dye molecules are embedded.

To test the validity of this view, we have estimated the ratio [C]/[U] from the fluorescence in the presence and absence of coupling of TDBC (Figure 2) and plotted it as a function of the Rabi splitting as shown in Figure 3. While a clear trend is visible, there are many assumptions underlying such a plot, most notably that the radiative rate constant of uncoupled molecules remains constant. To make a more accurate assessment of the dependence of K on the Rabi splitting, we have developed a method for deconvoluting the absorption spectra inside the cavity to estimate the fraction [C]/[U] as a function of Rabi splitting. A key difficulty is that the normal additivity of absorbances does not hold inside a Fabry–Perot cavity so that straightforward deconvolution is no longer possible. The details of our method, including the assumptions and the sources of error, are given in the Supporting Information.

Using this method, $\Delta G_C^{\ominus} = -k_B T \ln \frac{[C]}{[U]}$ at room temperature is plotted in Figure 3 as a function of Rabi splitting for two different molecules at various concentrations: BDAB and merocyanine, dissolved in PMMA (polymethylmethacrylate), all placed in Fabry–Perot cavities with one semi-transparent Ag mirror (Q-factor ≈ 25, see the Supporting Information for details). These molecules all reach the ultra-strong coupling regime where the Rabi splitting is a significant fraction (>0.1) of the transition energy involved in the coupling[22–24] (see also the Supporting information).

The proportionality tendency is quite clear, indicating that this is not fortuitous. It can be noticed in Figure 3 that ΔG_C^{Θ} is negative for all the measured splittings, indicating that strong coupling is spontaneous as expected, as the mere closing of the cavity generates the coupling. In terms of standard values used in chemistry, the observed ΔG_C^{Θ} values are in the range of a few kJ mol^{-1}e (for example, 25 meV corresponds to 2.4 kJ mole^{-1}). The large noise for the MC data stems mostly from the fact that when a very large fraction of molecules are coupled ($>90\,\%$), the fraction of uncoupled molecules can only be estimated within a few percent (see the Supporting Information).

To ascertain this interpretation and that the plot in Figure 3 has its origins in the thermodynamics of the formation of the dressed molecules, the temperature dependence of $-\ln[\mathrm{C}]/[\mathrm{U}]$ was analyzed. The analysis is made difficult by the fact that the absorption of the uncoupled dye molecule can shift and the cavity length can be slightly

modified by a change in temperature. Nevertheless by a careful choice of conditions, the analysis could be carried out for the BDAB over small temperature ranges from which the changes in standard entropy ΔS_C^Θ and standard enthalpy ΔH_C^Θ associated with coupling to the vacuum field can be extracted, because:

$$\Delta G_C^\Theta = -k_B T \ln \frac{[C]}{[U]} = \Delta H_C^\Theta - T\Delta S_C^\Theta \quad (2)$$

Figure 4a shows an example of the spectral changes associated with the temperature dependence of coupled BDAB and as insert the bare molecule. The changes are very small owing to the limited temperature range and the fact that the thermodynamic constants are tiny, as shown next. In Figure 4b, the deconvoluted spectral changes are replotted as a function of temperature, and the linear dependence enables the extraction of ΔS_C^Θ and ΔH_C^Θ for different values of $\hbar\Omega_{RV}$. The results are gathered in Table 1 for BDAB. ΔH_C^Θ is extremely small and negative, while $\Delta S_C^\Theta > 0$ and dominates the final ΔG_C^Θ at room temperature.

The possibility that solvation plays a role in the entropy and enthalpy was explored by comparing the data for BDAB in two different polymers: PMMA and polystyrene (PS), which have different molecular structures and (static) polarities. Indeed both ΔH_C^Θ and ΔS_C^Θ are significantly modified (Figure 4b and Table 1). As $\hbar\Omega_{RV}$ increases, the perturbation induced by the splitting pushes the ground state down affecting ΔH_C^Θ but mostly ΔS_C^Θ, the interaction with its immediate environment (solvation shell) being perturbed with a loss of microscopic order.

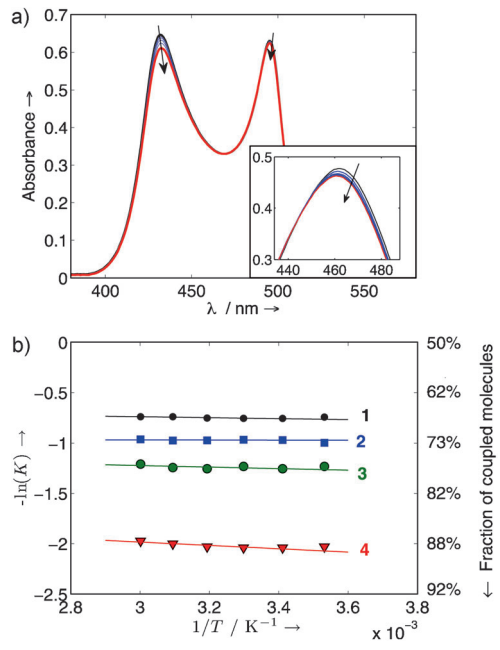

Figure 4. a) Example of changes in the absorption spectra of BDAB due to the increase of temperature, when the molecule is inside or outside (insert) the cavity between 10 °C (black curve) and 64 °C (red curve). b) $-\ln(K)$ $(=\Delta G_C^\Theta/k_BT)$ as a function of the inverse temperature. The symbols show the data points while the lines are their linear fits. The concentrations of BDAB are 1) 0.224 M, 2) 0.258 M, 3) 0.285 M in PMMA and 4) 0.285 M in PS.

Table 1: ΔH_C^Θ, ΔS_C^Θ, and ΔG_C^Θ for different values of $\hbar\Omega_{RV}$ for BDAB in PMMA and PS.

	$\hbar\Omega_{RV}$ at 298 K [meV]	ΔH_C^Θ [meV]	ΔS_C^Θ [meV K^{-1}]	ΔG_C^Θ at 298 K [meV]	Fraction of coupled molecules
BDAB (0.224 M/ PMMA)	431.1	−4.14	0.051	−19.13	68.1 %
BDAB (0.258 M/ PMMA)	491.3	−0.41	0.082	−24.52	72.5 %
BDAB (0.285 M/ PMMA)	526.5	−6.59	0.086	−31.71	77.8 %
BDAB (0.285 M/PS)	485.0	−14.34	0.128	−51.90	88.6 %

It has been known for a long time that not all molecules were coupled in a strongly coupled system.[8,9] In fact it has been assumed that only a very small fraction of the molecules are coupled. However the notion of thermodynamic equilibrium between uncoupled and coupled molecules was never considered as far as we know. When considering that the molecules go spontaneously and reversibly between uncoupled and coupled state by simply placing or removing one of the mirrors of the cavity, the two states of the systems must be in thermodynamic equilibrium.

Our results confirm that this is indeed the case and that there is a direct relationship between Rabi splitting and the ground state energies difference between the uncoupled and coupled molecules as reflected in ΔG_C^Θ, which is nevertheless modulated by solvation effects as can be seen notably in the entropy. As a consequence for a given initial concentration of molecules, Rabi splitting, ΔG_C^Θ and therefore the fraction of coupled molecules can be modulated by solvation. In fact the Rabi splitting dependence of the concentration of coupled molecules implies that:

$$\hbar\Omega_{VR} \propto \sqrt{C} = \sqrt{\frac{N}{1+\exp\left(\frac{\Delta G_C^\Theta}{k_B T}\right)}} \quad (3)$$

The shift of the ground level of the coupled system has been predicted[13] and observed[14] for the ultrastrong coupling regime and the dependence was supposed to be quadratic on the Rabi splitting, which would also be expected from Equation (3). A quadratic dependence can be fit to the BDAB data (Figure 3), but it might just be fortuitous. Indeed no such fit can be done for the merocyanine even within the large error bars of the data. Furthermore there is no clear reason why the ΔG_C^Θ has to be negative. Indeed if the fraction of coupled molecules is less than 50 %, ΔG_C^Θ must be positive.

At the microscopic level, the co-existence of uncoupled and coupled molecules can be understood in terms of distributions related to inhomogeneously broadening, such as molecular orientations and solvation. Furthermore, the location and orientation relative to the cavity field will generate a distribution of coupling strengths. As the Rabi splitting or coupling strength increases, the collective Dicke state will include more and more molecules with unfavorable

transition dipole orientations,locations, or transition energies. The equilibrium implies that each molecule is rapidly exchanging between the uncoupled and coupled states, the ratio of the rates in both directions being K. These rates must be very fast, and $< 10^{-13}$ s as perturbations induced by 150 fs pump probe experiments that we have carried out do not reveal any re-equilibration processes between the ground states. These rates are probably related to fluctuations within the inhomogenously broadened linewidth discussed above.

The large attainable fractional values of coupled molecules, opens the door for the controlled modification of properties of molecules and materials in the bulk as it has been reported for instance for the dynamics of a photoisomerization reaction and the work function of a material.[23,35] Such examples are only a sampling of what could be possible through the formation of hybrid light-matter states with the vacuum field. This will require well-defined conditions for which the thermodynamics presented here provides the framework of understanding. As we have demonstrated, the thermodynamics of strong coupling is mostly determined by the Rabi splitting modulated by both microscopic solvation effects and by macroscopic optical properties of the coupled molecule-cavity system. The findings reported here should thus be very useful for exploring the full potential of strong coupling in molecular and material science.

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[36] In the absence of dissipation, $\hbar\Omega_{RV}$ is given, for a simple two level system at resonance with a cavity mode, by the product of the electric field amplitude E of the cavity and the transition dipole moment d: $\hbar\Omega_R = 2\,E\cdot d\cdot\sqrt{n_{ph}+1} = 2\sqrt{\frac{\hbar\omega}{2\varepsilon_0 v}}\cdot d\cdot\sqrt{n_{ph}+1}$ (1), where $\hbar\omega$ is the cavity resonance or transition energy, ε_0 the vacuum permittivity, v the mode volume, and n_{ph} the number of photons in the cavity. As can be seen, even when n_{ph} goes to zero, there remains a finite value for the Rabi splitting, $\hbar\Omega_{RV}$, owing to the interaction with the vacuum field. This splitting is itself proportional to the square root of the number of molecules in the cavity $\sqrt{n_{mol}}$, which in turn implies that the $\hbar\Omega_{RV}$is proportional to the square root of the concentration ($\sqrt{\frac{n_{mol}}{v}}$).[26]
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