STRONG LIGHT-MATTER COUPLING TO MODIFY CHEMICAL AND PHOTO-PHYSICAL PROPERTIES

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INTRODUCTION

Electromagnetic field can interact with molecular systems by the exchange of photons. If the molecular transition energy is equal to the energy of incident radiation, the photon will be absorbed by the molecule. This is an example of weak light-matter coupling. If the molecule is placed inside an optical cavity, the interaction leads to strong coupling. Optical cavity is an arrangement of mirrors in which standing waves of light can be formed. Standing waves in the cavity are known as cavity modes (Figure 1). To form standing wave for a particular frequency, twice the separation between plane mirrors must be equal to an integral multiple of wavelength. The separation between mirrors can be adjusted to form cavity modes for a particular frequency. In order to have strong coupling, the cavity mode must be in resonance with molecular excitation. Here, two attempts to verify the effects of strong light-matter coupling on chemical and physical properties are reviewed.

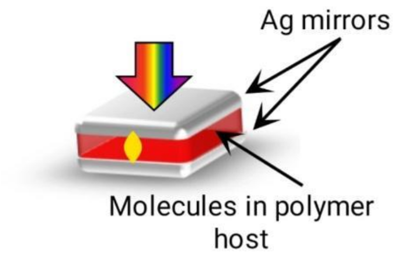

Figure 1. An optical cavity formed by two Ag mirrors with molecules in polymer host

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RABI SPLITTING

If a molecule is embedded in an optical cavity and the cavity mode is in resonance with molecular excitation, strong light-matter coupling occurs. The cavity mode and the molecule forms a coupled system in which the energy oscillates between the quantum systems as in the case of two simple harmonic oscillators coupled together. As a result of strong light-matter coupling, molecular energy levels are modified, leading to the formation of hybridized molecular photonic states known as polaritons. The excited molecular energy levels split into two polaritonic states – upper polariton and lower polariton (Figure 2). The energy difference between upper polariton and lower polariton is Rabi splitting. The coupled system can be thought of as a single entity with new energy levels and must have distinct chemical and physical properties.

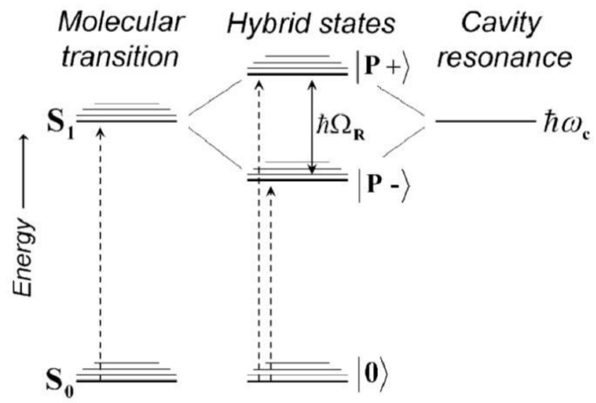

***Figure 2**. Simplified energy landscape showing the interaction of a HOMO–LUMO (S0–S1) transition of a molecule resonant with a cavity mode*[1]

STRONG COUPLING WITH VACUUM CAVITY MODES

The Rabi Splitting energy of a molecule embedded in a resonant optical cavity is given by

$$\hbar\Omega_R = 2Ed\sqrt{n_{ph}+1} = 2d\sqrt{\frac{\hbar\omega}{2\varepsilon_0 V}}\sqrt{n_{ph}+1}$$

Where ħω is the energy of cavity mode which is equal to molecular transition energy, V is the mode volume ie, the volume occupied by the cavity mode, d is the transition dipole moment and n_{ph} is the number of photons inside the optical cavity.

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Even if the number of photons in the cavity is equal to zero, there remains a finite Rabi Splitting due to strong coupling with vacuum electromagnetic field or vacuum cavity modes. The vacuum mode should be in resonance with molecular excitation.

MODIFICATION IN CHEMICAL REACTIONS

The effects of strong coupling of a molecular system with vacuum field on chemical reaction were verified by James A Hutchison and team in 2012[1]. They studied the photo isomerisation reaction of Spiropyran into Merocyanine, when the sample was embedded in a resonant cavity. The Spiropyran undergoes a bond cleavage following a photo excitation by UV light of wavelength around 330nm.

The Spiropyran in polymer host PMMA (Poly Methylmethacrylate) was embedded between two Ag mirrors insulated by PVA (Poly Vinyl alcohol) as shown in figure 3(d). Absorption spectra and reaction rate were studied with and without strong coupling with resonant optical cavity. Without coupling, Spiropyran and Merocyanine have absorption peaks at 330nm and 560nm respectively (Figure 3(c)). The cavity was adjusted to be in resonance with 560nm. Then, under strong coupling, Merocyanine shows two peaks at around 500nm and 650nm. The splitting of absorption (Figure 3(f)) into two new peaks is due to the strong coupling with cavity modes and the resulting formation of hybrid states. The spectrum of the coupled molecule is independent of the light intensity or no. Of photons which indicate that the coupling is with vacuum field.

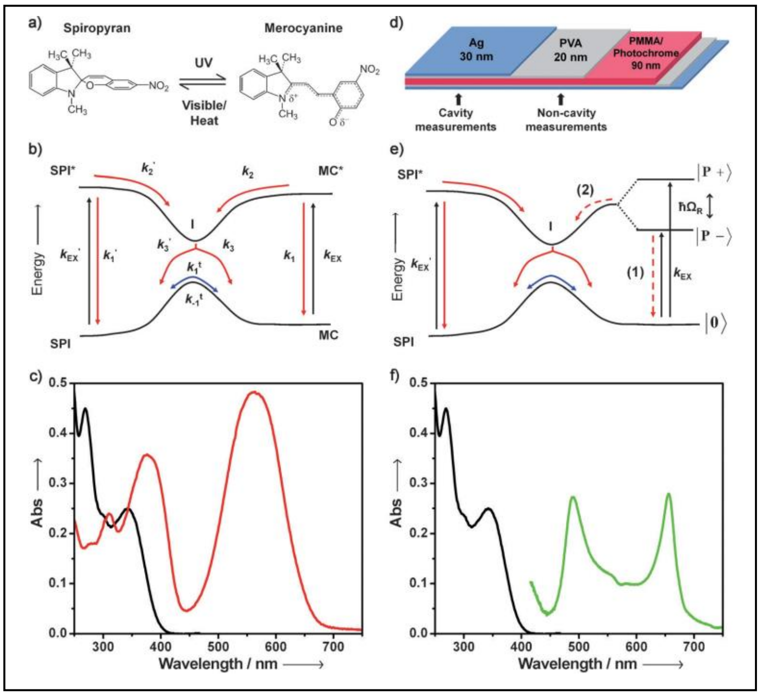

Figure 3. The molecular structure, cavity structure, energy landscapes and absorption spectra of Spiropyran and Merocyanine

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The energy landscapes of the molecule Merocyanine was modified as shown in figure 3(e). This modification will definitely modify the photo isomerisation reaction rate. The scientists measured the transmission amplitude of photo excitation radiation, from which the absorption amplitude was calculated. The value of absorption points towards the reaction rate and formation of Merocyanine. It was found that absorption was reduced due to Rabi Splitting. The observed photo isomerisation reaction rate was slowed down significantly in the cavity structure due to the modification of reaction potential by strong coupling with vacuum cavity modes. Thus, modification in molecular energy landscapes modifies the reaction rate and yield.

Strong coupling can either speed up or slow down a reaction depending on the reorganization specific energy levels. The coupling can be done to a specific vibration transition to modify the reactivity of a bond. Since the formation of hybrid states changes the energy levels at play, it will in principle modify the ionization potential and the electron affinity of the system. The work function of coupled material will be modified and measurements to verify this are under way. Fine tuning the work function by strong coupling to vacuum field could have significant consequences for device design and performance[1].

COLLECTIVE RAYLEIGH SCATTERING

The Rabi Splitting of energy levels of molecular system embedded in an optical cavity in the absence of photons is given by

$$\Omega_R = \frac{2d}{\hbar} \sqrt{\frac{\hbar\omega}{2\varepsilon_0 V} N}$$

Where, N is the number of molecules in the system. The $\sqrt{N}$ dependence indicates collective interaction between molecules and optical modes.

Adina Golombek, M Balasubrahmaniyam and team in 2020 studied the Rayleigh scattering from dye molecules in a polymer host under resonant and non-resonant conditions with vacuum cavity fields. They observed strong resonant Rayleigh scattering under strong coupling[2]. The Eigen states of the coupled system are delocalized across a macroscopically large ensemble of molecules. The molecules in the resonant cavity are coupled together by means of cavity modes and acquire distinct physical properties.

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CONCLUSION

Strongly coupling with a vacuum optical cavity i.e., by embedding the system between two plane mirrors finely tuned to be in resonance with molecular excitation, the reaction rates and yields can be controlled. Moreover, it was recently verified experimentally that the polaritonic states exhibit strong resonant Rayleigh scattering under strong coupling with vacuum cavity modes, and it indicates the modification in photo physical properties of materials also.

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