Cavity catalysis by Vibrational Strong Coupling

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Certificate of Examination

This is to certify that the dissertation titled “ Cavity catalysis by Vibrational Strong Coupling” submitted by Ms. Chithra P.R(MS15205) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be submitted.

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June 15, 2020

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Jino George at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Jino George
(Supervisor)

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Abbreviation

VSC - Vibrational strong coupling
V-USC - Vibrational ultra-strong coupling
ESC - Electronic strong coupling
PTA - 1-phenyl-2-trimethylsilylacetylene
TBAF - tetra-*n*-butylammonium fluoride
PIC - Phenyl isocyanate
PhOH - Phenol
F-P cavity - Fabry-Pérot cavity
J-C model - Jaynes- Cummings model
T-C model - Tavis - Cummings model
FWHM - Full width half maximum
DMF - Dimethylformamide
NMP - N-Methyl-2-pyrrolidone
FSR - Free spectral range
C-T complex - Charge transfer complex

CONTENT

Abstract

Polaritonic chemistry is a very promising research topic in the field of physical chemistry. In Polaritonic chemistry, selected vibrational band of a molecule gets strongly coupled to an infrared cavity mode, thereby modifying its energy-reaction co-ordinate. Strong coupling happens when a particular vibrational transition comes in resonance with an optical cavity mode and that exchange energy back and forth, creating hybrid vibro-polaritonic states. These vibro-polaritonic states possess very interesting properties: (1) their energy can be tuned depending upon the coupling strength and (2) are half-molecule like and half-photon like. This results in interesting chemical changes with respect to a reaction co-ordinate. So far, three examples are shown in the literature: vibrational strong coupling (VSC) of a desilination reaction, Prins cyclisation and an ester hydrolysis. In the earlier two cases the activation free energy increases, whereas in the later, activation free energy decreases. In the current work, we look into the effect of VSC of first order kinetics of adduct formation between phenylisocynate and a phenol derivative by coupling the isocyanate stretching mode to an infrared cavity mode.

CHAPTER 1

1. INTRODUCTION

Cavity quantum electrodynamics is a relatively new field of study in the atomic physic and quantum optics. This emerged in the early 80s with the new generation of experiments from Serge Haroche group at École Normale Supérieure, Paris. Cavity quantum electrodynamics deals with the interactions of the vacuum field with a two-level system. This interaction can be weak, strong and ultrastrong. In weak coupling, the losses like relaxation to ground state or decay rates are greater than coupling. But in the strong coupling regime, there is a coherent exchange of energy between the quantum emitter and the cavity. The rate of this exchange-Rabi frequency- is greater than any decay rate that can occur in the system. This energy exchange results in formation of new energy levels that have both light and matter properties. These states are called “Polaritonic states”. In ultra-strong coupling, the coupling strength is greater than 10% compared to the fundamental transition. Various experiments have been demonstrated that the properties of the materials can be modified, through the formation of polaritonic states. One of the fascinating developments in this direction is the introduction of polaritonic chemistry, where chemical systems are studied under light-matter coupling. In this chapter, we will be discussing the historical and theoretical background of strong interaction in polaritonic chemistry.

1.1 HISTORICAL PERSPECTIVE

Einstein’s demonstration of spontaneous emission as a culmination of thermal equilibrium between matter and radiation sparked the belief among physicists that excited atoms radiate inevitably.[1] Spontaneous emission is considered fundamental and an inherent property of an atom-vacuum system. One of the main characteristics of the spontaneous emission is its irreversibility and thus the exponential decay. Physicists have experimentally demonstrated that the spontaneous emission can be enhanced or inhibited by confining the radiation between two mirrors[2][3][4]. Purcell effect is one such pioneering work by the famous American scientist E.M Purcell, where the modification of spontaneous emission due to the enhancement or suppression of vacuum fluctuations inside a resonant cavity is observed[5]. But in those cases, specifically, it is the manifestation of the light-matter interaction in the weak coupling regime. The factor by which the emission rate altered inside the resonator with respect to that in free space is called Purcell factor. But in the succeeding researches, it was found that the interaction between matter and radiation inside a cavity exhibited properties of reversibility and thereby instead of exponentially decaying into the lower state it can exchange energy with the cavity. This occur when light-matter interaction is in the strong coupling regime. Although the theoretical framework of strong light-matter coupling was given in 1963 by Jaynes and cummings[6], the experimental attempt was done by Yakovlev *et al* in 1975 where it is shown that not only radiative decay rates are affected, but also new states are formed due to strong interaction between light and matter[7]. In 2012, Nobel prize in physics was awarded to Serge Heroche and David J. Wineland for their works on strong light-atom coupling. Initial experiments were done on Rydberg atoms. Strong light-matter interaction has been studied for the past 50 years in physics. Only a decade before the effect of strong coupling in physical chemistry and organic chemistry has started. This set of experiments paved a path for the emergence of a new field of study in chemistry itself, called polaritonic chemistry.

In the early stages of polaritonic chemistry, coupling was done to the electronic states of the molecule- electronic strong coupling (ESC). In 2012, T.W. Thomas Ebbesen and co-workers demonstrated some of the pioneering works in polaritonic chemistry. There are evidences that this strong coupling brings alterations on the chemical energy landscape of the photoisomerization of spiropyran and merocyanine photo-dyad[8]. Later on it was shown that, thermodynamics of the molecules under strong coupling[9], work function of organic molecules [10], conductivity of organic semiconductors[11] can be altered under strong coupling conditions. But the strong light-matter interaction is not just limited to electronic coupling. It was showed that vibrational band of a molecule can also be coupled to the vacuum field. This is called vibrational strong coupling(VSC). First experimental evidence was reported in 2015 by the Ebbesen group[12]. The experiment was done on the C=O vibrational band in polyvinyl acetate, a polymer and it was coupled to the vacuum field using a microcavity, in a Fabry- Pérot cavity configuration and a Rabi splitting of 167 cm^{-1} was achieved. Later in the same year, VSC in liquid phase was also reported for a series of functional groups like C=O, C=C, -CN[13] etc. After this, a series of studies are made not only in controlling chemical reaction, but also its implications in chemical and physical properties. In 2016, it was reported that a ground-state thermal collision reaction can be controlled under VSC to vacuum electromagnetic field[14]. The effect was demonstrated on the desilination reaction of alkynyl-silane and it was found that the rate of the reaction decreased by 5.5 times at ON resonance condition. The thermodynamic studies of this reaction reveal that the activation enthalpy and entropy changed significantly, indicating the modification of transition state from an associative to a dissociative type. It was also shown that by VSC it is possible to control a chemical reaction selectively[15]. Later, work by Hiura *et. al.* proved that there can be an acceleration in chemical reaction under VSC, named as cavity catalysis[16]. Later it was demonstrated that cavity catalysis can be achieved by another phenomenon called cooperative vibrational strong coupling[17].

1.2 THEORETICAL CONSIDERATIONS

1.2.1. STRONG COUPLING REGIME

In the extensive field of light-matter interaction, the term “strong coupling” is used specifically in two circumstances. In the first situation, it reffered to a scenario where there is a cavity of good enough quality factor such that the emitter inside can emit and reabsorb a photon multiple times before it decays irreversibly into the environment. Experiments in this case will be able to throw some light on Rabi splitting and its dynamics via spectroscopic techniques. Another scenario is ultra-strong coupling where the coupling strength is so strong that the approximations and formulas are not applicable. Let us go deep into the first scenario.

In strong coupling, there is a coherent exchange of energy between the quantum emitter and the cavity mode. The rate of this exchange Ω is faster than any other decay that can happen in that system. This energy exchange occurs only if the molecular transition and cavity mode are in resonance condition. If that is the case, then it will result in the generation of two new hybrid states both having the properties light as well as matter. The wavefunction of this polaritonic states is given by

$$| P+> = c_{11} |e>_m |0>_c + c_{12} |g>_m |1>_c$$

$$| P-> = c_{22} |e>_m |0>_c - c_{21} |g>_m |1>_c$$

P+ and P- are generated by the linear combination of the molecule in the excited state |e> with 0 photon and the molecule in the ground state |g> with 1 photon in the resonant cavity.[18] Figure 1.1 diagrammatically shows the formation of P+ and P- in the strong coupling regime

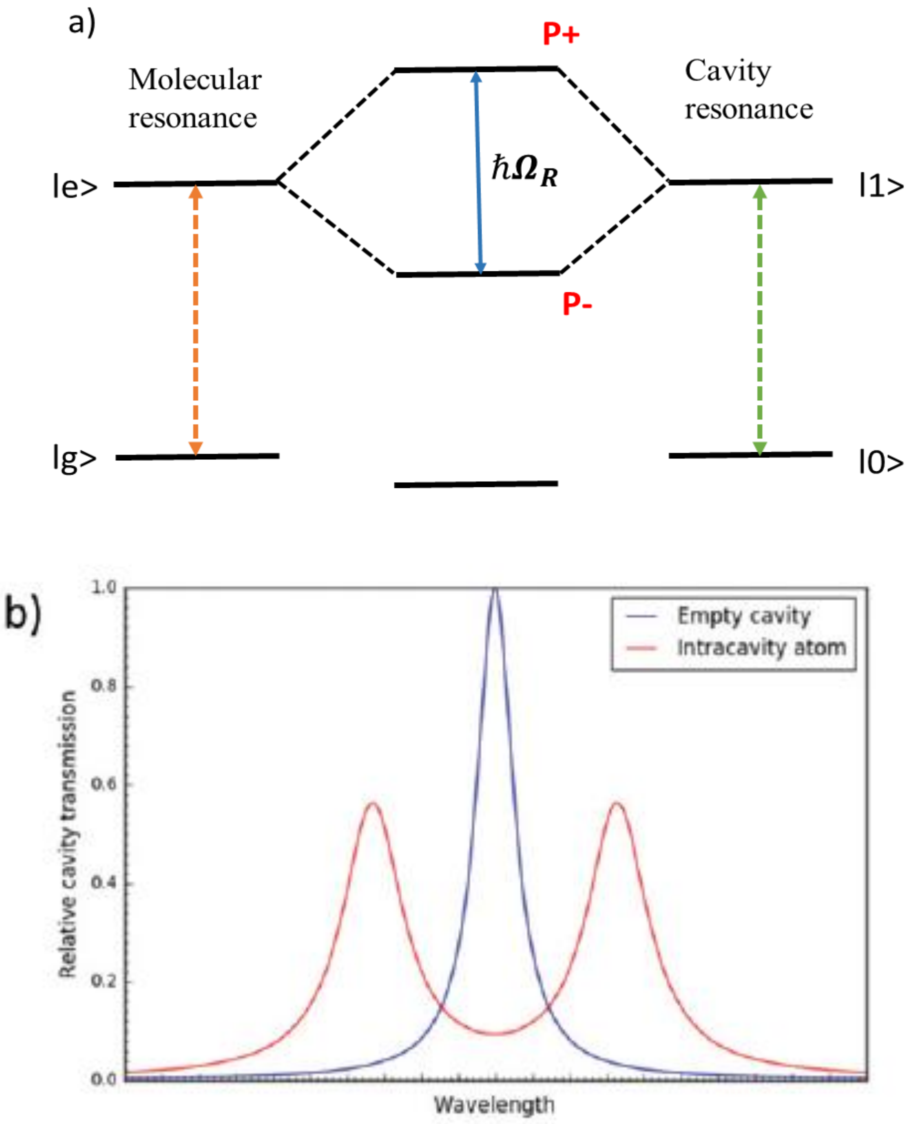


Figure 1.1 a) Resonance interaction between a two-level system and cavity mode leading to the formation of new hybrid light-matter states |P+> and |P->. b) Blue peak represents the relative transmission of the empty cavity and red spectrum with double peaks represents the relative transmission of resonant cavity due to the formation of polaritonic states. Figure is taken from ref.[19].

One of the important quantity that characterizes the strong coupling between light and matter is the Rabi frequency **Ω** and it is given by the expression

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

The energy difference between the two states- upper and lower polaritonic states is called Rabi splitting(**$\hbar\Omega_R$**). One of the key conditions for strong coupling as already mentioned is the rate of exchange of energy between the emitter and the resonant cavity should be greater than any decay processes in the system. This can be understood from Jaynes-Cummings two-state model;

$$\Delta E = E_+ - E_- = \hbar\Omega_R = \sqrt{4V_n^2 - (\gamma_c - \gamma_e)^2}$$

Where E_+ and E_- are the energies of polaritonic states P+ and P-, γ_c and γ_e are the decay constants (ħ/τ) of the photon in the cavity and the excited states, and V_n is the interaction energy between the electric component of the electromagmtic field in the cavity,**E_0**, and the transition dipole moment of the molecule, **d**. In the absence of dissipation, the equation for Rabi splitting is modified into

$$\hbar\Omega_R = 2V_n = 2d.E_0 = 2d\sqrt{\frac{\hbar\omega}{2\varepsilon_0 v}} \times \sqrt{n_{ph} + 1}$$

where ħω is the energy of the resonant cavity, ε_0 is the vacuum permittivity, v is the mode volume and n_{ph} is the number of photon involved in the coupling.

From the above expression it is clear that even in the absence of photons Rabi splitting has a residual value,ie, when n_{ph} = 0, is called "vacuum Rabi splitting". This happens when the molecular transition dipole interacts with the zero-point energy or fluctuations of cavity.[18] This is due to the exchange of virtual photons. The vacuum fluctuations or zero-point energy is the ground state energy of quantised electromagnetic field. Zero-point energy was first introduced by Max Planck in his second theory of black body radiation in 1911 and later by Einstein in 1913 to explain molecular agitation at zero temperature· [20][21] But in 1916, Nernst highlighted that the zero-point energy exists in a field mode, which was proved later·[22]

From the above equation, it is likely that the Rabi splitting is firmly dependent on few factors. One should be the strength of the electric field and another one is oscillator strength of the transition dipole. Field strength is maximum at the antinodes of the electromagntic wave. So Rabi splitting would be maximum if molecules are at the vicinity of antinodes.[23] Another one is the orientation of the molecular transition dipole moment. Every molecule is coupled at the same time as they are randomly oriented. So in an F-P cavity, $\hbar\Omega_R$ would be an average value of all the interactions and can be accounted for those molecules having a dipole parallel to the electromagnetic field.

One thing to keep in mind is that getting the polaritonic states is not enough to confirm that the system has entered into strong coupling[24]. One of the characteristics of the Rabi splitting is its dependence on concentration(C) of the molecules inside the resonant cavity.

$$\hbar\Omega_R \propto \sqrt{\frac{N}{v}} = \sqrt{C}$$

N is the number of molecules coupled to the cavity and v is the mode volume. So checking the concentration dependence of the Rabi splitting is one way to confirm whether the system has attained strong coupling.

Another important feature of strong coupling is that the bosonic nature of the polaritonic states. Since it has a bosonic (photonic) part along with fermionic (electronic) part, it can be called as quasi-boson. Cavity polaritons inherits dispersion behavior from the cavity photons who have a strong in-plane dispersion. Dispersion relation is the relation between energy or frequency and momentum of two states[25]. In the absence of any interaction the dispersive curve for two states intersect each other at the resonance condition. On the other hand, in the presence of strong interaction it shows anticrossing behavior and the difference between the energies at the resonance condition gives the Rabi splitting (see figure 1.2).

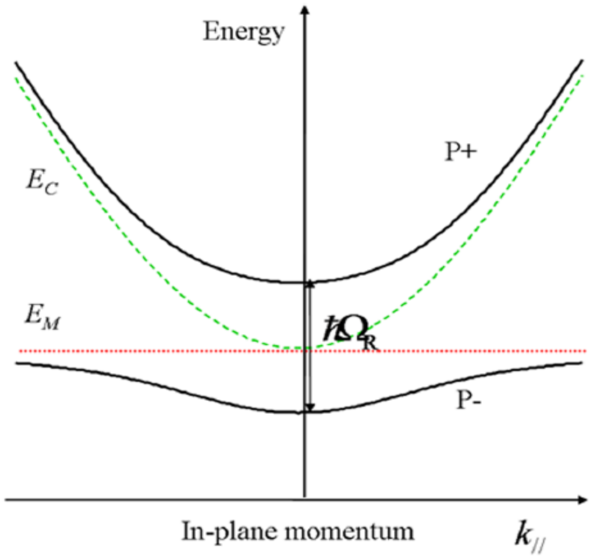


Figure 1.2 Illustration of a dispersion curve obtained in an F-P cavity in which the anticrossing appears at normal incidence ($k_{||} = 0$). E_C is the energy of the resonance cavity (green dotted line) and E_M is the energy of molecular transition (red dotted line). Figure is taken from ref [18].

In case of an F-P cavity, the formula that is usually used to plot the dispersive curves is

$$|k_{||}| = k_{||} = \frac{2\pi}{\lambda}\sin\theta$$

Where $k_{||}$ is the in-plane momentum, θ is the angle of incidence and λ is the peak wavelength. By exploiting the strong angle dependence of the cavity mode energy, one can tune the resonance frequency and thus the coupling itself. This is another way to confirm the Rabi splitting.

1.2.2 QUANTUM MECHANICAL MODEL FOR N MOLECULES

Many approximations have been made to explain the quantum mechanical explanation of strong light-matter interaction. One among them would be the dipole-dipole approximation which states that the wavelength of the electromagnetic field is much larger than the size of the molecule. This indicates that the coupling is only between the molecular transition dipole moment and the electromagnetic field. Another approximation is Thomson-Lorentz model of the atom which considers the atomic ensemble as a collective oscillator. Before getting deep into the quantum mechanical explanation, it is important to mention a significant parameter that need to be explained, transition dipole moment. It determines how strong is the interaction between a system and the electromagnetic wave or how strong would be a transition. It is given by an integral

$$\vec{d} = <\psi_f|\hat{d}|\psi_i> = \int \psi_f^* \,\hat{d}\, \psi_i d^3\vec{r}$$

The interaction energy or dipolar coupling V between the light and molecule is given by

$$V = -\vec{d}.\vec{\varepsilon}$$

Where $\vec{\varepsilon}$ is the electric field operator.

One of the early explanations for the coupling of molecules to the cavity on a pure theoretical framework was done by Jaynes and Cummings. In J-C model, the exciton is considered as a two-level atom(single emitter) and cavity field as a single mode with frequency ω_c. Thus the corresponding Hamiltonian would be

$$\begin{aligned}\hat{H}_{JC} &= \hat{H}_{mol} + \hat{H}_{cav} + \hat{H}_{int} \\ &= \frac{1}{2}\hbar\omega\hat{\sigma}_z + \hbar\omega_c\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) + \hbar g_0(\hat{a}^\dagger\hat{\sigma} + \hat{a}\hat{\sigma}^\dagger)\end{aligned}$$

Where g_0 is the magnitude of coupling strength, ω is the transition frequency of the molecule, $\hat{a}$ and $\hat{a}^\dagger$ are the creation and annhilation operators for the optical field, $\hat{\sigma}_z, \hat{\sigma}$ and $\hat{\sigma}^\dagger$ are the Pauli matrics for inversion, raising and lowering, respectively.

Later it was modified by Tavis and Cummings[26]. In T-C model, instead of single emitter it considered N molecules coupling to a single mode under rotating wave approximation. The Hamiltonian of T-C model (Dicke model) is

$$\hat{H}_{TC} \simeq \hbar\omega\left(-\frac{N}{2} + \hat{b}^{\dagger}\hat{b}\right) + \hbar\omega_c\hat{a}^{\dagger}\hat{a} + \hbar g_0\sqrt{N}\left(\hat{a}^{\dagger}\hat{b} + \hat{a}\hat{b}^{\dagger}\right)$$

Where $\hat{b}$ is the bosonic operator. $\sqrt{N}$ factor implies the collective coupling nature of the system and it has great importance that it contributes to the concentration dependence of the Rabi splitting. This collective coupling significantly increases the Rabi splitting and this enhancement can perturb the energy levels of other molecules which are not directly involved in the coupling[18] . That means coupling of N-molcules generates N+1 states and among that only two are spectroscopically measurable, P+ and P-, remaining N-1 states are called dark states and are forbidden transitions[24]. Figure 1.2 schematically shows T-C model.

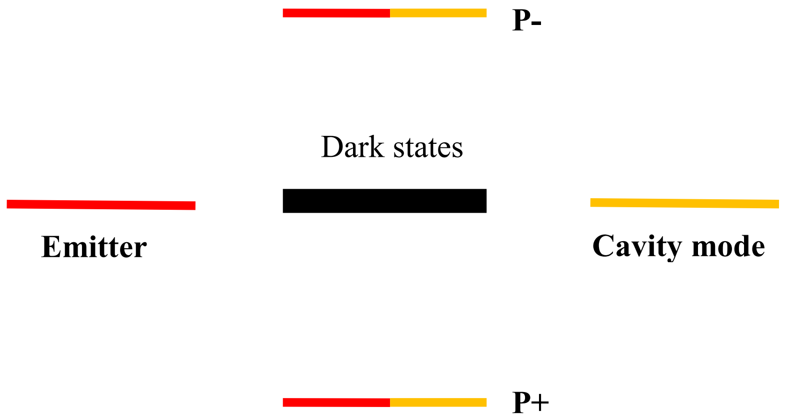


Figure 1.3 T-C model for N emitters (ref. 18)

1.2.3 OPTICAL CAVITY

The quality and properties of optical cavity is also another important experimental quantity. An optical cavity is usually an arrangement of two mirrors in which standing wave of electromagnetic wave forms. In polaritonic chemistry, a simple arrangement called Fabry-Pérot (F-P) cavity is generally used. As already mentioned, an F-P cavity has two plane mirrors facing each other and separated by an adjustable polymer spacer (See fig. 1.3). The parallel arrangement of the mirrors actually help to confine light, bounce back and forth between the mirrors, thus leads to the formation of a standing wave. By varying the distance between mirrors, standing wave pattern can be altered. The ON-resonance condition is expected to be when the light is in phase after one cycle and also when the cavity length, L_{cavity}, is an integral number of intercavity half wavelength.

$$L_{cavity} = \mathrm{m}\left(\frac{\lambda}{2n}\right)$$

Where λ is the wavelength, n is the refractive index and m is the mode order which is an integer. A very useful quantity for the quantitative measurement of strong coupling is free spectral range(FSR). FSR is the frequency difference between two consecutive modes and it is given by the expression

$$\nu_f = \frac{10^4}{\lambda} = \frac{(10^4)m}{2nL}$$

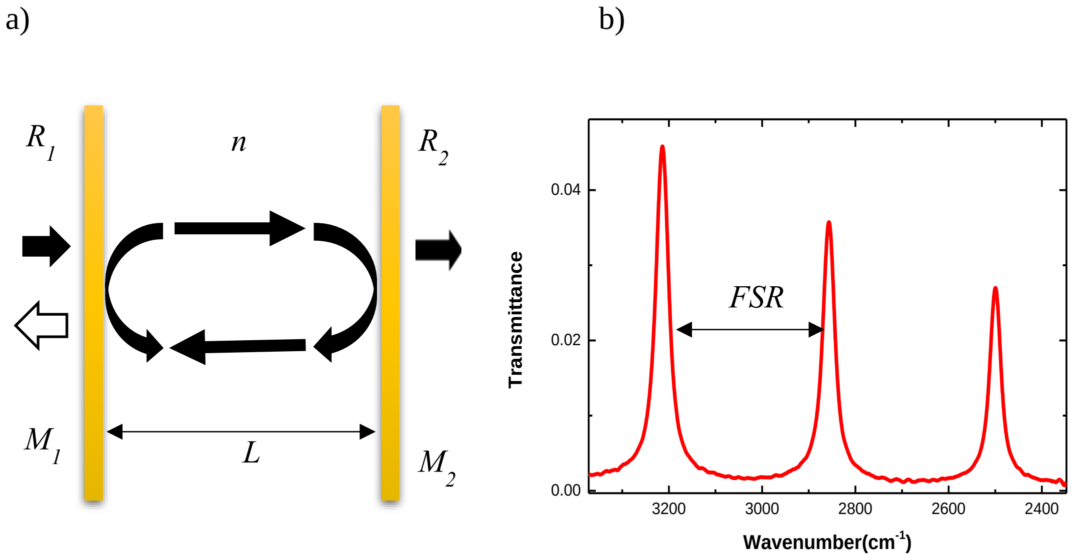


Figure 1.4 a) An F-P cavity formed by parallel mirrors, M_1 and M_2 placed parallel to each other. n is the refractive index of the medium, L is the length of the cavity and R_1 and R_2 are the reflections respectively. Light confined inside the microcavity undergoes multiple reflections before transmission. b) Transmission spectrum of an empty F-P cavity. The distance between two consecutive equi-spaced modes is given by FSR which can be calculated from the difference between the maximas of the respective peaks.

One of the parameters that determines the quality of the cavity is its Q-factor. It account for the overall dissipation rate of the cavity.

$$Q = \frac{\omega_r}{\Delta\omega_c}$$

ω_r is the resonant frequency and $\Delta\omega_c$ is the FWHM of the cavity mode. Strong coupling can be effective if the FWHM of the cavity mode as well as the molecular transition are almost similar.

1.2.4 VIBRATIONAL STRONG COUPLING

Conceptually, VSC is not very much different from ESC. A ground state molecule with a strong vibrational band can be hybridized with an infrared optical cavity mode leads to the formation of new states called vibro-polaritonic states. Figure 1.4 shows the coupling of the vibrational state to cavity mode. Like electronic coupling, VSC also changes the physical as well as chemical properties of the molecules as discussed earlier as the effective energy level get reshuffled. It is suggested that the formation of new vibro-polaritonic states can strengthens or weakens the bond as

$$\omega_v \propto \sqrt{\frac{f}{\mu}}$$

ω_v is the vibrational frequency, f is the bond strength and μ is the reduced mass of the atoms involved. It assumes that this might alter the Morse potential and therefore the chemical and thermodynamic properties of the systems.

As already mentioned, there has been a great development in VSC. One such would be the cavity catalysis by cooperative coupling of solvent molecules to the reactants[17]. In cooperative coupling, the condition is that there should be a vibrational overlap of the vibrational bands of reactants and solvent molecule. Due to the collective coupling, concentration strength or the Rabi splitting will not get affected during the course of the reaction. Since the reactants and solvents molecules have vibrational bands at same value, the number of molecules experienced by the cavity will be high. This causes large coupling strength and hence an effective control of a chemical reaction.

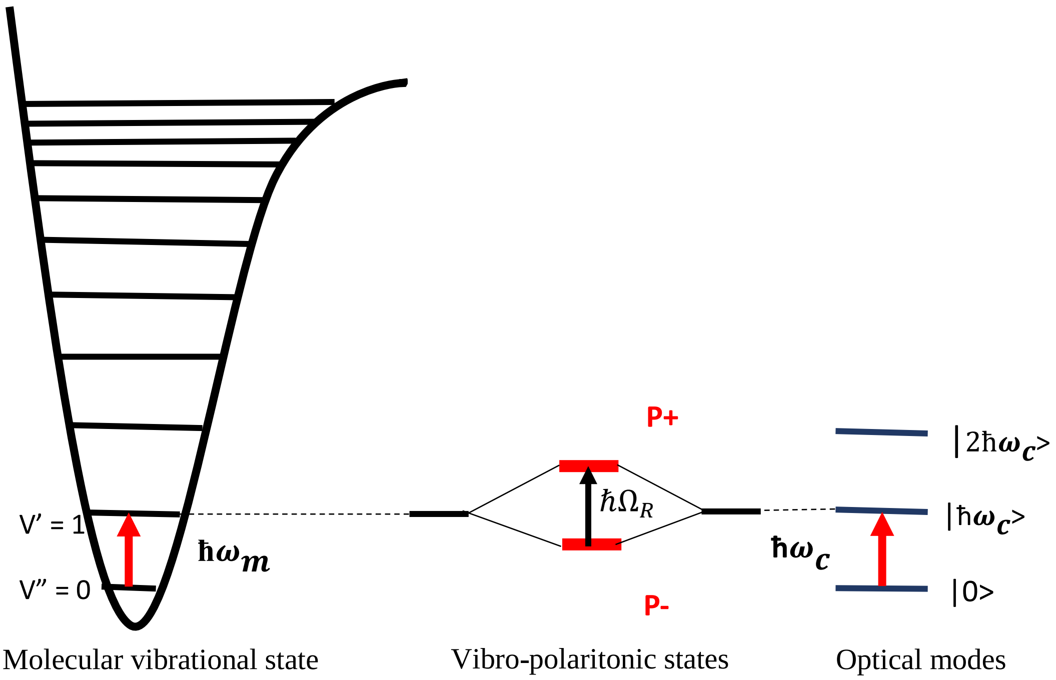


Figure 1.5 Schematic diagram showing the VSC and the formation of P+ and P-

CHAPTER 2

2.1 INTRODUCTION

As mentioned earlier, there have been many studies on the consequences of VSC on chemical reaction rates. One of the breakthrough experiments on this regard was the desilination reaction of alkynylsilane under VSC[14]. The chosen prototypical reaction is the deprotection reaction of 1-phenyl-2-trimethylsilylacetylene (PTA) with tetra-*n*-butylammonium fluoride (TBAF) in methanol (figure 2.1). The reactant is a pure liquid and is injected into an infrared F-P cavity for kinetic study of reaction. The reaction follows a pseudo-first order kinetics and the reaction rate is monitored by an FTIR spectrophotometer at different time intervals.

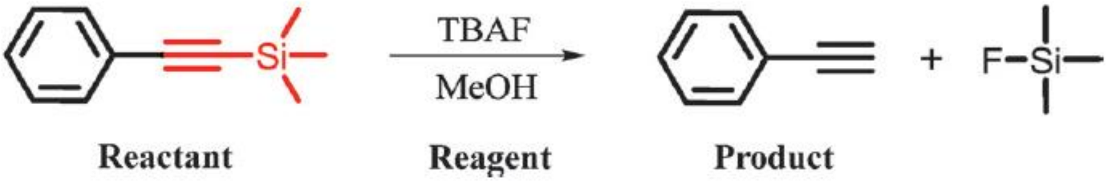


Figure 2.1 Desilination reaction of 1-phenyl-2-trimethylsilylacetylene. Figure is taken from ref [14].

The cavity is tuned in such a way that it is in resonance with the stretching transition of the $\mathrm{C-Si}$ bond at 860 cm^{-1}, a double peak corresponding to the $\mathrm{C\equiv C-Si}$ and $\mathrm{-Si(-Me)_3}$ modes. This ON-resonance condition resulted in a Rabi splitting of 98 cm^{-1} which is larger than the FWHM of both the vibrational transition of $\mathrm{C-Si}$ (39 cm^{-1}) and the cavity resonance (30 cm^{-1}). It was observed that as a consequence of the strong coupling of $\mathrm{C-Si}$ bond, $\mathrm{-C\equiv C-}$ vibrational transition at 2160 cm^{-1} was also weekly coupled to another cavity resonance, which allow the monitoring of the temporal evolution of the band.

The progress of the reaction was monitored by the shift in the position of cavity resonance which are far away from the vibrational transition leading to the change in FSR. The shift in the modes attributes to the fact that there is a difference in refractive indices of the reactant and product (figure 2.2 a). The kinetic study was demonstrated by plotting this difference in the FSR against time for both ON and OFF-resonance cavity (figure 2.2 b). Under ON-resonance condition, the rate constant was decreased by a factor of 5.5.

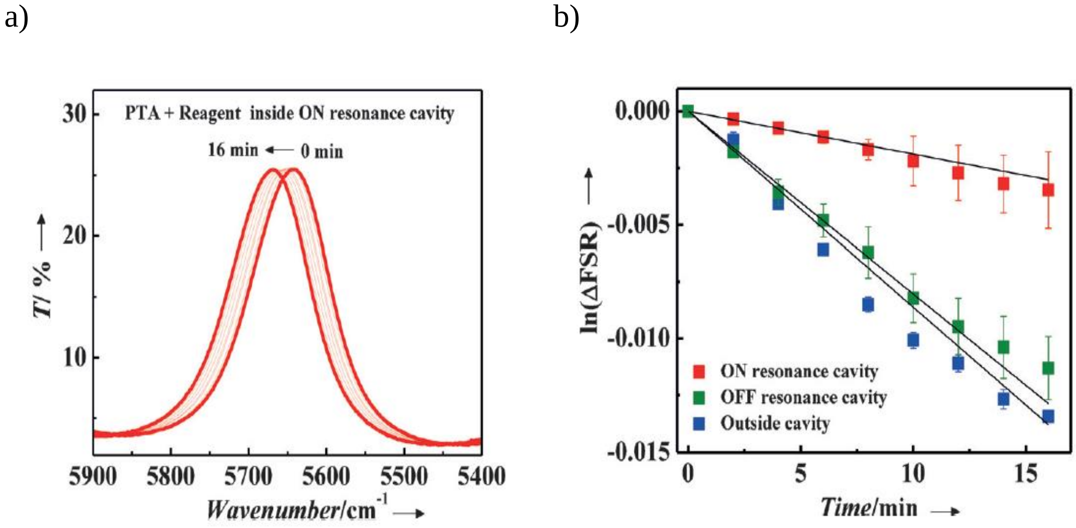


Figure 2.2 a) The shift in cavity resonance of the ON-resonance cavity during the reaction. b) Linear plot of difference in shift of cavity resonance against time giving the kinetics of the reaction at ON-resonance (red), OFF-resonance (green) and ouside the cavity (blue). Figure is taken from ref [14].

The thermodynamics studies of the reactions conducted also indicate the same conclusion. The associated thermodynamic parameters were extracted using the transition-state Eyring equation for a particular Rabi splitting

$$k = \frac{k_B T}{h}\exp(-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R})$$

Under VSC, the enthalpy of activation $\Delta H^\ddagger$ increased from 39 kJmol^{-1} to 96 kJmol^{-1} and the entropy of activation $\Delta S^\ddagger$ decreased from -171 to 7.4 JK^{-1}mol^{-1}. The changes in parameters suggest the change of transition state from an associative to dissociative.

Another experiment in this aspect was the modulationof Prins cyclisation by VSC[27]. In this experiment, Hirai *et.al* investigate the effect of VSC on a series of aldehydes and ketones undergoing Prins Cyclisation. Prins cyclisatin is a cycloaddition reaction to synthesis cyclic carbon compounds from two or more reactants (figure 2.3). The rate determining step of this reaction is the nucleophilic attack on the protonated carbonyl of an aldehyde or ketone by the alcohol group in 3-butene-1-ol and it follows a second-order kinetics. Thus it is greatly dependent on the reactivity of the carbonyl group.

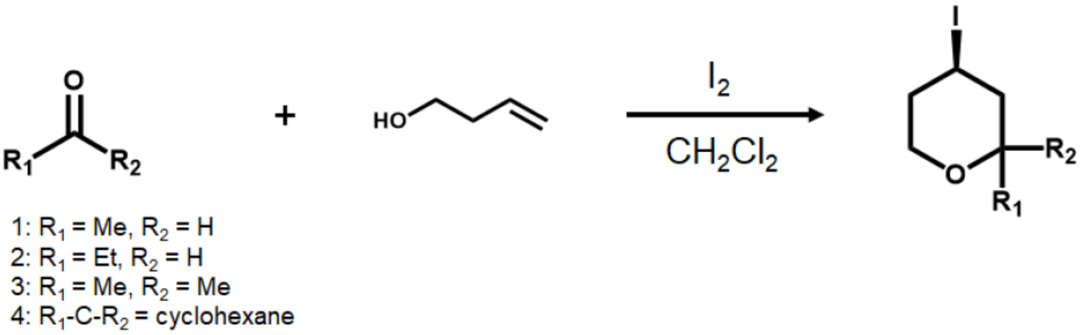


Figure 2.3 Prins cyclisation in the presence of I_2. Figure is taken from ref [27].

The coupling of the carbonyl stretching vibration of aldehyde to the cavity resonance resulted in the Rabi splitting of 105 cm^{-1} which is larger than both the carbonyl stretching vibration (FWHM = 27 cm^{-1}) as well as the cavity mode (FWHM = 54 cm^{-1}) (figure 2.4). In this experiment also there is a temporal shift in the higher order cavity resonance and as mentined earlier, the progress of the reaction is monitored. The kinetic studies under VSC showed decrease in the second-order reaction rate by 70%.

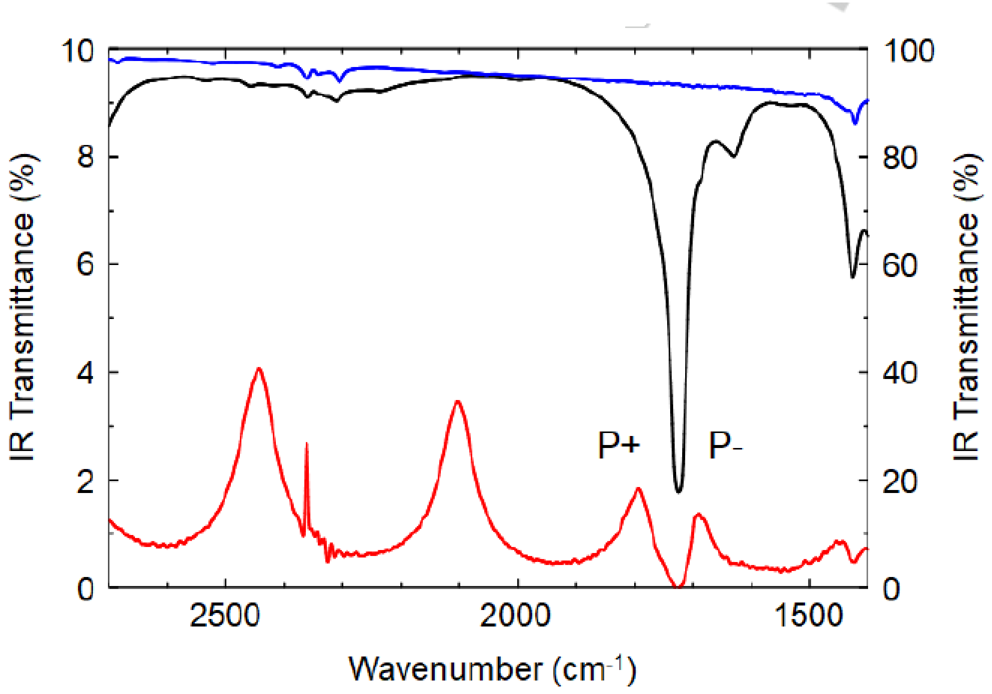


Figure 2.4 IR transmission spectra of acetaldehyde in dichloromethane(black). Vibro-polaritonic states, P+ and P-, formed by the coupling of carbonyl stretching vibration with the cavity resonance. Figure is taken from ref [27].

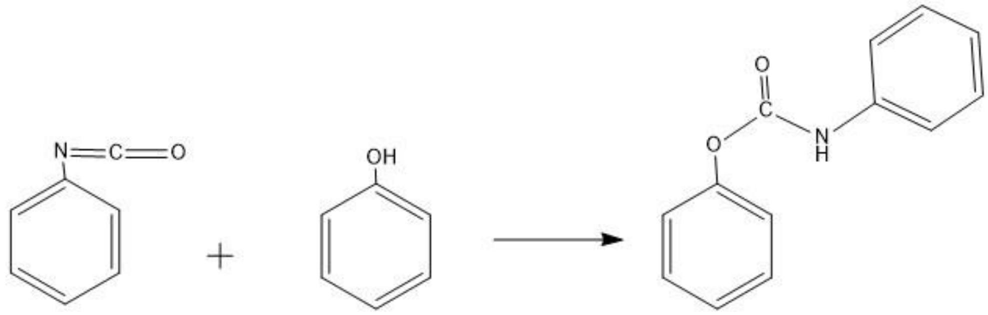
Thermodynamic studies of this reaction also found to be in agreement with the kinetic observations. In this reaction, the enthalpy of activation ($\Delta H^{\ddagger}$) of all reactants increased by ~ 10 kJ/mol under VSC while the entropy of activation did not alter much.

When both these experiments showed a decrease in rate of reaction and increase in activation enthalpy, work by Huira *et.al* demonstrates a catalysis in reaction by vibrational ultra-strong coupling (V-USC) of water molecules involved in hydrolysis reaction[16]. Coupling of –OH stretching vibration of water to the cavity resonance resulted in the Rabi splitting of 720 cm^{-1}. They also reported that there is an acceleration in reaction rate of the hydrolysis reaction of cyanate ions by 10^2 times and that of ammonia borane by 10^4 times. The acceleration of the reaction or the reduction of the enthalpy of activation is explained by the transition state theory. The possible explanation given is with respect to the relation between vibrational frequency and the force constant. Since vibrational frequqncy ω_0 is proportional to force constant,$\sqrt{k}$, the splitting of the first vibrational state will possibly change the force constant and thus lowers the activatin barrier(first-order approximation). Another aspect is that the light coupled water showed highest Rabi splitting ever reported for VSC and V-USC[28].

From above cases, it is clear that when molecules directly coupled to the vacuum field, there was a decrease in the rate of the reaction. whereas in the case of hydrolysis reaction, water acted as a reacting solvent. The molecules studied were mainly having functioinal groups like C=O and C=Si and –OH because of their strong oscillator strength. So this work will be addressing some of the obvious questions like what would be the case if we couple another functional group other than the above mentioned. In that case, can we achieve VSC and strong coupling? What will be the kinetic and thermodynamic properties of such a coupled system?

2.2 SYSTEM UNDER STUDY: PHENYL ISOCYANATE

Polyurethanes are an extensively used polymer and are very useful in the polymer and material engineering fields. In particular, the reaction of isocyanate with alcohol is a widely studied reaction. There has been extensive studies on the isocyanate-alcohol reaction[29][30][31]. Isocyanate reacts with alcohol gives carbamates[32]. Chemical reaction of phenyl isocyanate (PIC) and phenol (PhOH) is given in figure 2.5.



Phenyl isoyanate Phenol Phenyl phenyl carbamate

Figure 2.5 Reaction of PIC and phenol

There have been extensive studies on the factors like catalysis, temperature, reaction medium etc. based on PIC reactions[33]. Among these, the influence of solvents is one that has investigated much. It was proved that hydrogen bonding capacity of a solvent has a crucial influences on the reaction kinetics of the PIC reactions[34][35]. There are studies showing an increase in the reaction rate upon increasing thepolarity of the solvent[36]. In the earlier studies it was shown that the reaction kinetics is faster in aliphatic alcohols compared to phenol owing to the increased nucleophilicity of the alcohol[30]. Studies have made on many solvents like toluene, nitrobenzene, dioxane, acetonitrile, Dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP) etc. Among these DMF and NMP showed different behavior compared to the others. Reaction in DMF and NMP showed a first-order kinetics compared to the other solvent systems[31]. This difference can be understood from the reaction mechanism (figure 2.6).

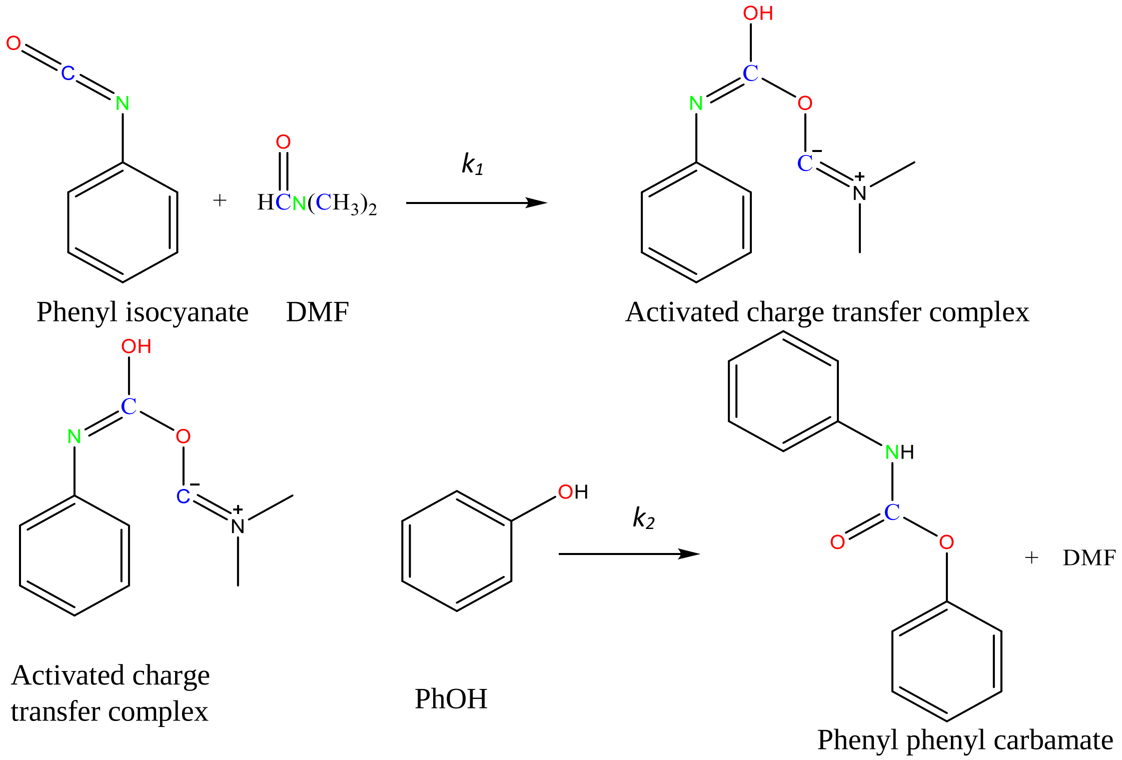


Figure 2.6 Reaction mechanism of PIC with PhOH (ref. [36])

Usually the reaction of isocyanates and phenol is carried out in the presence of a strong Lewis acid like aluminium chloride[37]. But it is reported that dipolar aprotic solvents like DMF and DMSO acts itself as a catalyst in the absence of external catalyst and forms a 1:1 charge transfer complex[38]. It is reported in literature if this is the case, then the reaction would follow a first-order kinetics and formation of C-T complex would be the rate determining step[31]. This C-T complex formation activates the isocyanate group in PIC.

Isocyanate group (-NCO) is a highly reactive moiety with two unsaturated bonds. PIC has a strong symmetric and asymmetric -NCO vibrational bands at 1448cm^{-1}(Raman – polarized line) and 2274cm^{-1}(Infrared)[39]. The IR spectrum of PIC is given in figure 2.7. The main task in the given thesis is to couple the asymmetric vibrational band of –NCO to the cavity and study the changes that will bring it to the reaction kinetics under VSC conditions.

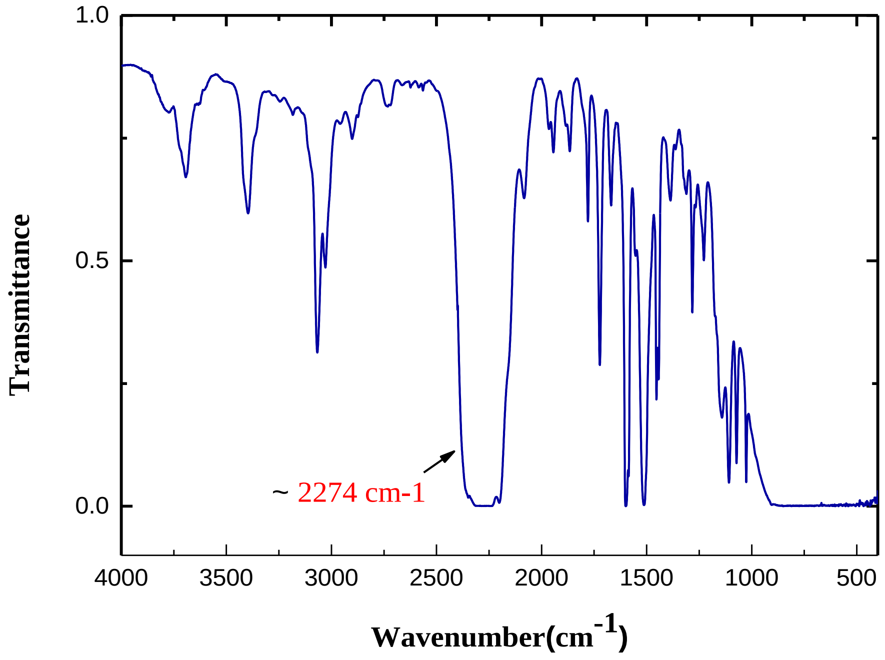


Figure 2.7 IR transmission spectrum of pure PIC in liquid phase. The strong –NCO bond and the corresponding vibrational frequency is shown.

2.3 EXPERIMENTAL METHODS

Phenyl isocyanate was purchased from Aura chemicals Pvt. LTd. All the other reagents were purchased from Sigma Aldrich. First, a solution of PhOH (0.5M) was prepared in DMF(2ml). 1M PIC was added immediately into the above solution and final reaction mixture was observed under FTIR spectrophotometer. The optimization step was done by varying the concentration of PIC in DMF. The system follows Beer-Lamberts law and self-dipolar interactions are much less even in 1M concentration of PIC which is taken further as standard of all the cavity and non-cavity experiments. IR spectra of each solution was recorded and a plot was made with absorption against concentration as shown in the figure 2.8.

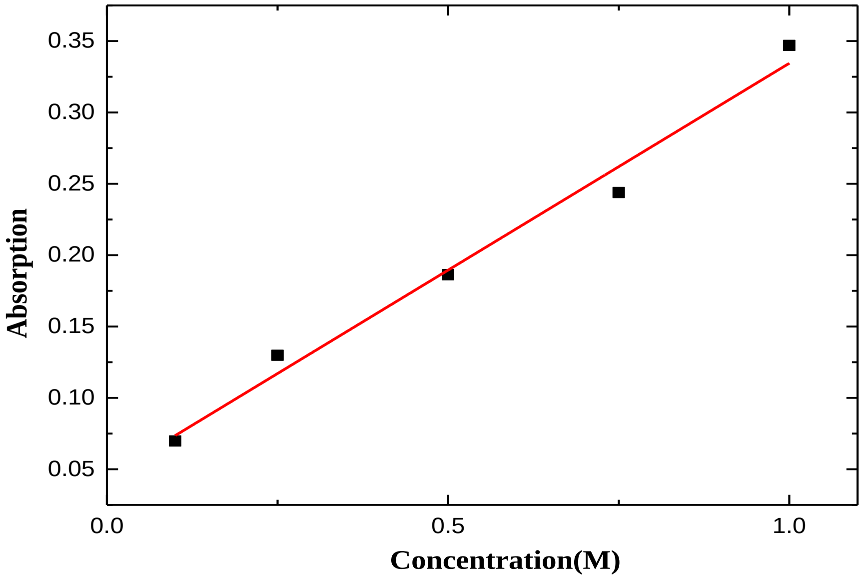


Figure 2.8 The best fit linear IR absorption of PIC –NCO band verses concentration of the PIC molecule in DMF.

Experiment in the non-cavity was carried out in a microfluidic cell by injecting the reaction mixture immediately after mixing. Figure 2.9 is the schematic of a microfluidic flow cell having the F-P configuration, in which the experiments were undertaken.

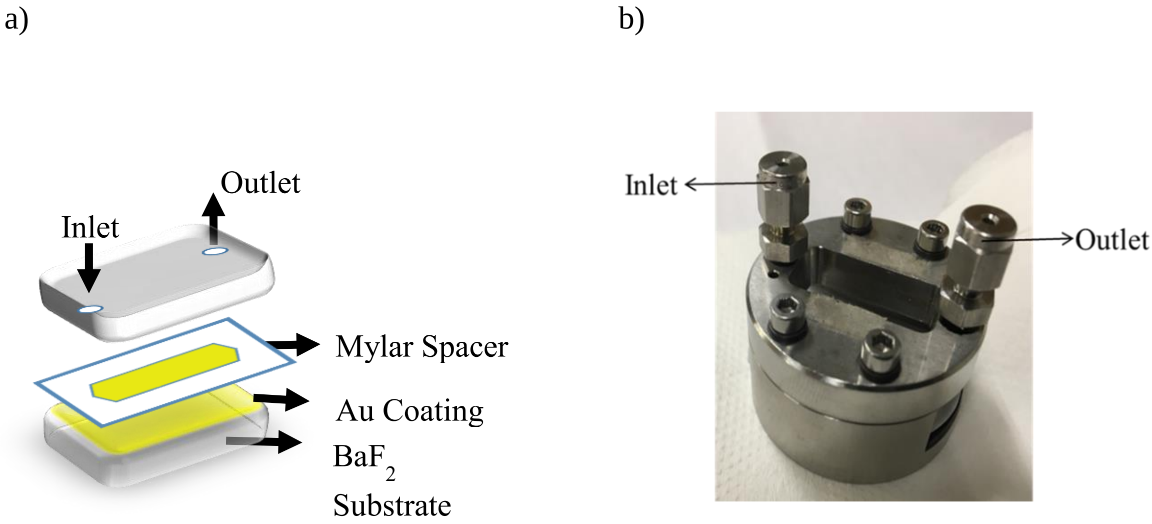


Figure 2.9 a) Schematic diagram of an F-P configuration. b) Image showing a microfluidic cell having the F-P resonator inbuilt.

A pair of BaF_2 substrates are used for the fabrication process. For strong coupling experiments, one side of each BaF_2 substrates are coated with Au (10 nm) by sputtering and they are placed parallel to each other for the confinement of light. 12 µm Mylar spacer was placed in between the substrates to define the cavity length. PTFE films were used to protect the substrates from metal contact. Figure 2.9 b shows the image of a microfluidic cell. Non-cavity condition is the same except the presence of Au coating present in cavity conditions. ON resonance condition is achieved by tuning the cavity pathlength to reach the vibrational transition of –N=C=O. IR spectra were recorded in kinetic mode by placing the cell inside an FTIR spectrometer. The course of the reaction is followed by observing the disappearance of –NCO peak at ~ 2274 cm^{-1} . Data was collected till the –NCO peak get completely diminished. From the transmittance, IR absorbance was calculated using the formula

$$A = -\log\left(\frac{I}{I_0}\right)$$

$$= -\log(T)$$

A plot of absorbance vs time was plotted and fitted into an exponential curve to extract the apparent rate of the reaction.

2.4 RESULTS AND DISCUSSION

2.4.1 C-T FORMATION STUDIES

To investigate the C-T formation, DMF was chosen as a dipolar aprotic solvent. Since DMF doesn't have any vibrational band at the isocyanate band region, it will not interfere in the coupling of isocyanate vibrational bands (IR transmission spectrum of pure DMF is shown in figure 2.10).

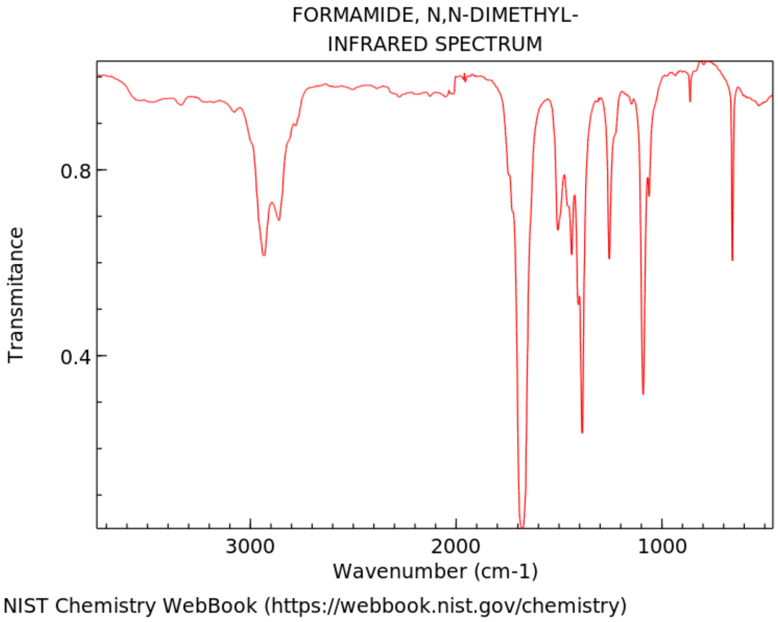


Figure 2.10 IR transmission spectrum of pure liquid DMF.

All the experiments were conducted at room temperature. The formation of activated C-T complex was confirmed by studying the reaction of pure PIC in DMF without PhOH. The reaction gave a first-order kinetic plot with $k = 8.979 \times 10^{-2}\ min^{-1}$, suggesting the formation of C-T complex. The absorbance vs time plot is given in figure 2.11.

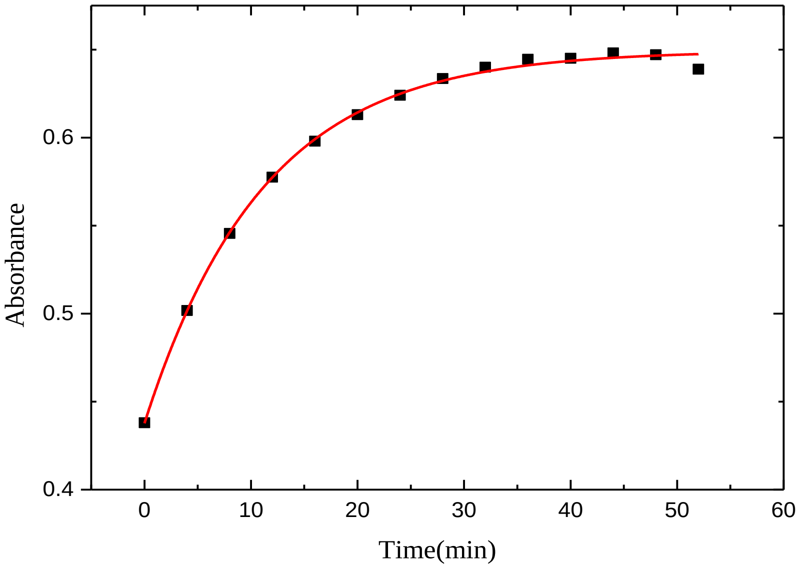
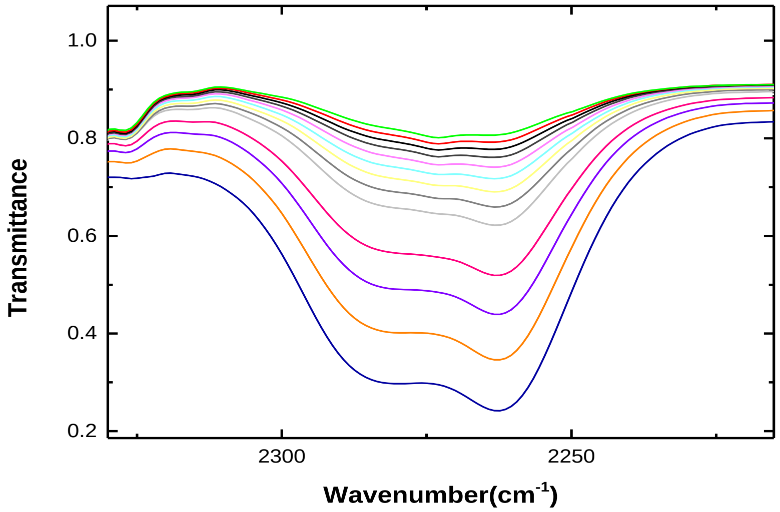


Figure 2.11 Best fit exponential graph with absorbance plotted against time of PIC and DMF reaction

2.4.2 ABSORBANCE STUDIES OF PIC UNDER NON-CAVITY CONDITION

99 % of PIC get reacted in 30 minutes under the given reaction conditions. We have repeated the experiment at least 4 times to obtain consistent results. Both the disappearance of –NCO band as well as the formation of –C-O bond at ~1199 cm^{-1} was taken as reference to follow the rate of the reaction . IR transmission spectra of the reaction mixture was taken at every 2-minutes. Figure 2.12 shows the temporal evolution of IR transmission spectra of both –NCO and –C-O over the course of the reaction. A first-order exponential graph was obtained for each trial when absorbance was plotted against time (figure 2.13). An average rate constant of $6.025 \times 10^{-2}. min^{-1}$ was obtained. Table 2.1 summarizes the apparent rate constants (k_{app}) obtained in each trial.

a)



b)

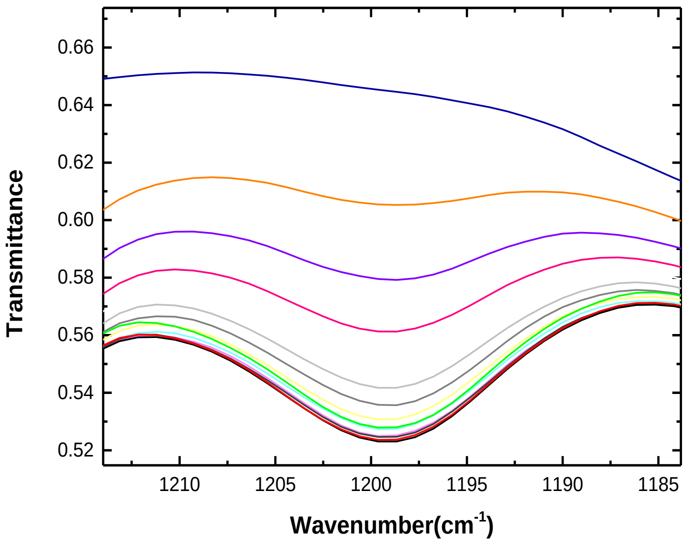


Figure 2.12 IR transmission spectra for the temporal evolution of (a) of –NCO stretching band disappearance at ~ 2274 cm^{-1} and a (b) growth curve of –C-O stretching band at ~ 1199 cm^{-1}.

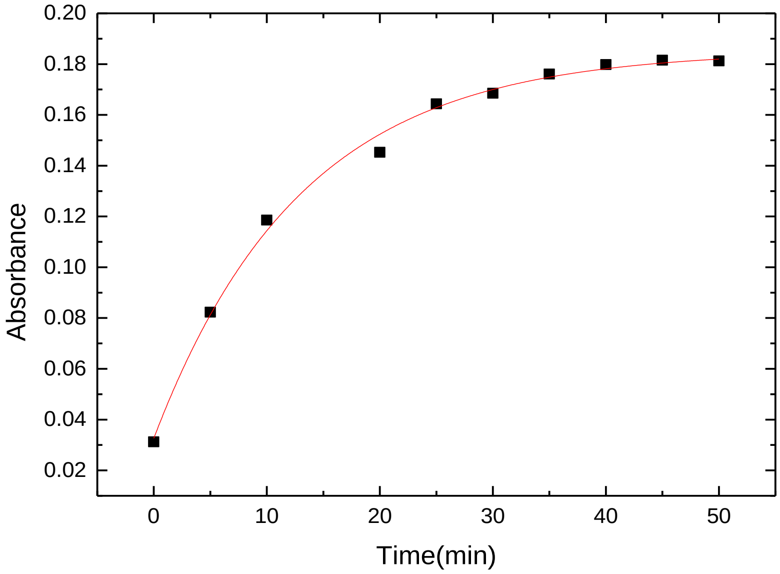


Figure 2.13 Best fit exponential graph of absorbance vs time of the reaction mixture in non-cavity condition (fitted for C-O stretching bond at 1199 cm^{-1}).

Trial	$k_{app} = \times 10^{-2}.min^{-1}$
1	7.672
2	6.261
3	6.616
4	3.551
Average	6.025

Table.2.1 Apparent rate constants obtained for each trial in non-cavity condition.

2.4.3 KINETIC STUDIES OF PIC UNDER VSC

Strong coupling kinetic experiments were carried out in similar manner except the presence of Au mirrors in the cavity. The distance between the mirrors are placed in such a way as to achieve VSC to the selected mode of a cavity. ON resonance cavity resulted in the formation of vibro-polaritonic states(VP), VP+ and VP- of 71 cm^{-1} ($\hbar\Omega_R$) which are coming at 2311 cm^{-1} and P- at 2240 cm^{-1}. Figure 2.14 shows how the transmission spectrum of the cavity(blue) is modified by the vibrational absorption spectrum of the reaction mixture(red).

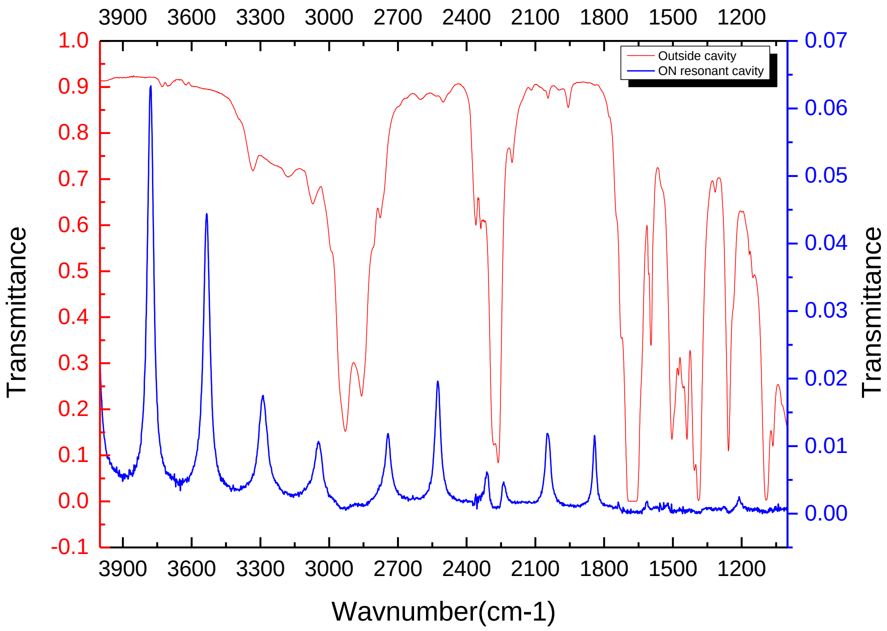


Figure 2.14 IR transmission spectrum of reaction mixture inside (blue) and ouside(red) the ON resonance cavity.

The reaction rate was monitored by observing the shift in the free spectral range (FSR) of the cavity (figure 2.15). As mentioned earlier, this shift happens due to the difference in the refractive indices of the reactant and the product. The refractive indices of the PIC, DMF and the product are1.535, 1.43 and 1.63 respectively. Since PIC is only 10% in the solvent DMF, the effective RI of the reaction mixture is still varying to observe a first-order change as shown in figures 2.15 and 2.16. Vibrational band of isocyanate was coupled to the 9th mode of the ON resonance cavity corresponding to a pathlength of 12 μm. Initially, an empty cavity, was set at 357 cm^{-1} to attain the ON resonance situation.

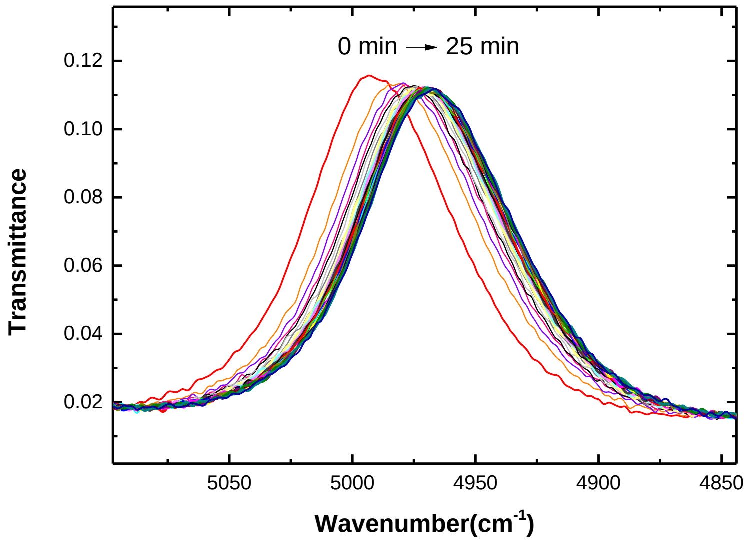


Figure 2.15 Temporal shift in higher order cavity modes of the ON resonance cavity during the reaction

To ensure a true VSC, the Rabi splitting should be greater than the FWHM of both the empty cavity as well as the vibrational transition of –N=C=O. The FWHM of the empty cavity is 47 cm^{-1} and the vibrational transition is 61 cm^{-1}, both are smaller than the Rabi splitting and hence one can say qualitatively that strong coupling limit is achieved by overcoming all the other decay rates in the cavity-molecule system.

The reaction in the resonant cavity was repeated for at least 3 times and a first-order average rate constant $k_{avg} = 1.3799 \times 10^{-1}.min^{-1}$ was obtained by exponential decay fitting method. The kinetic data for cavity experiments are given in the table 2.2.

Trial	$k_{app} = \times 10^{-1}.min^{-1}$
1	1.139
2	2.007
3	0.994
Average	1.379

Table 2.2 Apparent rate constants obtained for each trial with average rate constant at ON resonance condition.

An analysis of the kinetic data in all the conditions can be made by comparing the corresponding results obtained (see figure 2.16 and 2.17) and indicate that there is ~2.3 times enhancement in the rate of the reaction is achieved by VSC. This enhancement in rate can be accounted as cavity catalysis as mentioned earlier.

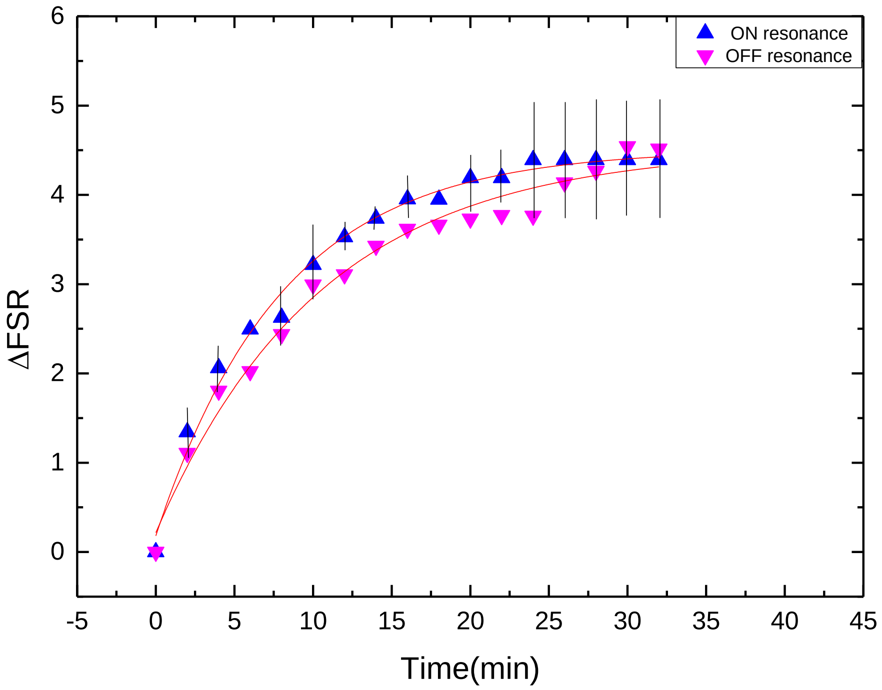
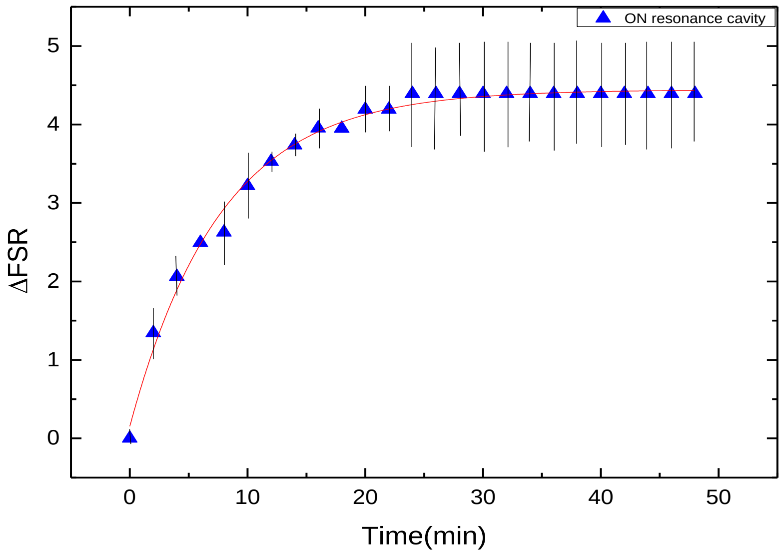


Figure 2.16 ΔFSR vs time plotted for both ON resonance (blue triangle) as well as OFF resonance (pink triangle) conditions.

a)



b)

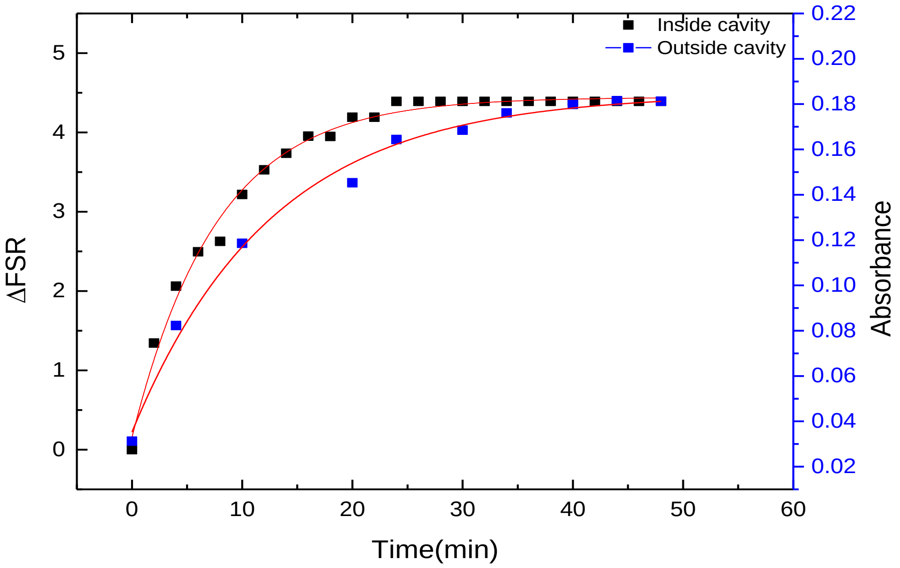


Figure 2.17 a) Averaged ΔFSR vs time plotted for ON resonance cavity with standard errors b) ΔFSR vs time plotted for inside cavity (black square) and absorbance vs time plot of outside cavity (blue square) conditions.

2.5 CONCLUSION

In the present work, reaction of phenyl isocyanate with phenol in dimethyl formamide medium was studied by vibrational strong coupling. The adduct formation was found to follow first-order kinetics. Strong coupling of the isocyanate band with the infrared cavity mode speed up the rate of the reaction by 2.3 times compared to the non-cavity condition. It was also found that the reaction is sensitive to tuning conditions as an OFF resonant coupling bring back the normal reaction rates. This is the first experimental evidence that direct coupling of the reaction co-ordinate can speed up the reaction through vibrational strong coupling. Please note that all the previous findings on cavity catalysis is through a solute-solvent interaction. Further studies are required to understand the free energy changes associated with isocyanate coupling .

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