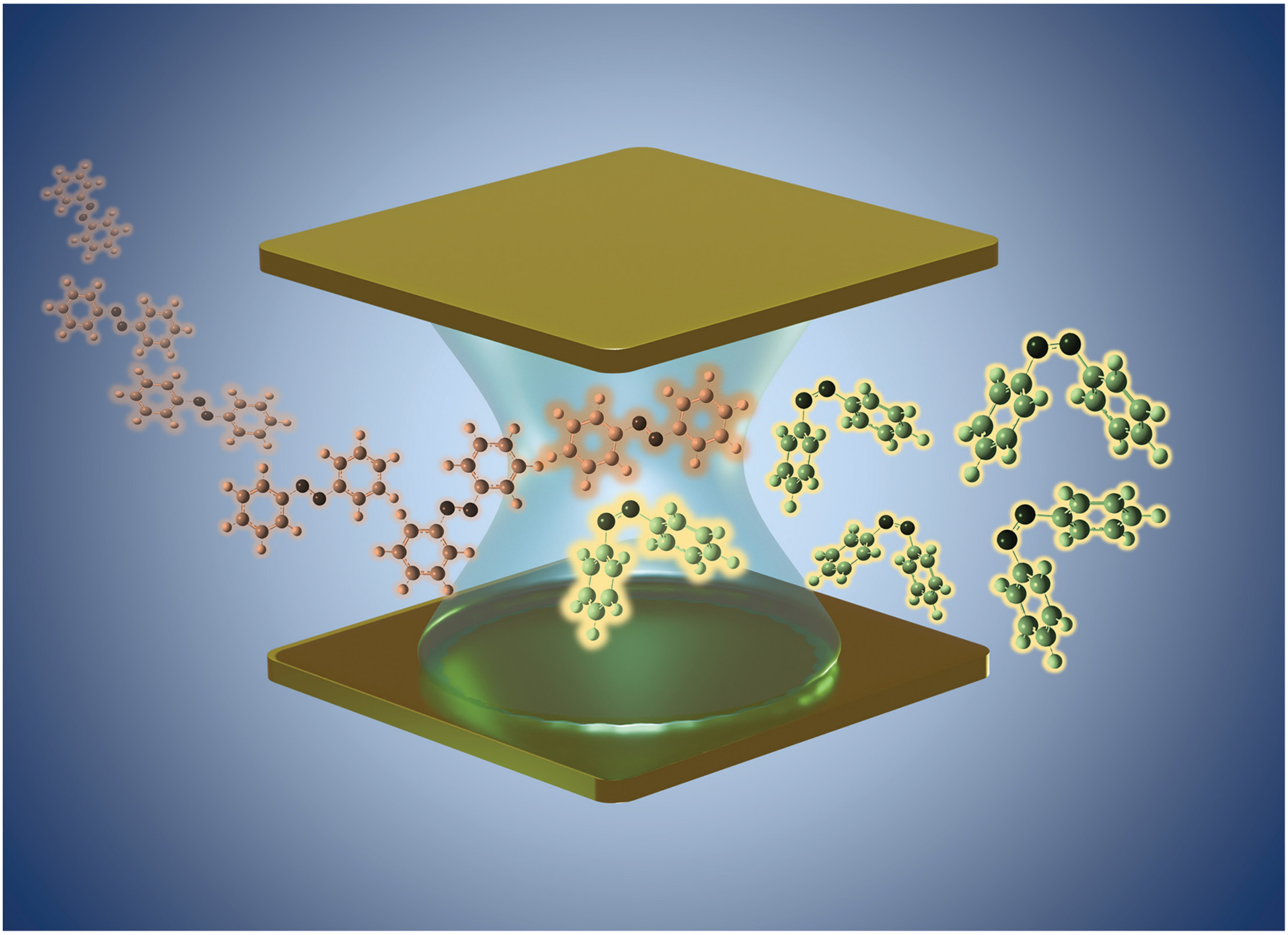

**Showcasing research from Professor Jino George's laboratory, Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, India.**

Stirring chemical reaction landscapes through strong light–matter interactions

This illustration shows a Fabry-Perot cavity used for strong coupling experiments. When molecules pass through the resonant cavity, polaritonic states are formed that modify their chemical reactivity. Azopyrrole photo-switching in the presence of a cavity is demonstrated here.

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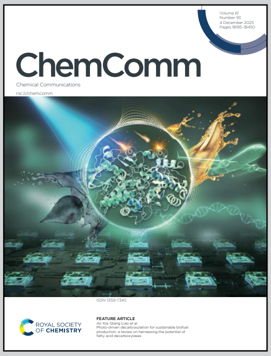

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# Stirring chemical reaction landscapes through strong light–matter interactions

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Recent experiments suggest that precise control of chemical reactions can now be achieved by strong light–matter coupling. This fueled a huge interest among researchers to use it as a spectroscopic tool to understand complex chemical relaxation pathways. In this review, we show the potential of polaritonic chemistry that can be used as a selective tool without using any external stimuli. Polariton-driven reactions are proposed based on photoswitches, all the way up to simple ester hydrolysis, that are otherwise mediated by light or thermal sources. We also discuss the cooperativity and collective nature of strong coupling that can tailor reaction rates by inter-/intramolecular interactions. Furthermore, we explain the pros and cons of this concept, its potential to be explored in different domains, and the challenges upfront.

## Introduction

Understanding the complexity of chemical reactions, finding new reaction schemes, and carrying out old ones in a much more efficient way have been some of the driving forces in chemistry. The use of catalysts to enhance chemical reactions is everywhere, even though theoretically predicting a catalyst is always a challenging task. The idea of using light as a catalyst was explored in the 19th century with the first synthetic photoconversion of the santonin molecule.[1] In the 1960s, when lasers were invented, it was thought that lasers could be used to catalyse chemical reactions, selectively targeting a chemical bond. This was explored extensively and is known as laser-controlled chemistry. Now, the field has developed pretty well, which will allow us to do precision photochemistry.[2] In this mini review, we discuss the original idea of polaritonic chemistry and its application in various perspectives, either as a spectroscopic tool or as a medium for selective bond breaking. Next, we will look into advancements of polaritonic chemistry by considering the examples pertaining to electronic strong coupling (ESC) and vibrational strong coupling (VSC). Next, we will briefly discuss the theoretical side of the polaritonic

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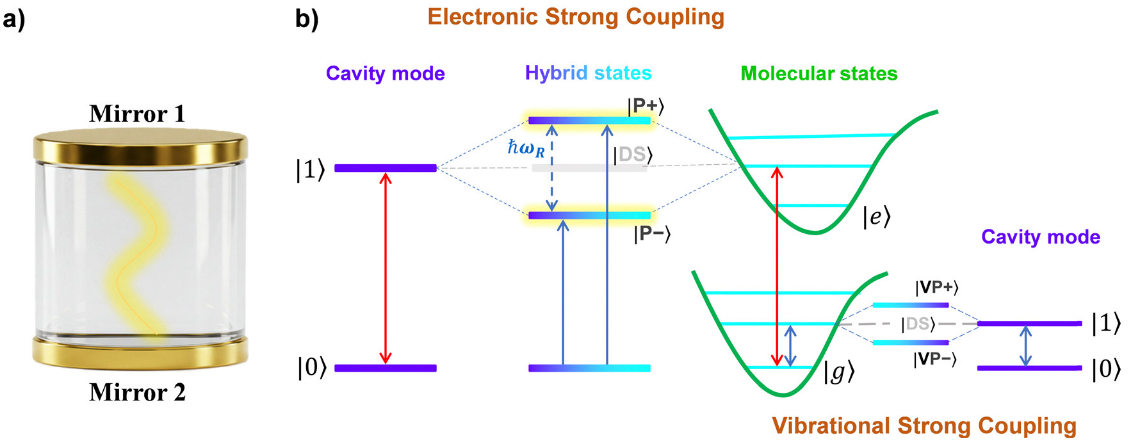

Fig. 1 Schematic illustration of strong light–matter interactions: (a) a Fabry–Perot cavity with a two-mirror closed configuration and (b) a scheme representing the formation of hybrid states from an electronic or a vibrational transition and a resonant cavity mode.

chemistry and shed light on current open questions. In the end, we will conclude with the potential future applications of the field.

The invention of lasers initiated resonant energy pumping of certain vibrational or electronic excited states to understand the role of the intermediates and even to trace transient species formed during a complex chemical reaction. In 1977, Odiorne *et al.* reported the reaction between K and HCl in the presence of a molecular beam that excites HCl.[3] In the excited state, HCl is 100 times more reactive than in the ground state. Interestingly, no increase in the reactivity is obtained when the laser is detuned from the fundamental ($\upsilon = 0 \rightarrow 1$) transition. In the same year, S. J. Harris reported an enhancement in the rate of a four-centred, concerted, and bimolecular reaction between ICl and $H_2$.[4] In the 80s, Frei and Pimentel reported in a series of articles the dependence of the excitation of the fundamental frequency of molecules by shining a laser.[5,6] Reactions with relatively low energy barriers include sparse vibrational levels, and all other rotational and translational degrees of freedom are arrested at cryogenic temperatures, so that a single degree of freedom can be examined. For the reaction between $F_2$ and $C_2H_4$, the product formation is increased nearly five times when the laser frequency corresponding to different vibrations of the ethylene molecule is used. On the other hand, many modes are also found to be ineffective in promoting the reaction. This helped researchers track the vibrational energy flow and the involvement of normal modes in the reaction coordinates to some extent. Here, it is also worth noting that this way of promoting the reaction with the help of resonant IR lasers also encountered hurdles in some cases, such as loss of excitation energy to the neighbouring modes through intramolecular vibrational energy redistribution (IVR), resulting in poor conversion yields.

In the past decade, strong light–matter interactions and their application in the field of polaritonic chemistry have also claimed to observe a similar control over the modification of chemical reactivity, without the use of any external stimuli. Strong coupling

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involves the hybridization of a photon with a molecular state that results in the formation of hybrid light–matter states by the linear combination of their wave functions. This is similar to the idea of molecular orbitals, in which the bonding and antibonding orbitals are obtained. However, one of the components here is a photon, and therefore, the hybrid states show anomalous properties. When a resonant photon interacts with the molecular transitions, be it an electronic or vibrational transition, in a confined space, two possibilities arise: weak or strong coupling. Weak coupling is where the rate of decay of molecular excitation is modified and thereby affects the emission properties of the molecules. However, when energy exchange is strong enough to overcome the rate of decay of the molecular excited state and the photon, new hybrid states are formed, as shown in Fig. 1. These newly formed hybrid states are called polaritonic states and are separated from each other by the so-called Rabi splitting energy, which quantifies the interaction strength between the excited state and the photon. In simple words, the stronger the interaction, the larger the Rabi splitting. Light has a dispersive nature, and therefore, polaritonic states inherit the same characteristics. For a simple system, the Rabi splitting energy can be estimated from the following equation:

$$\hbar\Omega_{\mathrm{R}} = 2\vec{E}\cdot\vec{d} = \sqrt{\frac{\hbar\omega}{\varepsilon_0 v}}\sqrt{(n+1)}$$

Here, $\vec{E}$ is the electromagnetic field strength of the resonant cavity, $\vec{d}$ is the oscillator strength of the molecular transition, $\hbar\omega$ is the resonant frequency, $\varepsilon_0$ is the vacuum permittivity, $v$ is the mode volume and $n$ is the number of photons present inside the cavity. Surprisingly, when $n = 0$, we still have some residual Rabi splitting. This is known as vacuum Rabi splitting, and it quantifies the strength of interaction between the molecule and cavity photon that originates from vacuum fluctuations. Initially, the field of polaritonic chemistry, particularly vibrational strong coupling, was welcomed with some sort of scepticism. But now, as many researchers around the world are also able to obtain the effect of VSC, the acceptability of the field is increased. But from a mechanistic point of view, it is still in its infancy, and there are so many open questions that need to be addressed. There are a few reviews that readers can glance through to get a detailed picture of polaritonic chemistry, along with the discussion on the contentious questions.[7–12] Here, our sole purpose is to discuss some of the main and important works, followed by our perspective on this field.

## Electronic strong coupling

Historically, strong light–matter interactions have been the area of interest for physicists.[13] In the late 90s, Lidzey and coworkers published various reports studying charge and

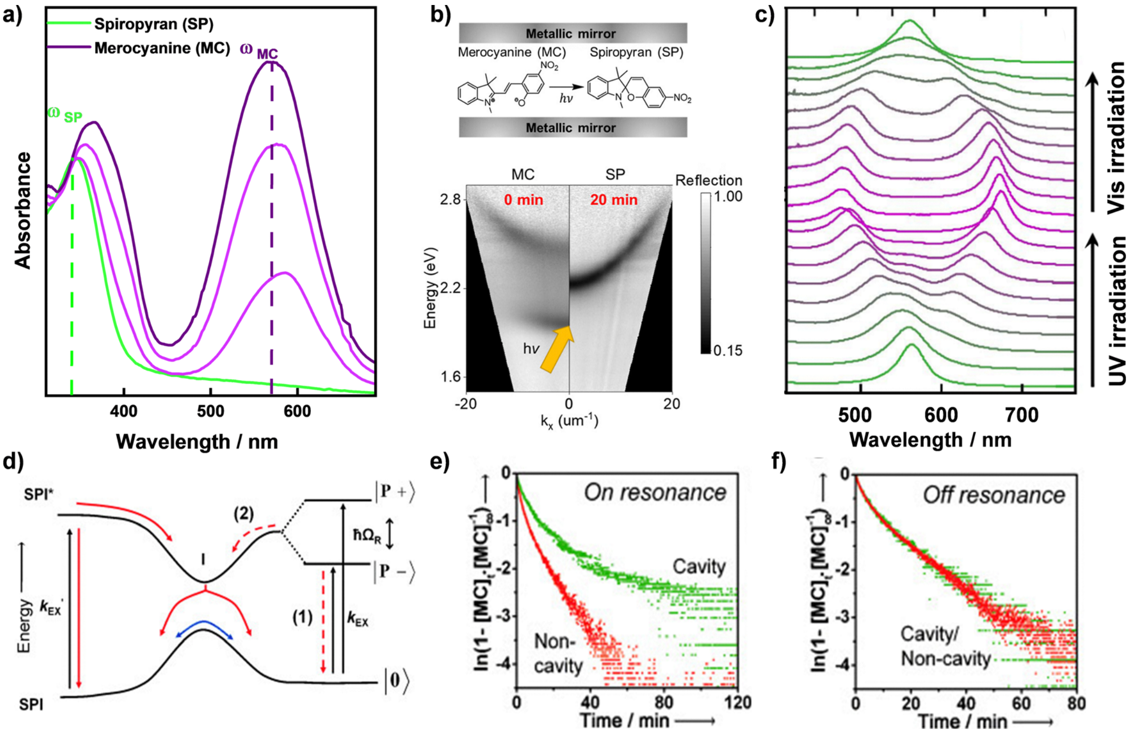


Fig. 2 Photoisomerization of SPI-MC under ESC. (a) UV-vis spectrum of SPI (green) and MC (purple) under non-cavity conditions; (b) FP cavity configuration used for the experiments along with polaritonic state dispersion of MC and SPI inside the cavity [(b) reproduced with permission from ref. 16. Copyright (2024) American Chemical Society]. (c) UV-Vis spectrum of the coupled system and its dynamic tuning upon irradiation of a UV or visible light source [(c) reproduced with permission from ref. 17. Copyright (2011) American Physical Society]. (d) Modification of potential energy (tentative) levels upon coupling of MC with the resonant cavity mode. The comparison of apparent rates of non-cavity (red) with respect to (e) ON-resonance and (f) OFF-resonance cavities (green) [(d)–(f) reproduced with permission from ref. 15. Copyright (2012) John Wiley and Sons].

energy transfer processes under strong coupling.[14] The most notable breakthrough from the chemistry perspective came in 2012, when Hutchison *et al.* showed the modification of a photochemical process by ESC for the very first time.[15] In all the above systems, a two-mirror configuration is used to confine the electromagnetic field, and this configuration is known as a Fabry–Perot (FP) cavity (Fig. 1a). The authors chose a model photochromic system, spiropyran (SPI), which undergoes a unimolecular ring opening reaction by irradiation with UV light, forming merocyanine (MC). MC has strong absorption around 560 nm due to the extended conjugation, while SPI is completely transparent in the visible part of the spectrum (Fig. 2a). MC forms with continuous irradiation and is increasingly coupled with the cavity mode, giving a Rabi splitting energy as high as 700 meV. The same behaviour is also tested and found to be sensitive to cavity conditions and the presence of other isomers of merocyanine.[16]

The system undergoes reversible switching while photoexciting with visible light (Fig. 2c).[17] Non-cavity measurements were carried out with the configuration having only one mirror. The photoisomerization in the non-cavity and cavity is found to be similar at initial times but significantly different at later times. The best control experiment in such a case is to move out the cavity mode from the molecular transition, making an OFF-resonant situation. In such a case, the observed behaviour of both the non-cavity and cavity is essentially the same. To understand this behaviour, the authors proposed a phenomenological kinetic model based on the modification of the energy landscape of the SPI-MC photoisomerization system. Formation of polaritonic states, particularly P-, acted as a barrier in the path of back conversion from the MC to SPI, resulting in the modification of the photostationary state (PSS), and the MC yield increased roughly up to 10% under ultra-strong coupling conditions. An ultra-strong coupling condition is when the Rabi splitting exceeds more than 10% of the molecular transition energy.

In another report, Zeng *et al.* studied the photoisomerization of a fulgide photoswitch and observed that the reaction rate is increased, contrary to the previously reported SPI-MC system.[18] Fulgide has two isomers mentioned as open and closed forms. Here, the cavity configuration is similar, whereas the measurement is carried out in the reflection mode. An important thing to note is that the closed form is coupled to the cavity mode. Upon irradiation, molecules start converting to the open form, therefore decreasing the coupling strength in an on-the-go reaction. Similarly, the kinetic rates of non-cavity are also measured and compared. Upon comparing the ON and OFF-resonant cavities, the system under strong coupling shows a faster switching initially and approaches the non-cavity rate in a longer time frame. This is par with our understanding that the cavity coupling goes negligibly as the oscillator strength collapses in the system upon irradiation. The authors subjected the results to a kinetic model fitting and suggested an alternative explanation for this effect other than the modification of the potential energy surface (PES). It is proposed that the increase in the rate of photoswitching is due to the fact that the cavity can promote the system into excited states where the reactivities of the coupled molecules are different from the non-cavity system.

In another case, Mony *et al.* studied the photoisomerization process of a norbornadiene–quadricyclane (NBD–QC) photoswitch under electronic strong coupling.[19] Here, stable NBD converts to metastable QC with an intramolecular [2+2] cycloaddition reaction, which can back convert to NBD through a thermal pathway. Electron donor and acceptor substitutions were made to shift the absorbance of NBD in the UV-vis range, and an absorption spectrum centered around 378 nm was obtained. 350 nm light was used to irradiate NBD to convert it into QC. While the half-life of back conversion of QC to NBD is roughly six days when kept in the dark. The photoisomerization process is first studied in the bare molecule case, and the quantum yield is calculated. It is then compared with the quantum yield obtained under strong coupling conditions with the irradiation of the upper polaritonic (UP) state, molecular absorption position, and lower polaritonic (LP) state. The authors observed that in the case of UP and dark state (DS)/uncoupled excitations, there is no significant change in the quantum yield, whereas it shows a drop when LP is excited. There is a sharp reduction in the quantum yield once we move away from the LP density of state (DOS). Please note that uncoupled to coupled comparison is not possible directly, as the coupled state behaves differently from the parent molecules. Here, it is important to note that in earlier experiments, the rate of the reactions inside the cavity was found to be decreased upon strong coupling. In contrast, the fulgide experiment shows an increased reaction rate. A recent study utilising ESC for enhancing the rate of 2+2 photocyclization of 2,4-dimethoxy-β-nitrostyrene (DN) is also worth mentioning. It was observed that under ESC, photocyclization is efficient even for lower-energy visible photons due to the formation of polaritonic states, particularly the lower polaritonic state, which helps in efficient absorption of visible photons. Here, the authors proposed that the effect of enhanced absorption of the visible photons inside the optical cavity and modifications in PES under strong coupling are the reasons for the rate modification.[20] Therefore, a much closer examination is required to understand the interplay of strong coupling in deciding the reaction rates. This is with the understanding that the polaritonic states are more stable; therefore, they are more protected.

There are many theoretical works available in the literature that use small molecules in order to understand the effect of strong coupling.[21–23] One interesting study in this direction is the photoisomerization of stilbene molecules under collective strong coupling.[21] Here, $N$-number of molecules can be coupled to a cavity mode (photon), thereby giving a collective coupling strength that scales as $\sqrt{N}$. The excited state PES is split into two as UP and LP branches with varying contributions of photon and exciton fractions. Photoexcitation of the polaritonic branches allows the system to dissipate the energy flow into $N$-molecules, thereby protecting the states as shown in Fig. 3. It is proposed that nuclear wave-packets get stuck in the well if the Rabi splitting energy is large, which supports the

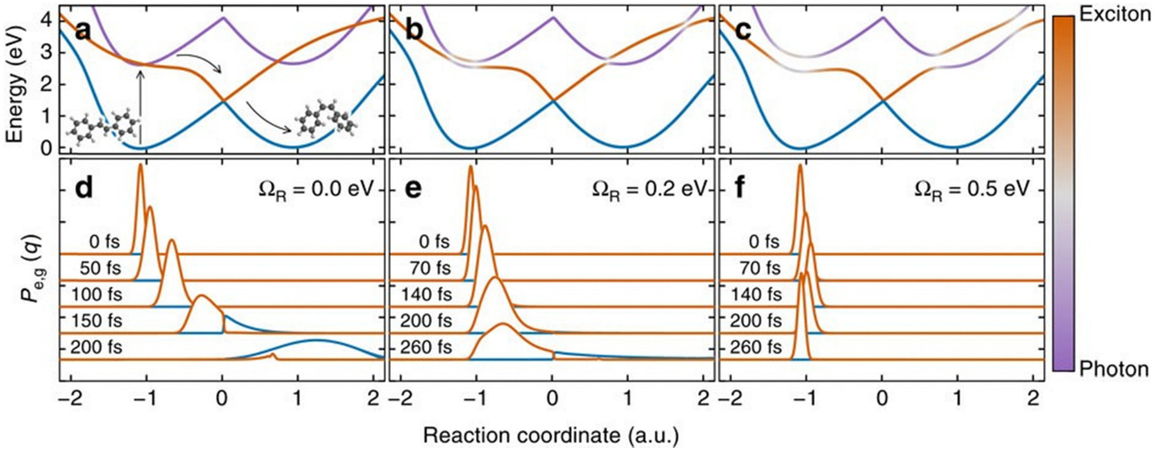


Fig. 3 Excited state reaction dynamics of light–matter states: (a–c) ground (blue) and excited (purple-orange colour scale) PES of the stilbene molecule coupled to a cavity mode ($\omega_c$ = 2.65 eV), with the light–matter coupling strength $\Omega_R$ increasing from (a) to (c). The continuous colour scale encodes the nature of the hybridized excited-PES. (d)–(f) Time propagation of the nuclear wave-packet after sudden excitation to the lowest excited state PES, shown separately for the parts in the LP surface (orange) and the ground state surface (blue) reached through the nonadiabatic transition at $q$ = 0 (at the equilibrium position). Contributions in the UP state surface are negligible and not shown [reproduced with permission from ref. 21. Copyright (2016) Springer Nature].

original finding of stabilization of MC molecules under strong coupling. However, the above theoretical study doesn't see a resonance effect in the system, as compared to many other single-molecule strong coupling predictions. Similar calculations and characterisation of polaritonic potential energy surface were also carried out for azobenzene molecules.[24] Photoprotection by strong coupling may not be true, as the process involves much more complicated energy transfer pathways through various available states.

A recent study focuses on an ultrafast proton transfer reaction of 10-hydroxybenzo[*h*]quinoline (HBQ) in an optical cavity (Fig. 4a).[25] Excited state intramolecular proton transfer (ESIPT) occurs from the phenol oxygen to the nitrogen atom when the samples are irradiated with a 375 nm light source (Fig. 4b). The timescale of the reaction is approximately 15 fs, which is similar to the cavity photon lifetime. The keto-form of HBQ formed after the proton transfer decays back to the electronic ground state ($S_0$) through photon emission, having a maximum around 620 nm. The performed DFT calculations show that the effect of strong light–matter coupling on modifying the PES leads to a minimum; otherwise, it would have been a barrierless proton transfer pathway from the S1 state (Fig. 4b).

However, no such suppression is observed experimentally, suggesting that alternate pathways such as thermal disorder are also present at room temperature. Owing to this disorder, the cavity mode contribution is redistributed over polaritonic states, along with a large population spread across the grey states that dominate the reaction dynamics. Fig. 4c represents the decay rate of the cavity ($\gamma_{\text{cav}} = 250\ \text{ps}^{-1}$) with a $Q$ factor of 15 and the overlap of dark states and polaritonic states with an increase in the number of HBQ molecules under strong coupling. When the overlap between the optically bright and dark states is greater, less suppression is observed in the formation of the photoproduct. Meanwhile, with an increase in HBQ concentration and thus the Rabi splitting, this overlap decreases after a certain limit of molecules, resulting in a 30% reduction in photoproduct formation. These results suggest that suppression in reaction is related to the Rabi splitting and the overlap between states, which is responsible for the radiative losses in the cavity due to population transfer from bright polaritonic states to dark states.[27] This theory works well with very fast reactions in which the photon fraction acts like a medium to propagate the energy flow. This interesting study paved the way for new perspectives in cavity-modified photochemical reactions.

To understand it further, we use the idea of *in situ* monitoring of a conventional photoisomerization reaction and allow the system to go through a weak-to-strong coupling transition through an intermediate coupling regime. An azopyrrole photoswitch is chosen for this study, which has a stable *trans* ($E$) form with a strong n–$\pi^*$ transition.[26] This system is special because the reactant and product are energetically degenerate here but exhibit different extinction coefficients. This helps study the reaction when the coupling strength changes dynamically as the reaction progresses. Photoswitching kinetics from stable $E$ to metastable *cis* ($Z$) are studied in ultra-strong and strong coupling regimes. It is found that under ultra-strong coupling (USC), the apparent rate of photoswitching decreases when the samples are irradiated at UP and molecular excitation positions ($\omega_0$) (Fig. 4e). In contrast, excitation at LP energy hastens the conversion to the $Z$ isomer. This was initially thought to be because of the cavity filter effect. An interesting highlight of this work is the deviation in the slope of reaction kinetics when the system moves through an intermediate coupling regime. It is found that the apparent rate of photoisomerization increases in the strong coupling regime when exciting the UP, $\omega_0$, and LP. Interestingly, entering the weak coupling regime, the apparent rate shoots up on UP and $\omega_0$ excitation (Fig. 4d). In the weak coupling regime, the photoisomerization rate decreases to the non-cavity rate when exciting at the LP

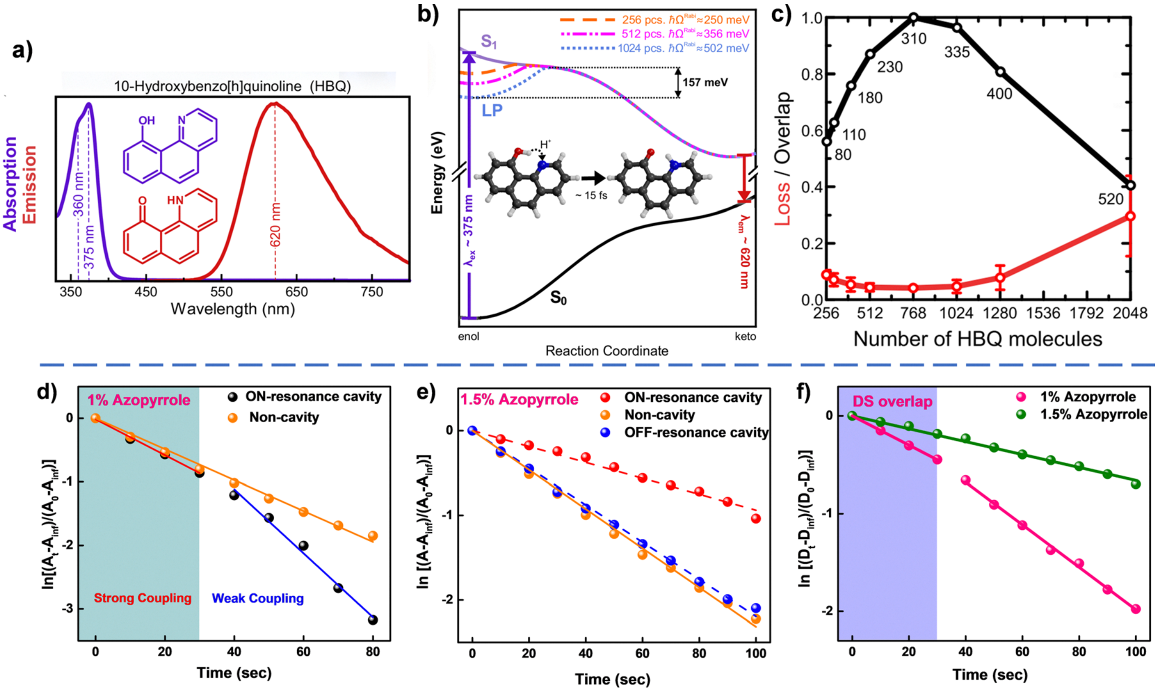


Fig. 4 Photochemistry under ESC: (a) normalized absorption and emission spectra of HBQ in the PMMA matrix. (b) PES for ESIPT in $S_0$ (black), $S_1$ (purple), and LP (dashed lines) representing the barrier induced by strong coupling. (c) Losses due to cavity decay (red) and overlap between the polaritonic absorption spectrum and molecular density states as a function of the number of strongly coupled molecules [(a)–(c) reproduced with permission from ref. 25. Copyright (2024) Springer Nature]. (d)–(f) Photoisomerization of *E*-azopyrrole in the cavity upon 490 nm excitation, (d) and (e) compared with the corresponding non-cavity (orange color) condition. (d) Deviation in the first-order kinetics of photoisomerization in the case of strong coupling regime on transitioning to a weak coupling regime; (e) slowing of the reaction inside the cavity under ON-resonance conditions; and (f) overlap integral of the cavity and dark states in an on-the-go reaction [(d) and (e) reproduced with permission from ref. 26. Copyright (2025) Springer Nature].

position. To understand the system's behaviour, theoretical calculations were performed at different coupling strengths of the cavity. For USC, it is observed that modification in PES plays a crucial role in controlling the photoisomerization reaction dynamics. In contrast, the strong and weak coupling regimes cannot be explained by the barrier in the PES of the polaritonic states. These results are then analysed using the overlap integral of the dark and bright states, and they align well with the experimental observations (Fig. 4f). Overlap of the dark states with the polaritonic states offers a better channel for energy migration, and therefore, the energy can be better redistributed across the reaction coordinates. Therefore, strong coupling can control the flow of energy through dark states, thus affecting the photoisomerization kinetics. These studies provide an alternate mechanistic understanding of photochemistry under strong coupling, which is not limited to the earlier idea of modification of PES. Here, it is also possible that the different mechanisms suggested by various studies are simultaneously at play or individually, depending on specific coupling strength conditions.

## Vibrational strong coupling

Motivated by the SPI-MC experiments, targeting a vibrational state and therefore controlling a chemical reaction is a straightforward thought in polaritonic chemistry. The same cavity configuration can be used for such experiments, given that the energy confinement falls in the infrared regime. The idea here is that if vibrational states responsible for a chemical reaction that undergoes light–matter strong coupling are used, could that modify the reaction dynamics? Earlier, there were attempts to target a given chemical bond by using an external stimulus, like lasers. Classically, one can increase the laser power and break a bond by allowing the system to cross the reaction barrier. However, achieving high efficiency is not possible due to the availability of large vibrational degrees of freedom that facilitate a better IVR within the molecule. In polaritonic chemistry, the confined cavity mode dresses the states and provides a platform for selective modification of the reaction coordinates. The original thought is to weaken the bond by vibrational strong coupling (VSC) and see whether reaction rates can be improved. However, it turned out that coupling slows down the reaction rates. Therefore, this initiated more elaborate experimental and theoretical studies in the VSC regime.

The first report of VSC appeared in 2015, where Shalabney *et al.* showed the coupling of a conventional polymer with an infrared cavity mode and the formation of vibro-polaritonic states.[28] Here, a well-known polymer, polyvinyl acetate (PVAc), which contains a strong carbonyl stretching band at around 1740 $cm^{-1}$, is used for the experiment (Fig. 5). A nearly 2 μm

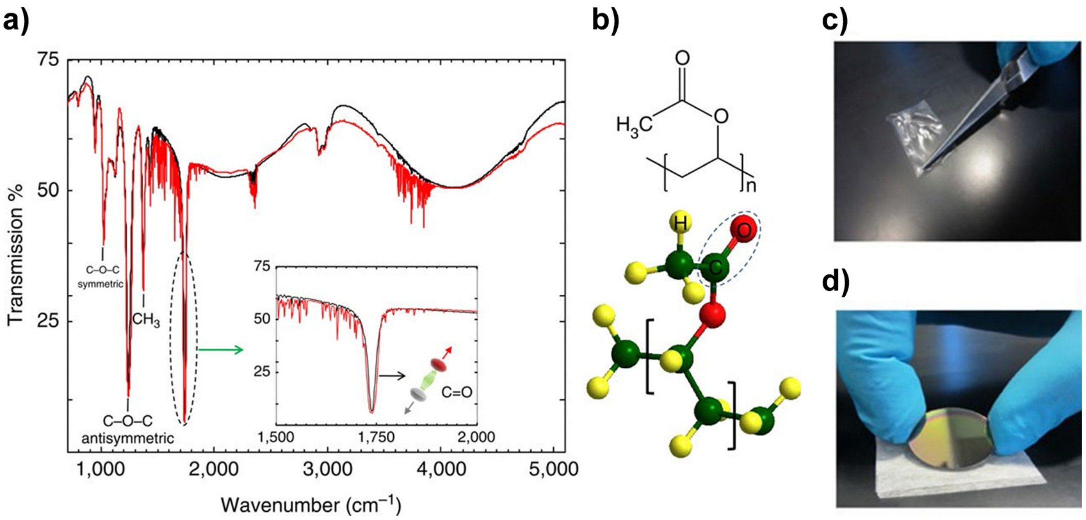


Fig. 5 Solid-state VSC: (a) infrared spectrum of a PVAc thin film; (b) molecular structure of PVAc, (c) free-standing PVAc thin film, and (d) a solid-state cavity containing spin-coated PVAc sandwiched between two gold mirrors on a germanium substrate [reproduced with permission from ref. 28. Copyright (2015) Springer Nature].

thin film of PVAc is sandwiched between two 10 nm Au mirrors deposited on the Ge substrate (Fig. 5d). The density of molecules is nearly $10^{21}$ cm$^{-3}$ in the thin film, sufficient to achieve strong coupling at room temperature. However, the estimated per-molecule coupling strength is approximately 0.1 μeV, which isn't enough to explain the observed spectroscopic signature. In this case, a Rabi splitting energy of ~21 meV is obtained. Therefore, it is convenient to say that the system responds collectively and enters into a strong coupling regime. This report demonstrates VSC in the solid state, and now there are many such experimental studies available with common polymer systems.[29–31]

Under ESC, only solid-state systems are tested due to technical issues in achieving sub-micrometer pathlength cavities in the liquid phase. However, most of the chemical reactions occur in the liquid phase and are ideal for VSC experiments. FP cavities for VSC are made of infrared transparent windows such as $BaF_2$, $CaF_2$, ZnSe, Ge, *etc.* The idea of coupling a molecular vibrational transition in the liquid phase is reported by coupling the vibrational bands of organic solvents in a microfluidic cavity (Fig. 6). Here, three solvent systems are studied, namely diphenyl phosphoryl azide, benzonitrile, and citronellal, having N=N=N (2169 cm$^{-1}$), C≡N (2229 cm$^{-1}$), and C=O (1726 cm$^{-1}$) stretching vibrational bands, respectively. Here, the microfluidic flow cell cavity allows tuning of the cavity mode position depending on the spacer thickness, and higher cavity modes give better finesses (Fig. 6c). The angle-dependent dispersion spectrum of the coupled states was also acquired and correlated with the TMM simulation.[32] Similar studies are carried out using ferrocyanide ions ($Fe(CN)_6{}^{4-}$).[33] These experiments opened a whole new paradigm of carrying out reactions in coupled states and explored how the strong coupling of the ground state can modify the reaction landscape, which is envisioned as progress from the earlier ESC experiments. This advancement also puts the field of VSC in the spotlight as selective control of chemical reactions by polaritonic chemistry, something that Pimentel and others

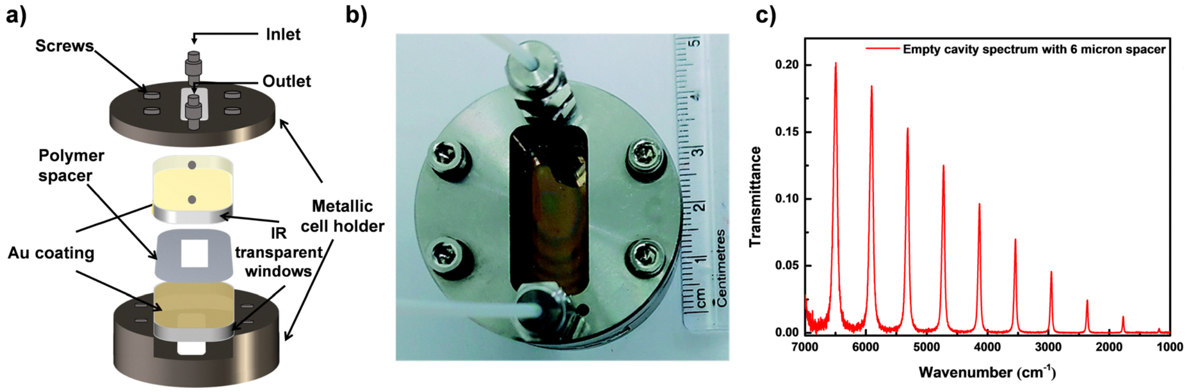


Fig. 6 Microfluidic cavity for VSC: (a) schematic of a disassembled microfluidic cavity with two parallel gold mirrors forming the FP cavity configuration, (b) picture of an assembled cavity, (c) infrared spectrum of an air-filled cavity [reproduced with permission from ref. 34. Copyright (2022) Royal Society of Chemistry].

were trying to do in the 1980s using lasers. In addition, a more exciting feature of VSC is that it is achieved in the dark without any external stimuli.

Thomas *et al.* first demonstrated the idea of ground-state chemical reaction control using VSC experiments in microfluidic cavities. A simple deprotection reaction of an alkylsilane using 1-phenyl-2-trimethylsilylacetylene (PTA) in a mild alkaline medium of tetra-*n*-butylammonium fluoride (TBAF) is used for the experiments. This system gave multiple advantages for this study, such as the reactant being a pure liquid, which can be injected into the cavity directly, and having well-defined vibrational modes for VSC experiments. The reaction follows a pseudo-first-order rate in the timescales of minutes and, therefore, can easily be monitored using an FTIR spectrophotometer (Fig. 7a). PTA has a vibrational transition at around 860 $cm^{-1}$ corresponding to the C–Si band. With the progress of the reaction, the refractive index (RI) of the reaction mixture changes; this, in turn, changes the free spectral range (Fig. 7b). Hence, the shift of the cavity mode position can be traced back to estimate the reaction rate. The reaction rate inside the cavity is decreased by nearly 5.5 times compared to outside the cavity (Fig. 7c). To confirm the ON-resonance effect, the cavity mode was moved away from the molecular transition energy by modulating the cavity thickness, and the reaction rate went to the non-cavity values (Fig. 7d). Later, to confirm that the product formation inside the cavity is reduced upon coupling to the cavity field, the reaction mixture was studied using gas chromatography (Fig. 7e). This also confirms that the formation of the product is hindered inside the cavity when the cavity mode is resonant with the molecular vibrational state. A temperature-dependent experiment proposed that the reaction mechanism is changing from initially being associative outside the cavity to dissociative inside the cavity. This experimental demonstration of modification in the chemical reactivity opened many new avenues for VSC.[35]

Furthermore, more complex systems are tested, especially competing reactions, and the selectivity is observed by coupling different functional groups. The competition between C–Si and O–Si bond breaking in the same molecule shows suppressed reactivity of one of the strongly coupled functional groups, and therefore, the product ratio is altered in favour of an uncoupled reactive site.[36] Similar works focusing on an intermolecular addition reaction are also reported using a well-known Prins cyclisation reaction between aldehyde/ketone and alcohol.[37] Here, the carbonyl stretching vibration of the aldehyde/ketone is coupled with a cavity to slow down the reaction. Upon coupling the carbonyl stretching vibration of the reactant, the reaction rate decreased by 70% compared to the OFF-resonance case. Here, the authors argued that there is no change in the reaction mechanism inside the cavity. Rather, it is proposed that VSC decreases the polarity of the coupled band and hence the reaction rate. The method shown above relies on RI change and, therefore, requires a very high concentration of the reactant and a difference in the RI of the reactant and the product. Also, this does not monitor the specific evolution of the product species; rather, it monitors the whole system as it evolves, making the reaction monitoring less informative. Recently, Ahn *et al.* reported VSC of an alcoholysis reaction between phenyl isocyanate (PHI) and cyclohexanol (CHol). In the non-cavity experiment, the rate of reaction was calculated

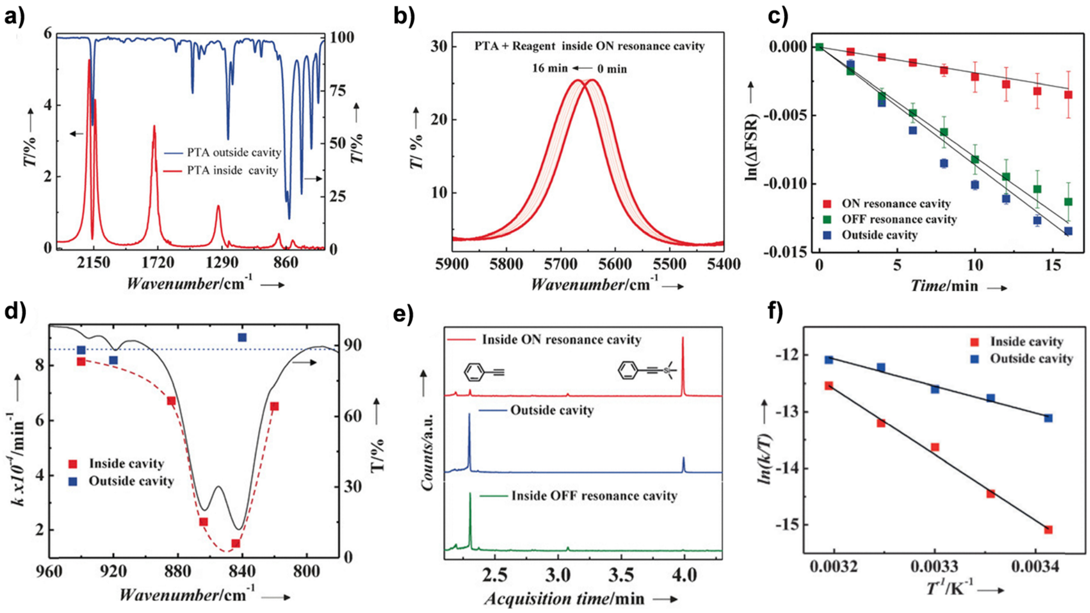


Fig. 7 Ground state chemical reactivity under VSC: (a) infrared spectrum of PTA outside (blue) and inside the cavity (red); (b) on-the-go changes in the cavity mode position measured for one of the higher cavity modes during the course of the reaction; and (c) first-order reaction rate fitting of ON-resonance (red), OFF-resonance (green) and outside (blue) cavities. (d) Plot of change in the reaction rate *versus* the mode detuning along the molecular infrared absorption of the C–Si band, (e) analysis of the product using gas chromatography, and (f) Eyring plot fitting of ON-resonance and outside cavities to extract the thermodynamic parameters [reproduced with permission from ref. 35. Copyright (2016) John Wiley and Sons].

by plotting the absorption of the NCO band *versus* time and extracting the concentration with respect to a calibration curve. Here, the approach is to measure the angular dispersion and directly extract the ON-resonance splitting energy. The ON-resonance energy is used to back-calculate the actual concentration of the reactant and further fitted to a second-order kinetic plot. An 80% decrease in the second-order rate is observed when the cavity mode is ON-resonance to the isocyanate (NCO) stretching band of the reactant.[38] Apart from the NCO stretch of PHI, the carbonyl stretch of CHol was also explored cooperatively and is also found to be effective, which we will discuss in the next section.

## Cooperative vibrational strong coupling

From a chemistry perspective, most of the reactions are carried out in the condensed phase, where almost 99% of the reaction mixture is constituted by the solvent molecules. In such cases, it is difficult to achieve strong coupling just with reactant molecules. Cooperative VSC offers to overcome this problem. Here, choosing the solvent vibrational frequency same as the reactant will allow the cavity coupling collectively, which can lead to a large Rabi splitting energy. Please note that cavity photons cannot discriminate between reactant and solvent vibrational states; hence, the reactant molecules can be cooperatively coupled through the solvent molecules. The first experimental demonstration of this idea is using a solvolysis reaction of *p*-nitrophenylacetate (PNPA) as the reactant and ethyl acetate (EtOAc) as the solvent (Fig. 8). PNPA and EtOAc contain a C═O stretching vibrational band at the same frequency, and strongly coupled to a cavity mode. The product formed here is *para*-nitrophenoxide, which shows a strong absorption in the visible spectrum at 400 nm. Therefore, the concentration of the product can be monitored using conventional methods such as UV-vis spectroscopy. The interesting point here is that the coupling of the reactant vibration is done in the infrared energy regime, while monitoring the reaction progress is done in the UV-vis region. The apparent rate for cavity experiments was nearly 250% higher than that of the non-cavity experiments (Fig. 8d). In addition, kinetic isotope experiments were performed in which isotopically substituted EtOAc was used. As EtOAc has $^{13}$C instead of $^{12}$C, the carbonyl stretching vibration shifts to a lower frequency and, therefore, cannot participate in the cooperative strong coupling process, and no change in reactivity is observed.[39]

In another report, PNPA hydrolysis is tested under enzymatic conditions with the coupling of OH stretching of water and α-chymotrypsin. It is observed that cooperative VSC can modify the enzyme catalytic efficiency.[41] A similar observation was made with the pepsin enzyme as well, in which the reaction rate constant was found to be decreased.[42] Furthermore, a group of substituted ester molecules is studied to extract the effect of VSC on the linear free energy relationship. It has been found that under the ON-resonance conditions, the system responds non-linearly as shown in Fig. 9.[34] The modification of the linear relation by the cavity is attributed to the complex interplay of energy flow between the substituent and the reaction centre through the benzene ring. The energy flow is getting perturbed while coupling the reaction coordinate to a cavity mode. However, there are no theoretical studies available so far to support the above mechanism proposed.

In order to get a better picture of the role of solvents in the cooperative strong coupling, a series of reactant and solvent combinations are tested in a detailed experimental study.

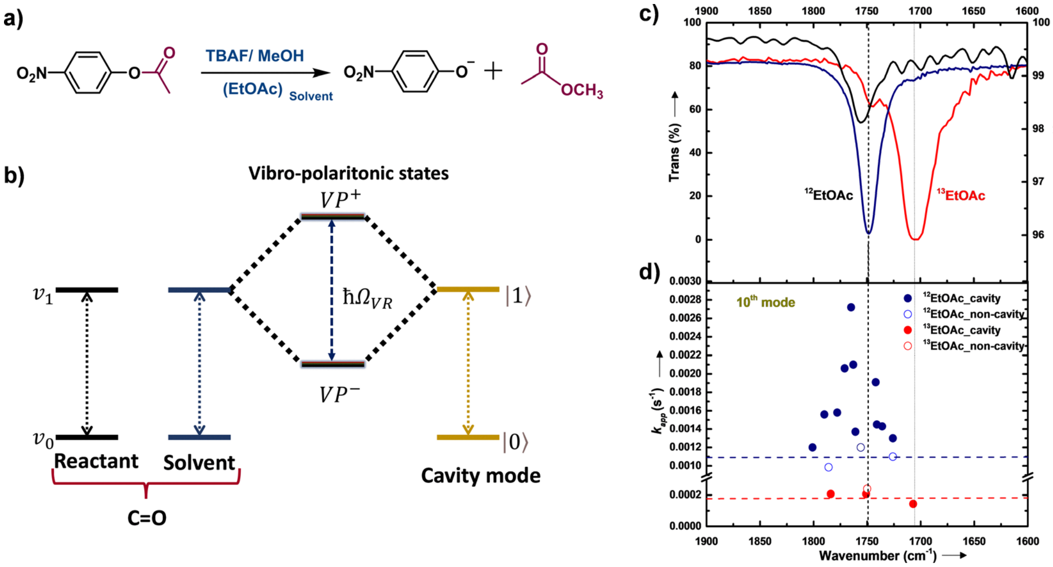


Fig. 8 Cooperative VSC of PNPA. (a) Scheme of the PNPA solvolysis reaction; (b) schematic illustration of cooperative VSC; (c) spectral overlap of reactant (PNPA) and solvent (EtOAc) carbonyl stretching bands; and (d) cavity detuning *versus* apparent rate constants at various mode positions. Reproduced with permission from J. Lather's PhD thesis.[40]

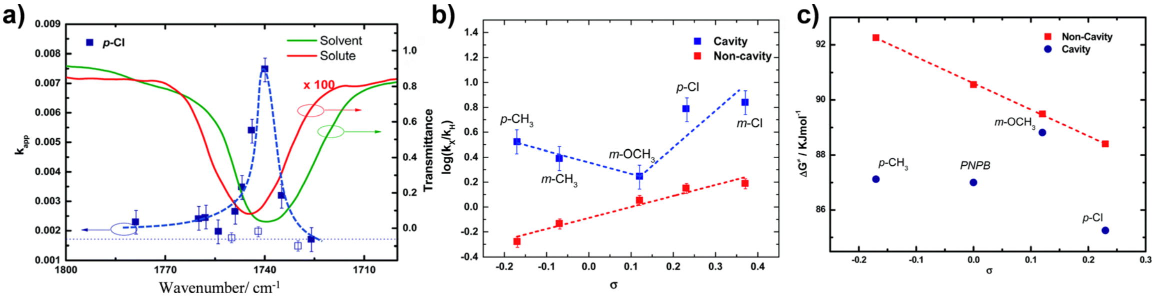


Fig. 9 VSC and linear free-energy relationship. (a) Kinetic action spectra for ester hydrolysis measured for the *p*-Cl derivative at 298 K. Cavity mode position (7th) moved slowly from 1680 cm$^{-1}$ to 1780 cm$^{-1}$ and the corresponding $k_{app}$ was plotted *versus* the infrared transmission spectra of the C=O stretching band of reactant (red trace) and solvent (IPAc; green trace) molecules. A sharp increase in the $k_{app}$ was observed (blue square) under the ON resonance condition. (b) Hammett plot for a series of ester solvolysis (*p*-CH$_3$, *m*-CH$_3$, *m*-OCH$_3$, *p*-Cl, and *m*-Cl) under non-cavity (red squares) and ON-resonance cavity conditions (blue squares). (c) Thermodynamic relation between free energy of activation *versus* $\sigma$ for cavity (blue) and non-cavity (red) systems. Dotted lines are a guide to the eyes [reproduced with permission from ref. 34. Copyright (2022) Royal Society of Chemistry].

A certain set of combinations is found to be more effective in changing the reaction rates, which also vary with the temperature of the bath. Thermodynamic studies suggest that VSC is not effective in some situations in which cooperative coupling is really visible. This is attributed to no change in the activation barriers at room temperature, even though the coupling is effective. Furthermore, the above study highlights that at a certain temperature range, the catalysis process turns down and becomes opposite, and the Eyring plot shows that the coupled system slows down the reaction rate. This means that modified-PES may not be a decisive factor here, and a more intricate dependence on the nature of solvents and the reactant has to be further tested.[43] Table 1 represents all the experiments tested under various conditions and also an indication of the possibilities that lie ahead to understand the use of polaritonic chemistry for various purposes.

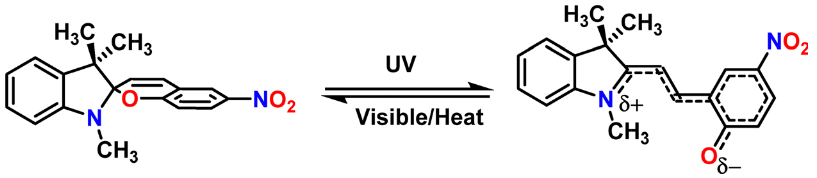
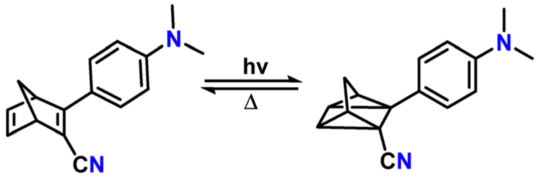
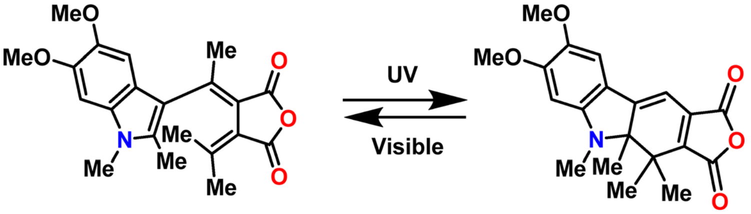
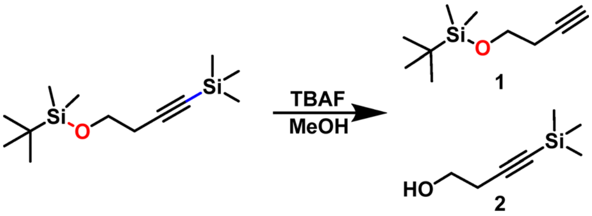
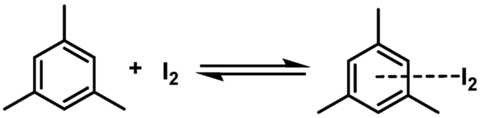
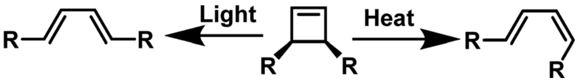
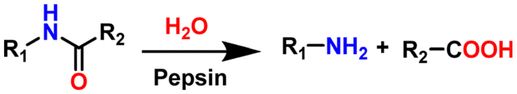
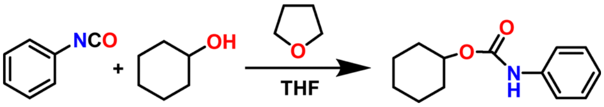
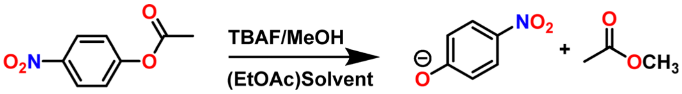
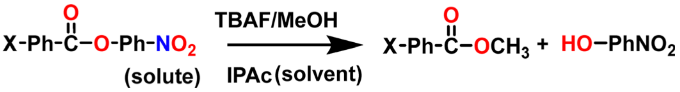
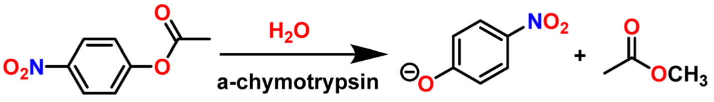
## Outlook and conclusion

So far, we have discussed different possibilities of achieving strong coupling in molecules, especially in the solid-state or in the liquid phase. This is done under the impression of testing conventional reactions in an unconventional platform. The resonance effect observed in the experiments shows the collective nature of the system; however, in many theoretical findings, the observation is not clear. ESC and VSC experiments so far have clearly shown the resonance effect. Most of the ESC experiments are carried out in photoswitches, whereas ESC can also affect other properties,[46] and even the photodegradation,[47] dimerization and complexation,[48] *etc.*, in a molecular system. Many of the theoretical studies so far have suggested the PES modification and protection of the state under strong coupling. However, a few reports suggest catalysis under certain conditions. This means that PES modification is not just the deciding factor here that controls the reaction pathways once the molecule is coupled to a cavity. There are other subtle features that also play along with these observed changes in the PES. This includes the modification of IVR channels by strong coupling. Sometimes, the polaritonic states open new IVR channels and sometimes block the existing channel, depending on the crossing of higher-order vibrational modes.[49,50] Considering the development in VSC-related ground state chemistry, there is now plenty of compelling evidence available (Table 1); however, the cavity-modified PES may not be the holy grail, as has now been seen and argued in many recent publications. There are also many cases in which strong coupling fails to give any conclusive evidence on the mechanistic aspect of reaction rate modification. The recent development in this direction is to study the symmetry of the vibrational states involved and see what the hybrid state symmetry looks like.[51]

Chiral cavities and stereoselective control of reactions are recent developments in the field. This comes from the motivation of using the symmetry role in deciding the fate of a reaction. Chiral cavities can be prepared in a laboratory and can be used for testing in a chiral discrimination experiment. Again, the magnetic field part is significant here, which may alter the chemistry of a chiral reaction, unless the electric field invokes it all alone.[52] A recent experimental study on a chiral reaction turned out not to affect enantioselectivity.[53] However, more experiments can be performed to demonstrate the involvement of a hybrid state in chiral discrimination, which is at least now predicted in a few theoretical studies.[54–56]

Apart from the chemical reactions, many other physical and chemical properties are found to be affected by strong coupling. For example, it has been shown that VSC can modify an equilibrium process,[36] improving the ionic conductivity of a solution,[57] crystallisation of the molecules,[58] supramolecular assemblies,[59–62] *etc.* As we have discussed many of the fascinating aspects of strong coupling, particularly VSC, it is worth mentioning that some reports claim to be unable to reproduce some of the published results in the literature.[63] On the other hand, some reports claim to observe the rate enhancement of the chemical reaction inside the plasmonic cavity.[64] In this work, the authors were able to successfully reproduce the original work, which was earlier done in a Fabry–Perot cavity configuration. Others also reproduced the original work inside Fabry–Perot cavities and, in fact, took it much further, such as carrying out the reaction under flow conditions, even

**Table 1** Representative polaritonic chemistry experiments for various chemical reactions under ESC and VSC conditions

| | Chemical reactions studied | Ref. |
|---|---|---|
| Electronic strong coupling |  | 15 |
| |  | 19 |
| |  | 18 |
| Vibrational strong coupling |  | 35 |
| |  | 36 |
| |  | 44 |
| |  | 45 |
| |  | 42 |
| |  | 38 |
| |  | 39,43 |
| |  $\mathrm{X\text{-}Ph\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}O\text{-}Ph\text{-}NO_2}$ (solute) $\xrightarrow[\text{IPAc(solvent)}]{\text{TBAF/MeOH}}$ $\mathrm{X\text{-}Ph\text{-}\overset{\overset{O}{\Vert}}{C}\text{-}OCH_3} + \mathrm{HO{-}PhNO_2}$ | 34 |
| |  | 41 |

connecting FP cavities in series.[65] Therefore, it is still an open area for research to optimise the experimental conditions. Recently, in some work, it has been observed that there are no VSC effects in a radical reaction.[66] In our view, coupling just a vibrational or a rotational state may not alter the reaction dynamics; at least, the band chosen for the experimentation must be involved in the rate-determining process or act as a spectator that may control the chemistry. In order to explicitly understand the role of VSC in the ground state chemistry, cleaner, gas-phase reactions – a unimolecular decomposition reaction – are required, so that a conventional tool like velocity mapping can be used to identify PES modification along with other players that control the intricacies of rate modification. In this perspective article, we attempt to discuss the recent understanding in the field. Finally, the experiments discussed above open new avenues and unequivocally prove the existence of a vacuum field that can be tailored to control chemistry.

## Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

The authors declare no competing financial interests.

## Data availability

No new data have been produced for this Feature Article.

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