

CHEMICAL REACTIVITY AND ELECTRICAL CONDUCTIVITY IN A CONFINED ELECTROMAGNETIC FIELD

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Present state of research on chemistry under light-matter strong coupling

The unique properties exhibited by nanomaterials, such as quantum dots, are attributed to the quantum confinement of electrons in such materials. Like electrons, it is possible to confine electromagnetic field (photons); however, not in a single material but in optical microcavities and photonic band gap structures. The confined photons and matter can interact and exchange energy to form the hybrid light-matter states or the polaritonic states in the so-called strong coupling regime[1]. An interesting aspect of light-matter strong coupling is that the wave function of the polaritonic states spreads across all molecules involved in the coupling, something like a delocalized orbital in a conjugated molecule. This collective character provides exciting avenues for engineering molecular or material properties through light-matter strong coupling[2]. Polaritonic chemistry originated[3] with the strong coupling of the molecular electronic transitions (ESC). However, the attention soon shifted to vibrational strong coupling (VSC), mostly because of the greater extent of changes under VSC and the vibrational mode selectivity that can be achieved under ambient conditions [4]. The VSC effect is not restricted to the ground-state chemical reactivity[5–8] alone. Ferromagnetism[9], superconductivity[10], energy transfer[11], and molecular self-assembly[12–14] have been impacted by VSC. However, finding the microscopic mechanism and generalizing the VSC effect has been challenging. Recent explanation of polaritonic chemistry based on molecular symmetry[15] and spin-glass effect[16] sheds light on a broad class of molecular and material properties impacted by VSC.

Chemistry in a confined electromagnetic field

The most exciting, at the same time, surprising aspect of VSC has been its impact on ground-state chemical reactivity. The seminal experiment in Strasbourg showed that the rate of silyl cleavage can be retarded by the VSC of the Si-C stretching vibrations[5]. Subsequent experiments from Strasbourg showed an even more remarkable impact of VSC on the chemical reactivity[6]. The VSC of the Si-C or Si-O stretching and Si-CH₃ bending

vibrational modes resulted in a reduced rate of silyl bond cleavage (Fig. 1A) and the tilting of the reactive landscape in favour of the relatively stronger Si-O bond cleavage compared to the Si-C bond (Fig. 1B).

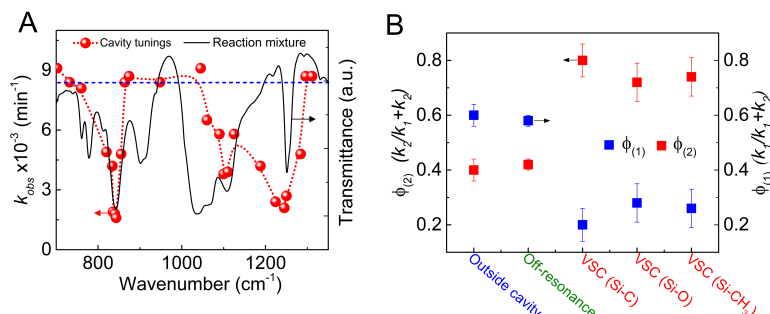


Fig. 1. (A) The variation of the observed silyl bond cleavage reaction rate constant inside the cavity as a function of cavity tuning (red spheres). The red dotted line is a guide for the eye. The black curve shows the IR spectrum of the reaction mixture. The blue dashed line represents the average rate constant outside the cavity. (B) Plot showing the yields (Φ) of product 1 (blue squares) and 2 (pink squares) under VSC, off-resonance, and outside cavity conditions (Reproduced from Ref. 6).

In a recent experiment in Bengaluru and repeated in Strasbourg inside NMR cavities, we observe that VSC selectively cleaves the O-SiMe₃ bond, sculpting a new reactive pathway, which is otherwise absent under non-cavity and off-resonance conditions. The beauty of polaritonic chemistry is that all these modifications are caused by the quantum fluctuations of the confined electromagnetic field, which does not need any photoexcitation.

Enhanced electrical conductivity under vibrational strong coupling :

Another exciting demonstration of how a confined electromagnetic field in a cavity can impact a material property is shown by the extraordinary electrical conductivity in non-conducting polymers such as polystyrene (PS) under VSC[17]. Strong coupling involves the interaction of matter with the quantum fluctuation of the electromagnetic field and can provide a permanent photonic content to matter. So we hypothesized that the VSC (Fig. 2A) should be an alternative to light excitation to obtain enhanced conductance. With this objective, we started working with PS, which has an aromatic -CH out-of-plane bending ($\delta(\text{Ar. CH})$) vibrational mode that supports vibronic coupling. The choice of PS was serendipitous, as we wanted an easily processable polymer with vibronic coupling attributes as a control. Surprisingly, the VSC of the PS $\delta(\text{Ar. CH})$ vibrational modes resulted in a conductance of the order of milli Amperes compared to the uncoupled PS (Fig. 2B). The observed conductivity in PS under VSC is c.a. 9 Sm^{-1} , equivalent to the conductivity shown by graphene-doped PS.

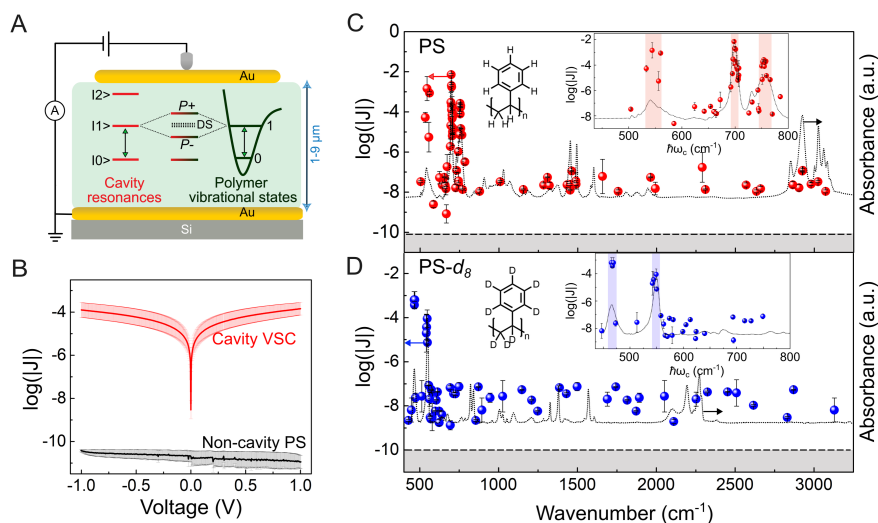


Fig. 2: (A) Schematic illustration of cavity VSC and the electrical measurement set-up. (B) The electrical conductance of PS under VSC (red curve) compared to the non-cavity (grey curve). (C, D) Electrical conductance through PS (red spheres) and PS- d_8 (blue spheres) as a function of cavity tuning. The grey-shaded region highlights the non-cavity conductance. The black dotted curve is the IR spectra of PS and PS- d_8 . The inset is the zoom in the $\delta(\text{Ar. CH})$ and $\delta(\text{Ar. CD})$ spectral region (Adopted from ref. 17).

We confirmed the VSC effect using deuterated polystyrene (PS- d_8). Tuning the cavity on resonance with the $\delta(\text{Ar. CD})$ mode resulted in the conductance enhancement similar to that of PS. The remarkable aspect of the experiment is the vibrational mode selectivity towards the enhanced conductance under VSC. Only the VSC of the $\delta(\text{Ar. CH(D)})$ vibrational modes of PS or PS- d_8 , belonging to the B_2 symmetry, leads to the electrical conductance (Fig. 2C, D). We then explored other aromatic and aliphatic polymers to check for any structure-property relationship under VSC. The aromatic polymers we investigated have C_{2v} local point group and B_2 symmetry for the $\delta(\text{Ar. CH})$ vibrational modes, but different frequencies compared to PS. The aromatic polymers showed enhanced conductivity under the VSC of their respective $\delta(\text{Ar. CH})$ vibrational modes. In contrast, the aliphatic polymers did not show any enhancement under VSC, as these polymers do not possess any out-of-plane bending vibrational modes that involve vibronic coupling. Their local symmetry is also different than that of the aromatic polymers. These experiments reveal an exciting molecular structure-property relationship and molecular symmetry correlation toward enhanced conductance under VSC.

Outlook on future developments of research on chemistry in confined spaces

Since the intermolecular interactions often govern the bulk properties, we emphasise that collective light-matter strong coupling must also modify these interactions to show the altered properties. At the atomic level, the interactions are mediated by the electromagnetic field. In this regard, a perturbation to the electromagnetic field in the form of light-matter

strong coupling can suppress or enhance the existing communication between atomic or molecular units, or open new pathways. The emergent properties from these modified interactions can appear in the form of altered kinetics[4], morphology[12,14], emission characteristics[18], charge transport[17], etc. It may lead to changes in chemical reactivity paths, but may not change the rate. It can also affect the vibrational energy flow and properties arising from it. Thus, light-matter strong coupling in a confined electromagnetic field can bring in completely new chemistry because the quantum fluctuations of the electromagnetic field may alter the fundamental interactions that hold the molecules together. However, one needs to get the right system to observe the changes, but predicting that right system remains challenging. We are steadily attaining the predictivity in VSC experiments with more generalised experiments, like the one based on molecular symmetry from Strasbourg[15] and the conductivity of polymers under VSC from Bengaluru[17]. Theory models based on spin glass effects developed in Hamburg[16] and intramolecular vibrational energy relaxation[19] will catalyse the predictivity towards the VSC-modified properties.

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