LIGHT-MATTER COUPLING

Manipulating matter by strong coupling to vacuum fields

Francisco J. Garcia-Vidal*, Cristiano Ciuti*, Thomas W. Ebbesen*

BACKGROUND: One of the most important phenomena in cavity quantum electrodynamics (cQED) is the so-called strong coupling regime, which appears when the interaction between a photon tightly confined in an optical cavity and a matter excitation creates hybrid light-matter states. When the latter are populated, hybrid particles called polaritons are formed. These particles are very attractive because they combine properties of their constituents, which enables applications ranging from low-threshold lasing in semiconductors to photon quantum information. Since its discovery, most of the investigations on strong coupling have been aimed mainly toward the modification of optical properties. During the past decade, an alternative area of research has emerged that takes advantage of collective strong coupling to take chemistry and materials science into new directions. For this purpose, no external light source is necessary as the hybrid light-matter states are formed even in the dark because the coupling occurs through the zero-point energy of the optical mode (i.e., the vacuum field). The mere presence of the hybrid states has a substantial effect on material properties, as reviewed here.

ADVANCES: Both experimental and theoretical studies have shown changes to photochemical reaction rates under strong coupling between the electronic excitations of molecules and cavity electromagnetic modes. Strong coupling modifies the shape of the potential energy surfaces associated with the excited states of the molecule, allowing for a manipulation of its photophysical properties. Moreover, ground-state chemical reactivity can also be completely modified when molecular vibrations are strongly coupled to infrared cavity modes. Although a detailed picture of the mechanism is still missing, symmetry seems to play a key role. Material properties can also be changed by strong coupling. Charge and energy transport in organic materials and magneto-conductivity in two-dimensional electron gases have been shown to be altered. Thanks to the intrinsic delocalized character of the polaritonic modes, transport properties can be then tuned at a macroscopic scale. It is also feasible to manipulate phases of matter by means of strong coupling. It has been reported that the critical temperature of a superconductor can be substantially enhanced by judiciously exploiting vibrational strong coupling and that the ferromagnetism of nanoparticles can be boosted by orders of magnitude. These examples illustrate the potential of using vacuum fields instead of intense laser fields to induce modification of material properties.

OUTLOOK: There are many classes of organic reactions that are currently being explored under strong coupling. As more results are collected, the underlying physical chemistry will be further clarified and should lead to some general principles to guide chemists and physicists in their use of vibrational strong coupling. The recent demonstrations that water, under vibrational strong coupling, modifies enzyme activity illustrates the potential for manipulating biological activity under strong coupling—an avenue that remains unexplored. Regarding solid-state material properties, the influence of strong coupling in phonon-based phase transitions should also be fully explored, aiming at inducing new condensed phases. Moreover, cavity-controlled magneto-transport might reach the quantum Hall regime. In general, two-dimensional materials are very well suited to be integrated in cavity resonators with deeply subwavelength photon confinement, which provides an intriguing platform to modify electronic properties through vacuum fields. ∎

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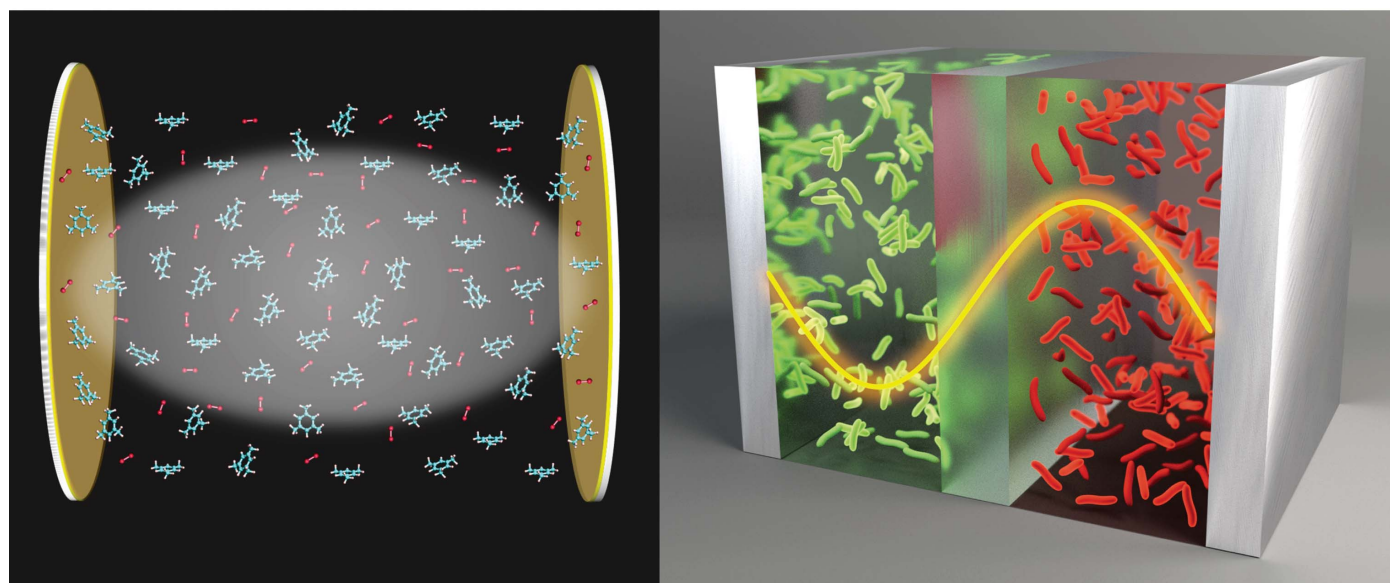
Illustration of modified molecular processes under strong coupling in optical cavities. (Left) Charge transfer complexation between mesitylene and iodide (courtesy of K. Nagarajan). (Right) Energy transfer between donor and acceptor molecules (courtesy of J. Galego).

LIGHT-MATTER COUPLING

Manipulating matter by strong coupling to vacuum fields

Francisco J. Garcia-Vidal[1,2]*, Cristiano Ciuti[3]*, Thomas W. Ebbesen[4]*

Over the past decade, there has been a surge of interest in the ability of hybrid light-matter states to control the properties of matter and chemical reactivity. Such hybrid states can be generated by simply placing a material in the spatially confined electromagnetic field of an optical resonator, such as that provided by two parallel mirrors. This occurs even in the dark because it is electromagnetic fluctuations of the cavity (the vacuum field) that strongly couple with the material. Experimental and theoretical studies have shown that the mere presence of these hybrid states can enhance properties such as transport, magnetism, and superconductivity and modify (bio)chemical reactivity. This emerging field is highly multidisciplinary, and much of its potential has yet to be explored.

I t has been well known since the work of Huygens in 17th century that two oscillators, such as pendula, can couple to generate new modes by the exchange of energy (Fig. 1A). Although there are numerous examples of coupled oscillators in nature, what is less well known is that it is possible to couple, in an analogous way, an optical mode and a state transition in a material to generate two new hybrid light-matter states by placing the material inside a resonant optical cavity (Fig. 1B). Perhaps the most notable aspect is that such coupling can also occur in the dark—a natural consequence of the quantum nature of both the electromagnetic (EM) fields and matter—as explained in detail in the next section. The emergence of new hybrid light-matter states, also known as polaritonic states, has the potential to change the material and chemical properties under appropriate conditions, even in the ground state. Furthermore, typical materials encompass a large number of oscillators coupled to a single optical mode, resulting in the formation of collective delocalized states, which also affect their properties. Since the first demonstration of a modified chemical reaction, numerous examples of cavity-controlled changes in properties have been reported from biological functions to solid-state properties. This approach to manipulating material and (bio)chemical properties has been generating tremendous interest during the past decade and is the subject of this Review. The interest is both in the fundamental

underpinnings as well as the technological potential.

Fundamentals of light-matter strong coupling

Normally we think of the vacuum as the absence of everything—in particular, the absence of radiation. In reality, empty space is filled with EM fluctuations. These so-called vacuum EM fluctuations originate from the fact that space is full of optical modes, which have zero-point energy as a result of their quantum nature. The presence of these vacuum fields has many consequences for molecular and material properties, such as, for example, spontaneous emission. It was Dirac (1) who, in laying the foundations of quantum electrodynamics (QED), provided the explanation that an emitter in an excited state interacts with those vacuum fields, allowing a transfer of energy to an unoccupied EM mode through the spontaneous emission of a photon. In free space, the EM field has a continuum of modes that typically interact weakly with the emitter. One way to enhance such interaction is to place the emitter inside a cavity, such as, for example, the one formed by two parallel metallic mirrors. In such confined geometry, the EM field presents a discrete spectrum of modes. Notably, the field can be much more localized than in free space, thereby increasing the emission quantum yield. This crucial prediction by Purcell in 1946 (2) began a whole field of research, today called cavity QED (cQED), which is devoted to exploiting different types of cavities and emitters to enhance and control light-matter interactions.

A very simple model to account for cQED scenarios was introduced by Jaynes and Cummings (JC) in 1963 (3). Within this JC model, only a single mode of the cavity with photon energy $\hbar\omega_c$ (where $\hbar$ is Planck's constant h divided by 2π) is taken into account, whereas the considered emitter is a two-level

system with transition energy $\hbar\omega_e$. Hybridization between the emitter excited state and a cavity single-photon state leads to the formation of two new eigenstates. When the photon and transition frequencies are equal, the hybrid eigenstates have an energy splitting $2\hbar g$, where g is the rate of energy exchange between light and matter. To describe real systems, one cannot neglect the photon leakage rate, κ, and nonradiative losses for the emitter, γ. Weak and strong light-matter coupling regimes can be quantitatively defined by just comparing $2g$ with κ and γ. When $2g < \kappa, \gamma$, the exchange rate is smaller than the loss rates, and, as a consequence, the excitation is lost before it can be shared between the emitter and the cavity components. In this case, the emitter-cavity system is said to operate in the weak coupling regime. In the opposite case, $2g > \kappa, \gamma$, there is an exchange of energy between the light and matter components, and the system resides in the strong coupling regime. Another paradigmatic quantum model is the one introduced by Hopfield (4). This model describes the coupling of the EM quantum field to collective material excitations, like excitons in semiconductors, which are bosonic and so behave as harmonic oscillators.

The hybrid light-matter excited states are known as polaritonic states (P+ and P− in Fig. 1B). As a result, the energy spectrum of the system in this regime displays two distinct peaks (Fig. 1C), separated by the so-called Rabi splitting, $\hbar\Omega_R = \hbar\sqrt{4g^2 - (\kappa - \gamma)^2}$ (Fig. 1B).

The huge potential and particular appeal of operating in this regime lie in the composite nature of the polaritonic states because they combine properties of their two constituents: the high coherence of light and the strong interaction of matter. In the extreme case, when the coupling is such that the Rabi frequency Ω_R is a significant fraction of the transition frequency (~>10%), the system enters the so-called ultrastrong coupling regime (5–7). Within this regime, antiresonant light-matter interaction processes that do not conserve the number of excitations in the system are allowed, which leads to a ground state that contains virtual bare excitations in addition to the emergence of polaritonic states in the excited manifold.

Attaining the strong or ultrastrong coupling regimes is enormously facilitated by the so-called collective coupling, in which a large number N of material oscillators—e.g., molecules—couple to one optical mode. As a consequence, the Rabi splitting increases as $\sqrt{N}$ (8). The collective coupling also results in the formation of a manifold of $N − 1$ collective states, which are known as dark states (DS) because they cannot be directly excited with light and therefore cannot be seen in an absorption spectrum (Fig. 1B). However, the

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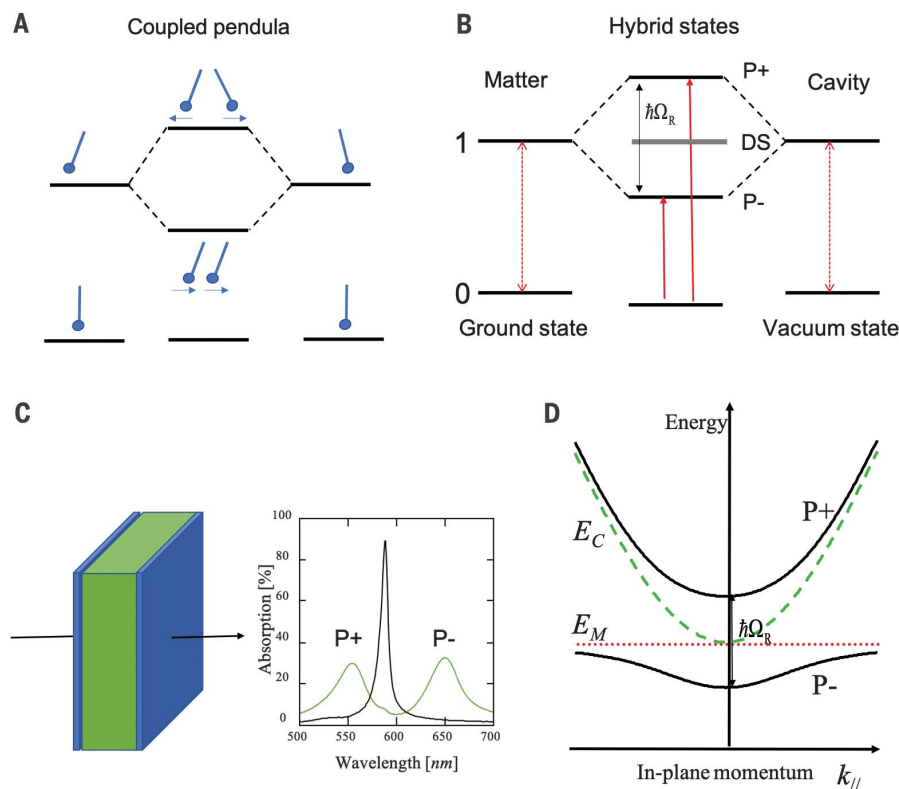
Fig. 1. Coupled oscillators and light-matter strong coupling. (**A**) Classical coupled pendula. (**B**) Strongly coupled material and optical transitions, leading to the formation of the hybrid light-matter or polaritonic states P+ and P− separated in energy by the Rabi splitting $\hbar\Omega_R$, and the DS in the case of collective coupling. (**C**) A FP cavity filled with a material. Under the right conditions for strong coupling, the formation of P+ and P− results in two new peaks in the absorption spectrum (in black, the original material transition; in green, the spectrum after strong coupling). Figure reproduced with permission from (64). (**D**) The dispersive optical mode of a FP cavity (E_C; green dashed line) intersects the material transition energy E_M (red dotted line) at normal incidence (where the parallel momentum $k_{//}$ = 0).

DS do not have the properties of the states of the uncoupled material, and notably, like the polaritonic states, they can acquire a delocalized character (9) that extends over the whole system (Box 1).

The first quantum experiments aiming for the strong coupling of matter excitations were performed using Rydberg atoms in microwave and optical cavities. A detailed account of these experiments can be found in (10). In parallel, phonons of inorganic materials were coupled to surface plasmons (SPs) in a more classical approach (11, 12). Later, advances in semiconductor microcavities led to the detection of strong coupling in various solid-state platforms, reaching Rabi splitting values of the order of tens of milli–electron volts (13), where experiments needed to be carried out at low temperatures. Within this scheme, it was possible to even achieve polariton lasing, condensation, and superfluidity (14, 15). To enhance light-matter interactions, organic materials provided a great opportunity (16–18). In fact, organic molecules display large oscillator strengths in the visible spectrum, giving rise to Rabi splitting values more than 10 times as high as those obtained with inorganic semiconductors, thereby enabling lasing and condensation of polaritons at room temperature (19–21). Molecules also paved the way to explore cavity-modified chemistry (22) and other material properties under strong coupling, as discussed in detail in the following sections.

From a practical point of view, strong coupling is achieved by placing a material in the confined EM field, such as typically provided by a Fabry-Perot (FP) cavity (two parallel mirrors), as illustrated in Fig. 1C, which results in two new peaks in the absorption spectrum. Alternatively, SPs or more-complex resonators, such as metallic split rings, can be used (23). The choice of the optical resonator can be tailored depending on the material properties to be measured, as detailed in the next sections. Many optical resonators are dispersive—i.e., the resonance energy varies with angle, such as in the case of a FP cavity, where it is minimal at normal incidence (Fig. 1D). Experiments with dispersive optical modes have shown that to maximize the effect of strong

coupling on organic material properties, the relevant transition needs to be resonant at the bottom of the dispersion curve—i.e., with the zero in-plane wavevector—probably because this is the equilibrium configuration where the properties are explored. Regarding material excitations, strong coupling can be achieved with different types of transitions that are optically allowed, such as electronic, phonon, and vibrational transitions, which can all affect both material and molecular properties. Most studies with organic molecules have involved coupling to electronic transitions or to vibrational transitions.

Modifying material properties

A large number of properties of solids have been explored under strong coupling to the vacuum field during the past decade, such as electrical conductivity, work-function, energy transfer probability, nonlinear optical response, and phase transitions. Here, we focus on a subset of properties on which much work has been carried out, starting with transport properties.

Enhanced transport of energy and charge

Organic semiconductors have generated great interest for large-scale fabrication of inexpensive and flexible devices. However, charge transport in disordered organic semiconductors displays a very low mobility of charge carriers (24), which severely limits their technological applications in electrical devices, such as field-effect transistors (25). On the other hand, energy transport in organic materials occurs through the motion of neutral electronic excitations—i.e., excitons—whose propagation is governed by short-range dipole-dipole interactions with a spatial range of only a few nanometers, in a process usually called Förster resonance energy transfer (FRET). Moreover, as most organic systems are disordered and possess relatively large dissipation and dephasing rates, exciton transport typically becomes incoherent and diffusive over long distances, which strongly limits optoelectronic applications of organic materials, such as organic photovoltaic cells (26).

As explained above, collective strong coupling leads to the formation of polaritonic states that are delocalized, extending over the whole structure in which the individual excitons and cavity EM mode(s) are interacting. This property is very appealing to enlarge the spatial range of both charge and energy transport in organic materials, as it could overcome the transport limitations linked to short-range interactions and disorder. In a first demonstration of this potential, the electrical conductivities of different n-type organic semiconductors deposited on top of a plasmonic resonator (holey metal Ag surface) were measured (27). This surface acts as an open

Box 1. Nomenclature and concepts.

Polaritonic states and DS: The collective coupling of *N* oscillators (e.g., molecules) to one optical mode generates two bright polaritonic states, P+ and P−, and *N* − 1 DS. The DS are also collective states generated by the strong coupling process: They are formed from a linear combination of all possible states with one excited molecule and *N* − 1 molecules in the ground state (*128*). Thus, their properties differ from those of the bare or uncoupled molecules. It has recently been suggested that if one considers the free energy, which depends on entropy, the DS can even have a lower energy than that of the lower polaritonic state (*116*). Moreover, in the presence of disorder and/or spatially inhomogeneous coupling, the *N* − 1 DS actually become gray, acquiring a photonic component that, even if small, can radically change the physical and chemical properties as catalysts or dopants do.

Reservoir of uncoupled excitons: The notion of a reservoir of uncoupled molecular excitons was introduced (*129*) because two types of disorder might lead to a large fraction of uncoupled molecules—namely orientation disorder (dipole moment is not aligned to couple with the cavity field) and spectral inhomogeneous broadening. It has been shown that for an inhomogeneously broadened absorber, the Rabi splitting does not occur from a subset of absorbers exactly resonant with the cavity, as confirmed by experiments (*128*). However, orientation disorder will necessarily lead to a fraction of uncoupled molecules. Recent experiments on chemical systems suggest that this fraction must be very small because it would preclude the observation of a large slowdown in chemical reaction rates and redistribution of products, among other things, as the coupled molecules could not compete with the faster uncoupled molecules.

Markovian versus non-Markovian dissipation regime: In the Markovian regime, the properties of the coupled system can be understood as simply derived from those of the uncoupled entities. In this regime, the dissipation rate of the coupled system is given by the sum of the cavity and exciton dissipation rates, such that the polaritonic states P+ and P− are expected to have the same lifetimes when the cavity mode is resonant to the material transition, contrary to experimental evidence. In the ultrastrong coupling regime, dissipation can be profoundly modified because the polaritonic states experience the effect of the bath (vacuum or thermal) at very different frequencies with respect to the bare modes (*130*). Additionally, the notably large changes in thermodynamics (PES and dynamics) observed in chemical reactions under strong coupling (*131*), and the effects of symmetry, clearly also point to a non-Markovian regime. In this regime, the dynamic properties must be calculated in the coupled basis, which can be challenging.

Cooperative coupling: When the absorption of the material to be coupled is weak as a result of low oscillator strength or low concentration, it is often not possible to attain the strong coupling regime. This limitation can be overcome by cooperative coupling whereby, for example, a solute has a vibrational absorption band at the same frequency as one of the vibrations of the solvent in which it is dissolved. Strong coupling of the solvent then acts on the solute as if it is coupled through intermolecular interactions (*115*, *117*).

EM cavity, and collective ultrastrong coupling between the excitons in the organic molecules and the SPs supported by the metal surface can emerge. At resonance, when the energy of the SP at $k_{//}$ = 0 coincides with the exciton energy of the molecule, the electrical current was shown to increase 10-fold at most, reflecting mostly a change in the carrier mobility. The fundamentals of this enhancement in electrical mobility are not straightforward to derive because the excitons that feed strong coupling are neutral quasiparticles. A theoretical model has suggested that, when losses in the cavity are larger than the bandwidth of electronic bands, the system can enter into a "collective dressing regime," in which strong coupling induces a large increase in the hole conductivity, leading to a substantial increase in the electrical mobility (*28*). More recently, p-type semiconductors have been also studied under ultrastrong coupling, revealing both enhanced conductivity and photoconductivity (*29*, *30*). By measuring changes in the photo-

conductivity of a p-doped organic semiconductor whose excitons were strongly coupled to the EM modes supported by a FP microcavity, it was found that the bare photoinduced electron transfer events can be modified by the presence of the two polaritonic states (upper and lower polaritons) in the energy spectrum: Moving from positive to negative detuning caused the upper and lower polariton photocurrents to swap their field dependence (*29*).

Inspired by the experimental findings reported in (*27*), two theoretical groups independently predicted in 2015 that energy transport in organic materials could also be enhanced when excitons are strongly coupled to a cavity EM field (*31*, *32*). By using a one-dimensional (1D) model system in which disorder was introduced both in the positions of the emitters and the orientations of their transition dipoles (Fig. 2A), they showed how the formation of a collective strongly coupled mode allows excitons to bypass the disordered array of emitters and jump directly from one end of the

structure to the other, concluding that polaritonic states can largely extend the spatial range of energy transport in organic materials. This capability has been experimentally verified several times since then. Room temperature ballistic propagation of excitons in an organic semiconductor was demonstrated for distances well beyond 100 micrometers thanks to their hybridization with propagating Bloch surface EM waves that act as open cavities (*33*). These EM modes appear at the surface of a truncated distributed back reflector, which is just a 1D photonic crystal made of two distinct dielectric materials. Similar results for the propagation length of this type of polaritonic modes have been reported more recently (*34*), as shown in Fig. 2B. Additionally, through analysis of the halo-like pattern of the polariton intensity, a coherence length of 20 micrometers was extracted, demonstrating the coherent character of the polariton-assisted transport of energy—a critical difference with the diffusive process occurring in bare organic materials. Along the same lines, long-range transport of organic excitons strongly coupled to EM modes supported by a FP cavity has been also reported (*35*) but with a much shorter propagation length of only a few micrometers, which could be due to the larger losses present in this type of metallic cavity. Such studies point nevertheless to the long lifetime of the polaritonic modes and to the non-Markovian regime of these systems (Box 1). In a properly designed strongly coupled system, it is also possible to induce efficient energy transfer over distances of 100 nm, well beyond the ~10-nm limit in the Förster regime, as shown both theoretically and experimentally (*36*, *37*). This long-range transport process, as illustrated in Fig. 2C, is discussed in more detail in the section devoted to the modification of molecular properties.

Modification of transport properties induced by strong light-matter coupling has also been reported for inorganic materials (*38*). When a 2D electron gas (2DEG) is inserted in a deeply subwavelength split-ring resonator, the 2DEG magneto-resistivity has been altered in the regime of low magnetic fields (*38*). As described theoretically (*39*), in the linear transport regime, the Drude scattering time is modified when the 2DEG cyclotron frequency is quasi-resonant to one mode of the resonator (Fig. 2D). Additionally, antiresonant interaction processes due to ultrastrong light-matter coupling can produce orbital renormalization effects (*39*) that, for example, are expected to modify the effective carrier mass and carrier hopping properties. Related effects have also been predicted for the vertical transport in semiconductor heterostructures with the possibility of controlling the dark current of quantum well infrared (IR) photodetectors (*40*).
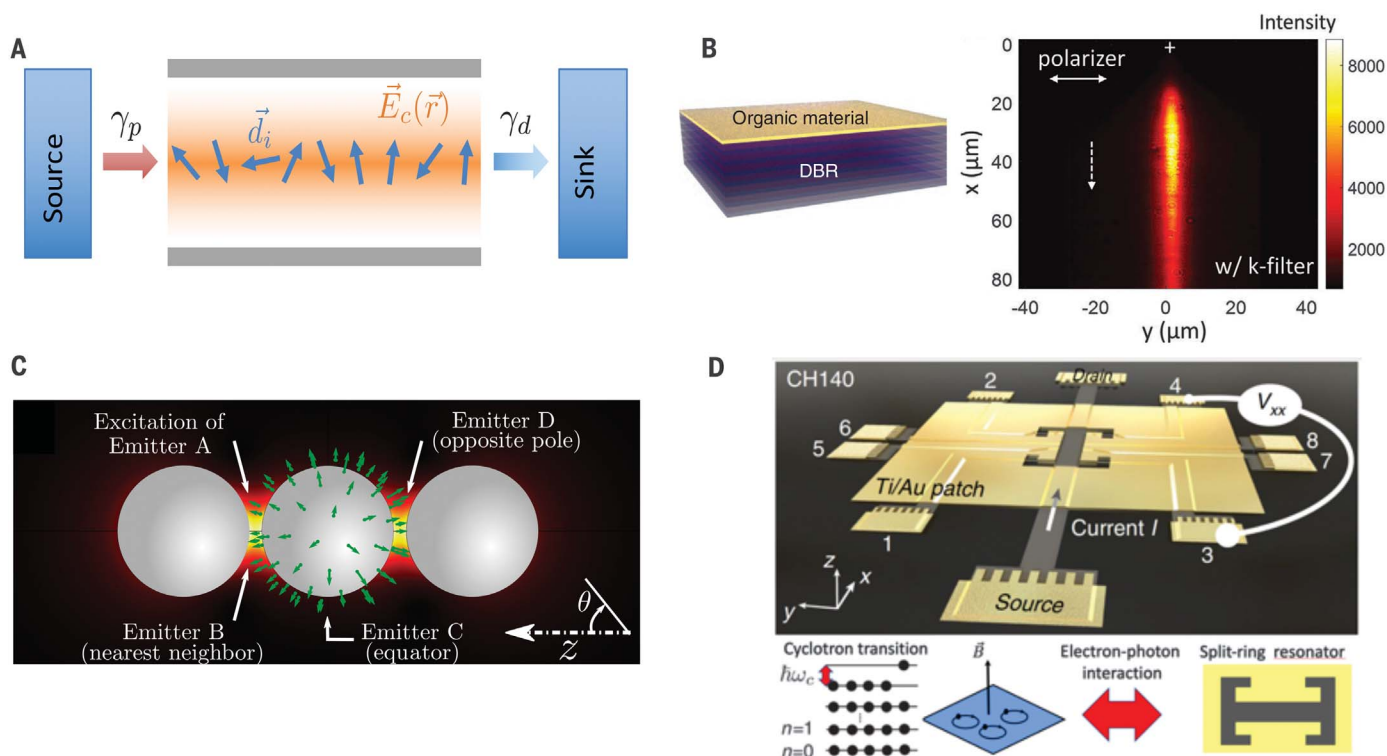
Fig. 2. Cavity-induced modification of transport. (**A**) Sketch of a 1D chain of disordered quantum emitters inside a cavity. Excitons are pumped into the system from the left reservoir, and the exciton current is measured when the excitons reach the sink reservoir on the right. Figure taken from (*31*). (**B**) An organic layer is deposited on a distributed Bragg reflector (DBR) composed of four pairs of ZnS/MgF$_2$ layers. Real-space photoluminescence image using a k-space filter is shown. The excitation laser spot is located at (0,0), indicated by the plus sign. Figure reproduced with permission from (*34*). (**C**) Illustration of a plasmonic cavity formed by three nanoparticles. A collection of quantum emitters couples strongly with the lowest energy EM mode (colored background), allowing for very efficient transfer of excitons from emitter A to emitter D. Figure reproduced with permission from (*36*). (**D**) The top panel depicts a setup to measure charge magneto-transport of a 2D electronic system coupled to a complementary split-ring resonator. In the presence of a perpendicular magnetic field, the light-matter interaction is responsible for electronic transitions between quantized Landau levels (bottom), whose energy separation is proportional to the cyclotron motion frequency. The bottom-right graphic shows a resonator with a subterahertz "LC" mode with deeply subwavelength spatial confinement, resulting in large vacuum fields coupled to the electrons. Figure reproduced with permission from (*38*).

Manipulating condensed phases of matter

Light-induced modification of material properties in the condensed phase dates back to pioneering experiments by Wyatt and Dayem (*41*, *42*), who observed that the critical current in BCS (Bardeen-Cooper-Schrieffer) (phonon-driven) superconductors could be increased when they are illuminated by coherent microwave radiation. More-recent pump-probe experiments have also shown that materials subjected to very intense terahertz pulses could exhibit transient superconducting properties at much higher temperatures than at equilibrium (*43*). This paradigm has led to the notion of quantum materials and the emergence of new properties through collective interactions (*44*–*46*). With the demonstration that material properties could be modified under strong coupling, several research groups have proposed replacement of the classical high-intensity light field by large vacuum EM fields obtained by tight spatial confinement—i.e., coupling of the system to the EM mode of a cavity. This approach holds the promise of engineering

a variety of material properties, not just transport, in the steady state and without the transient nature and excess heating associated with illumination by intense laser fields.

In this context, the effect of a cavity resonator on superconductivity has been explored both theoretically and experimentally. For example, a theoretical study has suggested that the exchange of virtual cavity photons could produce a pairing mechanism and lead to cavity-mediated superconductivity of a 2DEG (*47*). Other studies have discovered that, although strong coupling can lead to an enhancement of the electron-phonon interaction responsible for superconductivity, this change could not always translate to an increase of the superconducting critical temperature (*48*). Experimentally, two different superconductors [Rb$_3$C$_{60}$ and YBa$_2$Cu$_3$O$_{7-x}$ (YBCO)] have been tested in powder form and dispersed in various polymers (*49*). Whereas electron-electron pairing is driven by phonons in the case of Rb$_3$C$_{60}$, the origin of superconductivity in YBCO is proposed to be caused by antiferro-

magnetic spin fluctuations. The direct coupling of the phonon mode of Rb$_3$C$_{60}$ that drives its superconducting behavior with the IR EM modes of the cavity is very weak. To increase the coupling, a cooperative strong coupling mechanism (Box 1) was used whereby the strong vibrational bands of polystyrene that are resonant with that phonon mode of Rb$_3$C$_{60}$ act as a mediator in the phonon-EM mode interaction, leading to vibrational strong coupling (VSC). An increase of the critical temperature, T_C, from 30 to 45 K was observed for the case of Rb$_3$C$_{60}$. This was interpreted to be a result of the enhancement of the electron-phonon interaction induced by strong coupling, in accord with the theoretical studies discussed before (*47*, *48*). However, T_C in YBCO is decreased from 92 to 86 K when the phonon mode at ~700 cm^{-1} of the apical oxygen atoms of YBCO is coupled to the EM modes of the cavity. Further studies show that this is due to a 700-fold enhancement of the ferromagnetism of the YBCO particles under strong coupling, which competes with the

superconductivity at low temperatures (*50*). Further experiments and accurate theories need to be developed to elucidate the role of strong coupling in modifying such superconducting and magnetic properties.

In addition to superconductivity, the influence of vacuum EM fields on other quantum many-body phenomena has been also analyzed theoretically. It has been suggested that the interplay between electron-electron interaction and electron-photon strong coupling, as realized within a cavity, can lead to the formation of a "superradiant excitonic insulator" (*51*). Superradiant phases are characterized by a simultaneous condensation of excitons in the electronic system and photons in a given EM mode (*52*). On the other hand, it has been shown that resonant coupling between strongly correlated electrons and a single-mode cavity could result in the formation of new types of polaritonic states, which could help manipulate the insulating-conducting character of the electronic system (*53*). Along the same line, intertwined orders of strongly correlated electronic systems, such as charge density waves and different types of superconductivity, may possibly be selectively favored by a proper manipulation of their (strong) coupling to the EM modes of a cavity (*54*). As a final example, the possibility of inducing a phase transition from a paraelectric material to a ferroelectric one by just incorporating the bare material into a FP cavity has also been suggested (*55*). Apart from the exciting avenues for research that all these theoretical proposals have generated in recent times, they have also triggered an intense, sometimes controversial, but fruitful debate on how to model the interaction between a macroscopic quantum many-body system and a macroscopic cavity that can support many EM modes. In particular, we note the problems related to gauge invariance when describing the light-matter coupling in approximated models (*56*, *57*) and the role of spatial inhomogeneity of the cavity EM modes in the occurrence of phase transitions affecting the ground state (*58*, *59*).

Chemistry under strong coupling: QED or polaritonic chemistry

A study of molecules under electronic strong coupling (ESC) was reported as long ago as 1982 (*16*), but it is only in the last decade that the consequences of strong coupling for molecular properties and their ensuing chemical reactivity have been explored. Under ESC, photophysical properties are obviously modified by splitting, for instance, the first excited state into P+, P–, and DS. Emission quantum yields (*60*), intersystem crossing (*61*, *62*), singlet fission (*63*), and lifetimes (*60*, *64*) are affected, and experiments such as pump-probe cannot be carried out as straightforwardly as measurements outside cavities because of the mode

structure and the high reflectivity of the cavity optics (*64*). Additionally, resonant Rayleigh scattering is substantially enhanced as a result of the collective delocalized nature of the polaritonic states (*65*) that must be considered in the interpretation of results. Recall that there are $3n - 6$ vibrational modes for nonlinear molecules with n atoms, and, together with their harmonics, they form nearly a continuum of sublevels between P+, DS, and P– (see discussion on this issue in Box 1). As a consequence, at room temperature, only emission from P– is observed (*66*–*68*) because P+ decays too fast through nonradiative channels, mostly driven by internal vibration relaxation and dissipation into the surrounding bath. The P– emission quantum yield is only compatible with a long-lived emitter (*60*). Polariton propagation length also indicates a long lifetime (*34*, *35*). Such findings all point to a non-Markovian regime (Box 1).

Here, we will focus primarily on the consequences of strong coupling for chemical reactivity. The first demonstration of modified chemistry under strong coupling involved coupling an electronic transition of a photochrome (a molecule that photoisomerizes between two forms of different color) in a solid polymer matrix (*22*, *69*). The uncolored spiropyran was dissolved in a polymer solution and spin-coated on an Ag mirror so that when a second mirror was placed on the film, the resulting cavity was tuned so that it had a mode that could be coupled at normal incidence to its isomer, the colored merocyanine molecule, having a peak at 590 nm. As the sample was irradiated at its isobestic point (~326 nm), the evolution toward a photostationary state was monitored. As the reaction proceeded and merocyanine accumulated, the strong coupling increased as $\sqrt{N}$, the reaction slowed down markedly, and its quantum yield increased. This proof of principle that reactivity could be modified under strong coupling came as a surprise and generated much interest that led to numerous additional studies both theoretical and experimental (*70*–*114*). Theoretical studies (*81*, *82*) of model molecules, such as stilbene and azobenzene, agree with the earlier experimental results, which indicates that the distribution of a single excitation over many molecules effectively suppresses such photoisomerization (*81*). These theoretical studies and others (*70*, *71*, *73*–*80*) show that the potential energy surfaces (PES) of the various states at play are modified under strong coupling, which affects conical intersections and internal dynamics, as first pointed out in 2015 (*70*). Not surprisingly, not only chemical dynamics but also bond-lengths and charge density distributions are subject to modification (*73*, *76*). Electron transfer reactions are predicted to be strongly affected—either enhanced or suppressed depending on the exact conditions of

the reaction as a result of the decoupling between the electronic and nuclear degrees of freedom (*71*).

Experimentally, the photodegradation rate of different molecules has been studied and found to be suppressed (*84*, *85*). Photodegradation is typically a photo-oxidation process stemming from the reaction of O_2 with the long-lived triplet state of the molecules that must be populated competitively within the lifetime of the polaritonic states. The shorter this lifetime, the more photo-oxidation will be suppressed. Energy transfer between donor and acceptor molecules has also been studied by coupling both the donor and the acceptor to the same optical mode (*36*, *37*, *86*–*89*). It has been shown that the rate and the yields increase substantially in such conditions (*37*, *87*), which has inspired further experiments with vibrational energy transfer (*89*). Because the donor and acceptor molecules become quantum-mechanically entangled in this scheme, the possibility of separating the donor and acceptor molecules by a spacer layer was investigated, and energy transfer remained very efficient—well beyond the 10-nm limit typical of FRET (*37*). In fact, energy transfer enters a new regime that is no longer dependent on distance as long as the strong coupling condition is met (*36*, *37*, *88*). In the experimental study (*37*), it was also suggested that such a scheme could open the door to investigate chemical and molecular processes under entanglement—a prospect that was then analyzed theoretically (*90*).

The work reviewed above confirms the rich possibilities to modify photochemical and perhaps even ground-state thermally driven chemical reactions under ESC because ultrastrong coupling should change the ground state by lending it photonic character (*5*), even if the possibility of modifying ground-state chemistry has been questioned (*83*). Chemistry under ESC suffers nevertheless from one technical limitation—namely, that the cavity has to be resonant in the visible spectrum, which implies, when taking into account the refractive index of the material, that the cavity path length must be in the submicrometer range to avoid technical problems. Solution chemistry thus becomes extremely difficult. Not surprisingly, all of the experimental studies of chemical reactions under ESC have been done in solid solutions.

In a 2012 paper (*22*), a way to overcome these limitations was proposed—namely, to couple vibrational transitions in the IR and thereby also influence ground-state chemistry. This wavelength regime is compatible with microfluidic cells that have cavity path lengths in the 10-μm range. Through the use of flexible polymer spacers between the two mirrors, the cavity can be tuned to resonance with a given vibration simply by turning a screwdriver
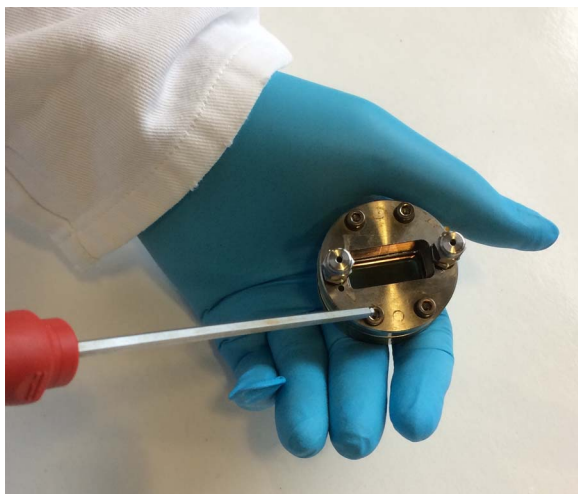
Fig. 3. QED or polaritonic chemistry in a microfluidic optical cavity. Photograph of a microfluidic IR FP cavity that can be tuned with a screwdriver to put it in resonance with a molecular vibration to achieve strong coupling (courtesy of T. W. Ebbesen).

(Fig. 3). Reactants can be injected into the cavity and the products extracted for further analysis using standard equipment, such as mass spectrometry and nuclear magnetic resonance.

Initial studies focused on establishing VSC (*91–94*), and it soon became apparent that VSC could have a substantial effect on chemical reactivity (*95*). Not only did the first reaction studied slow down but, more importantly, the enthalpy and entropy of activation both changed by more than 50 kJ/mole at room temperature, and the entropy changed sign, suggesting a change of reaction mechanism. The large modification of the activation energies came as a surprise because they are ~20 times as large as the collective Rabi splitting on the order of $k_B T$ (2.6 kJ/mole) (where k_B is the Boltzmann constant). Since then, a number of other reactions have been studied that show either deceleration or acceleration of the reaction rate, reflecting very large variations in the activation energies under VSC (*95–99*, *115*). Chemical landscapes can be tilted toward a desired product, and only VSC of vibrations closely linked to the bonds breaking induce an effect (*97*). Thus, by tuning cavities across the various vibrational bands of a reactant, VSC can be useful as a tool for elucidating reaction mechanisms. Theoretical studies of chemistry under VSC (*100–106*, *111–114*) have come to very different conclusions as to why reactions are modified. Notably, the variation in the density of states or the correction to the partition function (*105*, *106*) cannot account for the observed changes or the small magnitude of the Rabi splitting. Something else has to be modified under VSC to explain the large effect on the thermodynamics, and the most likely factor is symmetry. It is well known that

symmetry correlation diagrams between reactants and products play a key role in determining the PES of the reactivity landscape (*108*).

To investigate the role of symmetry in VSC, a very simple charge transfer (CT) equilibrium reaction between mesitylene and I_2 (Eq. 1)

$$\text{(structure)} + I_2 \underset{K_{DA}}{\rightleftharpoons} \text{(structure)} \cdots I_2 \qquad (1)$$
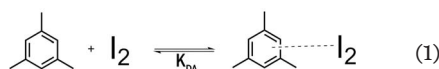
was studied for this purpose (*99*). This type of reaction, which has been investigated since the 1940s, has the advantage that the formation of the CT complex has a distinct and strong peak in the ultraviolet, which can be monitored to extract the equilibrium constant K_{DA}, all the while coupling the vibrational bands of mesitylene in the IR. Furthermore, mesitylene is highly symmetric and rigid, so the symmetry representations of the vibrations are well defined. Under VSC, the CT equilibrium favors complexation or decomplexation depending on the symmetry class of the vibration, as illustrated in Fig. 4A. The shift in K_{DA} is essentially independent of the type of vibration, its energy, and the Rabi splitting. Again, the thermodynamics (now the relative energy of the reactants and product, i.e., the Gibbs free energy, enthalpy, and entropy) are strongly modified by VSC (*99*). This result shows the central role of symmetry in VSC: The coupling acts on the symmetry, thereby modifying the electronic PES. This in turn implies that the vibronic coupling (interaction between the vibrational and electronic manifolds of the molecule) remains very strong under VSC, unlike for ESC, where they are expected to become decoupled (*71*). The complexation reaction also reveals the

transition from weak to strong coupling, akin to a phase transition, under variation of the mesitylene concentration, as can be seen in Fig. 4B. There is an abrupt change in the slope, reflecting the new K_{DA} and the change in the absorption cross section of the complex upon VSC. This also indicates that the reservoir of uncoupled molecules must be very small (Box 1).

Further studies confirm that symmetry plays a very important role in chemistry under VSC (*109*), but obviously other factors must also be involved. The modified shape of the PES, as seen in thermodynamic data, will influence the outcome and rate of the reaction. When either the solute, the solvent, or both are coupled under VSC, solvation must also be affected in view of the consequences for crystallization and enzymatic activity (*107*, *110*) and are probably the result of changes in the intermolecular interactions under strong coupling (*73*, *111*, *112*, *114*). Moreover, when molecules are large and floppy with ill-defined symmetry, the signature of symmetry is not obvious and can be obscured by such factors. The effect of VSC will probably be undetectable if it does not influence some limiting step in the reaction trajectory. The role of entropic reordering of energy levels of the DS could very well also play an important role in the chemistry (*116*).

Outlook

Matter owes many of its properties, such as spontaneous photon emission, Lamb spectral shifts, and Casimir and van der Waals forces, to the interaction with the vacuum EM field. The use of EM cavities or plasmonic resonators provides a platform to strengthen this interaction to the point that fundamental properties are modified by the introduction of hybrid light-matter states in the coupled material. This approach to manipulating the properties of matter, including modifying chemical reactivity and processes, appears very promising from the results that have been accumulating over the past decade. The interest is no longer purely fundamental, as technological applications should be quite straightforward to implement if there is an advantage. For example, some industrial chemical reactions are not optimal in terms of yields and reaction conditions despite decades of effort using traditional methods. Chemistry under VSC provides a new approach or tool to control chemical reactivity that could be scaled up with massively parallel microfluidic systems. It should not be very complicated to integrate confined optical fields in devices to modify solid-state properties, such as conductivity or magnetism.

Perhaps the biggest surprise of all recent developments in this field has been the magnitude of the effect of collective VSC on
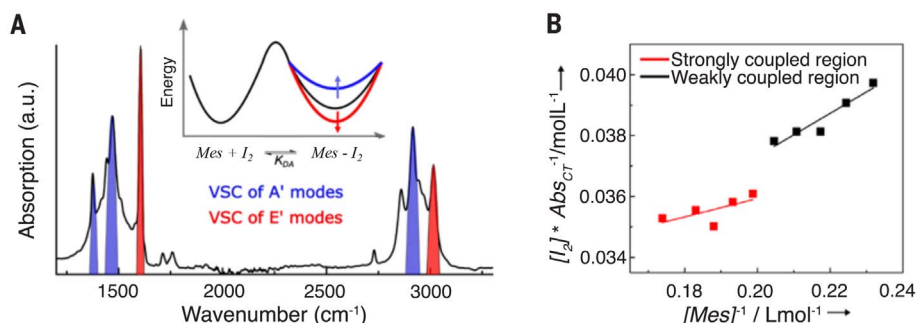
Fig. 4. VSC and symmetry. (**A**) IR absorption spectrum of the mesitylene coupled vibrations with their symmetries E' (red) and A' (blue), together with the consequences on the CT equilibrium landscape of the mesitylene (Mes)–I_2 complexation process in the inset. a.u., arbitrary units. (**B**) Change in the absorption of CT complex versus inverse mesitylene concentration, revealing the abrupt change at the transition from weak to strong coupling regimes. Figure reproduced with permission from (*99*).

ground-state chemistry. Strong coupling in general, but VSC in particular, is a new approach to chemistry. VSC can also be used as a mechanistic tool (*97*). Although concentration of the coupled species was a limiting factor, the introduction of cooperative strong coupling has opened the door to further advances in the field because reactants can now be coupled at low concentration through, for example, the solvent (*115*, *117*). There are many classes of organic reactions that are currently being explored under strong coupling. As more results are collected, the underlying physical chemistry will be further clarified and should lead to some general principles to guide chemists in their use of VSC. The possibilities of chemistry under entanglement through the cavity field could also open new directions for research. The demonstration that simply coupling water modifies enzyme activity (*96*, *110*) illustrates the potential for studying biological activity under strong coupling that remains otherwise unexplored. Here, the role of coherence in collective coupling (*118*, *119*) could open perspectives for quantum biology (*120*, *121*).

One of the open questions is whether the properties of solvents, such as water, are also modified upon strong coupling. With this idea in mind, selective crystallization of MOFs (metal-organic frameworks) has been demonstrated (*107*), opening an exciting avenue to reduce crystal polymorphism. This approach could potentially be used to favor one supramolecular assembly over another, with direct consequences for the dynamics and hierarchical organization of (bio)molecular materials. The exploration of weak intermolecular interactions under strong coupling with terahertz spectroscopy could reveal such modifications (*122*).

The cavity enhancement of solid-state material properties has already been shown for charge and energy transport, nonlinear processes, magnetism, and superconductivity, as discussed above. In general, phonon-based phase transitions should be good targets if the phonon bands have sufficiently large oscillator strength to be coupled to a cavity mode. The possibility of inducing new phases should also be explored (*55*, *123*). Particularly, 2D materials are well suited to be integrated in cavity resonators with deeply subwavelength photon confinement (*38*, *124*). Among the possible directions, we note quantum Hall systems and superconductivity in 2D van der Waals materials in particular (*125*–*127*). Clearly, strong coupling is a broad frontier, with implications and potential for fundamental science as well as technological applications.

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Science

Manipulating matter by strong coupling to vacuum fields

Francisco J. Garcia-Vidal, Cristiano Ciuti and Thomas W. Ebbesen

Captivating cavities

Laser technology is a familiar example of how confining light between two mirrors can tune its properties. Quantum mechanics also dictates that even without extraneous light, matter confined in a cavity resonant with its electronic or vibrational transitions can couple with vacuum electromagnetic field fluctuations. Garcia-Vidal *et al.* review the remarkable and still somewhat mysterious implications of this "strong-coupling" regime, with manifestations ranging from enhanced charge transport to site-selective chemical reactivity across a range of molecular and solid-state materials.

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