

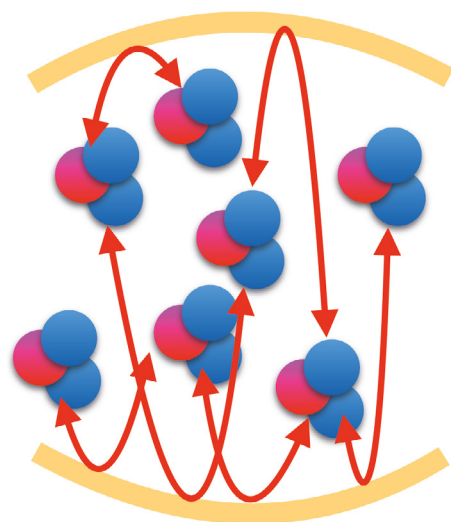
MOLECULAR STRONG COUPLING

William WARDLEY^{1,*}, Felipe HERRERA², William BARNES¹

¹ Department of Physics and Astronomy, Stocker Road, University of Exeter, EX4 4QL, United Kingdom

² Department of Physics, Universidad de Santiago de Chile, Av. Víctor Jara 3493, Santiago, Chile

*w.wardley@exeter.ac.uk



Strong coupling between an ensemble of molecules and an optical cavity mode offers exciting prospects in photonics, materials science and chemistry. We look at the conceptual background of strong coupling by making direct connection with cavity-QED. We then look at two topical areas in which researchers seek to exploit strong coupling, energy transport and chemical reactivity. We conclude with a summary and a look to the future.

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Think of an excited atom inside an optical cavity (Figure 1a), the cavity is tuned to be in resonance with the atomic transition by adjusting the path length between the mirrors. If the atom can exchange its energy with the cavity mode at a rate g that is faster than any dissipation rate – e.g. the rate of photon leakage from the cavity κ , and the decay rate of the atom γ – then the atomic transition and the cavity mode have time to interact with each other and form two new hybrid states, the excitations of these hybrid states are called polaritons. Polaritons inherit both light and matter character and are at frequencies different from the uncoupled atomic and cavity resonances, see Insert 1. The frequency gap that opens up between the new modes is known as the Rabi splitting of the system. Figure 1a shows

such an atom cavity system from the 1990s, when such systems were explored as part of a wider endeavour to better understand and exploit quantum mechanics, a field known as cavity quantum electrodynamics (c-QED) [1].

The extent of the Rabi-splitting in c-QED is sub meV, much too small to have an effect on the properties of a single molecule. However, experiments with several atoms in the cavity at one time showed that the energy level (Rabi) splitting scales with the square root of the number of atoms involved, see Insert 1. This scaling is exploited in molecular strong coupling such that systems involving millions/billions of molecules, Figure 1b, may show a Rabi splitting of a significant fraction of an electron volt. The hybrid nature of the newly formed states can have several useful consequences; giving photonic

modes mass (a matter characteristic) in this way has led to the creation of Bose-Einstein condensation, whilst giving material excitations (e.g. excitons) photonic properties leads them to have significant spatial coherence, enabling polariton lasing.

The large number of degrees of freedom associated with an ensemble of molecules in a cavity inevitably means that the picture we have just described is a very idealised one. In practice many other important phenomena are involved. Of particular interest are the dark states, collective states that do not emit or interact with far-field photons as they lack the electric dipole moment of the bright (polariton) states. Recent work suggests that the presence of disorder (inevitable in most experimental situations) can enable the dark states to contribute with the collective response of the system in a useful way,

see Insert 1 [2]. It has also become clear that all of the modes supported by a cavity need to be considered, not just the mode in resonance with the molecular transition.

What may be accomplished by harnessing strong coupling? Here we focus on two topics by way of example: intermolecular energy transfer and chemical reactivity.

ENERGY TRANSFER

The transfer of energy from donor to acceptor molecular species is a key part of nanophotonics, and harnessed very effectively by nature in photosynthesis. By strongly coupling either donor and/or acceptor molecules to a cavity mode, new energy transfer opportunities are opened up. Particularly appealing is the idea of extending the usual nanometre (nm) range of the transfer process by harnessing the delocalised yet coherent nature of polaritons, thereby bypassing the usual dependence on spatial separation. Energy from the donor may be coupled to a polariton state, from where it may in turn couple to the acceptor, a process known as polariton-assisted energy transfer. Several demonstrations of polariton-assisted molecular energy transfer have been reported in the past few years [3,4].

Figure 2, panel a, shows the arrangement used in both of these demonstrations. A planar microcavity is formed containing a layer of donor molecules (blue) separated from a layer of acceptor molecules (red) by a spacer layer (grey). The spacer is thick enough (>10 nm) to prevent the usual Förster energy transfer process. With appropriate tuning of the cavity resonance with respect to the molecular energy levels, clear evidence of polariton-assisted energy transfer is obtained, panel b. When the molecular system is pumped by a UV light source, and the cavity is ill-tuned, donor emission dominates (blue circle data points). When the tuning is correct then the emission is dominated by acceptor emission (red diamond data points) despite the acceptor molecules being located on the other side of the spacer layer; the 'bare' donor and acceptor spectra are shown for comparison.

These initial results now need to be translated into working opto-electronic devices, perhaps focussed on improving power conversion efficiencies in organic photovoltaics. Looking ahead one can envisage spatially manipulating the photonic landscape and in so doing provide a means to provide funnelled (directed) polariton-assisted energy transport.

CHEMICAL REACTIONS

The modified spectra that arise as a result of strong coupling naturally lead to the question of whether the formation of hybrid polariton states might also result in changes to chemical reactions. It is not obvious that this will be the case, since typically ground state reactions proceed through the cumulative effect of a large number of individual collision events, whilst strong coupling involves the collective response of the molecular ensemble. Electron transfer ●●●



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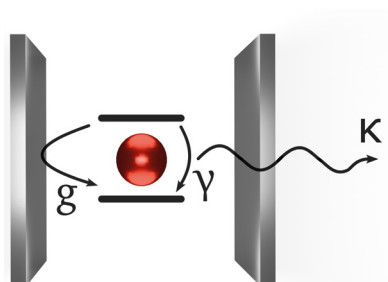
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reactions, such as those involved in photosynthesis, are different in the sense that the reactive event does not involve two-particle collisions, rather an excited electron undergoes a tunnelling transition from a donor to an acceptor state within a molecular complex. Interestingly, it was shown in 2016 that when donor excited states are coupled to a cavity field to form a donor-polariton state, the excited electron is delocalized over N molecules, and this increases the probability of tunnelling to a local acceptor state, increasing the electron transfer rate [5]. In contrast, if the acceptor states are coupled to the cavity, forming an acceptor-polariton, an excited electron localized in a donor state is now less likely to be transferred because the acceptor wavefunction is diluted over N molecules, decreasing the donor-acceptor charge density overlap. We can encapsulate this information in a ‘rule of thumb’: molecular transitions that are collective-to-single ($N \rightarrow 1$) can be enhanced by strong coupling, whilst single-to-collective transitions ($1 \rightarrow N$) are suppressed.

Should this simple rule of thumb also hold for thermodynamic reactions inside cavities? This question is the subject of ongoing theoretical debate about the microscopic mechanism behind observations of modified reaction rate constants for several chemical reactions in infrared cavities [6]. Since reactive collisions are local and strong coupling is collective, the $1 \rightarrow N$ scaling

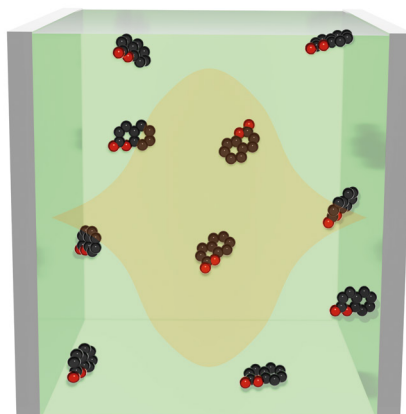


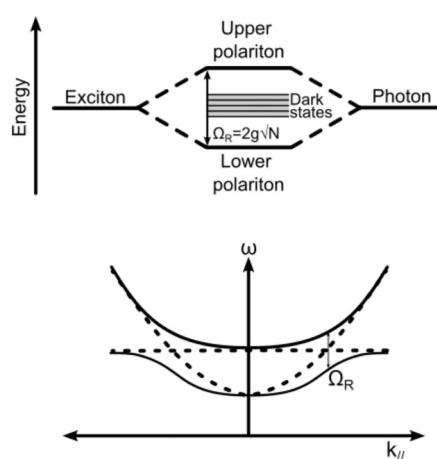
Figure 1. (a) Schematic of single atom c-QED cavity system, (b) Schematic of molecular strong coupling cavity, showing optical field profile for first order cavity mode. For clarity only a few molecules are shown.

argument should naively hold, so that no rate modifications are expected. However, thermodynamic chemical reactions do not proceed *via* ultrafast tunnelling transitions such as electron transfer, so this simple argument breaks down. The rate constant is a macroscopic observable that encodes an average over a very large number of individual reactive

collisions occurring over timescales much slower than the time it takes for strong coupling to be established in a cavity.

One suggested origin of the observed rate modifications is a change in the reaction energetics due to collective strong coupling. However, the cavity field ideally couples and modifies the energies of only a pair of collective molecular states that are bright. An overwhelming majority of dark molecular states, see Insert 1 (top), keep the same energy as in free space and effectively do not see a difference in the reaction energy landscape.

If spectral changes (polariton splitting) due to strong coupling do not have an influence on the reaction rate, another possibility is that somehow the strong light-matter interaction modifies the way in which reacting molecular ensembles thermalize. This is a macroscopic effect that affects all molecules and could modify the probability of overcoming the reaction barrier that separates reactants from products. Under what conditions this mechanism might be possible is the subject of intense debate, since our usual understanding of reaction rate



TOP. In molecular strong coupling the molecular and cavity modes interact to form upper (UP) and lower (LP) polariton states. This is similar to the interaction between atomic states to form bonding and antibonding orbitals. For N interacting molecules the difference in energy between the UP and LP is $2g\sqrt{N}$. In addition to the two bright collective states (UP and LP) there are $N-1$ dark states centred around the original molecular

BOTTOM. The simple energy level picture in the upper half of the figure is better indicated by a dispersion diagram, where the variation of the energy of the UP and LP states with momentum in the plane of the cavity, $k_{||}$, is shown. The dashed lines indicate the uncoupled photon and molecular states, the full lines the coupled modes (for clarity dark states are omitted).

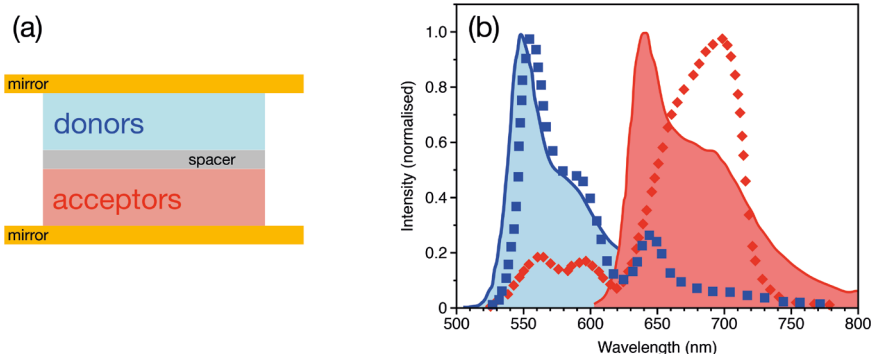


Figure 2. Polariton assisted energy transfer. (a): the cavity contains a layer of donor molecules (blue) and a layer of acceptor molecules (red) separated by a spacer layer (grey) that is thick enough to prevent Förster transfer. (b) Emission spectra of bare donors and bare acceptors are shown as blue- and red-filled spectra. When the donors in the donor and acceptor filled cavity are pumped by a UV light source the emission depends on the cavity tuning. For poor tuning there is very little energy transfer and donor emission dominates (blue squares). For correct tuning the emission is dominated by acceptor emission, despite the donors and acceptors being separated by more than the Förster distance. All spectra have been normalized, and are adapted from [4].

theory rests on canonical ideas of thermal equilibrium that, in principle, should also hold under strong coupling. All of these theoretical ideas need to be tested in carefully controlled experiments.

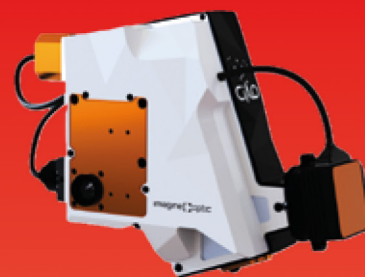
SUMMARY

Molecular strong coupling has caused much excitement as a result of the dramatic prospects on offer by using nanostructured optical environments to modify material behaviour, particularly the tantalising prospect of controlling chemical reactions. The field is currently at a cross-road because an underpinning theoretical and conceptual framework capable of explaining all strong coupling phenomena has yet to be developed [7],

and because some questions concerning reproducibility of experiments remain. In particular, the scope of what can be achieved with strong coupling, and what cannot, has still to be fully defined, *e.g.* what type of chemical reaction is amenable to control via strong coupling? Research on both experimental and theoretical fronts is intense. On the theoretical side a key challenge is to capture all of the relevant physics and chemistry in one model, on the experimental side a major challenge is to exploit non-optical ways to monitor cavity-based chemical reactions in real time. Many research groups are making good progress, but it is likely to be several years before we have a complete picture. ●

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