Ensemble strong coupling

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Abstract. Strong coupling between light and an ensemble of molecules leads to the formation of new hybrid states and offers the exciting prospect of a new route to control material properties. Now a theoretical model has been introduced to complement the recent observation of strong coupling between the vibrational modes of molecules and an electromagnetic (cavity) mode. This new work by del Pino *et al.* (New J. Phys. (2015) **17** 053040) makes an important contribution by offering fresh insight into the underlying physics, especially into the role of dephasing processes in determining the dynamics of ensemble strong coupling.

Submitted to: *New J. Phys.*

Strong coupling is an extreme form of light-matter interaction in which molecules exchange energy with an electromagnetic mode, often the mode is that of an optical cavity. For strong coupling to occur the exchange rate has to be faster than the rate of any competing dissipative process. When this happens new hybrid modes, polaritons, are created – part light, part matter – with energy levels very different from either parent [1, 2]. As with many coupled oscillators, the coupling lifts the degeneracy of the two uncoupled systems. In strong coupling the extent of the resulting level splitting is known as vacuum Rabi splitting [1].

Recent experiments involving large ensembles of molecules undergoing strong coupling – pioneered by Ebbesen and co-workers in Strasbourg – have shown that a remarkable degree of control over material properties may be achieved, examples include the modification of chemical reaction rates [3] and control over phase transitions [4]. The changes induced in material properties are a direct consequence of the modified energy levels, but the full theory underlying these phenomena is still not clear. The new theoretical work reported here by del Pino *et al.* [5] provides valuable insight into the physics behind these ensemble strong coupling phenomena.

These astonishing developments are the latest in a field that goes back more than 40 years, to the prediction by Agranovich and Malshukov of strong coupling between between the vibrational resonances in a thin film and the electromagnetic modes supported by the substrate adjacent to the film [6], an arrangement that is now important in the area of 2D (atomically thin) materials [7]. In the past few months new experiments showing strong coupling of the vibrational (the $C = O$ stretch) mode of large numbers of molecules embedded in an optical microcavity have been reported [8, 9]. This is an exciting development, not least because it opens up a new arena in which to test the concepts of ensemble strong coupling. Already we have seen vibrational strong coupling demonstrated in a liquid rather than a solid medium [10], thereby prompting the prospect of using strong coupling to control chemical reactions, even under physiological conditions.

Despite theses exciting prospects, many important questions concerning ensemble strong coupling remain, and it is here that the theoretical work reported by del Pino *et al.* [5] comes in. As the authors point out, when strong coupling involves an ensemble of molecules, the electromagnetic mode couples to a collective superposition of the molecular vibrations, the so-called bright-state. However other superpositions, the dark-states, are also possible. The authors address two key questions: what is the role of the dephasing processes associated with the environmental buffeting each molecule is inevitably subjected to?; and what role, if any, do the dark-sates play? To answer these questions del Pino *et al.* developed a quantum mechanical formalism directly including dephasing with which they considered two extreme scenarios. In the first, all vibrational modes are coupled to the same common bath (e.g. the long-range phonons of a crystalline environment). In the second, each molecular mode is coupled to an independent bath (e.g. the short range phonons of many molecular environments).

The authors found that in the common bath scenario dephasing does not introduce additional coupling between the bright-state and the dark-states, the bright-state thus behaves like a single oscillator that interacts with the cavity field. This is the situation that many authors have implicitly assumed in the past, and provides a good cross-over with what one expects from classical physics for such ensemble systems [11]. The situation is subtler for the independent bath scenario. However, provided the extent of the Rabi-splitting is greater than the energy typical of the bath modes, then the authors find that the single oscillator picture still applies. This last result lends support to a theoretical prediction made nearly 20 years ago that inhomogeneous broadening is suppressed in strong coupling [12]. It is perhaps not so surprising that the single oscillator picture survives in both situations since, as del Pino *et al.* point out, inhomogeneous broadening and dephasing are static and dynamic counterparts of each other. Interestingly, it now looks as though it may be possible to probe the effect of inhomogeneous broadening through experiment using 2D spectroscopy [13].

The authors of the present paper point out that vibrational strong coupling is important in the context of cavity optomechanics. Fascinating results have recently also been obtained by employing ensemble strong coupling to promote energy transfer between dye molecules [14], and even between chlorosomes associated with photosynthesis [15]. Strong coupling of ensemble systems is rapidly emerging as an exciting and important area of multidisciplinary research. A better understanding of the underlying physics is very much needed, del Pino *et al.*'s contribution provides an important step in that direction.

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