

## MANIPULATING MOLECULAR PROPERTIES WITH CONFINED ELECTROMAGNETIC FIELDS

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### Background to chemistry in confined spaces and fields

In 1927 Paul Dirac participated in the 5th Solvay Physics Congress and published a seminal paper on the "quantum theory of emission and absorption of radiation" coining the term quantum electrodynamics (QED). This explained for the first time that the phenomenon of so called "spontaneous" emission is actually not spontaneous but triggered by electromagnetic fluctuations of empty space. Such quantum fluctuations are omnipresent and determine many of the properties of matter such as the Lamb shift of the H atom, the existence of liquid He and the intermolecular London dispersion forces.

Of particular interest to molecular science is the field known as cavity QED where the electromagnetic field is typically confined between two parallel mirrors, a Fabry-Perot cavity. If molecules are placed inside such a cavity of wavelength dimensions in the direction normal to the mirrors, such as a microfluidic cell coated with gold films on either side, it is possible to induce QED effects known as weak and strong light-matter coupling. In the weak coupling regime, the emission probability can be modified, changing for instance the fluorescence quantum yield and lifetime. In the strong coupling regime, the interaction between the optical mode and a molecular transition is so strong that hybrid light-matter states are formed. What is surprising is that this occurs even in the dark because it is the quantum fluctuations of the confined optical mode that couples to the molecular transition dipole moment.

The mere presence of the hybrid light matter states, known as polaritonic states, should naturally lead to modified molecular and material properties, even in the ground state, something we started exploring 20 years ago. In 2012, we reported for the first time that chemical reactivity could indeed be changed under strong coupling of an electronic transition (ESC) of a photochrome [1]. We also proposed that perhaps coupling vibrational transition could modify the outcome of ground state reactivity. Unexpectedly, such vibrational strong coupling (VSC) leads to very large changes in molecular and material properties, not just chemical reactivity [2,3] but everything from self-assembly to conductivity and ferromagnetism [4-11]. Some of these will be presented in this Solvay conference together with our present understanding of the underlying physical chemistry. Indeed, the development of novel theoretical tools [12-15], such as QED chemistry, are gradually helping us get insight into the underlying mechanisms of VSC. This new field

has become known as polaritonic chemistry and its development has been largely possible thanks to support from the European Research Council. It is currently the subject of many projects around the world both for its fundamental aspects and its application as a new tool to control chemical and material properties.

### Recent progress in Strasbourg on chemistry in confined space and fields

In a typical VSC experiments, a very large number  $N$  of molecules inside the cavity are coupled to a single optical mode. This results in the formation of not only of two bright vibropolaritonic states  $VP+$  and  $VP-$  but also  $N-1$  dark states  $DS$  as shown in Fig. 1. These states are coherent collective states delocalized potentially over the extent of the mode ( $\mu\text{m}$ ). In reality these delocalized states are of course broken up by molecular motion. The  $VP+$  and  $VP-$  are separated in energy by what is called the Rabi splitting,  $\hbar\Omega_R$ , which is proportional to  $\sqrt{N}$ , leading to a separation on the order of  $k_B T$  (ie ca 2.5 kJ/mole). This is a very small energy perturbation and yet surprisingly it leads to very large thermodynamic changes (e.g. 50 kJ/mole in activation enthalpy [2,3]) of reactions under VSC. This raised immediately the question where the leverage comes from? Some other molecular property must be modified.

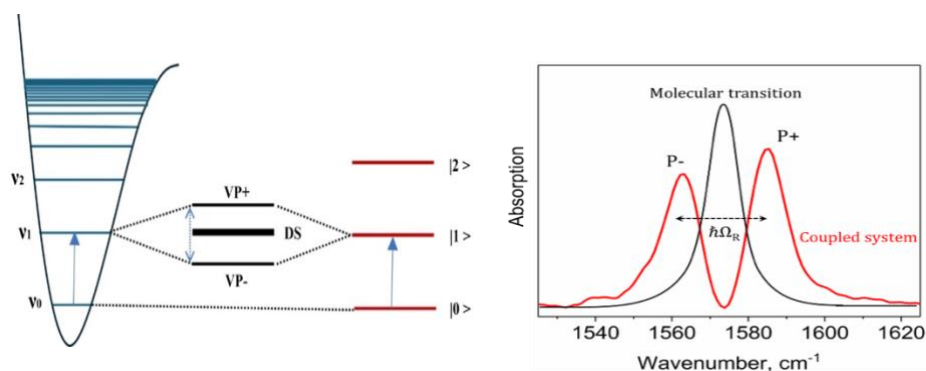


Fig.1 (left) Sketch of vibrational strong coupling (VSC) between a vibrational transition and a cavity mode leading to the formation of hybrid vibro-polaritonic states  $VP+$ ,  $VP-$  and dark states  $DS$  (reproduced from ref. 10); (right) spectral signature of a vibration coupled to an optical mode of a cavity (reproduced from ref. 5).

### NMR of Microfluidic Cavities

Having found that it is possible to modify the site selectivity [3], we thought at first that the electron density distribution of the molecules must be altered under VSC. So we designed NMR compatible cavities that can be inserted into standard NMR tubes (Fig. 2), to look for VSC induced chemical shifts. While this is challenging (only 2  $\mu\text{l}$  of liquid in a microfluidic cavity) and requires a precise protocol, it became quickly clear from  $^1\text{H}$ ,  $^{13}\text{C}$

and  $^{19}\text{F}$  NMR that chemical shifts are minor if any. So modification of the electron density distribution was not at the root of the induced changes under VSC.

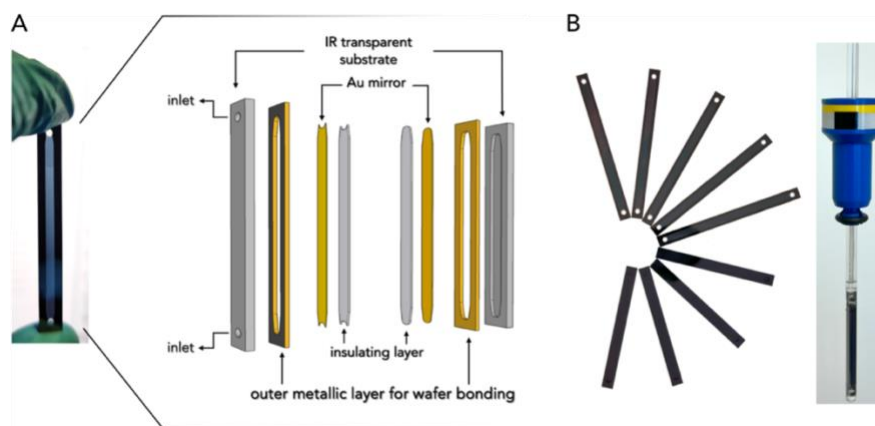


Fig. 2 Microfluidic cavities compatible with NMR spectroscopy. (a) Photograph of a cavity being filled with liquid along with its cross-section; (b) A set of NMR compatible cavities of different pathlengths and an NMR tube containing a sealed cavity immersed in deuterated water and plastic holders used to center the cavity inside the tube (reproduced from ref. 8).

#### *Role of Symmetry*

We had found earlier that the symmetry of the vibration plays a key role in controlling charge transfer equilibria under VSC [9]. The conclusion of that study was that the symmetry of the vibropolariton must be different from that of the uncoupled vibration. There remained to understand what was the new symmetry, how it came about and whether this would explain whether a reaction is favored or not under VSC. In the past year, we have found that there is a symmetry rule which answers these questions [10]. In essence, the vibropolariton is formed by the hybridization of a vibration and an optical mode each with their own symmetry (irreducible representations). By taking the symmetry product of the common subgroup, the vibropolariton has a new irreducible representation, orthogonal to the original vibration. As a consequence, it projects differently on the principal axis and on the reaction coordinate. Hence VSC modifies the pathway in the multidimensional reaction landscape and can therefore lead to large thermodynamic changes. This symmetry rule allows one to predict whether a chemical reaction will be favored or not by VSC.

#### *Cluster Formation and Phase transition*

Another VSC induced property that probably plays a critical in many reported observations is the formation of a new liquid mesophase consisting of cluster. This phase

is observed in all pure liquids studied so far but can be disrupted by temperature (phase transition) and the presence of another solvent in significant quantities. It is most easily studied by non-resonant Rayleigh scattering as the scattering intensity increases by one to two orders of magnitude under VSC depending on the solvent and coupled vibration. Rayleigh scattering of pure liquids is dependent on the density fluctuations within the liquid but here there is clearly something additional since adding another solvent brings the scattering down to normal levels, contrary to expectations. In such binary mixtures of solvents, the coupled system also undergoes a phase transition which itself is temperature dependent as shown in Fig. 3. Such observations indicate the formation of clusters within the solvent that are induced by changes in intermolecular interactions such as the London dispersion force [10]. This will have significant consequences for chemical reactivity and probably plays a role in the effects of VSC on self-assembly [6,7]. Further studies are under way to fully understand the consequences of this clustering mesophase.

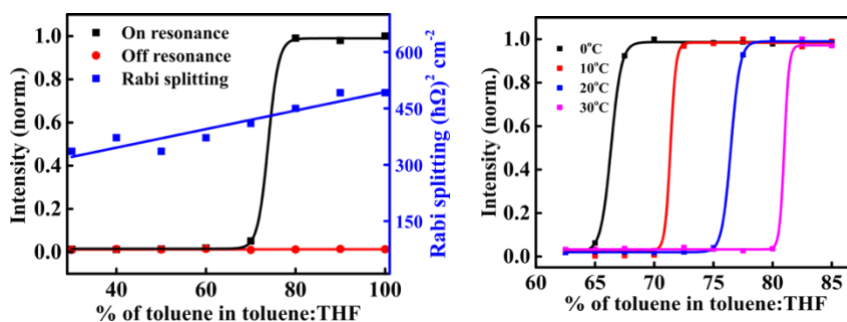


Fig. 3. Normalized non-resonant Rayleigh scattering of toluene when the C=C stretching vibration ( $1603\text{ cm}^{-1}$ ) is under VSC as a function of dilution with THF at room temperature (left) and as a function of temperature (right) (taken from ref. 11).

### Outlook on chemistry in confined spaces and fields

The possibility to control both ground state and excited state properties of molecules and materials through strong coupling explains the surge in interest in the polaritonics. It raises fundamental questions that will only be clarified through further experiments and theoretical studies. Many studies are under way in different labs to analyze reactivity of various types of chemical reactions. Obviously if VSC does not affect the limiting step, it will not be observable in the kinetics although could potentially be detected by NMR or mass spec. The changes in properties are significant and therefore it is already being explored for its technological applications. For instance, the development of cavities with chiral optical fields could lead to enantioselective biochemistry and circularly polarized emissive materials. Electronic and ionic conductivity, as well as ferromagnetism, have already been shown to be significantly enhanced so strong coupling could be used to improve electronic devices. While the concept of coupling material transitions to the

electromagnetic quantum fluctuations can be challenging, the experiments are straight forward. Strong coupling with confined fields will no doubt become a useful tool for the molecular and material sciences.

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