ACS central science

Polariton Chemistry: Action in the Dark

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Controlling chemical reactivity using vibrational strong coupling

In a pioneering experiment, Ebbesen and co-workers have recently demonstrated control of a thermally activated ground-state chemical reaction using vibrational strong coupling (VSC).[1] Within the Born–Oppenheimer approximation, (electronic) ground-state chemical reactions can often be viewed as occurring on a potential energy surface (PES). Reactions are described by pathways on the PES, starting from a minimum associated with the stable reactants, to another minimum, corresponding to the stable products. In many cases, at least one energy barrier along the reaction pathway will need to be thermally overcome, which is known as the transition state. In the gas phase, it has been shown that for "late barrier" reactions the best way to overcome this transition state is by imparting vibrational excitation energy to the reactants.[2] This begs the question of whether reactions can be triggered by directly exciting the vibrational mode of interest. Inspired by these ideas, significant efforts in the 1970s focused on "mode-selective chemistry", the use of infrared (IR) multiphoton excitation of specific molecular vibrations to induce a reaction in the condensed phase.[3] Only a handful of these efforts were successful, however, with most of them hindered by intramolecular vibrational energy redistribution (IVR)—the rapid thermalization of energy from the highly excited vibrational mode into other modes.[4] In fact, most contemporary efforts using light to control the outcome of chemical reactions bypass the exclusive use of IR-activated processes, instead invoking the richer photochemistry generated by UV–visible radiation.[5] However, the findings of Ebbesen and co-workers could revive the mode-selective chemistry program within the contemporary context of molecules in optical cavities or "polariton chemistry".

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between two metallic mirrors that form an optical cavity in the IR, as shown in Figure 1a. Under VSC, the energy exchange between photons and vibrations is faster than their respective decay rates,[6] leading to the hybridization of light and matter to form quasiparticles known as vibrational polaritons (VPs). This hybridization is mediated by the electric dipole interaction between the vacuum electromagnetic field of the resonant optical mode and a *collective* totally symmetric vibrational excitation which is delocalized across a large number of molecules, N, distributed with a density $\sim 10^{17}$ cm^{-2}. For identical photon and vibrational transition energies, the resulting VPs will be located symmetrically above (P+) and below (P−) the bare vibrational transition and separated by energies of $\hbar\Omega \approx 50-100$ cm^{-1} (see Figure 1a). These VPs can be understood to be symmetric (P+) and antisymmetric (P−) superpositions of the photon and the delocalized vibrational excitation, in analogy with bonding and antibonding orbitals in molecular orbital theory. However, just as in chemical bonding, the number of states before and after hybridization is equal, so there is a macroscopic reservoir of $N - 1$ subradiant ("non-bonding") states[6-9] which do not have the right symmetry to mix with the electric field of the cavity mode and remain parked at the bare vibrational transition energy.

Ebbesen and co-workers studied the cleavage of the Si−C and Si−O bonds in a model oxysilane compound under VSC with various vibrational transitions in the molecule (Si−C and Si−O stretching, Si−CH$_3$ bending). In this
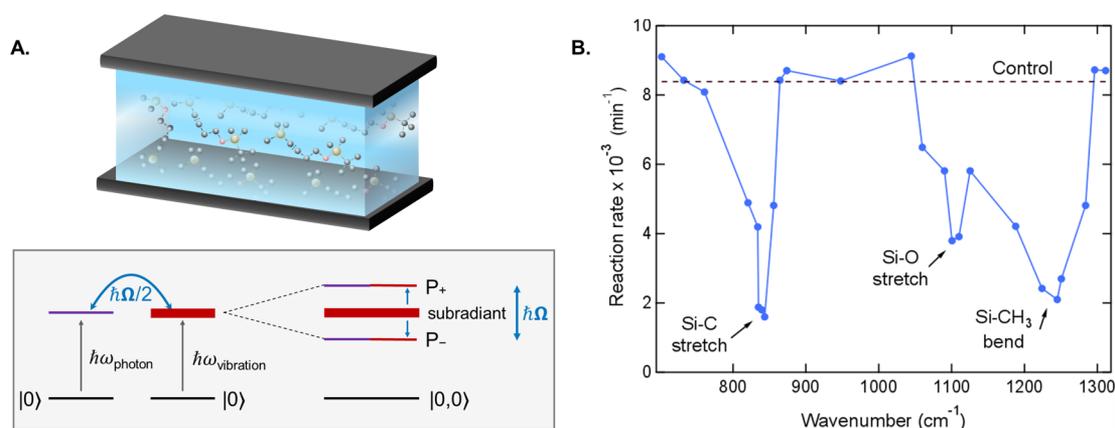
Figure 1. (A) The top panel shows a schematic of the microcavity enclosing a solution of the reagent. The bottom panel shows the bare single photon and single (collective) vibrational transitions and their corresponding vacuum state, $|0\rangle$. The coupling strength, $\hbar\Omega/2$, is half of the so-called Rabi energy. In the VSC regime, new hybrid modes, separated by $\hbar\Omega$, are created (the upper (P+) and lower (P−) VPs) at the expense of a large number of subradiant states remaining at the bare vibrational energy. The composite light-matter system ground state $|0,0\rangle$ corresponds to the absence of any photon or vibrational excitations. (B) The overall reaction rate measured by Ebbessen and co-workers as a function of the IR photon wavenumber. The out-of-cavity rate measured in a control experiment is shown as a dashed line. Clear reductions in rate are observed when the cavity is tuned to the vibrational transitions indicated in the figure.

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experiment, they adjusted the thickness of the cavity to match the IR photon mode to the different vibrations. In each experimental run, the oxysilane and tetrabutylammonium fluoride flowed through the cavity in a solution of methanol and tetrahydrofuran. By monitoring the change in refractive index via shifts in one of the higher-order (off-resonant) cavity modes, the reaction rates were extracted as shown in Figure 1b. With the exception of the area illuminated to probe the kinetics, the experiment took place in the dark. Variations in the overall reaction rate by up to a factor of 3.5 ± 0.2 were observed by changing the resonance conditions. Under off-resonance conditions, the reaction rate was shown to be nearly equal to that measured outside of the cavity. In contrast, under VSC with either the Si−C, Si−O, or Si-CH₃ modes, the reaction rate was slowed down.

More interestingly, the branching ratio of Si−C and Si−O cleavage was also modified under VSC. Off-resonance or outside of the cavity, the ratio was ∼1.5:1 toward Si−C

cleavage, while in the case of VSC with the Si−C bond, the branching ratio was changed to ∼3:1 toward Si−O cleavage. VSC with Si−O or Si−CH₃ vibrations also favored branching toward Si−O cleavage albeit with smaller branching ratios. These changes in branching ratios are an outstanding proof-of-principle demonstrating that VSC can induce mode-selective chemistry under thermally activated conditions, bypassing the stringent requirements of IR photoexcitation. However, many questions remain as to the mechanism responsible for the variations in rates and branching ratios. To start with, at room-temperature and under thermal equilibrium, most of the vibrationally excited population resides in the subradiant states rather than in the polaritons, due to the large multiplicity of the former. It is thus puzzling that such a small fraction of polaritons can induce any macroscopic changes in chemical reactivity under thermally activated conditions. Recently, a possible theoretical rationale to this VSC puzzle has been provided in a model for electron transfer reactions:[10] while the subradiant state channels outcompete the polariton ones from a thermodynamic standpoint, the latter might be the kinetically dominant reaction pathways due to their smaller activation barriers to surmount. Another puzzle is the systematic suppression of rates under VSC: is this phenomenon the result of an actual suppression of a pathway, or could it be a byproduct of the activation of another channel that competes with the dominant one? In addition, the reported branching ratios tilt toward the same product regardless of whether the Si−C, Si−O, or Si−CH₃ mode is resonant with the cavity. The reasons for this are far from understood. These considerations altogether beg the fascinating question: Is it possible to harness VSC to obtain regioselectivity that is

not possible with known synthetic routes? If so, VSC could constitute a novel and powerful strategy for chemical synthesis, where chemical bonds can be activated or suppressed on demand by simply placing them inside of an optical cavity and waiting, in the dark. To reach that stage, much (experimental and theoretical) light still needs to be shed into polariton chemistry.

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Notes

The authors declare no competing financial interest.

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