

Modifying chemical reactions with confined light modes

Clàudia Climent,* Javier Galego, Francisco J. Garcia-Vidal and Johannes Feist
*Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics Center
(IFIMAC), Universidad Autónoma de Madrid, Madrid, Spain*
*claudia.climent@uam.es

In this talk I will discuss how ground-state chemical reactivity may be modified in a cavity QED scenario [1]. I will first show, for a simplified model molecule, how energy barriers are altered when a molecular vibration and a cavity mode are coupled. With the aid of the cavity Born–Oppenheimer approximation [2], one can then rely on transition state theory to calculate the corresponding reaction rates. This is a very important point since it allows to study realistic molecular systems with quantum chemistry methods. I will then discuss the absence of resonance effects on the reaction rates and how, within perturbation theory, one can understand the energetic modifications we observe making a connection to Casimir-Polder interactions. In the second part of the talk, I will focus on specific examples we have studied by interfacing the above theory with quantum chemistry calculations [3]. In particular, I will discuss how nucleophilic substitution reactions can be catalyzed with plasmonic nanocavities. I will finally show how our proposal can serve as a novel strategy to modify static molecular properties, focusing on the transition temperature $T_{1/2}$ of spin-crossover transition metal complexes

References

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- [3] C. Climent, J. Galego, F. J. Garcia-Vidal, J. Feist, *Angew. Chem. Int. Ed.* 58, 8698 (2019).