

Articles: published in [Angewandte Chemie](#) and [Physical Review X](#) by Javier Galego, Clàudia Climent Biescas, [Johannes Feist](#) and [Francisco J. García-Vidal](#), IFIMAC researchers and members of Department of Theoretical Condensed Matter Physics.

Over the past few years it has become clear that strong electromagnetic coupling between a molecule and light confined in a nanoscale cavity can lead to significant modifications of the electromagnetic response of the hybrid system as well as the internal molecular properties. This has already been exploited to manipulate the fate of photochemical reactions, however, up to now there has been no general theory on how these interactions affect the chemical reactivity of a molecule in its ground state without any external input of energy.

In a theoretical study published in [Physical Review X](#), a group of researchers from the [Departamento de Física Teórica de la Materia Condensada](#) and the [Condensed Matter Physics Center](#) (IFIMAC) at the [Universidad Autónoma de Madrid](#) have developed a theoretical framework that combines quantum electrodynamics and the quantum theory of chemical reactivity. The authors implemented this approach for a simple model molecule that can be solved without approximations. This allowed to explore the general properties of cavity-induced ground-state chemical reactivity changes and develop a simplified theoretical model that can be applied to more complex molecules. They found that the induced changes on the molecular potential energy surfaces do not depend on any resonance condition between molecular transitions (such as vibrational or electronic excitations) and cavity modes, with the relevant interactions closely related to well-known electrostatic forces on the molecule due to other molecules or larger material bodies. In particular, the largest contribution to the modification of the energy landscape is typically determined by the change of the

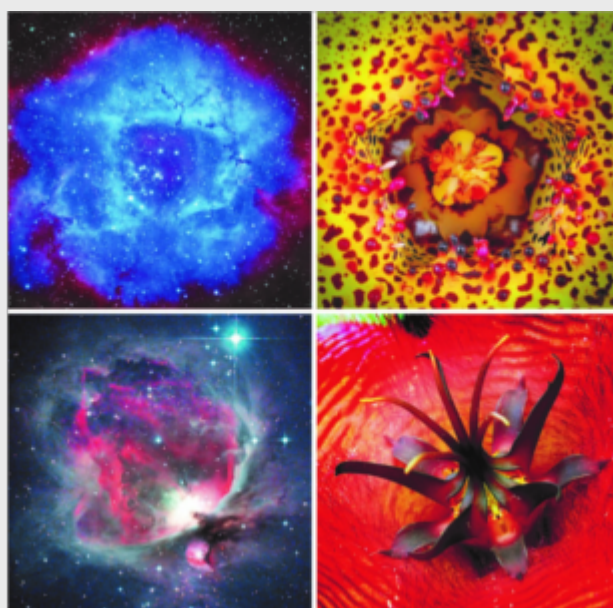
permanent dipole moment of the molecule between its equilibrium and transition state configuration. They have also shown that experimentally available nanocavities can induce changes in reaction rates by an order of magnitude in a single molecule, while for the case of many molecules, this effect becomes significant only if all the molecules are aligned.

In a second paper published in [Angewandte Chemie](#), the same authors have combined this theory with quantum chemistry calculations and have shown how plasmonic nanocavities can enable self-induced electrostatic catalysis of typical organic reactions, without any external driving, due to the interaction of the molecular permanent and fluctuating dipole moments with the plasmonic cavity modes. They have also exploited this interaction between molecules and electromagnetic modes to predict cavity-induced changes in the transition temperature of spin-crossover transition metal complexes, the prime example of molecular switches.

These studies contribute to the fundamental understanding of how nanoscale cavities can be used to manipulate chemical reactions of single molecules and open the path towards ground-state catalysis with plasmonic nanocavities. They also provide an example on how the interaction with plasmonic modes may be ultimately exploited to manipulate material properties. [[Angewandte Chemie - full article](#)] [[Physical Review X - full article](#)]

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## Universal Natural Shapes



Title: Universal Natural Shapes.

When: Tuesday, November 13, (2018), 12:00.

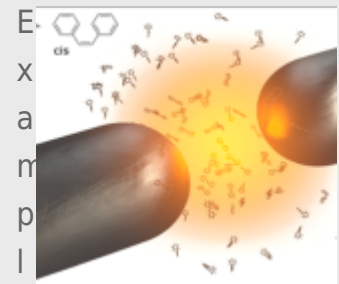
Place: Department of Theoretical Condensed Matter Physics, Faculty of Sciences, Module 5, Seminar Room (5th Floor).

Speaker: Johan Gielis, University of Antwerp, The Antenna Company, Belgium.

In the natural sciences, global anisotropies or (quasi-) periodic local deviations from isotropy or Euclidean perfection in many forms that occur in nature can be effectively dealt with by applying Gielis transformations to the basic forms that show up in Euclidean geometry, e.g. circle and spiral. Since their introduction in botany in 2003, Gielis curves, surfaces and transformations have been used in various fields of science and technology, including in nanotechnology. I will focus on 1) further generalizations and Pythagorean-compact representations, 2) Applications in biology and antennas, and 3) Generalized Möbius-Listing surfaces and bodies, in the context of possible further applications in nanotechnology and nanophotonics.

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### Suppressing Photochemical Reactions Through Strong Coupling



of a nanophotonic system where organic molecules are strongly coupled to a plasmon mode (confined light mode) in the gap between two metallic nanoparticles, thus suppressing the photochemical reaction sketched in the inset.

Article: published in [Nature Communications](#) by Javier Galego, [Francisco J. Garcia-Vidal](#) and [Johannes Feist](#), Department of Theoretical Condensed Matter Physics and IFIMAC researchers.

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hotoisomerization is a change in chemical structure of a molecule after the absorption of a photon. It plays a crucial role in biological processes, for example in human vision, as well as for technological applications such as solar energy storage, optical memories, or molecular switches. However, photoisomerization can also have detrimental effects, for example as an important damage pathway of DNA, or as a limiting factor for the efficiency of organic solar cells. While photoisomerization can be avoided by shielding the system from light, this is of course not a viable approach for devices that rely on the interaction with external light (such as solar cells).

In a theoretical study published in [Nature Communications](#), a group of researchers from the [Departamento de Física Teórica de la Materia Condensada](#) and the [Condensed Matter Physics Center \(IFIMAC\)](#) at the [Universidad Autónoma de Madrid](#) show how it is possible to take advantage of the phenomenon of strong light-matter coupling to significantly suppress photoisomerization and similar photochemical reactions.

Strong light-matter coupling is a well-known concept in quantum electrodynamics that has received a lot of attention in recent years. A quantum emitter (for example an organic molecule) and a light mode (a confined photon) become strongly coupled when the molecule can repeatedly emit a photon into the confined mode and reabsorb it before it is lost to the environment. The natural states of the system then become new hybrid states with mixed light-matter properties, known as polaritons. Strong coupling is chiefly achieved by exploiting the tools of nanophotonics and nanoplasmonics, which allow to create and design structures that can confine light to small spaces of only a few nanometers, such as in the gap between two metallic nanoparticles as sketched in the figure.

The researchers show that strong coupling in the molecule-photon system leads to a change in the energy landscape of the reacting molecule, creating an energy barrier that blocks the natural pathway from one isomer to the other. Under irradiation with an external light source (such as sunlight or a laser), the excited light-molecule state (polariton) then is significantly more stable than a molecule by itself.

Going beyond the single-molecule case, the researchers next studied the case of a large group of molecules coupled to a single electromagnetic mode. In this situation, the polariton is formed by distributing the excitation coherently over all of the molecules, enhancing the effective light-matter coupling. This is the most common way of achieving strong coupling experimentally. However, previous studies had found that the collective enhancement does not apply for changes to the internal structure, such that one could expect that the stabilization of the molecules would disappear in this setting. In a surprising twist, the opposite turns out to be the case: The researchers found that the stabilization effect becomes even more pronounced for a large number of molecules. The reason for this lies exactly in the collective nature of the excitation:

Because it is distributed over many molecules, each molecule spends most of the time in its chemically stable ground state, which does not undergo isomerization. This leads to an additional collective protection of the polariton when many molecules are involved.

The study thus shows that thanks to their hybrid light-matter nature, polariton modes can be significantly more chemically stable than excitations in bare molecule, and even more so in the common experimental case of collective strong coupling. This new kind of collective protection could pave the way towards novel polaritonic materials for devices such as solar cells. [\[Full article\]](#)

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