Chapter 1
Introduction

1.1 Motivation

From the first photosynthetic organisms, approximately three billion years ago, to the invention of the laser in the twentieth century, light has had a crucial role in shaping the universe and our lives. Light has always interacted with living organisms, providing energy and information from their environment. Evolution towards complex life forms was rendered possible due to the oxygenation of the Earth produced by early photosynthetic cyanobacterias [1]. In order to survive and thrive, animals need to assimilate information from their surroundings, for which they developed photosensitive cells which later evolved into sophisticated organs: the eyes [2]. Light is the means through which humans see each other and form societies, and people throughout the world and across history have understood its importance.

From the earliest times, philosophers in ancient India and Greece considered the question of light, writing on concepts such as reflection and refraction. Based on some of these texts, in the 11th century the arab scholar Ibn al-Haytham[1] (also known as Alhazen) wrote about optics and formulated precise laws of refraction [3]. During the 17th and 18th centuries, an intense scientific debate arose questioning the nature of light. On one hand, Isaac Newton developed his corpuscular theory, arguing that the straight rays of light demonstrated its particle nature. On the other hand, many of his contemporaries such as Robert Hooke and Christiaan Huygens maintained that light was composed of waves. This was later supported by Thomas Young's double-slit experiment, where wave characteristics such as interference could be seen on light, leading to the general acceptance of its wave nature.

We owe the first great revolution in the study of light to James Clerk Maxwell. By the middle of the 19th century a considerable amount of theoretical knowledge about electricity and magnetism had been gathered. In 1861 Maxwell condensed and

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[1] As a remark, the controlled experimental testing of his scientific hypotheses is considered the first achievement of the modern scientific method. Because of this, together with his pioneering studies on the behavior of light, he is considered the "father of modern optics".

J. Galego Pascual, *Polaritonic Chemistry*, Springer Theses,
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corrected it into a set of four equations,[2] and stated that electricity and magnetism are two manifestations from the same substance, and that light is an electromagnetic (EM) wave propagating according to those laws. With this, the corpuscular theory appeared to be completely dead, but soon a new revolution would yet again challenge our perception of reality: quantum mechanics.

In 1900 Max Plank found the solution to the ultraviolet catastrophe related to the radiation of a black body. In his explanation there was one revolutionary assumption: light was emitted and absorbed in discrete packets of energy. In 1905 this same hypothesis was used by Albert Einstein to explain the photoelectric effect. These two events eventually led to the birth of quantum mechanics and its concept of wave–particle duality, as well as to coining the idea of "photon". The quantum theory of light began in the 1920s when Paul Dirac introduced a full quantum description of light and matter [4], laying the foundations of the theory of quantum electrodynamics (QED). This stands as one of the most successful scientific theories in history, and its understanding soon brought a plethora of technological development and applications, such as the laser [5], nowadays a basic tool in medicine, industry, and scientific research among others, or the charge-coupled device (CCD) [6], central for digital imaging.

In the following decades, fundamental research and innovative experimental techniques allowed humanity to efficiently control light and matter at the nanoscale. This lead to the dawn of nanophotonics, which has emerged as a dynamic and prolific research area with the promise of a next generation of photonic devices [7]. Opportunities of avant-garde technology arise thanks to achievements such as superresolution microscopy [8], the discovery of metamaterials [9], improved solar cells [10], and nanolitography [11, 12], to cite just a few. Many of the different areas of nanophotonics have as a common ingredient the manipulation of the electromagnetic field at the nanoscale. Of particular interest to this thesis is the tailoring of EM fields to achieve strong interactions between light and matter. With this it is possible to enter the strong coupling regime, where light and matter become profoundly mixed. The excitations of such a hybrid system do not have a purely material or light nature, but rather they inherit properties of both constituents, giving rise to unusual phenomena. These novel excitations (which often can be understood as emerging quasiparticles) are known as *polaritons*, and constitute a promising pathway towards engineering novel materials [13].

One crucial realization of strong coupling is achieved with organic matter [14]. This has attracted a lot of interest in the last decades due to the possibility of achieving very strong interactions even at room temperature, a limit in which quantum features often are washed away by thermal fluctuations. Furthermore, in these materials strong coupling offers an efficient and elegant pathway to shape the material and chemical properties of organic molecules [15]. The work developed in this thesis constitutes a comprehensive theoretical study of the manipulation of chemical properties and reactions in organic materials. This introductory chapter first sum-

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[2] Originally Maxwell's equations were composed by 20 different expressions. The simplification to only four equations is credited to Oliver Heaviside.

marizes the fundamentals of light–matter interaction at the nanoscale, reviewing the possible experimental platforms to achieve strong coupling with organic molecules. Then we present a state-of-the-art review of the field which this thesis is focused on: polaritonic chemistry.

1.2 Strong Light–Matter Coupling

The lengthy development of quantum electrodynamics had plenty of difficulties on its path. Possibly one of the most notable ones is the appearance of diverging energies in vacuum, cured by renormalization theory. In simple terms, all measurable parameters of particles that can couple to the electromagnetic field are unavoidably "dressed" by local vacuum fluctuations. This effect produces small corrections in energy levels, first observed by Willis Lamb in the hydrogen spectrum [16]. While these corrections cannot be switched off, they do depend on the electromagnetic environment and can thus be modified by manipulating the distribution of modes upon imposing physical limitations to the field, e.g., by placing mirrors or conductors around the atoms. This was first noted by Purcell [17], who predicted that the rate of spontaneous emission for a nuclear magnetic moment should be enhanced by restricting the number of possible EM modes in a resonant electric circuit to only one strong mode. While the prediction was made for nuclear magnetic moments, the argument is valid for any kind of quantum emitter[3] in resonant cavities. In the consecutive years, several studies followed dealing with spontaneous emission rates in atoms near metallic surfaces. Of particular importance is the study by Casimir and Polder [18], where they discuss how vacuum fluctuations can produce a force between an atom and a conducting plane.

All of this new theoretical interest marked the birth of cavity quantum electrodynamics (CQED) [19]. In a nutshell, the goal of CQED is to isolate a quantum emitter inside a box so that the effects of the electromagnetic vacuum on the emitter are observable. This can be achieved by increasing the strength of the interaction between light and matter. The light–matter coupling strength is of course a relative concept, and we need to compare it to some energy scale to gauge it. Typically, two different regimes are considered: the weak and the strong coupling regimes. The regime of interaction depends on how large the energy scale of the coupling is compared to the decay rate of both the light and matter constituents. In the following, we offer a simple discussion of such interaction regimes, for a more involved analysis see Sect. 2.3.

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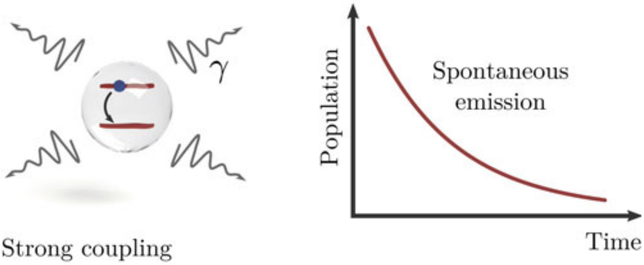
[3] We generalize this to "quantum emitters", which may represent any entity that can absorb or emit light, such as atoms, molecules, quantum dots, nanoparticles, etc.

(a) Weak coupling



(b) Strong coupling

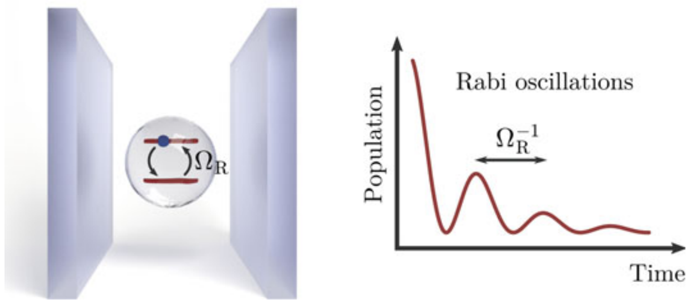


Fig. 1.1 The two main regimes of light and matter interaction in QED **a** weak and **b** strong coupling. Left: conceptual sketches of a single two-level quantum emitter (a qubit, the simplest matter description) in free space, weakly coupled to the EM field, and inside a cavity, strongly coupled to the cavity EM field. Right: time evolution of the population of the excited state of the qubit, showing simple spontaneous emission in weak coupling and Rabi oscillations in strong coupling

1.2.1 Regimes of Interaction Between Light and Matter

When the light–matter energy exchange is slower than the individual decay and dephasing rates (loss of excitation and quantum coherence respectively) of both elements, the system is said to be in the *weak coupling* regime. This is the most common scenario in nature, where the interaction between material (electronic and nuclear) and electromagnetic degrees of freedom can be treated perturbatively [20, 21]. This describes familiar processes such as absorption and emission. The excitation of a quantum emitter has a non-zero probability to be transmitted to the electromagnetic field in the form of a photon (spontaneous emission, see Fig. 1.1a). This is translated in terms of the excited-state lifetime, after which the emitter is said to have emitted a photon. This is typically described by a theory of open quantum systems [22, 23], where the emitter is coupled to a dissipative environment representing the continuum of EM modes that surrounds it. The transition probability depends on the local density of states of the electromagnetic environment of the emitter. Therefore, by placing the emitter inside a resonant cavity or near a conducting surface it is possible to control the emission rate via the so-called Purcell effect mentioned above.

If the relative coupling strength is further increased, the electromagnetic field can no longer be treated perturbatively, and ultimately the system will enter the *strong coupling* regime. Both photons and material excitations have to be treated on equal footing. The system then will be able to coherently exchange energy between both constituents. While typically the exponential decay of the excitations masks this energy exchange as simple emission or absorption phenomena, i.e., the excitation is transferred from the emitter to the electromagnetic field only once, and vice versa, in strong coupling an oscillatory behavior will be observed before loss of excitation, as a rapid series of emission and reabsorption processes (the so-called Rabi oscillations, see Fig. 1.1b). This population exchange between light and matter indicates that photons and material excitations are no longer the proper eigenstates of the system [21]. Instead, new hybrid excitations arise, called polaritons. These states can also absorb and emit light, but at different frequencies than the original emitter, being referred to *upper* and *lower* polaritons, for the larger and smaller energies respectively. The difference in energy is the so-called *Rabi frequency* Ω_R, and corresponds to the oscillation frequency of the emission-absorption cycle between the excited emitter and the photon.

One exceptional feature of strong coupling arises when a collection of emitters interact with the EM field. The entire ensemble collectively interacts with the field and can be understood as a "giant quantum emitter" with a very large dipole moment. The frequency of oscillations is enhanced $\Omega_\mathrm{R} = \sqrt{N}\Omega_0$, where N is the number of emitters and Ω_0 is the corresponding single-emitter Rabi frequency. This phenomenon is known as *collective strong coupling*, and is a very common approach to experimentally achieve strong coupling, since coupling strengths of individual emitters are often too weak to be notable. The collective nature of such systems is of utmost importance in many strong coupling effects, as it can correlate emitters that are far away in distance (and therefore not connected) through the EM field. We note that collective strong coupling and polaritons are not an inherently quantum phenomenon, but they arise when electromagnetic modes interact with classical Lorentzian (damped) oscillators, leading also to the $\sqrt{N}$ enhancement when a large number of oscillators are present. Indeed, polaritons appeared first in the context of classical optics as "collective oscillation of polarization charges in the matter" sustained by interfaces that separate media with permittivities of opposite signs [24, 25].

If the strength of the interactions keeps increasing, the system enters the *ultrastrong coupling* (USC) regime, where some additional counter-intuitive effects emerge. For example, the total number of excitations in the system is not conserved, which potentially leads to the global ground state of the system to being dressed by the EM field, even showing purely quantum properties such as squeezing and entanglement [26]. There is no clear agreement on the coupling strength required to consider the system to be in the USC regime, as it heavily depends on the particular system [27–31]. However, signatures typically connected to USC usually appear when the Rabi splitting energy becomes a significant fraction of the transition frequency of the quantum emitter excited state [32].

1.2.2 Experimental Strong Coupling Realizations

Up to now we have discussed the regimes of interaction in a very broad fashion, overlooking the different possibilities to achieve strong coupling in a realistic setup. Polaritons can be achieved in a wide range of systems of various natures, dimensionalities, and energy scales. Experiments can routinely achieve polaritons in solid-state and organic systems, for structures ranging from a few nanometers to milimetric distances, and for microwaves and ultraviolet light. The fundamental purpose or desired technological application is ultimately what determines the experimental realization. For example, some applications may require the device to work in microwave frequencies, such as in the case of superconducting artificial atoms coupled to on-chip cavities [33–35]. Or perhaps we favor the ability of the system to perform at room temperature, for which organic polaritons offer a more suitable platform [36–38]. Both the quantum emitter and the EM mode components of the system present fundamental advantages and restrictions that shape the possibilities for a particular strong coupling realization. In the following, we present these conditions and discuss some examples of possible single-emitter and collective strong coupling systems.

In order to discuss the fundamental limitations of the interaction, it is vital to analyze the nature of the light–matter coupling strength. As we present in detail in Chap. 2, this depends, to a very good approximation, on the electric field amplitude of the system at the position $\mathbf{r}_0$ of the emitter and the dipole moment of the emitter [21]:

$$g(\mathbf{r}_0) = \boldsymbol{\mu} \cdot \mathbf{E}(\mathbf{r}_0). \tag{1.1}$$

There are two main alternatives to effectively increase the coupling strength in order to reach the strong coupling regime.[4] The first is to efficiently choose the right quantum emitters, favoring large dipole moments. Note that in quantum mechanics the dipole moment is an operator, and finding a "large" and "aligned" dipole moment is not necessarily a straightforward task. For example, a quantum emitter may have a very small ground-state permanent dipole, but present a huge transition dipole moment between ground and excited states, making it suitable for strong coupling. The second approach is to engineer cavities that present very large electric field amplitudes. This can be achieved by confining the EM field in very small volumes, as the electric field associated to a EM mode depends on its mode volume as $|\mathbf{E}| \sim 1/\sqrt{V}$. We define this in a proper manner in Sect. 2.3; for now let us focus on the ability of a cavity to concentrate the electric field in very small volumes. Below we review some examples of experimental strong coupling realizations, focusing first on some different cavities presently used to tailor the EM field, and then discussing the variety of possible quantum emitters in which strong coupling is currently viable.

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[4] While not explicitly listed, increasing the emitter density is often the main approach to achieve strong coupling is some experimental realizations.

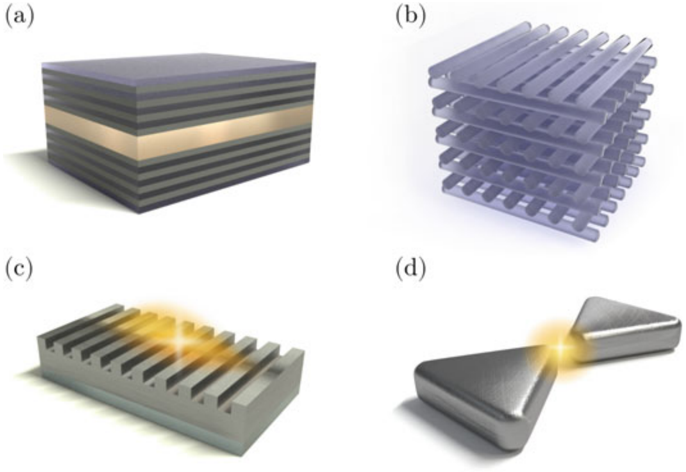

Fig. 1.2 Conceptual depictions of some model structures employed to confine light. **a** Fabry–Perot microcavity based on distributed Bragg reflectors. **b** Three-dimensional photonic crystal. **c** Surface plasmon polaritons on a structured metallic surface. **d** Bow-tie nanoantenna hosting a strongly localized surface plasmon resonance

1.2.2.1 Examples of EM Cavities

There are two fundamental approaches to experimentally achieve strong coupling by manipulating the EM environment of the quantum emitters. The first approach is to minimize the losses of the system so that Rabi oscillations can be observed within the lifetime of the cavity and the excited state of the emitter. This is based on a very efficient trapping of light so that a photon inside takes a very long time to exit the system. The second is to localize the light in tiny volumes, thus increasing the electric field amplitude and therefore boosting the light–matter coupling. The two methods are not mutually exclusive; an ideal cavity would incorporate a great confinement of the EM field while trapping light indefinitely (that is, without loss). Some reviews on different kinds of cavities can be found in the literature [39–41]. Let us now overview some examples of cavities that reach the strong coupling regime.

Possibly the simplest structures to achieve strong coupling are the planar microcavities in which two flat mirrors are brought close together so that only a few light wavelengths can fit in between them. The so-called Fabry–Perot microcavity can trap light very efficiently in rather large mode volumes (typically above the diffraction limit, $V \gtrsim \lambda_{\mathrm{EM}}^3$, where λ_{EM} is the mode wavelength), which often requires using very large number of emitters to enhance the interaction and achieve measurable Rabi splittings. Depending on the choice of material for the reflectors we can sort between metal and distributed Bragg reflector (DBR) microcavities. The former are easier to fabricate, composed of two parallel layers of a noble metal enclosing the material laterally. However, the fundamental parameters of the metals limit the efficiency of the cavity by introducing losses. This is greatly improved in the case of

DBR microcavities (see Fig. 1.2a), in which the metal planes are replaced by multilayers of alternating refractive index materials such that for certain wavelength ranges the reflectivity is close to unity. This offers very large photon lifetimes, even reaching hundreds of picoseconds [42]. Planar microcavities offer confinement in only one direction, while in the other two dimensions the EM modes can be arbitrarily extended. Therefore in these cavities photons can be excited with an in-plane momentum, thus displaying a continuous dispersion relation, which opens a wide range of possibilities for polariton condensation and superfluidity [43, 44]. A more intense confinement can be achieved by forming micropillars that exploit total internal reflection. While this greatly increases the losses, it also offers possibilities of novel devices that can present exotic features such as topological properties [45].

Photonic crystals [46] can be thought of extensions of the DBR structure to two and three dimensions. By generating a three-dimensional crystal (see for example Fig. 1.2b) with the appropriate combination of electromagnetic and electronic band structure, it is possible to rigorously forbid light propagation and scattering inside. By then creating a defect in this crystalline structure, light states can be confined without possibility of escaping, leading to the observation of a Rabi splitting [47]. This would theoretically provide one of the most efficient EM field confinement with tiny losses, however, current experimental realizations have not demonstrated this yet. Two-dimensional photonic crystals are presently the most promising option showing great figures of merit [48].

Plasmonic cavities [41] offer a great alternative to achieve strong coupling, offering sub-wavelength EM field confinement. In here we will consider two types of cavities that support plasmons of slightly different nature. The first type consists on engineered material interfaces which support surface plasmon polaritons (SPPs) [49, 50]. These arise when external light is coupled to the plasmonic excitations of a metal surface. Due to the momentum mismatch between surface plasmons in the metallic surface and light in air, these cannot straightforwardly be excited. Instead, it is possible to shine light passing through a high-refractive-index prism to the metal surface. Alternatively, it is possible to incorporate an extra wave vector to the system by devising a surface with a periodic grating [51] (see scheme in Fig. 1.2c). The quantum emitters located at the surface will be inside the evanescent field of the plasmonic mode, which can present very high electric field amplitudes. Experiments of organic materials on top of these systems have led to strong coupling between SPPs and electronic excitations [52] and nuclear vibrations [53].

Other plasmonic cavities commonly used in strong coupling are based on localized surface plasmons (LSPs). These cavities exploit the geometric properties of intricate metallic structures to achieve the best EM field confinement in the literature, however also showing great losses. Strong coupling has been investigated in a plethora of different cavities hosting LSPs, such as nanorods [54, 55], nanoprisms [37], and bow-tie nanoantennas [56–58] (see Fig. 1.2d). Recently the single-molecule strong coupling limit has been achieved at ambient conditions in the nanoparticle-on-mirror cavity [38], showing a mode volume for the optically active frequency of $\sim 40\,\text{nm}^3$. It even has been found that inside the gap of these cavities, atomic-sized defects can localize LSPs below one cubic nanometer [59].

1.2.2.2 Examples of Quantum Emitters

The choice of quantum emitters heavily relies on the desired properties of the strong coupling realization. As we discussed above, large transition dipole moments favor larger coupling strengths, which lead to an easier observation of the mode splitting. Moreover, the binding energy of the material excitation can also affect the conditions of the experiment, since relatively high temperatures can dissociate excitons with low-energy binding energies (e.g. quantum-well excitons in inorganic semiconductors are typically only supported at cryogenic temperatures). Another important quality of the emitters is the ability to achieve high densities, since strong coupling ultimately depends on $\sqrt{N/V}$. Note that the coupling strength increases as $\sim 1/\sqrt{V}$ and the Rabi splitting with $\sim \sqrt{N}$, therefore it is desirable to fit as many quantum emitters inside the mode volume of the EM field. More parameters that make each quantum emitter unique and potentially more suitable for achieving robust strong coupling are their inertness (i.e., chemical stability) or the possibility of manipulating them in order to fabricate distinct devices. In the following we will review some strong coupling realizations with different types of quantum emitters (Fig. 1.3).

The first experimental observation of Rabi oscillations was made for sodium Rydberg atoms inside Fabry–Perot cavities in the microwave domain [62]. Later, a

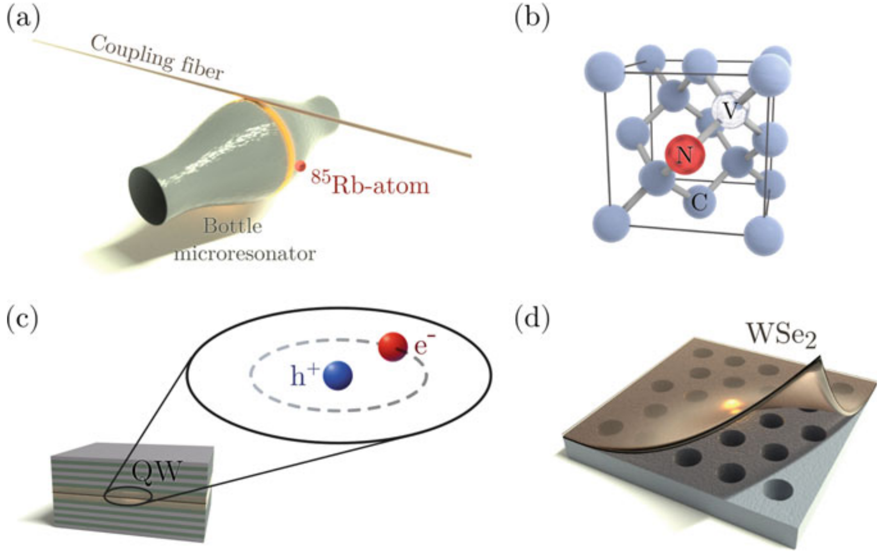

Fig. 1.3 Examples of different quantum emitters. **a** A rubidium atom strongly coupled to a whispering-gallery-mode microresonator, itself coupled to an optical waveguide, as in reference [60]. **b** Simplified atomistic structure of an nitrogen-vacancy center in diamond. **c** DBR microcavity with an inorganic semiconductor quantum well in the center hosting Wannier–Mott excitons (schematically depicted in zoom). **d** Monolayer of WSe$_2$ (a transition metal dichalcogenide) coupled to a photonic crystal cavity, as in reference [61]

direct observation of the energy splitting in the absorption spectrum was made in an optical cavity [63], achieving for caesium even single-atom strong coupling [64]. This lead to an elegant and sensitive way to detect single atoms and deterministically trap atoms near in the cavity [19, 65]. The great distance between the electron and the nucleus in a Rydberg state makes it possible to have a rather large dipole moment, achieving $\sim$1 Debye (D) in these experiments. This makes them highly attractive as single-photon sources [66]. Nevertheless, the convoluted experimental setups and required low temperatures for achieving robust strong coupling heavily restricts the potential of atoms for more sophisticated and practical photonic devices.

The success of CQED in atomic systems quickly brought the attention of the solid-state physics community [67]. The interest was first focused on inorganic semiconductors, where their intrinsic excitations (excitons) played the role of quantum emitters. These electronic excitations are called Wannier–Mott excitons [68], correlated electron–hole pairs, in many ways similar to hydrogen atoms, characterized by very large radius and relatively low binding energies. These states were found to be more stably confined inside quantum wells, quasi-2D regions enclosed by materials of wider bandgap. Solid-state cavity exciton-polaritons were first demonstrated for GaAs quantum wells inside Fabry–Perot microcavities [69], which later led to fascinating achievements such as polariton amplification devices [70] and Bose–Einstein condensation [71].

Quantum wells can be further confined into zero-dimensional systems with a set of bound and discrete electronic levels. These “artificial atoms” are known as quantum dots [72, 73], and constitute a central theme in nanotechnology. Other types of artificial atoms have been demonstrated in vacancy defects in crystals known as color centers, being nitrogen-vacancy centers in diamond the most commonly used [74]. In superconducting circuits, Cooper pairs can be quantum confined through Josephson junctions [75], playing the role of artificial atoms that can be brought into the strong coupling regime [34]. Due to the great dipole moment present in these types of qubits, the so-called field of circuit QED presents one of the best platforms to achieve the ultra-strong coupling regime [35], even achieving the best figures of merit in ratio coupling vs frequency [76], and one of the most promising ones to use for quantum computation [33].

In recent years, a new family of materials has emerged as very promising in the fields of nanotechnology. These are the van der Waals materials [77, 78], heterostructures composed of many atomic monolayers bonded by weak van der Waals interactions. In particular, two-dimensional transition metal dichalcogenides constitute a particularly promising platform for photonic devices [79]. In these rising materials very robust strong coupling is possible thanks to their large exciton binding energies, and it has been demonstrated in many different cavity systems such as DBRs [80], photonic crystals [81], and plasmonic structures [82, 83].

Currently one of the most interesting quantum emitters in nanophotonics are organic molecules. Among their numerous advantages they offer high photoluminescence quantum yields, very large dipole moments, and great flexibility in the building of photonic devices [14]. Since organic molecules are the main interest of this thesis, in the following we devote an entire subsection to review the field of strong coupling with organic molecules.

1.2.3 Strong Coupling with Organic Molecules

Organic molecules are chemical compounds that contain carbon in their composition. Due to its ability to form chains with other carbon atoms, there is a great variety of different organic molecules, ranging from simple molecules composed of a few atoms (e.g. methane CH_4), to immensely complex molecules such as DNA.

Organic materials still are one of the most interesting platforms to achieve light–matter strong coupling, even more than 20 years after its first realization in an optical microcavity [84]. Such materials present very localized excitations, known as Frenkel excitons [85], characterized by very large binding energies ($\sim$0.1–1 eV) and large transition dipole moments ($\sim$1–5 D), making them optimal for achieving robust strong coupling at room temperature. In general these excitations correspond to excited electronic states bound to single molecules inside the material, thus potentially allowing QED devices with single molecules at room temperature, an ideal scenario for studying quantum optical, nonlinear and saturation effects, such as photon blockade, previously achieved for atoms at cryogenic temperatures [86].

Another interesting quality of organic molecules is their ability to self-aggregate into different types of structures thanks to their weak intermolecular forces. Specifically, molecular aggregates generally present different absorption and emission spectra than the individual molecules they are composed of, potentially red- or blue-shifting the excitation frequency for J- and H-aggregates respectively [87]. Additionally, aggregation can further enhance dipole moments, which made J-aggregates the first class of organic material in which strong emission of polariton states was achieved at room temperature [88]. Due to the wide variety of molecular aggregates it is possible to create narrow absorption spectra tuned to the desired optical or near infrared frequency [89]. This feature is particularly interesting for imitating natural aggregates [90], such as photosynthetic complexes that present very efficient energy absorption and transfer [91]. Notably, strong coupling has been achieved with optically active biomolecules such as β-carotene [92], optical antenna structures in green sulphure bacteria [93], enhanced green fluorescent proteins [94], and reported even in living photosynthetic organisms [95].

Besides aggregates, the attractive van der Waals interactions between molecules can also lead to the formation of well-ordered molecular crystals [96]. In particular, anthracene crystals have been used to achieve strong coupling in the optical regime [97], and even room temperature lasing [36]. The latter achievement was done with a single anthracene crystal, motivated by the belief that strong structural and energetic disorder was the reason previous attempts at lasing did not succeed. However, later experiments demonstrated that it could be accomplished in amorphous small molecule and polymer films [98, 99]. These experiments demonstrated that molecular disorder, intrinsic to many organic material realizations, is not necessarily detrimental for organic polariton device fabrications, as it was previously thought. From a practical standpoint, it is easier to manufacture anything in a disordered state than in an ordered one, making organic materials possibly more advantageous [13].

The versatility of organic molecules has lead to strong coupling experiments in a wide variety of electromagnetic modes such as planar microcavity photons [84, 100–103], surface plasmon polaritons [52, 104–106], surface lattice resonances [107–109], localized surface plasmons [37, 38, 110], and even inside photonic crystals [111]. In the case of localized surface plasmon structures, organic molecules allow to reach strong coupling at the single-emitter level even at room temperature [38, 58, 112], an impressive achievement that promotes the technological development of room-temperature quantum devices. Among other important accomplishments not mentioned above are devices that present polariton–polariton nonlinear interactions [99], nonlinear optical responses [113, 114], and even broadband polariton lasing [115] and polariton-based transistors [116], both at room temperature. Furthermore, strong coupling constitutes a promising solution in material science. It has been demonstrated that it enables the possibility of tuning the work function of organic materials [117], enhancing electrical conductance [118, 119], improving propagation lengths of energy transport (typically of a few nanometers [120]) by several orders of magnitude [121–123], and using organic polaritons to harvest and direct excitations by tuning the cavity mode [124]. Organic systems present also an interesting platform to achieve energy transport between spatially separated molecules [125–128], thanks to nonlocal interactions induced by the cavity.

One unique aspect of organic materials is their internal complexity, apparent in Fig. 1.4a. Typically, organic molecules encompass tens to hundreds of atoms, forming rich structures that involve motion of both electrons and nuclei. Such abundance of degrees of freedom (DoF) opens new pathways for the electronic excitations to

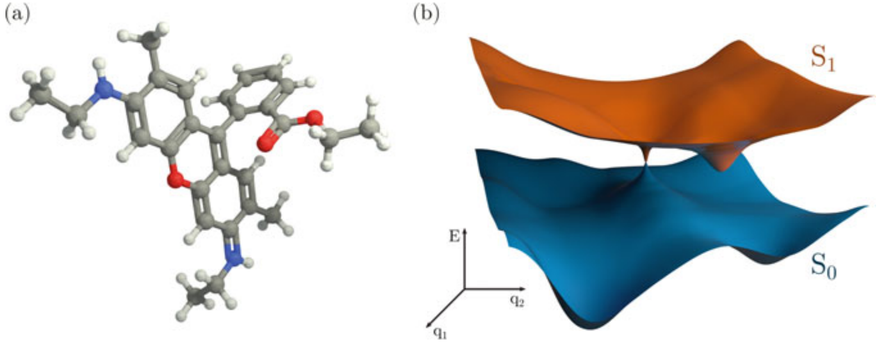

Fig. 1.4 Complexity of organic molecules. **a** Depiction of a rhodamine 6G molecule, commonly used for achieving organic polaritons. **b** Conceptual example of energy dependence with nuclear coordinates q_1 and q_2 of the first two electronic states (S_0 and S_1) of an organic molecule. These, in general, multidimensional hypersurfaces are known as potential energy surfaces. Typical energy landscapes have a dependence on many nuclear degrees of freedom and present multiple electronic states

relax (see an schematic of a typical energy dependence with nuclear coordinates in Fig. 1.4b). For example, the molecule can lose the excitation *nonradiatively*, i.e., without emitting a photon of the exciton frequency, but rather converting the energy into vibrational or rotational motion of the nuclei, i.e., essentially heat. Together with the high level of disorder in organic systems, the rates of dissipation and dephasing become more relevant than in their inorganic counterpart. Furthermore, the interaction between electronic and nuclear DoF (also known as *vibronic coupling*) becomes crucial to explain central features of organic molecules such as the Stokes shift, the difference in energy between absorption and emission spectra.

However, it should be noted that due to the high mass difference between electrons and nuclei, nuclear motion is usually much slower than electronic motion, leading to vibrational modes of lower energy,[5] typically in the mid-infrared spectral region. In some cases, the absorption intensity of certain nuclear bonds is very high, indicating large transition dipole moments [129]. For example, the C=O bond-stretching mode presents a dipole of $\sim$1 D [130] making it suitable for strong coupling. Indeed, this nuclear bond was exploited to achieve strong coupling with infrared modes, first in a polyvinyl acetate polymer [131] and in polymethyl methacrylate [132], even achieving in the latter spatial control over the coupling of vibrations [133]. Additionally, vibrational strong coupling of different molecules and functional groups in the liquid phase was later demonstrated [134].

The acknowledgment of this internal structure led to some pioneering experiments in which the nuclear DoF were exploited. In particular, the structure of some molecules can be altered, which in turn changed the energy of electronic excitation. This allows to turn on and off strong coupling by changing the molecular structure externally and thus detuning the exciton energy from the cavity mode. This was first achieved for a reaction of a porphyrin dye with nitrogen dioxide, which can be reversed through heating of the system [135]. Then, by using the molecule spiropyran, which can undergo reversible change to its isomer merocyanine by externally radiating with UV light [100]. Remarkably, it was shown that in this same setup strong coupling could be used to modify the photoisomerization reaction time from one species to another [136, 137]. Analogous experiments with strong coupling in a perovskite salt demonstrated that the energy barrier of a phase transition could be modified by cavity fields [138]. These experiments demonstrated that the internal structure does not only play a mayor role in organic polaritons, but that it can be exploited to modify the chemistry of a system.

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[5] Rotational modes have an even lower energy, and are typically not resolved in spectroscopy measurements, being thus reduced to giving fine structure to the vibrational modes. Therefore, usually these two modes are jointly referred to *rovibrational* modes.

1.3 Polaritonic Chemistry: State of the Art

Although the first realization of strong coupling with organic molecules was more than 20 years ago [84], it is only during the last few years that chemical aspects have begun to be explored. Indeed, many experimental works have reported chemical modifications inside cavities [117, 125, 136, 139–142], and much theoretical effort has been devoted to develop an adequate theory of polaritonic chemistry [143–150]. This young—but rapidly growing—field might open the doors to the next generation of polaritonic devices, paving the way towards completely tunable materials whose properties can be controlled for, e.g., optical sensing or energy harvesting applications, among others.

By placing an organic material in a suitable cavity it is possible to bring the system into the strong coupling regime. The molecules and the electromagnetic vacuum are coupled without the need of an external input of energy (as is the case with strong lasers [151]). Thanks to the large dipole moments of organic molecules, it is possible to achieve huge Rabi splittings, completely reshaping the energy structure of the system. This opens the possibility of altering the chemical properties and reactivity of a material, bypassing energy-consuming alternatives such as synthetic material design or control through a large external energy input (e.g., strong lasers or large temperatures).

In strong coupling, the molecules plus the cavity must be thought of a single entity with its own distinct energy levels. It is thus intuitively obvious that this in principle should influence processes that normally take place in the molecular excited state (see in Fig. 1.5 a Jablonski diagram illustrating many of the different process present in organic molecules). Moreover, strong coupling can also have an influence on the electronic ground state of molecules, in two different ways: by

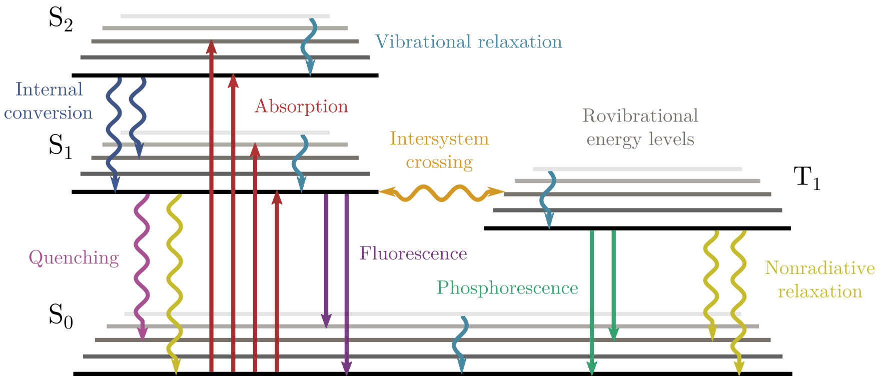

Fig. 1.5 Jablonski diagram depicting the possible processes typically present in organic molecules. Electronic states are denoted by their total spin (S for singlet and T for triplet) and are schematically represented by their rovibrational structure. Straight arrows represent events in which single optical photons are transferred, while wavy arrows depict processes in which energy is transmitted in the form of nuclear motion of the molecule and/or its environment

reaching electronic ultra-strong coupling, where molecule–cavity interactions can potentially “dress” the molecular ground state, and by achieving vibrational strong coupling with ground-state rovibrational states. We therefore separate the discussion of polaritonic chemistry by modifications of electronic excited state chemistry, and modifications of the ground state. In the following we review the experimental and theoretical efforts crucial to the early development of both of these scenarios.

1.3.1 Manipulating Excited-State Processes

The first experimental observation of chemical reactivity being modified in a cavity was done by Hutchison et al. [136] for a photoisomerization reaction. The process was observed in a spiropyran molecule, which undergoes ring opening after UV photoexcitation to form merocyanine, and the inverse reaction is achieved by thermal means. Spiropyran absorbs 330 nm light while merocyanine has an absorption maximum at 560 nm, which is resonant with the Fabry–Perot cavity the molecules are embedded in. Therefore, most of the product molecules are in the strong coupling regime, achieving a Rabi splitting of 700 meV. The authors observe a slow down of the rate of growth of the merocyanine concentration when measured inside the cavity on resonance. The larger the Rabi splitting, the slower the overall reaction is. By altering the energy landscape of the excited-state process, they observed a decrease of the reaction rate. While the system was in the ultra-strong coupling regime (in which the ground state can also be influenced by the cavity), they did not see any change in the thermally-driven back-reaction from merocyanine to spiropyran.

This experiment sparked many theoretical studies aiming to understand this phenomenon. At the time, most existing theoretical models were based on oversimplified descriptions, treating organic molecules as two-level systems. The presence of a more complex internal structure was generally ignored. However, some models took this into account by means of an open quantum systems theory (e.g., Lindblad theory [152]), that is, by assuming that rovibrational modes act like a thermalized bath that induces decay and dephasing on the molecular excitations. The most sophisticated descriptions explicitly treated single vibrational modes as harmonic oscillators around the equilibrium configuration. This model, the so-called Holstein–Tavis–Cummings model [153–155], was early used by Herrera and Spano to predict an enhancement of intramolecular electron transfer in collective strong coupling [156]. The authors discuss the mechanism of polaron decoupling, in which the electronic–nuclear interactions vanish in the thermodynamic limit. This model is a good approximation when the system is close to the equilibrium, which is decidedly not the case in an excited-state chemical reaction where the initial and final nuclear configurations are so different.

Strong coupling is a phenomenon typically studied from the point of view of quantum optics, a field of research that emphasizes the use of simple descriptions to study highly controllable systems. Organic polaritons were often viewed as a means to modify light, and little attention was paid to the intrinsic material properties. The first theory that embraced the complexity of organic systems with the aim to study molecular modifications in strong coupling was developed in [143], one of the studies that we focus on Chap. 3 of this thesis. In this work we aim for a microscopic description of the molecules, fully including their nuclear degrees of freedom. Because of the difficulty of such a task, we treated simple model molecules which could be fully solvable, and analyzed the validity of the Born–Openheimmer approximation, widely-used in chemistry. A related approach was soon after used by Kowalweski et al., in which they analyzed the important nonadiabatic dynamics that emerge in the single-excitation subspace in strong coupling [157, 158]. This method can be interfaced with state-of-the-art quantum chemistry approaches, achieving great accuracy and low computational cost without sacrificing the description of all the internal degrees of freedom [159].

An additional theoretical work was made by Flick et al. [147], where they analyzed matter–photon interactions from the point of view of a quantum-electrodynamical density-functional theory [160]. They demonstrate the potential of this powerful idea to calculate chemical quantities such as bond lengths, nonadiabatic couplings, or absorption spectra. The main challenge of this approach is finding suitable functionals that describe electron–nucleus–photon interactions based on the electron–photon density. It is also of great importance to this thesis (see Chap. 6) the cavity Born–Oppenheimer approximation [148], one of the possible adiabatic approximations that can be performed in an electron–nucleus–photon system. More ideas related to the quantum-electrodynamical density-functional theory were later further explored [161, 162], including additional insight into the intramolecular charge and energy transfer mechanics in strong coupling [163].

Up to now most of the microscopic descriptions mentioned above treated in somewhat detail the electronic and nuclear degrees of freedom such that no more that one or a few molecules could be considered simultaneously due to the exponential complexity of such computational task. Nevertheless, despite the potential of organic molecules, nowadays most strong coupling realizations consist on huge number of emitters. In this context, we extended the theory developed in [143] so that we can treat macroscopic number of molecules in terms of the concept of polaritonic potential energy surfaces [146], a generalization to light–matter system of the ubiquitous potential energy surfaces of chemistry. This theory is part of the focus of Chap. 4 of this thesis. Based on this, we published a theoretical work [164] in which a large collection of photoisomerizable molecules were studied. In particular we introduced a model that represented molecules such as stilbene, azobenzene, or rhodopsin, and studied the single-molecule dynamics and the energy landscape for collective strong coupling. In this study, presented in detail in Chap. 5, we predict a suppression of the reaction that grows more effective with the number of molecules. This effect is a generalization to any kind of energy landscape of the polaron decoupling effect described in [156]. Another collective effect is described in [165] (see Chap. 5), where we discuss the possibilities in polaritonic chemistry of opening new reaction pathways, previously not possible in standard chemistry, without relying on very specific conditions, such as in the case of singlet fission processes [166, 167].

The potential of this theory has been demonstrated by treating big molecular systems using well-known approaches such as QM/MM (quantum mechanics/molecular mechanics) [168, 169]. This accurate technique allows the simulation of realistic experiments while providing detailed insight at the atomistic level. Such method naturally includes nonradiative processes that contributes to the loss of excitation of the molecules, and spontaneous emission of the cavity photon can be straightforwardly added. These processes are often very important in strong coupling with organic molecules, and thus are incorporated in some other descriptions that do not treat explicitly the molecular complexity. For instance, despite it only treating electronic states close to the equilibrium, the aforementioned Holstein–Tavis–Cummings model has been used to theoretically predict polariton-assisted singlet fission [170].

Let us address more recent experiments dealing with polaritonic chemistry of the electronic excited state. One important landmark was achieved recently by Munkhbat et al., in an experiment demonstrating suppression of photobleaching of organic molecules [141]. In this process, a molecule can transfer its excitation from the singlet to the long-lived triplet state (see Fig. 1.5). In this state there is a higher probability of reacting with the atmospheric triplet oxygen ($^3O_2$), leading to chemically unstable species that can damage the photo-active organic molecules [171]. In this experiment it was demonstrated that because of the cavity hybridization of the singlet state, this inherited the short lifetime of the plasmonic modes it was coupled to. This significantly reduced the population transfer to the triplet state, which is the first step of this detrimental process, therefore strongly suppressing the overall photobleaching reaction. Another similar experiment was achieved for the polymer P3HT in a Fabry–Perot cavity, where a threefold reduction of molecular photodegradation is observed [172]. Finally, we note the possibility of using polaritonic chemistry to manipulate the so-called reverse intersystem crossing, that is, the transfer from triplet to singlet states, which has been studied in some experiments and recently discussed [173, 174].

1.3.2 Ground State Chemistry in a Cavity

Most of the research of polaritonic chemistry up to now has been devoted to influencing excited-state reactions and structure via electronic strong coupling. Despite the big relevance of these processes, most common chemical reactions occur in the electronic ground state and are triggered by thermal fluctuations, i.e., the energy contained in the internal motion of the participating molecules is used to overcome the transition state of a reaction. The difference in energy between the reactant state and the transition state is known as activation energy or energy barrier, and its manipulation is one of the main challenges in modern chemistry, for example, by applying external mechanical forces [175] or electric fields [176]. In the context of cavity-modified chemistry, the modification of the ground-state energy barrier was first analyzed for electronic ultra-strong coupling. In the original work of Hutchison et al., the ground-state back-reaction from merocyanine to spiropyran is thermally activated, but the authors did not observe any modification in strong coupling [136]. Indeed, subsequent theoretical studies confirmed that even in the ultra-strong coupling regime for electronic transitions, the ground-state effects are on the order of the single-molecule coupling, i.e., they are not influenced by collective strong coupling [31, 143].

More recently, a number of experiments reported changes in ground-state chemical reactivity, not by exploiting the usual electronic strong coupling, but by tailoring cavities that couple to the desired molecular vibrations [139, 140, 142, 177]. The first observation in 2016 by Thomas et al. reported up to a ∼5-fold decrease of the reaction rate of a alkynylsilane deprotection process by strongly coupling the Si–C stretching mode to a infrared cavity [139]. Following experiments achieved strong coupling catalysis, i.e., increments in the reaction rate. First, by achieving ultra-strong coupling with the O–H stretching mode in water, rate increments of 10^2 and 10^4 were achieved for two different hydrolysis reactions [140]. Then, by inducing strong coupling in a C=O bond, present both in the reacting molecule and the surrounding solvent, an increase of the reaction rate of over one order of magnitude has been reported [177].

An experiment of particular relevance is achieved again by Thomas et al. [142]. In this work the authors aim to recover the idea of "mode-selective chemistry" that was so prominent in the 1980s. The original idea was to externally excite specific infrared vibrational modes in order to induce thermally-drive chemical reactions [178]. However, the abundance of rovibrational states at thermal energies that competed with the selected mode made the realization of this idea only feasible at cryogenic temperatures, where relaxation processes were minimized. In this recent experimental study the branching ratio between two different products is modified when the system is in vibrational strong coupling. Not only the reaction rate is modified, but the final outcome of the reaction is changed inside a cavity. It should be emphasized that all of these experiments take place in the dark; there is no explicit input of energy, other than the intrinsic temperature of the sample.

At the time of writing of this thesis, current theoretical approaches do not explain these experiments, and many question remain unanswered. The work in [149] constitutes the first attempt for a microscopic description of ground-state reactivity in strong coupling. This theory, which is the focus of Chap. 6, explores the chemistry of ground-state CQED from a fundamental point of view, studying the formally exact quantum reaction rates and the widely-used transition state theory of chemistry in the context of strong light–matter interactions. Some predictions of this theory are discussed in detail in [179], where quantum chemistry methods are used to simulate realistic reactions in a cavity. In these works we find that the mechanisms that allow to influence the chemistry of the system are related to Casimir–Polder forces and do not explain the resonant condition that the experiments discussed above all share. More recently, a study by Angulo et al. [180] analyzed a particular ground-state charge transfer reaction in vibrational strong coupling. The reactant and product states are modeled as harmonic oscillators so that it is possible to generalize the widely-used Marcus theory to chemical species in vibrational strong coupling. This theory predicts an increase of the charge transfer rate that is most prominent under resonant conditions. However, this is a very specific model in which the reaction rate cannot possibly be slowed down, contrary to the original experiment of 2016. Therefore there is still a need to develop a satisfactory theory of molecule–cavity systems that successfully describes the mechanisms by which chemical reactions can be altered in the ground-state, so we can predict unusual phenomena and further design experimental realizations of interest.

1.4 Summary of Contents

This thesis explores from a theoretical point of view the field of polaritonic chemistry and in general the modification of molecular structure in strong coupling. It is written so that most concepts are supported with the appropriate theoretical background. In the following we explain in more detail the structure of this thesis.

In Chap. 2 we lay the fundamental theoretical background on which the thesis rests upon. We start by providing the crucial ingredients to understand the quantization of the electromagnetic field from Maxwell equations and the Lorentz force, aiming to achieve a quantum electrodynamical Hamiltonian that includes both light and matter. Then, we focus on the material part of this Hamiltonian and overview the theoretical tools used to treat it, such as the Born–Oppenheimer approximation, upon which most modern chemistry is built. Then, we go back to the light–matter Hamiltonian and focus on the possible treatments when the electromagnetic component is confined to a cavity. We overview different theoretical descriptions for cavity QED, such as the ubiquitous Tavis–Cummings model. Finally, we formally introduce the weak and the strong coupling regime based on a simple model, showing the key features of this phenomena.

Next, Chap. 3 is devoted to analyze from first principles the molecular structure in electronic strong coupling. In order to do this we exploit the concepts that we learned from previous cavity quantum electrodynamics models and try to combine them with the molecular description based on the Born–Oppenheimer approximation. We study the effects of strong coupling on the nuclear structure of two different molecules, rhodamine 6G and anthracene, which are reproduced through simplified theoretical descriptions. In particular, we focus on the validity of this approximation, discussing the nonadiabatic terms introduced by the photonic degree of freedom. We compare the absorption spectra for these molecules, with and without approximation, for one photonic mode strongly coupled to one and two molecules. In the case of two molecules, we analyze the nuclear correlations induced by the cavity in both the polaritonic and dark states. The results of this chapter have been published in Physical Review X [143].

The Chap. 4 is devoted to the theory of polaritonic chemistry. We formally introduce the molecular description developed previously into a proper CQED theory. We develop the concept of polaritonic potential energy surfaces, which generalizes the ubiquitous potential energy surfaces of chemistry to hybrid light–matter systems. We discuss this theory, analyzing the physical consequences of such description. In particular we consider the effects of collective strong coupling, which are crucial to understand polaritonic chemistry. These results were published in ACS Photonics [146].

In Chap. 5 we use the theory of polaritonic chemistry to study novel effects of strong coupling in photochemistry. In particular we study the suppression of a model photoisomerization reaction thanks to the hybridization between molecules and photons in a cavity. We present how this effect is remarkably enhanced in the case of collective strong coupling, leading to an almost complete suppression of the reaction. Additionally, we study another model molecule which after photoabsorption can isomerize to a different configuration with a quantum yield of less than unity. We then demonstrate how by tuning the cavity parameters, an increase of the reaction efficiency to essentially one can be achieved. Furthermore, we show how in the case of collective strong coupling this can lead to a succession of isomerization reactions of many molecules, one after another, by originally radiating the system with a single photon. With this we establish the potential of the delocalized nature of polaritons, achieving even the breakdown of the second law of photochemistry. The results of this chapter have been published in Nature Communications [164] and in Physical Review Letters [165].

Finally, in Chap. 6 we introduce the problem of influencing thermally-driven chemical reactions in the ground state. We study the formally exact quantum reaction rates of a model system, in which can apply the cavity Born–Oppenheimer approximation. We develop a theory that allows to explain and predict non-resonant energetic and structural changes to molecules coupled to a quasistatic cavity (e.g., metallic structures that can host plasmonic modes). We then validate our theory by applying it to realistic cavity and molecular systems. We furthermore study the orientation-dependent collective enhancement of the effect both for the reaction rates and the nuclear structural changes. We discuss how our theory can directly connected to well-known van der Waals forces, and more generally, to Casimir–Polder interactions.

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