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NEW VIEWS

Ultrafast coherent nanoscopy

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The dramatic advances of nanotechnology experienced in recent years enabled us to fabricate optical nanostructures or nano-antennas that greatly enhance the conversion of localised electromagnetic energy into radiation and vice versa. Nano-antennas offer the required improvements in terms of bandwidth, interaction strength and resolution for combining ultrafast spectroscopy, nano-optics and quantum optics to fundamentally push forward the possibility of the coherent optical access on individual nanostructures or even molecules above cryogenic temperatures, where dephasing processes typically occur at very short time scales. In this context, we discuss recent progress in the theoretical description of light-matter interaction at the nanoscale and related experimental findings. Moreover, we present concrete examples in support of our vision and propose a series of experiments that aim at exploring novel promising regimes of optical coherence and quantum optics in advanced spectroscopy. We envisage extensions to ultrafast and nonlinear phenomena, especially in the direction of multidimensional nanoscopy.

Keywords: light-matter interaction; nano-antenna; quantum optics; coherent spectroscopy; ultrafast phenomena

1. Introduction

There is a vast attention in the development of novel and more sophisticated technologies that exploit the laws of physics at the fundamental level, such as quantum information and communication or quantum sensing and metrology [1–3]. In this context, one typically focuses on the man-made suppression of decoherence in the quantum degrees of freedom, because it inhibits the functionality of devices or limits their performances. That has been achieved for example by laser trapping and cooling techniques [4], cryogeny [5] and high-finesse cavities [6]. In Chemistry, physico-chemical processes are fundamentally governed by quantum mechanics too and they may naturally occur at ambient conditions, where dephasing times are usually quite short. Here, quantum control is typically achieved using ultrafast light pulses that overcome decoherence [7,8]. Nonetheless, the interaction of light with single quantum systems at room temperature is very weak and its coherence can be hardly controlled [9–12]. Furthermore, such quantum phenomena may occur at nanometre length-scales that are difficult to explore with conventional experimental approaches (e.g. nano-composites and light-harvesting complexes) [13–15]. These deficiencies have a direct and severe impact on the possibility of addressing physical as well as physico-chemical processes at the quantum level under real-world conditions.

Nano-optics deals precisely with the challenge of controlling the interaction between few photons and tiny amounts of matter and with the ability to efficiently funnel light down to nanoscale volumes [16,17]. Advances in nano-optics may provide the missing link to place quantum physics and physical chemistry in a closer context and to probe quantum-optical as well as (photo) physico-chemical processes under new settings, hence providing deeper insight on the basic (quantum) mechanisms that govern them [18]. The past decades have witnessed the development of several successful attempts in this regard. For example, single-molecule spectroscopy has been an important tool to probe spatial and dynamical heterogeneities at the nanoscale without ensemble averaging [19–22]. However, the mismatch between light and a single emitter has limited the access to coherent and ultrafast dynamics.

Optical antennas or nano-antennas have recently emerged as a unique tool to greatly improve the exchange of optical energy with nanoscale matter [23–25]. These are metal nanostructures that exhibit electromagnetic resonances in the optical spectral range. In analogy to radio frequency antennas they may be exploited to efficiently receive photons or to radiate them into a preferential direction [26]. Furthermore, they have strong near fields that can be exploited to rapidly exchange electromagnetic energy with a nearby quantum system [27]. A longstanding problem

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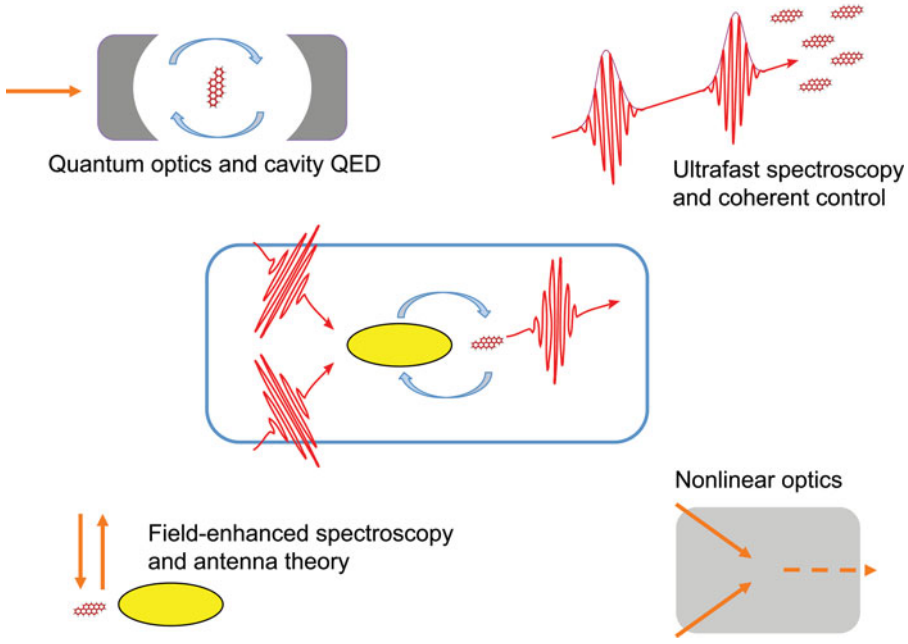

Figure 1. Vision and context at large: quantum optics and cavity QED combined (left-upper panel) focus on quantum coherence and dynamics at the single-photon/single-atom level; ultrafast spectroscopy and coherent control (right-upper panel) investigate quantum coherence and dynamics in the presence of strong dephasing processes; field-enhanced spectroscopy and antenna theory (left-bottom panel) boost the exchange of energy between light and nanoscale matter; nonlinear optics couples light with light through matter. Optical antennas establish a unique overlap among these research areas (centre panel).

was the competition between radiation enhancement and absorption in the near field due to real metals [28]. We have shown that this is not a fundamental constraint and that engineered nanostructures may lead to huge enhancements without quenching [29–31].

Optical antennas may establish unprecedented regimes for light-matter interaction, enabling the ultrafast coupling between photons and nanoscale material excitations in a situation where quantum phenomena may become important even in the presence of substantial dephasing. Moreover, these processes may be monitored if the time frame is faster than decoherence. That is possible owing to the large bandwidth of optical antennas, which makes them fully compatible with methods and techniques of ultrafast spectroscopy. Altogether, these settings hold great promise for interfacing photons to single quantum systems beyond the framework of cavity quantum electrodynamics (QED) and urge further thorough theoretical and experimental investigations.

The ambitious goal is to dramatically advance the possibility to investigate quantum-optical as well as photo-induced physico-chemical processes down to individual quanta on systems situated in realistic environments, with an unprecedented control over ultrafast few-photon linear and nonlinear optics, quantum dynamics and kinetics at the nanoscale. The research approach combines methods and techniques of advanced spectroscopy, quantum optics and cavity QED, as well as nano and nonlinear optics through the constructive combination of theory and experiments (see Figure 1 for an illustration of this vision).

2. Background context

2.1. *Optical antennas as nanoscale resonators*

Single-molecule detection found its way through a scheme based on fluorescence excitation spectroscopy [32]. However, the advent of quantum science and technology has renewed the interest for approaches that preserve coherence in the interaction process [33–35], which for many years have relied on single emitters suitably placed inside high-finesse cavities [6,36]. To gain insight on the potential of optical antennas as a new paradigm for coherent light-matter interaction, we compared them with optical microcavities [30] and discuss here some aspects related to quantum dynamics.

In practice, whether a two-level system (TLS) coupled to a resonator is in a regime where the addition or subtraction of one quantum (or a few) is observable physics depends essentially on two parameters: the critical photon number $N_S = \Gamma_1\Gamma_2/4g^2$ and the critical atomic number $N_A = k\Gamma_1/2g^2$, where Γ_1 and Γ_2 respectively are the spontaneous emission and dephasing rates of the TLS, k is the cavity loss rate and g is the coupling rate [37]. When both N_S and N_A are much smaller than 1, a single photon (or a TLS) can lead to significant dynamics. It means, for instance, that one atom may drastically change the

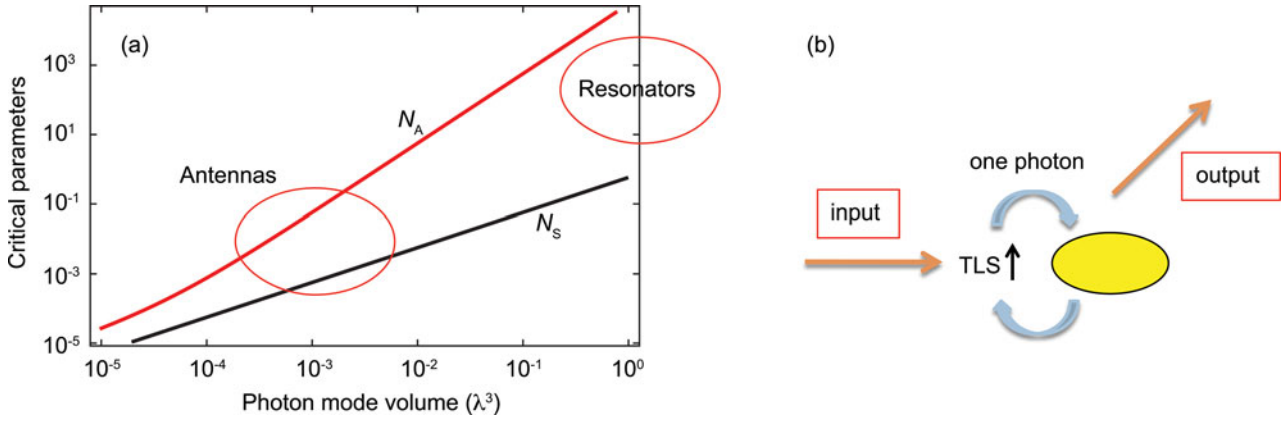

Figure 2. (a) Critical photon number (N_S) and critical atomic number (N_A) as a function of the photon mode volume V_m. The calculation was performed assuming dephasing times $T_2 = 100$ fs and $T_1 = 2.7$ ns for $\lambda = 2\pi c/\omega_o = 740$ nm, $\eta_o = 5\%$ and $L = 0.173$ (corresponding to a nanoparticle with an aspect ratio equal to 2). η_a has a value between 0 and 1, which depends on Q, V_m and materials absorption [30]. The red circles delimit the parameter space where optical antennas and microresonators operate. (b) Schematics of coherent light-matter interaction with a TLS, an optical antenna and an external (input) field. The output field carries some signature of the coherent coupling as exemplified in Figure 3.

reflectivity of a resonator [34] or lead to photon–photon interactions [38]. This is possible because in a typical cavity QED experiment with atoms, one obtains values like $N_S = 0.0029$ and $N_A = 0.018$, with $g \sim 10$ MHz [34]. In the late 1990s, progress in nanotechnology enabled the fabrication of miniaturised cavities that led to much larger g factors (~50 GHz) [36]. These allowed the observation of QED phenomena such as vacuum Rabi splitting in solid-state systems with much stronger dephasing [39,40]. Nonetheless, pushing such regime of light-matter interaction into situations with larger g and dephasing rates appears to be fundamentally limited by diffraction and new concepts need to be introduced.

Optical antennas may be the missing technology to eventually enable strong interactions with individual quantum systems under ambient conditions. In short, having a quality (Q) factor of the order of 10–100, optical antennas are fully compatible with ultrafast light-matter interactions. Moreover, the 'cavity' is in the strong Purcell regime, because the mode volume V_m is considerably smaller than the cubic wavelength λ^3. From the expressions for Q and V_m (see Ref. [30]), it is straightforward to derive the scaling laws

$$N_S = \frac{4\pi^2}{3\eta_o} V_m \frac{\Gamma_2}{\omega_o}, \quad N_A = \frac{32\pi^3}{9\eta_o\eta_a} \frac{(1-L)^2}{L^2} V_m^2. \qquad (1)$$

Here η_o represents the intrinsic quantum yield of the emitter, L is related to the antenna geometry and it is bound between 0 and 1/3, V_m is the mode volume in units of λ^3, η_a is the antenna radiation efficiency [29,30] and ω_o is the resonance frequency. The result for $T_1 = 1/\Gamma_1 = 2.7$ ns and $T_2 = 1/\Gamma_2 = 100$ fs is plotted in Figure 2(a). Note that both critical parameters are well below 1 if $V_m \ll 1$, even if the TLS and the cavity dephasing times are quite short.

2.2. *Advanced spectroscopy and nano-optics*

Time-resolved techniques, such as pump-probe spectroscopy, rely on ultrafast pulsed excitation. Here an important aspect as well is coherence, which allows monitoring and manipulating the quantum dynamics of matter [7,8]. Ultrafast pulses are being applied to single quantum systems with an increasing pace and breadth. Picosecond control of polaritons and spin states in a quantum dot has been recently achieved [41–43]. Similar ideas for the ultrafast storage and retrieval of quantum information are being pursued using warm atomic vapours [44,45]. Coherent state preparation is another important theme and, recently, single-molecule coherent vibrational wavepackets and quantum state controls were demonstrated at ambient conditions [11,12]. Moreover, there has been great progress in pushing these concepts towards nano-optical fields, where shaped femtosecond pulses interact with metal nanostructures to control the complex electromagnetic field in space and time [46–48]. The extension to nano-antennas and single emitters combined may push advanced spectroscopy into the quantum-optical domain further.

The advent of scanning near-field optical microscopy (SNOM) [49,50] and single-molecule fluorescence excitation spectroscopy [32] provided the experimental tools for controlled investigations of the interaction between an emitter and a metal nanostructure [51–55]. Recently, it has been demonstrated that an optical antenna strongly modifies the excitation rate, the spontaneous emission rate, and the radiation pattern of an emitter in its near field [56–60], but none of these studies have probed nanoscale coherence. Instead, a fibre-based aperture SNOM could perform coherent spectroscopy on a single molecule at 1.4 K [61,62], but the extremely low throughput of photons through the aperture did not allow to explore more degrees

of interaction. The throughput of a nanoscale sensor field next to $10^{-1} - 10^{0}$ is long expected and currently attempted by several groups [63–67]. Progress resulting from a successful outcome of these efforts would lead to fundamental advances in near-field optics and much beyond.

3. Discussion

3.1. *Quantum optics with an optical antenna*

We need to improve the theoretical description of light-matter interaction assisted by optical antennas to move from incoherent fluorescence excitation to coherent (ultrafast) spectroscopy. So far semiclassical approaches based on the optical Bloch equations have been chosen to tackle this problem [68–70]. Attempts have also been made for more complicated geometries using a suitably modified finite-difference time-domain (FDTD) algorithm [71]. Other groups have recently started to look into this problem by quantising the plasmon resonance of an optical antenna, treated as a polarisable object within the quasi-mode approach [72,73]. This allowed them to work with the standard tools of quantum optics to perform non-perturbative calculations of the scattering spectra at different excitation powers. Their studies indicated that there is a *qualitative* difference between the quantum and the semiclassical theory. However, the quasi-mode approach relies an electrostatic description of plasmon resonances (the so-called polarisability models used in the 1980s in field-enhanced spectroscopy [27]). We instead need a quantum optical formalism that treats the interactions in a non-perturbative manner, takes into account electrodynamics effect, including the vector nature of the electromagnetic field, and tackles arbitrary antenna geometries.

We chose a quantisation scheme based on the Green's function approach, which has been developed to investigate quantum-optical phenomena in electromagnetic environments characterised by absorption and dispersion [74]. In short, the Hamiltonian operator in the rotating wave approximation reads

$$\hat{H} = \int \mathrm{d}\mathbf{r} \int \mathrm{d}\omega \hbar\omega \hat{\mathbf{f}}^{\dagger}(\mathbf{r},\omega)\cdot\hat{\mathbf{f}}(\mathbf{r},\omega) + \frac{1}{2}\hbar\omega_o\hat{\sigma}_z - (\hat{\sigma}_+\hat{\mathbf{E}}^{\dagger}(\mathbf{r}_o)\cdot\mathbf{d} + \text{h.c.}), \quad (2)$$

where $\mathbf{r}_o$ denotes the TLS position and h.c. stands for Hermitian conjugate. The electric field operator sourced by the TLS is

$$\hat{\mathbf{E}}_{\mathrm{TLS}}(\mathbf{r}) = i\sqrt{\frac{\hbar}{\pi\epsilon_0}}\int \mathrm{d}\omega\frac{\omega^2}{c^2}\int \mathrm{d}\mathbf{r}' \times\sqrt{\epsilon_{\mathrm{i}}(\mathbf{r}',\omega)}\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\cdot\hat{\mathbf{f}}(\mathbf{r}',\omega). \quad (3)$$

Equation (3) contains the imaginary part of the dielectric medium $\epsilon_{\mathrm{i}}(\mathbf{r},\omega)$ and the classical electromagnetic Green's tensor $\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)$. $\hat{\mathbf{f}}(\mathbf{r},\omega)$ are bosonic fields that play the role of the dynamical variables of the composite system. $\hat{\sigma}_z$ and $\hat{\sigma}_+$ are Pauli operators for the TLS and $\mathbf{d}$ is the electric dipole moment. Other important quantities, like the emission spectrum and the photon statistics of the emitted light depend on the Green's tensor as well through field correlations. The fundamental equations are general and the relevant system parameters are included in the Green's tensor, which may be numerically obtained [68,75].

Figure 3 displays spectroscopic effects that occur in the absorption cross section of an optical antenna when a TLS is located at various distances from it and for different excitation powers. The asymmetric lineshape is commonly attributed to Fano interference [76], which is a signature

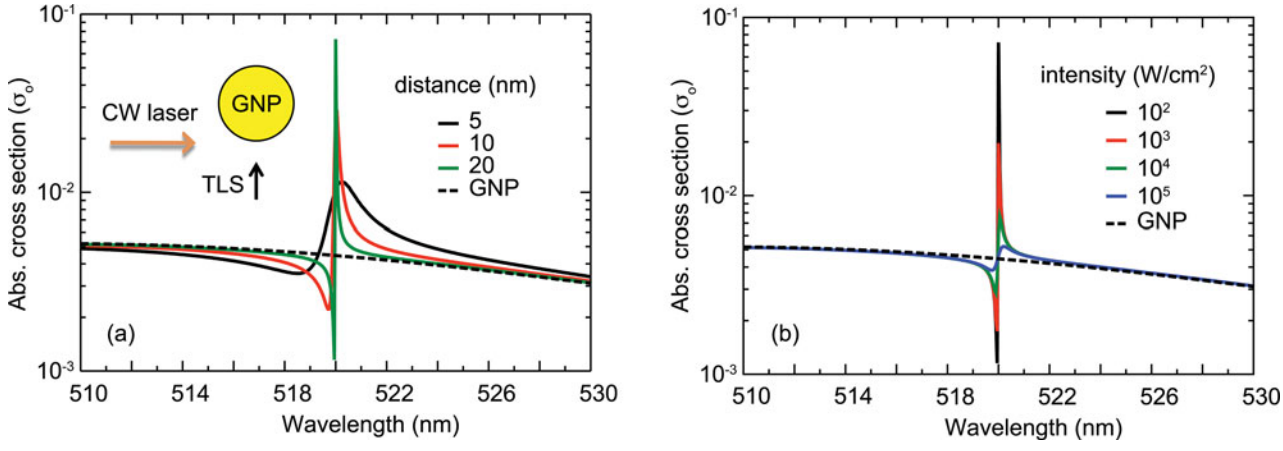

Figure 3. Absorption cross section for a TLS coupled to a 30 nm gold nanosphere (GNP), in units of $\sigma_o = 3\lambda^2/2\pi$, as a function of (a) distance and (b) power density. In (a) the intensity is 10^2 W/cm^2 and in (b) the distance is 20 nm. The dashed curves refer to the absorption cross section of the GNP without TLS. The latter is resonant at a wavelength of 520 nm and the intrinsic linewidth corresponds to a lifetime-limited transition. The continuous wave (CW) incident laser, the TLS and the GNP are sketched in (a).

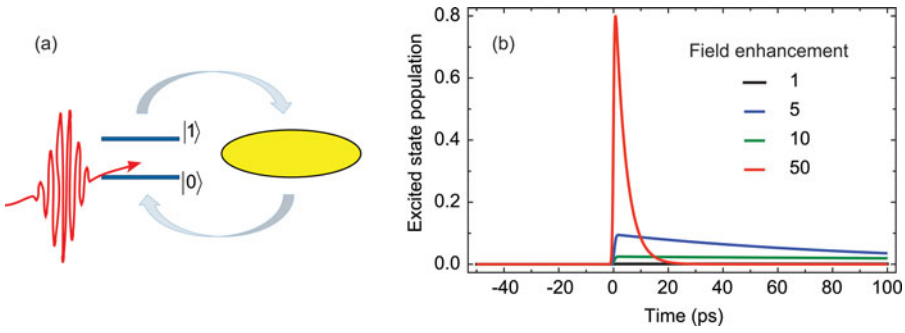

Figure 4. (a) Sketch of an ultrashort pulse interacting with a TLS coupled to an optical antenna. $|0\rangle$ and $|1\rangle$ are the ground and excited states of the TLS, respectively. (b) Excited state population as a function of time and field enhancement. The incident pulse has a duration of 1 ps, an energy of 10 optical photons and it is focused to the diffraction limit. The TLS has a transition wavelength of 600 nm, $T_1 = 10$ ns and $\Gamma_2 = 100$ GHz. The presence of an optical antenna is parametrised by a field enhancement ξ and a decay rate enhancement $|\xi|^2/\eta_a$, where $\eta_a = 1$. We remark that $\eta_a = 0.5$ leads to similar results.

of quantum coherence in atomic and molecular physics. Here it embodies the coherent interaction between the TLS and the optical antenna. A series of recent investigations show that it strongly depends on distance, optical antenna and emitter parameters, which lead to distinctive interaction regimes and phenomena [77].

The calculations are based on modified optical Bloch equations derived from the Heisenberg equations of motion under the Markov approximation [77],

$$\langle \dot{\hat{S}} \rangle = (-\Gamma_m + i\delta_L)\ \langle \hat{S} \rangle - i\frac{\Omega}{2}\langle \hat{\sigma}_z \rangle, \tag{4}$$

$$\langle \dot{\hat{\sigma}}_z \rangle = i(\Omega\langle \hat{S}^+ \rangle - \Omega^*\langle \hat{S} \rangle) - \Gamma_m(1 + \langle \hat{\sigma}_z \rangle), \tag{5}$$

where $\hat{S}(t) = \hat{\sigma}(t)\exp(i\omega t)$, $\delta_L = \omega_L - \omega_o$ is the frequency detuning, which implicitly includes the Lamb shift. $\Omega = 2\mathbf{d}\cdot\mathbf{E}_L/\hbar$ is the complex Rabi frequency, where $\mathbf{E}_L$ is the driving laser field, and

$$\Gamma_m = \frac{2\omega_o^2}{\epsilon_0\hbar^2}\mathbf{d}\cdot \mathrm{Im}\mathbf{G}(\mathbf{r}_o, \mathbf{r}_o, \omega_o)\cdot\mathbf{d} \tag{6}$$

is the modified decay rate of the excited state [78]. Equations (4) and (5) may be easily extended to deal with dephasing and non-radiative processes.

Note that $\hat{\mathbf{f}}(\mathbf{r}', \omega)$ reside in the optical antenna, where $\epsilon_i(\mathbf{r}, \omega) \neq 0$, and they are space dependent due to the presence of noise currents [79]. Another challenge is extending this quantisation scheme to input/output relations for treating an open quantum system driven by non-classical states of light [80]. This interaction regime places a number of fundamental and practical questions on light-matter interaction, quantum optics and spectroscopy, because large coupling efficiencies make a TLS a single-photon turnstile device, where the response to an incident photon is regulated by the presence of another photon [81,82].

3.2. *Interaction with ultrashort light pulses*

Coherent dynamical processes concern the interaction of short pulses with a TLS coupled to an optical antenna. The latter is expected to affect the TLS response in three different ways: (1) adjust the emitter linewidth to that of the pulse by modifying the spontaneous emission rate; (2) enhance the cross section by increasing the radiative decay rate with respect to other dephasing processes; (3) improve the excitation through field enhancement. To gain an intuitive picture of these effects, we considered a classical field interacting with a TLS and used modified optical Bloch equations to describe the system dynamics [68] (see also Equations (4) and (5)).

Figure 4(a) sketches an ultrashort pulse incident on the composite system. Here the quantum degrees of freedom are represented by the ground and excited states of a TLS. A preliminary result that indicates how critical the antenna and the TLS parameters are in determining the excitation level is shown in Figure 4(b). The curves refer to the excited state population when a resonant 1 ps Gaussian pulse with an average number of 10 photons is tightly focused on the TLS. The excited state of the TLS has an intrinsic lifetime of 10 ns and a dephasing rate of 100 GHz. When the field enhancement increases, corresponding to a situation where the optical antenna is closer to the TLS, the excitation probability gets larger and the excited-state lifetime becomes shorter. This may give rise to ultrafast nonlinearities that require a tiny amount of energy ($\sim$ aJ) notwithstanding the presence of strong dephasing. Such finding holds great promise for the implementation of nonlinear spectroscopy on individual systems near room temperature.

3.3. *From optical antennas to nanofocusing*

To pursue these ideas experimentally one needs to pay attention to a number of important practical aspects. First, the antenna should exhibit a strong field enhancement, a large radiation efficiency, and a high throughput in the

excitation/collection channel to obtain controllable few-photon interactions. Second, the experimental setup should allow a precise control of the coupling *on the same nanostructure*. We have recently proposed a high-throughput SNOM that fulfils these requirements [83,84]. The desired probe is a truncated metal nanocone with a high aspect ratio that is able to adiabatically focus surface plasmon-polariton waves down to nanoscale spots [85,86] (see the sketch in Figure 5(a)). We point out that contrary to conventional SNOMs our system can deliver 70% of far-field optical energy to the near field of the tip.

Nanofocusing presents some important, if not crucial, advantages from the experimental point of view. First, it is a non-resonant process, hence its bandwidth is larger, the sensitivity to fabrication imperfections is smaller and resonance shifts due to nearby dielectric interfaces are negligible. Second, the incident light is backreflected at the cone tip. Therefore, the scheme could be used in collection mode for homodyne detection as in a transmission experiment [88,89]. Third, nanofocusing substantially reduces background noise (fluorescence and scattering) as it spatially decouples the incident focused beam from the probe volume [84].

Our aim is to combine coherent spectroscopy with nanofocusing to explore how it may expand the detection limits of nanoscale objects, with particular attention on the competition between the enhancement of light-matter interaction with damping and dephasing processes. We have recently investigated the unique features of scattering under nanofocusing and derived expressions for the visibility and the phase shift caused by a point-like polarisable object placed in the near-field of the nanocone sharp end [89]. In subsequent studies, we are treating matter at the quantum level. Here the other important points of concern are saturation effects. Figure 5(b) displays a few femtoseconds pulse nanofocused by a gold nanocone (see Figure 5(c) for an SEM image of a nanofabricated structure). The field intensity increases by orders of magnitude, while the pulse does not exhibit significant dispersion. Then, it excites a thin film made of TLSs, which responds with the nanoscale coherence profile shown in the inset of Figure 5(b).

3.4. *Towards multidimensional coherent nanoscopy*

The previous discussion helped understanding how recent advances in nano-optics pave the way to the investigation of

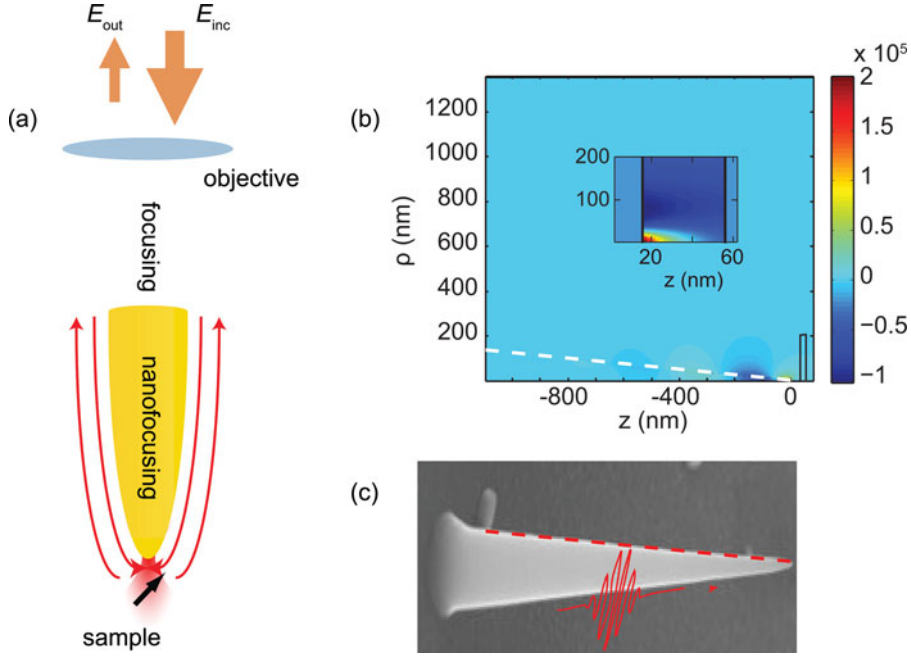

Figure 5. (a) Sketch of the nanofocusing principle and coupling with a nanoscale object. The incident field E_{inc} is focused on the nanocone base, where it excites surface plasmon-polariton waves that propagate to the tip (converging line arrows). There they interact with a sample and are backreflected towards the nanocone base (diverging line arrows), which eventually radiates a field E_{out}. (b) Longitudinal field component (E_z) of an incident femtosecond pulse. The dashed white line delimits the cone, with length 2000 nm, base radius 195 nm, tip radius 5 nm. Inset: Coherence induced by the pulse on a thin film made of TLSs near the cone tip. The zone between the thick vertical lines corresponds to a zoom-in of the small rectangular area delimited in the figure close to $z = 0$. Film parameters: thickness 40 nm, distance from the tip 20 nm, resonance wavelength 740 nm, $T_1 = T_2 = 25$ fs. The graphs display a cut in the radial dimension ρ. (c) Scanning electron microscope (SEM) image of a gold nanocone attached to an AFM cantilever (courtesy of Prof. Di Fabrizio, see also Ref. [87] for an overview on related nanofabrication strategies). The red dashed line corresponds to the white one in (b) to help associate the nanocone geometry with the nanofocusing process. Moreover, a fs pulse (red curve) is added to exemplify the field profile in (b).

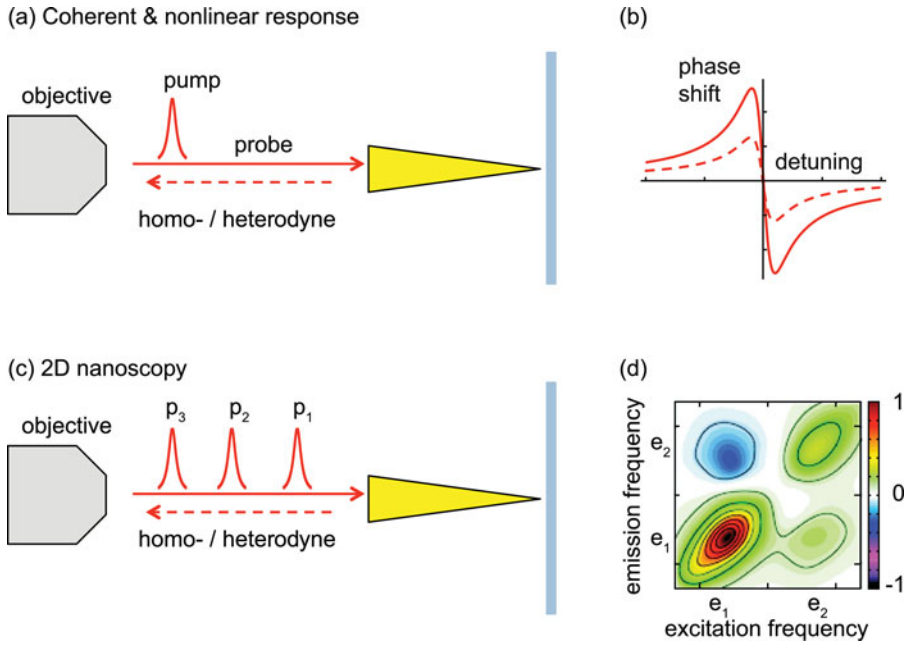

Figure 6. (a) Schematics of linear and nonlinear quantum-optical experiments with nanofocusing. An ultrashort pulse dynamically regulates the phase of a probe beam by pumping a saturable absorber placed near the nanocone tip. (b) Dynamical control of the phase shift: without (solid curve) and with (dashed curve) control beam. (c) Schematics of the proposed 2D nanoscopy. The position of the pulses p_i indicates time ordering. t_1 is the time between p_2 and p_1, t_2 the one between p_3 and p_2 and t_3 is the time between the read-out pulse and p_3. Since the pulses are collinear, we apply phase cycling to select the appropriate contribution to the nonlinear response [93,94]. (d) Example of a 2D spectrum of two coupled TLSs. The excitons e_1 and e_2 are superpositions of the original excited states, which split due to mutual coupling (Reprinted with permission from Ref. [95]. Copyright 2009. American Chemical Society).

quantum-optical phenomena under unexplored settings. To conclude, we would like to briefly discuss a few schemes that may enable their experimental study and also translate coherent, ultrafast and nonlinear spectroscopy into a powerful tool to explore nanoscale matter down to its quantum constituents.

We first focus on coherent control of the phase of a laser beam. This task may be effectively performed by a quantum emitter if the beam is tightly focused [90–92]. Therefore, we intuitively expect that nanofocusing be able to attain a comparable effect on systems that weakly interact with light because of dephasing, as recently verified by theoretical calculations [89]. The phase shift shall be detectable in homodyne measurements, where a reference beam of known intensity and phase is split in two parts. One is nanofocused and the other one interferes with the photons scattered by the sample, as exemplified in Figure 6(a). Next, based on the predictions of Figure 4(b) one may explore ultrafast few-photon nonlinearities by sending a weak ps/sub-ps pulse to dynamically regulate the phase shift on the probe beam (see Figure 6(a) and 6(b)).

These demonstrations would have immediate implications for advanced techniques, such as time-resolved, nonlinear and multidimensional spectroscopy. The latter has the advantage of combining time resolution (sub-picosecond scale) with the ability to directly observe and quantify couplings between quantum states involved in dynamical processes [95–99].

In its most general form, a two-dimensional (2D) spectroscopic experiment utilises a three-pulse arrangement where the third-order polarisation is measured by heterodyning it with a replica of the laser pulse (the so-called local oscillator) [99]. Ideally, if the pulse duration is short enough with respect to the internal dynamics of the sample, the measured signal yields directly the response function

$$S^{(3)}(t_3, t_2, t_1) \propto \int_0^\infty \mathrm{Im}(E_0(t)P^{(3)}(t))\,\mathrm{d}t. \qquad (7)$$

The times t_3, t_2 and t_1 are controlled by the experiment (see Figure 6(c)). Here $P^{(3)}$ is the nonlinear polarisation, whereas E_0 represents the local oscillator electric field. In 2D spectroscopy, $S^{(3)}$ is transformed into frequency domain with respect to the coherence times t_1 and t_3, while the waiting time t_2 gives dynamical information about the probed system. In particular, the existence of cross peaks in the 2D spectrum signifies the coupling between different excitations (see Figure 6(d)).

Multidimensional spectroscopy however lacks the ability to investigate single nanostructures due to difficulty in nonlinear interactions and it is unable to provide spectroscopic maps that resolve the complexity of nanocomposite

materials, although recent attempts have improved the resolution [100]. Therefore, the possibility of observing cross peaks and their transient behaviour, under schemes analogous to the one proposed in Figure 6(c), may provide invaluable information about electronic coupling strengths, coherence and population transfer or even structural changes at the nanoscale.

In coherent nonlinear spectroscopy a phase-matching geometry based on momentum conservation is used to collect and identify photons from the desired multidimensional process among isoenergetic photons resulting from other pathways. Furthermore, the fact that optical nonlinearities are weak demand for large sample volumes in order to obtain a sufficient signal to noise ratio [95,99]. At the nanoscale, the tiny probed volume may still give rise to a measurable response function because nonlinear interactions may be enhanced by orders of magnitude [101]. However, the phase-matching condition is relaxed and other solutions need to be implemented to select the desired nonlinear process. In this regard, we believe that phase cycling with collinear beams, already proposed and tested in conventional multidimensional spectroscopy [93,94], would be a promising approach for multidimensional nanoscopy as well. An additional benefit in the use of collinear beams is that all pulses are nanofocused (see Figure 6(c)), hence the enhancement of the nonlinear interaction is maximal.

4. Outlook

The coherent optical access of individual quantum systems in a realistic environment above cryogenic temperatures as well as the possibility to monitor and control quantum coherence under conditions where dephasing processes occur at very short time scales has been a longstanding challenge in physics and chemistry since the onset of single-molecule spectroscopy [8,102,103]. It represents a milestone in our ability to harness light-matter interaction and it paves the way to a deeper understanding as well as to the possibility of quantum engineering photo-induced physico-chemical processes. In the future, we aim at overcoming this barrier by advancing state-of-the-art experimental capabilities and developing theoretical techniques to quantitatively investigate these phenomena, including more realistic descriptions of molecular systems coupled to nanoscale optical fields [104–106].

Single-photon nonlinearities play an important role in quantum photonic technologies. In this context, it has been pointed out that photonic nanostructures could be exploited to enhance quantum nonlinear processes. For instance, a single-photon transistor could be attained based on the efficient coupling between a quantum emitter and a nanoscale optical field [107]. Several groups are indeed planning to couple photonic nanostructures with quantum emitters at low temperatures to demonstrate these proposals. Our ambition is to make a realistic attempt towards few-photon nonlinear optics above cryogenic temperatures, which would represent a breakthrough in classical and quantum information science, and also pave the way to extremely sensitive nonlinear spectroscopy. Furthermore, establishing a strong and ultrafast coherent interface with light and single quantum systems at ambient conditions may enable the experimental investigation of exquisite quantum phenomena under unexplored settings [108,109], hence opening new chapters in quantum optics as well as addressing the role of quantum physics into other areas of science and technology [14,110].

These efforts will also lay the ground for the investigation of innovative functional materials (e.g. diamond nanostructures, graphene, hybrid organic/inorganic) through the development of novel approaches at the interface between quantum optics, nano-optics and advanced spectroscopy. Most notably, we envision that coherent multidimensional spectroscopy may become capable of operating on individual nanostructures or even molecules, as well as single domains in nanocomposite media. For example, it could answer fundamental questions related to light absorption and charge transport in polymer blends, with immediate input for the rational design of organic solar cells [111]. In addition, the understanding of light-harvesting complexes may be largely improved by the possibility to address them one by one with multidimensional spectroscopic techniques, especially for what concerns the role of quantum coherence in energy transfer [112].

In summary, ultrafast coherent nanoscopy promises an unprecedented insight on ultrafast coherent phenomena in nanoscale matter. Significant input towards quantum engineering of energy harvesting and conversion, molecular functional materials and photochemical reactions, to cite a few, is expected. Furthermore, the application of advanced nanoscopy on single quantum systems may disclose additional information on the role of decoherence and more specifically on the possibility of pushing quantum technologies towards ambient conditions. Improved know-how in this domain will open up new fields of research with relevance to physics, chemistry and materials science.

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