The plasmon band in noble metal nanoparticles: an introduction to theory and applications

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Noble metal nanoparticles chemistry is a domain in rapid expansion, as those objects lead to interesting applications in the fields of catalysis, biosensing, electronics and optics. Because of their structure, intermediate between that of molecules and of bulk material, they enable to bridge the gap between molecular chemistry and surface science. In particular, their optical properties, known since antiquity, have already shown a part of their potential and further major discoveries can reasonably be expected. Their most insightful optical properties rely on a strong absorption in the visible spectrum, called the plasmon band, that colloidal solutions of gold, silver or copper feature. Herein we wish to present a comprehensible overview of the fundamentals of the theories explaining the phenomenon dedicated to chemists seeking an introduction to those features. We will also give a brief review of the recently published body of relevant literature with reference to the aforementioned theory.

Introduction

The first syntheses of metallic gold nanoparticles (NPs) most probably date back to the 5th or 4th century BC where gold specimens were reported in China and Egypt.[1] Since then, they have been exploited for both their curative and aesthetic properties. We will not focus here on the first aspect that made some alchemists see in gold colloidal solutions, called aurum potabile,[2] the elixir of youth. More interesting are their optical properties that were exploited for coloration of glass,[3] ceramics, china[4] and pottery.[5] One of the most fascinating examples of this technology is probably the famous Lycurgus cup which can be seen in the British Museum in London.[6] This object, crafted by the Romans in the 4th century, features an amazing property of changing colour depending on the light shed on it. Reflected light makes it appear green, whereas in transmission a bright red colour can be seen. Work of Barber evidenced the presence of mixed Au–Ag particles of approximately 70 nm in the glass matrix of the vase, the fact that the metal was an alloy of gold and silver being crucial for obtaining the scarlet red colour.[7,8] The optical properties of gold NPs indeed filled Faraday with enthusiasm when he

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reported in 1857 the synthesis of colloidal solutions of gold exhibiting colours ranging from ruby red to amethyst.[9] He started to list the factors impacting the colour of those solutions and evidenced that "the mere variation in the size of particles gave rise to a variety of resultant colours." Many applications of this property have arisen recently, leading to a plethoric bibliography. The subject is indeed so fashionable that a recent article of the New York Times focused on it.[10]

Besides their optical properties, noble metal nanoparticles have found applications in many different fields such as biochemistry, sensing science or catalysis. For example, gold nanoparticles immobilised in oxide matrixes are known to be active oxidation catalysts and devices using this technology are now commercialised in Japan for anti-odour systems.[11]

Nanoparticles or clusters, are defined as particles composed of a certain number of atoms ranging from 3 to 10^7.[12] Because of their size, they feature properties that are neither those of molecules, nor those of the bulk material. The surface plasmon band (SPB) is a strong and broad band observed in absorption in the UV-visible spectrum for metallic NPs bigger than 2 nm. This absorption is also referred to as Mie resonance from the name of one of the most prominent contributors to the SPB theory: Gustav Mie.[12] For smaller clusters, quantum effects are predominant and no SPB is observed. All metals feature this property. However, the series Au–Ag–Cu exhibits very intense SPBs that partly explains, alongside the ease of their synthesis and their robustness, the success of gold and silver NPs in this field. The position, the shape and the intensity of the SPB strongly depends on various factors: the dielectric constant of the surrounding medium, the electronic interactions between the stabilising ligands and the nanoparticle, which alter the electron density inside the nanoparticle and the size, shape and monodispersity of the NPs.

There are indeed other types of plasmonic signals, such as the surface plasmon band produced by metallic films, in reflection or transmission, some of them being called plasmon polaritons. Though the resulting physics is extremely exciting and the recent discoveries numerous, the present article will not discuss this matter further.

In recent years, many points of view were adopted by both chemists and physicists in order to give a clear description of the SPB and on the main factors impacting its position, intensity and broadness. The book of Kreibig and Vollmer gives a broad overview of the main existing plasmon band theories,[12] whereas Liz-Marzán recently wrote a comprehensive and well illustrated review focussing on Mie and effective medium theory.[13] Schatz and co-workers proposed methods to solve the Maxwell equations in order to describe the optical properties of NPs with arbitrary shape.[14] Other papers are specifically concerned with explaining given features such as the size dependence of the plasmon band width[15] or localized plasmon bands.[16] In the present review, we intend to explain as simply as possible the physics behind the phenomenon, using the two traditional theories: the Drude–Maxwell model and the theory exposed by Mie. This then leads to the present studies made to correlate the position, intensity and shape of the SPB with various factors. Interesting and insightful applications in various domains such as chemo- and bio-detection or electronics are then discussed.

Physical aspects

The surface plasmon band (SPB) is a phenomenon observed in transmission, due to the presence of nanoparticles, in solution or in the solid phase. For a special domain of frequency, nanoparticles interact with incident light, resulting in a global scattering of it. This macroscopic feature can be explained by the collective resonance of the conduction electrons of the nanoparticle. In order to understand this, one needs to evaluate all the parameters of the material and especially its dielectric constant. Usually, this quantity is approximated to that of the bulk metal (although it implies neglecting confinement effects and defects induced by edges or impurities): a study of electrostatics in bulk metal, using the Maxwell equations, is thus required. To express the dielectric constant as a function of known parameters, this theory needs to be completed by the Drude model, which describes the motion of free electrons in a metal. Then the question of the nanoparticles will be addressed: the conditions for conducting electrons resonance will be determined by several means. The ultimate goal will be the determination of the frequency of the absorption maximum (denoted ω_M, the frequency of the Mie resonance), the height of this maximum and the width of the peak. This electronic motion is specific of nanoparticles due to geometrical confinement effects of the free electrons. Indeed a nanoparticle can be seen as an immobile and periodical cationic network in which a cloud of conducting electrons move. The latter are usually considered as free electrons. NPs dimensions are very small compared to the wavelength of the UV-visible light for which the phenomenon is observed and also comparable to the mean free path of electrons. The SPB is due to the resonance of the electronic cloud with the incident wave and the mechanics of this phenomenon can be evaluated.

Determination of the dielectric constant $\varepsilon(\omega)$

Whatever way is chosen for solving the problem, one needs to know the expression of the dielectric constant of the bulk metal $\varepsilon(\omega)$. This value can be obtained phenomenologically or with the help of electroelectrostatics.[14] In the latter case, the Drude theory has been used. Besides, the Drude calculation offers an insight into the motion of electrons in metals, which is the quintessence of plasmon absorption.

Electromagnetism in the bulk metal

The Maxwell equations (eqn (1)–(6)) describing the propagation of an electromagnetic wave in a metal[17] link the electric field $\boldsymbol{E}$, the magnetic induction $\boldsymbol{B}$, the electric polarisation $\boldsymbol{P}$, the electric displacement $\boldsymbol{D}$, the magnetisation $\boldsymbol{M}$, the permittivity ε_0 and permeability μ_0 of free space; ε_∞ is the dielectric constant of the medium. The electrical current $\boldsymbol{j}$ and the current density ρ are usually that of free electrons.

$$\mathrm{div}\,\boldsymbol{B} = 0 \tag{1}$$

$$\mathrm{div}\,\boldsymbol{D} = \rho \tag{2}$$

$$\mathrm{rot}\,\boldsymbol{E} + \partial\boldsymbol{B}/\partial t = 0 \tag{3}$$

$$\mathrm{rot}\,\boldsymbol{H} = \boldsymbol{j} + \partial\boldsymbol{D}/\partial t \tag{4}$$

with

$$\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P} = \varepsilon_0\varepsilon_\infty\boldsymbol{E} \tag{5}$$

$$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M}) \tag{6}$$

Equations can be simplified stating: $\rho = 0$ (there is no charge accumulation in the metal) and $\boldsymbol{M} = 0$ (the medium considered does not retain magnetisation). To fully describe the system, we need to implement the Joule rule, linking $\boldsymbol{j}$ to $\boldsymbol{E}$ (eqn (7)):

$$\boldsymbol{j} = \sigma\boldsymbol{E} \tag{7}$$

Here σ is the conductivity of the medium. σ and ε_∞ are phenomenological coefficients dependent on the medium (supposed homogeneous and isotropic) and the frequency. Using eqn (3) and (4), the calculation of the double curl of $\boldsymbol{E}$ gives a new relation (8).

$$\begin{aligned}\mathrm{rot}(\mathrm{rot}\,\boldsymbol{E}) &= \mathrm{grad}(\mathrm{div}\,\boldsymbol{E}_{=0}) - \nabla^2\boldsymbol{E} = -\mu_0\sigma(\partial\boldsymbol{E}/\partial t)\\ &\quad - \mu_0\varepsilon_0\varepsilon_\infty(\partial^2\boldsymbol{E}/\partial t^2)\end{aligned} \tag{8}$$

The form of the electric field $\boldsymbol{E}$ can be defined further. Its spatial and temporal components are supposed independent. The electric field is taken as being periodical. As any periodical signal can be decomposed in time-harmonic functions by the Fourier transform, we chose $\boldsymbol{E}(\omega) = \boldsymbol{E}_0\mathrm{e}^{-\mathrm{i}\omega t}$ (complex representation). With this form, (8) becomes (9).

$$\nabla^2\boldsymbol{E} = -\mu_0\varepsilon_0\omega^2\left[\varepsilon_\infty + \frac{\mathrm{i}\sigma(\omega)}{\omega\varepsilon_0}\right]\boldsymbol{E} \tag{9}$$

$$\nabla^2\boldsymbol{E} = -\mu_0\varepsilon_0\omega^2\boldsymbol{E} \tag{10}$$

Eqn (9) has the same form as that of a wave propagating in the free space (10), but with ε_0 replaced by $\varepsilon(\omega)$ (expressed in eqn (11)).

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\mathrm{i}\sigma(\omega)}{\omega\varepsilon_0} \tag{11}$$

$\varepsilon(\omega)$ is the frequency dependent dielectric constant of the medium in the presence of a wave. Incident light causes a change in the metal behaviour that is thus taken into account. This value is complex, which expresses the fact that the wave and the response are not necessarily in phase.

Drude theory of free electrons

Although the problem in free space can be solved completely, it is much more complicated in other media as $\varepsilon(\omega)$ and $\sigma(\omega)$ have to be fully expressed. Experimental values have been determined for this but many theories have also been developed. Among them, the Drude theory describes the mechanics of the electrons inside a metal. Electrons are considered as free and independent. The motion of a whole cloud is then the sum of the motion of the individual electrons: the coupling between them is thus considered as maximum, electrons acting all in phase.[12] The motion of one electron is described by eqn (12) where m_e stands for the effective mass of the electron (taking into account the presence of a positively charge background), v is the electron speed and e the charge of the electron:

$$m_\mathrm{e}(\mathrm{d}v/\mathrm{d}t) + m_\mathrm{e}\Gamma v = e\boldsymbol{E} \tag{12}$$

the second term is a viscous friction due to different factors such as free electron inelastic collisions but also electron phonon coupling, defects, impurities, *etc.*[18] Γ is the corresponding damping constant, m_e and e the electron mass and charge, respectively. The second term is the force due to the electric field. Compared to that of the electric field, the force exerted on the electrons by the magnetic field is negligible. This approximation is justified since electrons are moving very slowly compared to light. It is stated again that $\boldsymbol{E}(\omega) = \boldsymbol{E}_0\mathrm{e}^{-\mathrm{i}\omega t}$. Then v will also be sinusoidal ($v = v_0\mathrm{e}^{-\mathrm{i}\omega t}$) and (12) becomes (13):

$$(-\mathrm{i}\omega m_\mathrm{e} + m_\mathrm{e}\Gamma)v_0\mathrm{e}^{-\mathrm{i}\omega t} = e\boldsymbol{E}_0\mathrm{e}^{-\mathrm{i}\omega t} \tag{13}$$

hence

$$v_0 = \frac{e}{m_\mathrm{e}\Gamma - \mathrm{i}\omega m_\mathrm{e}}\boldsymbol{E}_0 \tag{14}$$

Then $\boldsymbol{j}$ can be expressed as resulting from the individual motion of all electrons, with n, the electron density (eqn (15)).

$$\boldsymbol{j} = env = \frac{ne^2}{m_\mathrm{e}\Gamma - \mathrm{i}\omega m_\mathrm{e}}\boldsymbol{E}_0 = \sigma(\omega)\boldsymbol{E}_0 \tag{15}$$

$$\sigma(\omega) = \frac{ne^2}{m_\mathrm{e}\Gamma - \mathrm{i}\omega m_\mathrm{e}} \tag{16}$$

$\sigma(\omega)$ has then the form given by eqn (16). Injecting eqn (16) in (11), one can express the dielectric constant as a function of known constants: ε_∞, n, e, m_e and ε_0, of the frequency ω and of Γ (eqn (17)). Γ is a phenomenological parameter that is usually fitted utilising experimental data.[18–20]

$$\begin{aligned}\varepsilon(\omega) &= \varepsilon_\infty - \frac{\omega_\mathrm{P}^2}{\omega^2 + \mathrm{i}\omega\Gamma}\\ &= \varepsilon_\infty - \frac{\omega_\mathrm{P}^2}{\omega^2 + \Gamma^2} + \mathrm{i}\frac{\omega_\mathrm{P}^2\Gamma}{\omega(\omega^2 + \Gamma^2)}\end{aligned} \tag{17}$$

$$\omega_\mathrm{P}{}^2 = ne^2/\varepsilon_0 m_\mathrm{e} \tag{18}$$

Determination of the resonance conditions

Let us consider the case of nanoparticles. The idea is to determine the conditions for which the electron cloud will resonate. For that purpose, the expression of the dielectric constant found for the bulk will be used. Several postulates then become incorrect, but are kept as approximations: for example, $\rho = 0$, as in small particles the electron density is no longer uniform: charges will accumulate at particle edges, as we will discuss further. Besides, because NP size is very small with regard to the wavelength, one can consider that all the electrons confined in a nanoparticle see the same field at a given time t:[12] the electric field is considered as independent of the position. This hypothesis is called the quasi-static approximation. The displacement of the electron cloud under the effect of the electric field leads to the creation of surface charges, positive where the cloud is lacking, negative where it is concentrated (Fig. 1).[12] This aspect of the problem justifies the use of the term "surface" in the designation of the global phenomenon. However, one has to keep in mind that all the electrons are moving collectively while under the effect of the field. Such collective oscillation leads to plasmon polaritons,[3] in contrast to free plasmons occurring in the bulk metal.[12] The

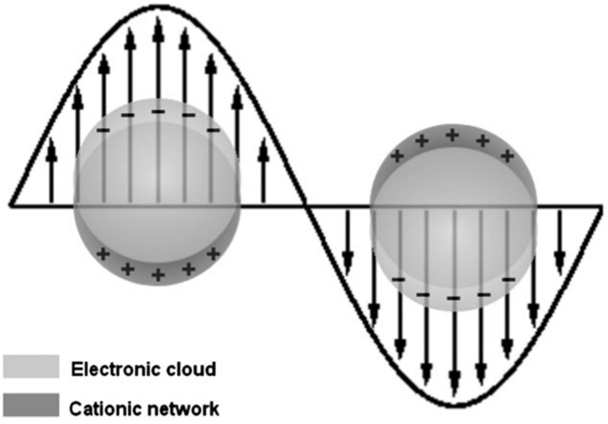

Fig. 1 Schematic description of electronic cloud displacements in nanoparticles under the effect of a electromagnetic wave.

notation "plasmon" was proposed by Shopper, in analogy to the bounded gaseous plasmon oscillations.[12] This dipolar charge repartition imposes a new force on the electron cloud. The electrons undergo a restoring force which conflicts with the external electric field. The position, x, of an electron placed in the oscillating cloud of a nanoparticle is then governed by eqn (19) where K is the restoring force.

$$m_e \frac{d^2x}{dt^2} + m_e \Gamma \frac{dx}{dt} + Kx = e\boldsymbol{E} \tag{19}$$

This approach has never been used for solving the problem, but it is a good model for understanding the SPB. This equation describes the movement of a forced, damped harmonic oscillator. This problem is equivalent to classical mechanical oscillators. The solution of such an equation is known and given in (20) with ω_R ($\omega_R = (K/m_e)^{-1}$) being the Eigen frequency of the system. Like for the Drude problem, the displacement and the field are not, in general, in phase, x being complex.

$$x = \frac{e\boldsymbol{E}}{m_e(\omega_R^2 - \omega^2 - i\Gamma\omega)} \tag{20}$$

$$x = \frac{e\boldsymbol{E}}{m_e}\sqrt{\frac{1}{(\omega_R^2 - \omega^2)^2 + \Gamma^2\omega^2}}\, e^{i\Theta}, \quad \text{with } \boldsymbol{\Theta} = \tan^{-1}\frac{\Gamma\omega}{\omega_R^2 - \omega^2} \tag{21}$$

The amplitude of x reaches a maximum for $\omega \approx \omega_R$, where the height of this maximum is inversely proportional to Γ and the width at half maximum is proportional to Γ (provided that $\Gamma \ll \omega_R$).

Another way of considering the problem is to say that the electric field seen by the nanoparticle is the external one altered by the effect of the polarisability of the medium. Using the boundary condition in a spherical particle, the internal field $\boldsymbol{E}_i$ in a nanoparticle surrounded by vacuum is expressed in eqn (22).[12,21]

$$\boldsymbol{E}_i = \boldsymbol{E}_0 \frac{3}{\varepsilon(\omega) + 2} \tag{22}$$

This gives a condition of resonance, which occurs when $\boldsymbol{E}_i$ is maximum, hence when $|\varepsilon(\omega) + 2|$, *i.e.* $|\varepsilon_1(\omega) + 2|^2 + |\varepsilon_2(\omega)|^2$ is minimum ($\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$). Thus ω_M, the resonance frequency, verifies $\varepsilon_1(\omega_M) = -2$. With the relation (17), considering that $\varepsilon_\infty = 1$ and $\Gamma \ll \omega$, eqn (23) is obtained:

$$\varepsilon_1(\omega_M) = 1 - ({\omega_P}^2/{\omega_M}^2) = -2, \text{ hence } \omega_M = \omega_P/\sqrt{3} \tag{23}$$

The description we have made of the phenomenon thus far is very simple: we envisaged one isolated, spherical nanoparticle in vacuum with several hypotheses such as $\varepsilon_\infty = 1$ and $\Gamma \ll \omega$. This is of course wrong, but the virtue of this model is to give a good insight into what happens physically: the electron cloud oscillates under the effect of incident light. The restoring force is provided by the surface charges formed at the edge. The value of the resonance frequency is given with a good approximation by eqn (23).[12]

Maxwell–Garnett, Debye and Mie theories

Historically the first approaches for describing interactions between light and nanostructures were published in the very beginning of the XXth century, some sixty years before those theories started to be exploited in the field of nanochemistry. These approaches enabled the complete description of the problem without having to proceed to complicated approximations. First in 1904–1905, Maxwell–Garnett described the so called "Effective medium theory".[22,23] The model developed gives the expression of the dielectric constant within a matrix (dielectric constant ε_m) containing small metallic spheres, provided that the size of the spheres is small compared to the wavelength and the material under consideration has a spatial extension larger than the wavelength. The spheres are seen as small Hertzian doublets that provides the polarisability of the medium. Thanks to the Maxwell equations and the expression of the electric field caused by a sphere, the average dielectric constant ε_{av} is given in eqn (24), where ϕ stands for the volumic fraction of the embedded particles and ε_∞ and ε_m are the dielectric constant of the metal and the embedding medium, respectively.

$$\varepsilon_{av} = \varepsilon_m\left(1 + \frac{3\phi\beta}{1 - \phi\beta}\right), \text{ with } \beta = \frac{\varepsilon_\infty - \varepsilon_m}{\varepsilon_\infty + 2\varepsilon_m} \tag{24}$$

This way of solving the problem rationalises the colours of different glasses containing copper, silver or gold particles. In this case wavelength dependence is taken into account by using the experimental values of ε_∞ and ε_m as they are expressed by Drude for each given wavelength. It is worth stressing here that the effect does not depend on the size or shape of the nanoparticles, as it is only the respective volume of nanoparticles and surrounding medium that is taken into account.

A few years later Debye developed another approach to the same problem. He envisaged the impact of light on nanoparticles as if light exerted a mechanical pressure on it.[24] This very elegant theory unfortunately lacked applications, mainly because of the difficulties encountered for measuring such a weak pressure at that time.[12] However, the most popular theory is without contest the one Mie published in 1908.[25] The problem was treated as a genuine scattering one. Indeed, the result of the SPB is a global absorption of the medium. Maxwell's equations were used for spherical particles embedded in a medium, boundary conditions being adequately chosen. The drawback of this arises in the fact that it is difficult to acquire an intuitive feeling of the physical phenomenon beyond the mathematics.[17] The power of this method though was that it divided the problem into two independent parts: the electromagnetic one, which could be totally solved, on one hand and the material one, which requires the determination of the dielectric constant $\varepsilon(\omega, R)$.[12] The latter obviously depends on ω, but also on R, the medium radius of particles. This approach enables to implement all important cluster effects *via* this phenomenological value. This constant could indeed be evaluated both by a theoretical approach or by experimental measurements.

The scattering approach leads to the following expression for the cross section C_{ext} (25).

$$C_{\text{ext}} = \frac{24\pi^2 R^3 \varepsilon_{\text{m}}^{2/3}}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_{\text{m}})^2 + \varepsilon_2^2} \qquad (25)$$

This quantity reaches a maximum for $\varepsilon_1 = -2\varepsilon_{\text{m}}$. We find here the condition furnished by the Drude treatment (eqn (23)) stating that $\varepsilon_{\text{m}} = 1$.

It is also very important to underline that the SPBs we are discussing here are of first order, which means that we only consider dipolar resonances. However, multipolar oscillations are also possible, as predicted by Mie,[25] and are indeed of great importance for addressing specific questions.[26–28]

Numerical methods

The above described theories are easily applicable to non-interacting and spherical shaped particles. To describe the absorption behaviour of more complex structures various numerical methods have been developed. Among them, discrete dipole approximation (DDA) and the finite difference time domain method (FDTD) have been intensively employed.

In DDA,[14,29] the whole particle and its environment are divided into elementary cubic volumes each characterised by their position and their polarisability. If the box size is small enough, they can be considered as dipoles (no higher multipole polarisabilities have to be taken into account). The polarisation of each cubic box results from the local electric field in the box. This field can be seen as the sum of an external field (induced by incoming light) and the field induced by the polarisation of the surrounding boxes. Various numerical methods can then be used to determine the time dependent value of the electric field in the boxes. DDA thus permits a very precise mapping of the field enhancement induced by incoming light in resonating NPs.

FDTD, also relies on the use of a discrete mapping of the space to resolve the Maxwell Curl equations (eqn (3) and (4)) replacing all the derivatives by finite differences (including the time differences). As underlined by Oubre and Nordlander,[30] this method enables one to follow the time evolution of the local electric field using a highly time saving algorithm. Chris Oubre's personal Home Page displays some movies showing such time evolutions.[31]

Analysis of some specific properties of nanoparticles

The above described physical aspects provide mathematical tools to rationalise the behaviour of the NP SPB while varying several factors such as the dielectric medium, the composition, the charge, the size and the shape of the particles.

Effect of the dielectric environment

It is obvious from the expression of the Mie extinction cross section (eqn (25)) that the dielectric constant of the surrounding medium plays a predominant role in determining both the plasmon peak position and intensity (Fig. 2).[12,32] Changing the medium surrounding the NPs for another medium having a markedly different refractive index strongly alters the plasmon behaviour of the NPs. This is, for instance, evidenced by the strong shifts induced by transferring NPs from water or ethanol to a transparent oxide matrix.[33] However, more subtle effects can occur; Mulvaney *et al.* have shown that gold NPs surrounded with thin silica shells of increasing thickness first feature a red shift (with shell thicknesses from 0 to 20 nm), due to an increase of the local dielectric constant. It is only with thicker shells that the blue-shift, expected while diminishing the dielectric constant, is observed.[34]

As mentioned above, all these considerations are relevant only if the particles are sufficiently far apart from one another to consider they are not interacting. However, this is not always the case, especially when the NPs are embedded in a matrix,[35] linked by oligomers[36] or when they self-organise.[37–39] Working on the previously mentioned silica coated gold nanoparticles, Ung *et al.* managed to synthesise composite layers with a fine tuning of the interparticle distances.[40] The latter were directly controlled through the silica shell thickness. The colour of those layers vary strongly with this parameter (the shorter the distances the lower the resonance frequency) as can be seen in Fig. 3.

Fig. 2 Changing in the plasmon peak position induced by varying the solvent refractive index. Refractive indices of the solutions at the absorption band maximum are 1.336, 1.407, 1.481, 1.525 and 1.583, respectively.[32] Reprinted with permission from *Langmuir*, 1994, **10**, 3427. © 1994, American Chemical Society.

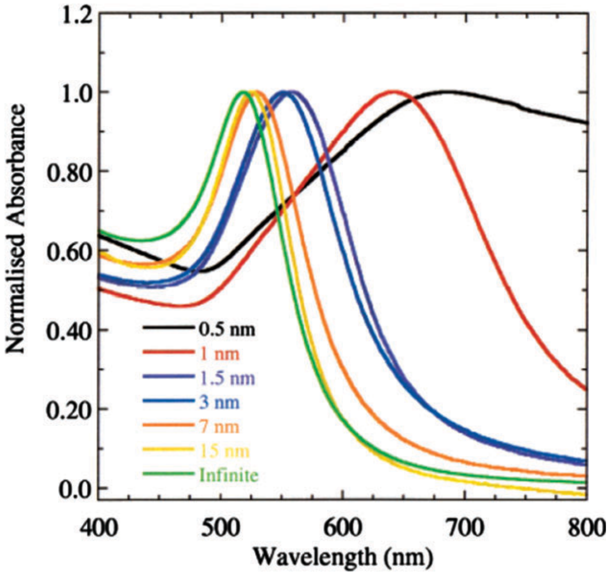

Fig. 3 Influence of the interparticle distance on the SPB position. From ref. 40. Reprinted in part with permission from *J. Phys. Chem. B*, 2001, **105**, 3441. © 2001, American Chemical Society.

In order to account for the observed red shifts, one still can use the usual solutions calculated for isolated NPs considering that the influence of the other NPs can be modelled as a modification of the medium dielectric constant (that thus becomes complex). This is the so-called effective medium theory.

A powerful approach to effective medium theory is to use the average electric constant of composite media, ε_{av}, defined by Maxwell–Garnet.[40] This way, the scattering properties of such systems can easily be derived from the theories presented above, provided that the dielectric constant of the surrounding medium, ε_M, is replaced by the average constant, ε_{av}. This approach proved to be very successful, as in the case of the films of Ung *et al.* the calculated peak positions fitted very well with the experimental data (Fig. 4).[40]

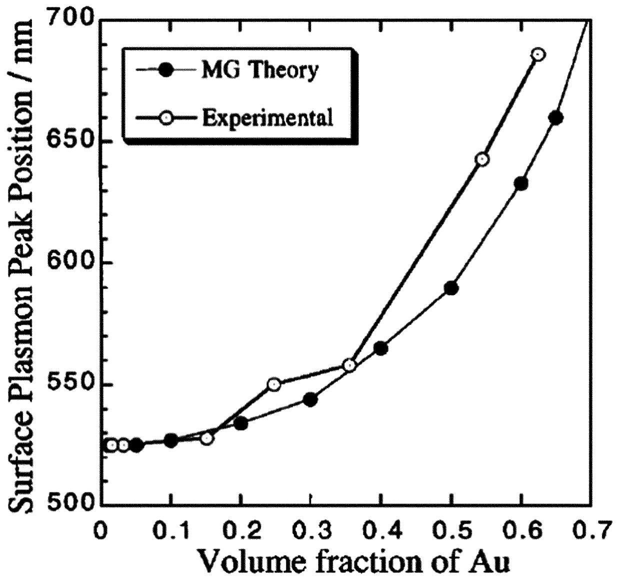

Fig. 4 Correlation between interparticle distance and plasmon position. Adapted from ref. 40. Reprinted with permission from *J. Phys. Chem. B*, 2001, **105**, 3441. © 2001, American Chemical Society.

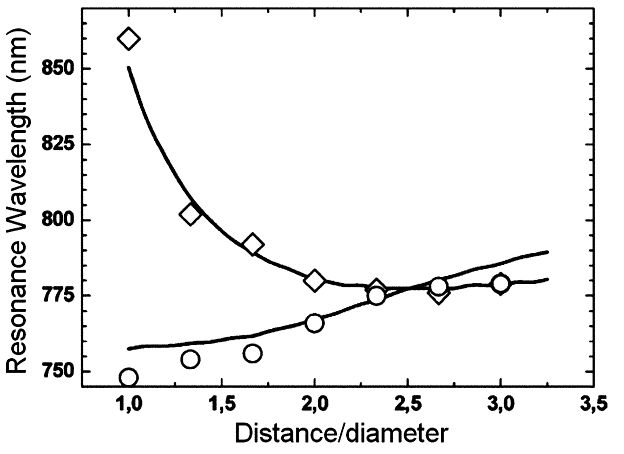

Fig. 5 Position of the plasmon absorptions of particle dimers *vs.* interparticle distance for the polarisation directions parallel (circles) and normal (squares) to the particle pair axis. Adapted from ref. 41. Reprinted with permission from *Opt. Commun.*, 2003, **220**, 137. © 2003, Elsevier.

When the coupling between the NPs is too strong however, effective medium theory cannot provide a good description of the observed phenomena. Such is the case for nanoparticle pairs deposited on a substrate, usually by nanolithography, the interparticle distance being monitored.[41–43] In that case, the optical response of the paired nanoparticles depends on the light polarisation axis, as can be seen from Fig. 5. The plasmon behaviour of those pairs can be very well reproduced using DDA calculations.[44] As any cubic element defined in this method can be of metallic or non-metallic type it is very easy to use it for calculating the behavior of NPs featuring complex shapes or interparticulate interactions. This very powerful tool, however, does not provide an intuitive view of the interaction between two neighbouring NPs. In order to understand the physical origin of the plasmon behaviour of a NP pair, plasmon hybridisation theory is much more convenient.[45] Indeed, in this model, oscillations of the conduction electrons, considered as an incompressible fluid, induced by incoming light only results in the appearance of a surface charge, which, in the case of a spherical particle, can be expressed as a spherical harmonic. A NP with more complex structure can be decomposed in its spherical components. The deformation of the whole particle electron cloud can then be modelled as resulting from the hybridisation of the spherical modes of its components.[46,47] Using this concept, the case of NP dimers is analogous to that of two atoms that interact through their molecular orbitals.[48]

Composition effects

The considered NPs are not necessarily constituted of one only element. Indeed alloy clusters and core–shell NPs have been described, all of these structures featuring new optical properties. The case of alloys seems to be the easiest to handle. Usually, a linear dependence of the absorption maxima with the molar ratio of the metals is found.[49–52] In Mie's approach no hypothesis was made on the chemical composition of the NP core. Introducing the dielectric constant of the alloy should allow a good modelling of the optical behaviour of those objects. El Sayed and co-workers, however, have nicely shown that the determination of the corresponding dielectric parameters was not an easy task.[53]

The case of core–shell nanoparticles[54] can be efficiently treated in the pure Mie model[55–57] but, again, plasmon hybridisation theory is more efficient for providing an intuitive view of the underlying phenomena.[47,58]

Electronic effects

According to eqn (23), the position of the plasmon band depends on ω_P, which itself varies as the square root of n, the electron density inside the NP. As a consequence, the plasmon band should be displaced upon adding or subtracting electrons to the overall metallic core. In earlier works, oxidation processes were carried out chemically[59] by the addition of free radicals[60] or under the action of dioxygen.[61] Chemical reductions similarly proceeded *via* the action of nucleophiles[62] or common reducing agents.[63] In all cases the increase (respectively, decrease) in electron density resulted in the postulated hypsochromic (respectively, bathochromic) shifts. Direct oxidation and reduction using electrochemical methods have been performed more recently.[64,65] The resulting devices are very promising for electro-optical applications.

The NPs in solution are rarely "naked". Their surface is, usually, covered with stabilising molecules, such as amines, thiols, phosphine, *etc.*, which, due to their affinity for the gold surface prevent the agglomeration and the further growth of the NPs.[1] By analogy with coordination chemistry these molecules are usually called ligands. A ligand shell, of course, strongly impacts the plasmon behaviour of NPs, first because it modifies the dielectric constant of the surrounding medium. Moreover, as these ligands interact electronically with the gold atoms, they also partially reduce or oxidise the NPs.[66] Such effects are well documented[33,67] and were rationalised in terms of ligand donating properties by Whetten and co-workers[68] In standard coordination chemistry, the electron density on the metal centre is not only directed by the ligands donating properties but also by their ability of back donation from the metal. Interestingly, the same is true for metallic NPs. Indeed, we reported that the use of phosphinine, the phosphorus equivalent of pyridine, which is well known for its strong π-accepting properties, resulted in a strong bathochromic shift of the plasmon band.[69]

Electron withdrawing effects may also partly explain the optical properties of so-called "nano-dumbbells" or "nano-snowmen".[70] Such objects consist of heterodimers of nanoparticles. The association of a metal oxide NP and a noble metal NP results in a red shift of the plasmon peak of the latter.[71] This can be rationalised considering that the oxide part deprives the noble metal NP from a part of its electron density.

We also recently evidenced that mixed ligand shell protected NPs with a bipolar repartition of their ligands featured strong hypsochromic shifts that could not be rationalised by standard SPB theories. This feature may rely on the Liebsch's spill-out effect (*vide infra*). Indeed, as both ligands did not have the same electronic properties their bipolar repartition polarised the NPs, inducing a stronger spill out of the electrons.[72]

Size and shape

The influence of the size of the NPs on the SPB is a question that has arisen very early. As the diameter R of the nanoparticles appears in its equation, the Mie SPB theory predicts a size dependence of the intensity of the SPB (eqn (25)). Position and bandwidth are also affected by R, but through intrinsic effects, which means that R modifies the expression of the dielectric constant of the metal and thus alters the resonance condition expressed as $\varepsilon_1 = -2\varepsilon_m$. Classically it is admitted that as NPs size becomes small enough (typically under 50 nm) the size of the NP becomes of the order of the mean free path, or even smaller, which strongly affects the dynamics of the system.[73] Many theories have been studied to correlate the size to the SPB position some predicting a blue shift, some a red one; others no shift at all, and Kreibig *et al.* reviewed them twenty years ago.[15] In fact, experimental results finally evidenced a blue shift of the SPB on decreasing the NPs size.[74,75] This result was subsequently rationalised by Liebsch.[76] For alkali metal NPs, the shift observed while decreasing the mean diameter is a red one. This can be explained by the fact that the electrons spill out of the cationic frame of the NPs and that thus the centroid of the fluctuating charge is located outside the metallic surface. On decreasing the size of the nanoparticle, spilling out electrons will have a bigger relative weight than the inner ones and then the SPB will be less energetic. In the case of noble metal, the existence of d electrons induce a mutual s–d polarisation. This mechanism is important enough to justify an inversion of the trend between simple and noble metals. In the same way, the bandwidth grows upon increasing the mean NPs size.[77]

The impact of the NPs shape on the SPB has been far less studied, because of both the intrinsic complexity of the problem and synthesis limitations. However, recently nanotechnology has enabled researchers to synthesise NPs featuring original shapes[78,79] such as rods,[80] disk,[81] squares,[82] triangles,[83] stars[84] and others, *etc.*[83,85] The SPB of oblate or prolate spheroidal NPs attracted attention very early, as Gans provided a solution for the problem based on Mie theory some seven years after the latter was published.[86] If the orientation of the observed nanorods is arbitrary, the optical signature is the existence of two bands, one corresponding to the longitudinal mode, one to the transverse one.[80] If the nanorods are embedded in a matrix in a parallel fashion, then only one band is visible and an increase in the aspect ratio causes a blue shift of the SPB.[87,88] This was rationalised utilising the Maxwell–Garnett theory. By contrast, in solution nanorods stabilised by micelles have two SPB bands that undergo red shifts on increasing the aspect ratio. For these objects though, the dielectric medium seems to be dependent on the aspect ratio in a non-linear fashion.[80,89] For more complicated shapes, other models had to be sought. The DDA, of course, appeared to be an ideal tool. As an example, Schatz *et al.* evidenced recently that three-tip-star like NPs featured SPB which are red-shifted (by 130 to 190 nm) compared to the spherical equivalents. Moreover, DDA evidenced that in this case the SPB phenomenon is mainly determined by the influence of the tips.[84]

Applications of SPBs

Among the possible applications of the above mentioned properties, detection is the one that has been the most successful thus far. Indeed, the ability of SPBs to be altered in an easy, controlled and reproducible way by a change in their environment naturally led chemists to use them as sensors to detect organic, inorganic or biological targets.[90]

Biodetection

Nano systems have already proved useful for potential applications in the biodetection field and may have a revolutionary impact in coming years. This new area at the meeting point of chemistry, biology and material science has recently been the subject of several reviews.[91–94] The ultimate goal of sensing a single molecule in a living cell (which has already been achieved by fluorescence of marked molecules[95]) seems now to be reachable using NPs. The properties of nanoparticles to feature a changing SPB in solution depending on the mean distance between them has been extensively exploited in the field of biodetection.[90] For example, Mirkin and co-workers provided polynucleotide sensors relying on this effect.[96–98] The 13 nm nanoparticles were functionalised with alkanethiol-capped oligonucleotides (single stranded DNA); once in presence of the complementary DNA strands, the cross-linking of the oligonucleotides directs the self assembly of the nanoparticles. As a result, the mean distance between them is then considerably reduced, which leads to the colour changes.[99] The advantages of their method upon other known biosensors are its sensitivity (down to 1 nM[100]), its selectivity (one base replacement is enough to have the test fail), its user-friendliness (the colour shift is clearly visible by the naked eye). Detection could even be quantitative down to 50 pM by using larger nanoparticles (Fig. 6).[100] More recently methods which do not involve cross-linking-hybridisation[101] or which even do not require any prefunctionalisation of the nanoparticle surface[102,103] have been designed. Recent progress in the field even permitted to access sensing of antigens in whole blood, based on the SPB of gold nanoshells, namely silica beads covered with a gold layer.[104] Another technique, nanosphere lithography (NSL) enables the patterning of a surface with an array of triangular shaped gold or silver nanoparticle.[105] In such systems, interparticle distances are fixed and it is rather the adsorption of the analytes to the particles that causes a detectable shift of the observed SPB, either by a electrical medium modification or by electronic exchange at the interface.[106] This method is also very practical as the sensor is an easy to handle solid device. In the same trend, Chilkoti and coworkers published on the coating of a glass substrate with nanoparticles, using self-assembled monolayers. The nanoparticles are functionalised so as to bind a given protein. The alteration of the dielectric medium around the nanoparticle is responsible for an SPB shift. User-friendly and sensitive protein sensors, based on the SPB response of the nanoparticle were thus designed.[107,108] One has also to underline that functionalised gold nanoparticles have also been used as a complement to metallic films utilised as DNA assay.[109–111] Indeed the surface plasmon band of a metallic film observed in transmission is a well known optical phenomenon that as also been used for detection especially of biological targets.[112]

Chemo-detection

Surprisingly, detection of organic molecules or inorganic ions has not yet attracted as much attention as biomolecule

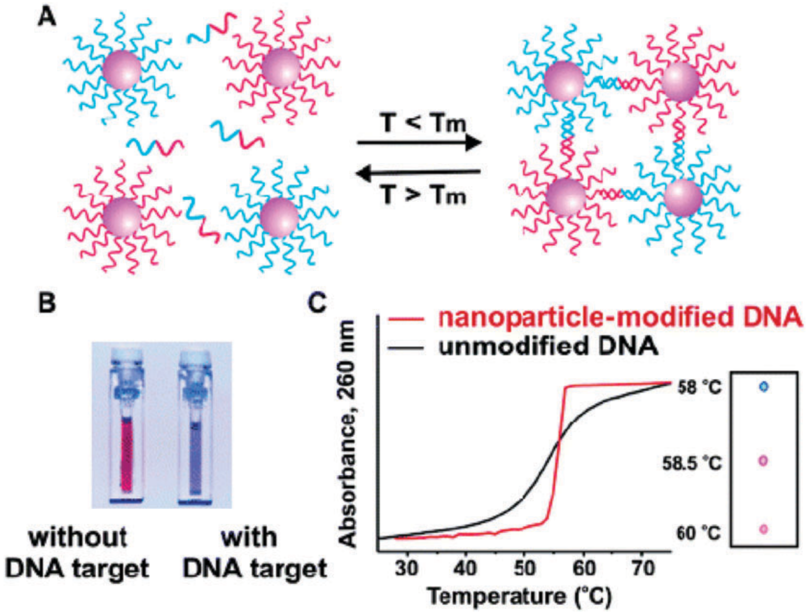

Fig. 6 In the presence of complementary target DNA, oligonucleotide-functionalised gold nanoparticles will aggregate (A), resulting in a change of solution colour from red to blue (B). The aggregation process can be monitored using UV-Vis spectroscopy or simply by spotting the solution on a silica support (C).[91] Reprinted with permission from *Chem. Rev.*, 2005, **105**, 1547. © 2005, American Chemical Society.

detection. The methods employed for chemosensing are often comparable to those just described, detection relaying on the SPB response to an alteration of either the dielectric medium, the aggregation of the particles or the electronic exchange between the particle and the adsorbed analyte. An interesting example of a potassium cation sensitive detector was developed by Chen and co-workers.[113] 15-Crown-5 functionalised nanoparticles have the property to aggregate when in presence of K^+, whereas other tested cations such as Na^+, Mg^{2+}, *etc.*, did not provide the same result. The aggregation caused a red to blue visible shift. Aggregation phenomenon was also used to reversibly follow a pH modification.[114] Carboxylic acid functionalised nanoparticles were used for that purpose, the red-to-purple shift was evident when adding an acid to the colloidal solution. More recently, work of Sun and Xia evidenced that the use of nanoshells that have a void core enhance the sensitivity of the system by almost one order of magnitude.[115] These objects feature an SPB shifted towards the red region compared to the solid nanoparticle and the size of their internal hollow and the thickness of their wall can be easily tuned. Another way of using the SPB for detection is to use its dependence upon the ligand electron donor/acceptor abilities detailed above. Indeed, ligands can easily be replaced at the surface of nanoparticles, provided the replacing ligand is in excess. We thus recently described the synthesis of a sensing device based on this principle. The gold NPs are immobilised in a mesoporous film, with a low metal loading, so that the analyte to be detected is in large excess even at low concentration. NPs are stabilised by a special ligand, the phosphinine, which enables a selective detection of phosphine, characterised by a blue shift, or of thiols which led to a red shift.[33]

Surface enhanced Raman spectroscopy (SERS)

Raman spectroscopy relies on inelastic light scattering by molecules in the infrared domain. Despite numerous advantages, it provides rich structural information, is non-invasive, does not require specific sample treatments, has a high space resolution allowing to realise mappings of solid samples, it suffers from one main drawback as the quantum yield of the Raman effect is low. Indeed Raman scattering cross sections are usually extremely small, so that large numbers of molecules have to be excited to yield high quality spectra.[116] The effectiveness of Raman spectroscopy depends, among other factors, on the intensity of the local electric field "seen" by the molecule. Plasmon resonance can result in huge magnification of the local field at the metallic surface. Therefore, rough metallic surfaces or metal nanoparticles under plasmonic excitation proved to act as antennae achieving scattering cross section enhancements of about eight orders of magnitude.[117] This so-called surface enhanced Raman scattering effect is so strong that it enables single molecule spectroscopy.[118–120] Recent examples of the use of SERS for detection purposes include the analysis of anthraquinone dyes in artefact objects,[121] the detection of viral DNA segments,[122] the detection of narcotics[123] or explosives.[124]

Interesting for the scope of this review is the fact that SERS promoted intensive work on predicting which particle shapes or assemblies would result in the strongest field enhancement at the NP surface and thus which systems would be the most effective for SERS experiments. For this purpose both DDA and FDTD methods have been successfully applied.[29,125]

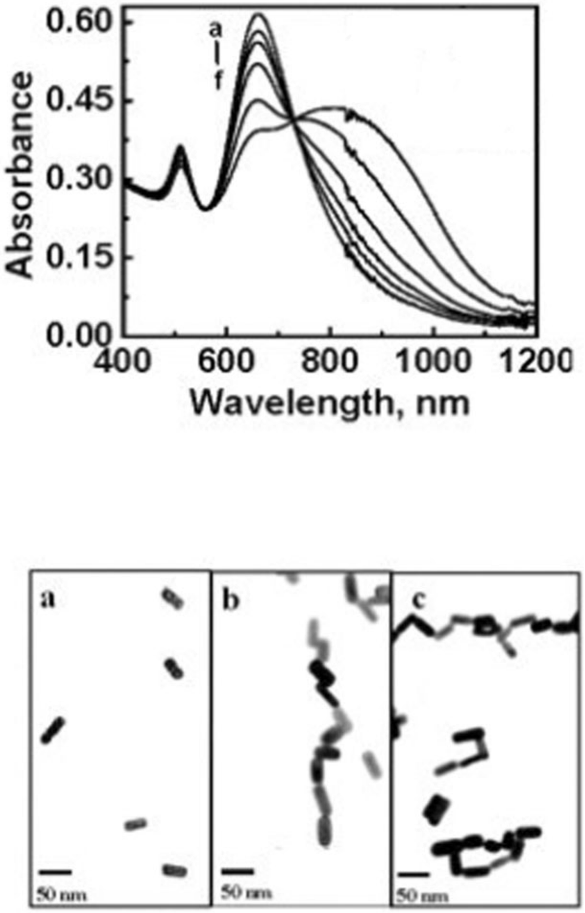

Fig. 7 Tripeptide detection with nanorods. Above: absorption spectral changes of Au nanorods on addition of cysteine at (a) 0, (b) 1.75, (c) 2.0, (d) 2.25, (e) 2.5 and (f) 3 μM. Below: TEM images of Au nanorods in the absence (a) and presence (b and c) of cysteine under identical conditions.[136] Reprinted with permission from *J. Am. Chem. Soc.*, 2005, **127**, 6516. © 2005, American Chemical Society.

Perspectives

The SPB is indeed a very powerful tool which has already shown a part of its capabilities. Further applications of it will surely be soon found in the fields of biodetection, electronics, *etc*. We would like to focus in this section on some areas that seem to open new opportunities.

Research in nanotechnology is growing rapidly and the opportunity of performing the synthesis of nanoparticles featuring new shapes and organisations[126] will enable to use the SPB to a wider range of applications. Schatz *et al.* performed calculations of silver nanoparticle arrays to produce a very sharp surface plasmon band.[127] Recent progress in nanosphere lithography are also very promising and arrays of complex three-dimensional metallic and bimetallic structures are accessible.[128] Complex interaction between two-dimensional arrays and a metallic surface have also started being investigated.[129] Even more powerful is the use of SPB as a chemical tool itself. By photoexciting triangular metallic plates with one or two appropriate visible beams whose wavelength corresponds to the surface plasmon mode of the tips of the prism, Mirkin *et al.* performed unimodal growth of those nanoobjects.[130,131] Interesting prospects can be expected from optical properties of multihierarchical structures. For example Osterloh *et al.* published results on gold nanoparticles stabilised on the surface of large silica nanoparticles. The ligands stabilising the gold particles induce different types of two-dimensional arrangements and thus special optical properties.[132] Core-shell nanoparticles are also very promising, a good example of the potential of this method for SPB tuning was furnished by Prasad *et al.* who grew gold nanoshells on polystyrene cores.[133]

Applications in the electronics domain have of course been sought as well. It was shown that the optical response of immobilised gold nanoparticle ensembles was modified by charge injection.[134] Other recent reports showed progress in this area.[64,135] Further developments in biodetection are also expected. One of the crucial aspects in the field is to produce very specific sensors. This goal was achieved for an amino acid and a tripeptide which can be detected by a shift of the longitudinal SPB of gold nanorods.[136] The key point in this detection is the presence of a thiol functionality in those molecules that enables a self organisation of the rods. Other amino acids failed completely to be detected by such means (Fig. 7). Eventually a great deal is expected in the field of electronics. Monolayers of silver[137] or gold[138] NPs have been found to undergo an insulator to metal transition upon mechanical compression. This phenomenon also causes a disappearance of the SPB of the NPs.

Conclusion

It might be that Qohelet, saying that there was nothing new under the sun,[139] was partly wrong. On the one hand we are still fascinated by the colours of metallic colloidal suspensions, like Faraday, stained glass makers of the Middle Age and even Roman craftsmen. On the other hand, however, they may be a real breakthrough in prospect. Indeed, after a long period devoted to understanding the physical principles rationalising the SPB phenomenon, chemists and physicists have started to use SPB for their own purposes. Applications in the field of detection have been milestones at the turn of this century. New breakthroughs are likely to come from the use of the SPB as a tool for nanosynthesis or for non-linear optics.

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