On the connection between optical absorption/extinction and SERS enhancements

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Several aspects of the connection between the absorption/extinction spectra and the enhancement in surface enhanced Raman scattering (SERS) are analyzed and discussed. It is shown that in many standard situations the *spatial distribution* of the resonance plays a role for the difference between extinction/absorption and SERS enhancement and that the connection between both can be very indirect and, in many cases, misleading. This clarifies several misconceptions often found in the literature.

We aim at clarifying the role of surface plasmon resonances—as seen in the optical absorption/extinction spectra—in relation to the presence of large signal enhancements seen in surface enhanced Raman scattering (SERS).[1] The connection has been sometimes the source of confusion. It is generally accepted that absorption/extinction does not reflect accurately SERS enhancement, but detailed quantitative studies have not been carried out. It is not strange to find publications where the presence of red-shifted collective plasmon resonances in metallic nanostructures is taken as a direct indication of a region with a favorable SERS enhancement. We argue, through simple examples, that the connection between absorption/extinction spectra and Raman enhancement is not necessarily straightforward. Moreover, in situations where the largest enhancements are observed, the absorption or extinction spectrum can be a bad indicator of where the maximum enhancements happen. Part of the problem comes from treating SERS as a sort of "resonant" Raman process with the excitation tuned to the absorption maximum of the SERS substrate to achieve the largest enhancement. This argument ignores the spatial distribution of the resonances and the fact that SERS enhancements can be very local and only dependent on what happens at a specific point in the geometry of the object. We aim at showing that the total contribution to the absorption/extinction from some of the resonances with the largest SERS enhancements can be small compared to others with much weaker enhancements and, therefore, the absorption spectrum/extinction is not a good indicator to judge the SERS activity in general.

The main topics of this paper are, accordingly: (i) the spatial distribution and localization of plasmon resonances in simple structures; and (ii) their connection with both absorption/extinction and SERS enhancements. Our results here will contribute to pinpoint several important aspects to take into account when a connection is sought between these two widely used techniques (SERS and absorption/extinction measurements). After its discovery in the 70's, SERS became a subject of intense research with interesting applications in analytical chemistry.[1] Interest has increased after two independent reports[2,3] in 1997 on the observation of single molecule SERS,[4] with potential advantages over fluorescence-based techniques. Electromagnetic modelling with a new generation of computational tools is coming as an aid to understand the details of the SERS phenomenon, including subtle effects like the possible contribution of optical forces.[5]

A collection of nanometer-sized interacting metallic objects made from Ag will typically display a distribution of plasmon resonances somewhere in the UV-visible-near IR range, depending on geometry and sizes. Analytes will be attached to their surfaces in SERS applications. If $\vec{E}(\vec{r})$ is the field at a specific point $\vec{r}$ and $\vec{E}_0$ the incident field, we call here the *maximum enhancement* the value of the maximum normalized local field factor $|\vec{E}(\vec{r})|^4/|\vec{E}_0|^4$ achieved anywhere *on the surface* of these objects; it is obviously expected to be strong at the resonances. The absorption/extinction is also expected to be strong at resonance for exactly the same reason: plasmon resonances maximize the interaction with the external field and should show as singularities in both the absorption/extinction and enhancement spectra. The questions we address are: How are the two spectra connected? Can we infer one from the other? We will show, in particular, that as soon as collective plasmon resonances are present the connection between absorption and SERS enhancements becomes more indirect. In a nutshell, the explanation of this effect is as follows: collective resonances at a given λ can be arbitrarily classified as having more of a *bulk-like* or *surface-like* character, depending on the spatial distribution of the intensity. A bulk-like resonance can have a large contribution to the absorption (proportional to the volume), but may have a relatively weaker field at the surface in a specific point. The opposite can happen for a surface-like resonance. One could argue that there might be a slight compensation effect for large surface-like resonances in the sense that the smaller overall penetration depth contributing to the absorption might be compensated by a much larger field. But in general this compensation is only partial. In addition, as we shall show later, for samples that consist of randomly oriented versions of

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the same basic units, it is found that resonances at different wavelengths have different spatial averaging properties. Ultimately, this translates into a lack of correlation between those resonances that matter the most for SERS and those seen in the absorption/extinction spectra, as we shall show in the examples that follow.

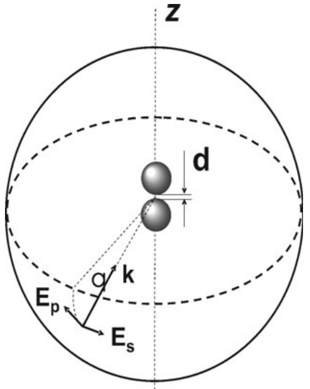

Fig. 1 A dimer formed by two Ag spherical particles with a 50 nm diameter separated by a distance *d*. The main axis of the dimer is along the *z*-axis. A plane wave impinges on the dimer with a wavevector $\vec{k}$ at an angle θ with respect to the equatorial plane and with either $\vec{E}_\mathrm{p}$ or $\vec{E}_\mathrm{s}$ polarization. $\vec{E}_\mathrm{p}$ is always polarized in the plane that contains the *z*-axis and $\vec{k}$, while $\vec{E}_\mathrm{s}$ is perpendicular to both $\vec{E}_\mathrm{p}$ and $\vec{k}$. The calculations shown in Fig. 2 and 3 make reference to this configuration.

The effect we report here is obviously very case-dependent. Each geometry has to be analyzed separately for its peculiarities. We only discuss here briefly two specific examples of the problem. We do a demonstration by antithesis; *i.e.* we show two simple examples where the concept we are trying to emphasize plays a role, thus proving that it is likely to play a role in general. For the sake of argument we take, for a start, the canonical SERS example of a dimer formed by two identical spherical colloids separated by a distance *d*. We calculate the extinction spectra and the SERS enhancement for different separations using generalized Mie theory as described in ref. 6, and the results are, accordingly, exact. We refer the reader to ref. 6 for the full details on the implementation of the theory, and we only highlight here basic aspects. Ref. 6 presents a very convenient implementation of Mie theory that works particularly well for the case of metallic (nanometer sized) spheres. According to ref. 6 *the effect of dipole–dipole indirect exchange through high polar order interactions is particularly important among metallic particles and such couplings should be included from the beginning*. Maxwell's equations are solved for an arbitrary cluster geometry and excitation condition by multipolar expansions of the fields with appropriate boundary conditions and interaction terms among the various components. The interaction terms are calculated by a recurrence relation for spherical vector wave functions. Convergence is rapidly achieved by using 20–50 multipolar terms depending on the exact geometry. The metallic colloids have the local dielectric function $\varepsilon(\lambda)$ that best fits the optical properties of Ag; namely a Drude model of the type:[7,8]

$$\varepsilon(\lambda) = \varepsilon_\infty - \frac{1}{\lambda_\mathrm{p}^2\left(\frac{1}{\lambda^2} + \frac{i}{\Gamma\lambda}\right)}, \qquad (1)$$

with parameters $\varepsilon_\infty = 4$, $\lambda_p = 141$ nm, $\Gamma = 17\,000$ nm.[8] We assume the colloids to be immersed in air ($\varepsilon = 1$). The same resonances will exist for colloids immersed in water but will be red-shifted in view of the different dielectric constant of the medium. As a guide, resonances at 360 and 450 nm in air correspond to resonances 410 nm and 550 nm in water ($\varepsilon = 1.77$).

Fig. 1 shows the geometry of the problem with the different incident polarizations ($\vec{E}_\mathrm{p}$ or $\vec{E}_\mathrm{s}$) and incident angles (θ). We make reference to this geometry in the next two figures. The "dimer" structure is arguably the simplest SERS structure and is widely used as a paradigm to understand experimental results of different origins. Fig. 2 shows the extinction and enhancement spectra for $\theta = 0$ only, but for different colloid–colloid separations: $d = \infty$ (isolated non-interacting colloids), and $d = 10$ and 2 nm. The main aspects of the results are summarized here. (i) For $d = \infty$ there is a single peak in the extinction spectra at 360 nm corresponding to the localized surface plasmon resonance of an individual colloid. (ii) For $d = 10$ and 2 nm, a red-shifted plasmon resonance develops and shifts further to the red for smaller *d*'s. This corresponds to the dipole–dipole interaction resonance of the dimer. (iii) The overall extinction and, in particular, the extinction at the maximum peak remain approximately unchanged within 20% for all *d*'s. (iv) There is a group of resonances in the region ~320–380 nm that always remain in the spectrum with comparable total oscillator strength, albeit showing some sub-structure depending on *d*. This corresponds to higher order interactions between the two objects (v) The effect of *d* on the enhancement spectra is completely different. Relatively large enhancements are predicted even in-between and beyond the main resonances. (vi) The most important difference between the behavior of enhancement and extinction is that the former *can vary by several orders of magnitude as a function of d even in regions where the extinction is not varying by much*. This stands as one of the main conclusions of this first calculation which is summarized at the bottom of Fig. 2 and in the corresponding caption.

The red-shifted collective resonance is usually the most relevant for SERS. This resonance behaves to a large extent like a "point-dipole" in the center of the dimer as far as its coupling to the external field is concerned. This can be shown by an angular study as a function of θ (see Fig. 1 for the geometry) and displayed in Fig. 3 for both $\vec{E}_\mathrm{p}$ and $\vec{E}_\mathrm{s}$ and for a fixed *d* of 2 nm. Note that the red-shifted resonance does not couple at all to $\vec{E}_\mathrm{s}$, as would be expected for a dipole-like excitation. Its intensity also disappears for $\vec{E}_\mathrm{p}$ when $\theta = 90°$, as expected, since for $\theta = 90°$ both $\vec{E}_\mathrm{p}$ and $\vec{E}_\mathrm{s}$ are equivalent by symmetry (see Fig. 1).

For all practical purposes, the red-shifted resonance has an angular dependence resembling a point-dipole centered in the middle of the colloids. The other group of resonances are also dipolar to a large extent but there are many such resonances that one can couple to by coming from different directions; *i.e.* at different wavelengths the *angular degeneracy* of the resonances is different. This results in a red-shifted resonance that

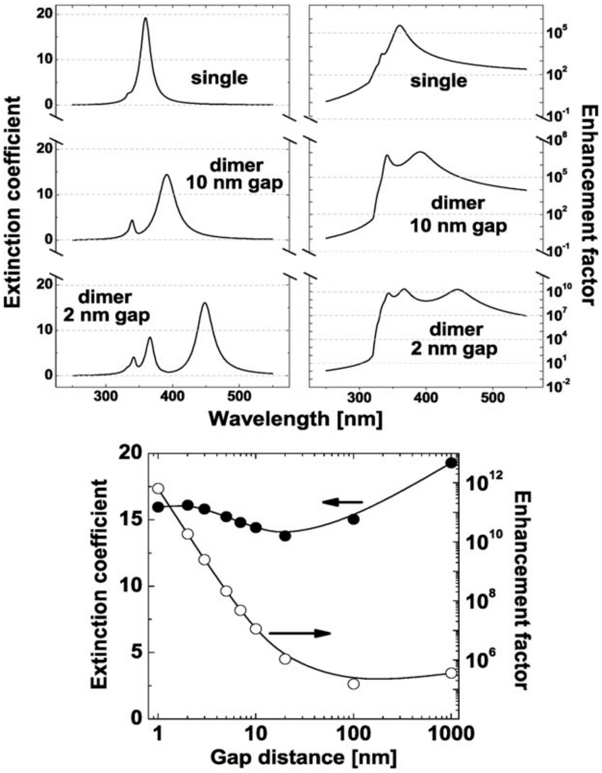

Fig. 2 Extinction coefficient, defined as the ratio of the extinction over the geometrical cross-sections (top left column) and maximum enhancement factor (top right column) for a single sphere ($d = 50$ nm), and dimers with $d = 10$ and 2 nm gap separation, respectively. Note that the enhancement is displayed on a log-scale while the extinction is plotted on a linear scale. All calculations have been performed with generalized Mie theory as described in ref. 6. The main message of these calculations is as follows: The overall extinction coefficient (including the maximum peak) does not change by much in magnitude when going from isolated spheres to a dimer with $d = 2$ nm. The maximum enhancement, on the contrary, changes by several orders of magnitude in the process. The red-shifted peak, where the maximum enhancement occurs in the gap, is often the most relevant to SERS. The variation with gap, d, of the enhancement and extinction for this peak, is shown in the plot at the bottom. While the extinction varies by no more than ~25% from 1 to 1000 nm separation, the enhancement varies by ~7 orders of magnitude in the same range.

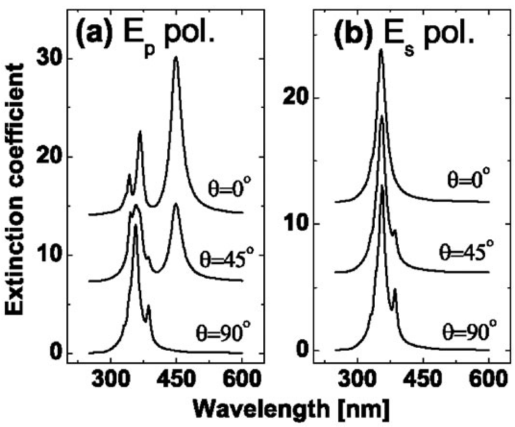

Fig. 3 Extinction spectra for a dimer with $d = 2$ nm for different angles of incidence (θ) and incident polarizations ($\vec{E}_\mathrm{p}$ in (a) or $\vec{E}_\mathrm{s}$ (b) according to the nomenclature in Fig. 1). The resonance that matters the most for SERS is the red-shifted resonance at ~450 nm (550 nm in water) for $\vec{E}_\mathrm{p}$ polarization. This resonance has a strong angular dependence (as seen on (a)) and it behaves essentially like an equivalent dipole ($\propto \cos^2(\theta)$). E_s does not couple to the resonance for any angle of incidence. Orientational averaging will reduce the resonance at ~450 nm to ~1/3 of the maximum at $\theta = 0°$ for $\vec{E}_\mathrm{p}$. This, together with the fact that the resonance moves in energy depending on the separation, d, creates a featureless "tail" in the extinction spectra of a real sample, with a peak dominating the spectrum at ~360 nm (410 nm in water). The SERS intensity is very large in a region where there is no obvious feature in the extinction spectrum. See the text for further details.

is more sensitive to the excitation geometry than the others which remain in the spectra with comparable oscillator strengths for all orientations. In short: the coupling to the light at the frequencies of the red-shifted resonance is more anisotropic than at other wavelengths. If we had a collection of randomly oriented dimers with different separations d's (a good simple model for a SERS active solution with partially aggregated colloids) two main effects will happen: (i) The red-shifted resonance will average to an intensity of 1/3 of the value for $\theta = 0°$ and $\vec{E}_\mathrm{p}$ polarization in its total contribution to the extinction, making it smaller in total intensity compared to the group of resonances around ~320–380 nm which exploit the angular degeneracy for different orientations and contribute approximately the same for all orientations, and (ii) The (now smaller) peak of the red shifted resonance will be distributed all over the visible and near-IR range depending on d. As a result of this, the extinction spectrum will consist of a main peak in the range ~320–380 nm and a long tail extending through the visible. This has been repeatedly observed experimentally for aggregated colloids.[9,10] The main peak will be produced by resonances which are more "single particle-like" and do not have large contributions to the enhancement in the gap of the dimer. A laser in the visible range, will profit from the SERS enhancement of the dimers which are oriented approximately in the same direction of the incoming polarization, and each of them will contribute by several orders of magnitude to the enhancement, as seen from Fig. 2, but in a region where the extinction is not at its maximum and is relatively featureless. There is nothing in the extinction spectra that can reveal the high SERS activity. All these facts respond to the basic phenomenology of SERS in liquids as reported in countless publications.[10,11]

The simple (exact) examples shown in Fig. 2 and 3 demonstrate that the connection between extinction/absorption and SERS enhancement is, at best, indirect and that a qualitative correspondence may be valid for single objects but may still cause problems if collective plasmon resonances are present. A key element of the difference is the spatial localization of the resonances and how this affects their relative contributions to the overall absorption/extinction or to the enhancement factor at one point. The different roles of the spatial localization of the resonances are present in a myriad of simple examples for more extended structures and different methods of calculation. Another example is shown explicitly in Fig. 4. Here we study

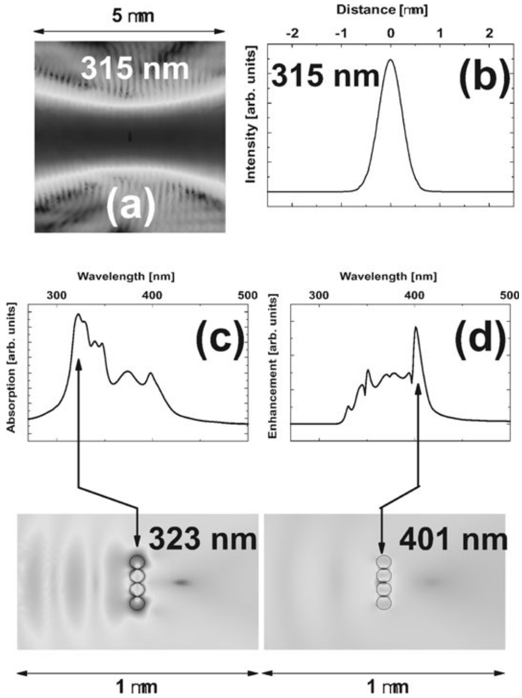

Fig. 4 The line quadrimer (four cylinders with d = 60 nm separated by 2 nm gaps and aligned in vertical direction) shown in the figures at the bottom is illuminated by a 2-D Gaussian beam coming from the side. In (a) the free-propagating beam at λ = 315 nm is shown in an intensity plot (with a black and white log-scale to see the details of the beam). In (b) the free-beam intensity profile at the focal plane is shown, displaying its Gaussian nature; while (c) and (d) show the corresponding absorption and enhancement spectra of the quadrimer. The absorption peaks at $\sim$323 nm correspond to resonances that are "bulk-like" mainly, while the enhancement peaks at $\sim$401 nm correspond to "surface-like" resonances mainly concentrated in the gaps and producing large hot-spots. The difference in the nature of the two types of resonances can be seen in the intensity plots at the bottom (log-intensity in false-color scale). The resonance at 401 nm has only a very localized high intensity in-between cylinders, while that at 323 nm is distributed throughout the volume of the quadrimer.

the SERS enhancement and absorption of a line quadrimer under Gaussian beam illumination in two dimensions for transverse magnetic (TM) propagation. Details of the calculation method have been reported elsewhere.[12] The main difference with the calculations in ref. 12 is the introduction of a *TM*-Gaussian beam (cylindrical beam[13]) excitation. Cylindrical (2-D) Gaussian beams are introduced by fixing the appropriate boundary conditions for the wave[13] on the boundary box of the finite element problem.[12] As in ref. 12 all simulations have been carried out by direct (finite element) numerical solutions of Maxwell's equations by using adaptive meshes. Simulations are performed by using modified Matlab codes (http://www.mathworks.com), with the geometry and meshes set up by FEMLAB (http://www.comsol.com). For clarity and ease of representation of the fields we work in a two-dimensional case as in ref. 12; this simplifies enormously the visualization of the field distributions and is by no means a limitation to the underlying concepts we highlight here. We choose to work in an electromagnetic 2-D transverse magnetic (TM) problem because this provides the polarization direction where the effects of "coupling" among objects are more important. As pointed out in ref. 12, a bounding box is set up with low reflecting (LR) boundaries to solve the electromagnetic problem. LR boundaries are strictly non-reflecting only for plane waves, but they provide an excellent approximation for open boundaries in general if the size of the box is not too small compared to the wavelength. However, the use of a Gaussian beam in this case has considerable advantages with respect to normal plane waves, as we shall point out later. We fix the boundary conditions to obtain the focal plane exactly in the center for all wavelengths with a beam waist[13] given by $w_0 = 1.4\lambda$, which is a reasonable value found in real systems. All calculations are normalized by the intensity of the free propagating beam. The free propagating beam solution (at λ = 315 nm) is shown in Fig. 4a. The free beam has a Gaussian cross section throughout, an example of which is shown in Fig. 4b at the beam waist. The advantage of a Gaussian beam lies in the fact that the simulation becomes less susceptible to imperfections produced by the finite size of the box and their corresponding boundary conditions. In particular, the upper and lower boundaries in Fig. 4a are particularly problematic for (TM) plane waves. When the latter boundaries are low reflecting they introduce a distortion in the plane wave that can cause artifacts in the numerical solution and if other types of boundary conditions are used (like "perfect electric conductor", which forces the electric field to remain perpendicular to the boundary at all times), they can modify and interfere with the scattered wave from the object. A Gaussian beam with low-reflecting top and bottom boundaries overcomes both problems at the same time. Fig. 4c and d show the corresponding absorption and enhancement spectra which are skewed in different directions and peak at different wavelengths. In this numerical method[12] it is more cumbersome to obtain the extinction as in generalized Mie theory;[6] we shall focus on the comparison between absorption and enhancement, accordingly. This is due to the difficulty in accounting for the *scattering component* of the extinction in these simulations (which is a property better evaluated in the far-field). The maximum of the absorption is a "bulk-like" resonance while the maximum of the enhancement is a "surface-like" one mainly concentrated in the gaps and producing intense hot-spots. Both are explicitly shown at the bottom of Fig. 4. This example further illustrates the different roles the spatial distribution of the resonances plays on either the absorption/extinction or the SERS enhancement, and further highlights the effect we want to discuss here: the connection between SERS enhancement and absorption/extinction is indirect, in particular when collective plasmon resonances are present. As a rule of thumb, the more complex the geometry with a large number of collective resonances and the more spatial averaging the weaker the connection between absorption/extinction and maximum SERS enhancement.

In closing, we demonstrated that the connection between absorption/extinction and SERS enhancement is not direct and can be even misleading in some circumstances. As mentioned before, highly SERS active colloids in solution have the maximum of their SERS efficiency in regions where there is no hint of a resonance in the absorption/extinction. This is due to the different spatial localization of collective resonances and their different spatial averaging properties. The SERS enhancement *cannot* be obtained directly from the absorption/extinction spectra in general, as assumed in some cases.

References

1 M. Moskovits, *Rev. Mod. Phys.*, 1985, **57**, 783.
2 S. Nie and S. R. Emory, *Science*, 1997, **275**, 1102.
3 K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari and M. S. Feld, *Phys. Rev. Lett.*, 1997, **78**, 1667.
4 E. C. Le Ru, M. Meyer and P. G. Etchegoin, *J. Phys. Chem. B*, 2006, **110**, 1944.
5 H. Xu and M. Käll, *Phys. Rev. Lett.*, 2002, **89**, 246802.
6 J. M. Gérardy and M. Ausloos, *Phys. Rev. B*, 1982, **25**, 4204.
7 *Handbook of Optical Constants of Solids III*, ed. E. D. Palik, Academic Press, New York, 1998.
8 R. Rojas and F. Claro, *J. Chem. Phys.*, 1993, **98**, 998.
9 S. Lecomte, P. Matejka and M. H. Baron, *Langmuir*, 1998, **14**, 4373.
10 K. Faulds, R. E. Littleford, D. Graham, G. Dent and W. E. Smith, *Anal. Chem.*, 2004, **76**, 592.
11 R. C. Maher, M. Dalley, E. C. Le Ru, L. F. Cohen, P. G. Etchegoin, H. Hartigan, R. J. C. Brown and M. J. T. Milton, *J. Chem. Phys.*, 2004, **121**, 8901.
12 P. G. Etchegoin and E. C. Le Ru, *J. Phys.: Condens. Matter*, 2006, **18**, 1175.
13 D. Oron and Y. Silberberg, *J. Opt. Soc. Am. B*, 2004, **21**, 1964.