

application of a consistent quantitative framework for species delimitation, numbers of known species will continue to grow — indisputably distinct species continue to be discovered at a remarkable rate, even in well-studied groups of organisms¹⁰. Indeed, the taxonomic challenge across most of the tree of life is not so much where to draw the line between species and subspecies, as it is in birds. Rather, it is that many, maybe most, species remain unnamed and undocumented, with too few hands on deck to help with this pressing task¹. Nevertheless, consistent species delimitation within the best-known taxonomic groups will surely help to bring into focus patterns that may apply more broadly across the tree of life. We

suspect that this approach² stands to ignite an operational revolution in taxonomy, tantamount to re-polishing the grail of the species as the fundamental unit of biology. ■

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NANOSCIENCE

Dark-hot resonances

The resonant behaviour of clusters of gold nanoparticles has been tuned by gradually bringing the particles together. The approach could have many applications, including chemical and biological sensing.

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Resonances are ubiquitous natural phenomena that occur on all spatial scales — from the largest distances in the Universe to the tiniest dimensions of elementary particles. They have great significance in both fundamental science and practical applications. Writing in *Nano Letters*, Hentschel *et al.*¹ describe the ability to switch a special type of resonance, termed Fano resonance², on and off in spectra of assemblies of nanometre-sized gold particles.

A resonant system, generically called an oscillator, undergoes an oscillatory motion that repeats in time with a certain frequency (or, correspondingly, period). When subjected to a periodically oscillating external force of nearly the same frequency as its own, an oscillator experiences resonance: with each new period, the oscillator gains some energy from the external force, which acts in unison with the oscillator's motion, and the amplitude of the motion increases. In atoms and molecules subjected to electromagnetic fields, resonances show up in spectra as narrow peaks of absorption, emission or scattering. (Other types of resonance exist that are caused by interactions with magnetic, nuclear and gravitational fields.) In certain cases of optical excitation, in which two quantum paths lead to the same final quantum state of the system, the resonance peaks have specific asymmetrical line shapes due to the interference of the paths' quantum amplitudes. Such resonances were first described by Ugo Fano in 1935 and are now widely called Fano resonances.

In the optical region of the electromagnetic

spectrum, the strongest resonances are caused by surface plasmons — collective oscillations of electrons in nanometre-scale metallic systems (nanoparticles). When they interact with light, surface plasmons lead to highly enhanced, nanolocalized optical fields ('hot spots')³ at the systems' metallic surfaces. Such nanoplasmonic resonances form the foundation

for many of the remarkable applications of the rapidly developing field of plasmonics⁴.

If the size of plasmonic nanoparticles — those composed of highly conducting metals — approaches or exceeds several tens of nanometres, they scatter light strongly. This is a beautiful phenomenon, and can be witnessed when sunlight obliquely strikes glass windows in churches and cathedrals (Fig. 1) — presumably, these contain gold, silver and copper nanoparticles. However, such light scattering causes broadening and dulling of the nanoplasmonic resonances, making them less significant in fundamental science and less suitable for applications. It would therefore be useful to use smaller nanoparticles, which do not suffer from such a drawback. But it is difficult to fabricate, assemble and tune them to specifications.



Figure 1 | The magnificent glass window of La Sainte Chapelle in Paris. The window's deep yellow and red colours (bottom) — seen on exposure to oblique sunlight — are probably caused by the scattering of light from silver, gold and copper nanoparticles.

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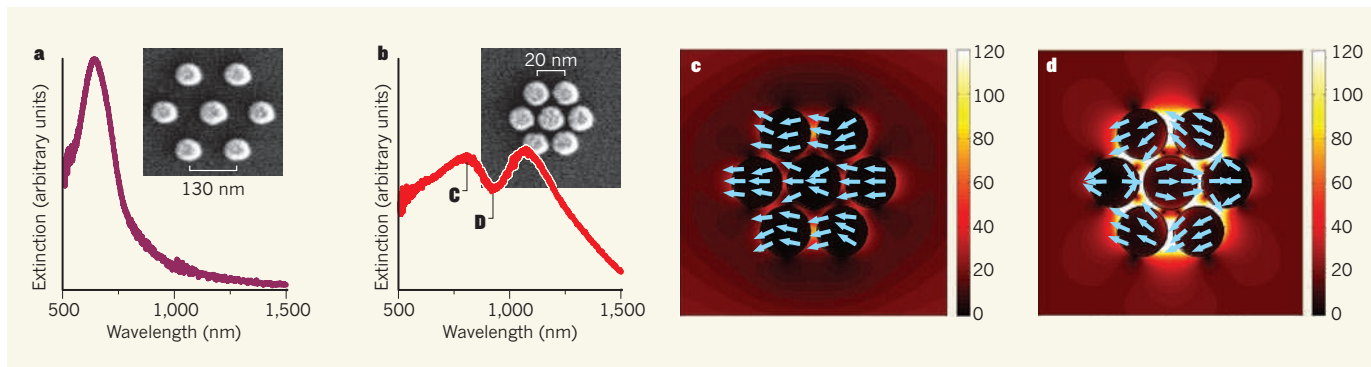


Figure 2 | The nanoclusters studied by Hentschel and colleagues¹.

The authors studied the optical response of clusters comprising seven gold nanoparticles and found that, for interparticle separations of less than 60 nanometres, the pronounced spectral dip of a plasmonic Fano resonance emerges. **a, b**, Absorption spectra for interparticle separation of 130 nm (**a**) and 20 nm (**b**); insets display images of the clusters taken with a scanning electron microscope. The Fano dip is marked in **b** with a D.

Fortunately, in addition to these 'bright' nanoplasmonic resonances, there are also 'dark' ones⁵, which by themselves are not very prominent in optical spectra. However, if a bright and a dark resonance coexist in a certain spectral range — which is not unlikely, because the bright resonances span relatively wide wavelength ranges — then their optical fields interfere. This interference significantly enhances the manifestation of the dark resonance: it acquires strength from the bright resonance and shows up as an asymmetrical peak-and-dip profile characteristic of a Fano resonance⁶. An important, albeit counter-intuitive, property of dark resonances is that, at exactly the frequency of the Fano dip, the hot spots of the nanolocalized optical fields in the nanosystem are strongest. This is because, at this frequency, the nanosystem emits minimal light and, consequently, does not wastefully deplete the energy of the plasmon oscillations.

In their study, Hentschel *et al.*¹ use state-of-the-art nanofabrication techniques to demonstrate the possibility of switching such a plasmonic Fano resonance on and off. They manufactured symmetrical clusters of gold nanoparticles and investigated the clusters' optical response as a function of the interparticle separation (Fig. 2). They found that, for interparticle separations smaller than 60 nanometres, the distinct spectral profile of a Fano resonance — two uneven peaks separated by a pronounced dip — emerges. What's more, on removal of the clusters' central nanoparticle, the Fano profile disappears.

Thus, the authors' study offers a means to circumvent the light-scattering problem that plagues the use of the bright nanoplasmonic resonances of relatively large nanosystems: by switching on the plasmonic Fano resonance in the dense symmetrical assemblies of nanoparticles, the internal electrical current driving the light scattering and absorption is drastically suppressed. Earlier studies^{7,8}

demonstrated other ways to control plasmonic Fano resonances, and to get around the light-scattering (radiative loss) problem: in the optical spectral region, by breaking the symmetry of the nanostructure⁷, and in the gigahertz regime, through the use of special, artificially engineered structures known as metamaterials⁸. An alternative to these and Hentschel and colleagues' approach may be not to fight the dragon of the radiative loss with the plasmonic Fano resonances but to avoid it altogether — by using smaller nanoparticles (of less than 20 nm) that scatter little light and so do not suffer from radiative loss and the subsequent broadening of the resonances.

What applications are there, then, for nanoplasmonic Fano resonances? One straightforward application is the sensing of ultrasmall amounts of chemical or biological substances. One approach to this is based on the fact that, when chemical or biological molecules bind to a plasmonic nanosystem, the enhanced optical fields of the nanosystem's hot spots polarize them. This causes a shift in the frequency of the nanosystem's nanoplasmonic resonance. Because nanoplasmonic Fano resonances are sharp, and the corresponding hot spots strong, this shift is relatively large and can be easily detected, thus revealing the presence of such molecules.

Another possible application is the widely used spectroscopic technique of surface-enhanced Raman scattering (SERS)^{9,10}, which relies on plasmonic hot spots to produce spectroscopic fingerprints that identify chemical structure, and changes in it, in minute amounts of molecules. Nanoplasmonic Fano resonances cause very bright hot spots (Fig. 2d) and, as a result, could be used to improve the sensitivity of SERS-based methods and devices. They could also be exploited in techniques such as surface-enhanced spectroscopy of fluorescence^{11,12} and absorption¹³.

Last, but not least, is the prospect of using the resonances to build a spaser (surface plasmon

c, d, Simulated local optical fields and corresponding electrical currents (blue arrows) at the spectral wavelengths marked C and D in **b**. The vertical bars indicate the colour scale for the magnitude of the optical field (relative to the field to which the clusters are subjected). The optical field at the Fano dip's wavelength is characterized by bright 'hot spots' — compare **d** with **c**, in which such an effect is absent. (Figure adapted from ref. 1.)

amplification by stimulated emission of radiation)^{14–18}, a nanometre-sized nanoplasmonic source of coherent, localized optical fields in which surface plasmons play the part that photons take in conventional lasers. ■

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CORRECTION

In the News & Views article "Nanotechnology: Holes with an edge" by Hagan Bayley (*Nature* **467**, 164–165; 2010), "6-mercaptohexanoic acid", mentioned in the fifth paragraph, should have read "16-mercaptohexadecanoic acid".