



HAL
open science

Anti-Stokes Thermometry in Nanoplasmonics

Guillaume Baffou

► **To cite this version:**

Guillaume Baffou. Anti-Stokes Thermometry in Nanoplasmonics. ACS Nano, 2021, 15 (4), pp.5785-5792. 10.1021/acsnano.1c01112 . hal-03353191

HAL Id: hal-03353191

<https://hal.science/hal-03353191>

Submitted on 5 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Anti-Stokes Thermometry in Nanoplasmonics

Guillaume Baffou

Institut Fresnel, CNRS, Aix Marseille University, Centrale Marseille, Marseille, France

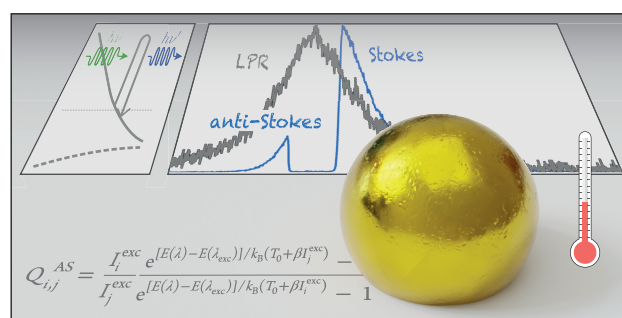
guillaume.baffou@fresnel.fr

Article reference : ACS Nano 2021, 15, 5785–5792

pdf: <http://guillaume.baffou.com/publications/054-Baffou-ACSNano.pdf>

Abstract

Whereas heating nanoparticles with light is straightforward, measuring the resulting nanoscale temperature increase is intricate, and still a matter of active research in plasmonics, with envisioned applications in nanochemistry, biomedicine, and solar light harvesting, among others. Interestingly, this research line mostly belongs to the optics community today, because light is not only used for heating but also often for temperature probing. In this Perspective, I present and discuss recent advances in the search for efficient and reliable thermometry techniques for nanoplasmonic systems by the nanooptics community. I focus on the recently proposed approach based on the spectral measurement of anti-Stokes emission from the plasmonic nanoparticles themselves.



Nanoscale heating is a fundamental concept that offers research opportunities in many scientific fields. The method of choice for achieving nanoscale heating has been the use of light to illuminate molecular dyes or absorbing nanoparticles. Nanoparticles have been the preferred light absorbers over molecules because they neither photo- nor thermo-bleach, and are thus more suited for applications requiring prolonged use. The best photothermal conversion efficiencies are reached using *metal* nanoparticles. Metals feature large electronic density, in comparison to semiconductors for example, which ensures much stronger interactions with light and subsequent absorption. In addition, metal nanoparticles can

exhibit localized plasmonic resonances, which further enhance light absorption by several orders of magnitude, especially with noble metals. This picture led to the field of *thermoplasmonics*,¹ which is the use of metal nanoparticles under illumination as nanosources of heat. In this field, gold nanoparticles in particular have played a major role for the past two decades because they feature strong plasmonic resonances, are biocompatible, and their resonance can be adjusted from the visible to the infrared range, as a function of their morphology.

The challenge in nanoscale heating research and applications is *not* in achieving nanoscale heating. This achievement is actually trivial, when using nanoparticles. Rather, the difficulty is in *measuring* the resulting nanoscale temperature increase.² After two decades, the lack of efficient and reliable nanoscale thermometry continues to cause problems in some applications of nanoplasmonics. In particular, in plasmonics-assisted chemistry, the possible occurrence of plasmonic heating has been disregarded for a decade, with some work recently questioning the interpretation of data from several impactful publications.^{3,4} In this field, heating is not the target, but rather a side effect. Nevertheless, it is crucial to quantify temperature increases properly to ensure correct interpretations of the experimental observations. Thus, thermometry is not only the concern of applications where heating is the target, it is ubiquitous in plasmonics, whether the resultant heating is desired or not.

Following the use of light for nanoscale heating, nanothermodynamics partly became a subfield of nanooptics. Because light can be used for nanoscale thermometry in addition to nanoscale heating, the entire field of nanoscale heating is a matter for the optics community. With far-field optical techniques, spatial resolution can reach a few 100s of nanometers, which is sufficient in most cases. The quest for efficient nanoscale thermometries in plasmonics started in the early 2010s.² So far, dozens of different optical approaches have been proposed. These approaches are based on the probing of physical quantities such as fluorescence (intensity, spectrum, polarization, life time), Raman (intensity, spectrum, surface-enhanced) or refractive index variations. The study by Barella *et al.* published in the February issue of *ACS Nano* stresses once more the particular interest in *anti-Stokes thermometry*.⁵ This approach lifts most of the limitations encountered by fluorescence thermometry: namely, it is label-free, it is more reliable due to its decreased sensitivity to other physical parameters, and it gives access to the temperature of the nanoparticles directly.

In this Perspective, I depict the evolution of ideas around nanothermometry in plasmonics over the past decade, with a special focus on anti-Stokes (AS) thermometry, based on the analysis of the anti-Stokes inelastic scattering of light by the plasmonic nanoparticles themselves. As an introduction to

the field, a first part of the Perspective briefly describes fluorescence microscopies developed for in plasmonics applications.

Fluorescence Thermometry

The fluorescence emitted by a material (molecule, particle, crystal defect, etc.) following the absorption of light at a shorter wavelength (see Figure 1a), is not only characterized by an intensity. Many other measurements can be undertaken to access valuable information on the material, such as spectrum, polarization, polarization anisotropy, life time, and correlation spectroscopy, among others.⁶ All these physical quantities are at the basis of countless microscopy techniques, which are especially useful in biology. But these emission characteristics are also dependent on the temperature of the material, making fluorescence the easy road toward thermometry.⁷ Provided a calibration is established, fluorescence microscopy can, thus, be used to achieve temperature mapping with a diffraction limited spatial resolution, using commercial set ups.

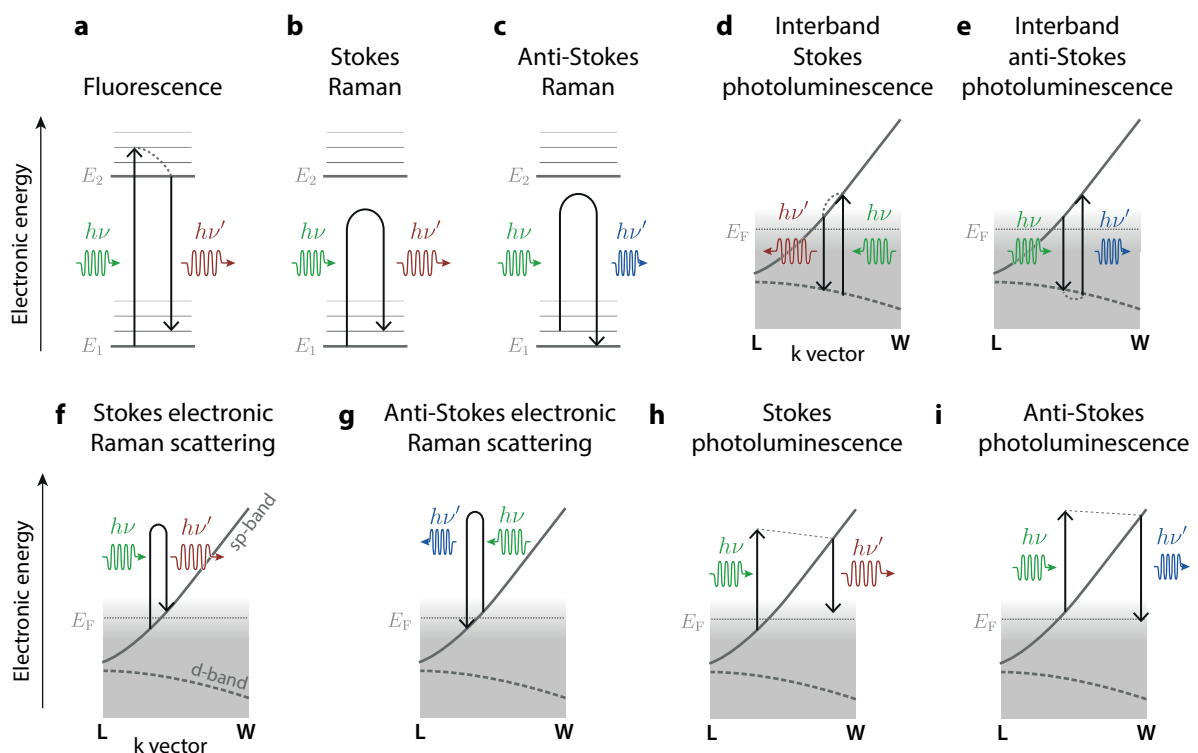


Figure 1: Mechanisms of inelastic light-matter interactions for molecules and gold nanoparticles. **(a)** Molecular fluorescence. **(b)** Molecular Stokes Raman emission. **(c)** Molecular anti-Stokes Raman emission. **(d)** Intraband Stokes photoluminescence (PL). **(e)** Intraband anti-Stokes PL. **(f)** Stokes electronic Raman scattering (ERS), **(g)**

anti-Stokes ERS, **(h)** Stokes PL (or hot luminescence), and **(i)** anti-Stokes PL (or hot luminescence) from a gold nanoparticle.

Fluorescence *intensity* is temperature dependent in most cases and usually decays with increasing temperature, due to decay of the quantum efficiency. However, fluorescence intensity is the least reliable fluorescence parameter as it also depends on many other effects, such as photo- and thermo-bleaching, and any subsequent variations of concentration. For example, studies in microscale molecular thermophoresis, a recent field of activity in thermoplasmonics,⁸ occasionally used thermosensitive fluorescent molecules dispersed in the liquid of interest to render the microscale temperature profile.⁹ However, these molecular probes are bound to feature variations of concentrations due to migration along the temperature gradients, leading to fluorescence variations that are not only due to temperature variations. This problem has been recognized,¹⁰ and may explain deviations of results compared with the rest of the community that is using alternative thermometries.¹¹ To avoid this issue, ratiometric fluorescence measurements are preferred, which can be achieved when considering fluorescence spectra.⁷ Some fluorescent compounds exhibit several fluorescence peaks with different temperature dependences, making a two-wavelength fluorescence intensity ratio a temperature readout that is no longer dependent on the molecular concentration. Monitoring a *shift* in wavelength of a fluorescence peak also fixes the issue.⁷

Interestingly, over the past decade, the search for effective nanothermometry techniques in plasmonics has been observed in live cell microscopy as well, quite independently, and the strategies that have been proposed were the same, all based on optical approaches. Drawing a parallel between these two research lines is instructive because the problems and solutions are the same, and the communities can learn from each other. In particular, monitoring fluorescence spectra has been the preferred approach for mapping the temperature in living cells as well, irrespectively of the exogenous and endogenous origin of the temperature variations. However, some unrealistic temperatures have been measured in living cells, casting some doubt on the reliability of fluorescence-based nanothermometries, no matter the measured fluorescence property (intensity, spectra, life time).¹²⁻¹⁴ For instance, researchers have noted temperature offsets of single living cells by a few degrees, albeit thermalized in a liquid bath,¹⁵ or even sometimes negative temperature variations,¹⁶ and, more recently, mitochondria at 50 °C.¹⁷ These issues highlight a fundamental problem with fluorescence as a temperature probe: Any fluorescence property is dependent on many physical quantities in addition to temperature, especially in a medium as complex as a living cell, including pH, ionicity, nonuniformity of the refractive index, hydrophilic/phobic surroundings, chemical near-environment, and aggregation.

Fluorescence properties can also be affected by the proximity of a metal surface,^{18,19} a common situation in plasmonics. For all these reasons, fluorescence thermometry has to be used with caution, especially in a complex environment.

The use of fluorescent *nanoparticles*, instead of molecules, may be more reliable because nanoparticles are more stable and less sensitive to external perturbations.⁷ In particular, nanodiamonds with nitrogen vacancy (NV) centers are fluorescent when excited around 530 nm. This fluorescence is not particularly temperature dependent, however, the frequency of spin resonance of NVs' center, which is in the microwave range, can be followed by fluorescence, and is temperature sensitive due to the dilation of the carbon lattice with temperature.^{20,21} NV-center thermometry requires the use of a microwave generator in addition to the excitation laser. In addition, NV-centers are insensitive to environmental factors, such as pH, ionicity, viscosity, molecular interactions, and organic solvents,²² and thus, seem to be a promising thermometry approach. To date NV-center thermometry has been used in several studies in live cell imaging,^{22,23} even involving plasmonic heating,²¹ and a couple of times for thermometry in plasmonic systems.^{24,25}

Irrespective of the approach, fluorescence-based thermometries require the use of labels in the nanoparticles' surroundings. In addition to the possible lack of reliability in complex environments, fluorescence microscopies are inherently invasive.

Anti-Stokes Thermometry

What is Raman scattering?

Raman emission is an inelastic scattering process that arises from the presence of vibrational states in the illuminated material, as depicted in Figures 1b,c. Raman spectroscopy provides valuable information on the chemical nature of the molecules or solid of interest, in a label-free manner. As a *scattering* process, it does not involve an electron promotion to another electronic state because the photon energy is too weak. To explain light-matter interactions despite the absence of an arrival electronic state, one usually refers to the transient access to a so-called *virtual* state. This appellation may be unfortunate, because nothing is virtual in physics, and because, once said, the mystery remains concerning what really happens, physically, during a scattering event. Actually, the molecule does reach this energy, not virtually. However, the electronic density at this energy is not a solution of the Hamiltonian of the system. In other words, it is not a steady state. As a consequence, the electronic density is not still, and radiates quasi-instantaneously. Thus, the unsteady (or virtual) state is short lived, and the coherence of light emission is kept in a scattering process. During this scattering process, which

only lasts around a period of the oscillation of the light electric field (a fraction of a femtosecond), the molecule can change its vibrational state, although it is very unlikely (1 out of 10^6 times). If this happens, one has a Raman scattering event. During a Raman process, depending on whether the final vibrational state has lower or higher energy than the initial state, the emission wavelength λ_{em} can be larger or smaller than the excitation wavelength λ_{laser} , leading to processes called respectively Stokes and anti-Stokes emissions (Figures 1b,c). The Raman energy shifts are usually expressed in wave numbers $\delta\sigma = 1/\lambda_{laser} - 1/\lambda_{em}$, expressed in cm^{-1} . $\delta\sigma$ is positive for Stokes and negative for anti-Stokes emission. This quantity is proportional to the photon energy shift $\delta E = hc\delta\sigma$.

Raman Spectroscopy for Thermometry

For an anti-Stokes (AS) process to happen, the initial state cannot be the ground state, but has to be one of the excited vibrational states (Figure 1c). However, these excited states are poorly populated at room temperature, following an exponential (Boltzmann-like) distribution, making AS signals weak compared to Stokes signals. As the temperature increases, these vibrational states become more populated, increasing the probability of AS Raman events. This temperature dependence offers the possibility to use Raman spectroscopy as a thermometry technique. In practice, the temperature of a material can be measured by monitoring the ratio of Stokes and AS emission intensities of a given Raman peak.²⁶ Given the small energy that thermal agitation can provide to molecules, around 24 meV at room temperature, AS Raman signals can only be found at the close proximity of the laser line, typically a few 10s of nm away in wavelength, or around a few 100s of cm^{-1} in wave number.

Anti-Stokes Emission from Metal Nanoparticles

Under laser illumination, metal nanoparticles exhibit weak AS emission at small energy shifts, just like molecules (Figures 2a,b). However, the origin of this emission is not clear, and not necessarily associated with a Raman scattering process as explained hereinafter. In general, an AS process designates any light emission that occurs at lower wavelength than the exciting light's wavelength, irrespective of the mechanism. This weak AS emission from metals may seem uninteresting at first glance, as it does not contain any information or any fingerprint of the nature of the material (Figure 2b). The AS spectra of metals merely resemble a featureless exponential decay, in contrast with the very rich AS emission of molecules. This lack of information may explain why AS emission from metals has been ignored for so long.

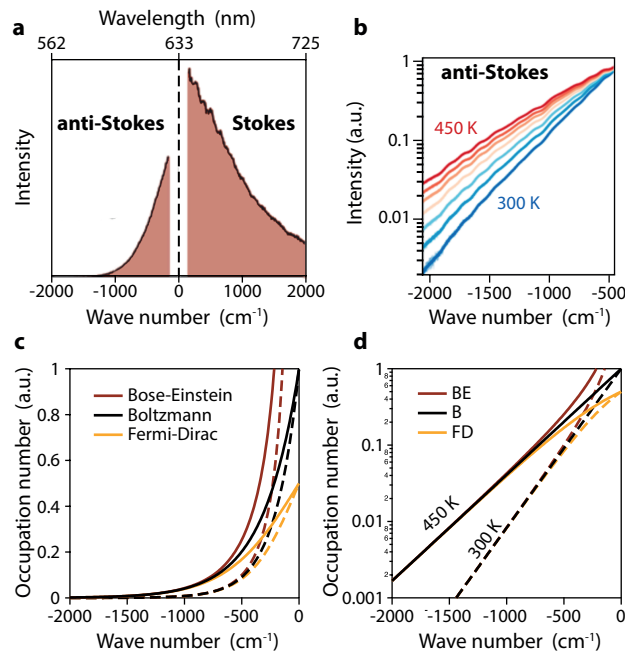


Figure 2: Photoluminescence from a gold nanoparticle. (a) Typical Stokes and anti-Stokes (AS) emission spectra for a laser excitation at 633 nm, and (b) semi-log plot of the normalized AS spectra associated to image (a). Reproduced from ref 27. Copyright 2018 American Chemical Society. (c) Plot of the different electron occupation statistics used to fit the AS emission profile (Eq. (1),(2),(3)), and (d) semi-log representation (dashed lines: $T = 300$ K, solid lines: $T = 450$ K).

The recently introduced thermometry technique in plasmonics based on the AS emission, and discussed hereinafter, is not based on the measurements of Stokes and AS intensity signals. Instead, this technique is based on the acquisition of exponential AS spectra, stemming from the metal, and its adjustment with a temperature-dependent fitting function (Figures 2a,b). This simple idea requires an appropriate fitting function, and determining the proper fitting function requires understanding the intimacy of the interaction between light and metal nanoparticles; this question is still a matter of debate. Although the characteristic emission spectra is simpler than that of molecules, the underlying physics of AS emission from metals is more complex and still under study. It is singular for at least three reasons. First, no vibrational states due to stretching or bending of chemical bonds enter into play with a metal. One rather has to deal with a continuum of phonons. Second, there are no discrete states. Only a continuous distribution of electronic energies has to be considered, along with a complex band structure and intra-/interband transitions. Finally, these electronic states have very short lifetimes, on the order of a few 10s of femtoseconds for gold, much shorter than the nanosecond range for excited electronic states of molecules. This short life time is due to the large probability of electron–electron

and electron–phonon scattering processes in metals. In the following section, I focus on gold because it is the metal that has attracted the most interest so far.

Photoluminescence or Light Scattering?

Two mechanisms have been proposed to explain the inelastic light emission from gold metal nanoparticles: electronic Raman scattering (ERS, a coherent inelastic light scattering process, Figures 1e,f), and photoluminescence (PL, an incoherent emission that involves effective electronic absorption, Figures 1g,h). When the photon energy is large enough (typically for wavelength below 550 nm), interband transitions are permitted and a PL process can explain the inelastic emission of light from metals, just like molecular fluorescence (Figures 1d,e).²⁸ Above typically 550 nm in excitation, only intraband transitions can occur. To explain the inelastic emission from metal nanoparticles, a dominant ERS mechanism has been considered,^{29–32} meaning that emission (unlike PL) should be prompt, coherent, and not require carrier relaxation, exactly like what happens with Raman emission from molecules (Figure 1). Yet, this process implies a change of momentum (horizontal shift, see Figure 1f) that cannot be supported by the re-emitted photon itself. It was proposed that this momentum compensation can occur when using nanoparticles due to the spatial confinement of the electronic wave functions over a characteristic length Δx , making wave vectors up to $\Delta k \sim \pi/\Delta x$ available.³¹ A PL process has been discarded because it is only favored when interband transitions can occur (Figure 1d,e), that is at illumination wavelengths below 550 nm. However, it does not mean that PL cannot occur with intraband transitions. If intraband PL was actually impossible or insignificant, compared with scattering processes, it would mean that the absorption would be insignificant compared with scattering in the near infrared (IR, the cross sections would obey the relation $\sigma_{\text{abs}} \ll \sigma_{\text{sca}}$), which is not the case in general. Substantial absorption does happen, even in the near-IR. This efficient absorption occurs due to inelastic scattering events with electrons, phonons, lattice crystallinity imperfections, and nanoparticle surfaces (Figures 1h,i). Thus, PL cannot be excluded by this sole argument, *a priori*. Incidentally, in 2019, going against the consensus that seemed to have been reached by the community regarding an ERS mechanism, Link's group instead proposed that the AS emission was due to the PL process, at least for gold nanorods.^{33,34} The authors noted that this result is not to be generalized to any plasmonic system, and that the involvement of one mechanism or the other may depend on the nature and morphology of the nanoparticles of interest. It seems likely that PL should be proportional to the *absorption* cross-section and ERS to the *scattering* cross-section of the particle, implying that the underlying mechanism of AS emission may indeed depend on the plasmonic system of interest.

Note that the term photoluminescence does not always have the same signification from one article to another. Whereas some researchers use PL to describe an incoherent process,^{31,32} in opposition to an inelastic scattering process, others consider PL to be a general name describing any inelastic light emission,^{29,35,36} being PL or ERS. In the latter case, PL is rather termed 'hot' luminescence.³⁶

Fermi-Dirac or Bose-Einstein?

In addition to the coherent/incoherent nature of the AS emission of metals piquing curiosity, the description of the electron occupation $f(E, T)$ near the Fermi level differs across studies. Because we are dealing with electrons, the natural occupation statistics to consider is a Fermi-Dirac (FD) distribution:

$$f_{\text{FD}}(E, T) = (e^{E/kT} + 1)^{-1}, \quad (1)$$

where E is the energy of the metal electron above the Fermi level (or more exactly above the chemical potential). This picture for metals has been adopted by the solid state physics community for decades,³⁷ and has been used more recently in plasmonics in the context of plasmonics-assisted nanochemistry under continuous wave (cw) illumination,³⁸ and by some researchers to develop the theory of AS emission from metal nanoparticles.^{29,31,32,39} However, in the context of this recent activity around AS emission from metal nanoparticles, some of the community considered the electrons near the Fermi level instead to follow Bose-Einstein (BE) statistics,^{30,33,35,40,41} because in interaction with phonons:

$$f_{\text{BE}}(E, T) = (e^{E/kT} - 1)^{-1}. \quad (2)$$

This latter description is justified when dealing with molecules, where the energy levels above the ground state are vibrational states (*i.e.*, identified as bosons), but with metals it seems less obvious. A hot electron created by photon absorption primarily thermalizes through electron–electron scattering. This process is more efficient at high energy, the interaction time scale τ_{e-e} being proportional to E^{-2} where E is the hot electron energy above the Fermi level.⁴² Thus, at low energy, the electron–electron interaction is less probable, and electron–phonon scattering may become the dominant process and set the electronic distribution.³⁶ This differentiation by energy level may explain why BE statistics could be privileged, although no evidence of this assumption has been derived. Consequently, when looking into detail, the occupation statistics in metals are not as simple as expected and deserve further investigation.

Orrit's group explained this subtlety in 2020,³⁶ and noticed, like others,³³ that within the range of AS energy shifts, the difference between one model or another is not dramatic, and both of them could be conveniently replaced with Boltzmann statistics, that is a simple exponential profile:

$$f(E, T) \approx \exp(-E/kT). \quad (3)$$

The three statistics (Eqs. (1),(2),(3)) are displayed in Figures 2c,d, where one can see that this assumption fails only at small energy shift, typically below 1000 cm⁻¹ where FD and BE distribution differ greatly. This region is generally cut by the filter of the laser excitation. It also fails when interband transitions enter into play, *i.e.*, at large wave numbers, or when the excitation laser wavelength is not red-shifted enough (Figures 3c,f).³⁶ Variations of 40% have been observed, though, in the temperature estimation when replacing BE with FD statistics (see Supplemental Information of ref 5). In semi-log representation (Figure 2d), at small wave numbers, the FD statistics are concave whereas the BE statistics are convex. Interestingly, most of the experimental semi-log AS profiles reported in the literature are concave (see Figures 2b and 3b,e), suggesting that the more natural FD distribution could be more appropriate than a BE profile as a fitting function, contrary to what most researchers are doing.

In AS thermometry, measurements usually do not exceed AS shifts of 2000 cm⁻¹, especially on single nanoparticle experiments because the signal becomes too low at high energy shifts. However, some researchers have measured signals above 3000 cm⁻¹ and observed strong deviation from the exponential law (Figure 3f).^{41,43,44} As a better fitting function, the authors used a combination of both BE and FD statistics that showed good agreement with experimental data:

$$f_{\chi}(E, T) = \chi f_{BE}(E, T) + (1 - \chi) f_{FD}(E, T). \quad (4)$$

To support this model, the authors assume that the nanoparticle hosts a thermalized hot electron population, an assumption also given in ref 33. However, under cw illumination, no such hot electron gas exists: It only exists transiently using pico- or femtosecond pulsed illumination. In cw illumination, hot electrons get excited one by one, and never meet each other, because they live only for 10s of fs. In addition, the thermalization with the lattice is too fast (0.5 ps) to enable the creation of a hot electron gas of several 1000s of degrees. The only case where the electron gas can feature a different temperature than the lattice under cw illumination is for very small nanoparticles (typically 10 nm big) as numerically demonstrated in ref 45. However, the temperature difference remains quite small. In plasmonics-assisted chemistry, the hot carriers are those charges that only live for 10s of fs and, more importantly, are not thermalized. Thus, their energy distribution cannot be modeled by a FD distribution, as proposed by the authors. The deviation from an exponential decay at large energies may come from another effect, rather than from an electron gas at a few 1000s of K. Perhaps some light leakage or dark noise of the sensor, which should necessarily be observed at some point for high energy shifts, may be responsible for this deviation, although it is difficult to believe that the authors

did not check these possibilities. As explained in ref 36 and shown in Figure 3c, deviations from the exponential law are expected when reaching wavelength below 550 nm due to interband transitions.

Effects of the Electronic and Photonic Density of States

The AS emission $I(\omega, T)$ from a nanoparticle follows the energy distribution of carriers above the Fermi level, which reads $n(E) = \rho(E)f(E, T)$, where $\rho(E)$ is the density of states, directly related to the energy band diagram. The AS emission is also proportional to the probability of far-field emission from an emitter, which is related to the local photonic density of state (PDOS). This effect can be understood as a Purcell effect mechanism.⁴⁶ For a plasmonic nanoparticle, the PDOS reproduces the localized plasmonic resonance (LPR) line shape I_{LPR} . The AS Raman spectrum is thus proportional to three functions:³⁶

$$I(\omega, T) = C I_{\text{LPR}}(\omega) \rho(\hbar(\omega - \omega_{\text{laser}})) f(\hbar(\omega - \omega_{\text{laser}}), T). \quad (5)$$

where C is a constant and ω_{laser} is the laser light angular frequency. In general, $I_{\text{LPR}}(\omega)$ cannot be considered as a constant over the frequency range of AS Raman emission, as observed in Figure 3a. $\rho(\hbar(\omega - \omega_{\text{laser}}))$ is usually not considered in AS Raman thermometry because it is assumed to be uniform. This assumption is valid if interband transitions do not occur.³⁶ I_{LPR} is usually assumed to be proportional to the scattering cross-section,^{29,33} or to the photoluminescence spectrum.³⁵ I_{LPR} is highly wavelength dependent, especially close to the plasmonic resonance, and thus significantly distorts the original exponential-like temperature-dependent emission. This distortion is where the complexity of AS thermometry in plasmonics lies as it prevents proper exponential fit of the AS spectra.

Anti-Stokes Thermometry in Nanoplasmonics: The Evolution of the Method

Several researchers have reported on the use of Raman spectroscopy measurements, including surface-enhanced Raman spectroscopy, to measure temperature in plasmonic systems.⁴⁷ However, these studies involved surrounding molecules, which require calibration, induce instability, and yield a temperature that is not necessarily the same as the nanoparticles'. In addition, some complexity arises from the presence of a fluctuating background continuum, the origin of which is not clearly established.³¹ The idea of using the AS emission from the nanoparticles themselves (and no longer from surrounding molecules) as a thermometry approach was briefly mentioned in 2015,²⁹ and introduced in greater detail in 2016 by Xie and Cahill.³⁰ With this pioneering work, the featureless AS emission spectrum of a *metal* nanoparticle finally found concrete application. The authors explained the temperature dependence of the AS emission, and considered BE statistics to fit its profile (Eq. (2)). They also introduced the main difficulty of the approach, which is dealing with the unknown I_{LPR} spectrum of the particle in Eq. (5). Their strategy consisted of acquiring the AS emission spectra at

room temperature T_0 as a normalization, *i.e.*, in computing $I(\omega, T)/I(\omega, T_0)$ to cancel $I_{\text{LPR}}(\omega)$ in Eq. (5). However, the probe laser was also the heating laser, and even at the lowest laser power required to achieve reasonable exposure time (on the order of 200 s), the laser was still heating the nanoparticle at a temperature that could not be determined. The authors fixed this issue by acquiring a series of measurements at various laser powers, and using an iterative algorithm to end up with consistent (linear) evolution of the temperature increase as a function of the laser power. The technique was taken up by several groups to conduct thermometry measurements in plasmonic trapping²⁷ or plasmonic photocatalysis.⁴⁸ In 2018, to eliminate the $I_{\text{LPR}}(\omega)$ factor in Eq. (5), Orrit's group proposed measuring it directly. This approach requires another laser, at shorter wavelength, to excite and to record the nanoparticle PL spectra, which is supposed to be proportional to $I_{\text{LPR}}(\omega)$. Using this method, the authors obtained the unperturbed distribution $f(E, T)$, up to a *constant* pre-factor, and achieved consistent temperature measurements (Figure 3b). In 2019, the same group extended the range of applications of AS thermometry in plasmonics by showing how it could be applied for temperature measurements under picosecond pulsed illumination.³⁶ In that case, transient electronic temperature increases as high as ~ 1000 K could be measured, as expected under pulsed illumination. The authors explained that their normalization procedure no longer applies when the laser excitation is close to interband transition and when using nanospheres instead of plasmonic nanoparticles resonating in the IR. To solve this issue, the authors noticed that with nanospheres, the plasmon resonance is not sharp and a simple exponential fit can be used without normalization (Eq. (3), Figure 3c). In 2019, Link's group used AS thermometry to investigate the underlying mechanism of AS emission from plasmonics nanoparticles. Some unrealistic electronic temperatures have been observed, as high as a few 1000s of K. Such high electronic temperatures are usually only observed under pulsed illumination. The huge heating laser intensity used in this study may partly explain this observation (100–300 mW/ μm^2).

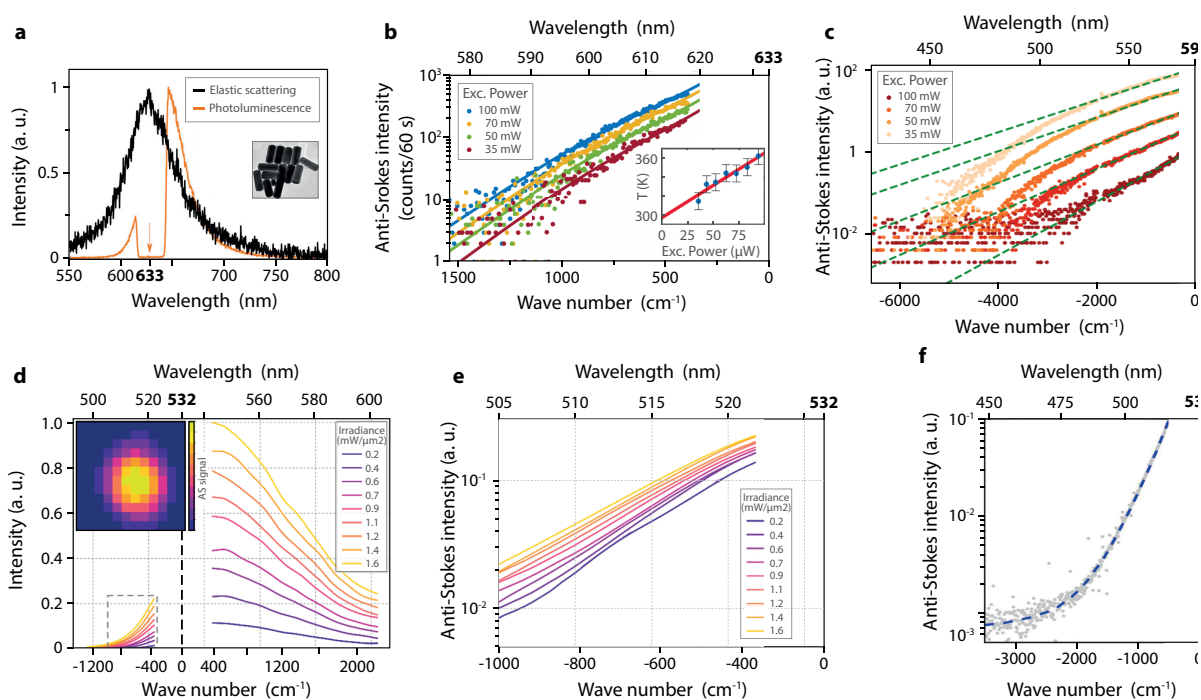


Figure 3: (a) Comparison of the inelastic emission spectra (orange) excited at $\lambda_{\text{laser}} = 633$ nm (the laser line was cut using a notch filter) and elastic scattering spectra (black) of a population of gold nanorods. Inset: scanning electron microscope image of gold nanorods. Reproduced with permission from ref 29. Copyright 2015 The Royal Society of Chemistry. (b) Anti-Stokes emission from a single gold nanorod excited at 633 nm for various laser powers. Solid lines are fits using Bose-Einstein statistics (Eqs. (2) and (5)). Inset: Temperatures retrieved from the fits. Reproduced from ref 35. Copyright 2018 American Chemical Society. (c) Same as (b) for a single gold nanosphere excited at 594 nm, under sub-picosecond pulsed illumination. Dashed lines are fit using a Boltzmann distribution (Eq. (3)). Reproduced from ref 36. Copyright 2020 American Chemical Society. (d) Photoluminescence spectra acquired from a 80-nm gold nanosphere, at various irradiance levels obtained from a hyperspectral confocal image (inset), along with (e) the semi-log plot of the anti-Stokes emission normalized by the excitation irradiance. Reproduced from ref 5. Copyright 2021 American Chemical Society. (f) Anti-Stokes emission spectra from an assembly of gold nanodisks, 100-nm in diameter, excited at 532 nm and fitted using Eq. (4). Reproduced with permission from ref 43. Copyright 2020 AIP Publishing.

Stefani and co-workers published a study along this line in the February issue of *ACS Nano*. The authors used the initial normalization procedure of Xie and Cahill,³⁰ but noticed that the nanoparticle temperature increase $\Delta T = T - T_0$ should be proportional to the laser intensity I_{exc} : $\delta T = \beta I_{\text{exc}}$.⁵ This simple, additional mathematical constraint enabled the authors to achieve temperature measurements without pre-calibration or use of another laser, making their approach more direct and simpler than current methods. In addition, the authors acquired hyperspectral images (Figures 3d,e) by raster scanning the laser beam over the nanoparticle of interest (2 s of integration time per pixel), eliminating the need for precise laser alignment with respect to the nanoparticle. Moreover, this image acquisition

procedure collects a large set of spectra at different laser irradiances, which can be processed to retrieve this β factor defined above, which is an intrinsic feature of the nanoparticle. This burgeoning activity in just 5 years is the sign of a rising trend, with applications not only for thermometry, but also for improving understanding of light–matter interactions in plasmonics.

Anti-Stokes Raman thermometry appears more powerful than fluorescence approaches in many aspects. In particular, it is less sensitive to environmental perturbation. The AS signal seems only to be affected by the photonic density of state of a metal particle (at least far from interband transitions), distorting the AS line shape. But this effect is well understood and several procedures have been proposed to take it into account. Raman thermometry also enables the achievement of sub-diffraction spatial resolution. The only issue when decreasing the nanoparticle size may be the signal-to-noise ratio. The major difference between fluorescence and AS thermometry is that they do not measure the same physical quantity: fluorescence provides measurements of the temperature in the nanoparticle's surroundings, whereas AS thermometry provides the inner nanoparticle temperature. This difference benefits fluorescence approaches in two ways. First, fluorescence microscopy enables temperature *mapping*, whereas nanoparticle AS thermometry probes temperature at a given location. Second, what really matters in most applications is the temperature in the surrounding medium, because it is where all the thermal-induced processes happen, being related to fluid dynamics, chemistry, phase transition, biology, etc. Fluorescence and AS thermometries, thus, are complementary, and the perfect nanothermometry approach in plasmonics is yet to be found, making this field of research still very active.

Conclusion and Outlook

Knowing the temperature of a plasmonic system under illumination, or just knowing whether heating occurs, are major concerns in plasmonics, both when heating is the target and also when it is not. The whole plasmonics community now has to face thermodynamics problems, with all the associated conceptual and technical difficulties, the first one being measuring the nanoscale temperature. After 10 years of active investigation and the development of a large variety of optical thermometries, the quest for the perfect nanothermometry is still ongoing. Fluorescence has been heavily used but can suffer from artefacts because fluorescence is dependent on many other parameters in addition to temperature, leading the community to look for noninvasive, label-free techniques. Considering the inelastic light scattering by the nanoparticles themselves looks promising. In particular, the AS emission from metal nanoparticles contains direct information on the nanoparticle temperature, a realization that gave birth to the new research line of AS thermometry in nanoplasmonics in 2015. This research

remains in its infancy and offers many possibilities for exciting new research activities. First, uncovering the origin of AS thermometry will also help us understand how metal nanoparticles interact with light, which remains a matter of debate. When a photon interacts with a metal nanoparticle, it is not clear where the electron comes from (FD or BE distribution) or what it does (PL or ERI). In other words, as soon as the description of the problem is not entirely illustrated by the Maxwell equations and some solid states physics enters into play, the problem increases in complexity and becomes a matter of debate. Currently, AS Raman thermometry has only been applied on conventional, primarily gold, nanoparticles. A large segment of the community is looking for alternative materials in plasmonics, and using AS Raman thermometry on other materials could help us better understand light–matter interactions in nanoplasmonics,⁴³ and potentially aid in the development of nanothermometers that are easier to handle than gold. Indeed, the major concern in nanoplasmonics thermometry today is no longer the search for new techniques, as a plethora have been proposed in the past decade. The next decade may instead be dedicated to finding new compounds and more reliable nanothermometers as a mean to improve established techniques.

References

1. Baffou, G.; Cichos, F.; Quidant, R. Applications and Challenges of Thermoplasmonics. *Nat. Mater.* **2020**, *19*, 946–958.
2. Quintanilla, M.; Liz-Marzán, L. M. Guiding Rules for Selecting a Nanothermometer. *Nano Today* **2018**, *19*, 126–145.
3. Baffou, G.; Bordacchini, I.; Baldi, A.; Quidant, R. Simple Experimental Procedures to Distinguish Photothermal from Hot-Carrier Processes in Plasmonics. *Light Sci. Appl.* **2020**, *9*, 108.
4. Dubi, Y.; Un, I. W.; Sivan, Y. Thermal Effects – An Alternative Mechanism for Plasmon-Assisted Photocatalysis. *Chem. Sci.* **2020**, *11*, 5017–5027.
5. Barella, M.; Violi, I. L.; Gargiulo, J.; Martinez, L. P.; Goschin, F.; Guglielmotti, V.; Pallarola, D.; Schlücker, S.; Pilo-Pais, M.; Acuna, G. P.; Maier, S. A.; Cortés, E.; Stefani, F. D. *In Situ* Photothermal Response of Single Gold Nanoparticles through Hyperspectral Imaging Anti-Stokes Thermometry. *ACS Nano* **2020**, doi:10.1021/acsnano.0c06185.
6. Valeur, Bernard. *Molecular Fluorescence: Principles and Applications*, 2nd Edition; Wiley.
7. Jaque, D.; Vetrone, F. Luminescence Nanothermometry. *Nanoscale* **2012**, *4*, 4301–4326.
8. Braun, M.; Cichos, F. Optically Controlled Thermophoretic Trapping of Single Nano-Objects. *ACS Nano* **2013**, *7*, 11200–11208.
9. Braun, D.; Libchaber, A. Trapping of DNA by Thermophoretic Depletion and Convection. *Phys. Rev. Lett.* **2002**, *89*, 188103.

10. Duhr, S.; Arduini, S.; Braun, D. Thermophoresis of DNA Determined by Microfluidic Fluorescence. *Eur. Phys. J. E* **2004**, *15*, 277–286.
11. Würger, A. Hydrodynamic Boundary Effects on Thermophoresis of Confined Colloids. *Phys. Rev. Lett.* **2016**, *116*, 138302.
12. Baffou, G.; Rigneault, H.; Marguet, D.; Jullien, L. A Critique of Methods for Temperature Imaging in Single Cells. *Nat. Methods* **2014**, *11*, 899–901.
13. Baffou, G.; Rigneault, H.; Marguet, D.; Jullien, L. Reply to: ‘Validating Subcellular Thermal Changes Revealed by Fluorescent Thermosensors’ and ‘The 10 5 Gap Issue between Calculation and Measurement in Single-Cell Thermometry’. *Nat. Methods* **2015**, *12*, 803–803.
14. Suzuki, M.; Plakhotnik, T. The Challenge of Intracellular Temperature. *Biophys. Rev.* **2020**, *12*, 593–600.
15. Yang, J.-M.; Yang, H.; Lin, L. Quantum Dot Nano Thermometers Reveal Heterogeneous Local Thermogenesis in Living Cells. *ACS Nano* **2011**, *5*, 5067–5071.
16. Okabe, K.; Inada, N.; Gota, C.; Harada, Y.; Funatsu, T.; Uchiyama, S. Intracellular Temperature Mapping with a Fluorescent Polymeric Thermometer and Fluorescence Lifetime Imaging Microscopy. *Nat. Commun.* **2012**, *3*, 705.
17. Chrétien, D.; Bénit, P.; Leroy, C.; El-Khoury, R.; Park, S.; Lee, J. Y.; Chang, Y.-T.; Lenaers, G.; Rustin, P.; Rak, M. Pitfalls in Monitoring Mitochondrial Temperature Using Charged Thermosensitive Fluorophores. *Chemosensors* **2020**, *8*, 124.
18. Anger, P.; Bharadwaj, P.; Novotny, L. Enhancement and Quenching of Single-Molecule Fluorescence. *Phys. Rev. Lett.* **2006**, *96*, 113002.
19. Carminati, R.; Greffet, J.-J.; Henkel, C.; Vigoureux, J. M. Radiative and Non-Radiative Decay of a Single Molecule Close to a Metallic Nanoparticle. *Opt. Commun.* **2006**, *261*, 368–375.
20. Neumann, P.; Jakobi, I.; Dolde, F.; Burk, C.; Reuter, R.; Waldherr, G.; Honert, J.; Wolf, T.; Brunner, A.; Shim, J. H.; Suter, D.; Sumiya, H.; Isoya, J.; Wrachtrup, J. High-Precision Nanoscale Temperature Sensing Using Single Defects in Diamond. *Nano Lett.* **2013**, *13*, 2738–2742.
21. Kucsko, G.; Maurer, P. C.; Yao, N. Y.; Kubo, M.; Noh, H. J.; Lo, P. K.; Park, H.; Lukin, M. D. Nanometre-Scale Thermometry in a Living Cell. *Nature* **2013**, *500*, 54–58.
22. Sekiguchi, T.; Sotoma, S.; Harada, Y. Fluorescent Nanodiamonds as a Robust Temperature Sensor Inside a Single Cell. *Biophys. Physicobiol.* **2018**, *15*, 229–234.
23. Simpson, D. A.; Morrisroe, E.; McCoey, J. M.; Lombard, A. H.; Mendis, D. C.; Treussart, F.; Hall, L. T.; Petrou, S.; Hollenberg, L. C. L. Non-Neurotoxic Nanodiamond Probes for Intraneuronal Temperature Mapping. *ACS Nano* **2017**, *11*, 12077–12086.
24. Tetienne, J.-P.; Lombard A.; Simpson, D. A.; Ritchie, C.; Lu, J.; Mulvaney, P.; Hollenberg, L. C.

- L. Scanning Nanospin Ensemble Microscope for Nanoscale Magnetic and Thermal Imaging. *Nano Lett.* **2016**, *16*, 326–333.
25. Sotoma, S.; Epperla, C. P.; Chang, H.-C. Diamond Nanothermometry. *ChemNanoMat* **2018**, *4*, 15–27.
26. McGrane, S. D.; Moore, D. S.; Goodwin, P. M.; Dattelbaum, D. M. Quantitative Tradeoffs between Spatial, Temporal, and Thermometric Resolution of Nonresonant Raman Thermometry for Dynamic Experiments. *Appl. Spectrosc.* **2014**, *68*, 1279–1288.
27. Jones, S.; Andr n, D.; Karpinski, P.; K ll, M. Photothermal Heating of Plasmonic Nanoantennas: Influence on Trapped Particle Dynamics and Colloid Distribution. *ACS Photonics* **2018**, *5*, 2878–2887.
28. Apell, P.; Monreal, R.; Lundqvist, S. Photoluminescence of Noble Metals. *Phys. Scr.* **1988**, *38*, 174–179.
29. He, Y.; Xia, K.; Lu, G.; Shen, H.; Cheng, Y.; Liu, Y.-c.; Shi, K.; Xiao, Y.-F.; Gong, Q. Surface Enhanced Anti-Stokes One-Photon Luminescence from Single Gold Nanorods. *Nanoscale* **2015**, *7*, 577–582.
30. Xie, X.; Cahill, D. G. Thermometry of Plasmonic Nanostructures by Anti-Stokes Electronic Raman Scattering. *Appl. Phys. Lett.* **2016**, *109*, 183104.
31. Hugall, J. T.; Baumberg, J. J. Demonstrating Photoluminescence from Au is Electronic Inelastic Light Scattering of a Plasmonic Metal: The Origin of SERS Backgrounds. *Nano Lett.* **2015**, *15*, 2600–2604.
32. Mertens, J.; Kleemann, M.-E.; Chikkaraddy, R.; Narang, P.; Baumberg, J. J. How Light Is Emitted by Plasmonic Metals. *Nano Lett.* **2017**, *17*, 2568–2574.
33. Cai, Y.-Y.; Sung, E.; Zhang, R.; Tazuin, L. J.; Liu, J. G.; Ostovar, B.; Zhang, Y.; Chang, W.-S.; Nordlander, P.; Link, S. Anti-Stokes Emission from Hot Carriers in Gold Nanorods. *Nano Lett.* **2019**, *19*, 1067–1073.
34. Ostovar, B.; Cai, Y.-Y.; Tazuin, L. J.; Lee, S. A.; Ahmadivand, A.; Zhang, R.; Nordlander, P.; Link, S. Increased Intraband Transitions in Smaller Gold Nanorods Enhance Light Emission. *ACS Nano* **2020**, *14*, 15757–15765.
35. Carattino, A.; Caldarola, M.; Orrit, M. Gold Nanoparticles as Absolute Nanothermometers. *Nano Lett.* **2018**, *18*, 874–880.
36. Jollans, T.; Caldarola, M.; Sivan, Y.; Orrit, M. Effective Electron Temperature Measurement Using Time-Resolved Anti-Stokes Photoluminescence. *J. Phys. Chem. A* **2020**, *124*, 6968–6976.
37. Ashcroft, N.; Mermin, N. *Solid State Physics*. Brooks/Cole, 1976.
38. Saavedra, J. R. M.; Asenjo-Garcia, A.; Garc a de Abajo, F. J. Hot-Electron Dynamics and Thermalization in Small Metallic Nanoparticles. *ACS Photonics* **2016**, *3*, 1637–1646.

39. Szczerbiński, J.; Gyr, L.; Kaeslin, J.; Zenobi, R. Plasmon-Driven Photocatalysis Leads to Products Known from E-Beam and X-Ray-Induced Surface Chemistry. *Nano Lett.* **2018**, *18*, 6740–6749.
40. Huang, J.; Wang, W.; Murphy, C. J.; Cahill, D. G. Resonant Secondary Light Emission from Plasmonic Au Nanostructures at High Electron Temperatures Created by Pulsed-Laser Excitation. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 906–911.
41. Wu, S.; Hogan, N.; Sheldon, M. Hot Electron Emission in Plasmonic Thermionic Converters. *ACS Energy Lett.* **2019**, *4*, 2508–2513.
42. Khurgin, J. B. Fundamental Limits of Hot Carrier Injection from Metal in Nanoplasmonics. *Nanophotonics* **2020**, *9*, 453–471.
43. Hogan, N.; Sheldon, M. Comparing Steady State Photothermalization Dynamics in Copper and Gold Nanostructures. *J. Chem. Phys.* **2020**, *152*, 061101.
44. Hogan, N.; Wu, S.; Sheldon, M. Photothermalization and Hot Electron Dynamics in the Steady State. *J. Phys. Chem. C* **2020**, *124*, 4931–4945.
45. Meng, L.; Yu, R.; Qiu, M.; García de Abajo, F. J. Plasmonic Nano-Oven by Concatenation of Multishell Photothermal Enhancement. *ACS Nano* **2017**, *11*, 7915–7924.
46. Cai, Y.-Y.; Liu, J. G.; Tauzin, L. J.; Huang, D.; Sung, E.; Zhang, H.; Joplin, A.; Chang, W.-S.; Nordlander, P.; Link, S. Photoluminescence of Gold Nanorods: Purcell Effect Enhanced Emission from Hot Carriers. *ACS Nano* **2018**, *12*, 976–985.
47. Pozzi, E. A.; Zrimsek, A. B.; Lethiec, C. M.; Schatz, G. C.; Hersam, M. C.; Van Duyne, R. P. Evaluating Single-Molecule Stokes and Anti-Stokes SERS for Nanoscale Thermometry. *J. Phys. Chem. C* **2015**, *119*, 21116–21124.
48. Pensa, E.; Gargiulo, J.; Lauri, A.; Schlücker, S.; Cortés, E.; Maier, S. A. Spectral Screening of the Energy of Hot Holes over a Particle Plasmon Resonance. *Nano Lett.* **2019**, *19*, 1867–1874.