



Molecular Spectroscopy Workbench

SERS: An Update of Progress Made

This column is a mini survey of progress that has been made in the area of surface enhancement over the last few years since my previous column on surface-enhanced Raman scattering (SERS) in 2008. The potential of SERS to provide signals of analytes at very low concentrations continues to beckon the analytical chemist. What the last few years has produced is a body of work describing the role of the plasmonic properties of metals, based on their geometrical and electronic properties, in enhancing the signals. As this field matures, we foresee production of surface-enhancing films and particles, engineered to provide large enhancements at selected wavelengths that will provide reproducible Raman signals for applications in areas such as environmental and biomedical studies.

Fran Adar

My earlier article on surface-enhanced Raman scattering (SERS) (1) did not include much discussion of particular applications except to mention improved sensitivity for bioclinical studies. Here, I provide a conceptual introduction to plasmonics to support the contention that, in the not-too-distant future, SERS will enable measurements at low concentrations.

Background Motivation

Aside from its potential to enhance analytical sensing measurements in manufacturing, biomedicine, and environmental testing, the United States military has shown a keen interest in surface enhancement for detection and identification of biological and chemical warfare agents. Because of reproducibility issues, workers at two of the US Army's laboratories have published a paper titled "Surface-Enhanced Raman Scattering (SERS) Evaluation Protocol for Nanometallic Surfaces" (2) to provide to the community "analytical and spectroscopic figures of merit to unambigu-

ously compare the sensitivity and reproducibility of various SERS substrates." But it is necessary to recognize that SERS measurement detects a two-dimensional (2D) area while a comparable bulk measurement detects molecules in a three-dimensional volume. Furthermore, it is difficult to calculate the number of adsorbed molecules on the SERS surface and in the detected volume of a normal Raman measurement; therefore, the assessment proposed in this article (2) is an empirical protocol. The SERS enhancement value (SEV) was defined as the ratio of the concentrations that produced, on a particular instrument, the same instrument responses for normal Raman scattering versus SERS scattering. In this case, the metric selected was the ratio of the area of a peak in the spectrum of BPE (*trans*-1,2-bis(4-pyridyl)-ethylene) to the ethanol in which the BPE was dissolved. This protocol provides a means to determine, for a particular type of SERS substrate, on a given instrument using standardized acquisition conditions, the minimum detectable concentration of an analyte and to determine SERS reproducibility, from spot

to spot on a given substrate, from substrate to substrate, and over time. And it also provides a qualitative means of comparing different substrate types. Because the military is interested not only in the detection of warfare agents, but also the identification of false positives and false negatives, it uses the receiver operating characteristic (ROC) curves for analysis of when, and how (warning versus evacuation) to react (3).

Clearly, if the Defense Advanced Research Projects Agency (DARPA) is investing so much effort into this technology, it is believed that the pay-off in terms of military capabilities and homeland security will be high. Because of this, DARPA put out a request for proposals to fund research that would determine, in a rigorous fashion, what is the origin of SERS so that it could be relied on as an analytical technique. The article cited above (2) describes the methods developed to evaluate and compare SERS substrates prepared by different laboratories, and to compare the heterogeneity of the substrates of a given type.

Evolution of SERS Research

The initial report on strongly enhancing Raman signals was published in 1974 (4). However, if one tried to follow the field during the first 20 years or so, you would see that the signals were highly variable from laboratory to laboratory, and a vigorous debate arose as to whether the origin of the enhancement was chemical or physical. Fleischman and colleagues (4) believed that the large enhancement arose from increased surface area produced by the substrate preparation, but by 1977 Jeanmaire and van Duyne (5) and Albrecht and Creighton (6) showed that the increased surface area could not account for all the enhancement. Already in a review published in 1985, Moskovits (7) reported that “the majority view is that the largest contributor to the intensity amplification results from the electric field enhancement that occurs in the vicinity of small, interacting metal particles that are illuminated with light resonant or near resonant with the localized surface-plasmon

frequency of the metal structure.” In 1997, Emory and Nie (8) reported super-enhancement from single silver colloidal nanoparticles in a heterogeneous population, with enhancement factors of the order of 10^{14} to 10^{15} . Certainly this publication went far in explaining the large discrepancies that had been noticed from laboratory to laboratory. The group of Louis Brus continued this type of work—associating SERS “hot spots” with particles of particular size, shape, and aggregation (9). By measuring Rayleigh and Mie scattering in addition to absorption and SERS they proposed modified enhancing mechanisms including the chemical mechanism of Otto (10) and a mechanism involving the interaction of ballistic electrons with chemisorbed molecules. Note that single-molecule SERS had been predicted a year earlier by Kneipp, and colleagues (11).

Moskovits published a second review (12) 20 years after the first in which he states “. . . that all of the major features of SERS . . . are essentially incomprehensible without invoking the electromagnetic theory,” but the controversy regarding the possibility of a strong chemical effect persists “because of the simplicity of its (SERS) experimental actualization, (which) is primarily a chemical (and lately a biochemical) tool whereas its origin requires a rather deep knowledge of condensed matter physics and especially the optical response of materials, which includes a number of physical subtleties.”

In his 1985 review, Moskovits described more than seven different preparation techniques from which he already inferred that the best enhancements occurred in the presence of coupled, microscopic metal domains (7). His 2005 article includes a clear explanation of why particle dimers produce such strong enhancement (12); his Figure 1 (which is derived from simple principles of electromagnetism that are shown here in my Figure 1) illustrates how an electric field (for example, from the photon) polarized along the interparticle axis induces a polarization along that direction that scales to the -8th power of the gap dimension.

If a molecule resides in the gap, it will experience a very large electric field. This large field in turn induces an enhanced polarizability and then an enhanced Raman signal. Moskovits summarizes that the electromagnetic theory accounts for all SERS observations—the nanostructure requirement, the behavior of the various metals (in terms of their enhancement capabilities), the increased enhancement from interacting metal nanoparticles, and the polarization sensitivity. He also mentions other electromagnetic mechanisms, in particular the lightening rod effect for ellipsoids and nanorods with sharp curvature. And he discusses single-molecule SERS. Single-molecule Raman scattering was more thoroughly reviewed in 2006 in *Applied Spectroscopy* (13). An interesting methodology was described in this 2006 article where solution concentrations of metallic clusters and target analyte were chosen to approximate 0 to several molecule–metal clusters in a focal volume of the order of picoliters to femtoliters when using a Raman microscope as the sampling tool. The integrated signal for a particular analyte line was plotted as a function of time, and represented the amount of detected analyte in the focal volume, which fluctuated because of Brownian motion. (A far red excitation, 830 nm, was used to couple the laser to the aggregated plasmon absorption, but its intensity was kept to a minimum to avoid “laser trapping.”) A histogram plot of the signal (frequency of events detected at given signal levels) indicated “quantized” detected levels; the histogram was fitted to Poisson statistics that indicated the presence of 0, 1, 2, and 3 molecules per detected event, with the total probability dropping with the number of molecules per event. At the end of this article, Kneipp and colleagues indicated the potential importance of the single-molecule SERS capability in detecting and differentiating chemicals such as DNA fragments or even single bases. Then in 2011, Volker Deckert’s group demonstrated that a tip-enhanced Raman spectroscopy (TERS) system has the capabilities to detect and differentiate

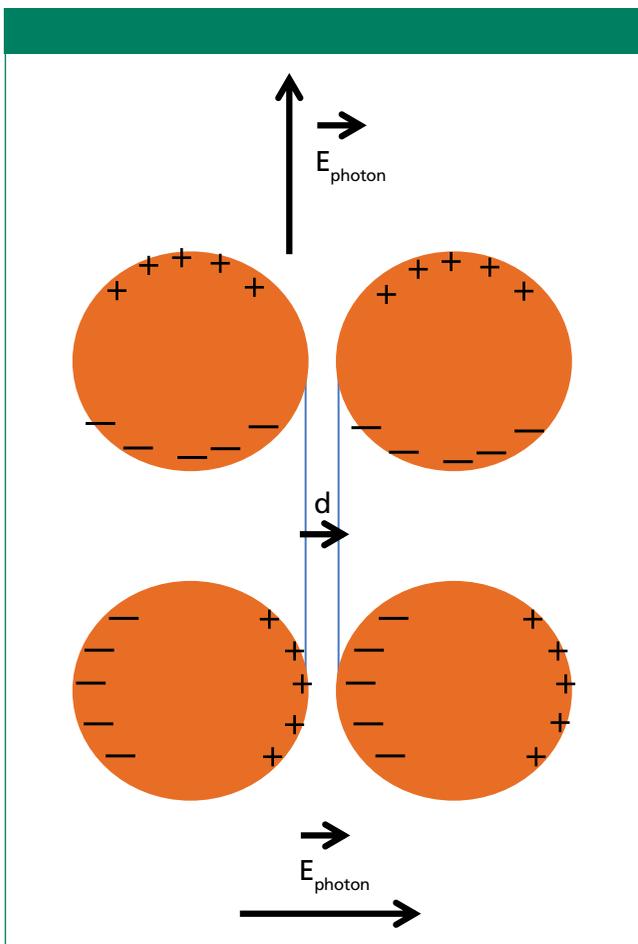


Figure 1: Depiction of how the photon field induces polarization on particles of dimension much smaller than the photon wavelength.

single nucleotides in single-stranded calf thymus DNA (14)!

Most of what has been said above could have been said in my first article on this topic, which appeared in 2008 (1). But in that article I really only indicated what the origin of intense interest in this field was. In recent years, because of the understanding of the origin of the SERS phenomenon, there has been a rational design of SERS substrates that really offers the expectation that SERS can become a reliable analytical tool. I cover some of those developments in the next section.

The Role of Strong Coupling in Metallic Nanostructures

I first became aware of the progress in the field when I heard the invited talk of Professor Naomi Halas of Rice University at the International Conference on Raman Spectroscopy (ICORS) in Jena, Germany, in August 2014. What really startled me was the demonstration of plasmonic properties in aluminum systems (15). Until recently it had been assumed that surface-enhancing conditions require coinage metals, but with the insights gained about the underlying physics, it is now clear that, in a proper configuration, aluminum will provide appropriate plasmonic properties. My abbreviated description, which will most certainly be inadequate for a physicist im-

mersed in the field, will be based on the review article by Halas and colleagues that appeared in 2011 (16) and includes more than 500 references to the field up until that time. My goal here is to provide a sparse introduction to a complex field that now really does show promise for producing reliable, reproducible, inexpensive SERS substrates. The interested reader is urged to access the literature.

As stated above, in his 1985 review Moskovits argued that electromagnetic theory can account for the SERS phenomenon. In his 2005 review he added that the SERS enhancement is increased dramatically when two SERS active particles are close together, the molecule of interest is in the space between the two particles, and the electric field is parallel to the two-particle axis. The plasmonics that have been developed over the last 10 or more years are based on this elemental SERS system. Figure 1 is a description of the SERS dimer from which plasmonics have evolved.

Because the wavelength of the photon is so much larger than that of the particles (~500 nm versus maybe 5–100 nm), the photon field sets up a charge distribution on the particle surface. When the field is parallel to the particle axis, the narrow charge separation in the gap produces a large field between the particles, which is the origin of the extra enhancement for SERS of interacting particles. As we all learned in classical electromagnetic theory (EM), as the interparticle distance is reduced, the size of the enhancing field increases. In addition, it has long been known that in solutions of aggregated particles, there is a color change. This is explained in terms of plasmon hybridization in which there is a resonance between the energies of the individual particles. Whereas there are degenerate electronic states of noninteracting particles, when they interact the states split into lower and higher energy states. The lower energy bonding mode of the “plasmonic dimer” has a large induced dipole with strong coupling to the far field accounting for the large, red-shifted absorption and the change in color that has been known since ancient times. This model is further developed to describe other types of interacting particles. For example, the electronic levels of a nanoshell, which is a configuration of great interest, are constructed from the levels of a metallic sphere interacting with a cavity in a metallic particle. Also, modeling of the interactions between two spherically capped nanorods enables one to start to visualize the behavior of arbitrarily shaped particles such as nanostars. Another interesting example is that of a metallic nanoparticle over a metallic surface. First there is the production of image charges in the substrate, and then the interaction between the localized plasmon of the nanoparticle with the propagating plasmon of the substrate. In this case, the red shift of the hybridized plasmon decreases more rapidly with separation distance because of larger contributions from higher order states. In addition, the propagating plasmons of the substrate provide a continuum of plasmon modes which, when coupled with the particle plasmon, results in Fano-type behavior (17). The importance in all of this is to know what laser wavelength will produce the best surface enhancement. Or to put it another way, one can envision engineering a SERS substrate, or SERS particles, for optimized signal generation with an available

laser wavelength.

While this description is quite satisfying, it ignores quantum mechanical effects that are expected for very small nanoparticle separations. To maximize the enhancement, one wants to minimize the gap between the particles, but if the gap becomes too small, electrons can tunnel between the particles which will clearly have very strong effects on the SERS phenomenon. A quantum mechanical description will include effects of tunneling as well as nonlocal screening of the induced fields due to evanescent electrons outside the particle surface, and to screening of the fields within 0.5 nm of the surface.

Initially Halas and colleagues (16) reviewed some quantum mechanical calculations of single particles, and found that the results were not much different than those of classical calculations, except at the surface of the particles. However, when nanoparticle dimers were considered, the behavior became characteristically different from the classical descriptions. As the dimer separation is decreased, the red shift of the plasmon absorption saturates and then begins to blue-shift; this is, in fact, consistent with what one would expect if electrons can start to tunnel across the gap and to screen the field. In particular, if one compares the results of the classical calculations to the quantum mechanical ones, one sees that the field enhancements are overestimated for gaps smaller than 1 nm.

The behavior of extended structures based on chains of nanoparticles where the size of the particles and distances between them were kept constant was also examined. Because of near-field coupling between nearest neighbors, the red shift of the longitudinal plasmon (E field parallel to the chain direction) increased until saturation at about 10 particles, which is determined by the near field interactions that scale as d^{-3} . In fact, both one-dimensional (1D) and 2D arrays have been studied; when the interparticle distance is comparable to the plasmon wavelength of a single particle, far-field interferences produces a narrowing of the plasmon mode, which will make the surface enhancement more intense because of better resonance with

a sharper plasmonic state.

The last topic of interest is that of plasmons with Fano resonances. A Fano resonance occurs when there is interference between a continuum of states and narrow localized modes (17). For example, in concentric ring-disk cavities (CRDC) the dipolar disk and ring modes hybridize; in both the calculations and measured spectra, the lower energy bonding mode is sharpened relative to the parent modes. Because the parent modes are often inequivalent (as in the cases of a ring and disk or a sphere on a substrate) there can be coupling between the bright (lower energy) and dark (higher energy) modes, which will result in multiple plasmon resonances in the optical absorption spectra. And because the effectiveness of hybridization increases with the proximity of the states, the state resulting from Fano interference becomes asymmetric. Not only have plasmonic calculations been done for the simple systems mentioned above, but oligomeric systems have been designed theoretically and manufactured to determine if the modeling predicts the states well, and that has been confirmed. The point is that using this information and experience, it is now feasible to tailor a plasmonic substrate that can predictably excite intense SERS at a selected wavelength.

(As an aside, I first became aware of Fano resonances when examining the Raman spectra of silicon that had been heavily doped with boron. The presence of the Fermi level of holes in the valence band near 500 cm^{-1} provides a continuum of transitions that can interfere with the phonon transition at 520.6 cm^{-1} . The result is an asymmetric Raman peak from which the doping level can be inferred.)

The question of how to produce these engineered structures effectively and inexpensively has to be addressed. Many of the demonstrated structures were fabricated with electron beam lithography, producing particles of uniform size and shape, but it has been noted that the surfaces of lithographic structures are often rough and produce scattering. On the other hand, chemically manufactured structures tend to have better crystalline quality, but the production yields are

expected to be quite low. It has been envisioned that superlattices of particles can be deposited by using controlled solvent evaporation or Langmuir-Blodgett techniques; in these schemes the interparticle distances would be controlled by the capping material and surface pressure. Other technologies for depositing nanoparticle arrays such as laser printing and nanoimprinting are being explored for precisely patterning particles.

Aluminum Plasmonics

The report of plasmonic structures based on aluminum (15) was especially surprising to me because it has always been assumed that coinage metals are required for SERS. Al was proposed as a plasmonic material for the UV and visible regions of the electromagnetic spectrum, and would take advantage of its low cost, high availability, and ease of processing (including complementary metal-oxide semiconductor [CMOS] technologies). However, in preparing Al plasmonic structures, it was found that the peak of the plasmon resonance was quite variable. In the work summarized in this publication (15), plasmonic structures were carefully prepared with controlled amounts of oxygen. It was found that the surface oxide on the metal, as well as the oxide included in the bulk material affected the plasmon resonance. X-ray photoelectron spectroscopy (XPS), used to derive the oxygen fraction, and ellipsometry modeled with the Bruggeman description of the composite Al/ Al_2O_3 dielectric function to describe the structure of the material, provided the necessary information for plasmonic modelling using the finite difference time domain method (FDTD) and showed the importance of the oxide in determining the plasmonic energy.

Summary

Even a superficial understanding of the physics of plasmonics goes a long way in explaining why SERS was so irreproducible in its early years; the detection of random "hot spots" explained the lack of experimental control. Following the observation that very large enhancements were mediated by aggregation, the earliest plasmonic model was proposed, based on a metallic nanoparticle dimer. From

this plasmonic fundamental, the field has evolved. Growth in our understanding of plasmonics, based on a rigorous numerical modeling of complex structures, provides a path to the predictive design of structures for practical chemical sensing with single-molecule sensitivity. While reviewing the galley of this manuscript, I was listening to a relevant webinar on photonics and plasmonics that provided additional information on the topics discussed in this column (18).

References

- (1) F. Adar, *Spectroscopy* **23**(2), 20–29 (2008).
- (2) J.A. Guicheteau, M.E. Farrell, S.D. Christesen, A.W. Fountain III, P.M. Pellegrino, E.D. Emmons, A. Tripath, P. Wilcox, and D. Emge, *Appl. Spectros.* **67**(4), 396–403 (2013).
- (3) T. Fawcett, *Pattern Recognit. Lett.* **27**(8), 861–874 (2006).
- (4) M. Fleischman, P.J. Hendra, and A.J. McQuillan, *Phys. Lett.* **26**, 123–126 (1974).
- (5) D.L. Jeanmaire and R.P. Van Duyne, *J. Electroanal. Chem.* **84**, 1–20 (1977).
- (6) M.G. Albrecht and J.A. Creighton, *J. Am. Chem. Soc.* **99**(15), 5215–5217 (1977).
- (7) M. Moskovits, *Rev. Modern Phys.* **57**(3), 783–826 (1985).
- (8) S. Nie and S.R. Emory, *Science* **275**, 1102–1106 (1997).
- (9) A.M. Michaels, M. Nirmal, and L.E. Brus, *J. Am. Chem. Soc.* **121**, 9932–9939 (1999).
- (10) A. Otto, I. Pockrand, J. Billmann and C. Pettenkofer, in *Surface Enhanced Raman Scattering*, R.K. Chang and T.E. Furtak, Eds. (Plenum Press, New York and London, 1982), pp. 147–173.
- (11) K. Kneipp, H. Kneipp, R. Anoharan, E.B. Hanlon, I. Itzkan, R.R. Dasari, and M. Feld, *Appl. Spec.* **52**(21), 1493–1497 (1998).
- (12) M. Moskovits, *J. Raman Spectrosc.* **36**, 485–496 (2005).
- (13) K. Kneipp and H. Kneipp, *Appl. Spec.* **60**(12), 322A–334A (2006).
- (14) R. Treffer, X. Lin, E. Bsailo, T. Deckert-Gaudig, and V. Deckert, *Beilstein J. Nanotechnol.* **2**, 628–637 (2011).
- (15) M.W. Knight, N.S. King, L. Liu, H.O. Everitt, P. Nordlander, and N.J. Halas, *ACS Nano* **8**(1), 834–840 (2014).
- (16) N.J. Halas, S. Lal, W.-S. Chang, S. Link, and P. Nordlander, *Chemical Reviews* **111**, 3913–3961 (2011).
- (17) U. Fano, *Phys. Rev.* **124**, 1866–1878 (1961).
- (18) <http://www.acs.org/content/acs/en/acs-webinars.html>.



Fran Adar is the Principal Raman Applications Scientist for Horiba Scientific in Edison, New Jersey. She can be reached by e-mail at fran.adar@horiba.com

For more information on this topic, please visit:
www.spectroscopyonline.com