

SERS assertions addressed **FREE**

Katrin Kneipp



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magnifies the enhancement by an artificial factor.¹ Simple characterizations of the bare Raman cross sections of these molecules show that using methanol as a reference induces an error in the enhancement by a factor of about 1200 at 785-nm laser excitation, and it is still a factor of about 350 at 1064 nm, further in the near-IR.

In 1999 Hongxing Xu and coworkers showed that a proper normalization with respect to the correct Raman cross section results in a maximum SERS enhancement factor of approximately 10^{10} , even for single-molecule conditions.² There is currently no strong experimental or theoretical evidence for SERS enhancements larger than around 10^{10} – 10^{11} . Moreover, SERS has been used more recently, with even smaller enhancements, for single-molecule detection of resonant molecules. Andreas Otto, in addition, argued on purely theoretical grounds that enhancement factors of approximately 10^7 are already sufficient to see single molecules.³ Recent experiments have confirmed those estimates.¹

Similar comments can be made regarding the claim that a Poisson distribution exists in the single-molecule SERS regime, as shown in figure 2 of Kneipp's article. Simple arguments can show that this apparent Poisson distribution is an artifact of the poor sampling of events over a long-tail distribution of SERS enhancement factors.⁴ Statistics over a much larger set of data would wash out completely the discrete peaks in the figure's histogram. Unfortunately, over the years, there has been a remarkable lack of disposition to substantiate those claims with more reliable statistics beyond a few hundred spectra. As a consequence, that approach cannot be used as proof of single-molecule sensitivity in SERS. Bruno Pettinger and coworkers discussed that issue in detail

for the related technique of tip-enhanced Raman spectroscopy (TERS).⁵

Fortunately, the single-molecule detection capability of SERS has since been proven unambiguously using other more reliable approaches, among them the Langmuir–Blodgett films used by Ricardo Aroca and coworkers,⁶ the technique of bi-analyte SERS developed by our group,¹ and TERS.

In short, we believe that Kneipp's article ignores the dynamic nature of the understanding in the field and the huge amount of work from many contributors over the past 10 years—work that has dramatically improved and in many cases radically corrected the interpretations of earlier pioneering studies.

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Kneipp replies: Pablo Etchegoin and coauthors raise two concerns in response to my article: the order of magnitude of surface-enhanced Raman scattering enhancement (10^{14}) and the Poisson distribution in the single-molecule SERS regime.

Achievable total SERS enhancement factors on the order of 10^{14} are supported by experimental and theoretical studies. Electromagnetic enhancement factors on the order of 10^{13} have been established.¹ Chemical enhancement can result in factors of 10^2 or greater.² Still, the relative contribution of electromagnetic and chemical effects to the total SERS enhancement remains under discussion. As an experimental example, effective SERS cross sections on the order of 10^{-16} cm² for the UV-absorbing molecule adenine have been inferred from vibrational pumping using 830-nm excitation. Such cross sections imply that a SERS enhancement factor of around 10^{14} is required to bring a typical nonresonant Raman cross section

on the order of 10^{-30} cm² to this level.³ Further, it is common knowledge that for larger intrinsic Raman cross sections of the analyte under resonant conditions, the requirements for the size of surface enhancement in single-molecule SERS can be greatly reduced.⁴ Moreover, the level of enhancement required for single-molecule SERS depends on the experimental parameters and improvements in the Raman technique, and reducing the background level in SERS samples may make it easier to see single molecules.

SERS signals measured from a sample with an average of approximately one analyte molecule in the probed volume follow a Poisson distribution that indicates the probability of probing 0, 1, 2, and 3 molecules during the actual measurement. With an order-of-magnitude increase in the average number of molecules, the Poisson distribution becomes a Gaussian distribution.^{3,5} One of the most important requirements to measure Poisson statistics is that all molecules experience a relatively uniform enhancement level. That can be achieved when the concentration of target molecules is one to two orders of magnitude below the concentration of silver nanoaggregates. In contrast to that requirement, Etchegoin and coauthors discuss experiments that measure the “long-tail distribution of SERS enhancement factors.” Those experiments, as set up by Etchegoin and coauthors, must fail in measuring a Poisson distribution and cannot be used as “proof” that, in general, a Poisson distribution in single-molecule SERS is an artifact. Also in single-molecule tip-enhanced Raman scattering, variations that occur in enhancement factors due to scanning the tip might preclude the observation of a Poisson distribution. Recently, Richard Van Duyne and coworkers demonstrated single-molecule SERS by tracking the statistics of appearances of the distinguishable spectral signatures of two similar molecules.⁶ I am pleased to have this opportunity to point out this complementary approach to proving single-molecule SERS, published after the PHYSICS TODAY article.

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Of hurricanes and fooling Mother Nature

The letter by Michael Binkley and the reply from Kerry Emanuel under the heading "Cool Shades for Hurricanes?" (PHYSICS TODAY, March 2008, page 9) attracted my attention. As a forester, hydrologist, ecologist, and student of atmospheric phenomena, I understand our atmosphere fairly well.

The function of hurricanes is to move excess heat energy from the equatorial regions toward the poles, particularly the North Pole. It is in humankind's best interest not to monkey around any more than we already have with Earth's powerful and yet delicately balanced energy sources, sinks, and pathways. An experiment in seeding hurricanes 40–50 years ago resulted in a near international incident when an errant seeded storm abruptly turned north and grazed Havana, Cuba, rather than taking its more normal path into the Gulf of Mexico. Fidel Castro complained bitterly that the event was a deliberate act of aggression by the US, but, of course, he received denials. A report later showed that the storm made a completely unnatural and sudden 90-degree turn northward. The proposed seeding program was later abandoned when potential perpetrators were required to write an environmental impact statement.

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LED efficiencies: Apples and oranges

The item "White LEDs Poised for Global Impact" (PHYSICS TODAY, December 2007, page 25) provides an interesting account of the use of LEDs in rural villages. Although the article correctly mentions that the energy efficiency of

LED technology continues to improve, I found the efficiency comparison with fluorescent lights misleading, for two reasons. First, some manufacturers show their specs as lumens per watt of light output, while others show lumens per watt used by the LED. The former does not include power wasted as heat. Second, some comparisons are made using LED light that is concentrated in a narrow beam while the fluorescent lights are tested without fixtures.

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Importance of double-blind reviews

I am amazed to learn from the letter by Lance Williams (PHYSICS TODAY, November 2007, page 12) that any academic journal would have only a single-blind referee process.

After finishing a postdoc in physics long ago, I went to trade school and learned how to practice medicine, which I have been doing ever since. I can assure you that the majority of physicians understand the scientific value of double-blind over single-blind evaluations of drugs. And those who don't use double-blind procedures often have a financial interest in the product they are evaluating. Is the accuracy of physics publications somehow not as important? Shouldn't physics and physicists have the highest standards, or perhaps even set the standards? Even old general practitioners who think "physics" is a quaint plural term for laxatives can tell you that single-blind evaluations are not worth much.

Are any of you physicists embarrassed by this practice?

Thomas J. Deal
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I couldn't help but applaud Lance Williams for writing his letter. On more than one occasion, I have seen the same piece of writing referred to as "poor English" and "well presented," depending on the names and affiliations of the coauthors. Why can't we adopt the double-blind system? It may not be perfect, but it is definitely better than the single-blind one.

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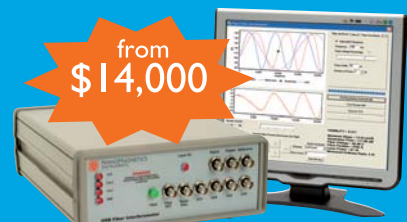
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