DISCUSSIONS

Theory of SERS enhancement: general discussion

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Dong-Ho Kim, Javier Aizpurua, [iD] William Lum, Alessandro Silvestri,
Bart de Nijs, [iD] Yikai Xu, Giuliana Di Martino, [iD] Michael Natan,
Sebastian Schlücker, Pieter Wuytens, Ian Bruzas, Christian Kuttner, [iD]
Mike Hardy, [iD] Rohit Chikkaraddy, Natalia Martín Sabanés, [iD]
Ines Delfino, [iD] Paul Dawson, [iD] Sylwester Gawinkowski, [iD]
Nicolò Bontempi, Sumeet Mahajan, Stephanie Reich, Ben Hourahine, [iD]
Steven Bell, [iD] Agata Królikowska, Marc Porter, [iD] Alex Keeler,
Marlous Kamp, Augustus Fountain, Claudia Fasolato, [iD] Fabrizio Giorgis,
Juan C. Otero, [iD] Cristiano Matricardi, Richard Van Duyne,
John Lombardi, Volker Deckert [iD] and Leonora Velleman

Rohit Chikkaraddy opened the discussion of the Introductory Lecture: Regarding quantifying the chemical enhancement, you showed a systematic change in the SERS enhancement for halide substituted molecules due to charge transfer from the metal. Is the extra enhancement due to an inherent increase in the Raman cross-section of the molecule? How do you go about referencing, as the charge transfer changes the vibrational frequency?

Richard Van Duyne answered: The extra enhancement is *not* due to an increase in the Raman cross section, as that is ratioed out in the calculation of the enhancement factor. The charge transfer (CT) process does not transfer a complete electron, it is a fractional degree of CT. Thus the change in vibrational frequency is small. DFT calculations that provide eigenvectors allow one to reference the vibrational modes of the free molecule with those of the adsorbed molecule.

Sylwester Gawinkowski asked: You have shown that the enhancement factor curve is redshifted relative to the plasmon resonance band and has a maximum at about 800 nm. This means that the SERS signal should be strongest for excitations in the near infrared spectral region. Why do most SERS reports, particularly related to single molecule SERS, have the excitation in the green or red spectral range and not in the near infrared?

Richard Van Duyne replied: The SERS excitation spectrum for isolated nanoparticles (*e.g.* the NSL nanotriangles that I showed in Fig. 1 of the introductory lecture[1]) is redshifted with respect to the localized surface plasmon resonance (LSPR) by half the Stokes frequency of the vibrational mode. As the nanoparticle size is decreased the LSPR shifts to the blue so it is only for a specific size that one gets an LSPR maximum at 800 nm. Essentially all single molecule SERS experiments are done with dye molecules and the laser excitation wavelength is chosen to get maximum resonance Raman (RR) as well as SERS enhancement. For Rhodamine 6G (R6G) the laser excitation wavelength of 532 nm is close to the absorption maximum of R6G. SMSERS should be possible in the NIR for a wide range of dye molecules with absorption maxima in that spectra region.

1 A.-I. Henry, T. W. Ueltschi, M. O. McAnally and R. P. Van Duyne, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00181a.

Marc Porter asked: Why is the oxidized form of nitrobenzene (I may not have the name of the reactant correct; my notes are a bit fuzzy, which I blame on jet lag) more sensitive to the local environment than its reduced from. Does the supporting electrolyte play a role here?

Richard Van Duyne replied: The redox system you are referring to is the dye Nile Blue. The oxidized form is positively charged and the adsorption has electrostatic character. Hence it is more sensitive to the electrostatics of the local environment than the neutral reduced form.

Sumeet Mahajan commented: In your work on surface-enhanced FSRS with a high rep rate laser why does the signal to noise not increase when there are 10× more pulses with the 1 MHz setup compared to the 100 kHz laser setup?

Richard Van Duyne responded: The S/N does increase by the square root of the number of laser pulses. 10× more pulses in the 1 MHz system does increase the S/N by a factor of ∼3.

Heike Arnolds remarked: What is the advantage of using tip-enhanced Raman scattering over inelastic tunneling spectroscopy?

Richard Van Duyne responded: Tip-enhanced Raman spectroscopy (TERS) has a more general application space than inelastic tunneling spectroscopy (IETS). TERS works in UHV, liquid, and gas environments for both small and large molecules and at both room and low temperature. IETS has a more restricted application space – UHV, small molecules, and low temperature.

Michael Natan asked: The best SERS-active particles, *i.e.* those with EFs on the order of 10^8, are not very useful as optical labels for most biological problems, because the particles are too big. How can you get a particle or assembly that is SERS active with only a 20 nm diameter (in total)?

Richard Van Duyne responded: Dr Natan is correct that there is a trade-off between the SERS enhancement factor and particle size. The smaller the

particles the lower the enhancement factor and the bluer the required excitation laser. Two 10 nm Ag particles in a dimer configuration would be the best SERS-active system that I know. My guess is that the enhancement factor for this construct would be 10^5. Thus, it would be usable for the type of biological problem discussed.

Christian Kuttner asked Richard Van Duyne: In the search for the highest SERS activity, the matching of the laser excitation to the optical properties of nano-structured materials is often still regarded as a mystery. In your talk, you pointed out that coupling particles behave completely different than single particles. Is this because of the more complex nature of their plasmonic modes and how can it be understood that in many cases the highest enhancement arises from mis-matched conditions?

George Schatz commented in response: As noted in the Van Duyne talk, the Raman excitation spectrum for SERS on isolated particles behaves quite differ-ently from that for dimers and smaller clusters. For isolated particles, the Raman excitation spectrum usually peaks when the incident wavelength is close to (or slightly blue shifted from) the dominant (usually dipole allowed) plasmon reso-nance. For small clusters where the particle separations are on the order of 1 nm or smaller, the Raman excitation spectrum often peaks at wavelengths corre-sponding to dark plasmon modes (such quadrupolar modes). In those studies, my group performed electrodynamics calculations for dimers and trimers, and we found that the dark modes have a similar near-field $|E|^4$ enhancement to the bright modes. In addition, we found that dark modes have dipole reradiation enhancement that can be larger than that of bright modes, due to the higher Q factors for these modes. Given that dark modes also have less interference from Rayleigh scattering than bright modes, there are important advantages to per-forming SERS measurements using clusters of particles.

Roy Goodacre communicated: In your SERS combined with pumped SRS system you observe signal degradation. Do you think this is heat related? And could you use the Stokes : anti-Stokes ratio to read out the temperature on the surface(s) in real time?

Richard Van Duyne communicated in response: The signal degradation is not temperature related as best we can measure. We have used the Stokes/anti-Stokes ratio method and can at most find temperature increases of ~10 ° C.

Ben Hourahine opened a discussion of the paper by Javier Aizpurua: Do you see any potential for impact due to the presence of multiple electromagnetic modes? There should be a mixture of both bright and dark modes present, and presumably these usually have somewhat different effective mode volumes.

For example Fig. 6 of ref. 1 shows that the imaginary part of the electromag-netic Green's function of various metallic structures has contributions from multiple independent modes, particularly when moving off resonance. The local density of states is a mixture of both bright and dark modes (Fig. 3), and the effective mode volumes (hence Purcell and Lamb shifts) for these are quite different.

While, as mentioned at the discussion session, a pseudo-mode description can be invoked for these multi-mode behaviors (for example in the case of the gold optical mode derived from the bulk response), and these have an associated entropy. Presumably, and particularly when heating or cooling the vibrational modes, this would also matter.

1 D. McArthur, B. Hourahine and F. Papoff, *Opt. Express*, 2017, **25**, 12189–12199. See also erratum, D. McArthur, B. Hourahine and F. Papoff, *Opt. Express*, 2017, **25**, 20950–20951.

Javier Aizpurua replied: Totally, we have worked out the optomechanical models in our Faraday paper, assuming a well-behaved single Lorentzian plasmonic mode, but as you point out, in realistic plasmonic systems, a plasmonic spectrum can be composed of a bunch of multiple electromagnetic modes, with the admixture of bright and dark modes which show completely different effective mode volumes and, therefore, optomechanical coupling strengths. This has to be included in the theory indeed. One possibility to incorporate the complex spectral structure of a plasmonic resonator (a metallic cavity for example) could be *via* the quantization of the electromagnetic fields through the Green's function of the system, as for example M. K. Dezfouli and S. Hughes have developed.[1] We have actually introduced a generalization of our optomechanical model to account for these complex situations in eqn (84) and (85) of Appendix C in our Faraday Discussion paper,[2] where we express the optomechanical transition rates (which give rise to the phonon population dynamics) in terms of the Green's function of the plasmonic system. This generalization of the optomechanical model would allow us to account for the effects of the complexity of the plasmonic spectrum, that you are correctly pointing out, in the Raman signal.

1 M. K. Dezfouli and S. Hughes, *ACS Photonics*, 2017, **4**, 1245–1256.
2 M. K. Schmidt, R. Esteban, F. Benz, J. J. Baumberg and J. Aizpurua, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00145b.

Jeremy Baumberg said: What happens if you have a dark mode in your model for the plasmon? Does it still interact optomechanically in the same way (it has a narrower linewidth as the radiative damping is lower).

Javier Aizpurua responded: To exploit a dark mode shows interesting aspects, as you point out. The narrower linewidth might facilitate more easily reaching the single photon strong coupling regime, as the optomechanical coupling rate could exceed that of the plasmonic decay rate (now slower for a dark mode). In this sense, it would be interesting to select a dark mode and try to reach strong coupling regimes so that the vibrational pumping effects such as nonlinearities of the Stokes and anti-Stokes photon emission, or the feedback action are revealed more easily in experiments. Very often though, a bunch of higher-order modes, a so-called pseudomode, is excited, and important changes in the electromagnetic couplings have been predicted, for example in plasmon–emitter coupling.[1] Now it would be good to explore this effect in optomechanical coupling as well.

1 R.-Q. Li, D. Hernángomez-Pérez, F. J. García-Vidal and A. I. Fernández-Domínguez, *Phys. Rev. Lett.*, 2016, **117**, 107401.

George Schatz commented: A very interesting aspect of your theoretical analysis arises in the blue detuning case, where the electromagnetic contribution to the width can become negative. Is this a physically meaningful result? Can the theory have artifacts? To what extent can this effect be seen in the experiments?

Javier Aizpurua replied: As in other optomechanical systems, and also in molecular optomechanics (non-resonant SERS), a blue detuning of the incident laser with respect to the plasmonic cavity mode produces an increase of the Raman signal, and a narrowing of the emission. In the optomechanical formalism this is clearly formulated and understood as a negative optomechanical damping due to the feedback action of plasmons and vibrations, which modifies the actual effective width of the molecular vibration. If this optomechanical damping (negative for the blue detuning case) equals the vibration intrinsic width, then strong nonlinear effects, which could give rise even to parametric instability, could be observed. This is not an electromagnetic effect, but rather a vibration–plasmon coupling effect mediated by the plasmon and phonon populations which interact with each other, *i.e.* an independent effect. The theory for the non-resonant case is quite robust and in this sense, to the best of my knowledge, free of artifacts. Now, the question of whether these optomechanical effects of blue detuning can be observed in experiments or not, is a very timely point. Certainly not every experiment in SERS will show these effects, and most of the nice experiments in SERS are mainly and fully explained in terms of electromagnetic and chemical effects. However, as we isolate single molecules, and work on more controlled plasmonic environments, including low temperatures, we open the door for these effects to be observed. Indeed, the enhancement of the SERS signal and narrowing of the Raman photon emission might have been experimentally observed "unconsciously", for example in ref. 1 and 2. We find in collaboration with our experimental colleagues in Cambridge, however, that often, right after entering the strongly nonlinear regime of optomechanics, many molecular systems burn and are chemically modified, so obtaining controlled experimental evidence of these effects is challenging in plasmonic resonators. I think that there is a door open for experimentalists to try to identify these effects systematically in SERS.

1 W. Zhu and K. B. Crozier, *Nat. Commun.*, 2014, **5**, 5228.
2 R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang and J. G. Hou, *Nature*, 2013, **498**, 82–86.

Jeremy Baumberg added: Our recent data shows that indeed one can see the regime Javier talks about in experiments. Using ps pulses to excite strong enough phonon populations, one sees a nonlinear increase in the Stokes signal. However this does not progress to the optomechanical instability, before damage sets in. This will be reported in a forthcoming paper.

Sumeet Mahajan asked: How does optomechanics relate to the terahertz regime?

Javier Aizpurua responded: I brought up the fact that by describing and analyzing the surface-enhanced Raman scattering of molecules as an optomechanical process, we open a new range of frequencies to explore in

optomechanics. In this optomechanical journey, we can go now from vibrations of few kilohertz frequencies in standard macroscopic optomechanical systems, with mirrors and microresonators, to a vibrational frequency range of several terahertz, typical of molecular vibrations. In this sense, molecular optomechanics opens the realm of terahertz and infrared frequencies, much faster than what has been explored in this field up to now.

Christian Kuttner remarked: Today, the optical properties of plasmonic nanostructures and particle assemblies are readily accessible by electromagnetic simulations (*e.g.* Generalized Multiparticle Mie Theory, GMMT).[1–3] Such optical properties allow the description and correlation of plasmonic modes, coupling mechanisms, and near-field enhancement. How can we incorporate these new insights about optomechanical back actions into our understanding of plasmonics and SERS activity? Especially the aspect of detuning, the energetic amplification and cooling, which depends on the excitation wavelength?

1 R. P. M. Höller, M. Dulle, S. Thomä, M. Mayer, A. M. Steiner, S. Förster, A. Fery, C. Kuttner and M. Chanana, *ACS Nano*, 2016, **10**, 5740–5750.
2 A. M. Steiner, M. Mayer, M. Seuss, N. Svetoslav, K. D. Harris, A. Alexeev, C. Kuttner, T. A. F. König and A. Fery, *ACS Nano*, 2017, **11**, 8871–8880.
3 C. Hanske, M. Tebbe, C. Kuttner, V. Bieber, V. V. Tsukruk, M. Chanana, T. A. F. König and A. Fery, *Nano Lett.*, 2014, **14**, 6863–6871.

Javier Aizpurua answered: I understand that in order to incorporate optomechanical effects in the analysis of Raman signals by experimentalists, a simple and direct methodology to make estimations and predictions is needed, to avoid complicated calculations of the dynamics of phonon and plasmon populations in the framework of quantum mechanics. It is precisely to that end that we brought up our current Faraday Discussion paper.[1] In this Faraday Discussion paper, we precisely establish the connection between the quantum description of the dynamics of phonons and that given by a simpler equation rate based on classical inputs. Section 3, and more specifically subsection 3.1.2, introduce a classical way of extracting the phonon population, expressed in terms of the scattering cross sections at each relevant frequency (Stokes or anti-Stokes), also including all the other relevant parameters, such as detuning with respect to the incident laser frequency. This phenomenological classical equation rate for the phonon population incorporates all the optomechanical aspects of vibrational pumping and feedback action, including parametric instability for large enough incident laser powers, and reproduces all the results of the quantum optomechanical model, and therefore we believe that eqn (65) of the paper will be of invaluable help to experimentalists in interpreting and predicting optomechanical effects in Raman signals with totally classical characterizations of their plasmonic systems.

There is one aspect though, which would still be missing in such a phenomenological classical approach, which is connected with the lack of information regarding the correlation of the emissions, and coherence aspects of the signals in general, but the other aforementioned aspects (nonlinearities, parametric instabilities and cooling and heating due to detuning) would be accounted for in classical eqn (65) of our Faraday Discussion paper.

1 M. K. Schmidt, R. Esteban, F. Benz, J. J. Baumberg and J. Aizpurua, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00145b.

Richard Van Duyne asked: The nonlinearity of the TERS intensity *vs.* the excitation laser power reported in the 2013 *Nature* paper by Dong *et al.*[1] is not a widely accepted piece of experimental data. Our group has not been able to reproduce this data. We always see a linear or sublinear dependence of the TERS intensity on the laser power. What guidance can you give for choosing a molecular system that would enable us to observe the kind of intensity *vs.* power curve reported by Dong?

1 R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang and J. G. Hou, *Nature*, 2013, **498**, 82–86.

Javier Aizpurua responded: The non-linear dependence of the TERS signal reported in the supplementary material of the 2013 Nature paper by Dong *et al.*[1] was obtained reproducibly one a molecular island at 80 K, without any data manipulation. Such non-linear power-dependence behavior has also been confirmed by better-controlled low-temperature TERS experiments at about 7 K for the same molecular system [*i.e.*, H2TBPP on Ag(111)] using Ag tips and 532 nm laser. Of course, the type of molecules, their stability and the junction might be an issue that may affect the results. Other situations, such as ZnPc on Ag(100) at liquid helium temperature, seemed to show a linear power dependency, according to what the experimental collaborators in Hefei (Zhenchao Dong *et al.*) tell me, although the exact origin for such different behavior is still unclear

However, as a theoretician describing the optomechanical dynamics of molecules in plasmonic cavities, I believe that the nonlinear behavior of the Raman signal with power is a robust result that cannot be discarded. Another issue is whether this non-linear effect is revealed systematically in many systems; probably not.

We now have alternative experimental evidence from the Cambridge group (Prof. Baumberg) with molecules in particle-on-a-mirror cavities that this nonlinear behavior with incident power clearly occurs in pulsed illumination, and we will soon be reporting on it.

My feeling is that one needs to analyze the data on a one-to-one basis for each molecule and each plasmonic cavity configuration, trying to isolate any other spurious effect, which can jeopardize the observation of the optomechanical dynamics. Sometimes the power required to achieve the evidence of this non-linear effect is so large that the molecules do not survive for reliable data, therefore my suggestion would be to try to work with pulsed illumination to avoid destroying the sample, as well as to use robust molecules and plasmonic configurations. Nevertheless, it would be nice to have more diverse and clear experimental data for final conclusions, along the lines of the experiments suggested above.

1 R. Zhang, Y. Zhang, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang and J. G. Hou, *Nature*, 2013, **498**, 82–86.

Rohit Chikkaraddy communicated: In your paper[1] (Section 4.3) you mention the Stokes and anti-Stokes photon statistics. Can you comment on how the coherence is lost due to the ohmic loss of the metal? Because now it seems like the coherence is not just a function of the coupling strength but also of the pump laser power.

1 M. K. Schmidt, R. Esteban, F. Benz, J. J. Baumberg and J. Aizpurua, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00145b.

Javier Aizpurua communicated in reply: The model used throughout our work does not explicitly account for the radiative or non-radiative origin of the decay of the plasmon population, or for the pure dephasing of the plasmon; instead, we choose to derive the effective decay rate of the relevant plasmon mode only from its spectral width. Such an approximation has been widely adopted in the field of quantum plasmonics, and should be satisfying for all of the results reported here. In particular, the inclusion of pure dephasing of the plasmon or the phonon would not significantly change the strength of the correlations between the Stokes and anti-Stokes emission, as they are not dependent on phase correlations between excitations in the system. In fact, a purely classical model of the Stokes–anti-Stokes correlations developed by Kasperczyk *et al.*,[1] based solely on analysis of the population of phonons, reveals very similar dependencies of the Stokes–anti-Stokes correlations to the ones shown in our work (see the explicit study of these correlations in, for example, M. Schmidt *et al.*[2]).

1 M. Kasperczyk, A. Jorio, E. Neu, Pa. Maletinsky and L. Novotny, *Opt. Lett.*, 2015, **40**, 2393–2396.
2 M. K. Schmidt, R. Esteban, A. González-Tudela, G. Giedke and J. Aizpurua, *ACS Nano*, 2016, **10**, 6291–6298.

Giuliana Di Martino opened a discussion of the paper by Leonora Velleman: In the paper 40 nm nanoparticles have been used. What is the range of sizes you can handle?

Leonora Velleman replied: We have assembled up to 500 nm nanoparticles before. However, it is one thing to assemble, or simply flocculate, particles to sit at the interface, it's another thing to be able to assemble with order, which may prove more difficult for larger sized particles. Indeed, this type of assembly technique is also commonly used for micron-sized samples (polystyrene beads, long carbon nanotubes *etc.*). And therefore, there is potentially no particle size limit. But in general, these samples lack spacing control and order.

Steven Bell commented: I'm really interested in your views on the way the particles arrange themselves in 2 dimensions at the interface. Under your water flooding conditions, where the particles approach 2 nm separation, are there islands of packed particles and areas of the surface which are empty of particles, or do more particles move to the interface? Similarly, under conditions which give a larger spacing is the average separation set by the fixed area of the interfacial surface layer and the number of particles available to cover it, or is there a balance of forces which determines the interparticle separation?

Leonora Velleman replied: After preparing the film, the number of nano-particles at the interface is absolute. Therefore during the water flooding experiments, as the nanoparticles are brought closer together, areas void of nanoparticles will form. Macroscopic holes are seen to pop up in areas of the film as shown in Fig. 2 of the manuscript[1] and the supplementary videos. For very sparse films however, as there are so few nanoparticles present, small clusters of

nanoparticles can form when flooded with water. We are unsure yet what the threshold of coverage is where the nanoparticles will be more prone to cluster with neighbouring particles rather than evenly shift together and form a large macroscopic void within the film.

Nanoparticle spacing is determined by a balance of forces (electrostatic repulsion, van der Waals attraction, *etc.*). For example, for a fixed interfacial area, a film with large nanoparticle spacing can be formed and a film with dense interparticle spacing can be created simply by controlling the balance of forces.

1 L. Velleman, L. Scarabelli, D. Sikdar, A. A. Kornyshev, L. M. Liz-Marzán and J. B. Edel, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00162b.

Roy Goodacre asked: For nanoparticles at the liquid–liquid interface it's nice that you can control the *x* and *y* coordinates. Do you observe any tumbling of the NPs (*i.e.*, in the *z* axis)?

This could be important, especially for the gold nanorods (GNR) where the tips would be exposed to the polar and organic layers as they rotate/tumble; especially so in GNRs as this where the main SERS enhancements are occurring.

Leonora Velleman answered: For the spherical citrate-stabilised nanoparticles, we have observed the nanoparticles leaving the interface when the aqueous phase is replaced with a high concentration of citrate solution (*e.g.* 10× the original citrate concentration). Therefore the nanoparticles can potentially be moved in the *z* direction.

For gold nanorods, we are not able to observe tumbling. It would be particularly interesting to be able to direct the orientation of the nanorods to be lying down or positioned vertically at the interface and to control the rotation. Polarised light and X-ray diffraction experiments would be useful to probe any rotating/ tumbling but we have not currently performed these measurements.

Rohit Chikkaraddy asked: Do the nanoparticles assembled at the interface scavenge across the two different media, to capture molecules from the different media and bring them to the interface?

Leonora Velleman responded: One of the advantages of this system is the ability for the nanoparticle to bind with a target analyte in the bulk and then bring it to the interface for analysis, a much quicker scenario than waiting for the analyte to diffuse down to a SERS surface. Examples of the ability of nanoparticles to capture molecules from both the oil and water phase can be found in our previous publications.[1,2] Molecules can be scavenged in either phase by using two sets of nanoparticles, stable in each phase. Alternatively, it would be possible for aqueous-stable nanoparticles to encounter a molecule in the organic phase while the emulsion is formed as the distance between the nanoparticles and organic phase is shortened. Furthermore, the nanoparticles can sit in contact with both phases, allowing an analyte from either phase to diffuse to the nanoparticles at the interface for detection. For example, we have previously found that 13 nm gold nanospheres settle at a *z* position of 90% within the organic phase and 10% in the aqueous phase.[3]

1 M. P. Cecchini, V. A. Turek, J. Paget, A. A. Kornyshev and J. B. Edel, *Nat. Mater.*, 2013, **12**, 165–171.
2 M. P. Cecchini, V. A. Turek, A. Demetriadou, G. Britovsek, T. Welton, A. A. Kornyshev, J. D. E. T. Wilton-Ely and J. B. Edel, *Adv. Opt. Mater.*, 2014, **2**, 966–977.
3 L. Velleman, D. Sikdar, V. A. Turek, A. R. Kucernak, S. J. Roser, A. A. Kornyshev and J. B. Edel, *Nanoscale*, 2016, **8**, 19229–19241.

Sumeet Mahajan asked: In 2D planar plasmonic arrays, both long and short range plasmon coupling is seen. Your system is essentially a 2D planar array of nanoparticles at an interface. At long range, that is when the spacing between the NPs is much larger than the size of the NPs, a blue shift of the plasmon resonance is predicted/seen. See for example George Schatz's paper.[1] In your spectra only a red shift is shown which really happens at short range. So why has a blue shifting of the plasmon resonance not been observed in your tuneable system where clearly you would have had a very large spacing between the NPs initially? Also, it should have been reversible.

1 L. L. Zhao, K. L. Kelly and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 7343–7350.

Leonora Velleman responded: We do not observe blue shifting for the inter-particle spacings shown in the paper as we have produced layers with a high enough density that the distance between the particles is never large enough to observe any blue shift. However, in other experiments we have indeed observed a blue shift (relative to the bulk nanoparticle LSPR) for samples at a very sparse coverage/interparticle spacing, consistent with the observations of George Schatz's group.

Natalia Martín Sabanés asked: You obtain enhancement factors of 4.3×10^4 and 8.4×10^5 for interparticle spacings of 30 nm and 1.9 nm respectively. When comparing these values to the theoretically predicted numbers reported in Fig. 5 of your supplementary information, you find a pretty good agreement between theory and experiment for an interparticle distance of 1.9 nm. However the value measured for 30 nm deviates strongly from the theoretical prediction. Theoretically, you predict differences in the EF of several orders of magnitude between 1.9 and 30 nm (3.85×10^5 *vs.* almost zero), while in reality you measure EFs that are much closer in absolute numbers (8.4×10^5 *vs.* 4.3×10^4). Could you comment on the reasons for this discrepancy?

You argue in the manuscript that the theoretical model only takes into account perfectly spherical particles which is not the case in the real experiment, but isn't this true also for the calculation at 1.9 nm? Is your theoretical model more precise for describing the EF at a small interparticle distance?

Leonora Velleman answered: It is important to note that the theoretical EF corresponds to the maximum EF whereas the experimental EF is an average EF and so it is difficult to compare values directly. Only ~7% of our nanoparticle surface is tagged with the Raman reporter molecule, so there are chances that they are not sitting within the hottest spot between the nanoparticles. The theoretical data can be used to help support our experimental trends, but due to the discrepancies between the theoretical model and the experimental scenario, it is hazardous to perform a direct comparison between the values.

Theoretically as we assume that nanoparticles are perfectly spherical, hotspots are dominant in the inter-nanoparticle gaps. For large gaps of 30 nm, inter-nanoparticle coupling is very weak and so is the hotspot, resulting in very low theoretical EF calculations. But in practice, there are irregularities on the nanoparticle surface that could host stronger hotspots near them, which can't be seen theoretically. This brings about a huge difference between theoretical and experimental values at a large interparticle spacing.

Alessandro Silvestri asked: The system proposed in the article is based on the ionic strengths of the media and the superficial charge of the nanoparticles. Rod like nanoparticles have a reduced curvature radius on the tips. This variation of the curvature radius can be reflected in a different ligand density and charge distribution on the extremities of the rods. What effects can this phenomenon have on the nanorods' self-assembly?

Leonora Velleman answered: Yes, ligands are known to preferentially attach to the tips of the rods. This can indeed affect the assembly of the nanorods. One interesting phenomenon to investigate would be whether the tips could be functionalised in such a way that they will be prone to standing up vertically at the interface.

Jeremy Baumberg asked: What happens when you try to bring the nanorods close together. Do they reversibly come apart after? I think this may be rather more difficult than with the spheres.

Leonora Velleman responded: Indeed, control over the assembly of nanorods and the ability to bring them apart and push them together is far more complex than the situation with spheres due to their anisotropic shape and the preference for functional groups to attach to the tips. However, the premise of moving the nanoparticles together and further apart is simply based on controlling their repulsion (through nanoparticle surface functionalisation and altering the degree of repulsion by modifying the nanoparticles' overall charge/double layer thickness). And so, under the right conditions there is the potential to reversibly push the nanorods apart. The correct surface functionalisation will be key in this situation, as ligands are more preferentially adsorbed at the tips of the rods. Furthermore, care will need to be taken to inhibit the van der Waals attraction between the sides of the rods so that irreversible aggregation does not occur.

Ines Delfino said: Can you please give an estimate of the sample thickness and of the laser spot size on it? What was the laser intensity at the sample during the measurements?

Leonora Velleman responded: In general, the nanoparticle layer is one monolayer in thickness. The laser spot size is ∼2 μm. The laser intensity is 380 μW. However, this is the laser power measured at the objective. At the nanoparticle layer, the laser has also travelled through the glass vial and a ∼5 mm thickness of dichloroethane and so the laser power at the sample may be slightly lower.

Yikai Xu remarked: There are indeed many advantages to using 2-dimensional arrays formed at liquid–liquid interfaces for SERS. It has been studied in past literature and also shown in this work that the stability of such particle arrays relies on a delicate balance between numerous forces (van der Waals attraction, electrostatic repulsion, steric repulsion, surface tension *etc.*). Here the authors take advantage of this and demonstrate that the distance between adjacent particles within the particle array can be manipulated for better SERS responses by tuning the amount of electrolyte present and thus the electrostatic repulsion between particles in the system. However, in practice to obtain SERS signals the analyte would have to adsorb onto the surface of the particles which would bring a significant change to the various forces between the particles. How does the author see this affecting the fine-tuned distances between the particles and the overall stability of the particle array? Here the authors demonstrate SERS with a Raman tag added prior to particle self-assembly, it would be interesting to monitor changes within the particle array with the "plasmon ruler" when the SERS tag is added into the system after particle assembly.

Leonora Velleman replied: It is definitely possible to add a Raman reporter after assembly and monitor the effects. Depending on the reporter and its concentration, its introduction may alter the stability of the nanoparticle array. This could be a favourable scenario; when the analyte is added, the nanoparticles could shift together, forming hotspots and a Raman signal could be detected. The detection of the Raman reporter is also dependent on the ligand length on the nanoparticles, and whether the nanoparticles can come close enough together and the Raman reporter squeeze itself within the hotspot to enact a Raman signal.

Mike Hardy asked: Hi Leonora, you mention that you have recently achieved 200 cycles of the spherical nanoparticles moving between the small and large spacing regimes. Contrariwise, in your paper the lack of full reversibility in this process is highlighted; it is suggested that the nanoparticles are sticking together somewhat. Thus, I am wondering how you have optimised this process since. Could you provide some details? Thank you.

Leonora Velleman replied: Yes, we have achieved cycling between small and large spacing regimes. However, we still see a slight increase in the Raman signal when returning to a large interparticle spacing over time. Therefore, on each cycle there are gradually more particles sticking together, although the effect is minimal. We have optimised to this point (200 cycles) with almost full reversibility, by cycling between water and a high concentration of citrate solution ($>4 \times$ higher than the original citrate concentration). Furthermore, you could potentially refrain from bringing the nanoparticles too close together by not reducing the citrate concentration to zero, however, your maximum Raman signal will not be as intense.

Alex Keeler communicated: You mention that the self-assembled films of nanoparticles can be transferred onto solid surfaces, rather than being kept at the liquid–liquid interface. How stable are these films on these surfaces and have you tried doing this with metals other than Au?

Leonora Velleman communicated in response: This depends on the adhesion of the nanoparticles to the support (*i.e.* the type of support material, whether it is functionalised, *etc.*) and drying treatments such as annealing. We have dried silver or gold nanoparticles onto glass/silicon wafers. The nanoparticles are simply physisorbed and therefore we found that there is some delamination of the nanoparticles when they are re-immersed in water (with nanoparticles deposited on unfunctionalised glass and dried at room temperature). Therefore for stability, it is advisable to functionalise the glass slide, with a thiol terminated silane for instance.

Marlous Kamp communicated: For applications it will be interesting to turn your LLI systems into Pickering emulsions, that is, to have an emulsion of water and an organic solvent stabilized by the gold NPs. In that way, a higher surface area – and thus stronger total Raman signal – is more easily attained, and the emulsion could be observed from different angles (although one must make efforts to reduce scattering). To achieve this goal, one typically needs extra surface modification such as a thiolated PEG (see ref. 1). Do you see possibilities for such a modification, or will it for example be problematic because of the Raman reporter that is required to be present at the surface? And, will the tuning of the inter-particle spacing still be possible? It would be great if you could comment on this, and possibly you have already observed some temporary formation of a Pickering emulsion. Thank you.

1 K. Larson-Smith and D. C. Pozzo, *Langmuir*, 2012, **28**, 11725–11732.

Leonora Velleman communicated in reply: This is a very interesting avenue and not one that we have pursued. In general, for the functional ligands we have tried, we find that the two phases separate out over time, but there have been instances where a stable emulsion will form, however this was observed to occur randomly. Perhaps those times were when a thiolated PEG was used.

There is the capability to modify the nanoparticle with the correct ligand to form a stable emulsion without causing a problem for the Raman reporter accessing the surface. Factors such as the ligand length and packing density would need to be carefully adjusted to factor for space for the Raman reporter.

Control over the interparticle spacing should still be possible, but again, a careful choice of ligand, stabilisers and electrolyte should be devised.

Yikai Xu communicated: In the manuscript the authors show a neat experiment where DDI water is injected into the particle array at the liquid–liquid interface to provide a localised region of pure water. They observed that the colour of the particle array at the area changes from pink to blue indicating a stronger coupling between neighbouring particles, in other words a reduction in the interparticle spacing, and claim that this is due to the temporary loss of citrate ions. In this system the two major forces acting on the particles laterally at the interface would be electrostatic repulsion and van der Waals attraction. Without electrolytes in the system (TBATPB in the organic phase and trisodium citrate in the aqueous phase) in theory the electrostatic repulsion would become dominant and the particles should be repelled from each other by their surface charge which would be the opposite of the reported experimental observations. Indeed this is

why the authors need to add TBATPB into the organic phase to promote particle self-assembly at the interface in the first case. Thus, I am wondering if there are also other forces at play, such as the direction of the water flow or the space occupied by the pipette tip at the interface.

Leonora Velleman communicated in response: The flow rate, distance of the pipette to the surface and angle all effect the rate at which the nanoparticle spacing can be modulated as the nanoparticles shift dependent on what their local environment is. If the pipette is far away and flow rate low, the water being pumped in may not reach the interface to dilute the concentration of the citrate stabiliser and the nanoparticles will not move closer together.

In general, we hold the pipette ~300 μm above the interface and use a low flow rate (*e.g.* 10 μL min^{-1}) to ensure that turbulence of the film at the interface is minimised. Movement in the film can be easily be seen by tracking a defect, if the defect is pushed away once the flooding commences then the flow rate must be reduced or pipette pulled further away.

Fabrizio Giorgis communicated: In the paper, a nice method aimed to control the spacing between nanoparticles (NPs) is presented showing that the Raman enhancement can be optimized by matching the plasmon resonance of the assembly with respect to the optical excitation. This allows one to perform fundamental analyses on the Raman response of the nanostructured liquid system. In the recent past, several groups have presented results concerning plasmonic nanoparticles grown on an elastomeric matrix (*e.g.* ref. 1–3), where the interstitial gap between the NPs is changed by applying a controlled strain on the polymeric membranes; such systems yield SERS tunability. Could you comment on the similarities and differences in the potential of your approach *versus* these metal–elastomeric nanostructures, also in terms of tunable plasmon resonances?

1 M. K. Hossain, G. R. Willmott, P. G. Etchegoin, R. J. Blaikie and J. L. Tallon, *Nanoscale*, 2013, **5**, 8945–8950.
2 M. Kang, J.-J. Kim, Y.-J. Oh, S.-G. Park and K.-H. Jeong, *Adv. Mater.*, 2014, **26**, 4510–4514.
3 A. Lamberti, A. Virga, A. Angelini, A. Ricci, E. Descrovi, M. Cocuzza and Fabrizio Giorgis, *RSC Adv.*, 2015, **5**, 4404–4410.

Leonora Velleman communicated in reply: An elastomeric substrate is another convenient method to observe the SERS and plasmon resonance dependence on nanoparticle gap. Some notable differences are the range of interparticle spacings that can be achieved. For example, with nanoparticle assembly at liquid interfaces we can control the spacing from <2 nm with potentially no upward limitation on interparticle spacing. Elastomeric substrates can only stretch so far. In general, these studies performed 50–100% strain in their elastomers.

The interface between two immiscible liquids is essentially atomically flat and defect free. The nanoparticles arrange themselves evenly over the interfacial area producing homogeneous interparticle spacing and minimising multi-layers. With any solid substrate, problems can arise from nanoparticle attachment, uneven deposition over the surface and macroscopic surface roughness. Further, there may be uneven strain in each direction of the elastomer as it is stretched.

Cristiano Matricardi communicated: Considering nanoparticles in SERS, when they are close to each other hot spots further increase the signal. However when we have dimers or more extended clusters, the extinction peak and the maximum of the EF can appear in different parts of the spectrum, and the best EF can even fall far away from the maximum of the extinction peak. In the case of NP aggregates, what are the optical properties that determine the most suitable and optimized substrates for SERS? Is the scattering intensity *vs.* wavelength a property that has more importance in this case?

Leonora Velleman communicated in response: The interparticle spacing will have the greatest impact on the SERS enhancement, as the large local field enhancement within a nanoparticle junction results in some of the largest single molecule enhancement factors. But as you mention, the maximum EF can drop off relative to the position of the extinction peak. By tailoring the closest interparticle spacing so that the LSPR and laser excitation match, the Raman enhancement could be boosted further. Therefore, it will be important to take both the interparticle spacing and extinction spectra into account.

Agata Królikowska communicated: You used trifluoroacetic acid (TFA) to protonate 4-MBA molecules and screen the charge between the GNRs to induce nanoparticle assembly. You could probably see the SERS signature of the protonation of the initially dissociated carboxylic groups of 4-MBA. Have you noticed any correspondence between the progress of this protonation process and the temporal evolution of the SERS spectra (Fig. 4c in your paper[1]) during GNR assembly, as in the paper you only analyze the SERS intensity changes (Fig. 4d).

1 L. Velleman, L. Scarabelli, D. Sikdar, A. A. Kornyshev, L. M. Liz-Marzán and J. B. Edel, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00162b.

Leonora Velleman communicated in reply: The peaks commonly used to monitor 4-MBA protonation are the peak at ∼1430 cm^{-1} (COO$^-$) and the peak at ∼1710 cm^{-1} (C=O). By taking the ratio of these peaks an indication of the degree of protonation can be determined and has been used previously as a sensitive pH probe.[1] In our case the ratio between the intensities of the COO$^-$ and C=O peaks decreases from 2 to 0.6 as TFA is added, signifying the protonation of the COO$^-$ group as the pH is decreased.

1 S. W. Bishnoi, C. J. Rozell, C. S. Levin, M. K. Gheith, B. R. Johnson, D. H. Johnson and N. J. Halas, *Nano Lett.*, 2006, **6**, 1687–1692.

Bart de Nijs opened a discussion of the paper by Stephanie Reich: The dye and carbon nanotube seem a complicated system to model. Could you elaborate on how much area/volume the carbon nanotube takes up in your nanogap and if or how you take this into consideration in your modeling?

Stephanie Reich replied: The area of the CNT bundle is approximately 80 nm^2. The area of the plasmonic hotspot is on the order of 10^3 nm^2. The CNT takes up 5–10% of the hotspot cross section. We performed FDTD simulations of the gold nanodimer with a graphite cylinder in the gap to model the presence of the CNTs. The presence of the graphite altered the plasmonic near field, but when

normalizing the simulations to a free-standing graphite cylinder as a reference, we recovered the original SERS hotspots. The key in considering the effect of the CNT is to realize that our reference system was likewise 6T molecules in CNTs that are subjected to external electromagnetic fields.

Jeremy Baumberg asked: The field in the gap is not uniform, and thus your results are very sensitive to the exact position of the CNTs in this gap. How accurately can you capture this?

Also, the CNTs have very high conductivity both along the tube and around the tube. How have you included this in the EM field modelling, as the conductivity strongly screens the fields but also allows them to build up locally? I would suggest that this is very important, and your modelling must take account of the complex dielectric constants of the CNT bundle (which since they are close to each other will not show sharp discrete resonances).

Stephanie Reich responded: We estimated the uncertainty in the CNT position as 5 nm. However, in the discussion paper[1] we present simulations were we moved the CNT in the gap as much as physically possible (the CNT is constrained by the gold discs). The changes in the enhancement were below 30%, whereas the discrepancy with respect to the experimental data is two orders of magnitude. The original simulation of the SERS enhancement considered only the nano-plasmonic system (as is the standard in the field). We performed additional FDTD simulations of the gold nanodimer with a graphite cylinder in the gap to model the presence of the CNTs. The presence of the graphite altered the plasmonic near field, but when normalizing the simulations to a free-standing graphite cylinder as a reference, we recovered the original SERS hotspots. The key in considering the effect of the CNT is to realize that our reference system was likewise 6T molecules in CNTs that are subjected to external electromagnetic fields.

1 N. S. Mueller, S. Heeg, P. Kusch, E. Gaufrès, N. Tang, U. Hübner, R. Martel, A. Vijayar-aghavan and S. Reich, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00127d.

Jean-Francois Masson asked: In the original experiments of Martel *et al.* in Nature Photonics, they reported a high Raman signal for the same carbon nanotube–6T construct. When the Raman signal is compared to SERS, it seems that there is not much enhancement from the carbon nanotube–6T construct. Can you explain the difference between the original Raman data of the carbon nanotube–6T system that showed a high Raman intensity and the current data showing an apparent low intensity? If one were to change the molecule in the carbon nanotube, would there be a different conclusion?

Stephanie Reich responded: There is no difference between the original data of the Martel group[1] and our measurements. The absolute Raman cross section of the 6T molecules in the CNTs is very high. We get a Raman peak with an excellent signal to noise ratio from only 5000 molecules with 532 nm excitation, with a $100\times$ objective, 350 µW µm^{-2}, and a 30 s integration time. This is comparable to the signal observed by the Martel group (532 nm excitation, $100\times$ objective, 95 µW µm^{-2}, 60s integration time). However, the total scattering intensity increases by another factor of 10^4–10^5 when the 6T@CNT hybrids are placed in

the plasmonic cavity. We note that our measurements were performed at 633 nm, whereas Gaufrès *et al.* focus on 514 nm excitation. The 6T peak is somewhat less pronounced for red excitation compared to the CNT signal as already reported in the 2014 *Nature Photonics* paper.

1 E. Gaufrès, N. Y.-W. Tang, F. Lapointe, J. Cabana, M.-A. Nadon, N. Cottenye, F. Raymond, T. Szkopek and R. Martel, *Nat. Photonics*, 2014, **8**, 72–78.

Paul Dawson commented: You have mentioned the passive nature of the carbon nanotubes with regard to Raman scattering from the molecules contained within the nanotubes. Can you confirm this with regard to the properties of the nanotubes – since these are single-walled nanotubes, can you specify the chirality? Are they metallic or semiconducting and does it make any difference?

Stephanie Reich replied: The tubes are mix of metallic and semiconducting. The papers by the Canadian group studied the 6T@CNT hybrids in great detail finding no difference between semiconducting and metallic nanotubes for the encapsulated molecules.[1] The radial breathing modes of the CNTs used in the experiment are below 150 cm^{-1} (1.5 nm diameter, see *e.g.* ref. 2). In our current measurement setup we cannot measure Raman spectra below 200 cm^{-1}, because we optimized the system for SERS measurements at high phonon energies.

1 E. Gaufrès, N. Y.-W. Tang, F. Lapointe, J. Cabana, M.-A. Nadon, N. Cottenye, F. Raymond, T. Szkopek and R. Martel, *Nat. Photonics*, 2014, **8**, 72–78.
2 J. Maultzsch, H. Telg, S. Reich and C. Thomsen, *Phys. Rev. B*, 2005, **72**, 205438.

Pieter Wuytens remarked: The simulated enhancement factor is calculated based on the field enhancement at the Stokes and pump wavelengths. Would it make a difference if the enhancement at the Stokes frequency is calculated from the enhanced dipole radiation? Possibly, this emission has a different polarization, can this (partially) explain a discrepancy between the simulation and the experiment?

Stephanie Reich replied: The consequence of accounting for dipole reradiation in SERS was investigated in previous works by Ausman *et al.*[1–2] This effect can indeed lead to a different enhancement factor (by factors of 2–3) for special scattering configurations, when the Raman scattered light is detected at a large angle towards the incoming light. However, in a backscattering configuration, there was no difference in enhancement to the standard EM modelling. As our experiments are performed in the backscattering configuration, we expect this effect to be negligible.

1 L. K. Ausman and G. C. Schatz, *J. Chem. Phys.*, 2009, **131**, 084708.
2 L. K. Ausman and G. C. Schatz, in *The Mie Theory - Basics and Applications*, ed. W. Hergert and T. Wriedt, Springer Series in Optical Sciences, Springer, 2012, ch. 5, pp. 135–155.

Richard Van Duyne commented: With regards to the polarization conditions, I assume the experiment is done with polarized light. Isn't the orientation of the nanoparticle wrong?

Stephanie Reich answered: In the experiments reported in the paper, the incoming and scattered light was polarized along the axis of the nanodimer. The

angle between the nanotube and the axis of the nanodimer is 70°. Enhancement is provided by the projection of the near-field onto the nanotube axis. The polarization is "correct" for the nanoplasmonic system, but "almost wrong" for the nanotube. We also performed polarization-dependent experiments, where we rotated the polarization direction with respect to the dimer axis. We observe that the enhancement is strongest, if the light is polarized along the dimer. For green excitation (no plasmonic enhancement), in contrast, the maximum of the Raman intensity occurs for polarization along the nanotube. We reported similar experiments for unfilled nanotubes in ref. 1.

Another interesting situation arises (unpublished data) when we look at nanotubes where the intrinsic resonance of the tube matches the plasmonic resonance of the nanocavity. We observe a polarization dependence with four maxima between 0 and 360°: two maxima correspond to the SERS spectrum and are aligned with the nanodimer axis; two maxima correspond to the Raman spectrum and are aligned with the nanotube axis.

1 Heeg et al., Nano Lett., 2013, **13**, 301–308.

George Schatz remarked: The results in your paper address fundamental questions about SERS enhancement mechanisms. One issue is whether the enhanced fields generated in the experiments might be high enough to cause nonlinear optical effects in the metal particles to be important. A second issue is whether the higher order Raman effects that are thought to explain the experiments are unique to carbon nanotubes, or whether they are universal to all molecules.

Stephanie Reich answered: Our plasmonic nanostructures are gold nanodiscs with a 100 nm diameter and 20–30 nm separation. The maximum SERS enhancement is on the order of 10^6–10^7, rather low/average for SERS structures. We think that nonlinear optical effects are negligible for this system. Our published description of SERS as a higher-order Raman effect is applicable to molecules.[2] The predicted enhancement is independent of the molecular species and depends only on the plasmonic system (resonances, resonance line width, and strength of the coupling). We also note that the experimental enhancement factors we obtained for the 6T inside the CNTs agree very well with the measured enhancement of thiol-functionalized gold nanostructures.[1]

1 W. Zhu and K. B. Crozier, Nat. Commun., 2014, **5**, 5228.
2 N. S. Mueller, S. Heeg, S. Reich, Phys. Rev. A, 2015, **94**(2), 023813.

Rohit Chikkaraddy asked: My question is two fold: What does the dark-field scattering look like? Does it match with the simulated scattering spectrum?

Do you observe any features of strong coupling?

Stephanie Reich responded: We have no dark-field spectra of the devices. There was no signature of strong coupling in our experiment. The gold nanodimers have disc diameters of around 100 nm and a gap size of 20–30 nm. We do not expect such a system to reach the strong coupling regime for single CNT bundles in the gap. The strong coupling regime has been observed for plasmonic structures comparable to ours, but with a large number of chirality-sorted individual CNTs of small diameter; see ref. 1.

1 A. Graf, L. Tropf, Y. Zakharko, J. Zaumseil and M. C. Gather, *Nat. Commun.*, 2016 7, 13078.

Pieter Wuytens said: Does the far-field absorption of the measured structure match that of the simulated structure? Is it possible that discrepancies in the material dispersion give a shift in the resonance, changing the field enhancement at one single wavelength?

Stephanie Reich responded: We did not measure the far-field absorption of the structures; indeed with the current sample it is impossible to measure absorption, because the plasmonic structures were fabricated on silicon. We may attempt preparing plasmonic nanostructures on transparent samples using electron-beam lithography and/or producing individual plasmonic hotspots through alternative forms of assembly for absorption measurements. This will require modulation-type absorption spectroscopy.

Ian Bruzas said: The NTs are probably metallic. Could scattering from a tip be causing some kind of strange effect that's not particularly wavelength dependent?

Stephanie Reich replied: The CNTs are a mixture of metallic and semi-conducting. Probably the best approximation to describe this material is to consider the properties of graphite (the typical one-dimensional features of isolated CNTs are almost absent for the mixed bundles of tubes with 1.5–2 nm diameters as used by us). We performed FDTD simulations of the gold nanodimer with a graphite cylinder in the gap to model the presence of the CNTs. The presence of the graphite altered the plasmonic near field, but when normalizing the simulations to a free-standing graphite cylinder as a reference, we recovered the original SERS hotspots. The key in considering the effect of the CNT is to realize that our reference system was likewise 6T molecules in CNTs that are subjected to external electromagnetic fields.

Roy Goodacre communicated: Have you considered that these CNTs may be acting as a kind of waveguide where the reporter molecule (6T) is effectively exposed to more laser light due to the properties of the waveguide and internal reflections within the CNT?

Stephanie Reich communicated in answer: Additional enhancement induced by the CNT will act on the molecules in the plasmonic cavity as well as on the reference molecules, because both were encapsulated in CNTs. When calculating the enhancement as the ratio of the SERS-enhanced intensity and the reference Raman intensity of 6T@CNT these effects cancel.

Augustus Fountain communicated: People have measured graphene-enhanced Raman. Have you considered that you are plasmonically enhancing the CNT which is then coupling with the molecule inside?

Stephanie Reich communicated in reply: Additional enhancement induced by the CNT will act on the molecules in the plasmonic cavity as well as on the reference molecules, because both were encapsulated in CNTs. When calculating

the enhancement as the ratio of the SERS-enhanced intensity and the reference Raman intensity of 6T@CNT these effects cancel.

Christian Kuttner communicated: You examined the plasmonic contribution of organic molecules encapsulated in CNTs. Can you rule out the possibility that the delocalised electrons of the CNTs contribute to the SERS activity of the hotspot?

Stephanie Reich communicated in answer: Additional enhancement induced by the CNT will act on the molecules in the plasmonic cavity as well as on the reference molecules, because both were encapsulated in CNTs. When calculating the enhancement as the ratio of the SERS-enhanced intensity and the reference Raman intensity of 6T@CNT these effects cancel. Furthermore, we performed FDTD simulations of the gold nanodimer with a graphite cylinder in the gap to model the presence of the CNTs. The presence of the graphite altered the plasmonic near field, but when normalizing the simulations to a free-standing graphite cylinder as a reference, we recovered the original SERS hotspots. The key in considering the effect of the CNT is to realize that our reference system was likewise 6T molecules in CNTs that are subjected to external electromagnetic fields.

Heike Arnolds addressed Javier Aizpurua and Stephanie Reich: The discussion of nonlinear effects in SERS is often very focussed on the enhancement factor, EF, but the EF can be a very difficult number to determine or reproduce experimentally. Are there any other experimental characteristics one can look for, such as a spatial emission pattern or the existence of second harmonic Raman scattering?

Javier Aizpurua answered: Precisely this is the focus of our Faraday discussion paper: to stress the fact that there might be certain situations where the coupling of vibrations and plasmonic modes can be strong enough (due to the small effective mode volumes provided by plasmonic resonators) so that nonlinearities start emerging. In this regime of vibrational pumping, the optomechanical coupling between vibrations and plasmonic modes can provide a nonlinear evolution of the Raman signal. This should be more traceable in an experiment than the absolute or even relative EF provided by a plasmonic antenna. Our suggestion to experimentalists is to try to create situations where these effects are revealed.

Regarding the emission pattern and the existence of second harmonic Raman scattering, I believe that the directionality of the emission is mainly governed by the plasmonic mode, which is finally responsible for taking the signal out to the detector, so I am not sure how much more additional information this analysis might provide regarding the Raman process itself. For the nonlinear signal, however, in panel c of Fig. 6 of our Faraday Discussion paper[1] we show how for increasing optomechanical coupling strengths, Stokes and anti-Stokes peaks at twice the energy of the phonon clearly emerge, showing the existence of 2-phonon scattering events. This should be observable in experiments under the right conditions.

1 M. K. Schmidt, R. Esteban, F. Benz, J. J. Baumberg and J. Aizpurua, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00145b.

Stephanie Reich replied: This is a very interesting and valid point you are making. Currently, we cannot offer an alternative fingerprint of plasmonic systems, but we will keep actively considering this. As to the enhancement factors and their reproducibility, it would be very helpful to develop a standardized system of a SERS probe (molecular type, concentration) and reference system. The reference would be a different molecule and it needs to be accessible with the types of Raman setups we use for SERS. Maybe this is a route the community wants to consider (like the high degree of standardization in measuring the efficiency of solar cells).

Claudia Fasolato opened a discussion of the paper by John Lombardi: My question is about the contribution of excitonic resonances to the chemical enhancement from semiconductor surfaces. You mentioned the tunability of semiconductors in terms of electronic transitions as one of the advantages of these substrates, but often in these systems a change in the excitonic resonance is related to a change in the semiconductor structure and brings along a consequent modification of the energy gap, *e.g.* from indirect to direct (as in the transition from few-layer to monolayer MoS_2). In your opinion, would this modification represent an advantage for exciting charge transfer resonances, or a drawback because of the enhanced carrier recombination within the substrate, not involving the analytes probed by SERS?

John Lombardi answered: Yes, if the exciton changes from a direct to indirect band gap structure, it will make the exciton resonance forbidden, and therefore not eligible for lending intensity to the charge transfer transition. Of course, as you mention the opposite can be true, as in the case of MoS_2. In all cases, we have to ascertain the locations of the possible resonances in the system, and adjust the parameters under our control (such as laser excitation wavelength, particle shape and size) to find the optimum conditions for Raman enhancement

Jeremy Baumberg addressed George Schatz and John Lombardi: It would seem to me that organic substrates would be a very bad idea, as then one picks up a huge background SERS component. Is there any way around this?

George Schatz commented: This question refers to a recent article that I was involved in.[1] In this work, strong Raman enhancement (3.4×10^3) was observed when methylene blue (MB) was adsorbed onto the organic molecular semi-conductor, α,ω-diperfluorohexylquaterthiophene (DFH-4T). The measurements show Raman modes from both the semiconductor and MB, but MB is a resonant Raman scatterer, so the MB modes are easily observed. Our calculations (using the same INDO method as in our paper[2]) show the presence of a charge transfer resonance at very close to the excitation wavelength (785 nm) so long as the resonance is sufficiently narrow.

1 M. Yilmaz, E. Babur, M. Ozdemir, R. L. Gieseking, Y. Dede, U. Tamer, G. C. Schatz, A. Facchetti, H. Usta and G. Demirel, *Nat. Mater.*, 2017, **16**, 918–924.
2 R. L. Gieseking, M. A. Ratner and G. C. Schatz, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00122c.

John Lombardi responded: I agree that the phonon spectrum of a substrate composed of an organic semiconductor will produce problems of spectral

interference in SERS. For inorganic substrates, the phonon modes are, in most cases, confined to the region below 500 cm^{-1}, and do not pose a problem. However, organic semiconductors tend to have higher lying phonon modes, and these have to be taken into account in choosing a semiconductor to use with a given molecule. Perhaps the ability to finely tailor the band edges will be valuable enough to mitigate the phonon interference. Or a substrate can be chosen such that there is little interference with enough modes to allow discrimination. It may also be that the substrate modes will not be as enhanced as much as the adsorbate modes. In any case this problem must be addressed in any application of organic substrates.

Ben Hourahine remarked: Since these are semiconductor systems, effects such as surface band bending, charge transfer to adsorbed species (which can be very strong in some cases[1]), or charging of the system should be expected to perturb the response. Do you see any prospect for rules of thumb to design around these effects or to tailor systems to be more sensitive to specific analytes?

1 J. Ristein, *J. Phys. D: Appl. Phys.*, 2006, **39**, R71.

John Lombardi replied: Certainly the theory, as is, does not account for the problems you raise. In some cases, such as band bending, it may be simply that we need to change the band edge level to the bent level. In cases of doping, we might have to revert to the Fermi level of the theory as applied to metals. In cases where these effects are not known, I believe more experiments are needed in order to account for such problems.

Jeremy Baumberg addressed John Lombardi and George Schatz: How does bringing the molecule down on the substrate affect the electronic structure at that position on the substrate?

How do you know what the effect will be? How will molecule "land"? Can you rely on DFT to accurately model the orientation and position of the molecule, and then predict how it interacts with the semiconductor/metal underneath?

George Schatz answered: Electronic structure calculations can be used to determine how the adsorbate molecule binds to the substrate. Often this requires using a dispersion-corrected DFT method, but such calculations are routinely available now, and they provide accurate estimates of orientation and position, including for subtrates that can be metals, semiconductors and insulators. The semiempirical INDO method is less accurate for these ground state structural properties, so typically we would use DFT to determine the structure, and then INDO to determine optical properties for that structure.

John Lombardi answered: It is well-known that the addition of a surface molecule can affect the conduction or valence band edge, and in this case, we need to adjust the theory to take these changes into account. The problem is that these effects are hard to measure, and experiments have not been carried out in too many cases. There are also valid concerns as to the reliability of DFT predictions of the optimized molecular orientation on surfaces. There is no assurance that these calculations produce the global minimum of the orientation

potential, and we may possibly have to use comparison to experiments (such as the relative intensities of Raman lines of different symmetry species, or EELS measurements).

Dong-Ho Kim asked:
(1) If we put MoS_2 on a normal metallic SERS substrate, can we expect a synergic effect? If possible, I want to know the references that you think are meaningful and reliable.
(2) Then, is there any logical step to match the synergic effect? Maybe the band alignment and/or work function matching can be a guideline for that?

John Lombardi answered: I suggest for example ref. 1–3.
I suggest that, if possible, the metal Fermi level be adjusted to match the charge transfer resonance. This, of course, is not always possible, although it may be worth trying this in an electrochemical environment, with potential control over the Fermi level. This is a throwback to the early days of SERS, but if it works, it might be well worth the effort.

1 X. Yang, H. Yu, X. Guo, Q. Ding, T. Pullerits, R. Wang, G. Zhang, W. Liang and M. Sun, *Materials Today Energy*, 2016, **5**, 72–78.
2 X. Fei, Z. Liu, Y. Hou, Y. Li, G. Yang, C. Su, Z. Wang, H. Zhong, Z. Zhuang and Z. Guo, *Materials*, 2017, **10**, 650.
3 Y. Sun, K. Liu, X. Hong, M. Chen, J. Kim, S. Shi, J. Wu, A. Zettl and F. Wang, *Nano Lett.*, 2014, **14**, 5329–5334.

Rohit Chikkaraddy asked: The SERS spectrum on MoS_2 of 4-mercapto pyridine (4-MPy) is different from bulk 4-MPy, is this due to field gradients breaking Raman selection rules or different Raman lines excited due to charge transfer?

John Lombardi responded: We clearly believe the relative enhancements of the observed spectrum of 4-MPy are due to charge transfer effects. This belief is backed up by the selection rules, which are obeyed. However, these selection rules depend on the orientation of the molecule at the surface, which we obtain by DFT calculations (see the answer to the question from Jeremy Baumberg), which are possibly not in the correct optimized orientation. This presents the possibility, as suggested, that field gradient effects could also be the cause of the observed spectrum. If I am not mistaken, the selection rules are very similar for both cases, but the Herzberg–Teller selection rules also involve an intensity "borrowing" mechanism, which predicts the relative enhancements of lines of different symmetry (depending on the oscillator strengths of the "lending" transitions). These have been observed to be followed in many cases.[1] However, in the case of 4-MPy on MoS_2, the possibility of field gradient effects cannot be ruled out as of now.

1 J. R. Lombardi and R. L. Birke, *J. Phys. Chem. C*, 2008, **112**, 5605–5617.

Christian Kuttner commented: You stated that one main objective is to coincide plasmonic modes because of possible benefits for increased SERS activity. I expect that there are also situations where perturbation by overlapping modes might negatively affect the SERS activity. Are there examples where overlapping modes can be "bad"?

John Lombardi answered: Your suspicions are correct. All the resonances which contribute to the SERS effect are coupled, and in many circumstances the polarizability expression involves a sum over various terms, which must then be squared to obtain the correct intensity. The terms in this sum can interfere either positively or negatively, the latter producing lower intensity, rather than enhancement. I know of no report in which the latter has definitely been observed, but that is perhaps because people tend not to report negative results. (If you don't see a spectrum, how do you know it's there?)

Nicolò Bontempi remarked: Prof. Lombardi in his work[1] says that, in presence of a precise analyte, it is possible to tune *a priori* the band gap of a semiconductor and obtain an enhancement of the Raman signal due to a charge transfer effect between the analyte and the substrate itself. I completely agree with this possibility, but I would like to present the possibility to also get SERS in semiconductors exploiting the electromagnetic enhancement. For example by exploiting morphology-dependent resonances[2] or light trapping effects[3] it is possible to obtain excellent sensing results. Of course semiconductors, up to now, are far from the sensing performance of metals, which can reach a single molecule detection level. However, if the aim is not ultrasensitive sensing, semiconductors may help in avoiding some of the known drawbacks of metallic SERS,[4] for example their lossless nature increases their thermal stability preventing heating damage in the analyte.[5] Moreover the exploitation of surface evanescent fields may allow us to study chemical reactions avoiding the denaturation of the analyte[6] or it may give us the possibility of easily functionalizing it with specific supramolecular receptor.[7] In conclusion I would like to underline that the homogenous structures fabricated for dielectric SERS present a higher reproducibility with respect to the random hotspots generated with traditional metallic SERS.

1 J. R. Lombardi, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00138j.
2 I. Alessandri, *J. Am. Chem. Soc.*, 2013, **135**, 5541–5544.
3 N. Bontempi, M. Salmistraro, M. Ferroni, L. E. Depero and I. Alessandri, *Nanotechnology*, 2014, **25**, 465705.
4 I. Alessandri and J. R. Lombardi, *Chem. Rev.*, 2016, **116**, 14921–14981.
5 M. Caldarola, P. Albella, E. Cortés, M. Rahmani, T. Roschuk, G. Grinblat, R. F. Oulton, A. V. Bragas and S. A. Maier, *Nat. Commun.*, 2015, **6**, 7915.
6 I. Alessandri and L. E. Depero, *Small*, 2014, **10**, 1294–1298.
7 N. Bontempi, E. Biavardi, D. Bordiga, G. Candiani, I. Alessandri, P. Bergese and E. Dalcanale, *Nanoscale*, 2017, **9**, 8639–8646.

John Lombardi responded: I am in total agreement with this analysis.

Duncan Graham commented: I think there's a lot of attractive features in using semiconductors including lots of ligands that can be used. What might happen if a thin shell of a semiconductor such as the ones you suggest is used around a plasmonic NP?

John Lombardi responded: This is really a good idea. If the semiconductor shell is thin enough, it enables the addition of plasmon resonance to the enhancement, providing a larger enhancement factor. It also gives greater flexibility of design, as well as independent adjustment of the conduction or valence

band edge. If the shell thickness is less than the exciton Bohr radius, quantum confinement effects can also be harnessed (see for example ref. 1 and 2). Some of these issues are discussed in a recent review article.[3]

1 X. Fu, Y. Pan, X. Wang and J. R. Lombardi, *J. Chem. Phys.*, 2011, **134**, 024707.
2 S. K. Islam, M. A. Sohel and J. R. Lombardi, *J. Phys. Chem. C*, 2014, **118**, 19415–19421.
3 I. Alessandri and J. R. Lombardi, *Chem. Rev.*, 2016, **116**, 14921–14981.

Giuliana Di Martino opened a discussion of the paper by Paul Dawson:

What happens in your system if you have a molecule inside the gap? How would you take this into account in your model? What do you think will be the strongest effect: the fact that you are changing the plasmonic mode or the fact that you are changing the molecular system?

Paul Dawson responded: One could readily accommodate, say, a molecular monolayer in the gap in terms of an adlayer on the Au substrate with an effective dielectric function. Any infilling of the gap with a medium of $n > 1.0$ will cause a red shift of the localised plasmon resonances of the gap. This, of course, is speaking from a purely optical perspective, assuming a constant gap dimension – which will not be the case. A more significant influence on the spectral profile of gap mode plasmons is likely to arise from changes in the gap dimension due to variation in the local density of states and the local work function brought about by the introduction of the molecule.

Agata Królikowska commented: You are trying to simulate a real TERS experiment. According to your results, when you decrease the absolute value of the bias, the TERS intensity is also decreased (*e.g.* Fig. 4b in your paper for the 633 nm laser line[1]).

However, this theoretically predicted behaviour seems to be just the opposite to what is known from experiment. How can you explain this, apart from the humidity issues mentioned in the paper?

1 P. Dawson, D. Frey, V. Kalathingal, R. Mehfuz and J. Mitra, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00128b.

Paul Dawson replied: I'm not sure we are trying to simulate a real TERS experiment. Our primary goal here is to establish why gap-mode plasmon resonances exist at all toward the red end of the visible spectrum and into the near IR. We are suggesting this comes about by a manifestation of a $\chi^{(3)}$ non-linearity in gold which manifests as an $|E|^2$ dependence in the dielectric function. We have thus systematically varied the applied bias across an STM junction of constant gap dimension (1.0 nm) in order to illustrate the physics involved, whereas a more realistic simulation of an experiment would incorporate some basic tunnelling theory to imitate, say, a constant current mode of operation. We haven't done that at this stage since the bias dependence of the gap dimension (at constant current) would convolute changes in the resonance positions (in wavelength) due to changes in the tip–sample coupling with those due to the changes in the junction electric field.

The changes as reported in some TERS experiments are not necessarily in conflict with the model presented in the Discussion paper. In Fig. 4b, to which

you refer specifically, it is the case that for the range ~1200 cm^{-1} to ~3200 cm^{-1} in Stokes scattering (with an excitation wavelength of 633 nm) the modelled enhancement factor is greater at biases of 1.25 V and 1.50 V than at 1.75 V (or even 2.0 V). In other words the Raman signal would increase with decreasing bias in this range.

The other matter that I specifically highlighted during the discussion of relevance to the point you raise was with reference to the light emission intensity in STM, both experimental and modelled, as reported in Fig. 4 of ref. 1. This figure brings together the optical analysis with basic tunnelling theory – at constant bias a decrease in tunnel current (from 40 nA to 10 nA) leads to an increase in the gap dimension (from 1.0 to 1.06 nm in the model) which in turn causes a (slightly super-linear) decrease in the emission intensity of the main intensity peak, along with a small blue shift in the peak emission wavelength. While this is a constant-bias rather than constant-current operating mode it does demonstrate that the our model of the emission optics may be combined with basic tunnelling considerations to produce a reasonable, physically-based description of experimental data.

1 V. Kalathingal, P. Dawson and J. Mitra, *Phys. Rev. B*, 2016, **94**, 035443.

Giuliana Di Martino communicated: Why do you think you see a different trend compared to what was seen in Paper 14063[1] and in ref. 2?

1 G. Di Martino, V. A. Turek, C. Tserkezis, A. Lombardi, A. Kuhn and J. J. Baumberg, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00130d.
2 G. Di Martino, V. A. Turek, A. Lombardi, I. Szabó, B. de Nijs, A. Kuhn, E. Rosta and J. J. Baumberg, *Nano Lett.*, 2017, **17**, 4840–4845.

Paul Dawson communicated in reply: First of all, to avoid repetition, please refer to our response to the earlier question from Agata Królikowska which points out that there are regions in the modelled response of the enhancement factor (EF) which indicate that the Raman signal will decrease with increasing applied bias.

Note that the two situations – localised gap modes in a vacuum or air gap ($n = 1.0$) in the context of STM (Paper 14168[1]) and the modes in a dielectric-filled gap in an electrochemical cell – are non-equivalent systems, so it is not clear why it should be thought that the trends should match. Our first pass at these gap mode configurations is to apply the empirical model based on the theory of Rendell and Scalapino (RS).[2] For the set-up in Di Martino *et al.*[3] this approach shows the "zero-order" mode at ~680 nm using a bulk plasmon energy of 8 eV and a self-assembled molecular layer of $n = 1.45$ in a gap of dimension $d = 1.1$ nm (n and d as given for the same nanoparticle-on-mirror system in ref. 4). This is pretty well aligned with the experimental result of Di Martino *et al.* shown as Fig. 1b in Paper 14063[3] and Fig. 1c in ref. 5 which means that there is no need to take recourse to arguing for modification to the dielectric function of the Au. The screening offered by the dielectric filler brings about a very significant red shift of the localised plasmon modes relative to the vacuum-gap case, with any modification to the Au optical data playing a secondary role. This red-shifting of gap mode plasmons due to dielectric infill of the gap has been directly addressed in Paper 14168[1] in relation to similar Au nanoparticle-on-mirror systems, namely those of Lumdee *et al.* and Mock *et al.* (ref. 6 and 7 respectively). By contrast,

application of the RS-based model to explain the spectral emission from STM (*i.e.* with no dielectric filler in the gap) requires the reduction of the effective bulk plasmon energy to ~3.5 eV which has been consistently argued in our previous work (ref. 8–10) on an empirical basis with qualitative interpretation. The interpretation was then developed in ref. 11 where we place the argument on a more physical footing.

In the case of the electrochemical cell, to fully develop the effects of a strong dc field in the gap requires all of the potential drop to occur between the Au nanoparticle and the Au substrate across the ~1 nm dielectric spacer and none to occur across the macroscopic volume of the cell between the ITO counter electrode the Au nanoparticle. We are not sure that this has been definitively established in the paper by di Martino *et al.*

The final point, again, is that the gap is filled with a dielectric medium. It is more likely that the changes monitored optically (a change of the peak position or the half-width of the scattering peak associated with the coupled or gap mode) are to do with the linear polarizability of the molecular layer, rather than a third order effect in the polarizability of the metal. Indeed this seems to be the interpretation that is offered in the paper you cite.

1 P. Dawson, D. Frey, V. Kalathingal, R. Mehfuz and J. Mitra, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00128b.
2 R. W. Rendell and D. J. Scalapino, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1981, **24**, 3276–3294.
3 G. Di Martino, V. A. Turek, C. Tserkezis, A. Lombardi, A. Kuhn and J. J. Baumberg, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00130d.
4 F. Benz *et al.*, Nano Lett., 2017, **15**, 669–674.
5 G. Di Martino, V. A. Turek, A. Lombardi, I. Szabó, B. de Nijs, A. Kuhn, E. Rosta and J. J. Baumberg, *Nano Lett.*, 2017, 17, 4840–4845.
6 C. Lumdee, B. F. Yun and P. G. Kik, *ACS Photonics*, 2014, **1**, 1224–1230.
7 2 J. J. Mock, R. T. Hill, Y. J. Tsai, A. Chilkoti and D. R. Smith, *Nano Lett.*, 2012, **12**, 1757–1764.
8 J. Mitra, L. Feng, M. G. Boyle and P. Dawson, *J. Phys. D: Appl. Phys.*, 2009, **42**, 215101.
9 M. G. Boyle, J. Mitra and P. Dawson, *Appl. Phys. Lett.*, 2009, **94**, 233118.
10 M. G. Boyle, J. Mitra and P. Dawson, *Nanotechnology*, 2009, **20**, 335202.
11 V. Kalathingal, P. Dawson and J. Mitra, *Phys. Rev. B*, 2016, **94**, 035443.

Natalia Martín Sabanés commented: In the STM-TERS modelling, you find that increasing the bias voltage results in a significant increase of the TERS signal, and argue that even considering the gap distance increase from 0.1 V to 1 V reported by Pettinger *et al.* in ref. 84[1] of your paper, the TERS intensity should increase as a result of the strong increase of the electric field in the junction. Experimentally, few reports have shown a decrease of the TERS intensity upon bias increase in different environments[2] and for different molecules, generally attributed to a gap distance increase. In ref. 3, it is found that bias tuning has the additional effect of altering the molecular geometry (bending of the monolayer) which further affects the TERS intensity.

Your model doesn't include molecules in the junction, nor a gap distance change that will occur experimentally when operating the STM. Probably a convolution of different effects (plasmon shifts, gap distance change, maybe molecular reordering) will define the final intensity of the spectra for a given bias value. Have you considered including (some of) these effects in your model in order to theoretically understand the different contributions and bring the theoretical simulations and experimental data to a closer agreement? Would it

be feasible to include in your model in a simple way the gap distance change resulting from the bias change? In ref. 2, we found a decrease of intensity upon bias increase in a voltage range between 0.01 and 0.5 V. What does your model predict in such a small bias regime? At such low values, the gap distance is expected to be very small and therefore a small distance change will affect the TERS signal dramatically (Pettinger *et al.*[1]), do you think then that in that regime the distance change will predominate instead of the change in **E** at the junction?

1 B. Pettinger, K. F. Domke, D. Zhang, G. Picardi and R. Schuster, *Surf. Sci.*, 2009, **603**, 1335–1341.
2 N. Martín Sabanés, A. Elizabeth, J. H. Pfisterer and K. F. Domke, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00164a.
3 C. Toccafondi, G. Picardi and R. Ossikovski, *J. Phys. Chem. C*, 2016, **120**, 18209–18219.

Paul Dawson responded: Thank you for the comprehensive and considered nature of your comments and questions. You are quite correct in stating that the bias-dependent response will be a convolution of the effect on the localised gap modes of a change in the gap dimension (under constant-current STM operation), the change in the optical properties of the Au in the near tip–sample region, as well as molecule-specific changes.

To run through the points that you raise: The anticipated TERS signal in our model generally does increase with increasing bias, but this is not the case across all of the range of Raman shift and tip dimensions as specifically noted in the response to the earlier question by Agata Królikowska – please refer to that response. The variation of the gap dimension in ref. 84[1] covers a large range up to ∼5 nm while our modelling, for the purposes of isolating the effect of the change in electric field, has the gap fixed at 1.0 nm. Increasing the gap dimension will of course lead to a dramatic decrease in the coupling between the tip and substrate and thus a corresponding decrease in the TERS signal. This may be as important as, or possibly even be of more significance than the effect of detuning from a given gap mode (*i.e.* of a particular order) or a transition from one gap mode to another (of a different order) driving a particular Raman transition as the gap conditions change (dimension, electric field). This will be more so the case at low bias (less than 0.5 V), as you suggest, where the gap modes are not well developed (Fig. 4a and 5a of paper 14168[2]). In passing it is interesting to note that the analysis presented in ref. 1 uses a value for the bulk plasmon frequency in the Rendell and Scalapino model (ref. 3) that is much reduced from the ideal Drude value. This is exactly the issue that we were pointing out contemporaneously in 2009 in the context of detailed, fundamental studies in STM light emission (ref. 4–6), though our considerations didn't extend to TERS at the time.

Regarding molecular inclusions in the gap, starting from a vacuum or air gap it would be relatively straightforward to optically include a molecular monolayer in the gap, represented by an adlayer with some effective refractive index. However, there are the additional issues of alteration in the gap dimension due to changes in the local density of states and workfunction, as already noted in our response to the earlier question by Giuliana Di Martino. Moreover, as you mention in your comment, other effects such as changes in the molecular conformation, orientation *etc.* can come into play which is beyond the scope of our model. With regard to variation of the gap dimension as a function of bias which you also raise,

please refer to the response to the earlier question from Agata Królikowska where
this issue was addressed.

1 B. Pettinger, K. F. Domke, D. Zhang, G. Picardi and R. Schuster, *Surf. Sci.*, 2009, **603**, 1335–
    1341.
2 P. Dawson, D. Frey, V. Kalathingal, R. Mehfuz and J. Mitra, *Faraday Discuss.*, 2017, DOI:
    10.1039/c7fd00128b.
3 R. W. Rendell and D. J. Scalapino, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1981, **24**,
    3276–3294.
4 J. Mitra, L. Feng, M. G. Boyle and P. Dawson, *J. Phys. D: Appl. Phys.*, 2009, **42**, 215101.
5 M. G. Boyle, J. Mitra and P. Dawson, *Appl. Phys. Lett.*, 2009, **94**, 233118.
6 M. G. Boyle, J. Mitra and P. Dawson, *Nanotechnology*, 2009, **20**, 335202.

Jeremy Baumberg said: If your model for the depletion of carriers in Au is
correct, it would mean that I can make an FET from a thin Au layer. However this
is absolutely not the case – you can never change the charge density of Au as the
screening is much too strong. What is the problem in your model that over-
estimates the change in the electron density in gold? If you look at paper 14063,[1]
you will see the plasmon shifts for the voltages you discuss are extremely small,
and do not seem to come from the changes in the Au dielectric constant that you
suggest.

1 G. Di Martino, V. A. Turek, C. Tserkezis, A. Lombardi, A. Kuhn and J. J. Baumberg, *Faraday
    Discuss.*, 2017, DOI: 10.1039/c7fd00130d.

Paul Dawson replied: This is the core of what we postulate in our model which
is effectively that the Thomas–Fermi (T–F) screening length is not applicable in
this situation, *i.e.* in relation to the material in the immediate vicinity of the
junction. Here the dc fields involved are extremely high ($>10^9$ V m^{-1} typically)
which means that the assumptions underlying the T–F length – the expression
normally quoted is based on a Taylor series expansion to the first order term only
– are not applicable. The assumptions are that the external potential should vary
slowly on the scale of the Fermi wavelength and that the externally applied charge
is weak enough to produce only a linear response in the electron gas. There is also
the implicit assumption that the specimen is semi-infinite in nature and not
a nanostructure. In relation to the field strength it should be noted that it is only
a few times less than that required to remove Au atoms from the tip or sample –
pulses of several V applied in STM constituted one of the first nano-writing
experiments in scanning probe microscopy. As far as dimensional nanoscaling
is concerned it has been experimentally observed that the chemical potential of
metal nanoparticles increases with decreasing nanoparticle dimension,[1,2] which
will adversely affect the effective screening length in such confined systems, in the
present case a sharp metal tip under the influence of an extremely high electric
field.

The modified screening length, though substantially relaxed from the T–F
screening length, is ~2 nm, indicating a "depletion" on a similar length scale.
Evidently this alone is not sufficient to envisage a gold thin film FET, where
confinement along the direction of the applied electric field is essential along
with delocalisation along the perpendicular directions for charge transport.

We agree that the plasmon shifts noted in Paper 14063[3] do not originate with
changes in the Au dielectric constant for two reasons. First, in the electrochemical
cell scheme of Paper 14063[3] the Au nanoparticle is separated from the Au

substrate by a dielectric spacer layer. In common with other nanoparticle-on-mirror configurations the energies of the coupled or gap mode plasmons can be evaluated reasonably accurately with use of the Rendell and Scalapino model (ref. 4) using an unmodified Drude value for the bulk plasmon frequency of ∼8 eV – further detail is given in the response to the earlier question from Giuliana Di Martino. This applies to the zero-bias condition and stands in marked contrast to the vacuum/air gap STM scenario. The screening afforded by the dielectric spacer significantly red-shifts the localised gap modes relative to the vacuum gap case. The presence of a molecular spacer layer also significantly attenuates any dc field induced modification to the Au optical properties. Secondly, to even approach the regime where any noticeable change to the Au properties would be induced by a dc field would require all of the potential applied across the electrochemical cell to drop across the ∼1 nm spacer between nanoparticle and substrate – is that really the case? In summary, we concur that the shifts in plasmon energy observed in paper 14063[3] are due to the response of the molecular spacer layer itself.

Finally, one should also bear in mind that there does not appear to be any explanation of the remarkable red shift of localised plasmon modes in STM arising from considerations of non-locality or quantum plasmonics.

1 C. T. Campbell, S. C. Parker and D. E. Starr, *Science*, 2002, **298**, 811–814.
2 C. T. Campbell and J. R. V. Sellers, *Faraday Discuss.*, 2013, **162**, 9–30.
3 G. Di Martino, V. A. Turek, C. Tserkezis, A. Lombardi, A. Kuhn and J. J. Baumberg, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00130d.
4 R. W. Rendell and D. J. Scalapino, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1981, **24**, 3276–3294.

Javier Aizpurua said: When you describe light emission from a STM cavity, you show how you need non-linear terms to properly describe the spectral features of the emission. The description of the dielectric response of the metal is made in terms of Drude-like functions. Could one not get a good spectral fit of the emission if one used a dielectric function scaled by the interband transitions which would shift the resonances to the red and might provide a good fit? In other words what makes you discard a linear description? On a separate thought, have you tried the reverse process: photon-in instead of photon-out to achieve photo-induced current?

Paul Dawson responded: The backdrop of our work on STM is photon emission examined in the wavelength range above 620 nm (below 2 eV in energy), mostly in the window of 690–1050 nm (1.8–1.18 eV) where the low wavelength, high energy limit is determined by junction stability under ambient conditions and the long wavelength limit by the Si CCD detector. In this spectral range the observed optical properties of Au are well replicated by the Drude model with a bulk plasmon energy of ∼8 eV (8.17 eV in the case of our fit to literature data). The presence of interband transitions coming into play above 2 eV does not influence the behaviour of the metal below 2 eV and in no way serves to somehow scale or compress the localised plasmon energy range. The use of the actual optical data as reported in the literature would make no difference to our analysis – we use a model because it is convenient for modelling. The huge disparity between experimental observation (in STM light emission) and what a purely linear description of the dielectric function predicts was our reason for exploring non-linear contributions.

Our experimental work concerns "electron-in, photon-out"; the modelling presented in Paper 14168[1] addresses "photon-in" and projects to "inelastic photon-out" in terms of plots of the Raman enhancement factor. The reverse effect of photo-induced current change in a tunnel junction has been investigated in terms of photo-induced rectification, which however is not mediated by plasmon excitation. However the effect of photon absorption in inelastic tunnelling would be fundamentally interesting.

1 P. Dawson, D. Frey, V. Kalathingal, R. Mehfuz and J. Mitra, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00128b.

William Lum asked: Do you see longer range coupling/electric fields in the hybrid plasmon waveguide substrates, such as those seen in Fabry–Pérot substrates? If yes, can you comment on using the longer range coupling to probe molecules further away from the metallic surface with SERS (> 10 nm).

Paul Dawson responded: The metallic component in HPWG systems is necessarily present and always in close proximity to the high index dielectric (or semiconductor) in order to achieve the necessary field confinement within the thin, interposed low-index layer in the structure. The only variable, in terms of increasing the distance from the metallic surface, is the thickness of the low-index material where the mode is confined. This could, for example, be increased to 20 nm (the modelling presented in paper 14168[1] assumes a 10 nm low-index "gap" in all cases). However, if you mean by long range coupling that the HPWG mode could be used as a "feed" to a remote SERS active region then I think the answer is "no". But we may expand a little on this as follows:

In the suggested enhanced Raman schemes of Fig. 1d of paper 14168 the Si-based structure represents the usual single-pass amplification feed to the Raman signal (though the great benefit in Raman scattering is that the single pass comprises 2 stages, excitation and scattering, with $|E|^2$ amplification in each stage); this conforms to the usual surface enhanced Raman description. Since the molecular layer of interest is envisaged as being deposited on an end-facet of the structure, the close proximity of the metal surface is a potential "problem" due to the appearance of hot-spots at the corners of the Ag substrate (Fig. 14 of the paper) and the fact that the molecular deposit will be present there also. This is not an issue in the sense that Raman enhancement will still be produced from the hot-spots, but the characteristics of the hot-spots will depend on the detail of the nm-scale geometry of the Ag corners and so could be quite variable. In contrast, the scheme depicted for the GaAs nanorod-based system (Fig. 1d) offers a continuous amplification feed-stage to the Raman signal and could be better described as a thin-film Raman enhancement scheme. Here the molecular layer is located in the middle of the low-index region, isolated from the metal. As noted above the structure could be engineered to have the probe molecules 10 nm or more from the metal interface, but at the expense of decreased field confinement and thus decreased enhancement of the Raman signal.

You mention Fabry–Pérot substrates as a means of effecting longer range coupling to the molecular species. This could be regarded as a Raman enhancement scheme with discrete multi-pass amplification, contrasting in different ways with both schemes shown in Fig. 1d. In the structure described by Vanco *et al.*[2] the

molecules are deposited on a (particulate Ag) mirror surface (the second partially reflecting surface being an Si/Si oxide interface), and so are not remote from the metal. To meet your metal/molecule separation criterion the molecules would have to be deposited in the middle of an odd-order mode FP cavity (*i.e.* with an anti-node in the middle) such as described by Kern *et al.*[3] However, the excitation and emission intensity enhancements in such a scheme are modest (for example, 40 and 3 respectively in ref. 3) and so the Raman enhancement factor would not appear to be competitive with the proposed HPWG scheme.

1 P. Dawson, D. Frey, V. Kalathingal, R. Mehfuz and J. Mitra, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00128b.
2 L. Vanco, M. Kadlečíková, J. Breza, M. Vojs, P. Michniak and M. Marton, *Vib. Spectrosc.*, 2017, **90**, 31–37.
3 A. M. Kern, D. Zhang, M. Brecht, A. I. Chizhik, A. V. Failla, F. Wackenhut and A. J. Meixner, *Chem. Soc. Rev.*, 2014, **43**, 1263–1286.

Ben Hourahine opened a discussion of the paper by George Schatz: I'm curious about the reference density functional choice for these systems, BP86.[1,2] Was there any specific reason for this choice?

This functional is known to outperform hybrid functionals for the ground state properties of systems containing transition metal–carbon bonds (for example ref. 3). However, since both the hybrid and more recent range separated functionals can obey the generalized Koopmans' theorem, they appear much more reliable in the prediction of charge transfer molecular excitations (for example the results and discussion of ref. 4).

1 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
2 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
3 H. Hirato, *J. Phys. Chem. A*, 2011, **115**, 9308–9313.
4 M. Wanko, P. García-Risueño and A. Rubio, *Phys. Status Solidi B*, 2012, **249**, 392–400.

George Schatz replied: We've used BP86 in past studies of silver clusters, as well as functionals that have been optimized for excited state properties, such as SAOP. The plasmon excitation energies are similar for these two choices, but the charge transfer states can vary a lot. In the present study we did not use DFT for excited state properties, so BP86 should be adequate. In past work, Lasse Jensen (Penn State) has studied a broader range of functionals, including range-corrected functionals, but the problems with poor charge transfer energies were not fixed. This was a motivation for our use of INDO in the present work, as this method is known to give accurate charge transfer energies, and also does well for the plasmonic excitations.

Sebastian Schlücker remarked: One important advantage of semi-empirical over DFT approaches is that they are computationally less expensive. What is the largest system size you can currently calculate in a reasonable amount of time? How feasible is the computation of an entire metal nanoparticle with ten thousand atoms? What are most significant additional physical insights you would expect from this approach compared with the system molecule@metal cluster?

George Schatz answered: INDO methods are simpler than DFT so there is an opportunity for using INDO to treat larger clusters than we have done in the past with DFT. Currently the code we have is limited to clusters with less than about

100 atoms, as this code was not developed to take advantage of high performance computers. However with a more scalable code, it should be possible to treat systems with thousands of atoms. This would be very useful, as the most significant quantum size effects arise with clusters of smaller than 1000 atoms. However it should be noted that even with 10000 atoms, we are still dealing with clusters that are significantly smaller than have been studied experimentally, so it is also important to develop "mixed" quantum/classical theories to circumvent this issue. Recent work in Lasse Jensen's group (Penn State) has made important progress in this direction, including studies that describe 10 nm particles. However this approach makes important approximations concerning the treatment of chemical effects, so that challenges remain.

Stephanie Reich asked: I have two questions regarding the chemical enhancement.

(1) Charge transfer may contribute to Raman resonances as dynamic and transient charge transfer. Which type of charge transfer do you address in your calculations?

(2) Please comment on the dependence of chemical enhancement on the distance between the molecule and the metal. How close were the two constituents in your simulation? How close do you think they need to be for chemical enhancement to play an important role?

George Schatz replied: Our INDO calculations should, in principle, include all aspects of charge transfer, at least for the cluster models we are using to describe plasmon excitation. There is static charge transfer between the metal and molecule that influences the static limit Raman intensity (the static chemical effect). In addition, there is charge transfer at optical frequencies that contributes to resonance Raman effects, and also to chemical interface damping. Our calculations can describe the dependence of these effects on the distance between the molecule and the surface (something that is a problem for DFT), but we haven't studied this issue yet. The distance we have used for these calculations is the equilibrium geometry that comes from the DFT calculations, and for pyridine–silver this distance should reflect weak donor–acceptor interactions. At longer distances one expects charge transfer effects to decay exponentially as they are determined by wavefunction overlap. However there are open questions as to what sort of distance dependence can be found as one transitions between physisorption and chemisorption.

Jeremy Baumberg remarked: I like this approach but I am puzzled that the EM enhancement is seen to be lower for the vertex position than the surface face. Aizpurua has shown clearly that one can get field enhancement at a single atom vertex, but you do not seem to see this in your model.

George Schatz replied: What we have found is that excitation of small silver clusters at the plasmon frequency leads to an induced dipole near that center of the cluster. Since the field of a dipole varies as $1/R^3$, molecules at the vertex position are farther away from the dipole and therefore have a smaller field than molecules at the surface position. This behavior is therefore different from what one gets from classical electrodynamics for a large particle, where the vertex

would be an electromagnetic hot spot compared to the surface site. This issue for our modeling appears to be a problem associated with small cluster models, and it points to the need to study larger clusters in order to generate results that are more representative of the nanoparticles that are used in SERS work.

Duncan Graham commented: You've not put any oxygen into this system – is there going to be any silver oxide in this and could/should that be part of the model? What about halide ligands too? We know chloride has a beneficial effect on SERS but that's not well understood. Some speculation on the surface affinity for the target molecule but maybe it's more than this and your modelling could show this?

George Schatz responded: The cluster models that I discussed have the capability of including oxygen, halogens and other species that might influence the SERS intensities but this has not been done so far. However this is an exciting opportunity for this type of theory study, as there have long been questions about the role of these species, both in determining adsorbed molecule densities and in their optical properties.

Heike Arnolds asked: One issue I find is often missing in SERS theory is the collective nature of adsorbed layers. Adsorbates such as pyridine will lower the work function of a coinage metal by up to 3 eV and any excited states will shift with the work function (although not exactly parallel to it). It is also conceivable that the polarizability will change with surface coverage, perhaps due to some shielding or collective effects. Do you see this as an important issue to address or can we neglect coverage, perhaps because hot spots and therefore very small assemblies of molecules overwhelm the signal?

George Schatz answered: The coverage dependence of SERS intensities was studied experimentally long ago by Murray and Bodoff.[1,2] They found that SERS intensities for a cyanide ion on roughened silver maximized as coverage increased, peaking at about half monolayer coverage. They were able to interpret their results in terms of collective interactions of the induced dipoles in the molecules, which results in depolarization for higher coverage. While this was adequate at the time, we now know much more about coverage effects, and the correct situation is probably more complicated, reflecting chemical interactions that are now much better understood. It would be of great interest to revisit this issue with a combination of theory and experiment. The INDO-based theory that my group has developed is capable of studying coverage effects, but so far we have not considered this issue.

1 C. A. Murray and S. Bodoff, *Phys. Rev. Lett.*, 1984, **52**, 2273.
2 C. A. Murray and S. Bodoff, *Phys. Rev. B*, 1985, **32**, 671.

John Lombardi added: This is a worthy question. It is partly addressed in my reply to the earlier question from Jeremy Baumberg. In our work, we always try for less-than-monolayer coverage, in order to mitigate these problems. It is also possible that the collective alignment of the molecules changes when a full monolayer is approached (for example a molecule such as pyridine might lie flat

in low coverage, but align perpendicular to the surface at high coverage). Apparently not everyone is so careful, and I have seen articles in which the SERS spectrum looked suspiciously like a normal Raman solid spectrum. In any case, you are correct in suggesting that this problem be addressed more vigorously in the SERS community, and perhaps reliable experiments can be designed to sort out the difficulties you suggest.

Christian Kuttner communicated: The paper presents data for clusters of 20 atoms. Already nanoparticles of 4 nm in diameter possess roughly 2000 atoms – about 2 orders of magnitude more. Could you comment on the required computational effort and the usefulness of extending such simulations to larger particle sizes?

George Schatz communicated in reply: The small clusters studied in our paper are useful, but there are good reasons to be able to study much larger clusters as well, so we hope we can extend the INDO calculations in future work. In previous work my group showed that the plasmon red-shifts with increasing cluster size due to quantum size effects, so one problem with small clusters is that the plasmon energy is to the blue of what the experimental value is for the nano-particles that are normally used for SERS measurements. Another issue that was addressed in a question from Aizpurua is that the variation in the local field with distance from the cluster is different for small clusters than for larger ones. The sort of calculations we are doing should be extendable to clusters with thousands of atoms, so as noted we should be able to consider clusters of 4 nm or so at the all electron level of theory. Note, however, that most SERS experiments are done with nanoparticles that are 50–100 nm, so doing purely quantum calculations for these is never going to be possible. This means that a class of theory that mixes quantum and classical electrodynamics is also important to consider.

Juan C. Otero communicated: Gieseking, Ratner and Schatz[1] have introduced a new theoretical tool for modeling voltage effects in SERS. Voltage plays a key role in the chemical mechanism and therefore, it is very important to provide reliable theoretical approaches for predicting its effect on the spectra.

It is stated in the article[1] that previous theoretical works studying the effect of the electrode potential on the SERS relative intensities are limited to references 72[2] and 73[3] of the paper, but Tian et al.[4] have also modeled the voltage dependence of the SERS intensities of pyridine by means of cation-modified clusters. In this last case, the discussion is centered on the ground electronic state of the surface complex[4] while ref. 2 and 3 are focused on resonant Raman processes involving excited states of the metal–molecule system with charge transfer character (the CT mechanism).

In ref. 2 (and other related papers) the effect of the voltage on the relative intensities of pyridine and its analogues is modeled by changing the density of charge of linear silver clusters. The obtained results are useful for recognizing the presence of resonant CT processes in a particular spectrum. This same approach has recently been able to account for the unexplained enhancement of mode 9a in the SERS of pyridine recorded at negative electrode potentials.[5] The selective enhancement of mode 9a is not related to any CT process but to the very particular

electronic structure of the metal–molecule complex at a high negative surface excess of charge.

Uniform electric fields are used in turn in ref. 3 for modeling the effect of the electrode potential on silver–pyridine complexes, but the powerfulness of the proposed methodology can not be assessed until the questions raised in a recent Comment[6] have been clarified.

There is another issue related to the dependence of the energies of the metal–molecule surface states on the applied potential. This is an intriguing subject in classical electrochemistry[7] as well as in electrochemical SERS.[8,9] The voltage (E_V/V) modifies the position of the Fermi level of the metal (E_F/eV), and tunes the energies of the metal–molecule CT states (E_{CT}/eV), and therefore controls the presence of resonant CT processes in a particular SERS recorded at a fixed excitation wavelength. Schatz et al.[1] have assumed that a change of 1 V in the applied potential shifts the orbital energies of the metal cluster by 1 eV. As a result, the calculated CT states of the metal–molecule complex are shifted by similar energies of 1 eV, i.e., $e\Delta E_V = \Delta E_F \approx \Delta E_{CT}$. But electrochemical SERS experiments point to a huge effectiveness of the electrode potential in tuning the CT states ($e\Delta E_V \ll \Delta E_{CT}$) amounting to up to 3–4 eV/V.[8,9] The origin of this unexpected energy gain is discussed in ref. 10.

1 R. L. Gieseking, M. A. Ratner and G. C. Schatz, Faraday Discuss., 2017, DOI: 10.1039/c7fd00122c.
2 F. Avila, C. Ruano, I. López-Tocón, J. F. Arenas, J. Soto and J. C. Otero, Chem. Commun., 2011, 47, 4213–4215.
3 M. Mohammadpour, M. H. Khodabandeh, L. Visscher and Z. Jamshidi, Phys. Chem. Chem. Phys., 2017, 19, 7833–27891.
4 S.-Y. Ding, B.-J. Liu, Q.-N. Jiang, D.-Y. Wu, B. Ren, X. Xu and Z.-Q. Tian, Chem. Commun., 2012, 48, 4962–4964.
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6 D. Aranda, J. Román-Pérez, I. López-Tocón, J. Soto, F. Avila and J. C. Otero, Phys. Chem. Chem. Phys., 2017, 19, 27888–27891.
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8 L. Cui, D. W. Wu, A. Wang, B. Ren and Z.-Q. Tian, J. Phys. Chem. C, 2010, 114, 16588–16595.
9 A. Otto, J. Billmann, J. Eickmans, U. Ertürk and C. Pettenkofer, Surf. Sci., 1984, 138, 319–338.
10 J. Román-Pérez, C. Ruano, S. P. Centeno, I. López-Tocón, J. F. Arenas, J. Soto and J. C. Otero, J. Phys. Chem. C, 2014, 118, 2718–2725.

Javier Aizpurua communicated: In your calculation of the optical spectrum of a molecule near metallic clusters, you show little difference when the molecule is attached to a tip-like rather than a flat surface-like structure. We find in our TDDFT calculations of the field induced in such protrusions a strong lightning rod effect which produces a stronger field in tip-like structures (M. Barbry et al.[1]). What would be the local field distribution of the field in your case? Do you think that this lack of difference that you find between tips and surfaces might be due to the presence of the molecule itself or maybe due to the small size of the metallic clusters?

1 M. Barbry, P. Koval, F. Marchesin, R. Esteban, A. G. Borisov, J. Aizpurua and D. Sánchez-Portal, Nano Lett., 2015, 15, 3410–3419.

George Schatz communicated in reply: We think the issue here is with the small size of the cluster used for the SERS modeling. We studied this issue using TDDFT long ago,[1] where we found that small clusters produce Raman enhancements that

are mostly determined by the distance from the center of the cluster, rather than by local shape effects such as the lightning rod effect. This shows why it is important to study larger clusters to provide realistic SERS modeling. We hope to do this for our INDO studies once a more efficient code (currently a work in progress) is available.

1 L. Jensen, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. C*, 2007, **111**, 4756–4764.

Roy Goodacre asked: In his Introductory Lecture[1] Rick highlighted the great growth in the field, as is also highlighted in the introductory material to this meeting, and currently there are approximately 10 papers on SERS published each day.[2]

The Chair of this year's SERS Faraday Discussion suggested in the last SERS Faraday Discussion in 2005 (and it's on the record[3]) that there is no need to have a full understanding of the underlying process for SERS and it's better just to use it. Would you agree that the same sentiment is true today? And how far do you think we are in understanding the actual physical mechanism of SERS, so that SERS of an unknown molecule can be predicted accurately?

1 A.-I. Henry, T. W. Ueltschi, M. O. McAnally and R. P. Van Duyne, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00181a.
2 Based on a search of Web of Science with "TOPIC(surface enhanced Raman)".
3 Prof. Graham stated: "Knowing all the mechanisms of enhancement is not necessary to use SERS in anger". *Faraday Discuss.*, 2006, **132**, 147–158.

George Schatz responded: There are different aspects to this question. First, with respect to the electromagnetic mechanism of SERS, I think we are now comfortable with the idea that accurate electrodynamics calculations can determine enhancements to within a factor of 10 or so provided we know the nanoparticle structures and their dielectric environment. It is very hard to do better than this, as small uncertainties in nanoparticle structure can lead to factor-of-10 variations. However for many applications there is no need to do better. For the chemical effect, the theoretical models are getting developed, but there are important uncertainties in how best to generate results. The chemical effect is smaller than the electromagnetic one, but at this point there are important qualitative issues that need to be settled before we'll have confidence that we aren't making important errors. A third aspect of the theory refers to issues such as cavity quantum electrodynamics where there are serious fundamental questions, and theory/experiment comparisons are fraught we ambiguity. I expect this area to evolve considerably in the next few years.

Paul Dawson added: And where has the "blind" application of SERS got us so far? I suppose the answer is quite a long way in terms of interesting things to do in the research lab, but not so far in terms of routine commercial application. In that regard the key issue is more the precise control of the enhancement component that we do understand well, namely the electromagnetic enhancement. That, in turn, requires very precise control of substrate fabrication that is highly repeatable and very affordable, a combination that has proved remarkably elusive over the years. Hopefully this situation is currently changing.

The main challenge to detailed understanding beyond that of the electromagnetic enhancement appears to lie in the detail of the molecule–substrate

interaction. As a rather general comment, to that end it should be useful to study the enhancement of the same molecular species on metal, dielectric and semi-conducting substrates, provided the electromagnetic component can be "tied down" in each case. Interestingly, the first session, "Theory of SERS enhancement", covered all three scenarios, though not necessarily addressing the molecular interaction in each case.

Christian Kuttner addressed Paul Dawson, George Schatz and John Lombardi: The most commonly applied estimation of the electromagnetic enhancement factor is the $|E_{exc}|^4$ approximation at the excitation wavelength. Alternatively, in some situations it is recommended to evaluate $|E_{exc}|^2 \times |E_{sca}|^2$ at the excitation wavelength and scattering wavelength, respectively. Could you comment on the appropriate use of both approximations, especially for plasmonic nanostructures with hybridized modes?

George Schatz replied: What we find is that $|E_{exc}|^4$ is adequate when one considers isolated particles. $|E_{exc}|^2 \times |E_{sca}|^2$ is always preferred, and will generally give lower enhancement factors, but for isolated particles this is not a major issue. An even better expression would include dipole reradiation effects, which is something that we did in ref. 1 and 2. For dimers and other clusters, dipole reradiation has an important effect on the results.

1 L. K. Ausman and G. C. Schatz, *J. Chem. Phys.*, 2009, **131**, 084708.
2 S. L. Kleinman, B. Sharma, M. G. Blaber, A.-I. Henry, N. Valley, R. G. Freeman, M. J. Natan, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2013, **135**, 301–308.

John Lombardi responded: I believe that the second suggestion (*i.e.* $|E_{exc}|^2 \times |E_{sca}|^2$) is preferable, since it accounts more accurately for the spectral shift of the scattered light from the exciting light. This actually leads in to the problem of the reliability of calculations of enhancement factors. It is known that different lines in each SERS spectrum have different enhancement factors, often wildly different. For example, I posed the problem of what the enhancement factor is for a line that is forbidden in the normal Raman spectrum, and allowed by the SERS (Herzberg–Teller) selection rules (it is infinity, which is unreasonable). This means that even comparisons of enhancement factors within a single SERS spectrum are questionable. This is a problem that should be addressed by the wider SERS community.

Paul Dawson replied: The $|E_{exc}|^4$ approximation is OK provided that there are no strong resonant responses in the enhancement factor (EF) as a function of Raman shift and/or the Raman shift is small. Otherwise this approximation can be seriously in error, so it is always best to use $|E_{exc}|^2 \times |E_{sca}|^2$ if possible. In the context of our paper (number 14168[1]) it would generally be very inaccurate to apply the $|E_{exc}|^4$ approximation in STM-TERS unless the Raman shift is very small, on the scale of $\sim$100 cm^{-1}, but it would be acceptable in HPWG-SERS provided the Raman shift is not very large (refer to Fig. 12 of Paper 14168[1]).

The same principle applies in the case of hybridized modes and Fano modes and so on. In general the magnitude of the electric field should always be evaluated separately at the excitation and scattering wavelengths and the electromagnetic Raman EF evaluated on that basis.

1 P. Dawson, D. Frey, V. Kalathingal, R. Mehfuz and J. Mitra, *Faraday Discuss.*, 2017, DOI: 10.1039/c7fd00128b.

Volker Deckert added: I would agree basically with the previous comment. However, it should be noted that the $|E_{exc}|^4$ is very often used as an estimation and not as a quantitative measure. As such the $|E_{exc}|^4$ expression is a good way to qualitatively estimate enhancement and I do not see too much of a problem if it used in this context. If quantitative data is required one must of course use the exact expression. Particularly when hybridised modes are involved I would not expect that the simple expression yield reliable results.