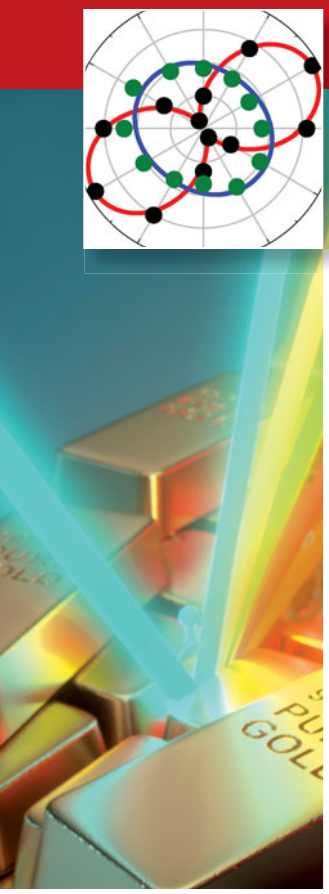


Optical activity in single-molecule surface-enhanced Raman scattering: Role of symmetry

Lev Chuntonov and Gilad Haran

Light emitted by molecules embedded within metal nanoparticle clusters is strongly enhanced by interaction with surface plasmons. This allows, for example, the observation of Raman scattering from individual molecules. The symmetry of the metal cluster may affect the Raman-scattered light by generating new polarization states. This article reviews the use of symmetry theory to analyze the plasmonic normal modes of metal nanoparticle trimers. The lowest bright energy modes are degenerate for an equilateral triangle but split when the symmetry is broken. When a single molecule in the gap between two of the particles emits, it excites the plasmon modes, typically off-resonance, and the ensuing interference between the modes rotates the polarization of the emitted light. This so-called Raman optical activity can generate circularly polarized light at the Raman frequency. This curious phenomenon, which was demonstrated experimentally, may prove useful for future plasmonic devices.

Introduction

The ability to detect surface-enhanced Raman scattering (SERS)[1,2] from single molecules[3–6] located in the vicinity of noble metal plasmonic nanostructures has opened unique opportunities for probing the nanoscale environment and has provided the basis for ultrasensitive diagnostics and nano-optical applications.[7–13] From a basic science point of view, single-molecule SERS (SM-SERS) is an excellent tool for probing local dynamics at metallic surfaces, including phenomena such as charge transfer[14] and surface diffusion.[6,15] The strong electromagnetic field localization required for the observation of SM-SERS is readily achieved when a molecule is adsorbed inside the nanometer gap between closely adjacent nanoparticles, especially when these particles possess a localized plasmon resonance of frequency close to that of the excitation source and the Raman band.[4,16–20]

State-of-the-art strategies for nanoparticle synthesis have rendered possible precise control of nanoparticle size and shape,[21,22] the inter-particle gap, and even molecular binding within the gap.[23] When a gap-bound molecule is excited with the enhanced local electric field at the laser frequency, it is the scattering of its Raman-shifted emission by the localized surface plasmon excitations on the nanoparticles that determines the light characteristics, for example, its directivity and polarization.[24–28] These excitations depend on two factors: The metal dielectric function[29,30] and the way the nanoparticles are arranged.[17,18,31–38] It has been shown that by manipulating these properties, one can build new materials with improved optical characteristics.[39–43]

SM-SERS is a new field of spectroscopy that has developed rapidly in the last decade. Our interest in better understanding the mechanisms behind the interactions of molecules with localized surface plasmons has motivated a series of spectroscopic and theoretical studies that are summarized in this review.[24,44–46] In particular, we examined the relation between the polarization of Raman-scattered light and the plasmon mode structure of nanoparticle clusters, an aspect that has not received much attention.[28] We focused on trimers, which are the smallest nanoparticle clusters that may show Raman optical activity (ROA) (i.e., conversion of linearly polarized light into circularly polarized light at the Raman frequency) in SM-SERS.

We start our discussion with the question of how the plasmon mode structure of nanoparticle trimers depends on their symmetry. We then demonstrate a relation between mode structure and the SM-SERS light polarization using a simple physical model of harmonic oscillators. **Figure 1** shows the main take-home message of this review: When a molecule trapped within a nanoparticle cluster emits light (e.g., Raman scattering), it may excite either one or multiple plasmon

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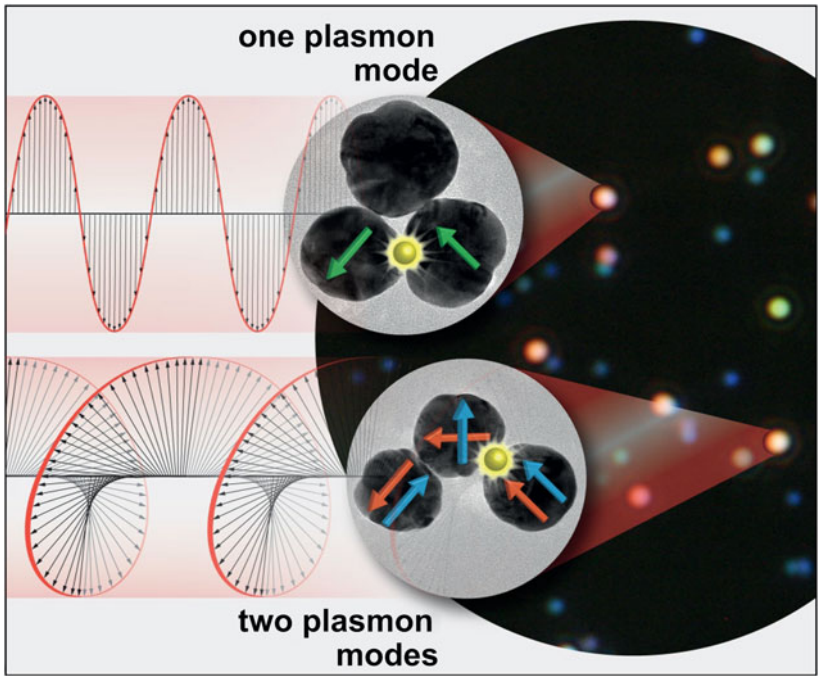


Figure 1. Plasmonic clusters and Raman optical activity. A dark-field image of silver plasmonic nanoparticle clusters is shown on the right; nanoparticle monomers appear in blue and clusters (e.g., trimers), in more orange color as determined by their dominant plasmon resonances. Transmission electron microscope images taken from the same clusters studied optically are also shown (insets). The arrows drawn on the nanoparticles represent excited plasmon normal modes of the clusters. The single-molecule surface-enhanced Raman spectroscopy reporter occupying the interparticle gap is shown in yellow. Upper trimer: only one plasmon mode is excited in a cluster of D_{3h} symmetry, leading to the linear polarization of the emitted light. Lower trimer: two orthogonal plasmon modes are excited in a cluster of C_{2v} symmetry, which generally results in elliptical polarization of the emitted light.

modes, depending on the symmetry of the cluster. In the case of multiple-mode excitation, the interference between modes can lead to elliptical and even circular polarization of the Raman-scattered light in the far field. Understanding the connection between plasmon modes and the characteristics of emitted light may facilitate the design of novel plasmonic devices based on well-defined polarization states of light.

Plasmon mode structure of nanoparticle trimers

The plasmon modes of metal nanoparticle clusters can be studied with single-particle dark-field optical spectroscopy, sometimes called plasmon spectroscopy in the current context.[44] Spectra of single nanoparticle clusters obtained in this manner can be analyzed based on their structural symmetry using symmetry-adapted linear combinations (SALCs) of the individual nanoparticle plasmon modes.[35,45–47] When the symmetry of the cluster is lowered due to the change in its geometry, the irreducible representations of the symmetry group are transformed, as summarized in relevant correlation tables, in a similar way to molecular vibrations.[48,49] However, correlation tables alone provide only information on the symmetry changes and are not sufficient to track the plasmon mode transformation in detail. The explicit shapes and energies of the plasmon modes for arbitrary cluster geometries can be calculated using plasmon hybridization theory.[35–38] For simplicity, here we focus only on the dipolar modes of the multipole expansion. The dipolar model is valid in the long wavelength limit ($ka << 1$, where k is the scattering wave vector, and a is the radius of a nanoparticle), which holds approximately for silver nanoparticles of ca. 50 nm excited with visible light.

Different clusters of three silver nanoparticles are shown in **Figure 2** together with their plasmon scattering spectra, corresponding to two orthogonal orientations of the linearly polarized excitation light: Longitudinal and transverse. In the former orientation, the polarization is parallel to one of the bases of the triangle formed by the nanoparticles, while in the latter, it is perpendicular to this base. The equilateral triangle, which belongs to symmetry point group D_{3h}, possesses two degenerate low-energy plasmon resonances. They correspond to the doubly degenerate irreducible representation of symmetry E′, as dictated by the presence of the rotational subgroup C_3.[48,49] This assignment was made based on the correlation between surface charge distributions calculated numerically for each of the cluster resonances and dipolar SALCs constructed based on the D_{3h} group character table. The corresponding dipolar SALCs, which also agree with the results of plasmon hybridization theory,[38] are illustrated in **Figure 3** (left column). In addition to the degenerate E′ plasmon modes, it is important to consider the ring-like A_2' mode of the D_{3h} trimer. This mode is dark owing to its zero net dipole moment. Nevertheless, when the symmetry of this trimer is broken, it plays an important role in the interaction with light.

The symmetry of the D_{3h} cluster can be broken in several ways, for example, by opening one of the vertex angles of the triangle or by "re-sizing" one of the nanoparticles, such that the resulting clusters have C_{2v} symmetry. Gradual opening of the vertex angle eventually leads to a linear chain of three nanoparticles, while reducing the size of one of the nanoparticles leads to a dimer (linear chain of two nanoparticles). Both linear clusters have $D_{\infty h}$ symmetry. Representative examples of symmetry-broken trimers are shown in Figure 2 together with their plasmon spectra. It is evident from the figure that breaking the symmetry of the trimer lifts the degeneracy of the E′ modes and facilitates the appearance of new peaks in the plasmon spectrum.

Using the group theoretical framework and plasmon hybridization theory, we constructed a correlation table for the

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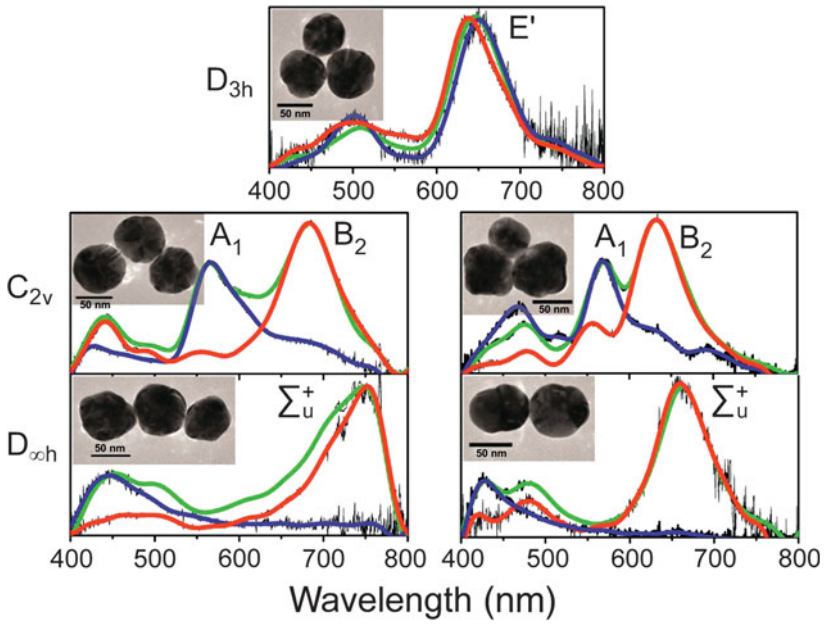


Figure 2. Scattering spectra of silver nanoparticle trimers showing mode splitting due to gradual symmetry breaking. Thin black lines, raw experimental data; color lines, low pass filter applied. The clusters are excited by either nonpolarized light (green) or light linearly polarized along the longitudinal (red) and transverse (blue) directions. The polarized spectra are normalized to the corresponding peaks of the nonpolarized spectra. Plasmon mode symmetries of the bonding modes are marked. Transmission electron microscopy images of the clusters are shown in the insets (scale bars are 50 nm). Adapted with permission from Reference 44. © 2011 American Chemical Society.

plasmon modes in the sequence of shapes, as shown in Figure 3. As the C_3 rotation operation becomes invalid, two new plasmon bands, selectively excited by light linearly polarized along the cluster's longitudinal and transverse directions, appear. As shown in the correlation table, the transverse and longitudinal in-plane E′ modes transform to modes A_1 and B_2 of C_{2v}, respectively, which are symmetric and anti-symmetric with respect to the σ_v reflection plane. The net dipoles of the A_1 and B_2 modes are oriented along the cluster's transverse and longitudinal directions.

As the symmetry breaking further increases, the cluster attains $D_{\infty h}$ symmetry corresponding to a linear chain of nanoparticles. Here, only the single bright bonding mode Σ_u^+ exists, corresponding to a parallel alignment of the individual dipoles. All other modes of the C_{2v} cluster transform to various dark modes (with no net dipole) in the $D_{\infty h}$ limit (see Figure 3). The interchange of the mode dipole moments and the associated energy shifts obtained from hybridization theory are in full agreement, with detailed electromagnetic numerical simulations that were performed for all possible cluster geometries.

Effect of plasmon modes on the polarization of SM-SERS

As we already noted, single molecules can provide valuable information on their immediate environment within the interparticle gaps through their enhanced Raman spectra. SM-SERS is being used to probe an ever-increasing list of nanoscale phenomena, and we cite only a few examples here. Thus, blinking and spectral jumps of single molecules were studied in order to understand molecular diffusion on metallic surfaces[50] and were also correlated with electrical conductance through a molecular junction.[51] Single molecules were also used to probe charge transfer phenomena[14,52] and to study chemical reactions on the nanoscale.[52] Finally, the structure of electromagnetic hot spots was mapped by super-resolution imaging of Raman scattering from individual molecules[53] (see the Introductory and Jokerst et al. articles in this issue).

One important observation that can provide information on the interaction of the electromagnetic field generated by a molecule and the plasmon modes of the cluster on which it resides is the polarization state of Raman-scattered light.[54] We studied SM-SERS from single Rhodamine 6G molecules embedded within nanoparticle clusters.[24] The polarization function of the Raman-scattered light, $\rho(\theta) = \left[I_{\parallel}(\theta) - I_{\perp}(\theta)\right]/\left[I_{\parallel}(\theta) + I_{\perp}(\theta)\right]$, was measured in our lab for different orientations of each cluster in the laboratory frame defined by the angle θ. Here $I_{\parallel}$ and $I_{\perp}$ are two orthogonally polarized intensity components of the SERS spectrum that were measured simultaneously.[24] Note that the emitting molecule, excited within the interparticle gap by the plasmon-enhanced electric field normal to the surface, is the only source of light observed at the Raman-scattered wavelength.[56] Therefore, only the interaction of the Raman emission with the plasmonic cluster affects the polarization of the far-field signal, as can be formally shown.[24]

Consider that a molecule adsorbed within one of the interparticle gaps in a cluster excites the cluster's plasmon modes. Therefore, the far field measured in SM-SERS experiments can be modeled as a superposition of electromagnetic fields emitted by each plasmon mode excited by the molecule. The electric field of light observed at the zenith point can be written simply as a linear combination of complex amplitudes of these modes. Each plasmon mode can be represented as a harmonic oscillator, with the amplitude and phase determined by the resonance frequency, spectral width, and its net dipole moment. To a good approximation, these parameters can be obtained directly from the plasmon spectrum of the cluster. The linear combination of the electric field components includes all possible transverse or longitudinal modes of the cluster.[57]

In general, the interference between excited plasmon modes implies that light emitted by the plasmonic cluster has elliptical polarization even though linearly polarized light

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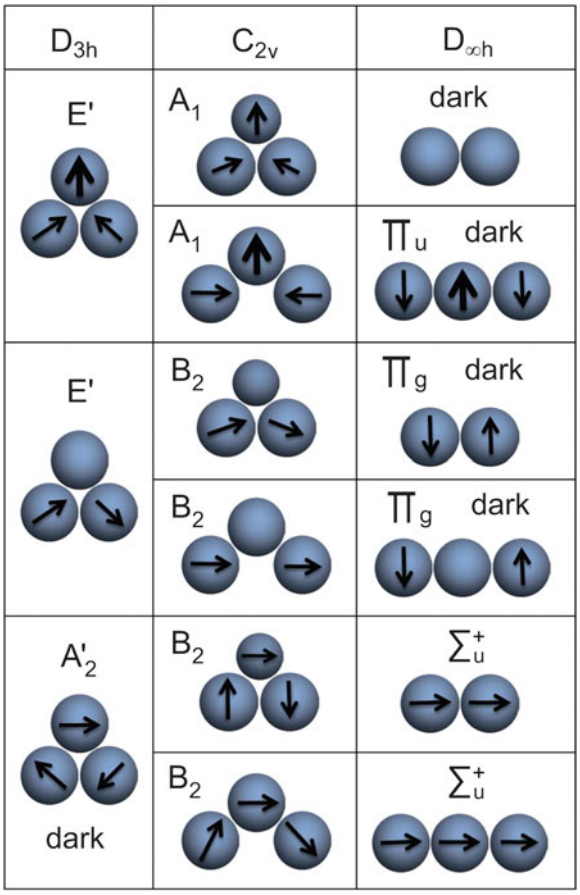


Figure 3. Correlation table of bonding dipolar plasmon eigenmodes of trimers obtained using plasmon hybridization theory. The symbols of the corresponding irreducible representations are shown. Adapted with permission from Reference 45. © 2011 American Chemical Society.

was used for the excitation. This phenomenon is similar to ROA, a well-known phenomenon in molecular spectroscopy.[58] ROA is defined as $\Delta = \frac{I_R - I_L}{I_R + I_L}$, where $I_{R,L}$ is the intensity of the right- (or left-)handed circularly polarized light at the Raman-scattered frequency. It is typically observed in chiral molecules, due to the interference between the molecular polarizability and optical activity tensors, the latter involving both induced electric quadrupole and magnetic dipole moments of the molecule. ROA serves as the basis for an emerging powerful characterization tool for structural biology. However, the effect in chiral molecules is weak, with typical Δ values of several tenths of a percent only.[58,59]

We found that single molecules adsorbed on symmetry-broken trimers such as those described previously show giant ROA, with values as high as the maximal $\Delta = \pm 1$, which corresponds to pure circular polarization at the Raman-scattered wavelength.[57] Notably, the ROA observed in the present case originates from the interaction between the molecular electric dipole and multiple electric dipole resonances of the nanoparticle cluster, as opposed to the case of optical activity observed in bare plasmonic nanostructures that originates from the interaction between electric and magnetic modes.[60–62] No magnetic dipole of the molecule is involved, which is unique to the present effect when compared to Raman optically active chiral molecules.[58]

To understand how such a giant ROA is obtained, consider C_{2v} trimers of the shape shown in **Figure 4**a, with a dipolar emitter (a molecule) residing in one of the interparticle gaps, marked by an arrow.[57] The two possible geometries shown in the figure are related to each other as mirror images, and therefore serve as an example for a plane-chiral pair.[63,64] One of the structures will convert linear polarization preferentially into right-handed circular polarization and will therefore be called dextrorotatory (*d*), while the other will generate left-handed circular polarization (levorotatory, *l*). This behavior arises from the interference between the two plasmon normal modes of A_1 and B_2 symmetry excited by the emitting molecule, as shown in the numerically simulated emission spectrum in Figure 4b. At around 650 nm, the electric fields emitted by the cluster along two perpendicular axes are equal in amplitude and in quadrature phase. This corresponds to purely circularly polarized light, with values of $\Delta = +1$ and -1 obtained for the *d* and *l* clusters, respectively. Modeling the cluster emission using two harmonic oscillators (whose parameters are found from fitting the spectral resonances of the cluster's emission spectrum in Figure 4b to Lorentzian line shapes), we calculated the ROA and found it to be in very good agreement with the numerical results, as compared in Figure 4c.[57] This approach can be readily generalized for multiple plasmon resonances.

We also tested the harmonic oscillator model of plasmonic ROA by analysis of experimental SM-SERS results reported in Reference 24. As an example, we show an SEM image of a cluster in **Figure 5**a. The parameters of the harmonic oscillators used in the model were obtained from a fit to the simulated emission spectrum shown in Figure 5b. The experimentally measured $\rho(\theta)$ is shown in Figure 5c for two specific choices of wavelength in black and green dots. While the pattern measured at 555 nm (black) shows that the polarization is very close to linear, the polarization at 583 nm (green) is essentially circular. The ROA values calculated from the experimental data are plotted for several wavelengths in Figure 5d as red dots. The ROA spectrum calculated by electromagnetic simulation (black line) and the harmonic oscillator model results (blue line) are in a very good agreement with the experimental data. While for excitation at 550 nm, one plasmon resonance clearly dominates the spectrum and results in an almost linear polarization of the scattered light; for excitation at 583 nm, the contributions of both resonances are of the same magnitude, and their spectral distance from the excitation results in amplitudes and phases of the electric field components corresponding to circularly polarized scattered light.

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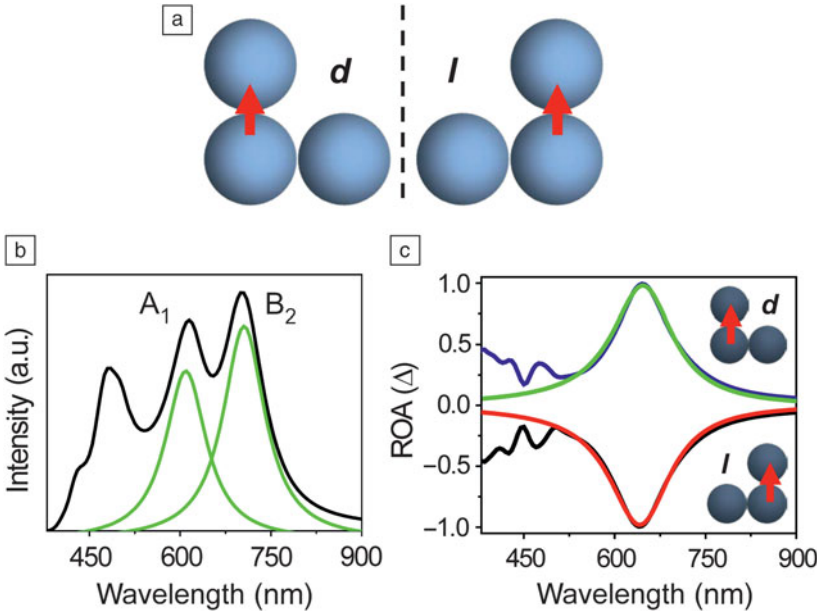


Figure 4. Raman optical activity (ROA) in a silver trimer of C_{2v} symmetry. (a) Two plane-chiral configurations of the cluster, related by mirror symmetry and corresponding to dextrorotatory (*d*) and levorotatory (*l*) behavior (see text). Molecular dipoles residing within the interparticle gaps are depicted by the red arrows. (b) Plasmon spectrum of the trimer in either configuration, with the symmetries of the excited plasmon modes marked. Green lines show Lorentzian fits of the spectral peaks. (c) ROA of the *d* and *l* configurations. Black and blue lines, electromagnetic simulation; red and green lines, harmonic oscillator model. Adapted with permission from Reference 56. © 2013 American Chemical Society.

Conclusions

The symmetry of a noble metal nanoparticle cluster defines the shapes and general structure of its plasmon normal modes, which, along with the metallic dielectric function, define the cluster's optical response. Raman light emitted by a molecule trapped within the interparticle gap of the plasmonic cluster is shaped by the interaction with the plasmon modes. In this review, we have shown how plasmon modes of small clusters can be studied and analyzed using concepts from the theory of symmetry. This analysis helps in explaining the formation of these modes, their evolution with changes in cluster geometry, and the impact they have on the properties of SM-SERS light. The broad spectrum of analytical tools used in the present study, including group theoretical analysis, plasmon hybridization theory, full electrodynamic simulations, and harmonic oscillator models, enabled an in-depth understanding of the physical systems studied here. Although we have discussed clusters of three nanoparticles, this approach can, in principle, be applied to more complex clusters. However, increasing the number of nanoparticles in a cluster leads to a more complex plasmon mode structure and congested plasmon spectra, and will therefore make the application of harmonic oscillator models more difficult, requiring detailed case-specific analysis.

The importance of the novel insights gained from this study is twofold. First, the availability of a simple model of molecule-cluster interaction, based on the concept of plasmon modes and their interference, will substantially assist the correct interpretation of SM-SERS experiments. Second, the present approach paves the way for designing future subwavelength devices, in which control over light characteristics will be crucial for the efficient coupling of electromagnetic fields into plasmon modes and back.

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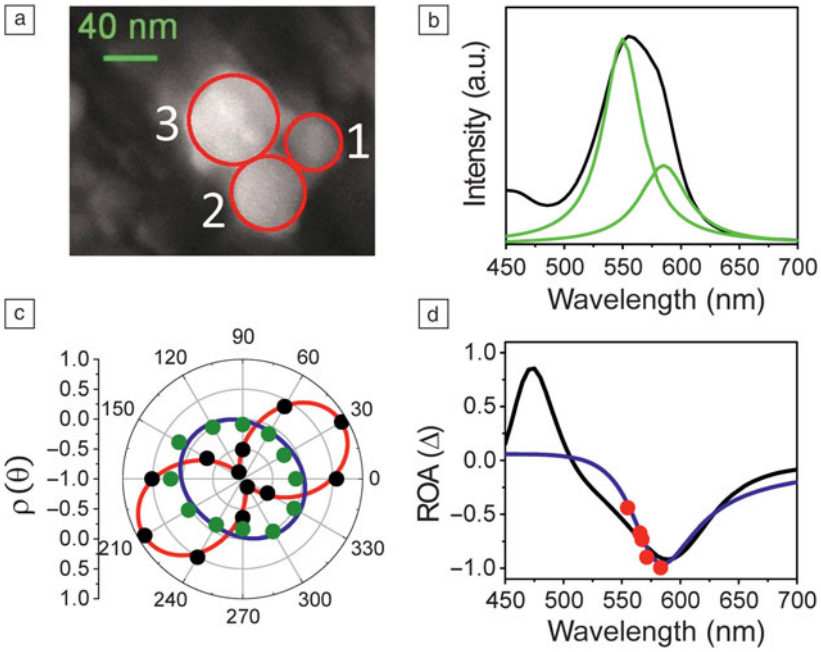


Figure 5. Experimental observation of the effect of a symmetry broken trimer on the polarization of surface-enhanced Raman spectroscopy from a single molecule. (a) Scanning electron microscopy image of a silver trimer on which a single Rhodamine 6G molecule was adsorbed. Our calculations show that the molecule resided in the gap between particles 1 and 2. (b) Simulated emission spectrum (black) using nanoparticle dimensions and gap sizes estimated from the image (see text). (c) Experimental polarization functions $\rho(\theta)$ of the Raman-scattered light measured at 555 nm (black dots) and 583 nm (green dots). Red and blue lines show a fit. (d) Raman optical activity (ROA) calculated from the experimental data (red dots), from the electromagnetic simulation (black line), and from the harmonic oscillator model (blue line). Adapted with permission from Reference 56. © 2013 American Chemical Society.

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University Chapters

The Materials Research Society® (MRS) University Chapter Program is a passionate and talented network of students from universities around the world. Supported by the Materials Research Society Foundation, the program fosters an environment for collaboration and open exchange of ideas across all scientific disciplines, spanning campuses and continents. These students represent the next generation of materials research and are preparing to carry the torch forward, advancing materials and improving the quality of life.

You'll find starting an MRS University Chapter is a fun and exceptionally valuable experience. Working through your Chapter—hosting events, creating special projects and connecting with experts from around the world—will prepare you for future professional and leadership roles in the materials community. Your Chapter can also play a vital role in bringing science to a broader audience. Now more than ever, the goal is to successfully bring research out of the laboratory and into the classroom and to the general public … to show how materials have changed our history and continue to shape our future.

MRS continues to explore new ways to effectively foster growth of virtual global materials communities, using emerging technologies that are smart, fresh and innovative … and that includes our University Chapters. With social media, MRS OnDemand® and two-way live streaming, we're already tapping into today's technologies to engage Chapters unable to attend our Meetings, but with the promise of new innovations, tools and devices, we continue to look ahead. **Help us build the Chapter of the Future!** Together we can design and develop virtual events to better collaborate, educate, participate and fascinate—across Chapters, across disciplines, across borders.

Now's the time to use your excitement, expertise and unique scientific perspectives to forge a new path. Join this international student community.

Start an MRS University Chapter today!

MATERIALS RESEARCH SOCIETY FOUNDATION

HELP US BUILD THE FUTURE

An International Community

One of the main objectives as graduate students and future researchers is to acquire the ability to build scientific networks for enhancing our vision, mission and scientific cooperation. MRS offers multiple tools to accomplish this with annual meetings, workshops, the MRS Bulletin and useful applications such as career connections or MRS OnDemand. Our MRS Student Chapter allowed us to obtain support from the Sociedad Mexicana de Materiales (SMM) that expands our national network. The formation of MRS Cinvestav Student Chapter not only allows us to integrate and exchange ideas as materials science students at Cinvestav, but also have the opportunity to know the science beyond our borders.

Natalia Tapia, Chapter President
Centro de Investigación y de Estudios Avanzados
del Instituto Politécnico Nacional (Cinvestav-IPN)
Mexico City, MEXICO

Interdisciplinary Collaboration

The MRS Student Chapter at WSU was organized by students who recognized the need to bring together a diverse group of students who were working in materials science. The campus is spread out geographically and students pursuing PhD degrees in MSE can be advised by chemistry or physics professors who are located far from the MSE department located in the engineering buildings. There is no distinction made between students whose advisors are in different departments or colleges, and the MRS student Chapter has been a great vehicle to promote unity within the disciplines here.

David Field, Chapter Faculty Advisor
Washington State University
Pullman, Washington, USA

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The MRS University Chapter Experience

The MRS University Chapter Program provides invaluable experiences and benefits for student members, but don't take our word for it. **Our Chapter Members Say It Best!**

Leadership Development

The Materials Research Society, along with our local Binghamton University Chapter, has positively influenced my commitment to materials science and technology. We were inspired by our advisor, Professor M. Stanley Whittingham, to start this Chapter … and motivated by his enthusiasm and our faith to bring science to the general public, we continue to hold numerous events taken from MRS, i.e. MAKING STUFF and NanoDays. As our organization grows, we keep growing our events, and have found a solid and welcoming place in our community. Apart from the target audience, our events also benefit the volunteers, who gained valuable experience both from preparation, interaction, and activities. We feel proud and grateful to be part of an MRS University Chapter.

Tianchan Jiang, Chapter President
Binghamton University
Binghamton, New York, USA

Education Outreach

Our Chapter has enabled us to establish collaborations among the scientists on campus through informal social events, in addition to providing opportunities to participate in outreach. Integrating the science outreach efforts of Vanderbilt's community into our local community is one of our primary goals. As a University Chapter, we received a grant through the Materials Research Society Foundation to bring emerging materials science and hands-on activities to disadvantaged students and teachers in rural Tennessee. Without these seed funds, our Vanderbilt program, Materials Outreach for Rural Education (MORE), would not have been possible.

Amy Ng, Chapter President
Vanderbilt/Fisk Universities
Nashville, Tennessee, USA

Professional Growth

Starting and advising an MRS University Chapter is truly a rewarding experience. One can see professional growth of students, who start feeling like members of the worldwide materials research community. I come to MRS meetings with a "team," not just a couple of my students. Exciting initiatives and project ideas generated by students are amazing. Not surprisingly, some of the most prominent materials scientists, such as Millie Dresselhaus (MIT) or Stan Whittingham (SUNY Binghamton), have been acting as Faculty Advisors for many years.

Yury Gogotsi, Chapter Faculty Advisor
Drexel University
Philadelphia, Pennsylvania, USA

Building Chapters of the Future

I had the chance to present at the 2012 MRS Fall Meeting's Sustainability Forum, while being over 9000 km away from the meeting venue. I felt as if I was actually in Boston, being able to take questions, address them and getting into discussions with the committee. Thanks to the Materials Research Society and our local MRS-KAUST University Chapter for making this possible.

Ahmed E. Mansour, Chapter Vice President
King Abdulla University of Science and Technology (KAUST)
Thuwal, SAUDI ARABIA

Chapter Support

As a graduate student, it is key to broaden your spectrum of what is taking place in the research world in real time. MRS opens up many avenues, especially when working from a University Chapter. Direct contact with MRS associates helps keep everyone abreast on conferences, Chapter opportunities and activities that otherwise may not have been as easily accessible. MRS also rewards student memberships with rebates and travel expenditures, helping promote student involvement as well as Chapter building. We were able to host a multitude of meetings and seminars as well as send students to attend MRS conferences to promote their research.

Chinedu Okoro, Chapter President
Tuskegee University
Tuskegee, Alabama, USA

FOR MORE INFORMATION

on the MRS University Chapters Program,
visit **www.mrs.org/university-chapters**

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