Supplementary Material (ESI) for Nanoscale

Electronic Supplementary Information

Determining Molecular Orientation via Single Molecule SERS in a Plasmonic Nano-gap

Addison R L Marshall,[a] Jamie Stokes,[a] Francesco. N. Viscomi,[a] John E. Proctor,[a,b] Johannes Gierschner,[c] Jean-Sebastien Bouillard,*[a,d,e] and Ali M Adawi *[a,d]

[a] School of Mathematics and Physical Sciences, Department of Physics and Mathematics, University of Hull, Cottingham road, HU6 7RX, UK

[b] Materials and Physics Research Group, School of Computing, Science and Engineering, University of Salford, Manchester M5 4WT, United Kingdom

[c] Madrid Institute for Advanced Studies - IMDEA Nanoscience, Calle Faraday 9, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain

[d] G. W. Gray Centre for Advanced Materials, University of Hull, Cottingham road, HU6 7RX, UK

[e] Department of Physics, King's College London, Strand, London, WC2R 2LS
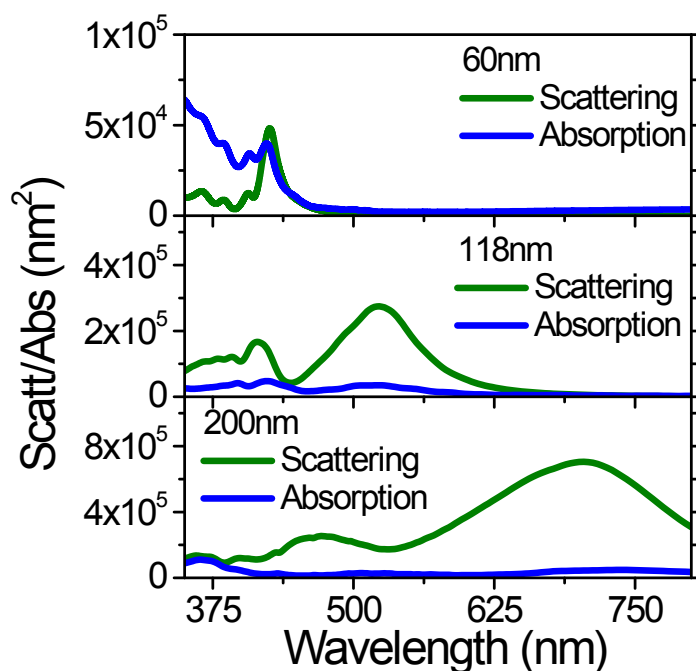
*a.adawi@hull.ac.uk and j.bouillard@hull.ac.uk

Figure S1: The calculated scattering and absorption cross section spectra vs. wavelength for a 5 nm nano-gap width for different particle sizes.
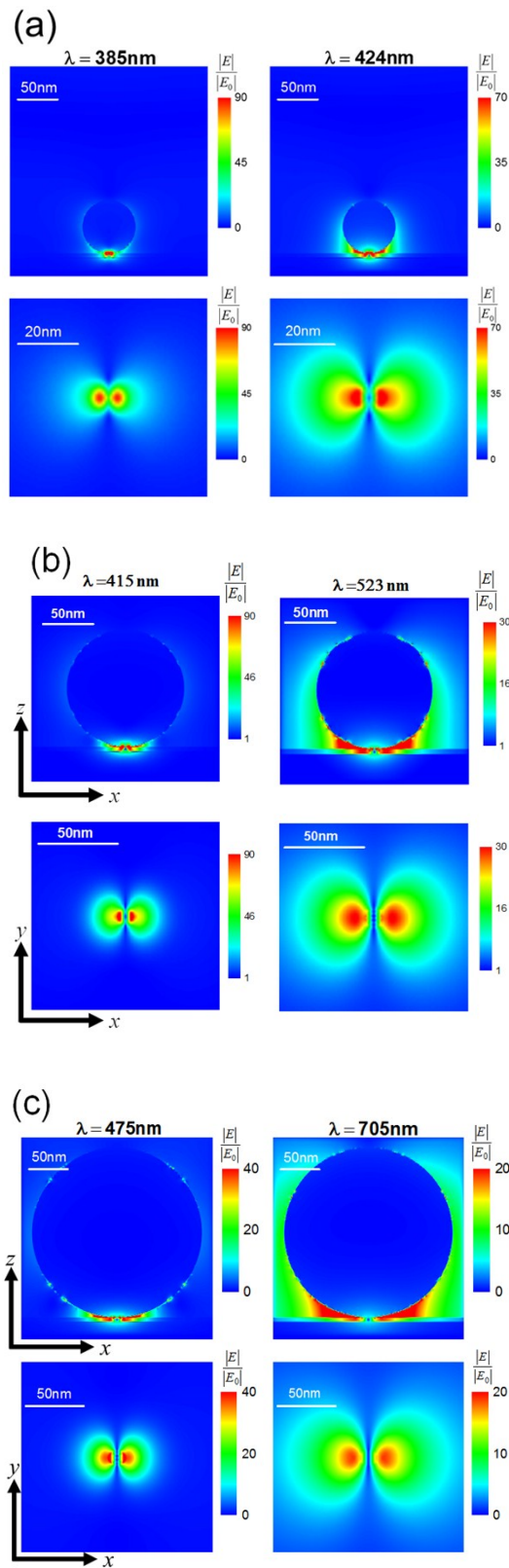
Figure S2: The calculated field enhancements associated with a 5 nm nano-gap using a particle size of 60 nm (a) 118 nm (b) and 200 nm (b) and a 100 nm extended silver film. The x-y field enhancements were taken from the centre of the nano-gap.
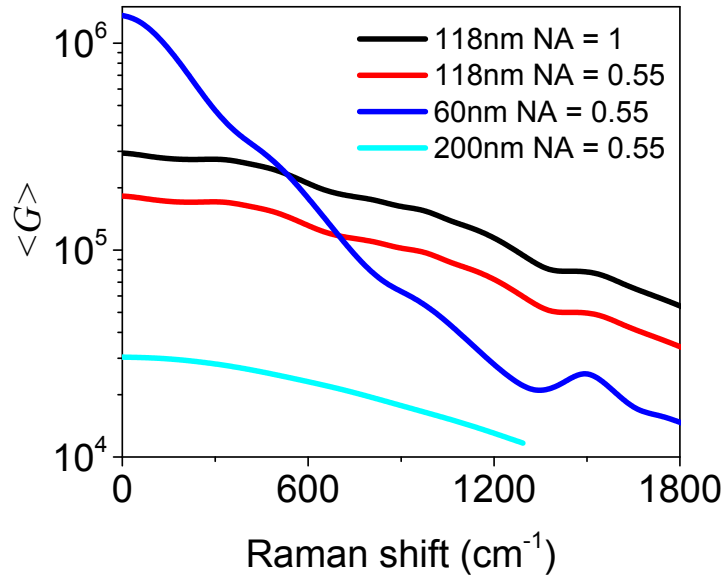
Figure S3: The calculated effective figure of merit $\langle G(\lambda) \rangle$ for a 5 nm nano-gap of different particle size 60 nm, 118 nm and 200 nm as a function of Raman shift. In each case the Raman shift is calculated relative to the nano-gap wavelength peak maximum.
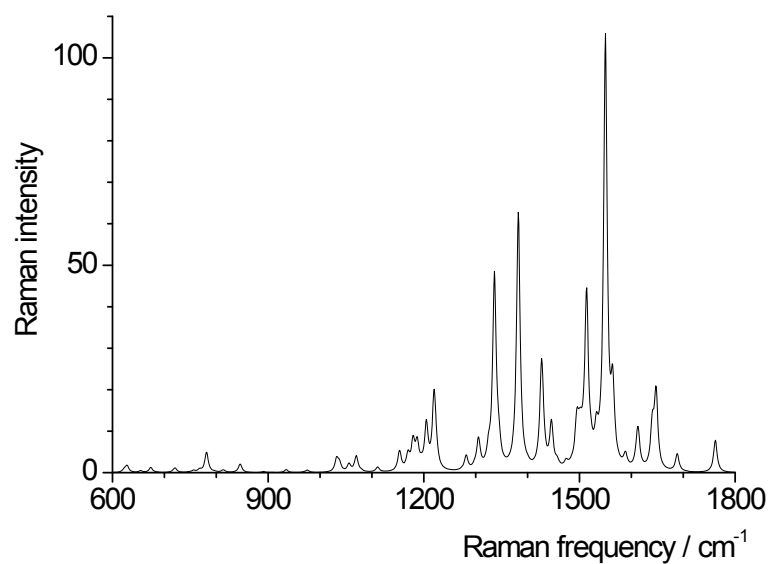
Figure S4: DFT-calculated Raman spectrum under off resonant condition.

628 cm^{-1} 781 cm^{-1}
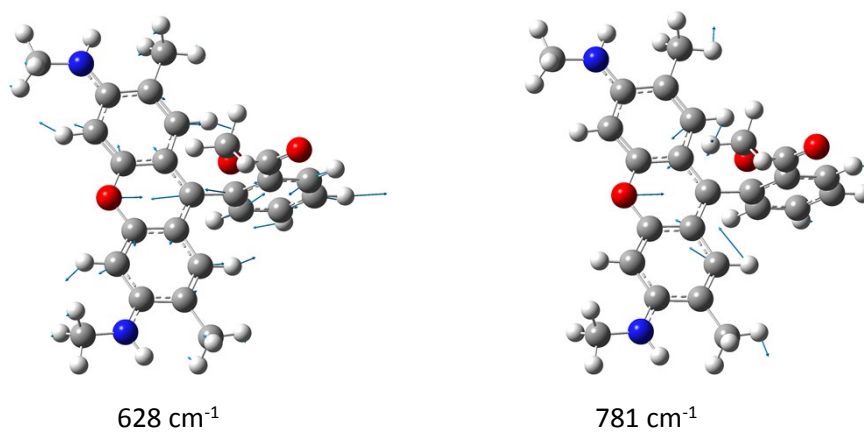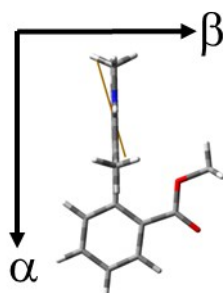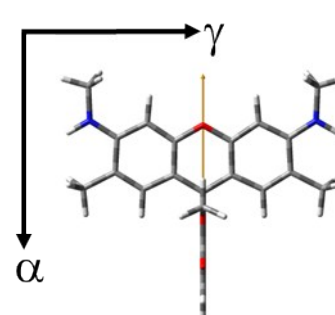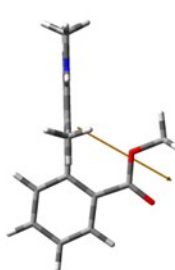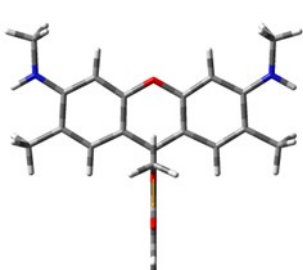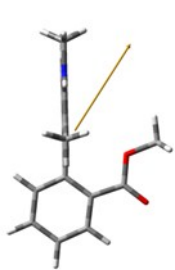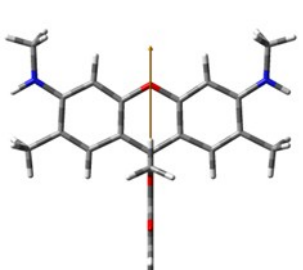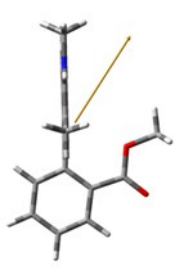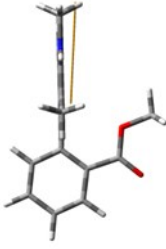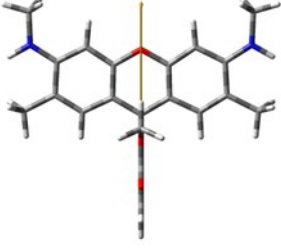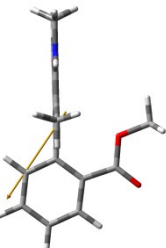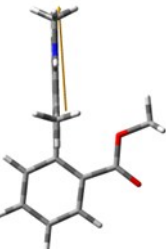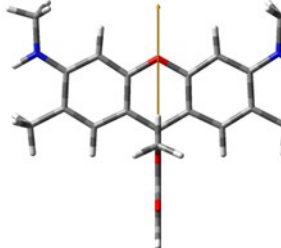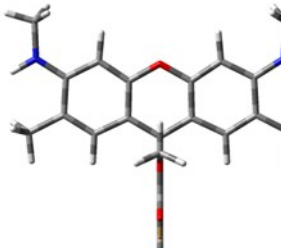
Figure S5: Calculated atomic displacements for selected modes

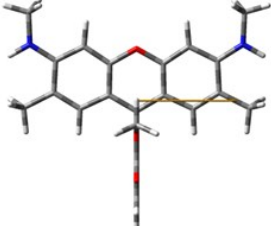| Table S1: dipole moment direction for the measured Raman modes in Figure 5.			
Measured Frequency (cm^{-1})	Calculated Frequency (cm^{-1})	Dipole moment in $\alpha-\beta$ plane	Dipole moment in $\alpha-\gamma$ plane
621	628		
778	781		
1193	1205		
1237	1220		

1318	1336		
1367	1382		
1427	1427		
1511	1514		
1583	1550		

1652	1647		