iSOCS Short Course Winter 2023

16 - 19 January 2023 – Bormio, Italy

ENVIRONMENTAL GAS & ODOUR SENSING

in collaboration with EU project

SENSOFT

Develop your knowledge of environmental gas & odour sensing at the ISOCS Short Course in Bormio, Italy

This Short Course will cover topics including:

- Environmental odour monitoring
- Environmental data analysis and processing
- Advanced applications with drones
- Trace detection of air pollutants
- Wireless gas sensing networks
- Sensor calibration techniques

Speakers including:

- Prof. Saverio De Vito, ENEA; President ISOCS
- Prof. Laura Capelli, Politecnico di Milano
- Prof. Agustin Gutierrez Galvez, University of Barcelona
- Prof. Eduard Llobet Valero, Universitat Rovira I Virgili
- Prof. Achim J. Lilienthal, Örebro University
- Dr. Jan Mitrovics, JLM Innovation GmbH, Germany

SENSOFT: Smart Sensing for Rapid Response to chemical threats on soft targets

http://deeea.urv.cat/sensoft/

SENSOFT-VOGAS- ISOCS Meeting See (Austria), 27-30 Jan 2020
From nanomaterials for sensing and preconcentration to trace lecel detection applications

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Universidad Zaragoza

INMA
INSTITUTO DE NANOCIENCIA Y MATERIALES DE ARAGÓN

SERS for Sensing in Gas Phase

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Universidad Zaragoza
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INMA
Instituto de Nanociencia y Materiales de Aragón

SERS stands for...

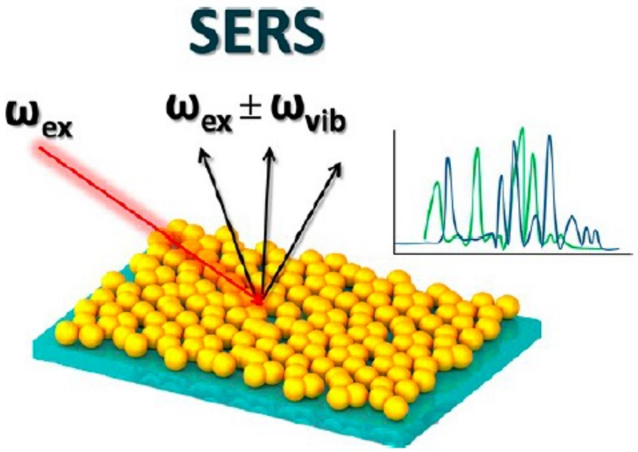
1. Ship Emergency Response Service

2. State Employees' Retirement System

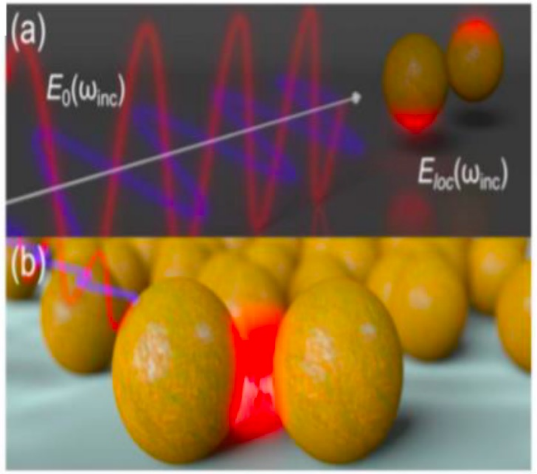
3. Software Engineering Release System

4. ?

- Absorption
- Vibrational Excitation
- Re-emission



ACS Nano 2020, 14, 28–117



OUTLINE

1. Chemical Sensing & Scenario Driven Requirements

2. SERS Fundamentals
   - Spectroscopy & Raman Spectroscopy
   - Surface Enhanced Raman Spectroscopy: SERS Effect & substrates
   - Measuring SERS
   - Portable Instrumentation
   - Application Fields

3. SERS for Gas Sensing
   - Challenges & Strategies
   - Our Approach
   - Future Work

4. Take-Home Messages

1. Chemical Sensing & Scenario Driven Applications

Security and Public Safety

providing real-time monitoring and early detection

Healthcare and Life Science

helping to diagnose and access general health

Home Sensing and Automation

providing safety and security within your home

Reliability

Robustness

Selectivity

KPIs

Ultra sensitivity

Response time

Portability

Cost

User friendly

Agriculture

providing valuable information throughout the growth cycle

Manufacturing

providing consistency within manufacturing

Industrial

providing optimization, monitoring and environmental compliance

Personal Health

monitor exercise, sleep, and health information

Social Challenge: Secure Societies & Chemical Threats

Smart **Sens**ing for Rapid Response to chemical threats on **soft** targets (SENSOFT)
Exploiting Surface Enhanced Raman Spectroscopy (**SERS**) and Advanced Algorithms For Guidi**ng** Responses to Potential Chemical Threats (SERSING)

… From Odours to CWAs* & TICs

**A Clear Example…Nerve Agents (NAs) Detection*

SERSing Sensoft

This work has received funding from the *European Union's Horizon 2020 research and innovation programme* under grant agreements N° 823895 & N° 883390.

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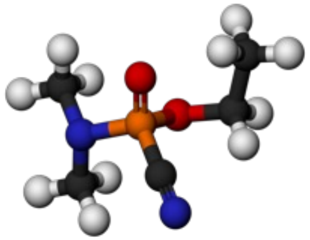
*A Clear Example…Nerve Agents (NAs) Detection**



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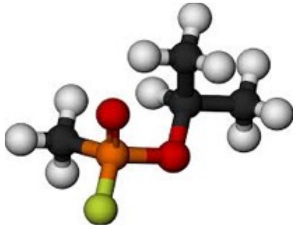
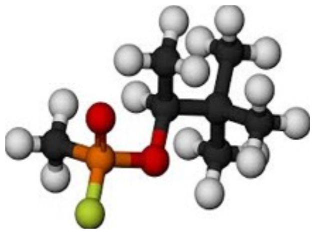
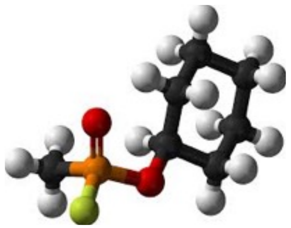


SARIN



Soman



Cyclosarin

Phosphorous P
Nitrogen N
Fluorine F
Oxygen O
Carbon C
Hydrogen H

	Tabun	Sarin	Soman	Cyclosarin
NATO designation	GA	GB	GD	GF
Chemical formula	$C_5H_{11}N_2O_2P$	$C_4H_{10}FO_2P$	$C_7H_{16}FO_2P$	$C_7H_{14}FO_2P$
Appearance	Colorless to brown liquid	Colorless liquid	Colorless liquid	Colorless liquid
Odor	None	None	Fruity	None
Vapor density *(relative to air)*	5.6	4.9	6.3	6.2
Vapor pressure (@ 20ºC)	**5 Pa**	**280 Pa**	**53 Pa**	**6 Pa**

Data extracted from www.epa.gov

****Common Surrogate: DMMP Dimethyl methyl phosphonate CAS Number**: 756-79-6*

Social Challenge: Secure Societies & Chemical Threats

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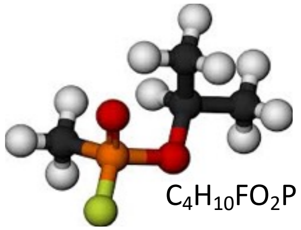
Exploiting Surface Enhanced Raman Spectroscopy (**SERS**) and Advanced Algorithms For Guid**ing** Responses to Potential Chemical Threats (SERSING)



SARIN

- Accute toxicity.......................SHORT RESPONSE TIME
- Reliable response..............LOW FALSE ALARM RATE
- **Trace** detection.............SENSITIVITY @ ppt-ppb level
- Presence of **interferences**...................ON FIELD USE

	Effect	SARIN exposure time				
		10 min	30 min	60 min	240 min	480 min
Discomfort	AEGL-1 *Nondisabling*	1.2 ppb *(6.9 µg/m³)*	0.68 ppb *(4.0 µg/m³)*	0.48 ppb *(2.8 µg/m³)*	0.24 ppb *(1.4 µg/m³)*	0.17 ppb *(1.0 µg/m³)*
Impaired ability to escape	AEGL-2 *Disabling*	15 ppb *(87 µg/m³)*	8.5 ppb *(50 µg/m³)*	6.0 ppb *(35 µg/m³)*	2.9 ppb *(17 µg/m³)*	2.2 ppb *(13 µg/m³)*
Life-threatening Effects	**AEGL-3** ***Lethal***	**64 ppb** ***(380 µg/m³)***	32 ppb *(190 µg/m³)*	22 ppb *(130 µg/m³)*	12 ppb *(70 µg/m³)*	8.7 ppb *(51 µg/m³)*

AEGL: Acute Exposure Guideline Levels

Data extracted from www.epa.gov

**Common NA Surrogate: DMMP Dimethyl methyl phosphonate CAS Number: 756-79-6*

Sensoft SERSing

Social Challenge: Secure Societies & Chemical Threats

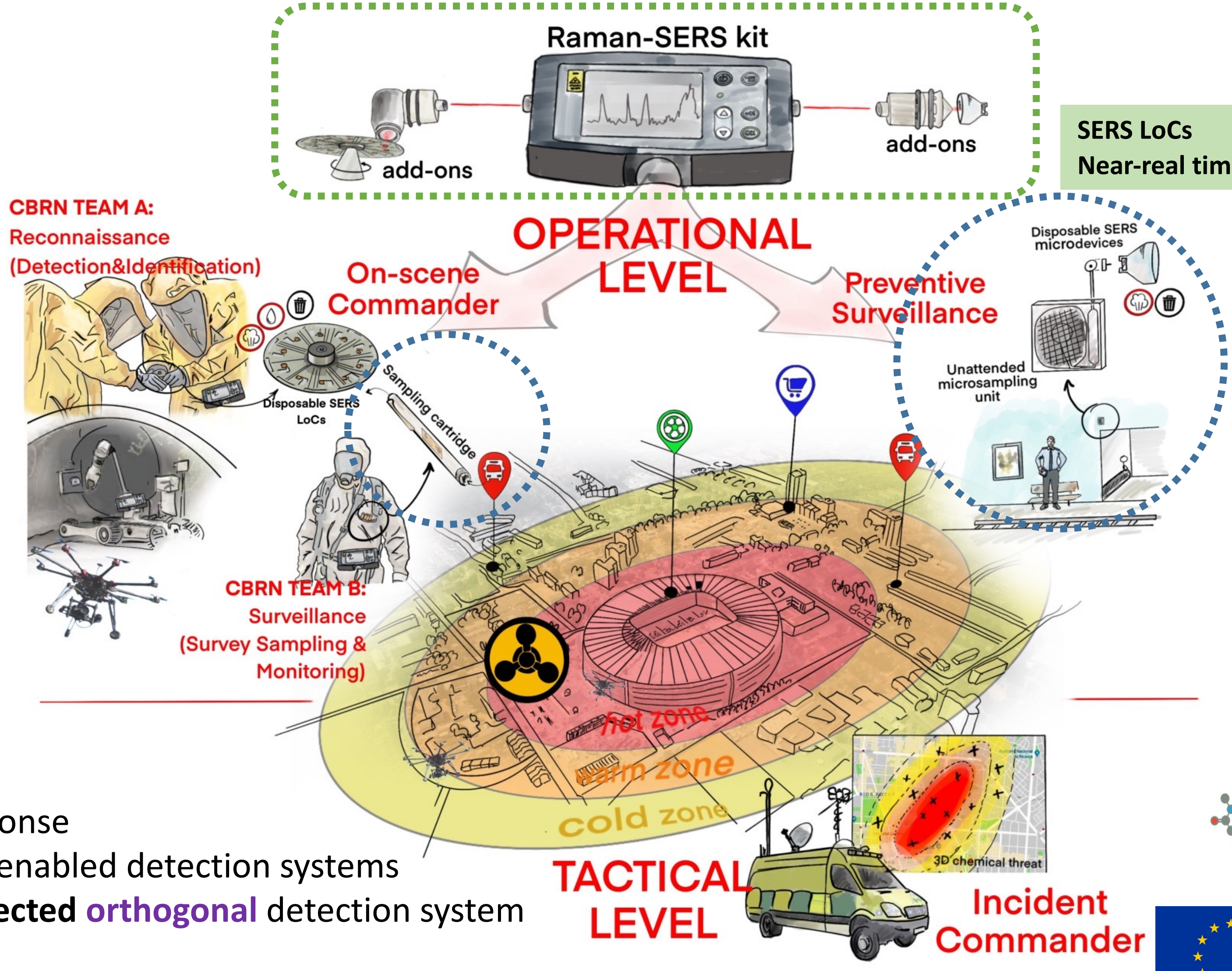
Smart **Sens**ing for Rapid Response to chemical threats on **soft** targets (SENSOFT)
Exploiting Surface Enhanced Raman Spectroscopy (**SERS**) and Advanced Algorithms For Guid**ing** Responses to Potential Chemical Threats (SERSING)

International Forum to Advance
FIRST RESPONDER INNOVATION

Lack of **miniature**, **fieldable** and **affordable** tools and systems for **detection**, **identification** and **monitoring (DIM)** of **Chemical Threats (AEGLs @ ppb level)**

Social Challenge: Secure Societies & Chemical Threats

Smart **Sens**ing for Rapid Response to chemical threats on **soft** targets (SENSOFT)
Exploiting Surface Enhanced Raman Spectroscopy (**SERS**) and Advanced Algorithms For Guid**ing** Responses to Potential Chemical Threats (SERSING)



SERS LoCs
Near-real time or on-demand DIM

Unattended Microsampling Units
Sampling Cartridges

- **fast** and **reliable** response
- **early warming** nano-enabled detection systems
- **pervasive, interconnected orthogonal** detection system

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   - Our Approach
   - Main Results

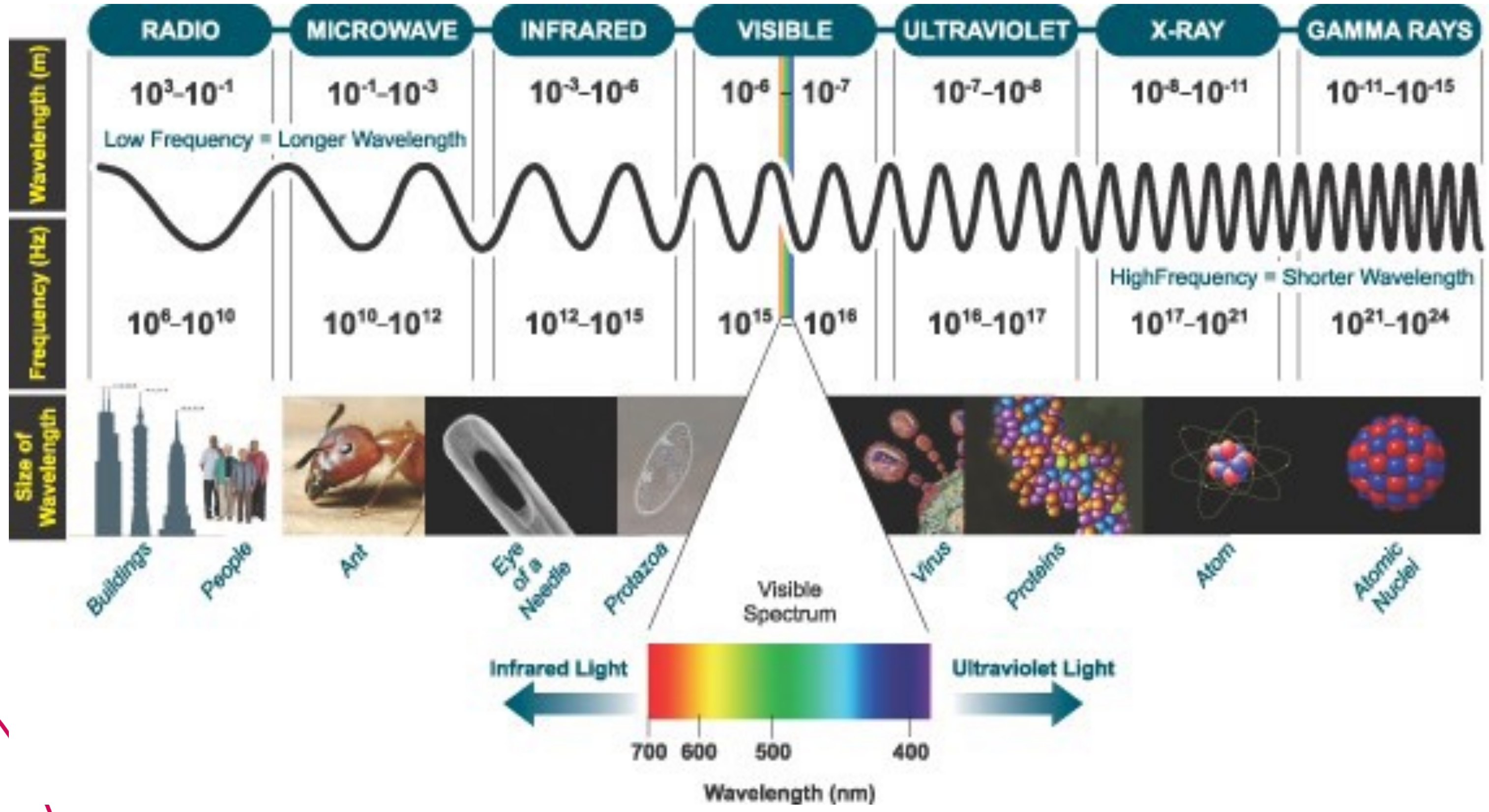
4. Take-Home Messages

2. SERS Fundamentals

INMA

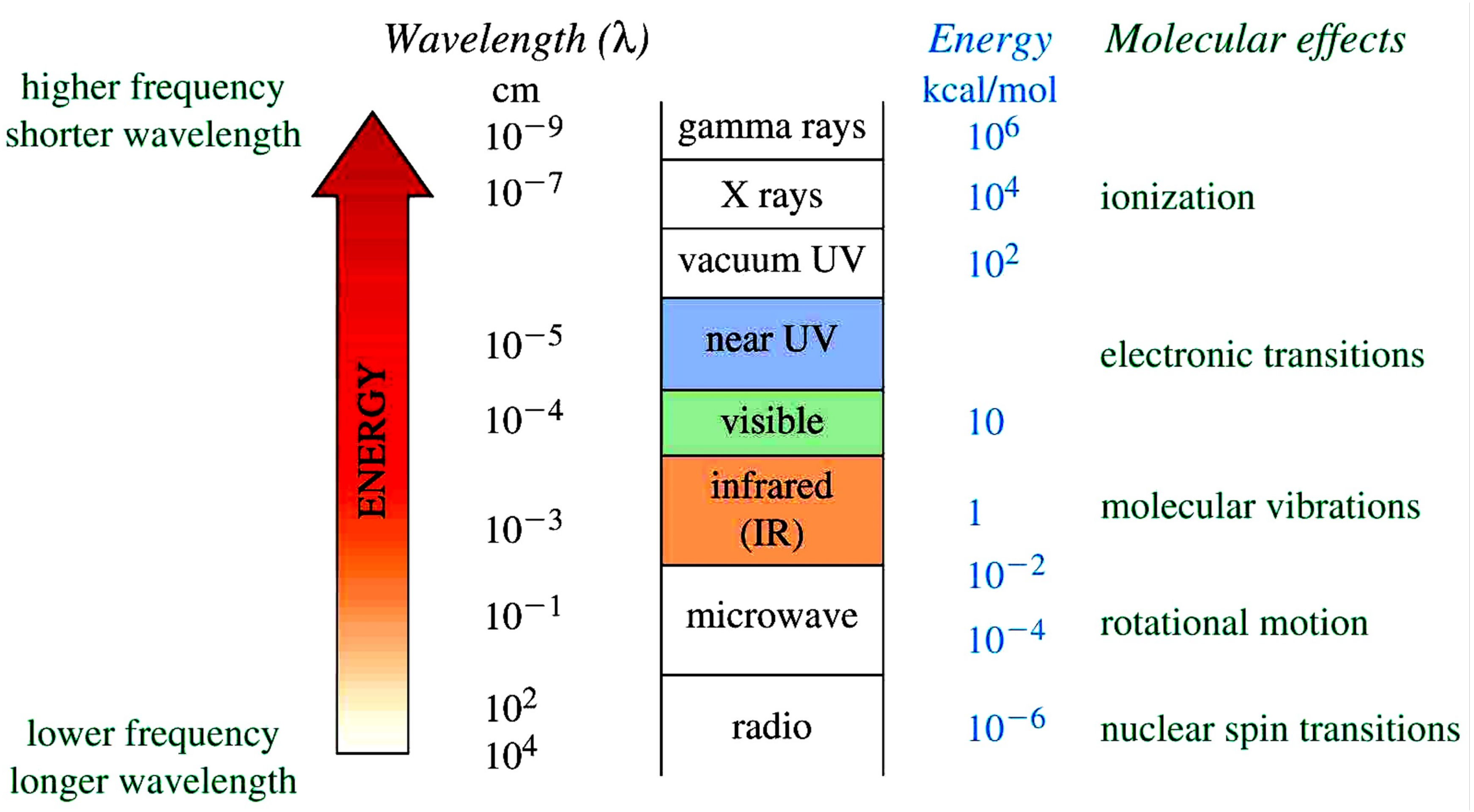
SPECTROSCOPY DEFINITION

It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.



2. SERS Fundamentals

EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES



Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

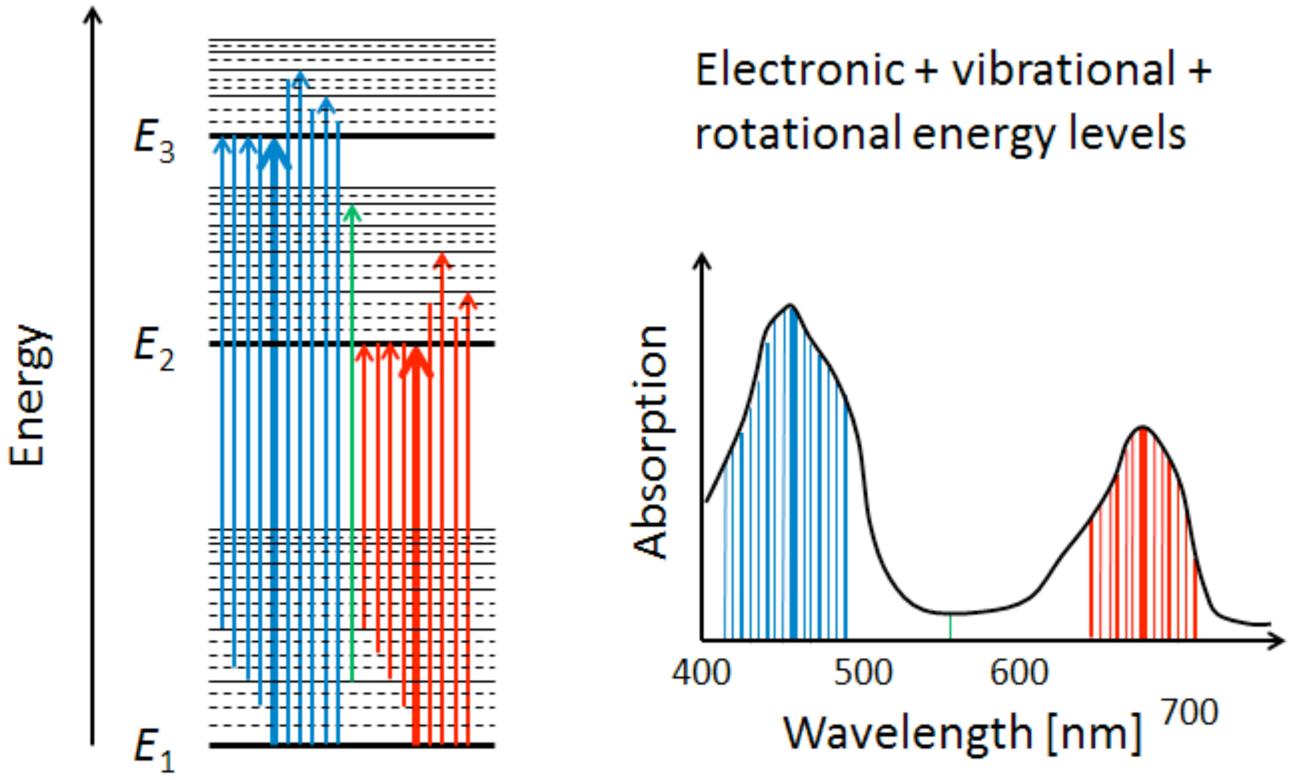
2. SERS Fundamentals

INMA

SPECTROSCOPY

Spectrum = the intensity (or flux) of radiation as a function of wavelength

Energy levels



$\Delta E_{rotational} < \Delta E_{vibrational} < \Delta E_{electronic}$

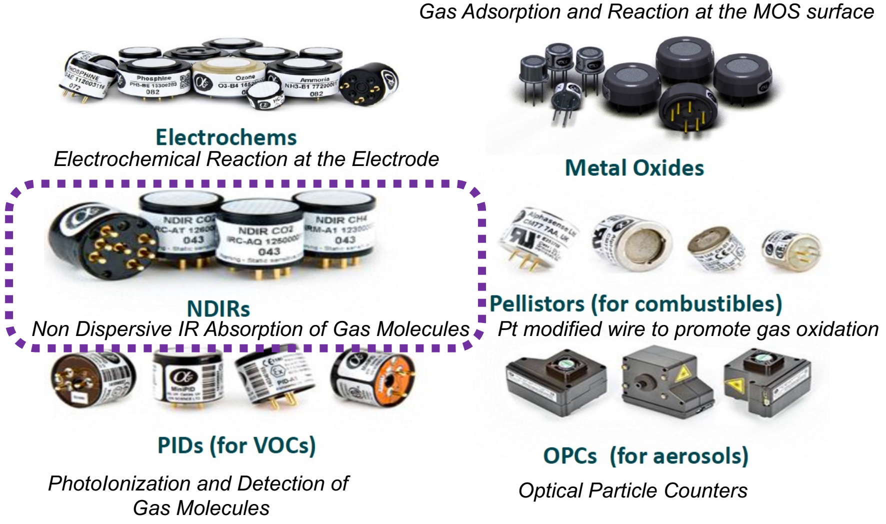
ABSORPTION Spectroscopy

UV-Vis	Electronic levels
IR	Vibrational and rotational levels

EMISSION spectroscopy

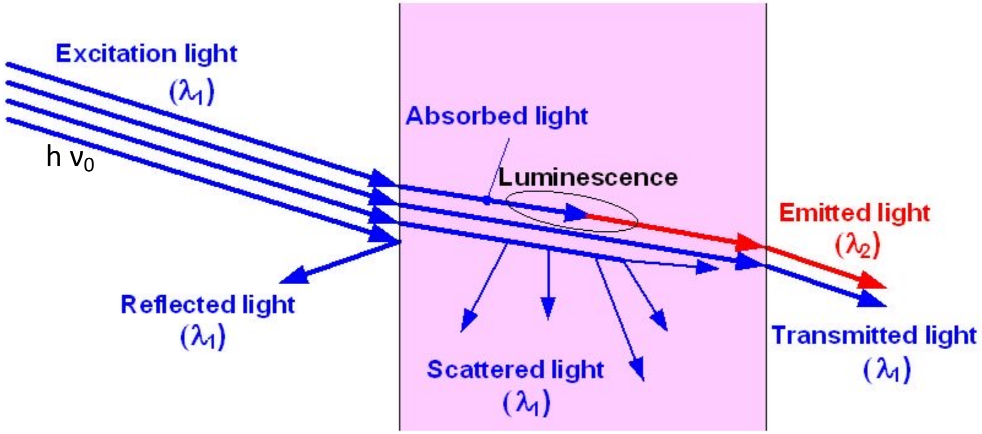
Fluorescence	Singlet excited state

Well Stablished Sensing Technologies

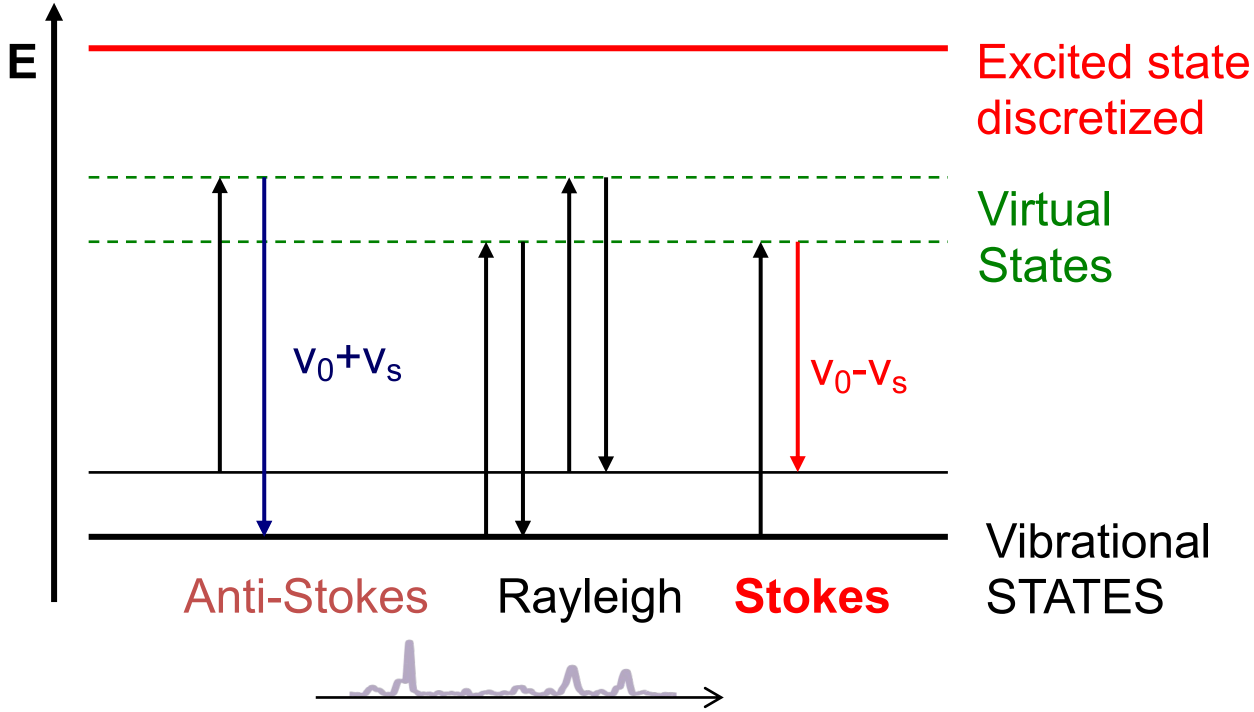


2. SERS Fundamentals

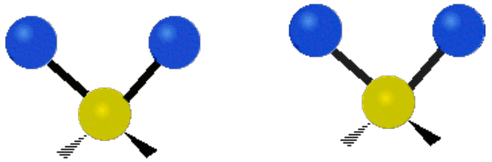
RAMAN SPECTROSCOPY: INELASTIC SCATTERING PROCESS (1929´s)



- **Absorption v_0 & Molecule/Atoms Polarization to a virtual state**
- **Elastic Scattering RAYLEIGH (only polarization of electrons): Re-emission of photons at = v_o**
- **Ineslatic Scattering RAMAN (+ nuclear motion): Re-emission of photons at $v_s \neq v_o$**



cm⁻¹
RAMAN SHIFT
VIBRATIONAL SPECTROSCOPY



Modern Raman Spectroscopy – A Practical Approach W.E. Smith and G. Dent 2005 John Wiley & Sons, Ltd

2. SERS Fundamentals

RAMAN SCATTERING: INHERENT WEEK EFFECT, POOR RAMAN SIGNALS

1 in every 10^6–10^8 photons which scatter is Raman scattered

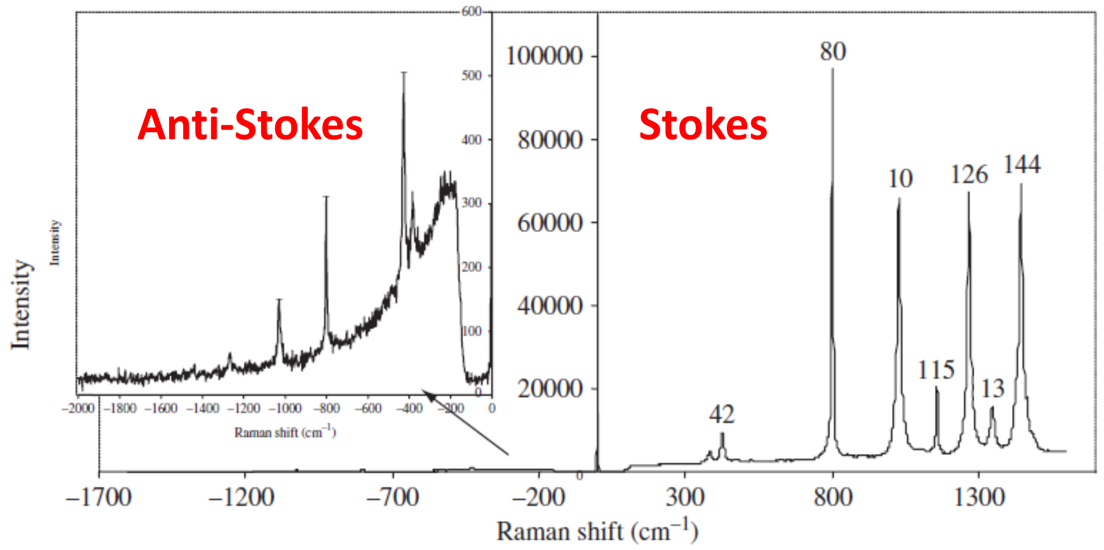
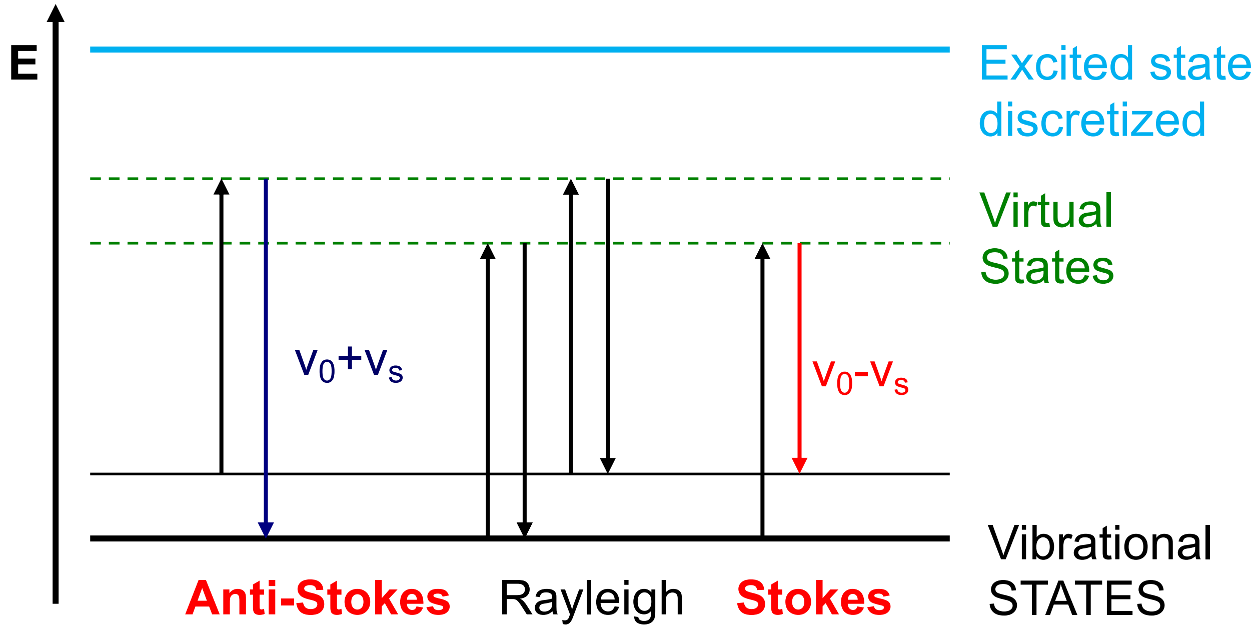


Figure 1.3. Stokes and anti-Stokes scattering for cyclohexane. To show the weak anti-Stokes spectrum, the *y*-axis has been extended in the inset.



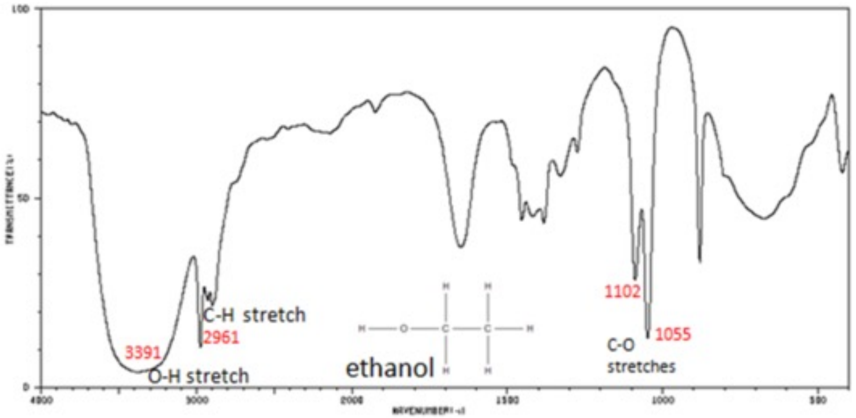
Modern Raman Spectroscopy – A Practical Approach W.E. Smith and G. Dent 2005 John Wiley & Sons, Ltd

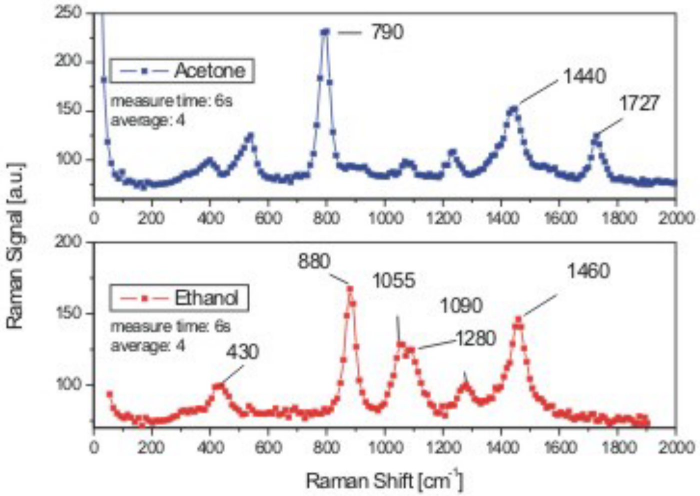
2. SERS Fundamentals

VIBRATIONAL SPECTROSCOPIES

*"The main **spectroscopies** to detect **"vibrations in molecules"** are based on the processes of Infrared Absorption and **Raman Scattering**"*

*"They are widely used to provide information on chemical structures and physical forms, to identify substances from the characteristic spectral patterns (**'fingerprinting')**, and to determine quantitatively or semi-quantitatively the amount of a substance in a sample"*





Modern Raman Spectroscopy – A Practical Approach W.E. Smith and G. Dent 2005 John Wiley & Sons, Ltd

2. SERS Fundamentals

VIBRATIONAL SPECTROSCOPIES: SELECTION RULES

*"Intense **Raman** vibrations occurs from vibrations* which causes a **change in the polarizability (distorsion) of the electron cloud** around the molecule"*

Bulky molecules, unpaired delocalized electrons: LARGE RAMAN CROSS SECTION

*"The most intense **Infrared absorption** occurs by a change in the **dipole moment** of the molecule when the molecule is vibrating"*

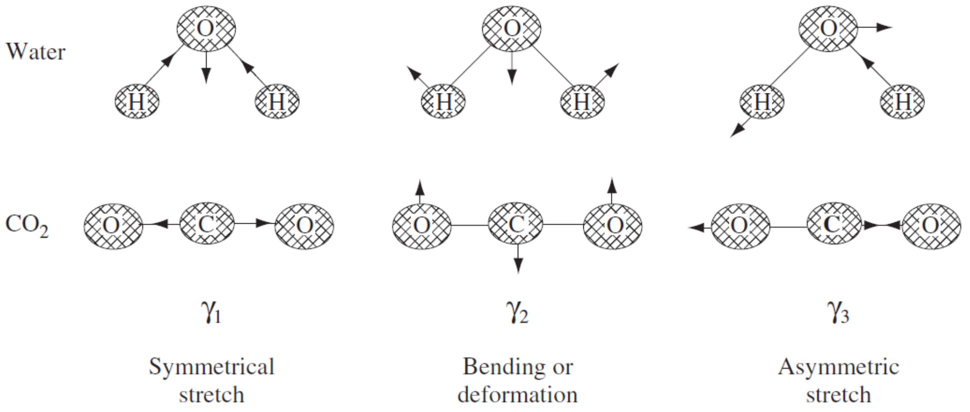


Figure 1.5. Spring and ball model – three modes of vibration for H_2O and CO_2.

- **H_2O is poorly Raman scattered**
- **H_2O is a stronger IR absorber**

**Vibrational degrees of freedom in a molecule: 3N-6 or 3N-5 (lineal molecules) N: nº. atoms*

Modern Raman Spectroscopy – A Practical Approach W.E. Smith and G. Dent 2005 John Wiley & Sons, Ltd

Functional Group/ Vibration	Region	Raman	InfraRed
Lattice vibrations in crystals, LA modes	10 - 200 cm^{-1}	strong	strong
δ(CC) aliphatic chains	250 - 400 cm^{-1}	strong	weak
υ(Se-Se)	290 -330 cm^{-1}	strong	weak
υ(S-S)	430 -550 cm^{-1}	strong	weak
υ(Si-O-Si)	450 -550 cm^{-1}	strong	weak
υ(Xmetal-O)	150-450 cm^{-1}	strong	med-weak
υ(C-I)	480 - 660 cm^{-1}	strong	strong
υ(C-Br)	500 - 700 cm^{-1}	strong	strong
υ(C-Cl)	550 - 800 cm^{-1}	strong	strong
υ(C-S) aliphatic	630 - 790 cm^{-1}	strong	medium
υ(C-S) aromatic	1080 - 1100 cm^{-1}	strong	medium
υ(O-O)	845 -900 cm^{-1}	strong	weak
υ(C-O-C)	800 -970 cm^{-1}	medium	weak
υ(C-O-C) asym	1060 - 1150 cm^{-1}	weak	strong

Continue…

υ(CC) alicyclic, aliphatic chain vibrations	600 - 1300 cm^{-1}	medium	Medium
υ(C=S)	1000 - 1250 cm^{-1}	strong	weak
υ(CC) aromatic ring chain vibrations	*1580, 1600 cm^{-1}	strong	medium
	*1450, 1500 cm^{-1}	medium	medium
	*1000 cm^{-1}	strong/medium	weak
δ(CH3)	1380 cm^{-1}	medium	strong
δ(CH2) δ(CH3) asym	1400 - 1470 cm^{-1}	medium	medium
δ(CH2) δ(CH3) asym	1400 - 1470 cm^{-1}	medium	medium
υ(C-(NO2))	1340 - 1380 cm^{-1}	strong	medium
υ(C-(NO2)) asym	1530 - 1590 cm^{-1}	medium	strong
υ(N=N) aromatic	1410 - 1440 cm^{-1}	medium	-
υ(N=N) aliphatic	1550 - 1580 cm^{-1}	medium	-
δ(H2O)	~1640 cm^{-1}	weak broad	strong
υ(C=N)	1610 - 1680 cm^{-1}	strong	medium
υ(C=C)	1500 - 1900 cm^{-1}	strong	weak
υ(C=O)	1680 - 1820 cm^{-1}	medium	strong
υ(C≅C)	2100 - 2250 cm^{-1}	strong	weak
υ(C≅N)	2220 - 2255 cm^{-1}	medium	strong
υ(-S-H)	2550 - 2600 cm^{-1}	strong	weak
υ(C–H)	2800 - 3000 cm^{-1}	strong	strong
υ(=(C-H))	3000 - 3100 cm^{-1}	strong	medium
υ(≅(C-H))	3300 cm^{-1}	weak	strong
υ(N-H)	3300 - 3500 cm^{-1}	medium	medium
υ(O-H)	3100 - 3650 cm^{-1}	weak	strong

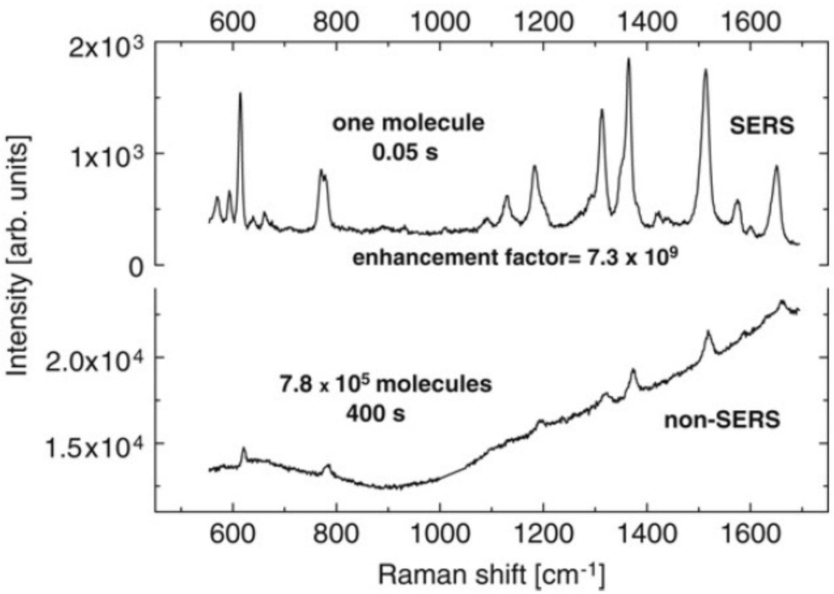
Look for the specific vibrations (literature) before going to the lab/selecting the optical sensor….

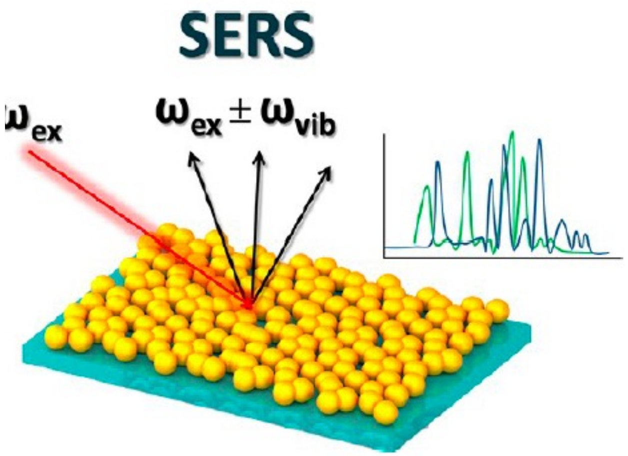
2. SERS Fundamentals

Surface Enhanced Raman Spectroscopy (1974´s):

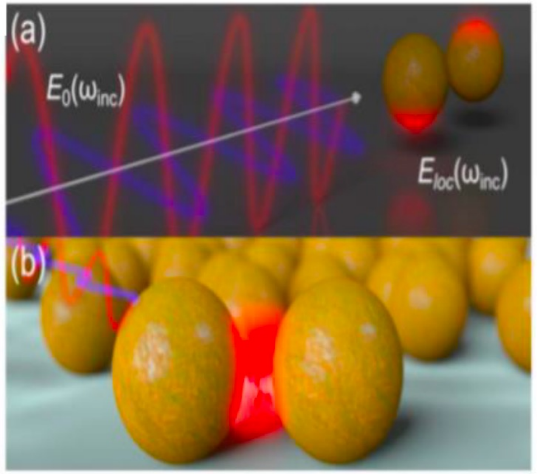
*…About **amplifying** Raman signals by several orders of magnitude, through the electromagnetic interaction of light with **metals***

*…To profit from these, the molecules must typically be adsorbed on the metal **surface**, or at least very close to it (typ. maximum 10nm)…*





ACS Nano 2020, 14, 28–117



2. SERS Fundamentals

Surface Enhanced Raman Spectroscopy: SERS Effect & substrates

Electromagnetic Enhancement ⇒ Metallic Nanostructures ⇒ Surface Plasmons

Localized SPR

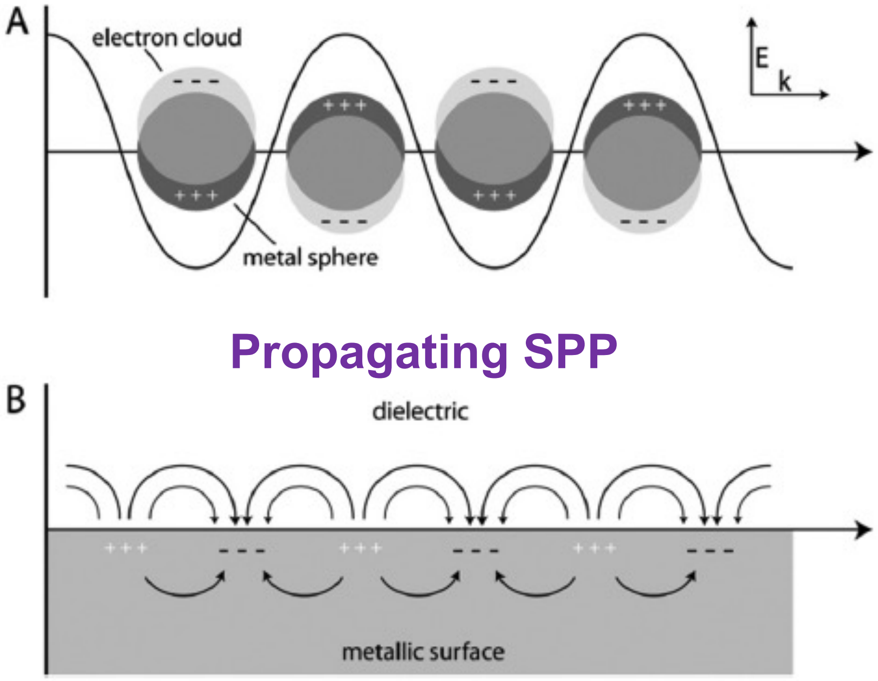
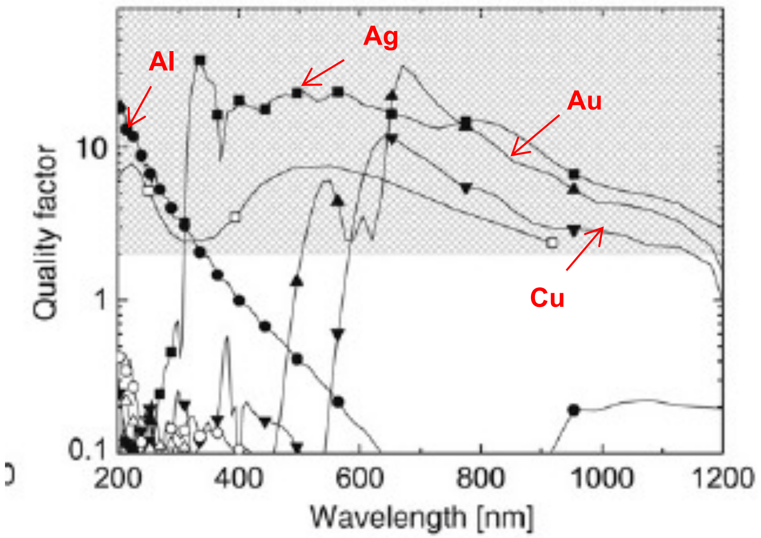


Fig. 1 Schematic illustration of (A) localized and (B) propagating surface plasmon polaritons. *E* depicts the electric field vector and *k* the wave vector.

➡ **Metals: dielectric function**



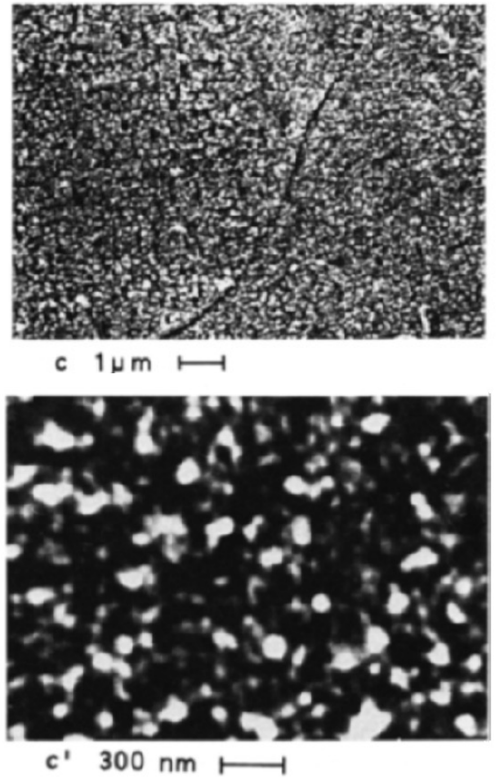
➡ **To consider: reactivity of the Surface: Ag vs. Au**

- EM enhancement up to 10^8
- Chemical Enhancement up to 10^6

2. SERS Fundamentals

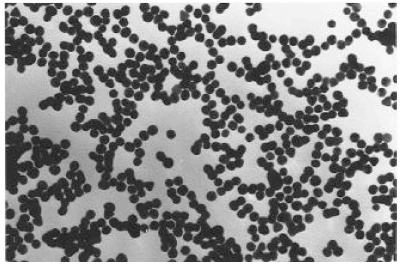
Surface Enhanced Raman Spectroscopy: SERS substrates

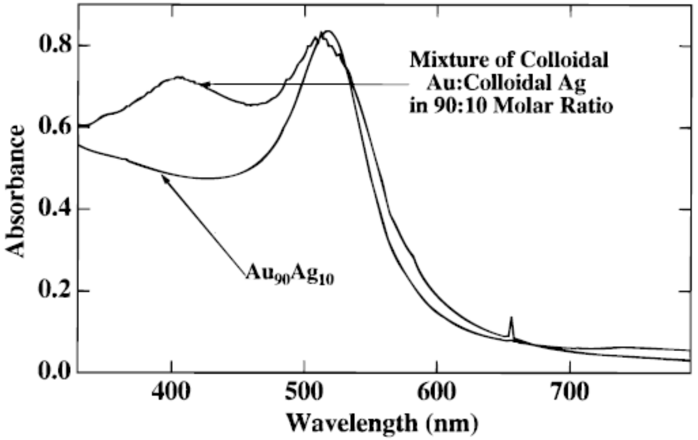
Silver coated electrodes (70's)



Fleischmann, M et al. Chem. Phys. Lett. 1974, 26,163–166.

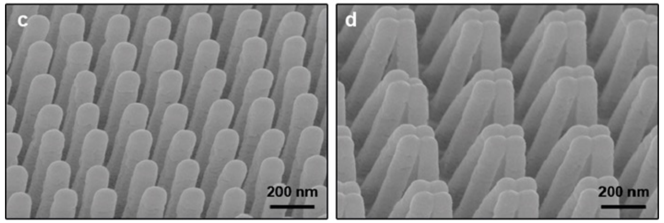
Metallic nanoparticles (end 90's)



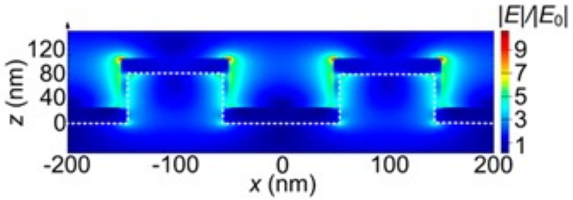


Freeman et al. J. Phys. Chem., Vol. 100, No. 2, 1996

Ordered nanostructures … last years
Nanophotonics



Hu, M. et al. JACS, 2010, 132, p. 12820-2822.

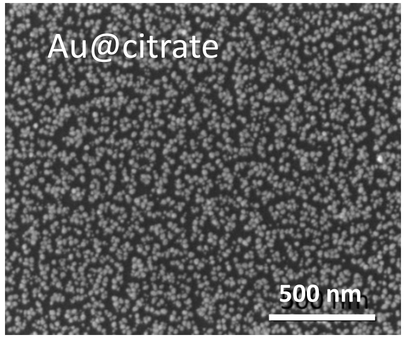


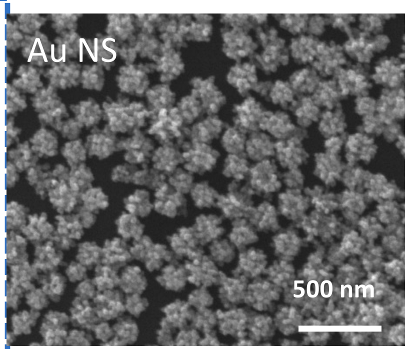
Liu, X. et al. ACS Nano, 2015, 9 (1), p. 260-270.

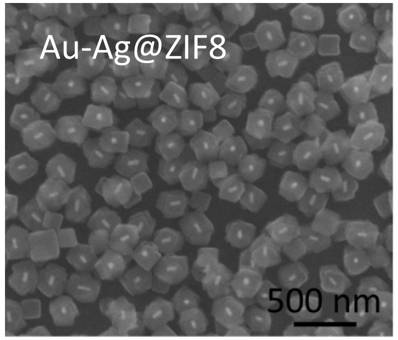
2. SERS Fundamentals

SERS substrates @ INMA

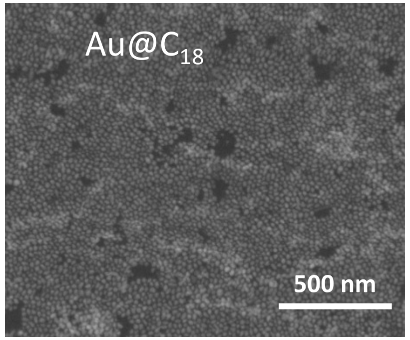
Layer by Layer





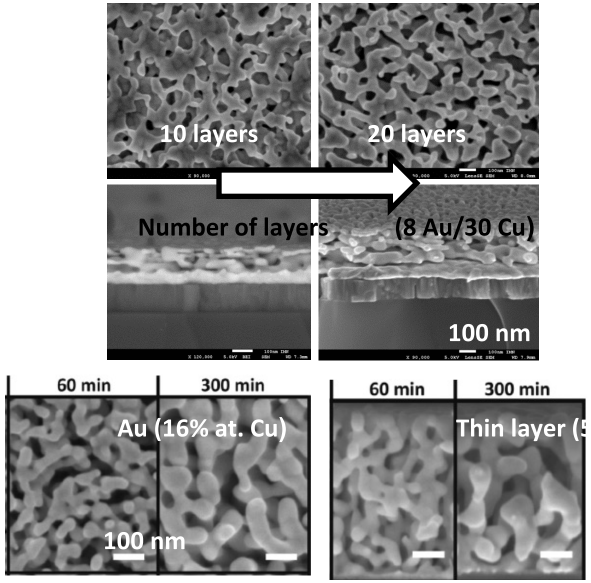


Langmuir-Schaefer

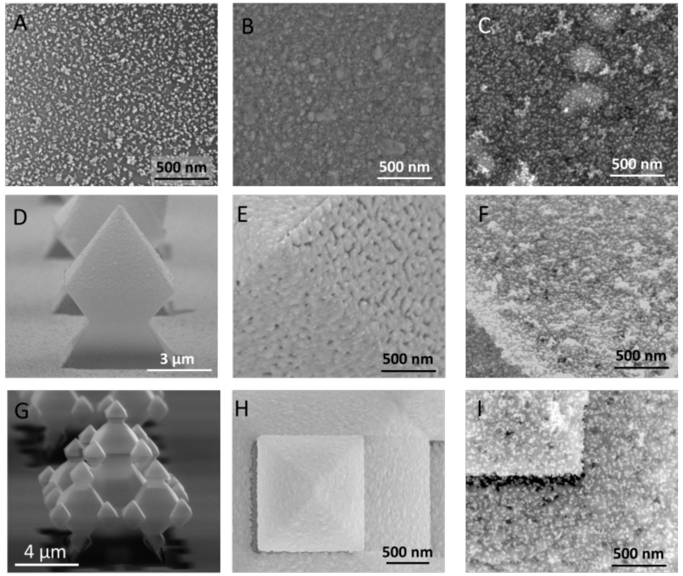


2D SERS substrates “bottom-up”
vs.
3D SERS substrates “top-down”

Institut des Matériaux Jean Rouxel



MESA+ Institute for Nanotechnology



2. SERS Fundamentals

Surface Enhanced Raman Spectroscopy: SERS substrates based on Colloids Transfer

Metallic Nanostructures: Size – **Shape** - Gap

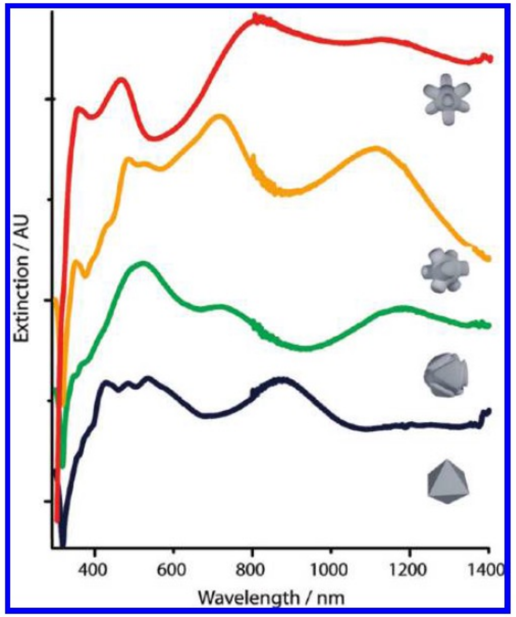


Figure 4. UV−vis−NIR characterization of the octahedral-shaped particles as a function of the etching progress when starting from octahedral nanoparticles. Interestingly, as the etching progresses the octapod structures have LSPs with greater intensity in the red and near-infrared regions.

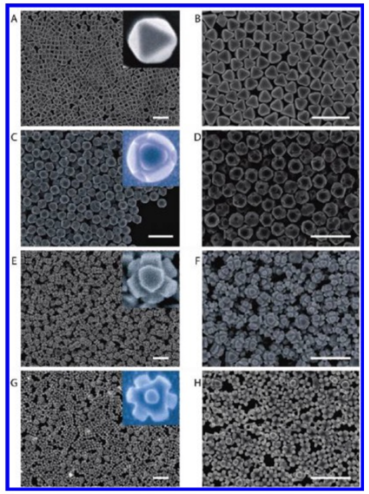


Figure 2. SEM images following the etching progress of the silver octahedral-shaped nanoparticles. (A, B) Octahedra-shaped starting material showing regular size and shape, which are essential for controlled etching reactions; (C, D) using a small amount of etchant, the edges and corners can be selectively etched leaving gaps of 5−10 nm; (E, F) when exposed to a slightly higher concentration of etching solution, eight distinct arms develop; and (G, H) finally, at relatively high concentrations of etching solution, octapod-shaped nanoparticles are isolated in high yield. All scale bars shown represent 1 μm.

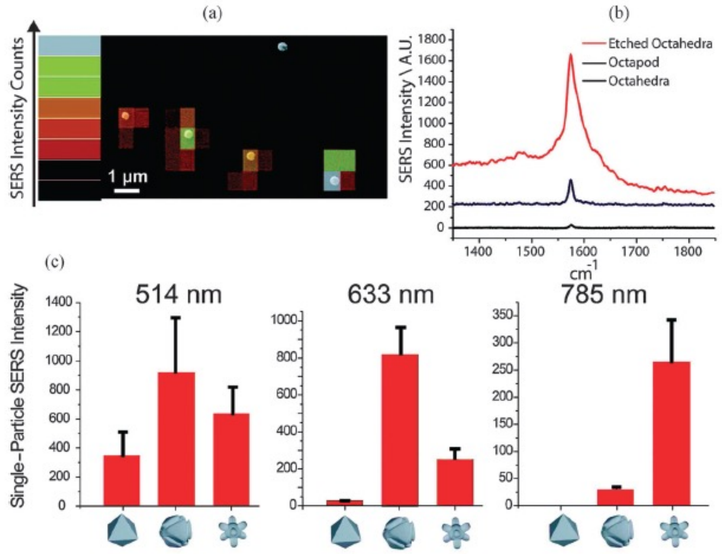


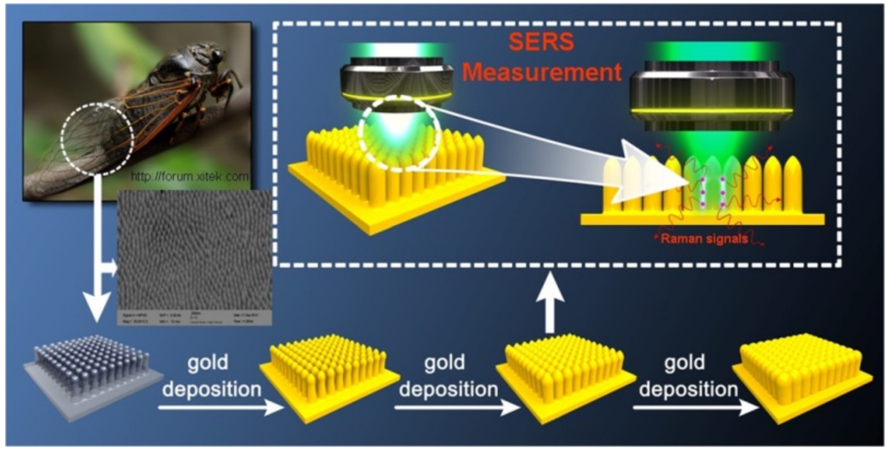
Fig. 8 Surface-enhanced Raman scattering of benzenethiol on single Ag nanoparticles. (a) SEM image of particles overlaid with SERS intensity map of the 1584 cm^{-1} mode of benzenethiol. (b) SERS spectra for each shape particle obtained with 633 nm excitation. (c) Average single particle SERS intensity as a function of shape and excitation wavelength. Reproduced with permission from ref. 168.

J. AM. CHEM. SOC. 9 VOL. 132, NO. 1, 2010

2. SERS Fundamentals

Surface Enhanced Raman Spectroscopy: SERS substrates based on Colloids Transfer

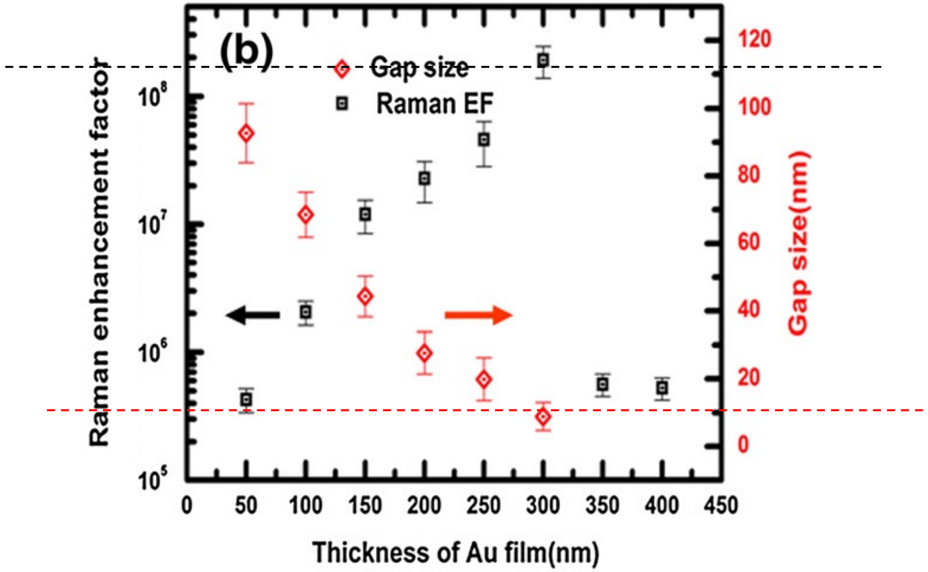
Metallic Nanostructures: Size – Shape - **Gap**



400 nm length, 65 nm diameter

Nanoscale Research Letters, 2013, 8, 437

HOT SPOTS FORMATION



2. SERS Fundamentals

Measuring SERS

SERS probes (analytes or labels)

- Dyes produce larger signals in Raman and are typical probes but….(Raman intensity is characterized by Raman cross-section)
- Can any molecule be measured with SERS?
- Can any molecule be attached (or at least brought close) to a metallic substrate?
- Will the resulting SERS signal be sufficiently strong to be observed (and distinguished from any other unavoidable signal and noise)?
- Photo stability of the probe (power, time, dosis laser line) should be considered

↓

Necessary to optimize acquisition parameters to maximize the enhacement

2. SERS Fundamentals

Measuring SERS: Analytical Enhancement Factor (AEF) or SERS Gain

$$\mathrm{AEF} = \frac{I_{\mathrm{SERS}}/c_{\mathrm{SERS}}}{I_{\mathrm{RS}}/c_{\mathrm{RS}}}.$$

- Measurement is easily implemented and reproducible
- Identical Raman and SERS adquisition conditions
- Shortcomings:
  - C_{SERS} is clearly affected by the adsorption efficiency (intercomparison conditions)
  - C_{RS} carefully selected for dyes to avoid photobleaching, molecular aggregation, molecular absorption… (low concentrations are preferable)

2. SERS Fundamentals

Measuring SERS: Analytical Enhancement Factor (AEF)

$$\mathrm{AEF} = \frac{I_{\mathrm{SERS}}/c_{\mathrm{SERS}}}{I_{\mathrm{RS}}/c_{\mathrm{RS}}}.$$

Table 1 Characteristics of SERS hot spot substrates discussed in the text. Values are a best estimate given reported literature values. See text for details. The following are acronyms used in the table: MFONs—metal film over nanospheres; TERS—tip-enhanced Raman spectroscopy; SHINERS—shell-isolated nanoparticle enhanced Raman spectroscopy; NR—not reported; NA—not applicable; Fs—femtosecond

	EF range	Estimated gap size (nm)	Cost ($-$$)	Analyte specificity	Proven SM sensitivity	Ref.
Non-hot spot substrates						
Island films	10^4	10–100	$$	No	Yes	22–24
Periodic particle array	10^7	10–100	$$	No	No	4, 25
Nanorods	10^3–10^7	NA	$	No	No	26
Nanoshells	$\sim 10^6$	NA	$	No	No	27
Fabricated substrates						
MFONs	10^3–10^{11}	0.1–10	$$	No	No	28, 29
Lace-shell NPs	$\sim 10^2$	1–10	$$	No	No	30
Fs laser etching	$< 10^9$	NR	$$	No	No	31, 32
E-beam lithography	10^3–10^5	1–100	$$	No	No	33–35
Templated nanowires	10^2–10^3	5–100	$$	No	No	36–38
Bowtie electromigration	10^8	0.1–10	$$	No	No	39
Spheres on E-beam posts	10^8	0–1	$$	Yes	No	40
Assembled structures						
Aggregated colloids	10^6–10^{10}	0–10	$	No	Yes	7, 41
DNA hybridization	10^8–10^{12}	1–100	$$	Yes	Yes	42–44
Embedded polymers	$\sim 10^5$	10–100	$	No	No	45, 46
SiO_2 encapsulated cores	10^6–10^8	0–10	$$	Yes	No	47
Particles in wells	10^9	0–10	$	No	No	48, 49
Nanofingers	10^{10}–10^{11}	0–10	$$	No	No	50, 51
TERS	10^4–10^9	0–100	$$	No	Yes	52–54
SHINERS	10^5–10^8	1–10	$	No	No	55, 56

Huge variability due to the long list of influencing parameters (apart from the substrate):

- Laser excitation, Detection Set-up
- SERS probe: Raman polarizability, adsorption efficiency, analyte concentration, preferential orientation
- **CHEM mechanism: molecule-substrate specific**

2. SERS Fundamentals

Measuring SERS: AEF vs. Spatial uniformity-Reproducibility

Table 2 Distribution of EFs on AgFON substrate. Adapted with permission from ref. 29

Raman enhancement factor	Percentage of molecules	Percent contribution to average SERS signal
$<2.8 \times 10^4$	0%	0%
2.8×10^4 to 1×10^5	61%	4%
10^5 to 10^6	33%	11%
10^6 to 10^7	5.1%	16%
10^7 to 10^8	0.7%	22%
10^8 to 10^9	0.08%	23%
10^9 to 10^{10}	0.006%	17%
$>10^{10}$	0.0003%	7%

¡¡ < 1% of the target molecules adsorbed on the hot spots accounts for > 69% SERS signal!!

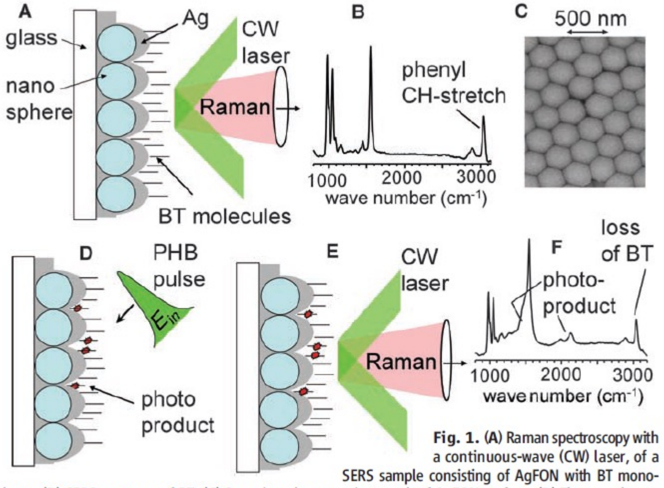


Fig. 1. (**A**) Raman spectroscopy with a continuous-wave (CW) laser, of a SERS sample consisting of AgFON with BT monolayer. (**B**) SERS spectrum of BT. (**C**) Scanning electron micrograph of AgFON surface. (**D**) The sample was exposed to an intense PHB pulse with laser field E_{in}. BT molecules at sites with local field enhancement g were damaged if $gE_{in} \geq E_{th}$, where E_{th} is the threshold field needed to damage BT. (**E** and **F**) The Raman spectrum after PHB shows loss of BT plus new transitions from photoproduct molecules. The loss of BT is quantified by using the integrated area of the phenyl CH-stretch transition at 3050 cm^{-1}.

SCIENCE VOL 321 18 JULY 2008

- Are Hot Spots really beneficial for "real" applications?
- SERS fluctuations; SERS blinking; Photobleaching…

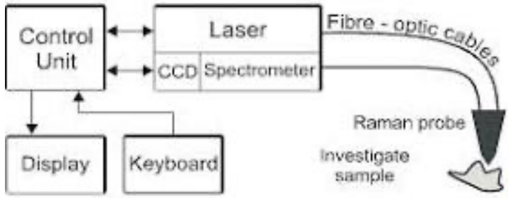
Average EF (Substrate) vs. Single Molecule EF (SMEF)

2. SERS Fundamentals

INMA

Measuring SERS: Hand-held Raman spectrometers

Key advantage for CBRNe applications: liquid/solid phase material identification through container walls (optically transparent and even semi-opaque)



Handheld systems

									
Spec	B&W Tek NanoRam®	B&W Tek TacticID®-GP	B&W Tek TacticID®-N	Bruker Bravo	Cobalt Resolve	ThermoFisher Scientific Gemini	ThermoFisher Scientific FirstDefender RMX FirstDefender RM TruNarc TruScan GP TruScan RM	Rigaku Progeny RESQ	Rigaku Progeny
Lasers	785nm	785nm	785nm	700 - 1100 nm (Duo LASER™) 758 nm and 852 nm	830 nm	785 nm	785 nm	1064 nm	1064 nm
Laser output power	300mW Max Adjustable in 10% Increments	300mW Max Software Adjustable	300mW Max Software Adjustable	low laser power, < 100 mW for both LASERs	Adjustable laser power (475 mW maximum)	300mW	300mW	30-495 mW Adjustable laser power	30-495 mW Adjustable laser power
Range	176cm^{-1} to 2900cm^{-1}	176cm^{-1} to 2900cm^{-1}	176cm^{-1} to 2900cm^{-1}	300cm^{-1} to 3200cm^{-1}		250-2875cm^{-1}	250-2875cm^{-1}	200-2500cm^{-1}	200-2500cm^{-1}
Resolution	~ 9cm^{-1}@ 912nm	~ 9cm^{-1}@ 912nm	~ 9cm^{-1}@ 912nm	10-12 cm^{-1}		7-10.5 cm^{-1}	7-10.5 cm^{-1}	8-11 cm^{-1}	8-11 cm^{-1}
Detector	TE-Cooled Linear CCD Array	Linear CCD Array	Linear CCD Array	CCD				TE Cooled InGaAs	TE Cooled InGaAs
Other	Point-and-shoot	Point-and-shoot	Point-and-shoot	Point-and-shoot	Point-and-shoot SORS™	FT-IR combined	Point-and-shoot	Point-and-shoot	Point-and-shoot

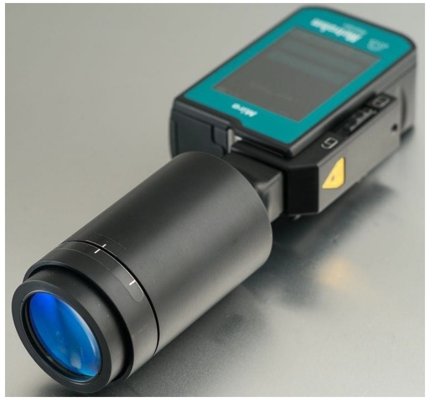
2. SERS Fundamentals

Measuring SERS: Hand-held Raman spectrometers

Key advantage for CBRNe applications: liquid/solid phase material identification through container walls (optically transparent and even semi-opaque)

								
Spec	SersTech SersTech100	Metrohm Mira M-1 M-2 M-3	Snowy Range Instruments SnRI CBEx	Ocean Optics IDRaman Mini	SmithsDetection ACE-ID	Airsense Analytics LS-ID	TSI ASSURx Raman Hanheld Analyzer	TSI EZRaman-H Series Raman Hanheld Analyzer
Lasers	785 nm	785 nm 1064 nm	785 nm 1064 nm	633 nm 785 nm	785 nm	785 nm	785 nm	785 nm
Laser output power		≤ 100 mW	≤ 100 mW	100 mW		100mW	300mW	300mW
Range		400cm^{-1} to 2300cm^{-1}	400cm^{-1} to 2300cm^{-1}	400-2300 cm^{-1}			250-2350cm^{-1}	250-2350cm^{-1}
Resolution		12-14 cm^{-1}	12-14 cm^{-1}	16 cm^{-1} (633 nm) 18-20 cm^{-1} (785 nm)			6 cm^{-1}	6 cm^{-1}
Detector				CCD			CCD	CCD
Other	Point-and-shoot	Point-and-shoot ORS	Point-and-shoot ORS	Point-and-shoot ORS	Point-and-shoot ORS	Point-and-shoot	Point-and-shoot	Point-and-shoot

Standoff material identification
Metrohm, Mira accessory
Distance: up to 1.5 m



2. SERS Fundamentals

Application Fields

Biomolecule Sensing & Bioimaging

…degenerative disorders[1]
…infectious diseases[2]
…genetic diseases[3]
…cancer[4]

[1] Bhowmik et al., *ACS Nano*, 2015.
[2] Shanmukh et al., *Nano Lett.*, 2006.
[3] Garcia-Rico et al., *Chem. Soc. Rev.*, 2018.
[4] Pazos et al., *J. Am. Chem. Soc.*, 2016.

Environmental Monitoring & Industrial Control

…enviromental toxins[5]
…chemicals[6]
…heavy metals[7]
…pesticides[8]
…monitoring chemical reactions[9]
…discrimination quiral molecules[10]

[5] Feng et al. *Biosens. Bioelectron.*, 2016.
[6] Li et al. *Nanoscale*, 2016.
[7] Xu et al. *Biosens. Bioelectron.*, 2015.
[8] Lafuente et al. *ACS Appl. Mat. Interfaces*, 2020.
[9] Han et al. *ACS Appl. Mater. Interfaces*, 2017.
[10] Tkachenko et al. *Nat. Commun.*, 2014.

Emerging Field: Homeland Security

Raman Spectroscopy + **Nano and Micro-technology**

- ✔ Spectral Fingerprint → **MOLECULAR SELECTIVITY/SPECIFICTY**
- ✖ **Low signal (inelastic scattering)**
- ✔ Universal Technique
- 🔍 **Raman Cross Section (polarizability)**
- ✔ Outperforming Portable Instrumentation

- ✔ Surface Plasmon Resonance Engineering → **"SINGLE MOLECULE DETECTION"**
- 🔍 **SERS effect is a Surface Effect → DETECTION IN GAS PHASE???**

OUTLINE

1. Chemical Sensing & Scenario Driven Requirements

2. SERS Fundamentals
   - Spectroscopy & Raman Spectroscopy
   - Surface Enhanced Raman Spectroscopy: SERS Effect & substrates
   - Measuring SERS
   - Portable Instrumentation
   - Application Fields

3. SERS for Gas Sensing
   - Challenges & Strategies
   - Our Approach
   - Future Work

4. Take-Home Messages

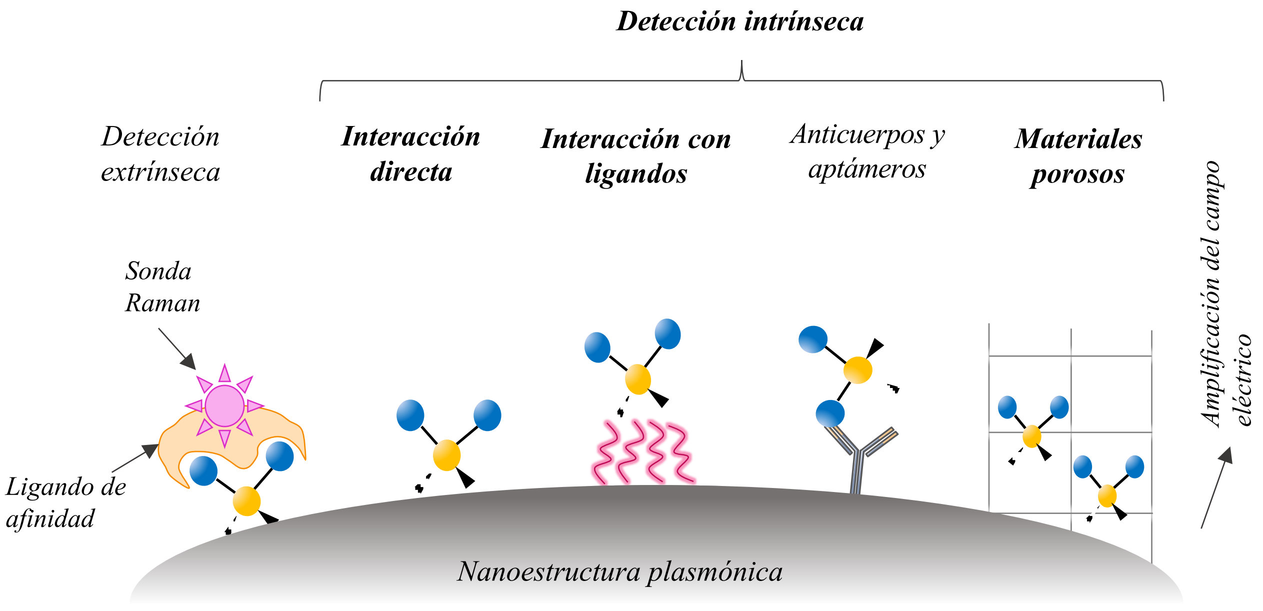
3. SERS for Gas Sensing: Challenges & Opportunities

INMA

- Gas phase: low number of molecules per unit volumen $\rho_{gas} = \rho_{liq}/1000$
- Low Sticking probability of gas/vapor molecules on the Enhancing Surface: low C_{SERS}
- Raman Cross- Section of Target Molecules

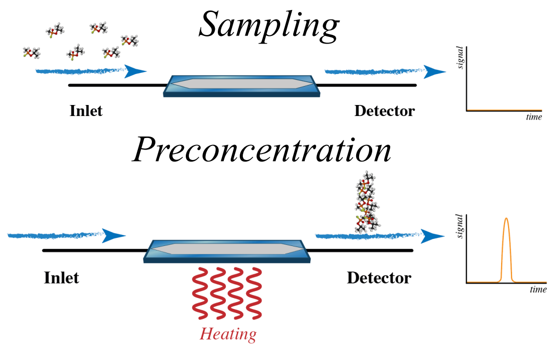
- Engineering SERS susbtrates/chips
  - Electrochemical Assisted SERS
  - Temperature Assisted SERS

  - Surface Chemistry
  - Partition Layers or Porous Surfaces

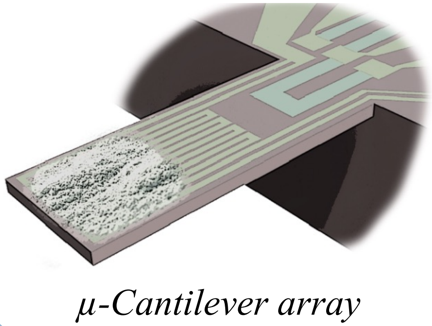


3. SERS for Gas Sensing

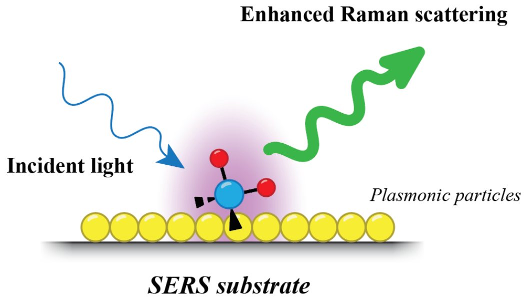
Our Approach: From Nanoporous Sorbents to Plasmonic Sorbents



Sampling
Preconcentration



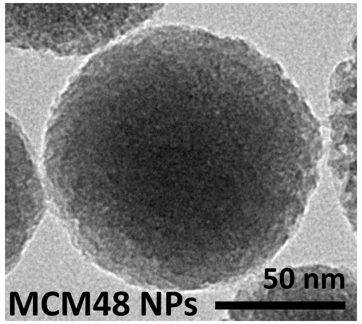
Detection

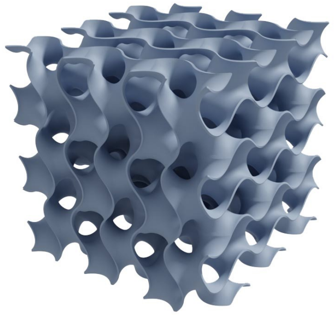


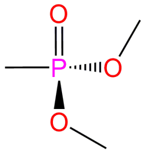
IDENTIFICATION

3. SERS for Gas Sensing

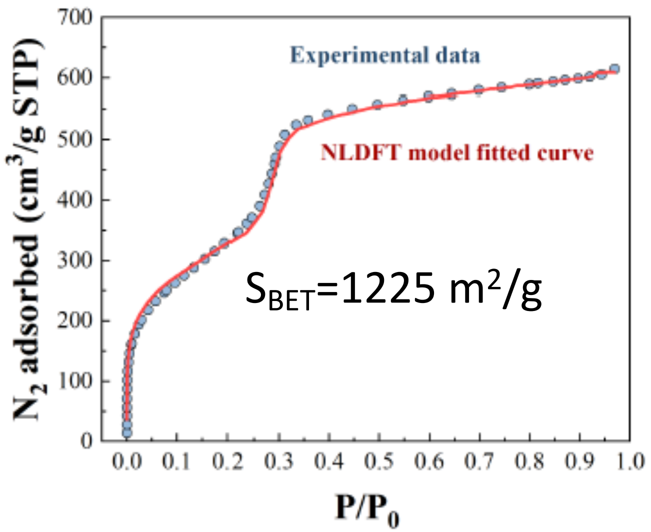
Our Approach: From Nanoporous Sorbents to Plasmonic Sorbents

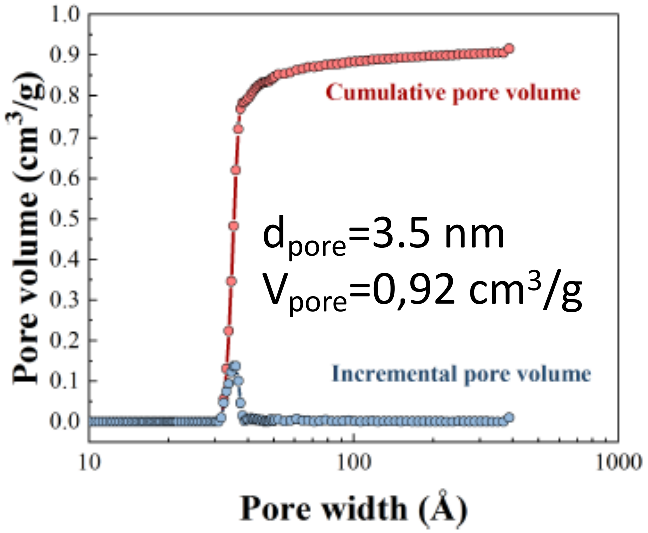






DMMP
Sarin Gas Surrogate

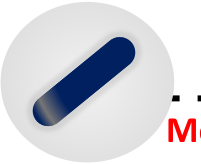




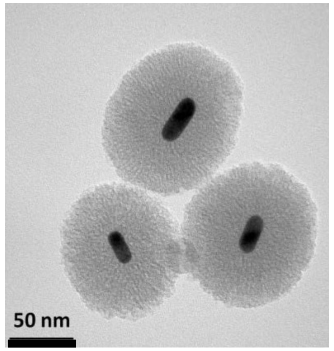
Material	Control		After exposure to 747 ppmV DMMP					
	Δm mg/gsorbent	T (ºC)	Δm mg/gsorbent	T (ºC)	Δm mg/gsorbent	T (ºC)	Δm mg/gsorbent	T (ºC)
Dense SiO_2	66.8	36	21.5	52	-	-	-	-
MCM48	31.4	42	40.0	39	132.8	97	222.7	170
MCM48-NH_2	62.4	45	109.5	39	82.1	61	51.6	110

3. SERS for Gas Sensing: Our Approach

❖ <u>Films based on Core-Shell nanoparticles based on Mesoporous Silica</u>

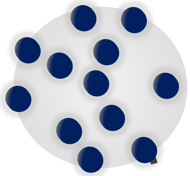


Mesoporous Silica Shell

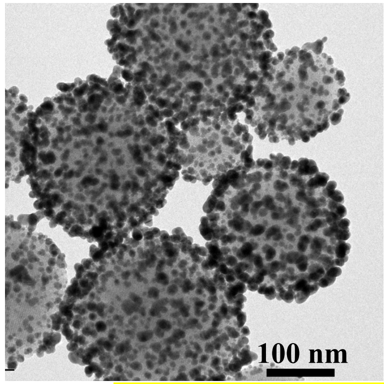


100 ± 25 nm
Shell 45 ± 8 nm

V_{pores} = 0,92 cm^3/g
D_{pore} = 3,5 nm
S_{BET} = 1230 m^2/g

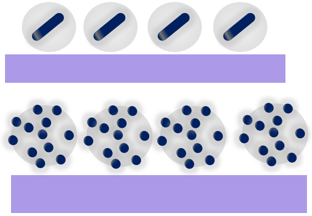


Mesoporous Silica Core



Silica:
180 ± 9 nm
AuNP:
15 ± 3 nm

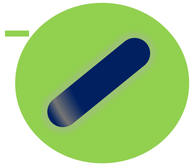
DMMP sorption= 317 mg/g
(750 ppmV-25°C)



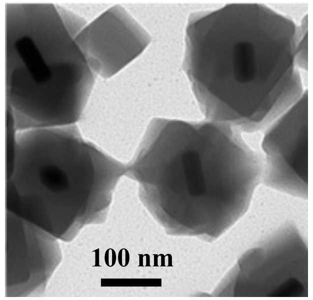
- ❖ **Ordered Mesopores 2.8 to 3.5 nm in pore size**
- ❖ **User-frienly Functionalization of Mesoporous Silica**
- ❖ **Higher DMMP Uptake on Mesoporous Silica**
- ❖ **Thickness of the Porous Moities: preconcentration effect vs response time & LSPR position**

❖ **Films based on Au@Ag nanorods encapsulated in Microporous ZIF8 (Zn based MOF)***

ZIF-8 Shell



ZIF8 (Zn based)



241 ± 25 nm
Shell 90 ± 17 nm

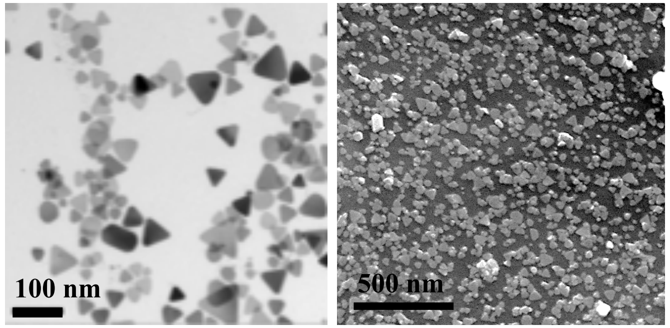
V_{pores} = 0,70 cm^3/g
D_{pore} = 1,2 nm
S_{BET} = 2000 m^2/gr

DMMP sorption= 83 mg/g
(750 ppmV-25°C)

*https://doi.org/10.1021/acssensors.1c00178

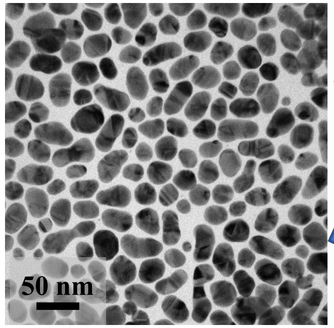
3. SERS for Gas Sensing

SERS substrates validated with nerve agents and vessicants



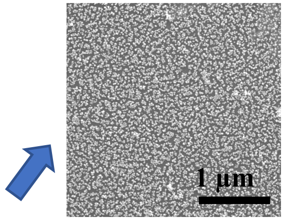
Silver nanoplates *electrostatically self-assembled to flat graphite*

https://doi.org/10.1016/j.jhazmat.2019.121279



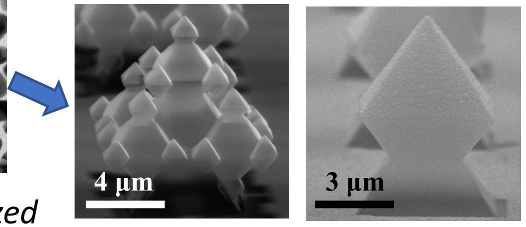
Gold nanoparticles *stabilized by citrate ions*

https://doi.org/ 10.1016/j.snb.2018.04.058



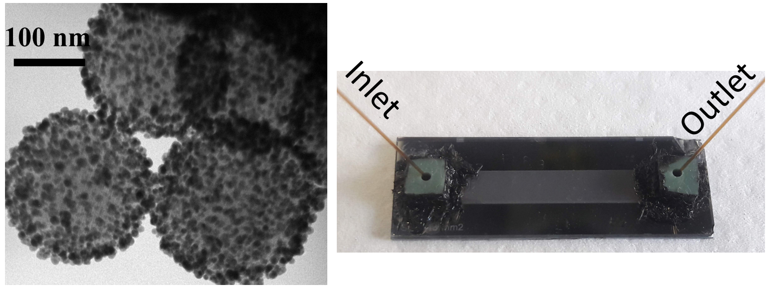
Electrostatically self-assembled…
to flat SiO_2

https://doi.org/10.1016/j.apsusc.2019.144663



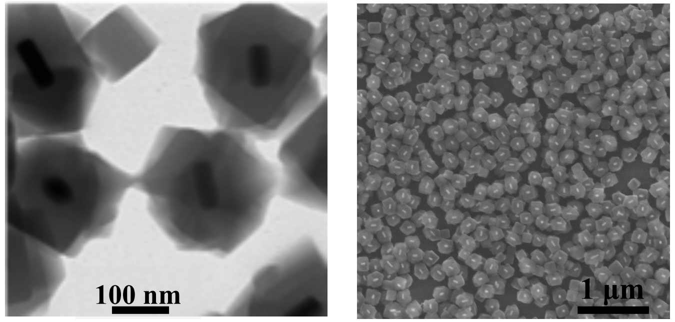
3D fractals

https://doi.org/10.1007/s00604-020-4216-9



MCM48@Au nanoparticles *spin coated inside Si microfluidic chip*

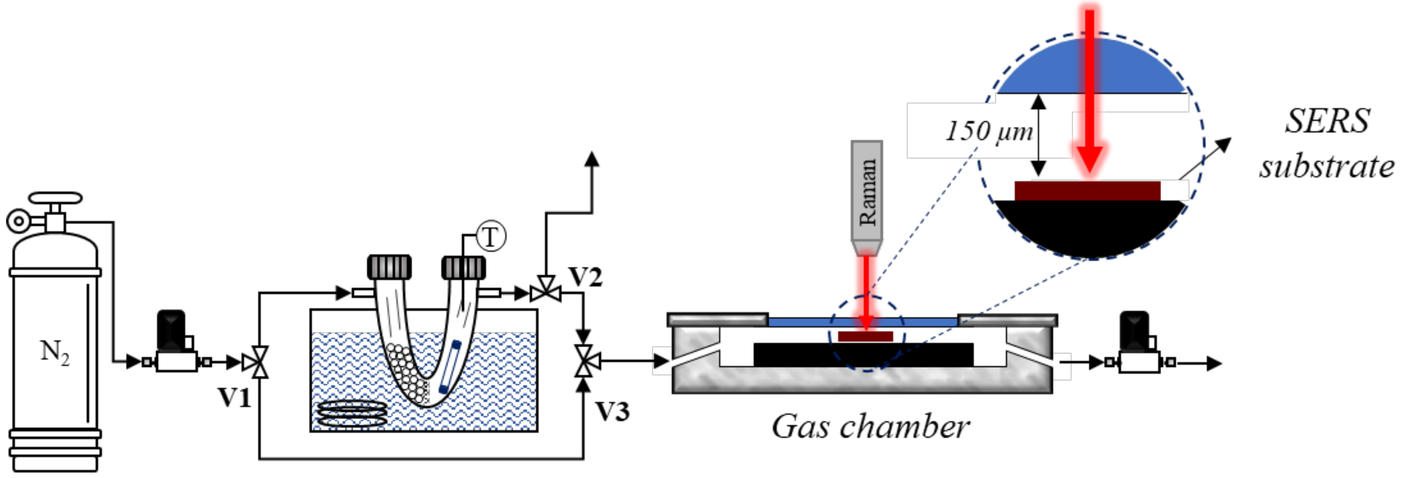
DOI: 10.1109/TRANSDUCERS.2019.8808289

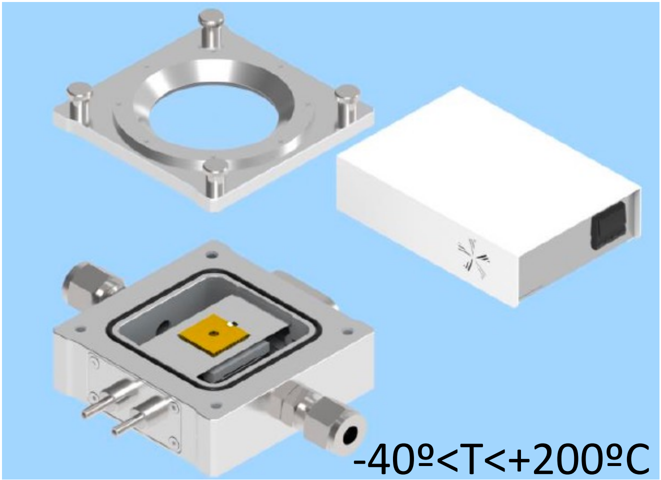


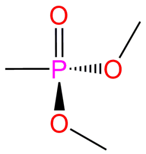
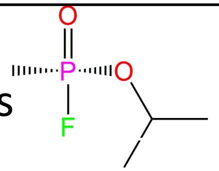
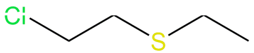
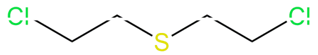
Au@Ag@ZIF8 nanoparticles
spin coated onto flat SiO_2

https://doi.org/10.1021/acssensors.1c00178

Basic Experimental set-up for SERS in gas phase





Surrogate/TIC	Real CWA/TIC	Lab testing*	AEGL1** at 10´
DMMP (Dimethyl methylphosphonate) 	Sarin gas & G family NAs 	< 2.5 ppmV	1.2 ppbV
CEES (2-chloroethyl ethyl sulphide) 	Vesiccant mustard gas 	< 100 ppbV	60 ppbV
NH_3 (Ammonia)	Toxic industrial compound	< 30 ppmV	30 ppmV
H_2S (Hydrogen sulfide)	Toxic industrial compound	< 1 ppmV	0.75 ppmV

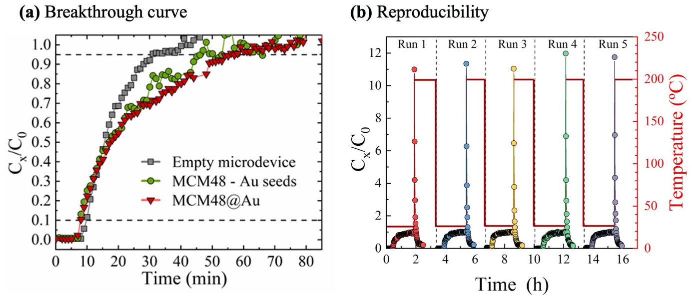
** Concentration values for Metrics definition;*

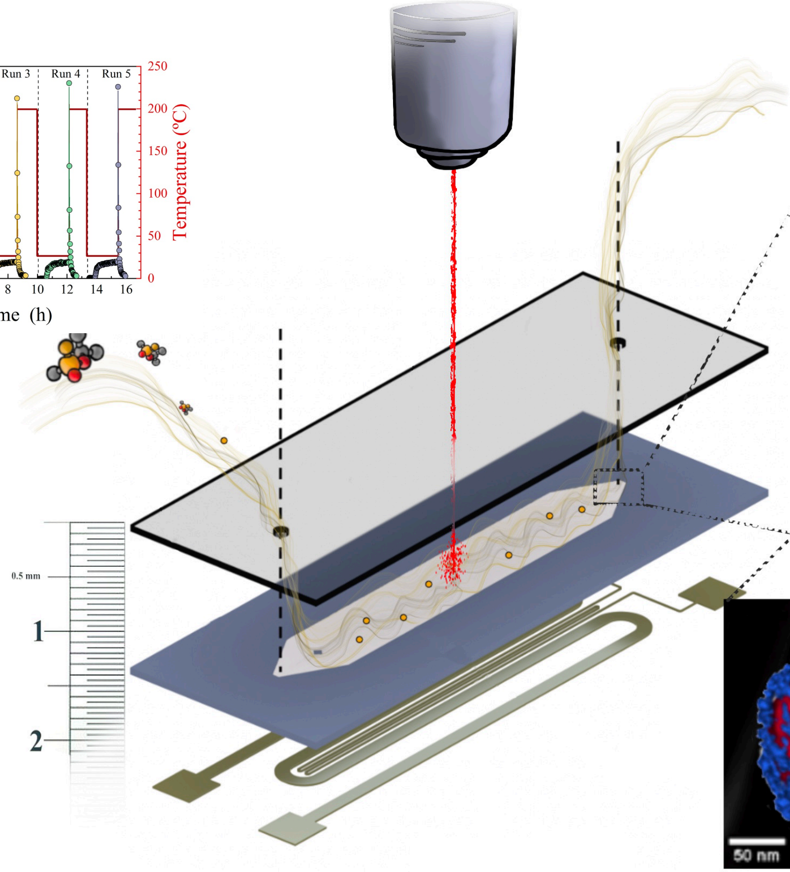
*** Irritation and discomfort (non irreversible health effects)*

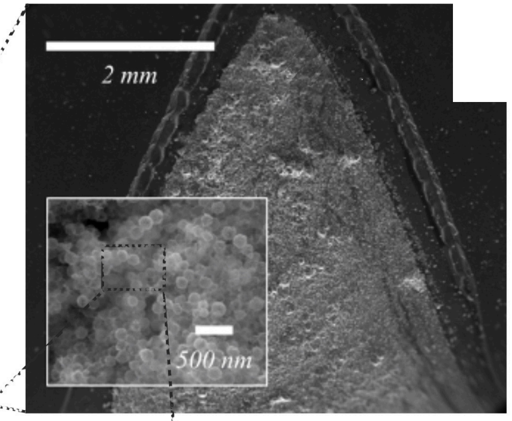
3. SERS for Gas Sensing

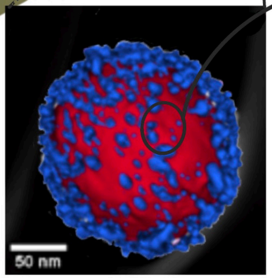
Our Approach: From Nanoporous Sorbents to Plasmonic Sorbents

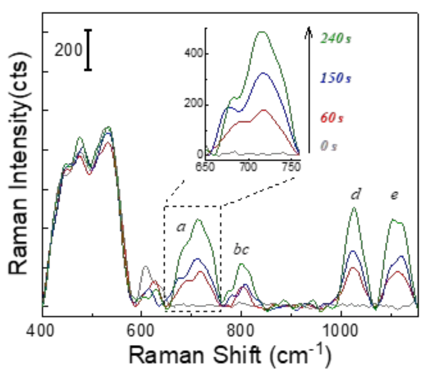
*On-Chip Monitoring of toxic gases: capture and label-free SERS detection with plasmonic mesoporous sorbents**

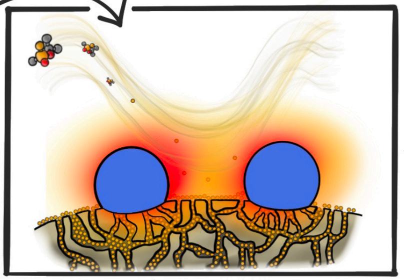


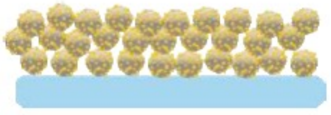












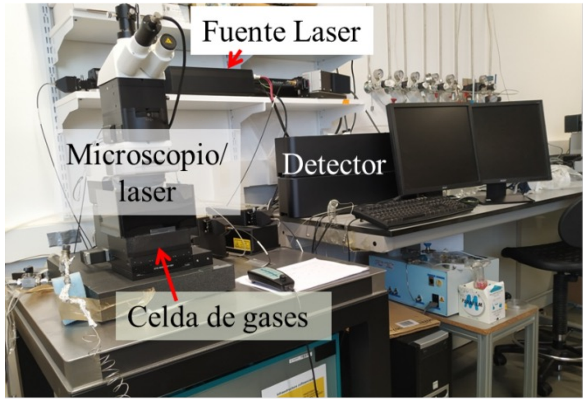
Conventional deposition of plasmonic nanostructures

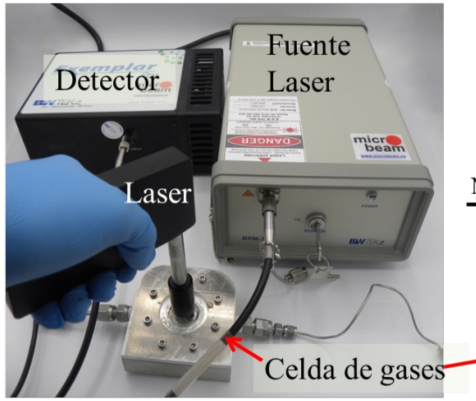
*Manuscript sent to Lab on a Chip Nov 22: Under Revision

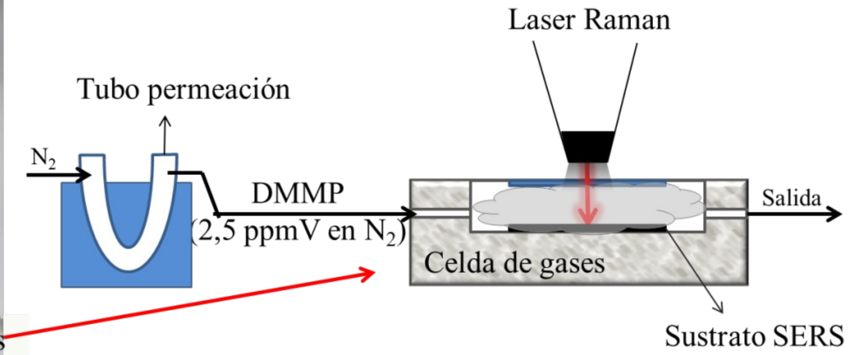
Universidad Zaragoza

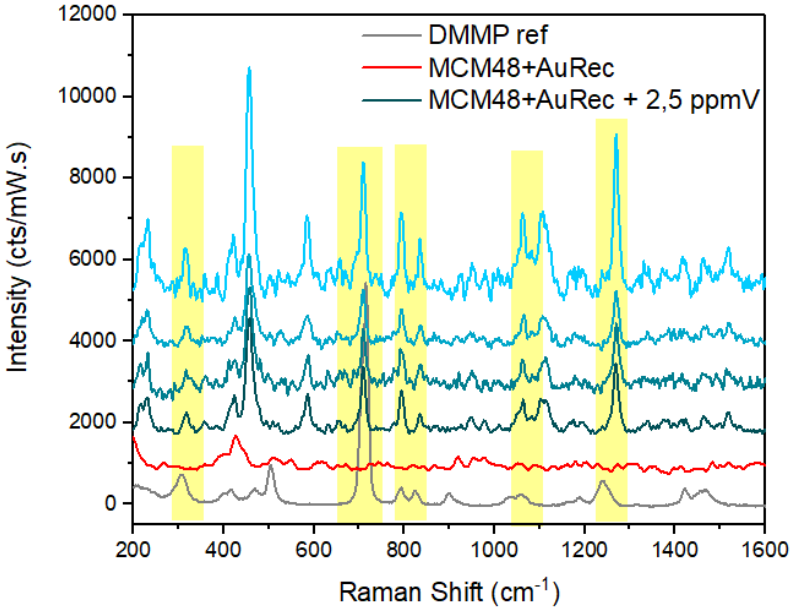
3. SERS for Gas Sensing

Our Approach: From Nanoporous Sorbents to Plasmonic Sorbents*

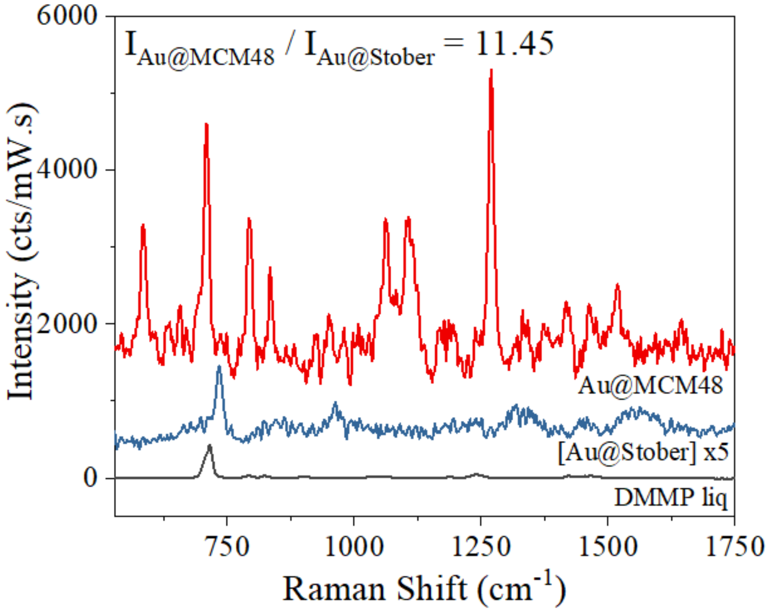








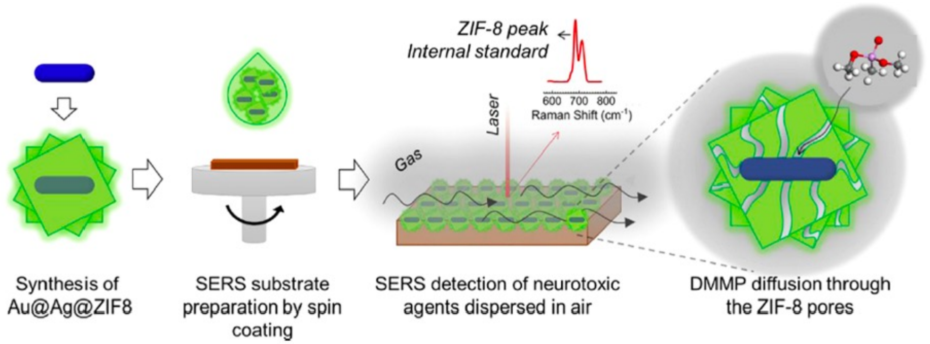
- ✓ Selective Fingerprint of the target molecule: 5 characteristic Raman Bands
- ✓ Outperformance vs. Au@ dense Silica



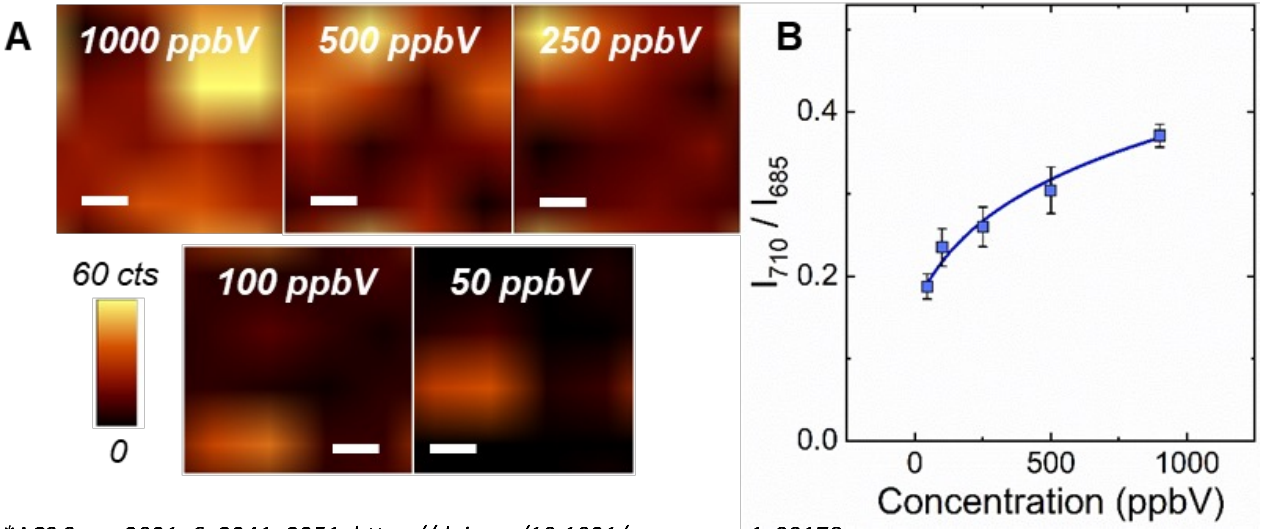
*Manuscript sent to Lab on a Chip Nov 22: Under Revision

3. SERS for Gas Sensing

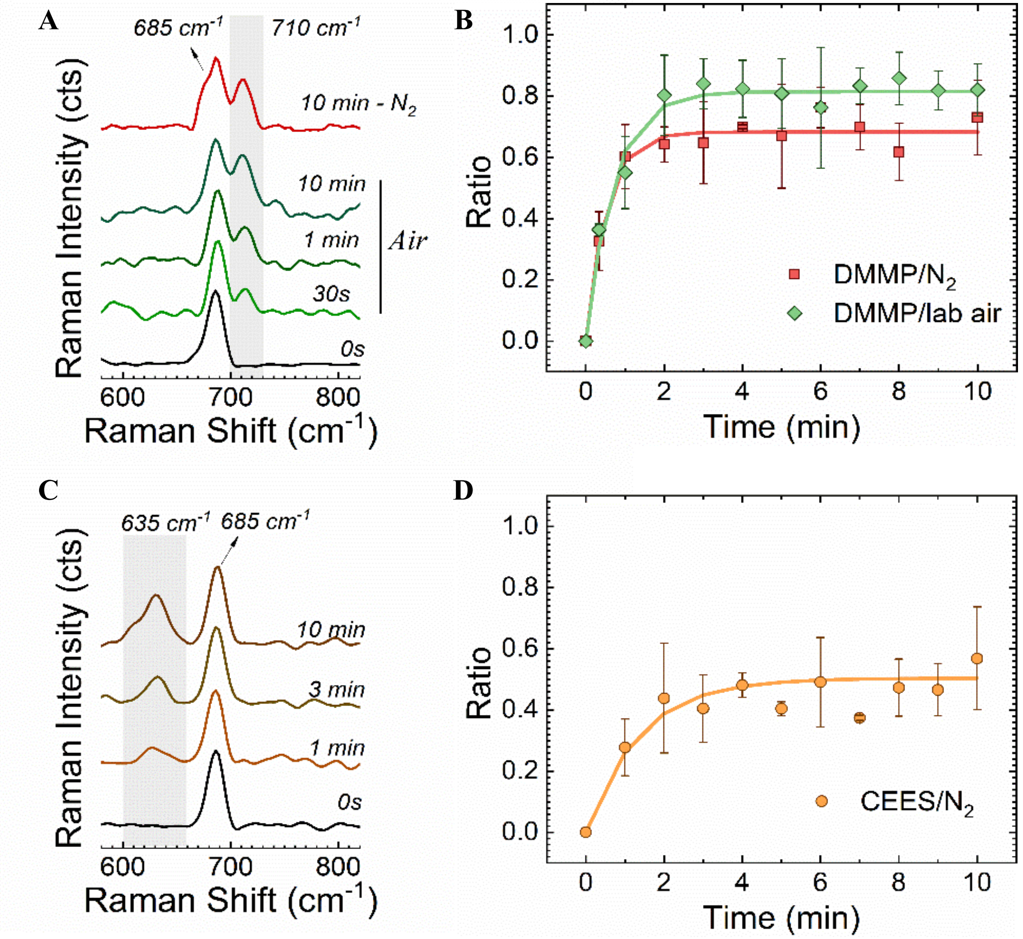
*Plasmonic MOF Thin Films with Raman Internal Standard for Fast and Ultrasensitive SERS Detection of Chemical Warfare Agents in Ambient Air**



SERS detection of gaseous DMMP in N_2 using Ag@Au@ZIF-8 thin film as sensing platform: LOD_t=6 ppbV; $t_{response,50\%}$<30s



On-field detection capabilities of Ag@Au@ZIF-8 substrate using a portable Raman equipment (DMMP-2500 ppbV; CEES-76 ppbV)



*ACS Sens. 2021, 6, 2241–2251. https://doi.org /10.1021/acssensors.1c00178

3. SERS for Gas Sensing

Future Work

Lack of **miniature**, **fieldable** and **affordable** tools and systems for **detection**, **identification** and **monitoring (DIM)** of **Chemical Threats (AEGLs @ ppb level)**

International Forum to Advance
FIRST RESPONDER INNOVATION

- SERS Ad-ons for Near-real time or on-demand detection and identification of chemical threats
- Handheld or robot-mounted instrumentation
- Develop machine learning based algorithms for SERS/Raman data analysis
- Provide data map to aid first reponders and incident commanders in hazard assessment and decision-making

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UNIVERSITY OF TWENTE.

Universidade de Vigo

DTU Compute
Department of Applied Mathematics and Computer Science

DTU Health Tech
Department of Health Technology

National Institute for Nuclear, Chemical and Biological Protection SUJCHBO

FOI

SERSTECH

SILMECO
SERS substrates

4. Take-Home Messages

- Multidisciplinary Field
- Universal and Ultrasensitive Analytical Technique
- Rapid Development of Portable Instrumentation
- SERS Community is devoted to demonstrate perfomance in Practical Applications, including DIM of traces

Main Areas Contributing to SERS at the Present