Inelastic light scattering by the free vibrations of gold nanocrystals: how much does shape matter?

Lucien Saviot

Laboratoire Interdisciplinaire Carnot de Bourgogne
UMR 6303 CNRS-Université de Bourgogne Franche-Comté
Dijon – France

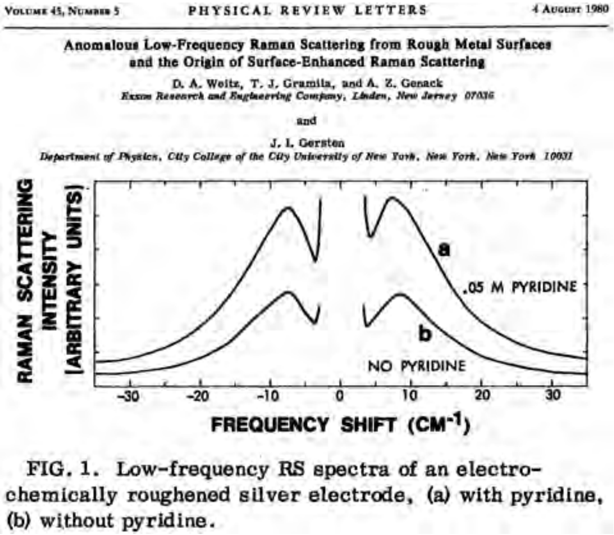
Introduction

Non-spherical shapes

Nanorods

Nanocubes

Low-frequency Raman scattering


VOLUME 45, NUMBER 5 PHYSICAL REVIEW LETTERS 4 AUGUST 1980

Anomalous Low-Frequency Raman Scattering from Rough Metal Surfaces and the Origin of Surface-Enhanced Raman Scattering

D. A. Weitz, T. J. Gramila, and A. Z. Genack
Exxon Research and Engineering Company, Linden, New Jersey 07036

and

J. I. Gersten
Department of Physics, City College of the City University of New York, New York, New York 10031

FIG. 1. Low-frequency RS spectra of an electrochemically roughened silver electrode, (a) with pyridine, (b) without pyridine.

Low-frequency Raman scattering

VOLUME 56, NUMBER 19 PHYSICAL REVIEW LETTERS 12 MAY 1986

Vibration Eigenmodes and Size of Microcrystallites in Glass: Observation by Very-Low-Frequency Raman Scattering

E. Duval, A. Boukenter, and B. Champagnon

Physico-Chimie des Matériaux Luminescents, Campus la Doua, Université Lyon I, 69622 Villeurbanne, France

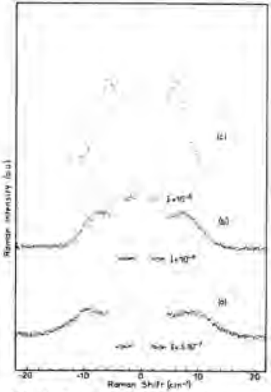


FIG. 2. Stokes and anti-Stokes very-low-frequency Raman-scattering bands due to microcrystallites after heat treatment. (a) 4 h at 875 °C and 2 h at 900 °C, (b) 4 h at 875 °C and 4 h at 900 °C, (c) 2 h at 875 °C and 10 min at 1050 °C.

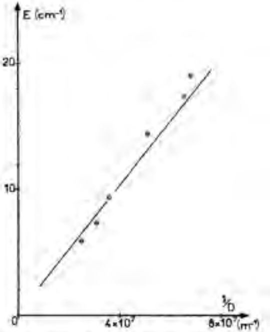
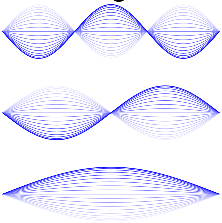


FIG. 3. Position of the very low-frequency Raman peak as a function of the inverse of the particle diameter as obtained by small-angle neutron scattering.

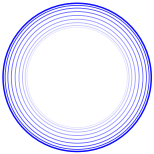
Free vibrations of nanoparticles

Eigenvibrations

1D – string

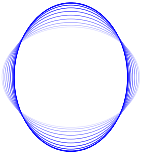


3D – sphere



breathing

spheroidal, $\ell = 0$



quadrupolar

spheroidal, $\ell = 2$

Vibration frequency

$$\text{frequency} \quad \propto \quad \frac{1}{\text{diameter}}$$

Introduction

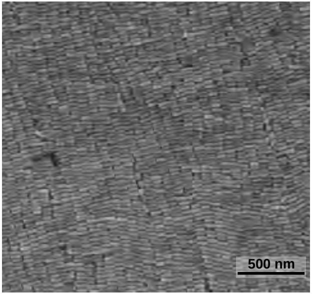
Non-spherical shapes

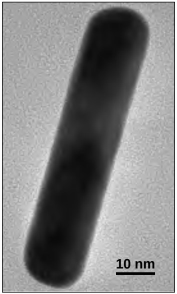
- Nanorods
- Nanocubes

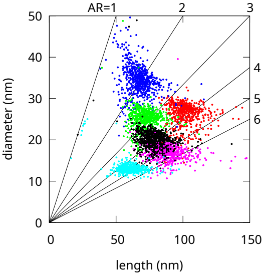
Monodomain Au nanorods

ACS Nano 2020

Synthesis: H. Portalès & N. Goubet (MONARIS)





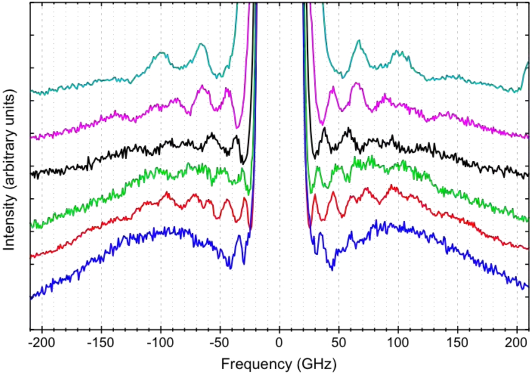


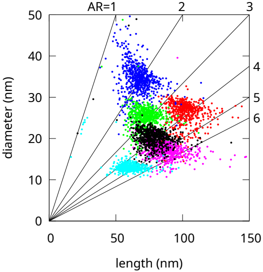
Inelastic light scattering spectra

ACS Nano 2020

Experiments: H. Portalès (MONARIS), J. Margueritat (ILM)

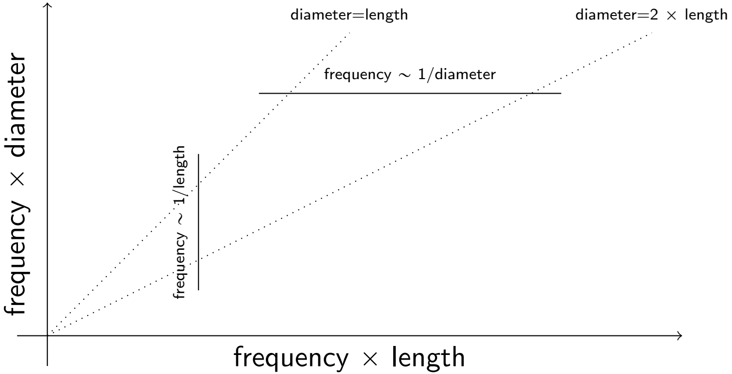
Tandem Fabry-Pérot interferometer, $\lambda = 647$ nm





Plotting frequency *vs* length and diameter

- size $\gtrsim$ few nm $\Rightarrow$ continuum elasticity $\Rightarrow$ frequency $\propto \frac{1}{\text{size}}$
- nanorod: frequency = f(diameter,length)



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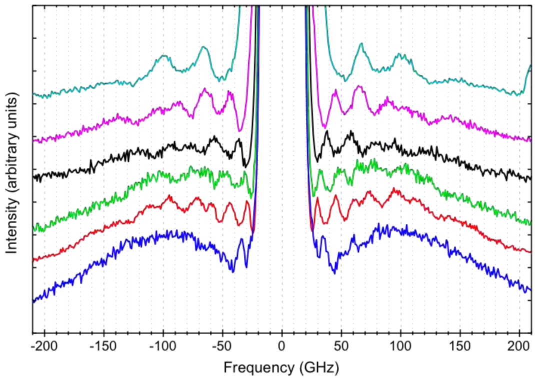

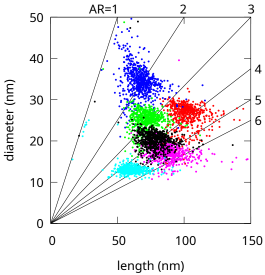

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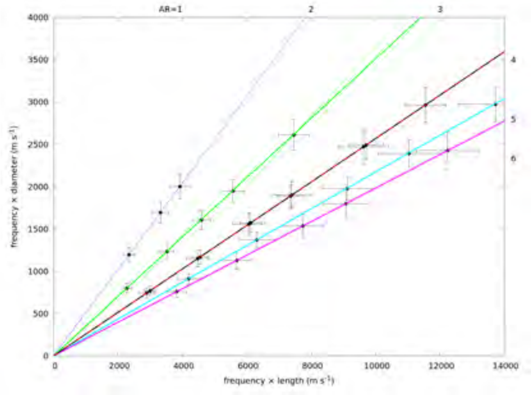

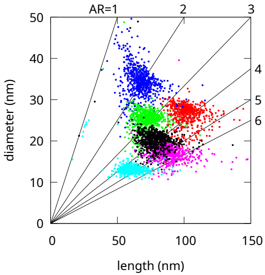

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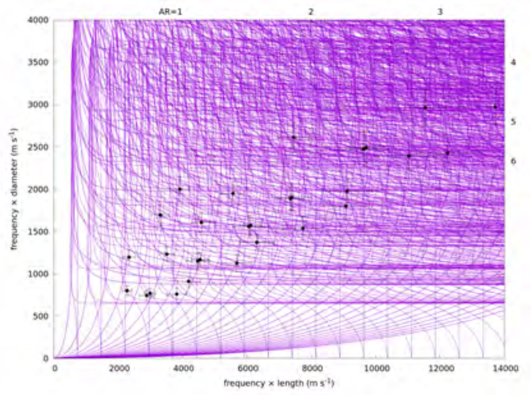

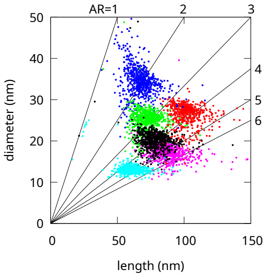

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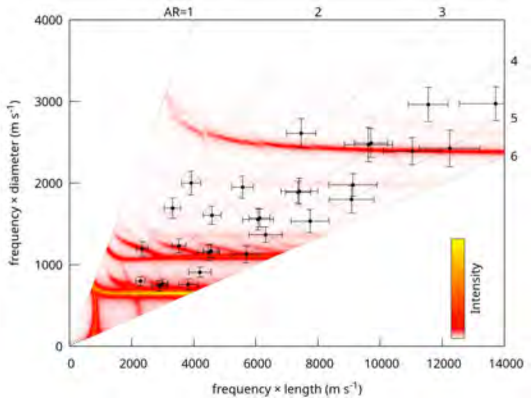
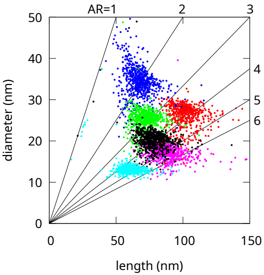
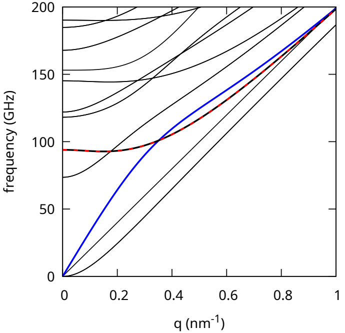




Nanowires

isotropic Au, d=10 nm

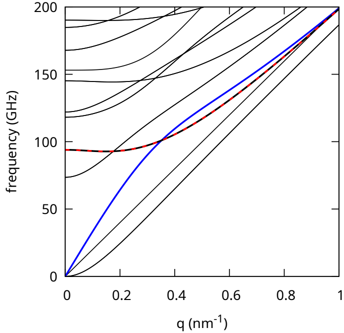


94 GHz ($m = 2$)

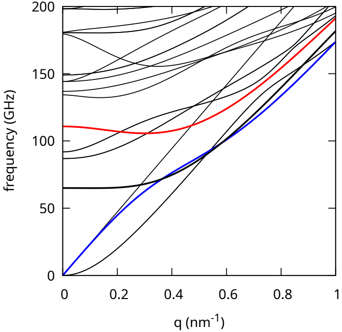
Nanowires

Nanowires

isotropic Au, d=10 nm



cubic Au, d=10 nm



94 GHz ($m = 2$)

65 GHz (B_{1g})

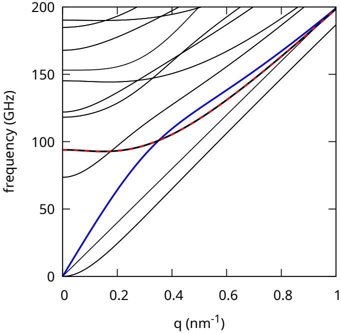
111 GHz (B_{2g})

Nanowires

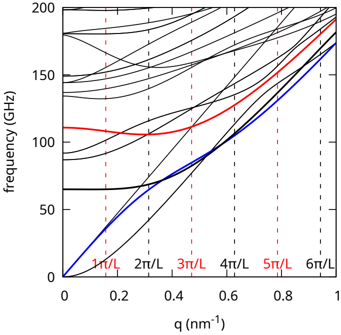
PRB 2018

Nanowires

isotropic Au, d=10 nm



cubic Au, d=10 nm



94 GHz ($m = 2$)

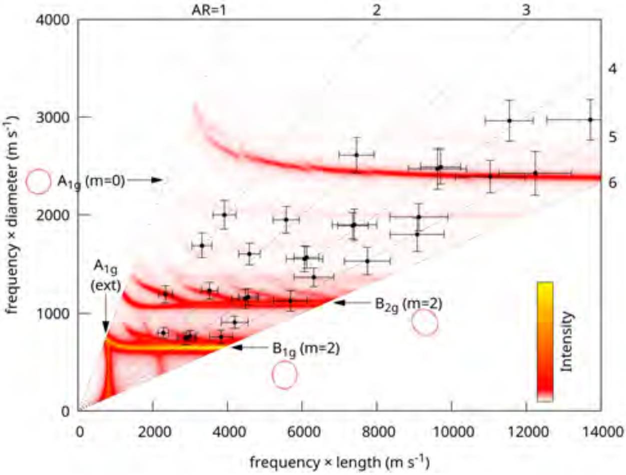
65 GHz (B_{1g})

111 GHz (B_{2g})

Assignment of the peaks II

ACS Nano 2020

Raman



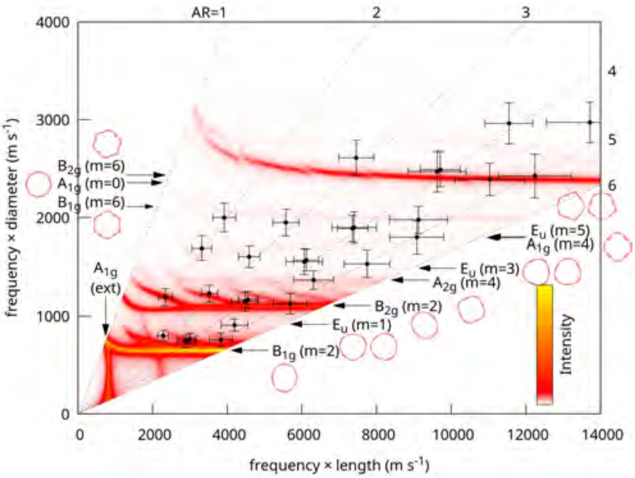
Assignment of the peaks II

ACS Nano 2020

Raman

$+$

$m = 3, 4, \cdots$

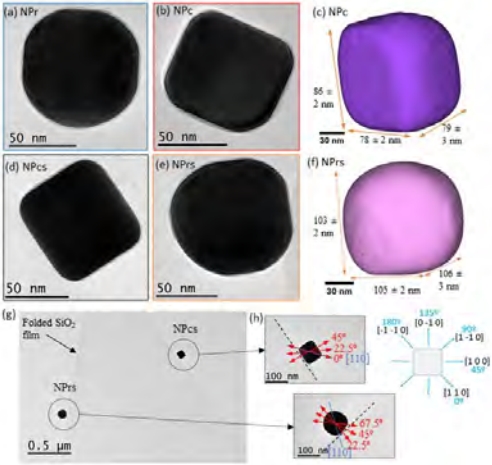


Nanocubes

JPCC 2022

Single Au nanocubes

Experiments: M. M. Timm, J. Margueritat (ILM)



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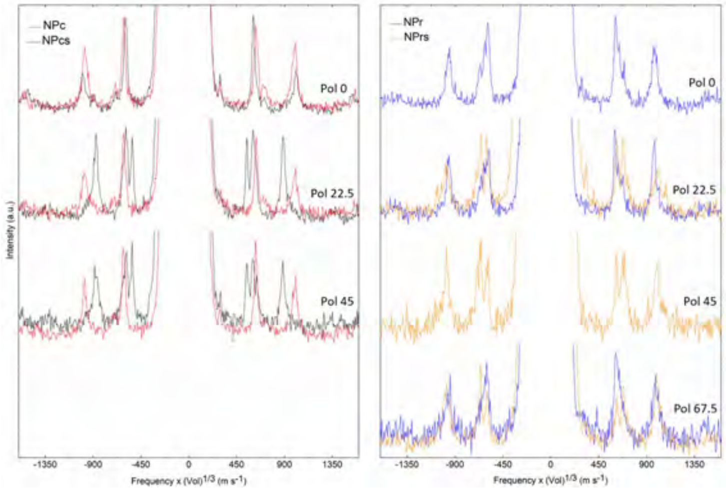

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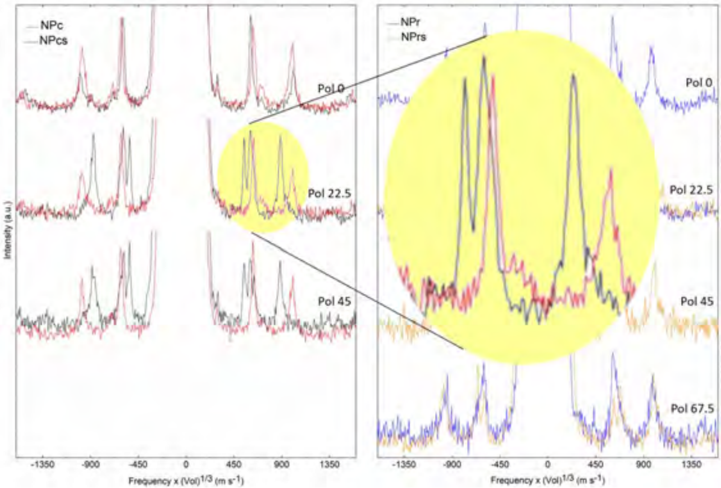

Nanocubes

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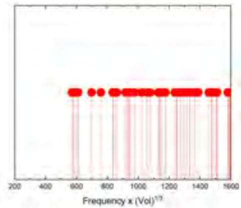
Shape used for the calculations

- FEM with 3D tomography →



Nanocubes

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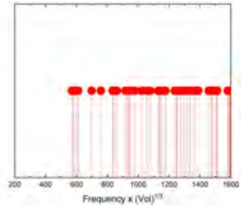
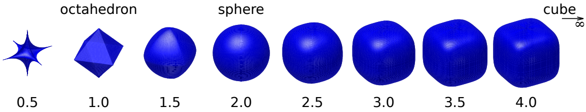


- RUS with superquadrics: $|x|^n + |y|^n + |z|^n = R^n$ Nanomaterials 2021



  - take advantage of cubic symmetry (O_h)
  - fast (web application)

https://saviot.cnrs.fr/rus/cubic/index.en.html

Nanocubes

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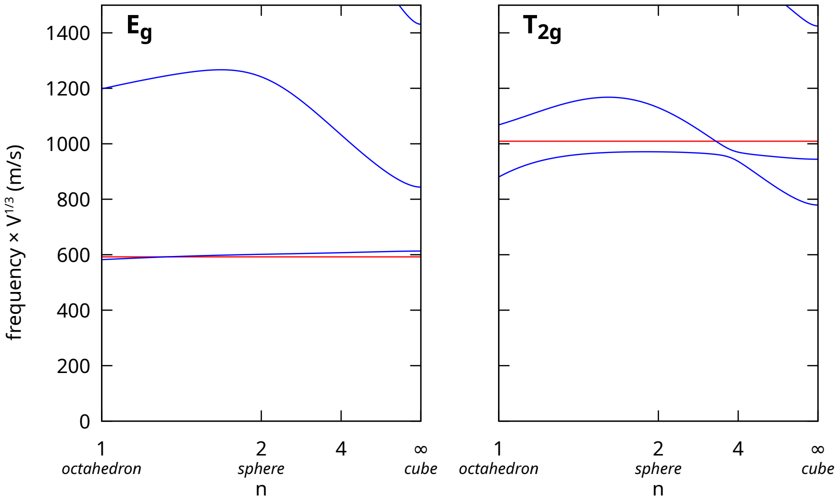
E_g-T_{2g} and shape

https://saviot.cnrs.fr/rus/cubic/index.en.html#ir=Eg&nq=2



Nanocubes

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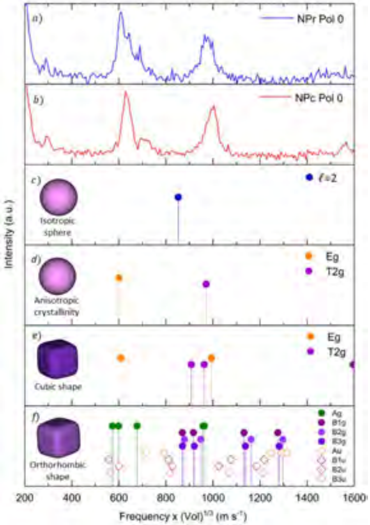
E_g-T_{2g} and shape

https://saviot.cnrs.fr/rus/cubic/index.en.html#ir=Eg&nq=2



Nanocubes

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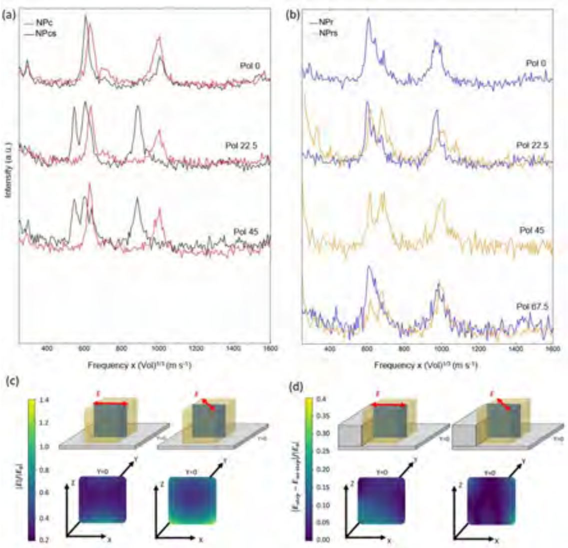
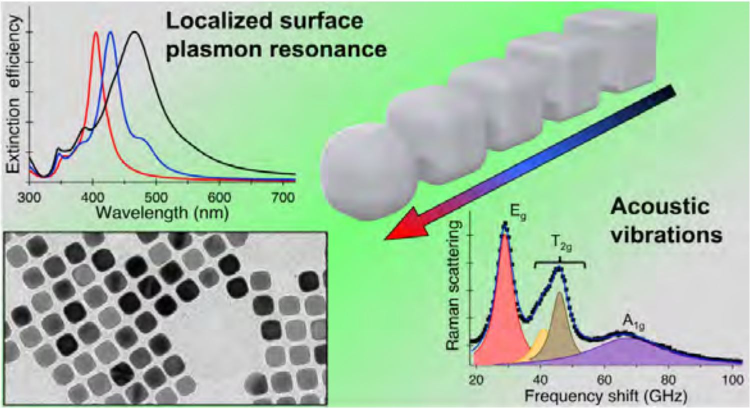
Do the Raman selection rules apply?



Nanocubes

Ensemble measurements – Ag nanocubes ACS Nano 2023

C. Vernier, H. Portalès, Y. Fan, A. Courty (MONARIS)



Nanocubes

Ensemble measurements – Ag nanocubes **ACS Nano 2023**

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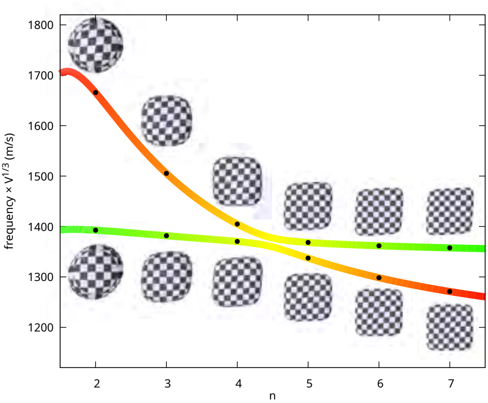

Conclusion

Does shape matter?

- Elastic anisotropy matters even more
- "breathing" and "quadrupolar"
  - nanoparticles: frequency $\times \sqrt[3]{V} \sim$ constant
  - nanowires: frequency $\times \sqrt{S} \sim$ constant

Perspectives

- more single particle measurements
- calculation of intensities

$\rightarrow$ assessing the electric field <u>inside</u> the NPs

Acknowledgments

MONARIS, UPMC

- Nicolas Goubet, Hervé Portalès

ILM, Lyon I

- Jérémie Margueritat, Alain Mermet, Mariana Timm