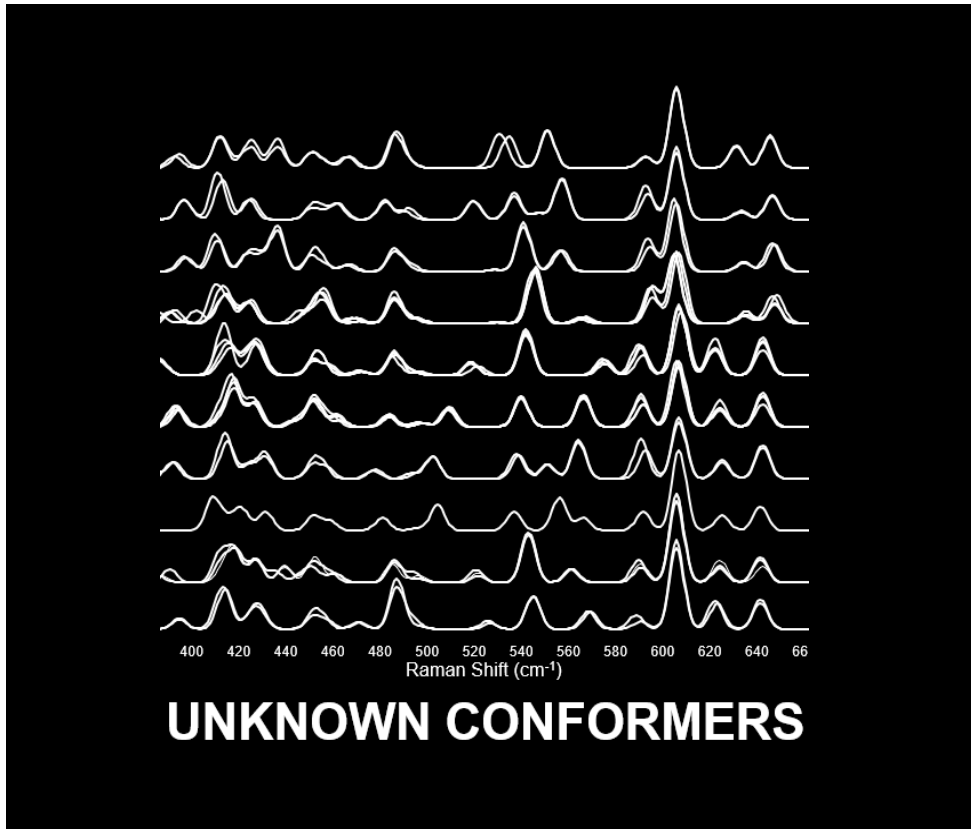
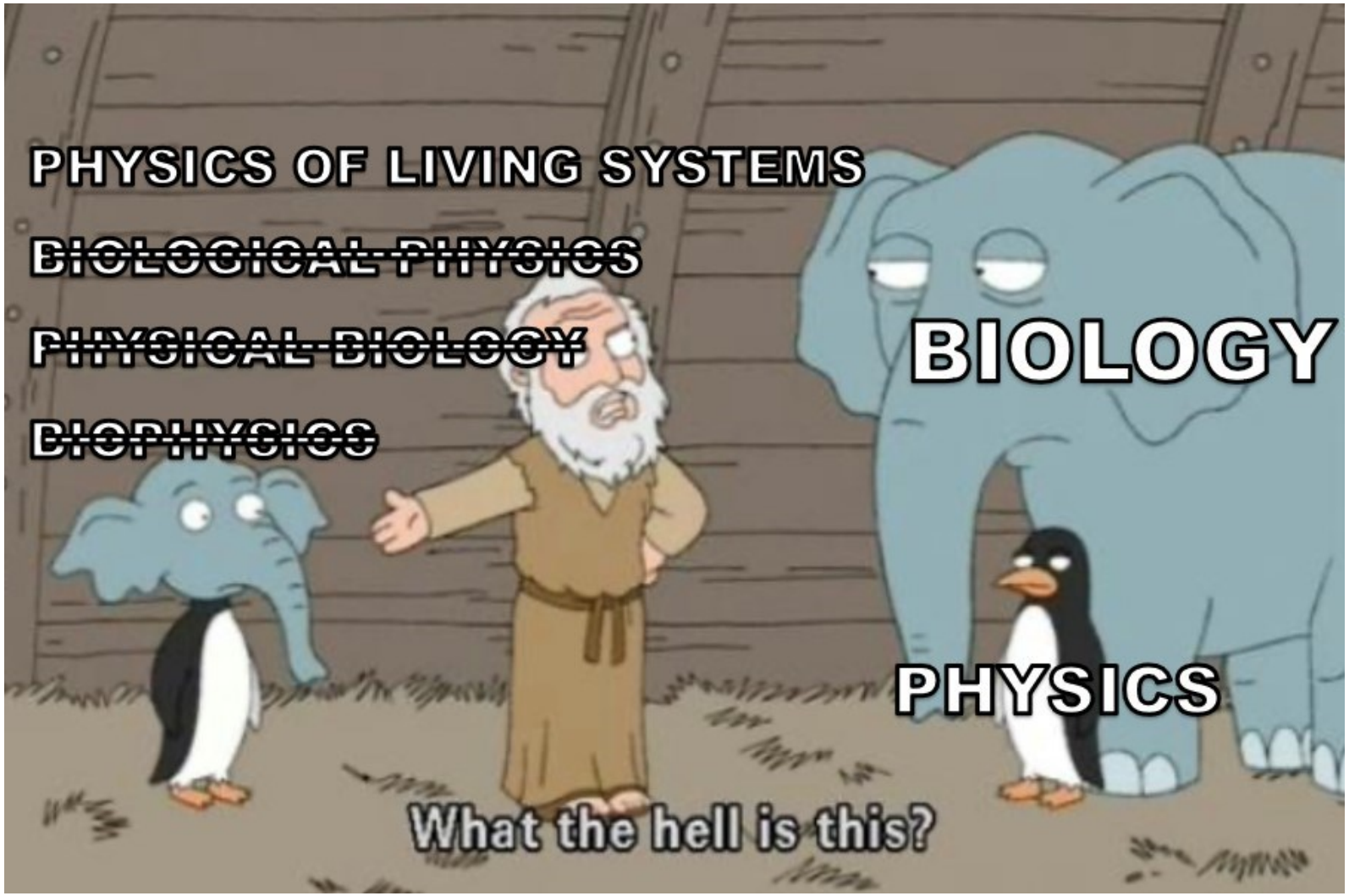
Watching Molecules Vibrate

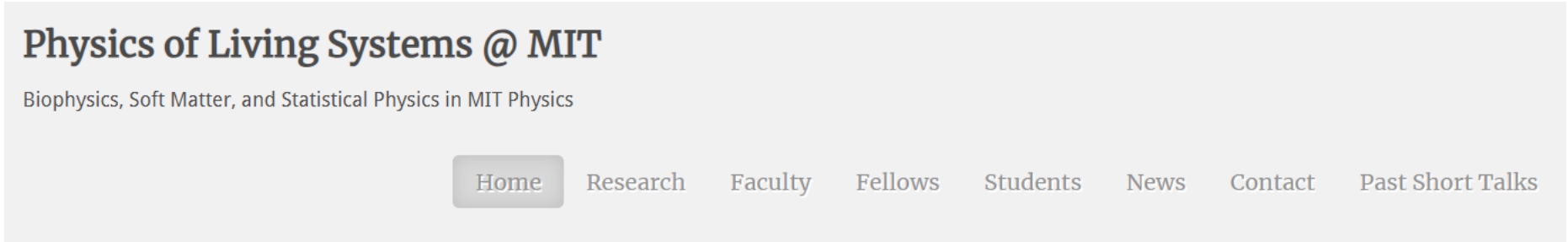


Jason Hafner
Dept. of Physics & Astronomy
Rice University

What is Biophysics?



What is Biophysics?



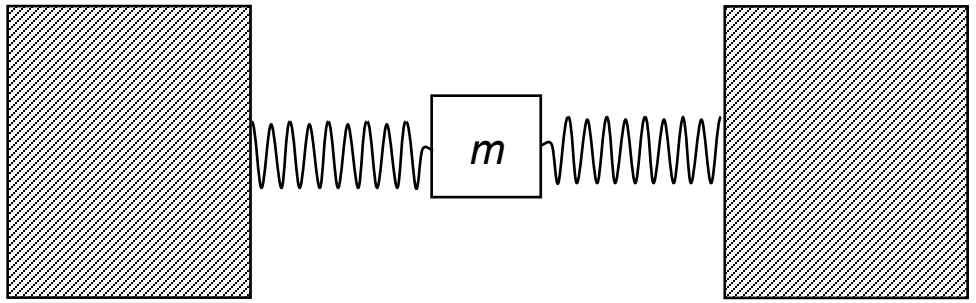
Deciphering the physical principles of organization in living and non-equilibrium systems

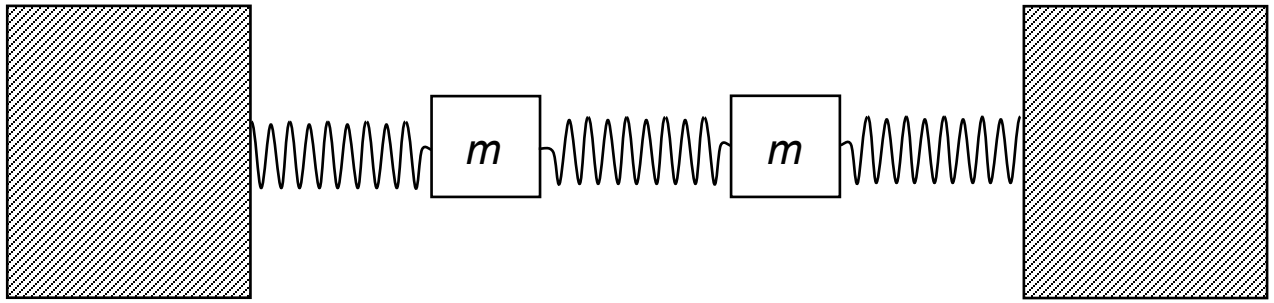
The mission of Physics of Living Systems @ MIT is to advance our understanding of living and other emergent systems across scales and to train the next generation of leaders pushing the forefront of research at the interface of physics and biology. PLS brings together biophysics, soft matter, and statistical physics researchers from across the Department of Physics at MIT. Research is conducted in eight different groups that include a total of over 70 scientists, as well as by the PLS Postdoctoral Fellows, a group of independent researchers working alongside and contributing to the PLS community.

The fields of biophysics and soft matter have experienced tremendous growth and excitement in recent years, with areas of focus ranging across all scales, from the structural organization of polymers to the evolutionary and ecological dynamics of populations.

Masses and Springs

Normal Modes – vibrations where all masses move at the same frequency.





https://www.falstad.com/coupled/

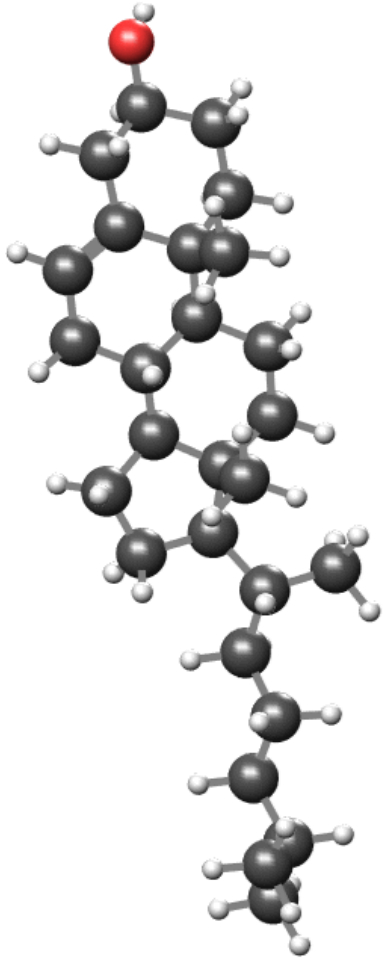
Masses and Springs

Molecules can be very accurately approximated as masses on springs.

-Nuclei are masses

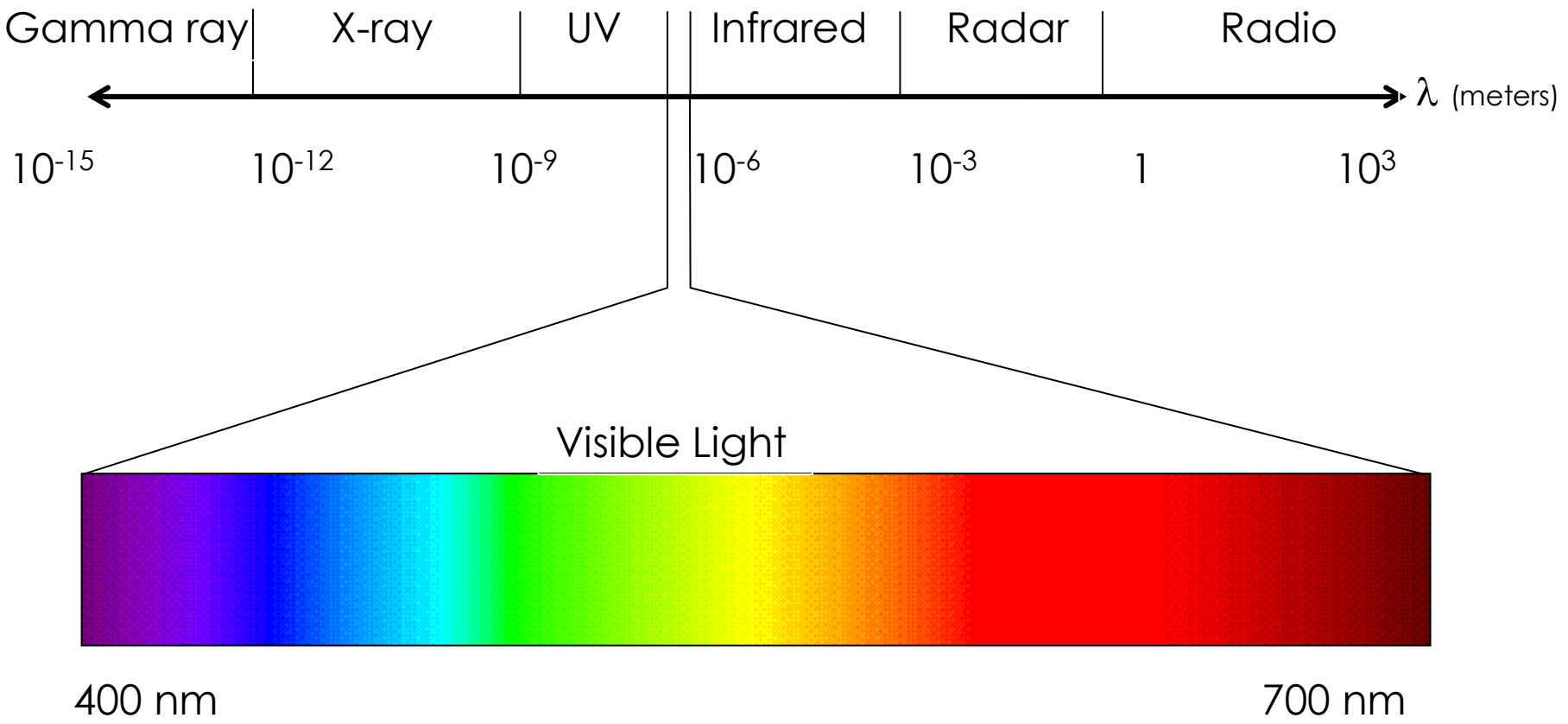
-Bonds are springs

-They are arranged in 3D



Vibrational Spectroscopy

Measure molecular and crystalline vibrations through their interaction with EM radiation.

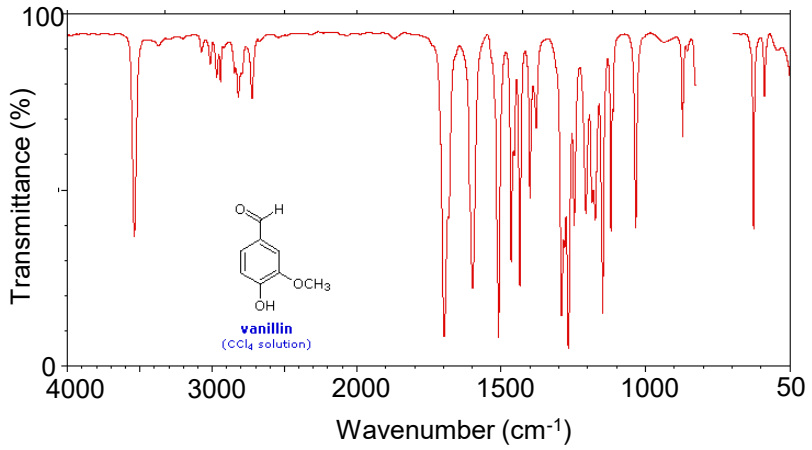


Vibrational Spectroscopy

Measure molecular and crystalline vibrations through their interaction with EM radiation.

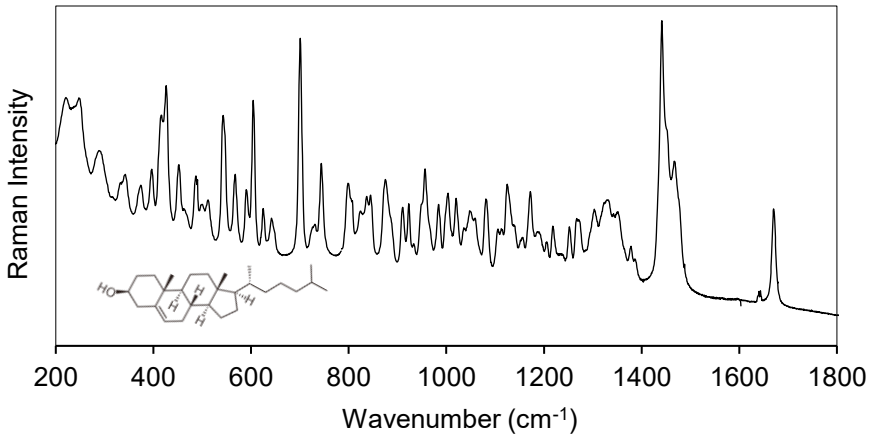
Direct Absorption (IR)

- Dipole moment oscillates with vibration
- Infrared light (λ = 2 – 20 microns)
- Water absorbs very strongly

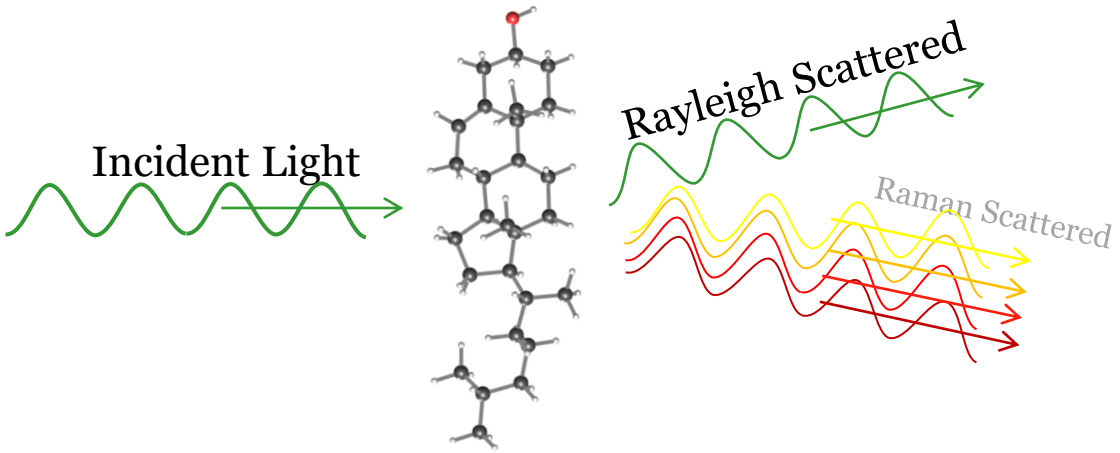


Inelastic Scattering (Raman)

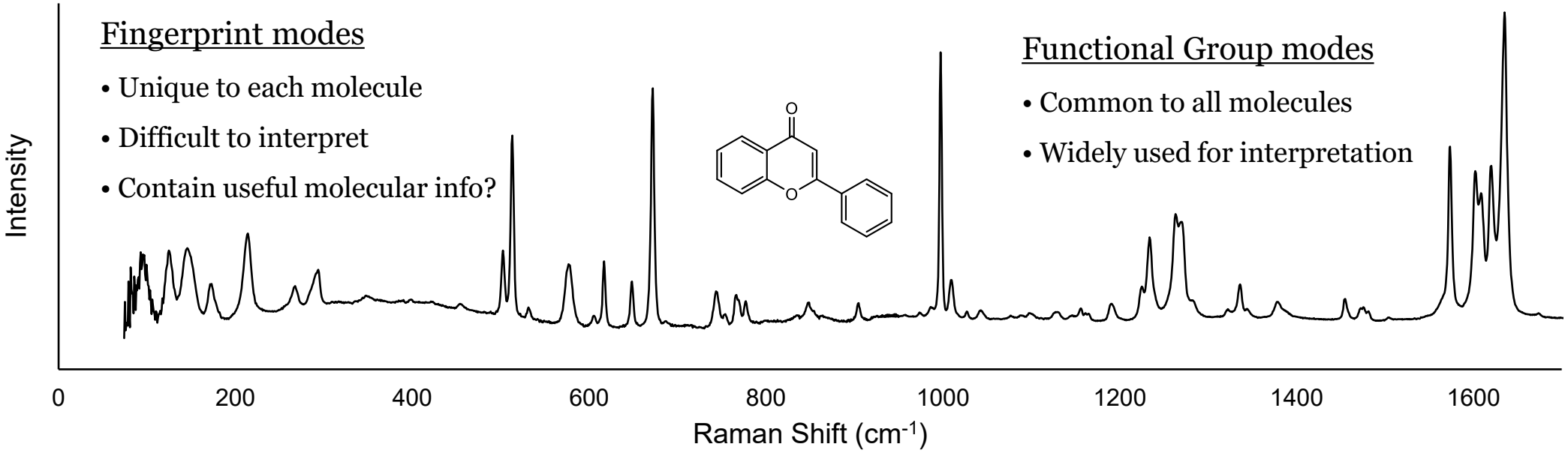
- Polarizability changes with vibration
- Visible light (λ = 300 – 1000 nm)
- Very weak signal from water



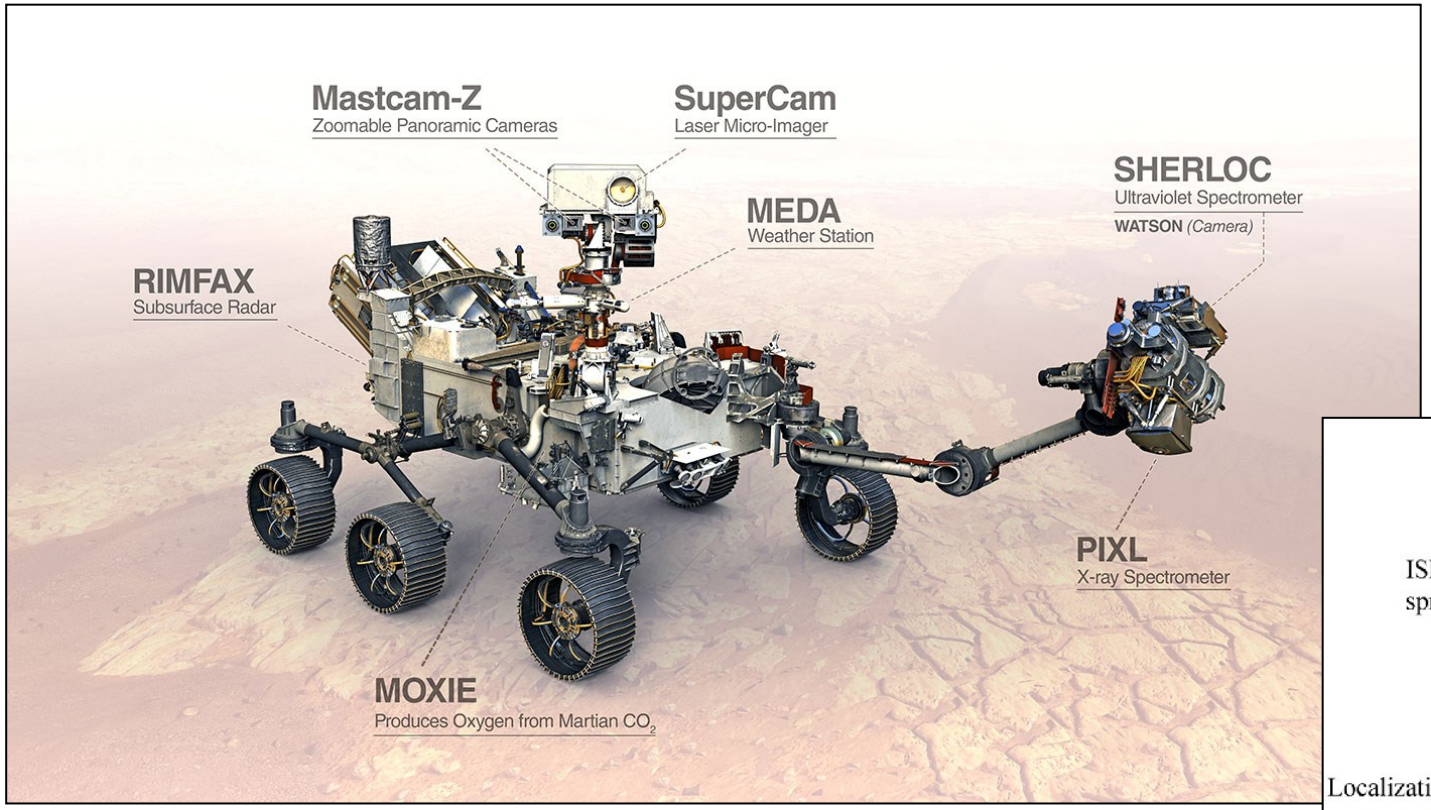
Raman Spectroscopy

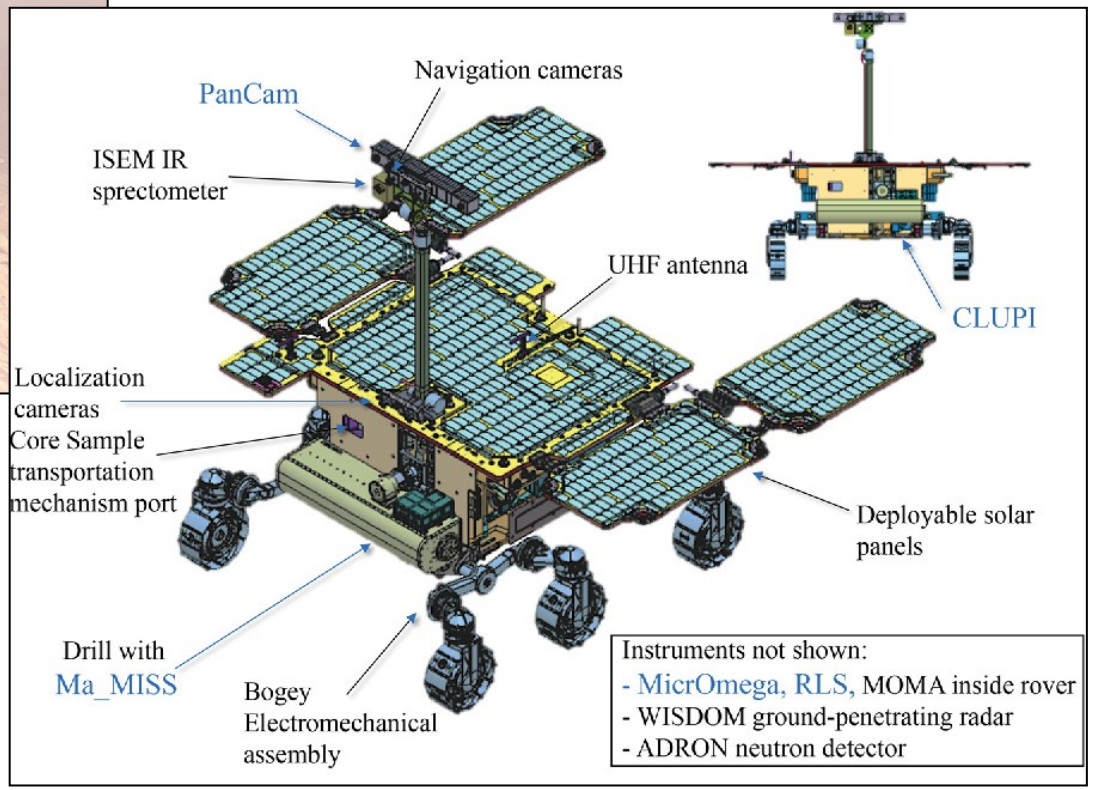


- Detect specific molecules/minerals by comparing measured spectrum to a spectral database.
- Detect common functional groups.
- Study changes in molecular conformation, environment, or assembly.



Raman in Astrobiology!





Extremophiles

JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2004; **35**: 463–469
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jrs.1172

JRS

Protective pigmentation in UVB-screened Antarctic lichens studied by Fourier transform Raman spectroscopy: an extremophile bioresponse to radiation stress

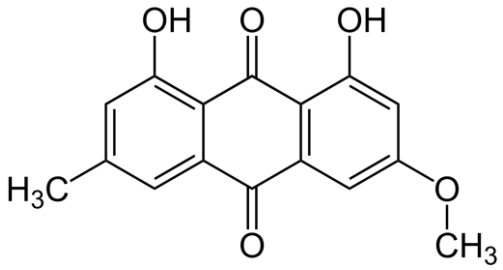
Howell G. M. Edwards,[1]* Charles S. Cockell,[2] Emma M. Newton[1] and the late David D. Wynn-Williams[2]

[1] Department of Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK
[2] British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK

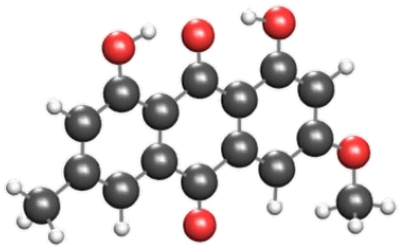
Plate 1. Colonies of *Xanthoria* and *Caloplaca* epilithic lichen on Leonie Island, maritime Antarctica; specimens of the extremophile lichens studied in this work.

Extremophiles

Parietin



4



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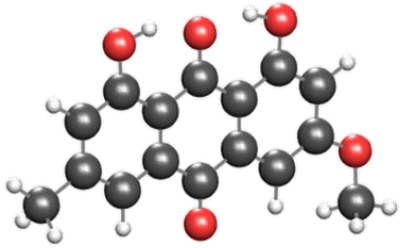
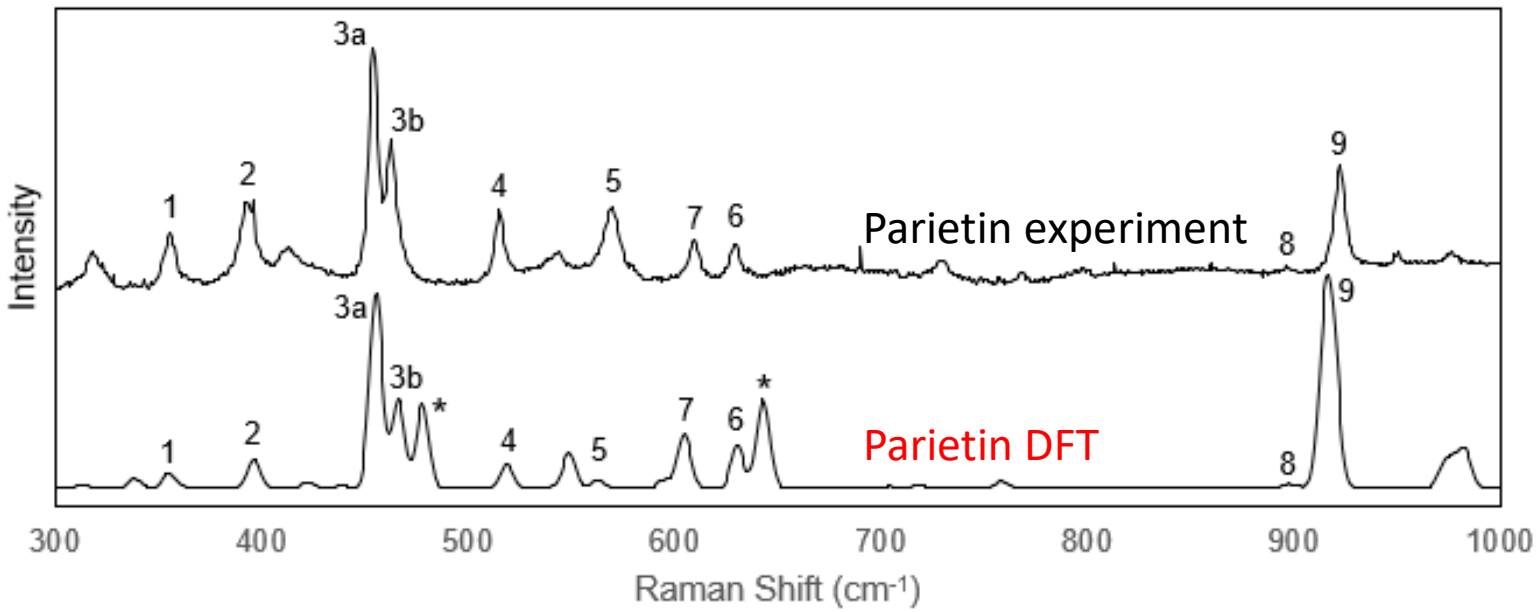




Simeral, Hafner, Astrobiology v. 22, p. 1165-1175 (2022).

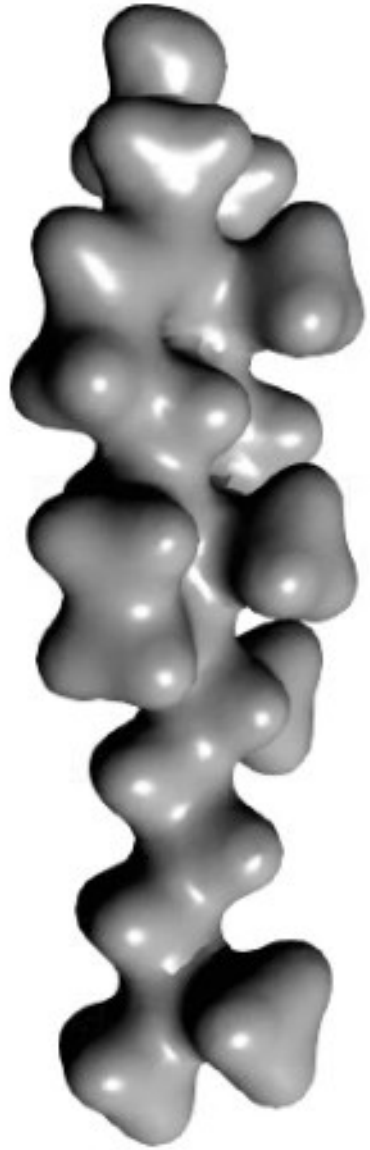
Density Functional Theory

Solve Schrodinger's Equation

Optimize Structure (minimize E)

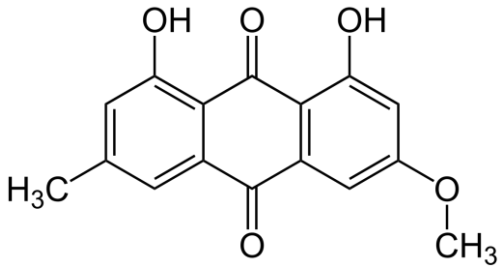
Calculate Normal Mode Frequencies

Calculate Pol Change (Raman)



Extremophiles

Parietin



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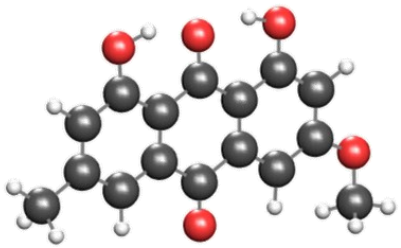

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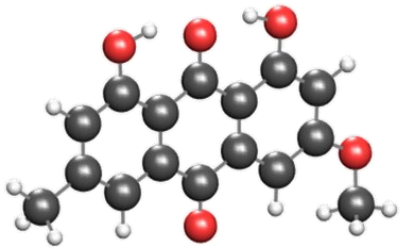
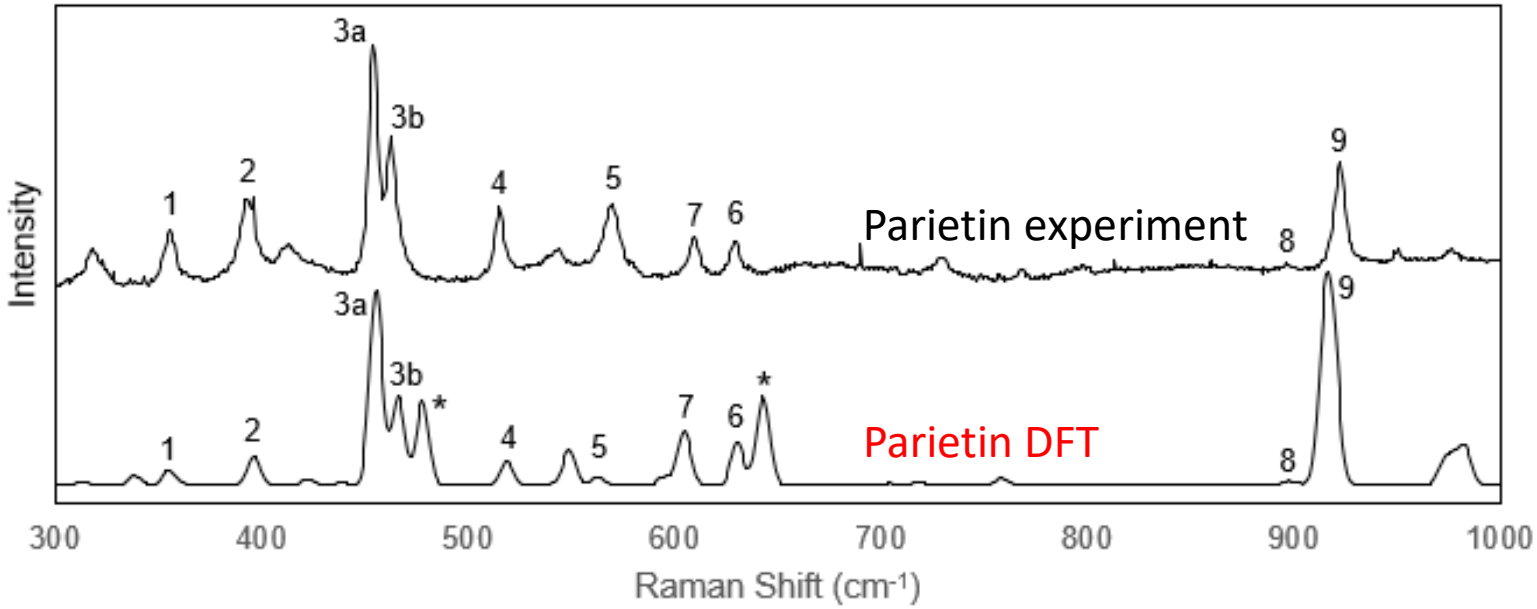
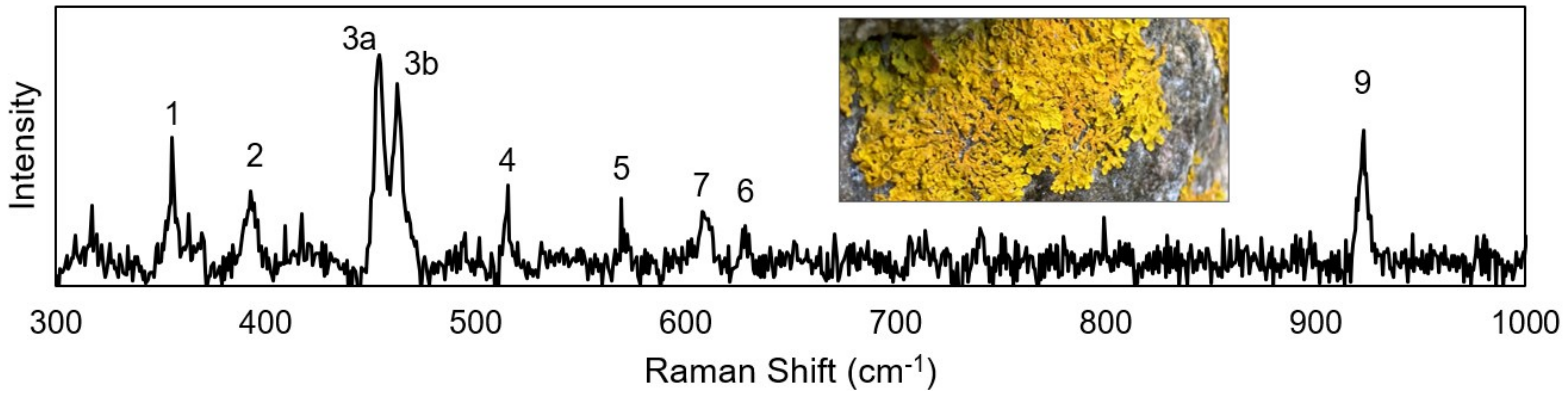


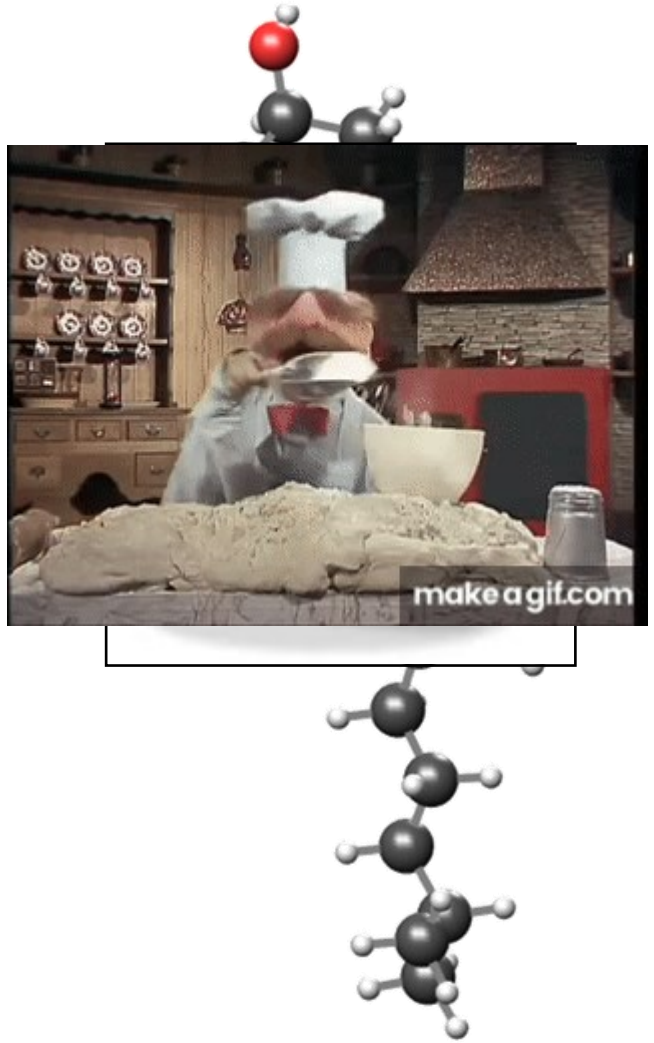


Xanthoria parietina

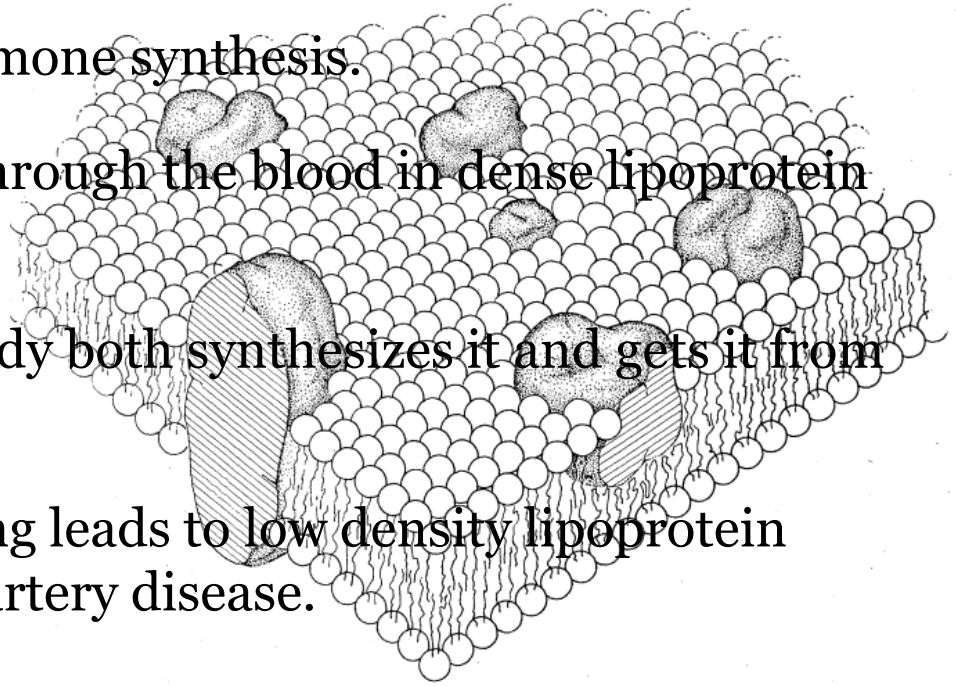


Simeral, Hafner, Astrobiology v. 22, p. 1165-1175 (2022).

Cholesterol

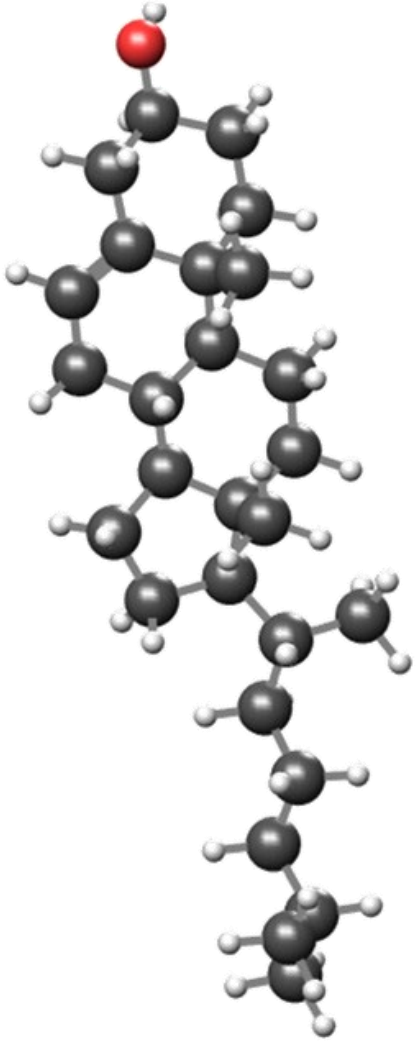


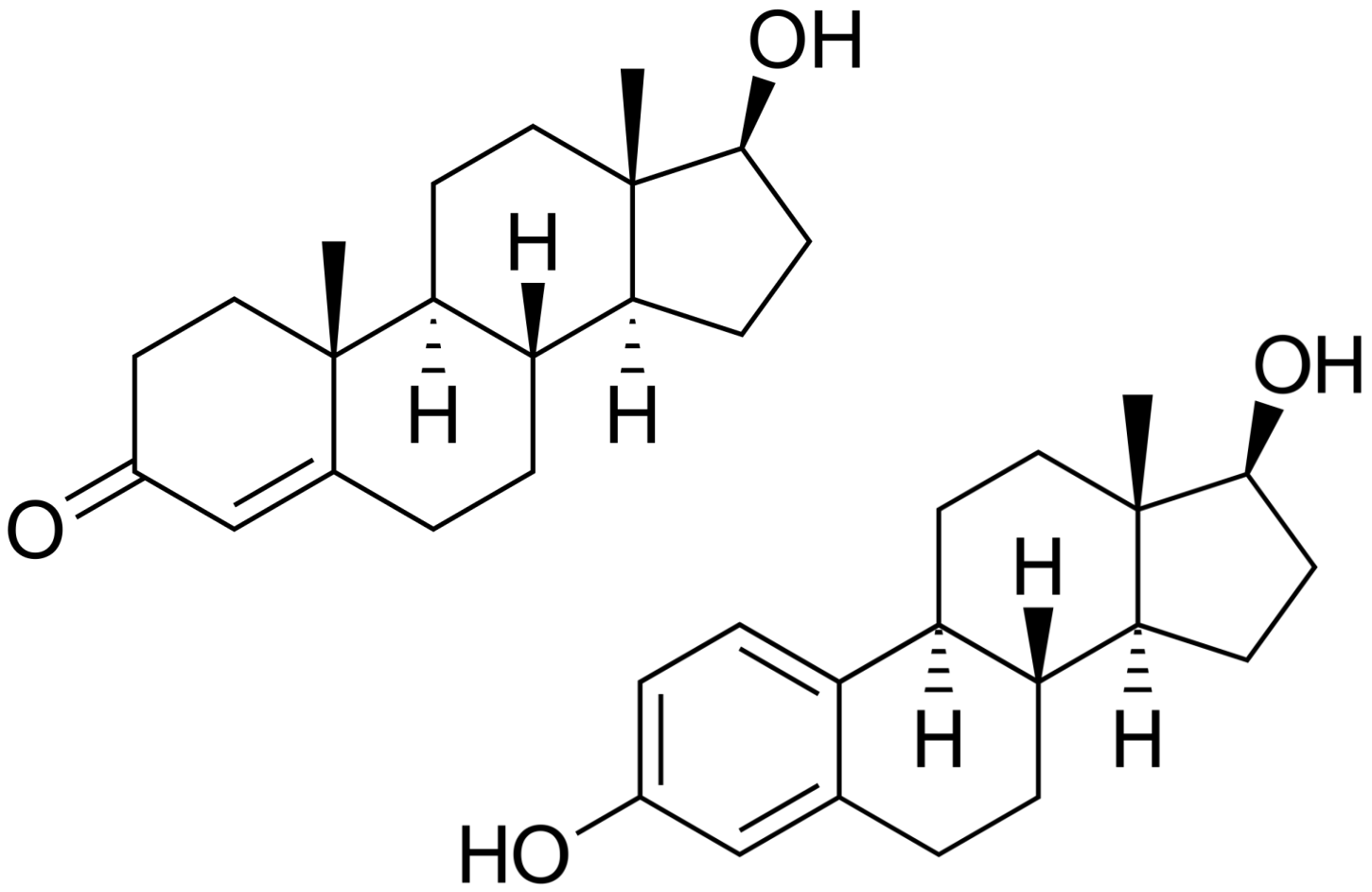
- Cholesterol makes up ~40% of mammalian plasma membrane and modulates membrane “mechanical” properties.
- It is a component of “lipid rafts”.
- It directly interacts with membrane proteins to affect function.
- It is a precursor for hormone synthesis.
- It is heavily trafficked through the blood in dense lipoprotein particles.
- You need a lot - your body both synthesizes it and gets it from your diet.
- Too much of a good thing leads to low density lipoprotein particles and coronary artery disease.



Singer and Nicolson, Science v. 175, p 720, 1972

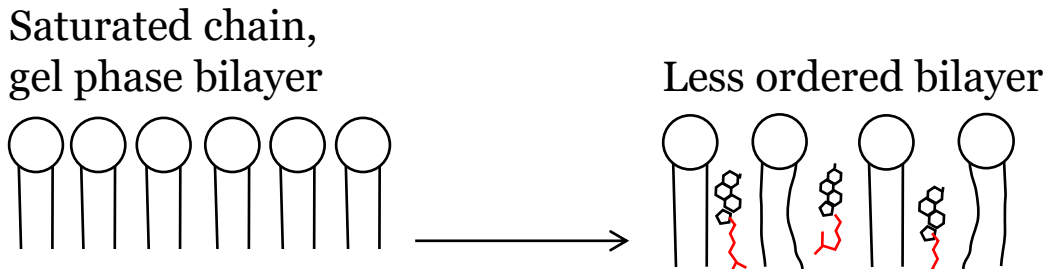
Steroids

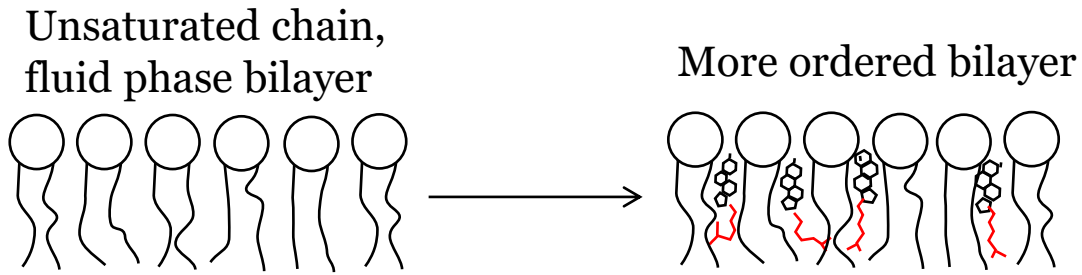




Cholesterol in Lipid Membranes

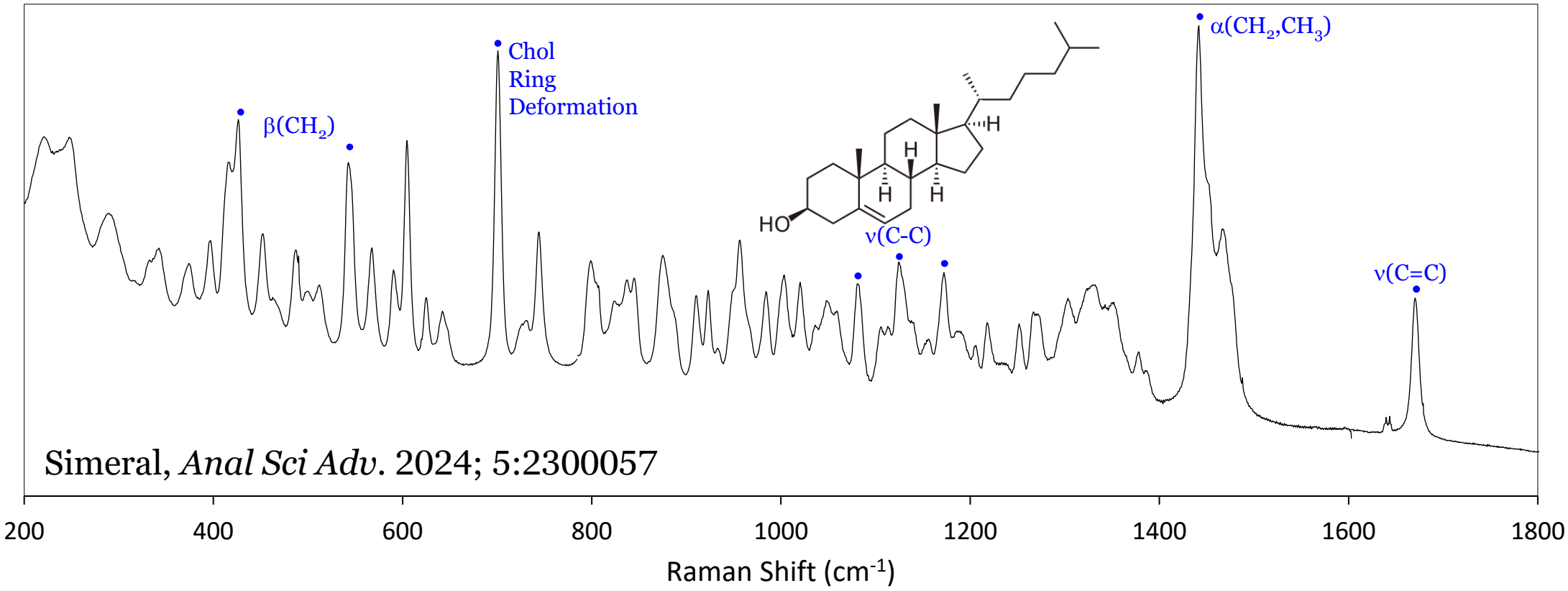
Cholesterol makes crystalline membranes more fluid by reducing order, and makes fluid membranes more ordered (condensation). How?





Detailed structures and mechanisms unclear. Main tools available are NMR and snapshots from Molecular Dynamics.

Molecular Vibrations of Cholesterol

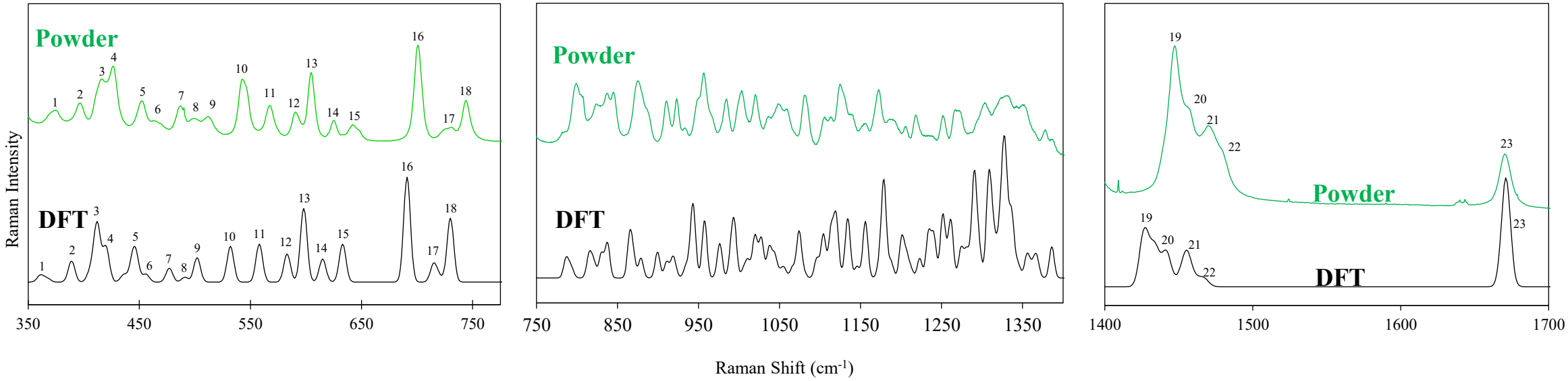


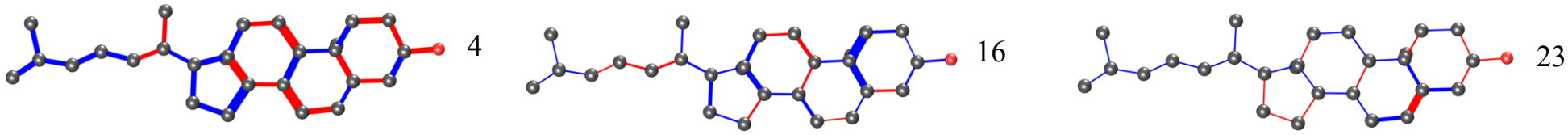
bone vibrations, is exceptionally characteristic for CHL. Their assignment is ambiguous; most probably, the band at 701 cm^{-1} is associated with the in-plane deformations of the ring involving the double bond, whereas the bands at 424 and 548 cm^{-1} result from a combination of bending vibrations of the C–H groups in the chain and rings.

Czamara et al, J. Raman Spectroscopy v 46 p 4-10, 2015

DFT of the Cholesterol Raman Spectrum

- BP86 functional, dispersion corrected, damped
- Quad Z all-electron basis set
- 0.004 mHartree bond energy accuracy
- ~ 1 week on an 8-core PC

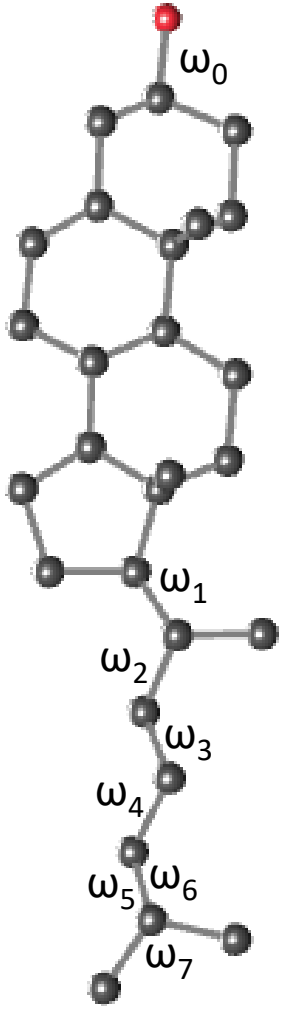




Simeral, *Anal Sci Adv*. 2024; 5:2300057

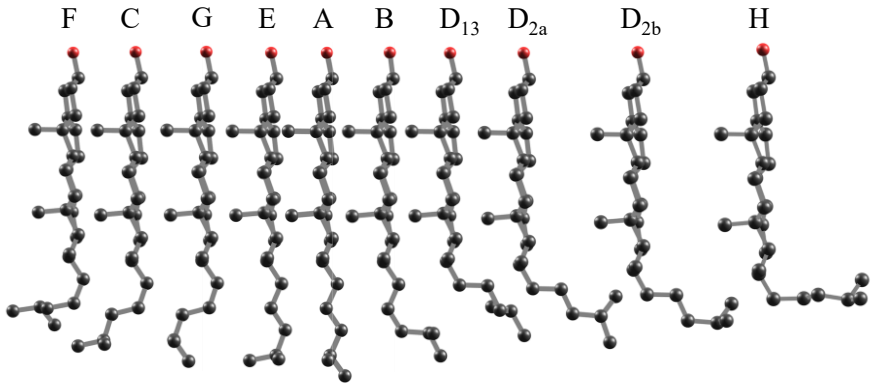
Chain Conformers

Consider 7 dihedral angles:



Type	Conf	chol	ω_0	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	E(kcal/mol)
A	1	5	182	180	190	176	176	187	63	-56	0.63
A	2	8	182	180	192	178	185	-63	173	56	0.66
A	3	7	57	180	191	176	176	187	63	-56	0.76
A	4	12	-63	180	192	177	185	-63	174	56	0.77
B	1	16	182	180	195	181	-59	-57	180	62	0.7
B	2	26	-63	180	195	180	-59	-57	180	62	0.8
B	3	22	-63	180	191	173	60	181	58	-61	0.73
B	4	17	57	179	195	180	-59	-57	180	62	0.82
C	1	15	58	180	184	59	172	187	63	-56	0.57
C	2	21	-63	180	183	59	173	187	63	-55	0.59
C	3	13	182	180	183	59	179	-65	172	54	0.69
$D_{1,3}$	1	10	-62	176	62	174	60	182	58	-61	0.42
$D_{1,3}$	2	1	57	176	62	175	61	182	58	-61	0.43
$D_{1,3}$	3	20	58	176	62	177	96	-61	175	58	2.06
$D_{1,3}$	4	9	163	174	63	183	-63	-57	179	62	0.54
D_{2a}	1	0	180	176	61	179	183	-63	174	56	0.36
D_{2a}	2	3	-62	176	61	178	175	187	63	-56	0.5
D_{2b}	1	4	180	176	61	178	179	63	-63	180	0.98
D_{2b}	2	11	-61	174	61	176	179	63	-63	180	1.08
E	1	14	181	180	189	175	180	63	-63	180	1.25
E	2	23	-63	180	190	176	180	63	-63	180	1.37
F	1	19	181	179	187	55	55	183	59	-59	0
F	2	58	-63	180	187	55	55	183	59	-59	0.11
G	1	24	182	180	183	59	177	63	-63	180	1.28
G	2	49	297	180	184	59	174	61	-65	178	1.38
H	1	30	179	177	50	65	169	186	63	-56	1.86
H	2	59	182	177	49.3	63	172	-68	168	51	2.24

Structure types correlate to chain deviation from steroid ring plane.

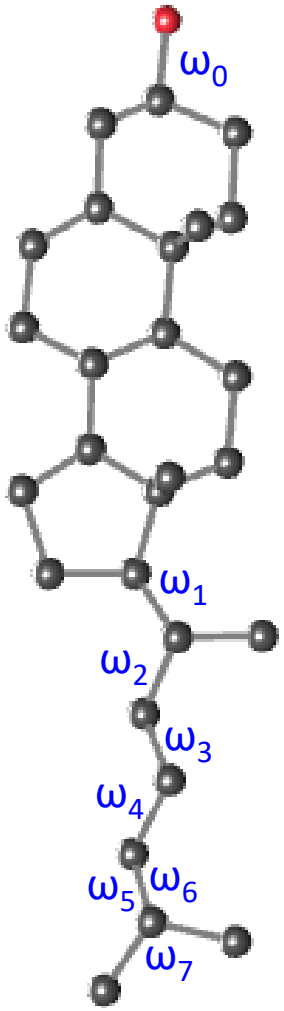


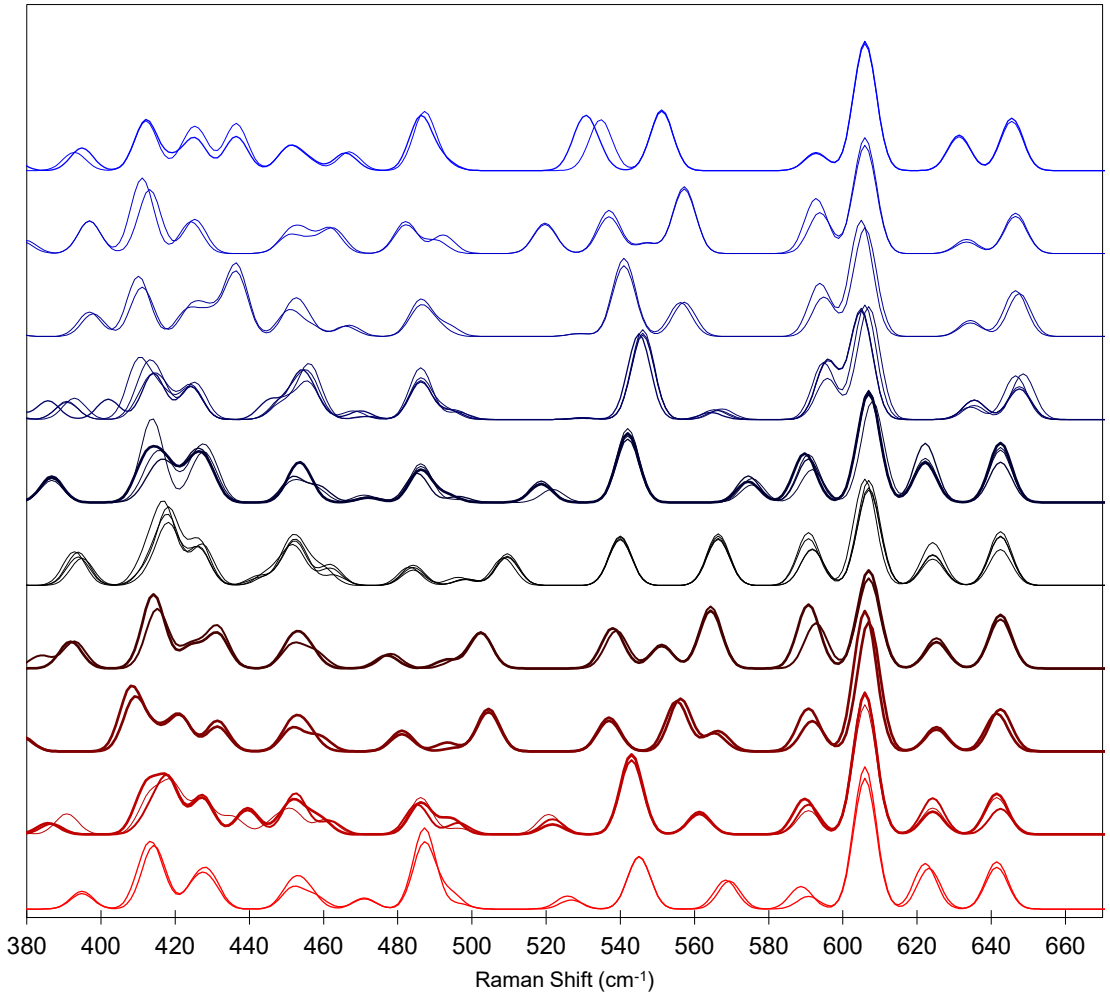
Original A-D structure type assignments:
Duax et al, *Lipids* v. 15, p. 783-792, 1980

Birkenfeld, Hafner, in preparation

Chain Conformers

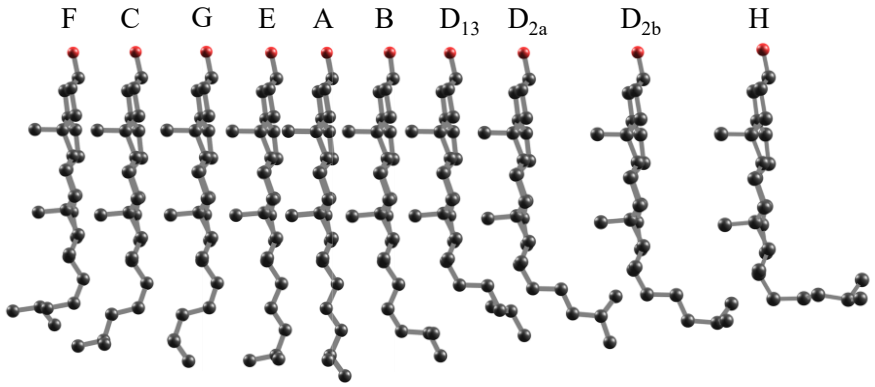
Consider 7 dihedral angles:





Structure types are also spectral types in the low frequency region!!

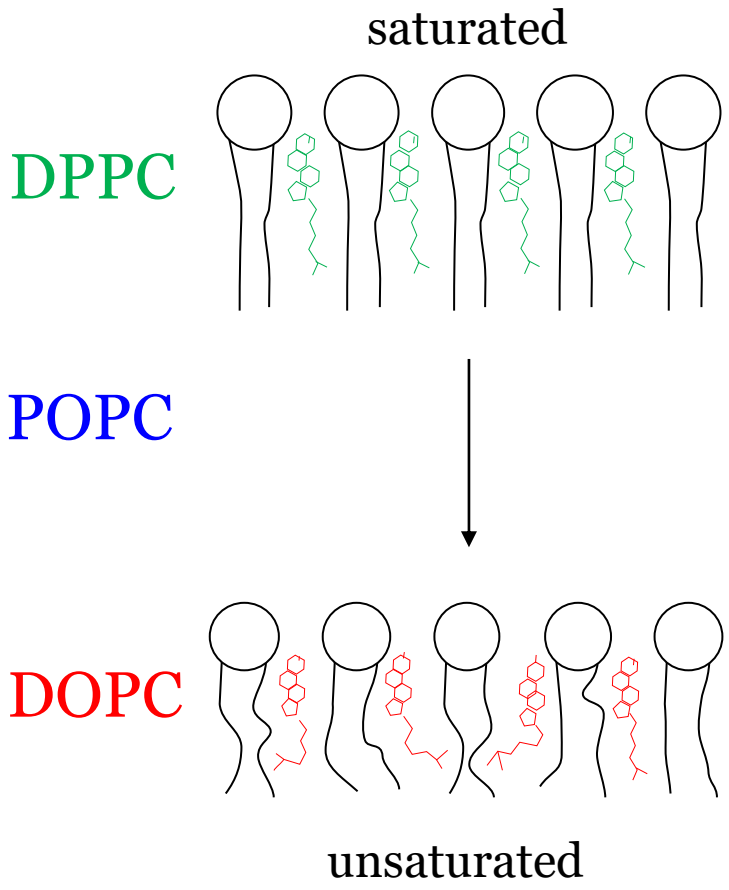
Structure types correlate to chain deviation from steroid ring plane.

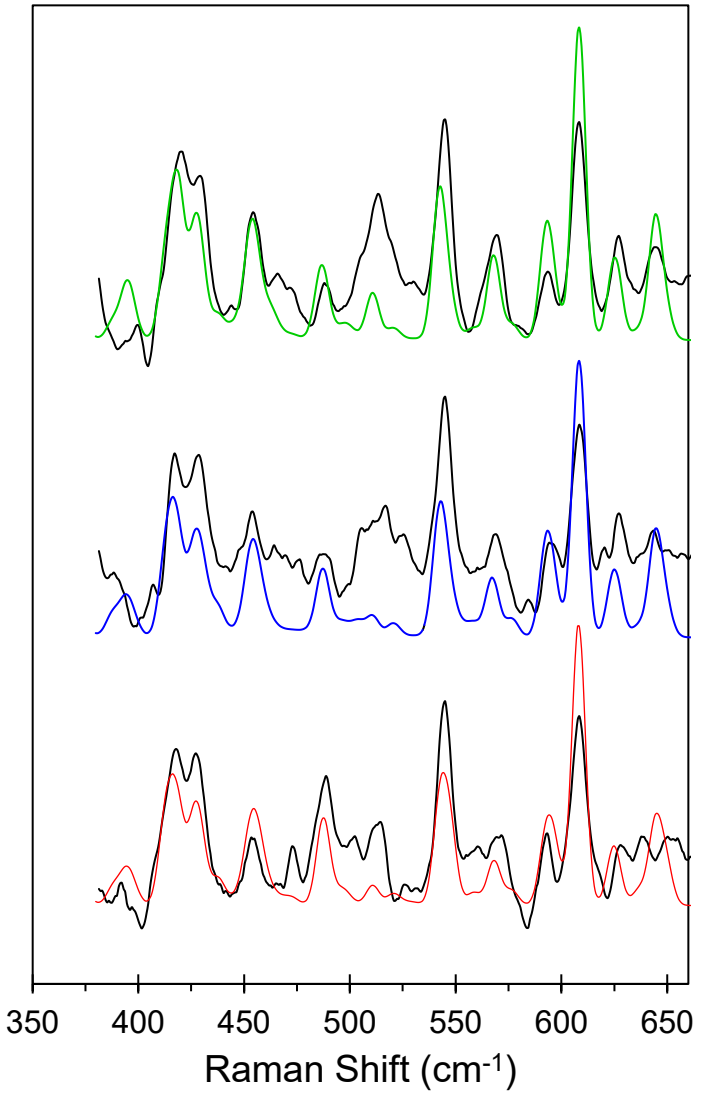


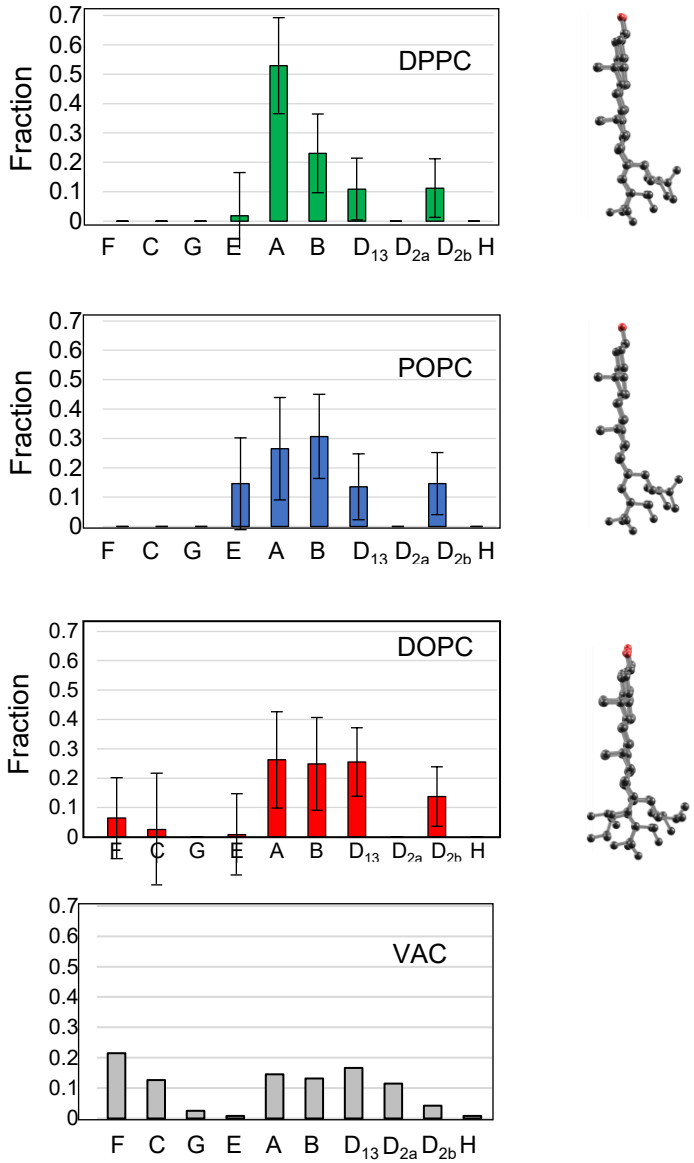
Original A-D structure type assignments:
Duax et al, *Lipids* v. 15, p. 783-792, 1980

Birkenfeld, Hafner, in preparation

Cholesterol in Phospholipids with Different Order







Birkenfeld, Hafner, in revision

Cholesterol's Role in Phospholipid Membrane Properties

THE LANCET, APRIL 25, 1925.

Croonian Lectures

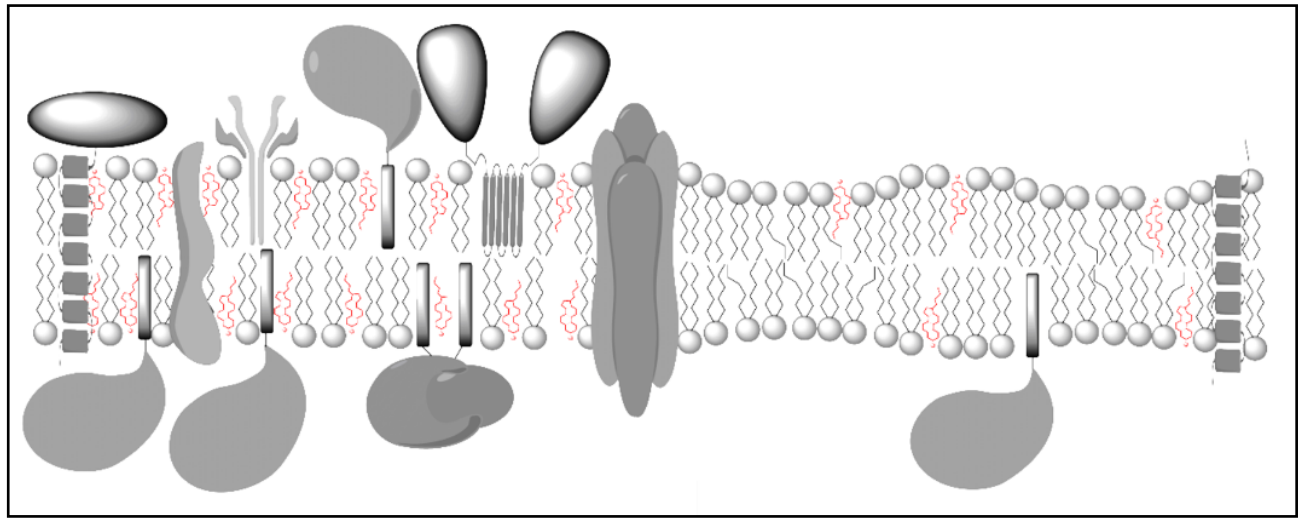
ON THE

RÔLE OF FATS IN VITAL PHENOMENA.

BY J. B. LEATHES, F.R.C.P. LOND., F.R.S.,
PROFESSOR OF PHYSIOLOGY, UNIVERSITY OF SHEFFIELD.

LECTURE II.*

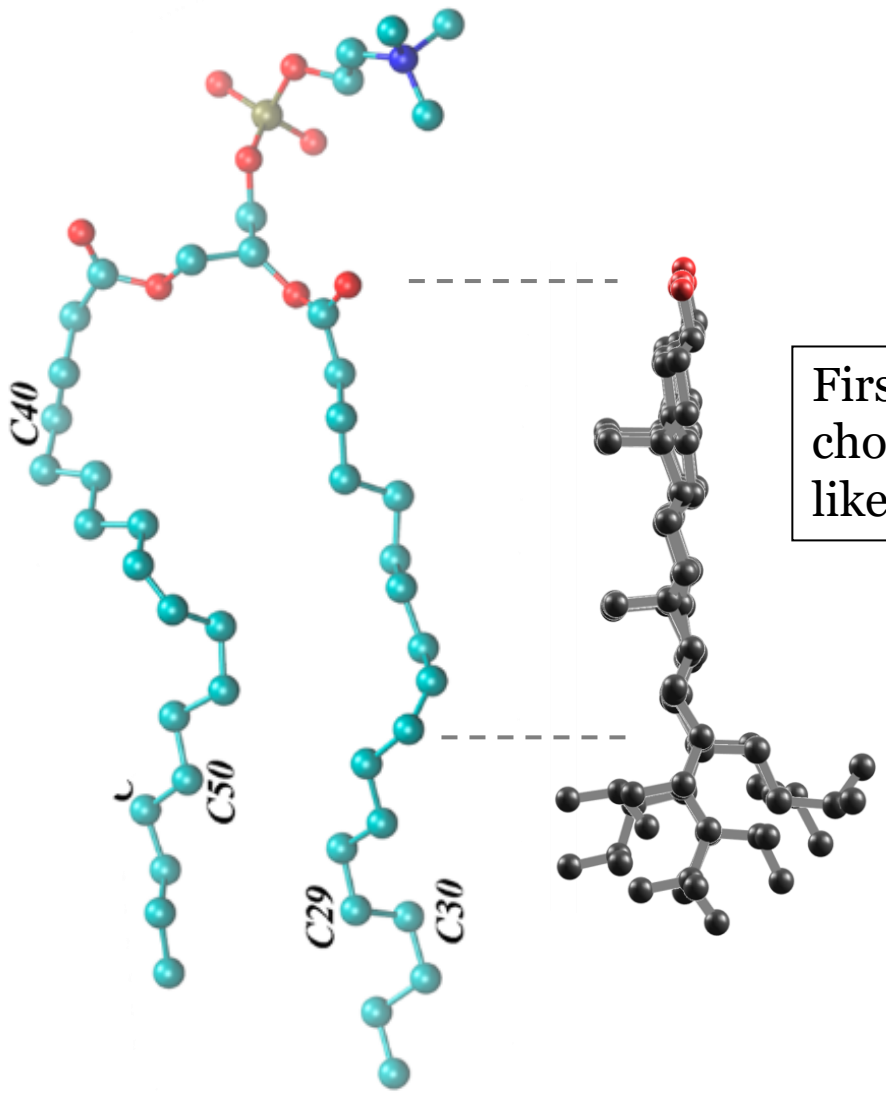
THE attempts to make intelligible the rôle of fats in the life of the cell which I tried to review in Lecture I. fail to satisfy the needs, and we have to search for further knowledge of the physical behaviour of fatty substances insoluble in water before we can form ideas that approach the truth. How near we may hope to get with available data we can only determine after taking count of certain facts that have not yet been generally incorporated in the scheme of biological studies.



Krause and Regen, *Acc. Chem. Res.* 2014

- Cholesterol provides a surface for van der Waals interaction with phospholipid chains that reduce their conformational space (lengthens and orders).
- Both rings and chain contribute to these effects. Their precise structures are important.
- Cholesterol has a stronger interaction with saturated phospholipid chains.

Cholesterol's Role in Phospholipid Membrane Properties



Khelasvili and Harries, *JPCB* 2013

First three carbons of the cholesterol chain are "rigid" like the rings.

The variable part of the cholesterol chain begins at the unsaturated bond position of the phospholipid chain.

Stone Tools

The Origin of The Acheulean: The 1.7 Million-Year-Old Site of FLK West, Olduvai Gorge (Tanzania)

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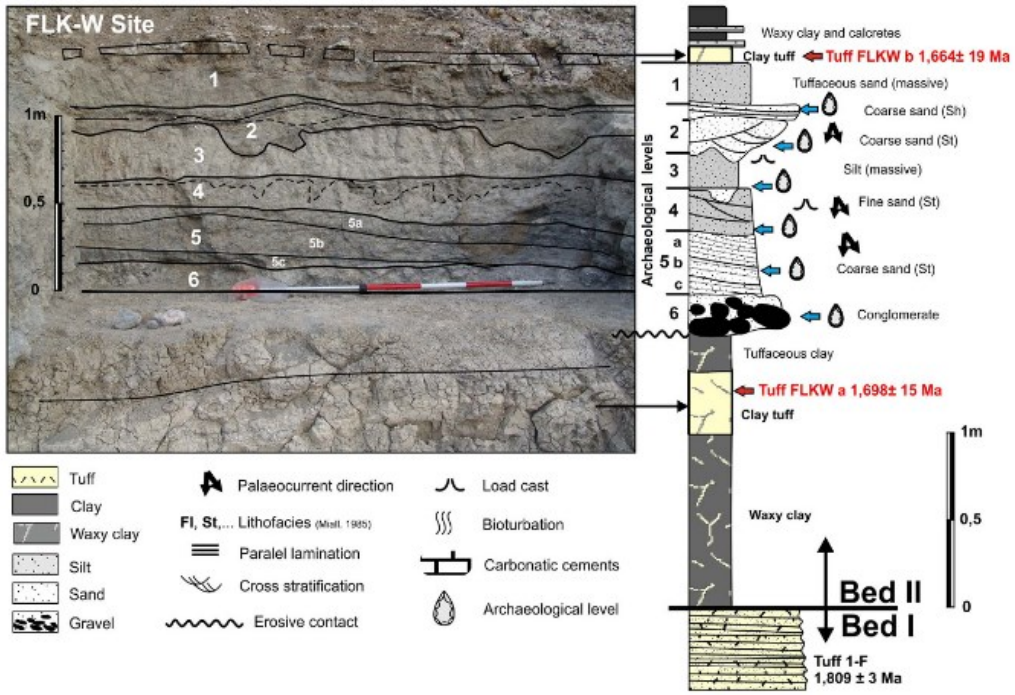
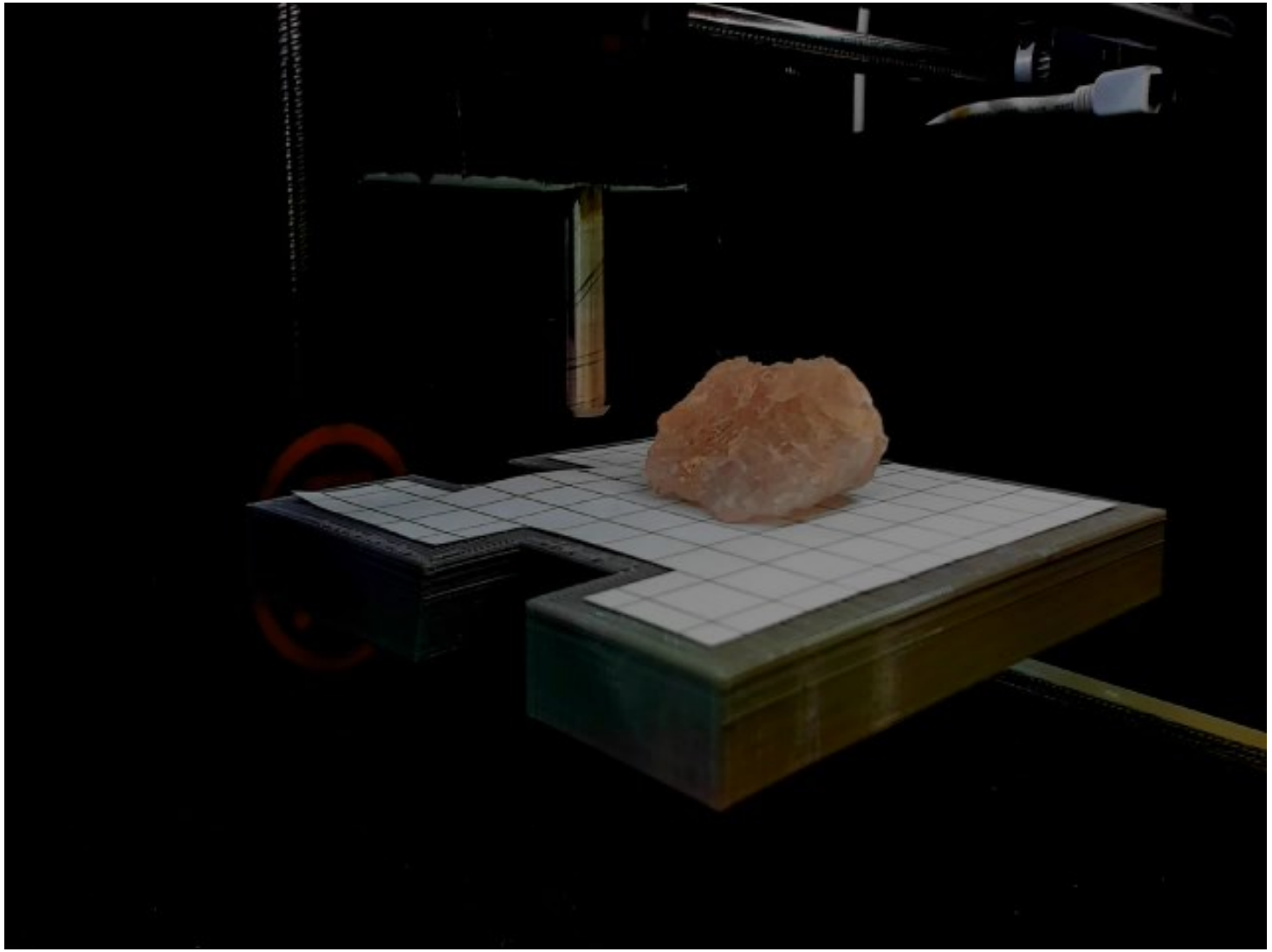


Figure 1. Left, detail of geometry and contacts of geological levels 1 to 6 in FLKW site. Right, stratigraphic section from Tuff 1-F to Tuff FLKW b. Drawing and photo by D. Uribelarrea.

What can micro-residues on the edges tell us?

Manuel Dominguez-Rodrigo, University of Alcalá in Spain.

Macro Raman Scanner



Q: Where to record Raman spectra from a macroscopic object?

A:

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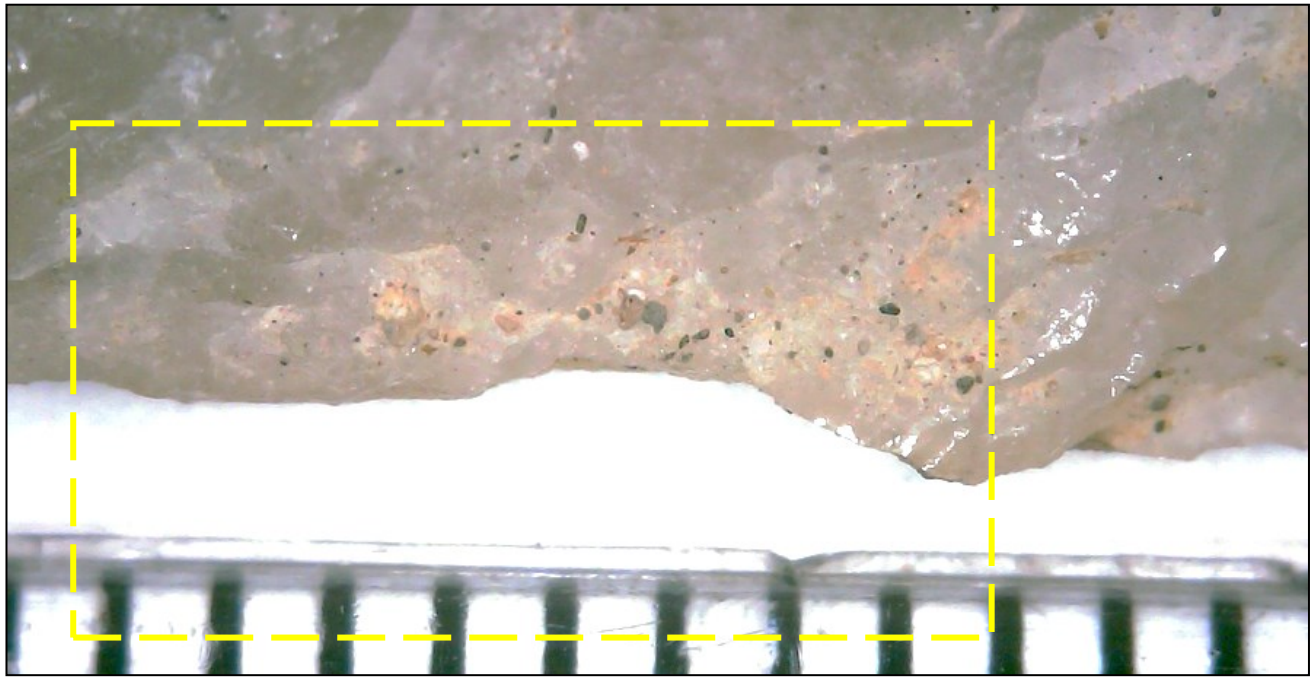

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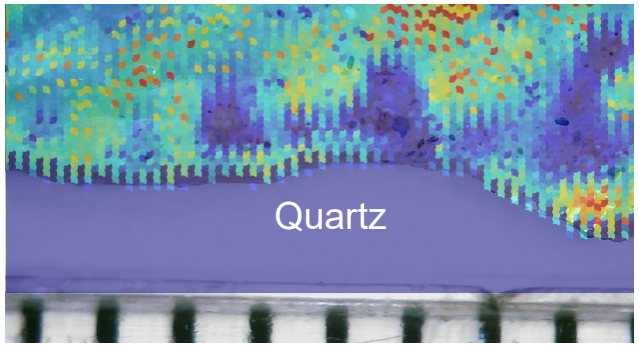

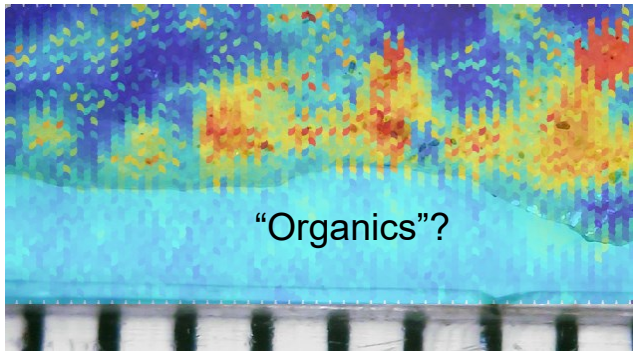

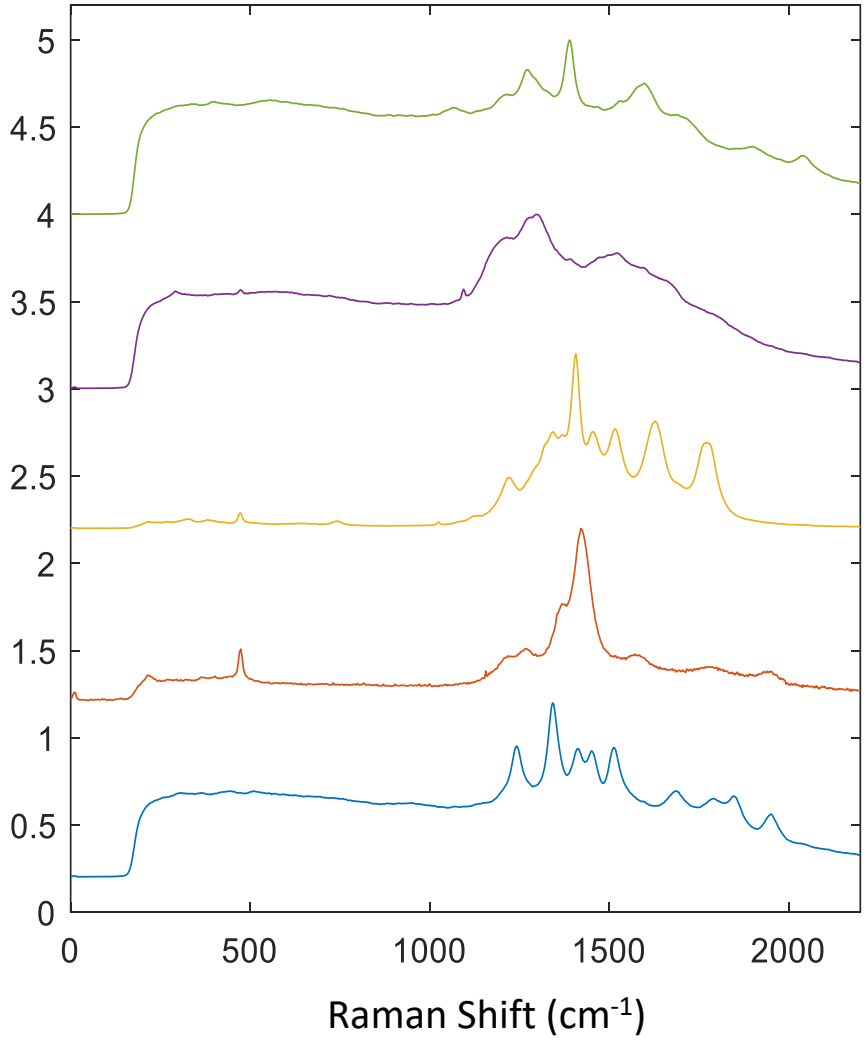

Mining Asteroids with Microbes

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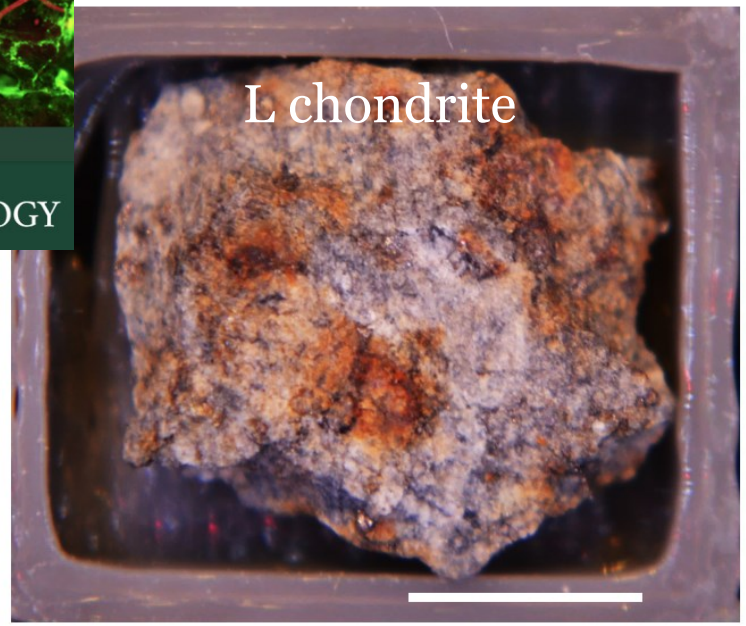
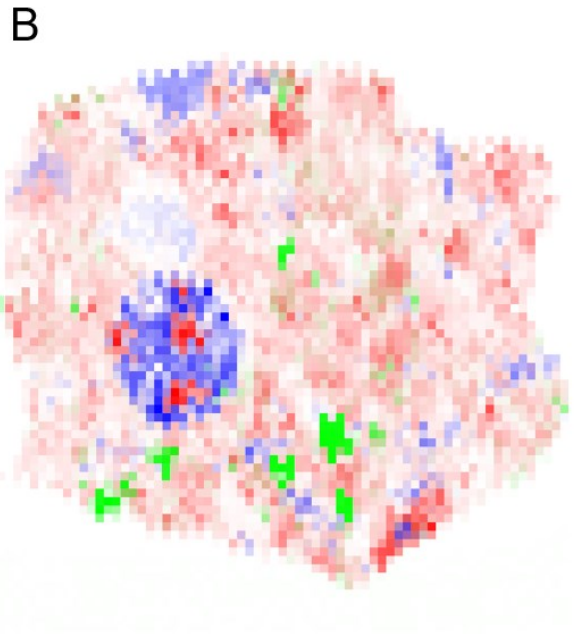
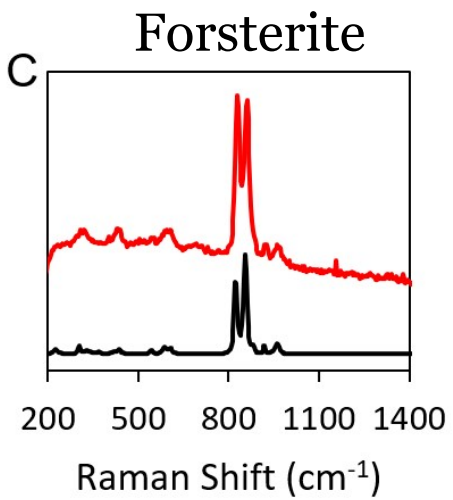
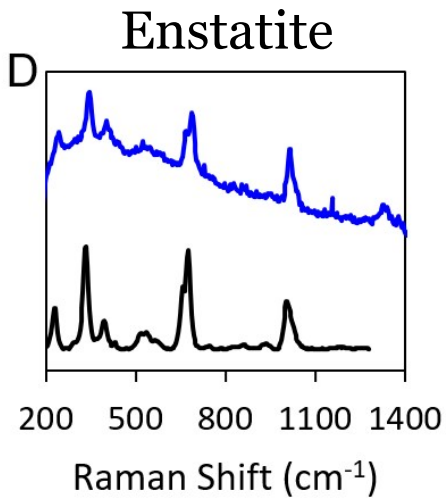
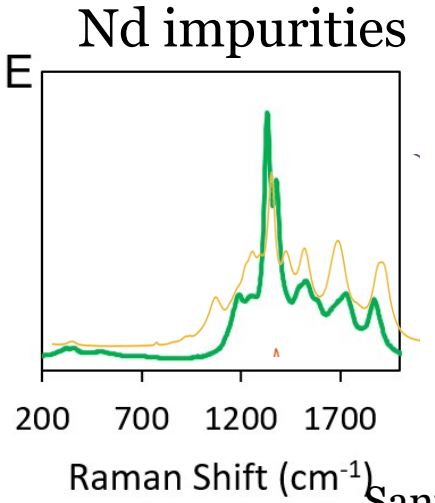










Santomartino et al, submitted

Sulfates from Mars Analog Sites

Ziyao Fang, UK Centre for Astrobiology, Edinburgh

Polyhalite
Evaporite mine
Boulby, UK

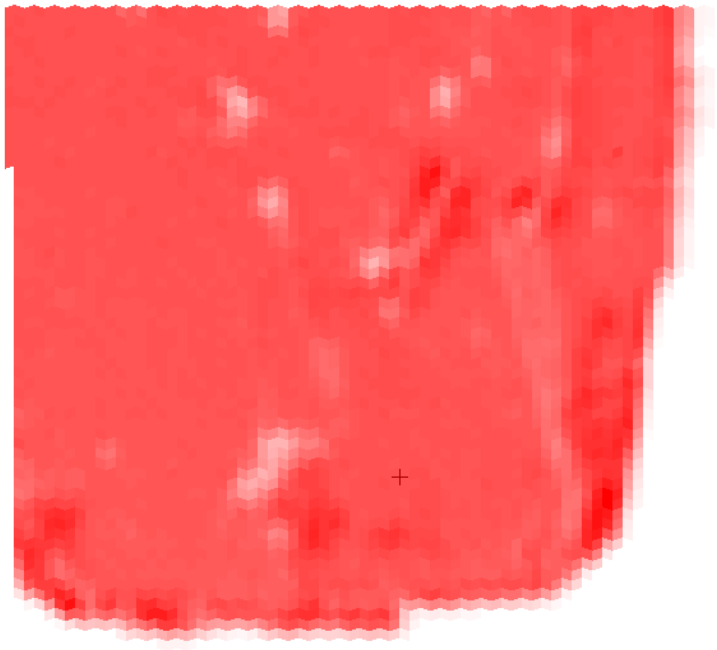
Gypsum
Qaidam Basin,
Tibetan Plateau

Anhydrite
Evaporite mine
Boulby, UK

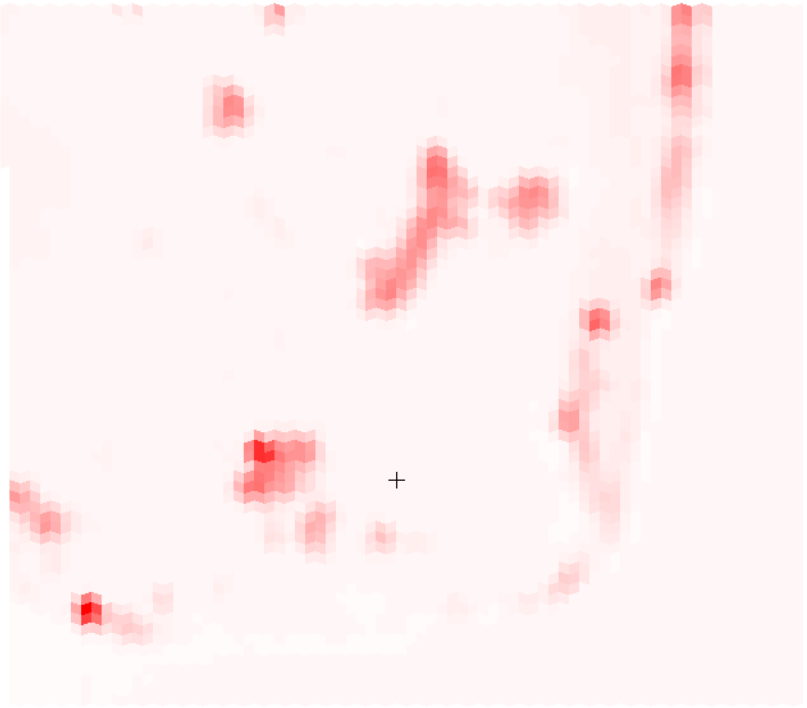
Gypsum with inclusions

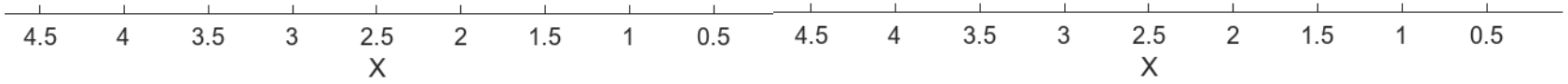
Dark Field

Gypsum peak map

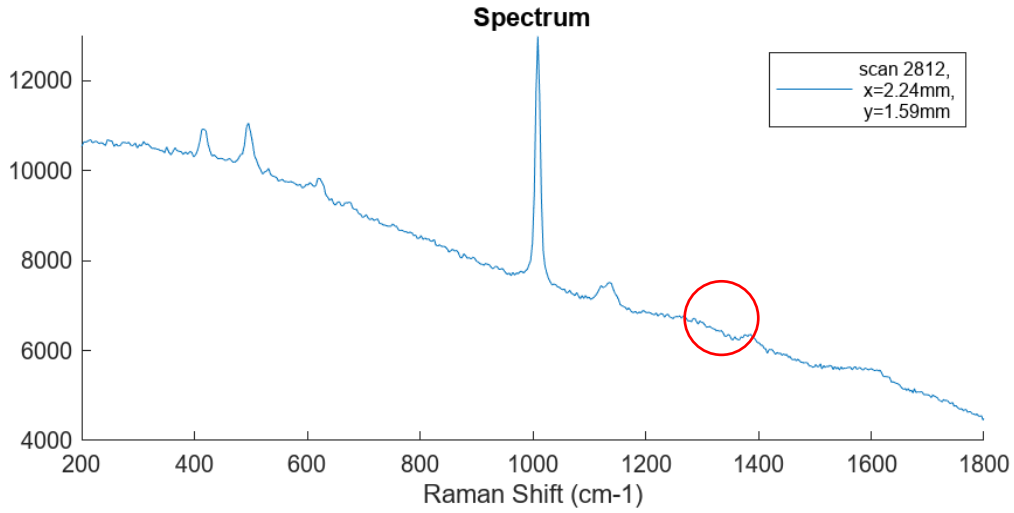


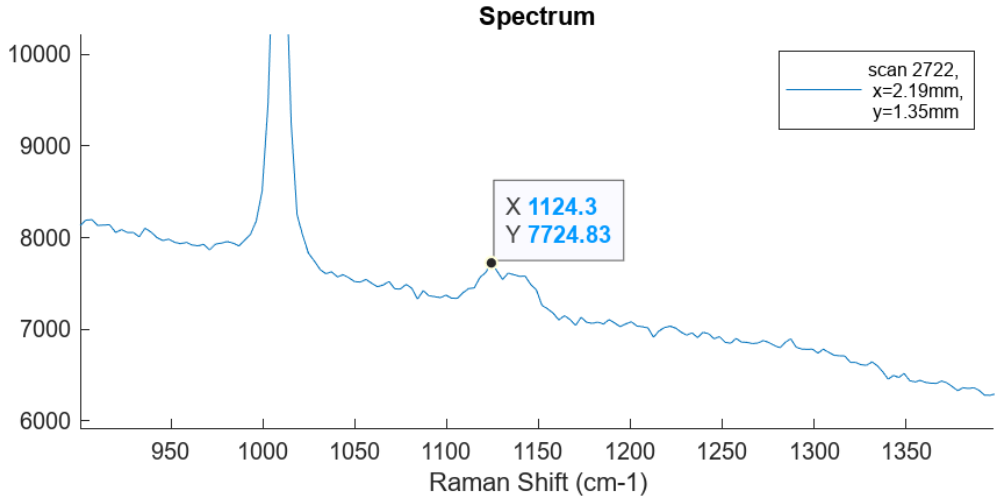
“Organic” 1400-1700 cm^{-1} peak map

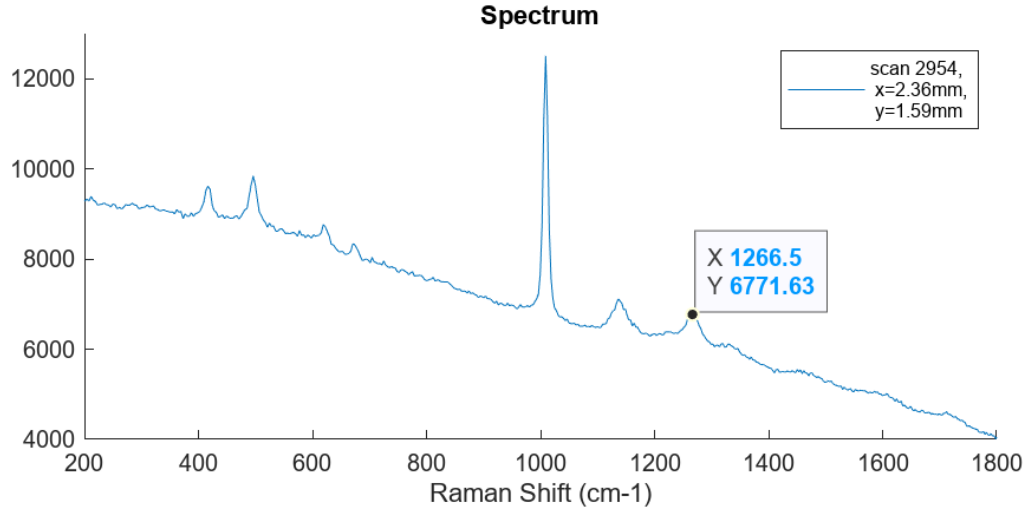




“Organic” peaks in Gypsum







Starship IFT 1

Starship IFT 1

A new launch pad failure mode: Analysis of fine particles from the launch of the first Starship orbital test flight

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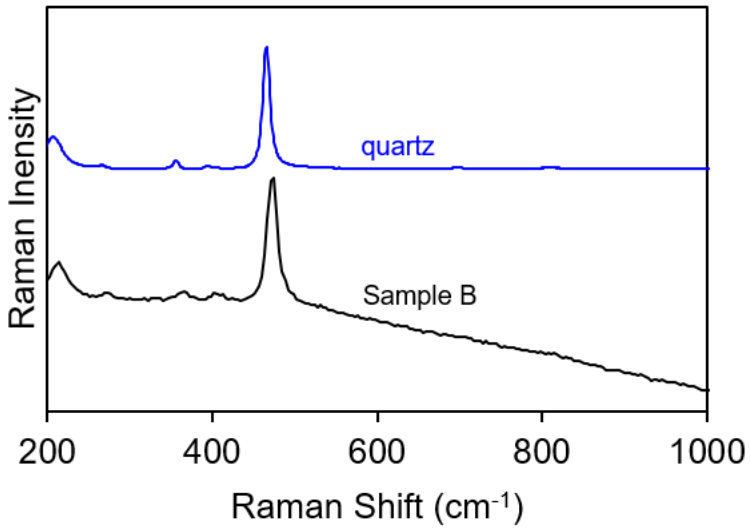
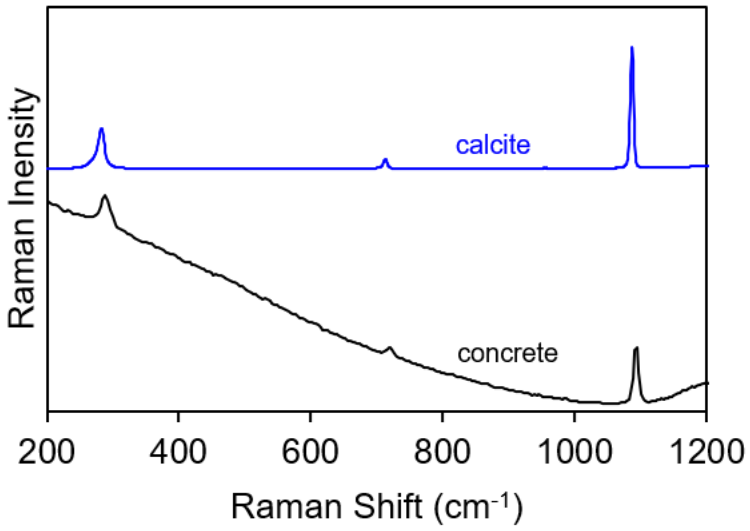
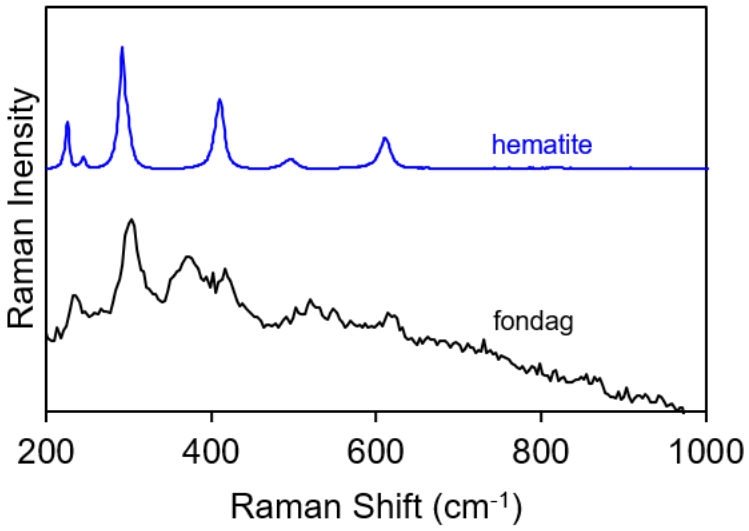
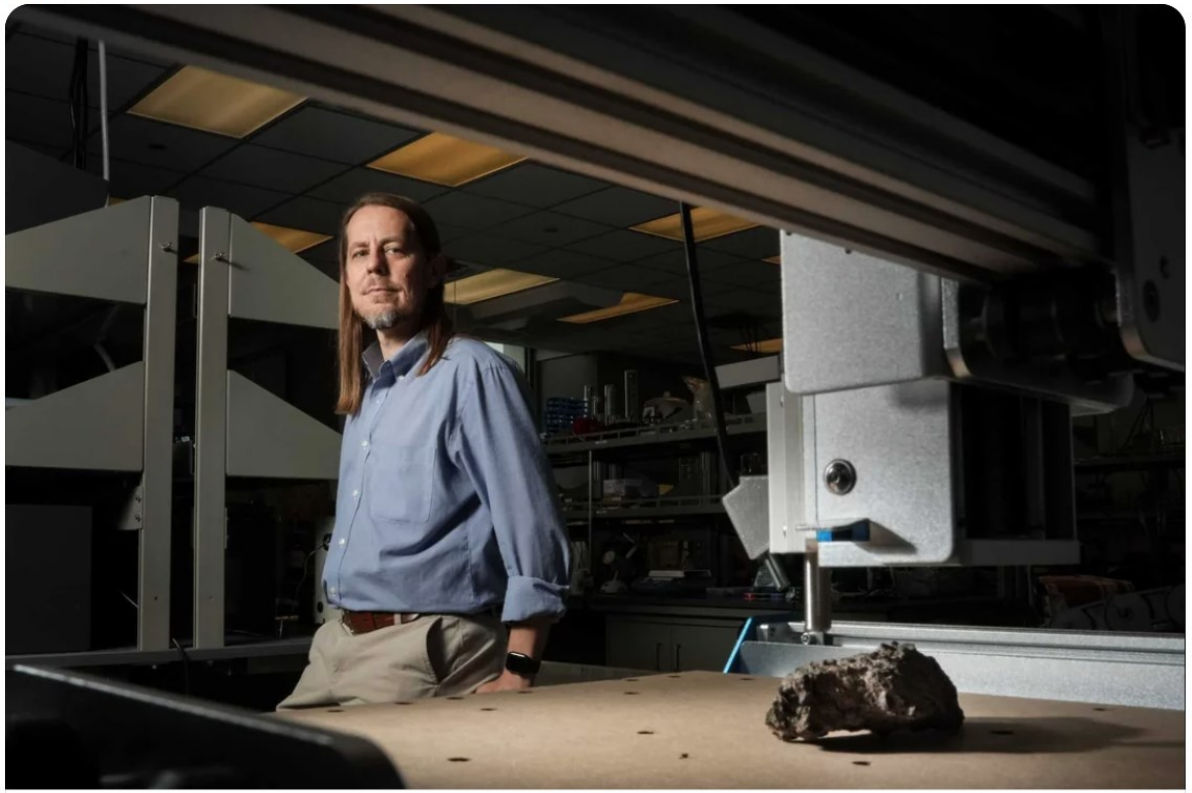




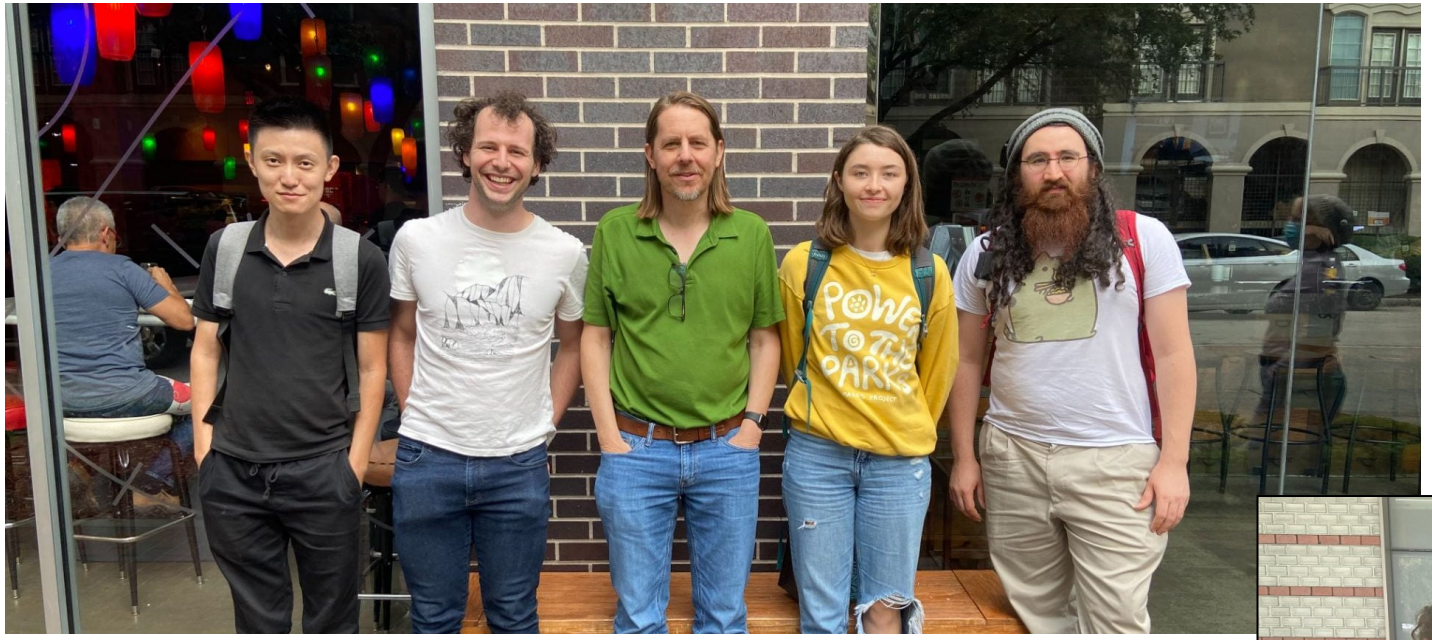


SpaceX Starship sprinkled South Texas with mystery material. Here's what it was.

it was sand



Mathieu Simeral Campbell Uyeki Charles Pacheco



Kyra Birkenfeld

Tia Gandhi