Optical Spectroscopy Techniques: Astrobiological Applications

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McMaster University

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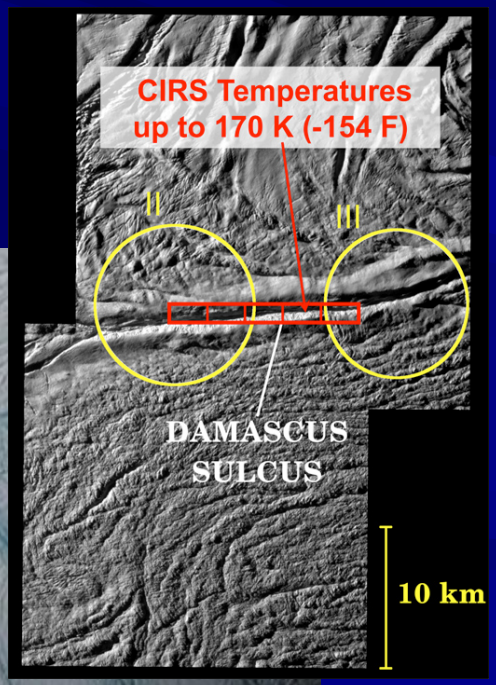
Outline

- Possible techniques
- Types of optical spectroscopies
- Principles of different types of optical spectroscopies
- Advantages/disadvantages of each
- Status and outlook for optical spectroscopies
- Roles for astrobiologists

Introduction

- Detecting life (past or present) on another planetary body is a difficult task for many reasons:
  - Where on a planet to search?
  - What to look for?



Detecting life

- Tons of techniques are available, with varying degrees of:
  - Specificity:
    - E.g., how many types of potential life forms can they detect?
  - Practicality:
    - can they be sent to another planet? (power, weight, ruggedness, data volumes, automation, ease of use)
    - Do they require sample prep?
    - Are they one time or multi-use tests?

Optical spectroscopies

- As a group of techniques, we use various forms of light to interrogate a target or sample. Major techniques are:
  1. Reflectance and emittance spectroscopy
  2. Raman spectroscopy
  3. Laser-induced breakdown spectroscopy (LIBS)
  4. Fluorescence spectroscopy
- This list is by no means complete
- These are ones that have flown or likely will fly soon

Optical spectroscopies

- We can use the fact that light interacts with matter in different ways to interrogate targets

Most important for us is "absorbed" (i.e., light that interacts directly with the target in some way prior to us detecting it)

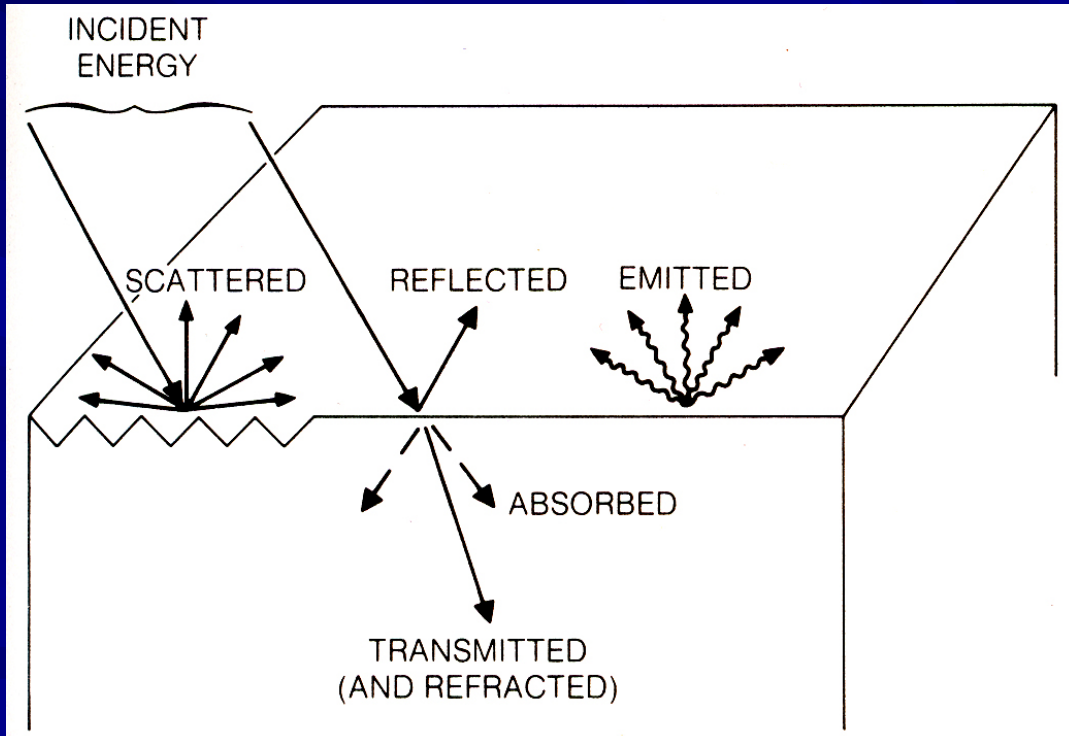


Figure 1-1 Interaction processes between electromagnetic energy and matter.

1. What are photons?

- Photons are discrete quanta of energy, that can be characterized in terms of their wavelength or frequency- its sometime more convenient to talk about them in terms of energy, sometimes in terms of wavelength – they are interchangeable

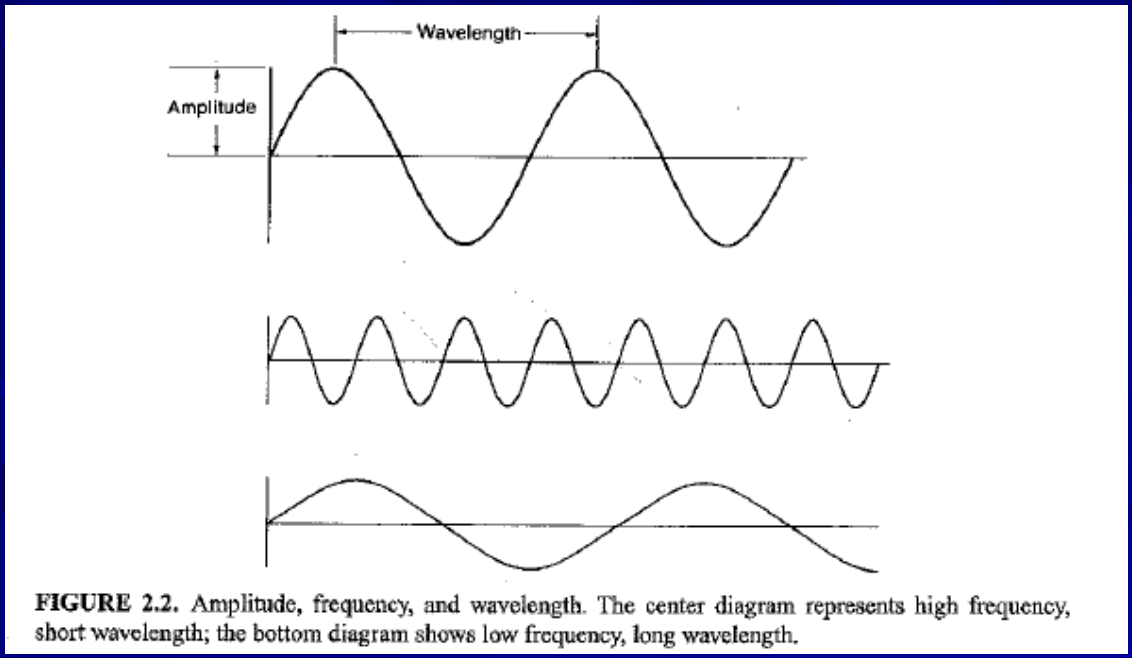
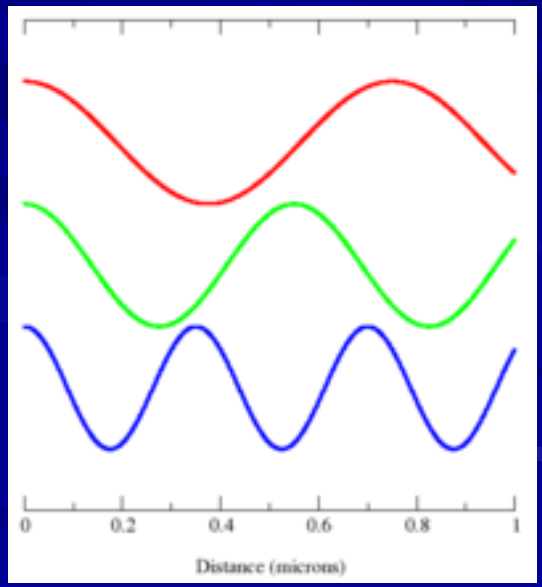


FIGURE 2.2. Amplitude, frequency, and wavelength. The center diagram represents high frequency, short wavelength; the bottom diagram shows low frequency, long wavelength.



1. What are photons?

- For purposes of remote sensing, a convenient fiction is to think of photons as packets of energy, and the longer the wavelength, the lower the energy. Long wavelength photons are slackers, and short wavelength photons are hopped up on coffee.

2. Reflectance/emittance spectroscopy

- Relies on light-matter interactions to probe the composition of a target
- Specifically looks at light reflected by or emitted from a target
- Can use ambient light or an active light source

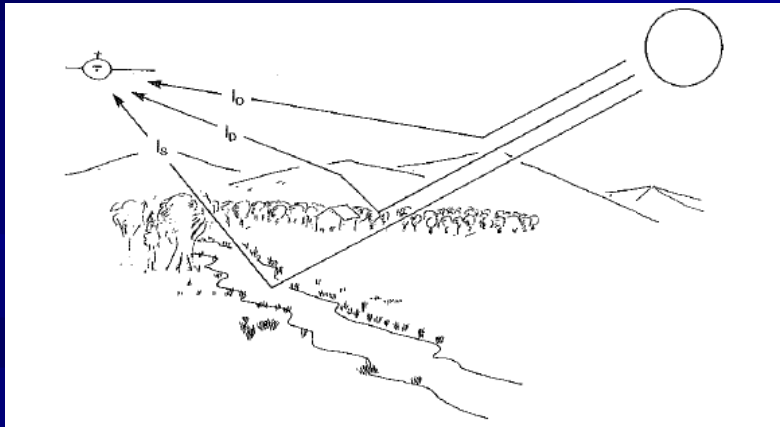
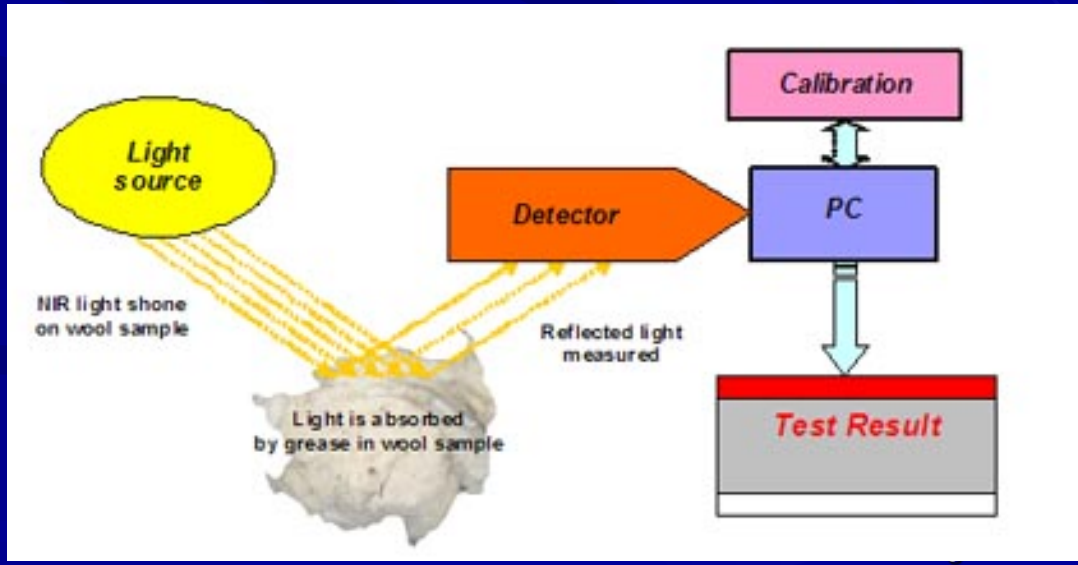
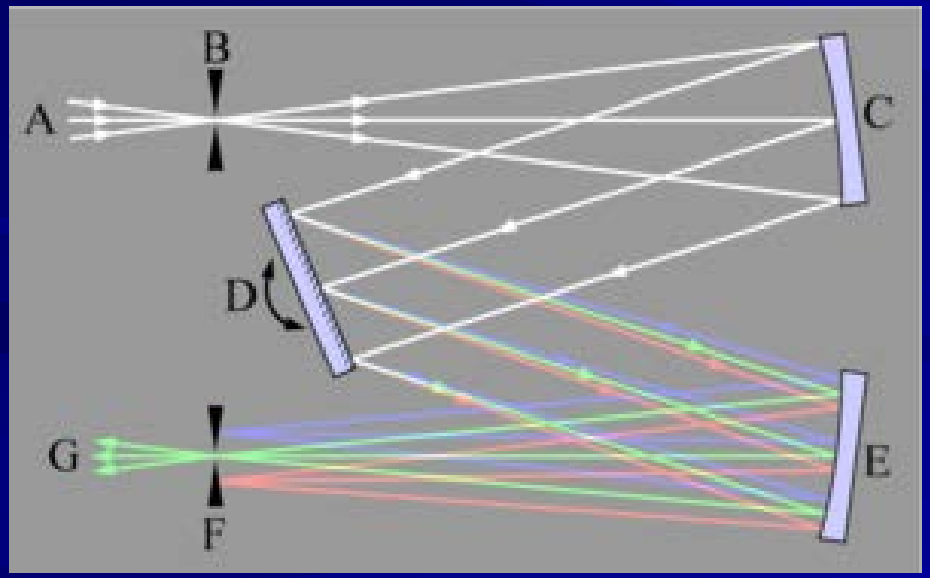


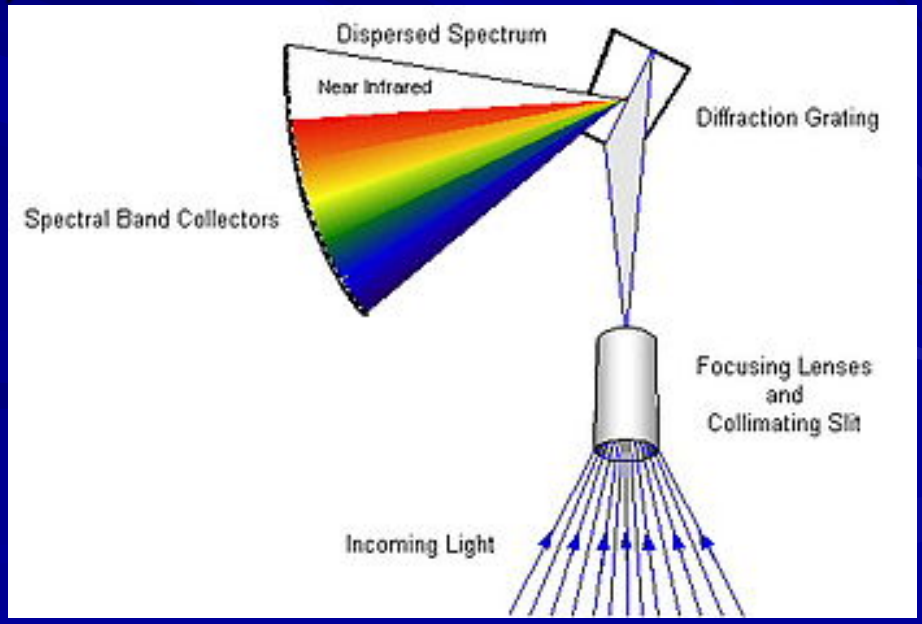
FIGURE 2.8. Principal components of observed brightness. I_S represents radiation reflected from the ground surface, I_O is energy scattered by the atmosphere directly to the sensor, and I_D represents diffuse light, directed to the ground, then to the atmosphere before reaching the sensor. This diagram describes behavior of radiation in and near the visible region of the spectrum. From Campbell and Ran (1993). Copyright 1993 by Elsevier Science Ltd. Reproduced by permission.



2.1. Reflectance/emittance spectroscopy concept

- Simple concept:
  - Look at light that has interacted with a target – break it up into constituent wavelengths (“rainbow”) and look at how intensity varies with wavelength – affected by how the light has interacted with the target which depends, in turn on target composition (and physical structure)



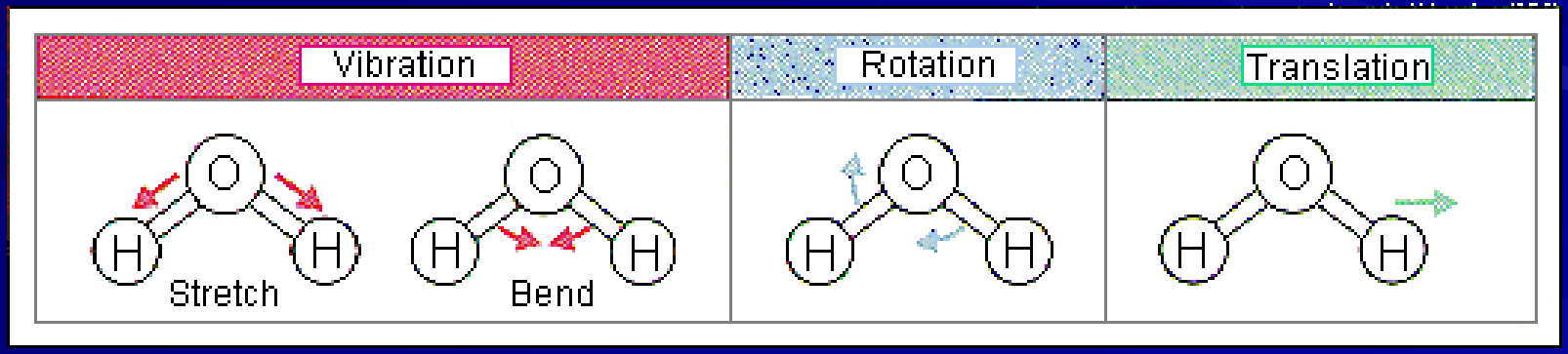


2.2. Reflectance/emittance spectroscopy

- Probes targets at the level of individual atoms and small molecular clusters
- For organics/biology it can detect the presence of heteroatomic molecules (e.g., C-H, C-N, C-O, N-H, H-O – pick your favourite organic (bio)molecule

2.3. How it works – part 1

- Low-energy photons can make a molecule "dance": the molecule can be made to:
  - Move as a solid object
  - Rotate in place about an axis
  - Change the angle between atoms (bend)
  - Change atom-atom distances (stretch)



2.3. How it works – part 2

- Higher energy photons can affect a single atom – can make an electron move from one energy level (orbit) to another (some restrictions apply)

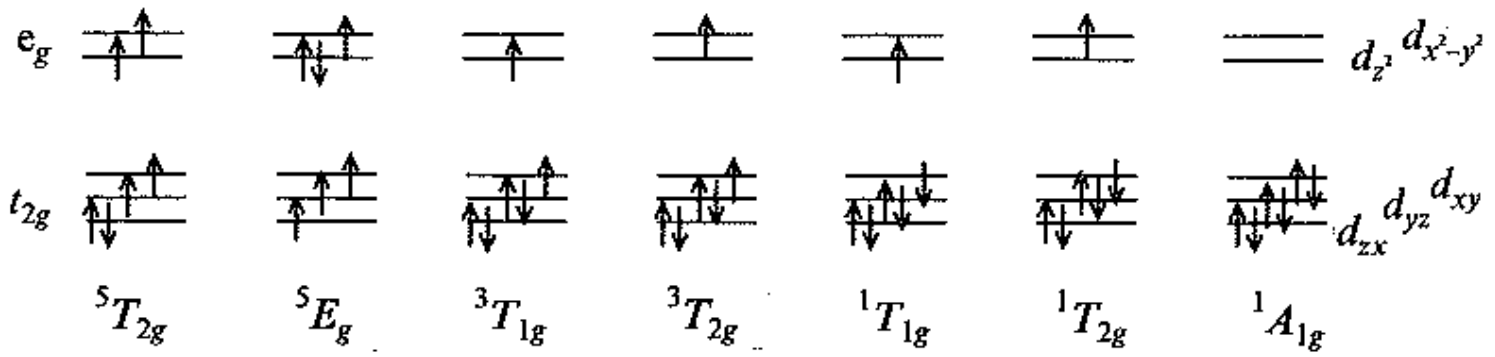
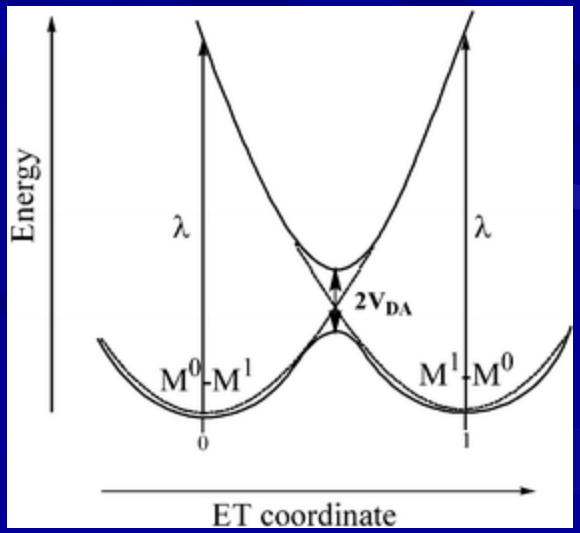


Figure 3.6. Electronic configurations of the ground state and some of the excited crystal field states of the Fe^{2+} ($3d^6$) ion in octahedral coordination.

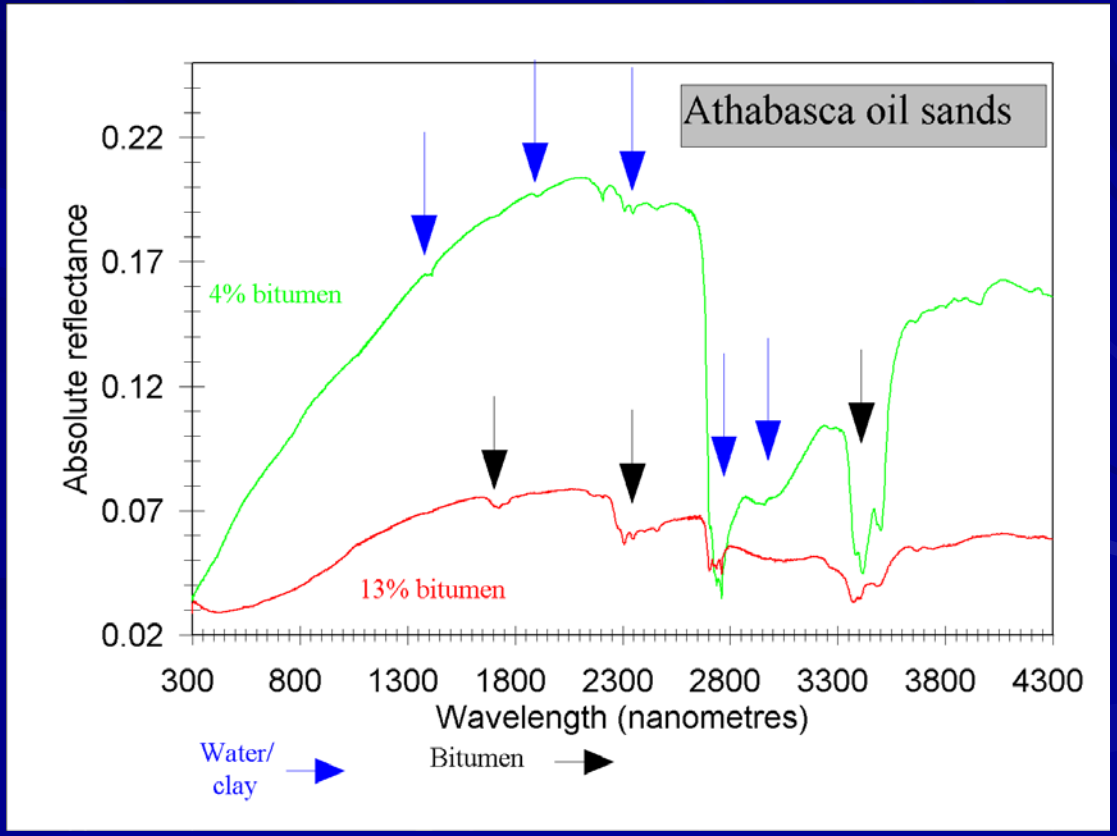
2.3. How it works – part 3

- Highest energy photons can make an electron jump from one atom to another (charge transfer bands).
- For instance, can be used to probe oxidation state of iron



2.4. Reflectance/emittance – organic targets

- Have used it to characterize oil sands, coals, etc.

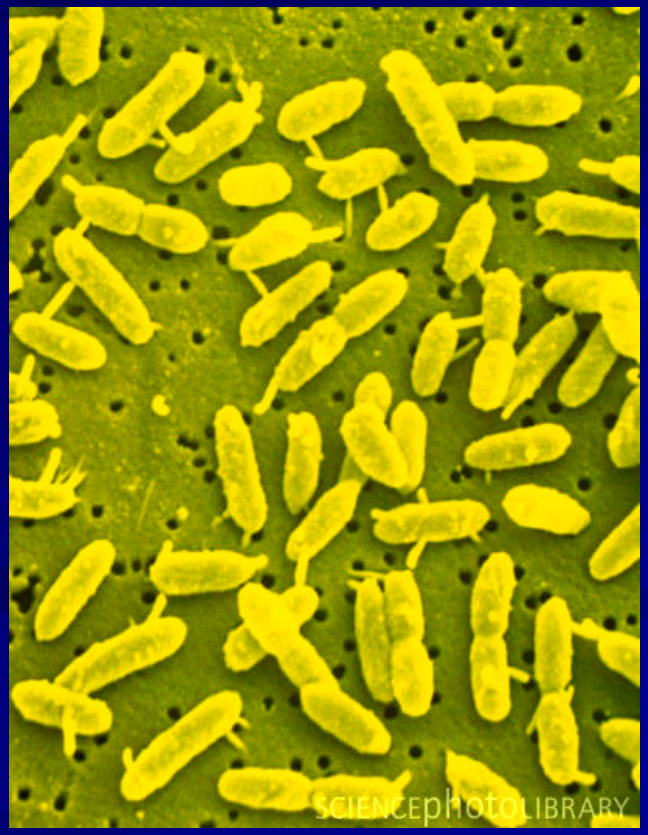


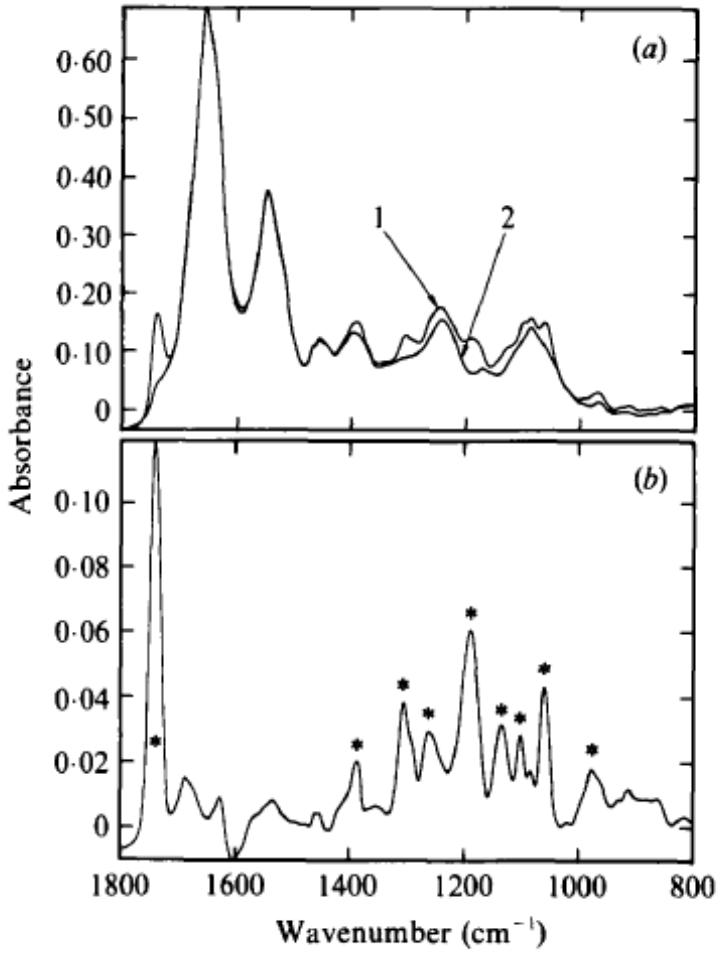
Journal of General Microbiology (1991), **137**, 69–79. *Printed in Great Britain*

Classification and identification of bacteria by Fourier-transform infrared spectroscopy

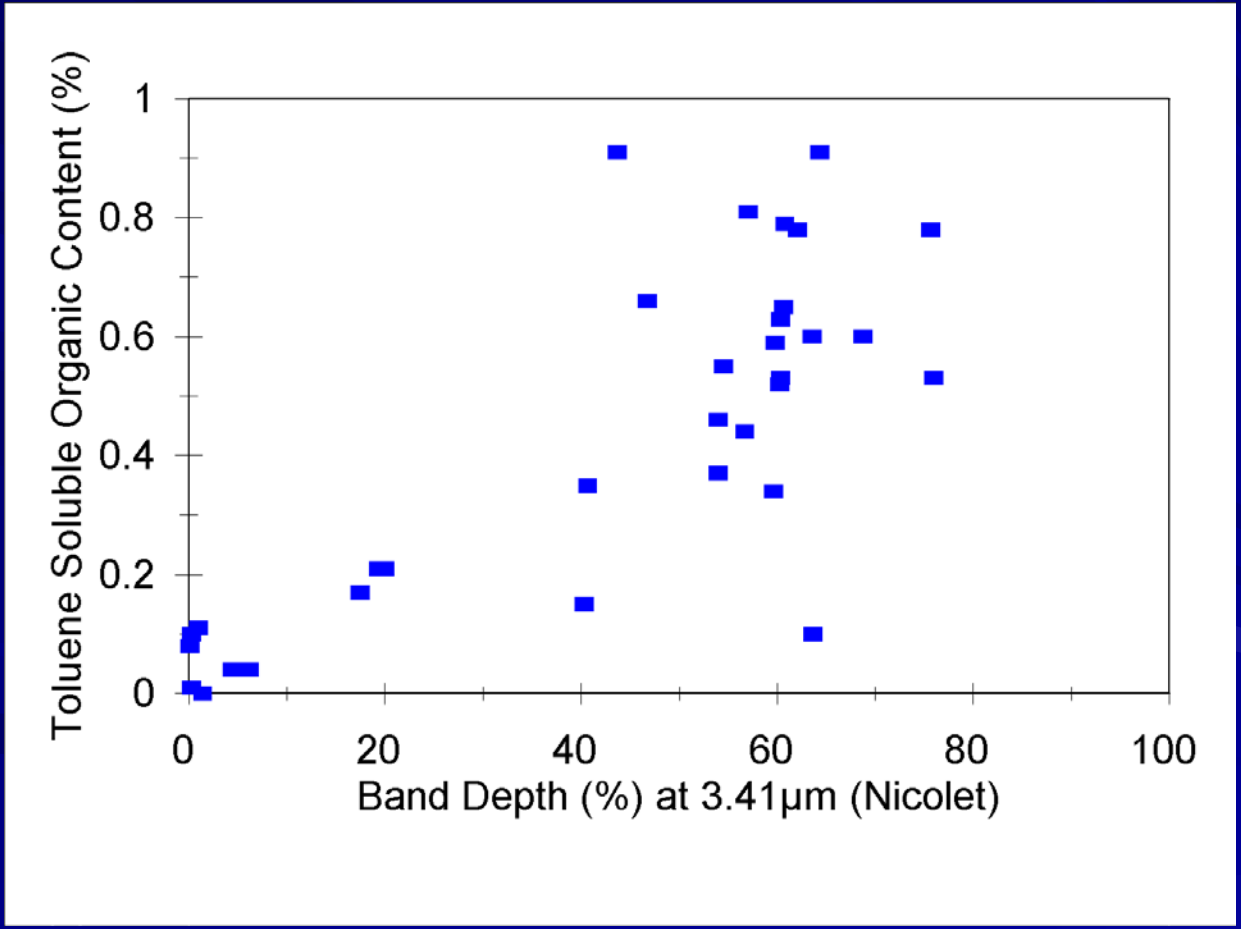
D. HELM,[1]* H. LABISCHINSKI,[1] GISELA SCHALLEHN[2] and D. NAUMANN[1]

- Works on bacteria!





Detection limits can be über-low if absorption bands are intense.



E.g. Spectrum of purified biopolymer

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Enzyme and Microbial Technology 34 (2004) 673–681

ENZYME and MICROBIAL TECHNOLOGY

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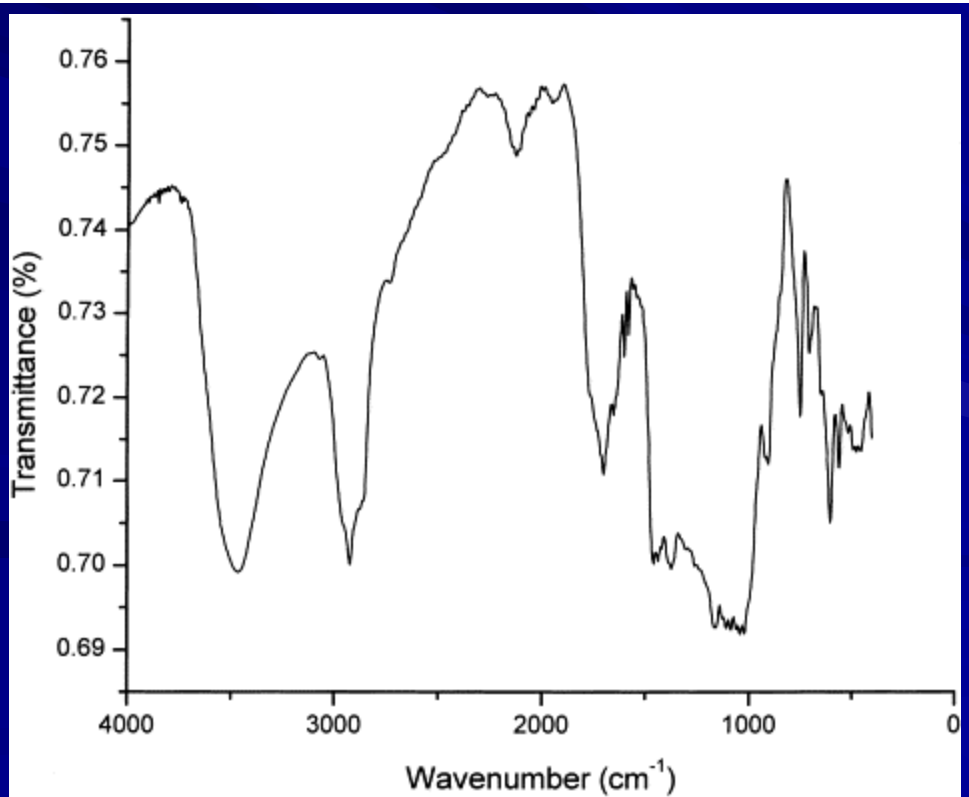
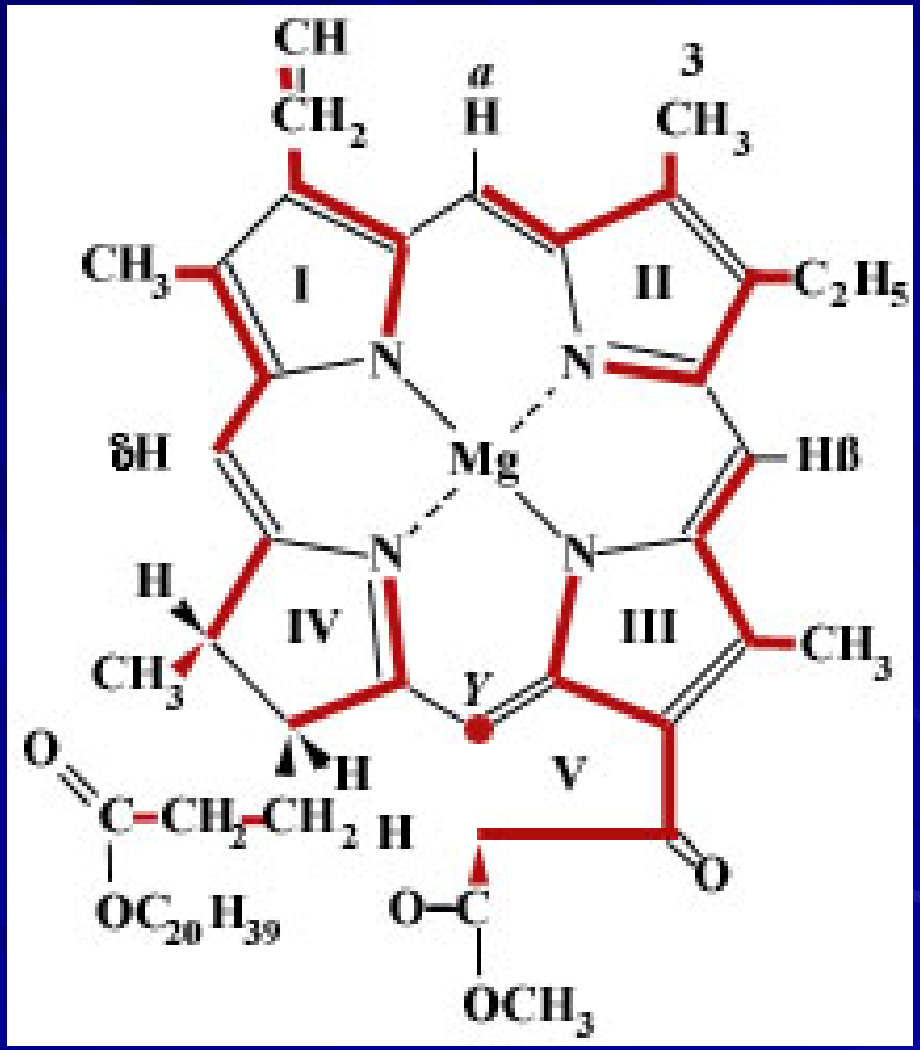
Purification and characterization of an extracellular polysaccharide from haloalkalophilic *Bacillus* sp. I-450

Microbes or microbe component spectra can have a lot of detail



Chlorophyll as an example

- N-C stretches/bends
- C-H stretches/bends
- O-C stretches/bends
- Aromatic pi bonds
- If Fe substitutes for Mg can get additional bands

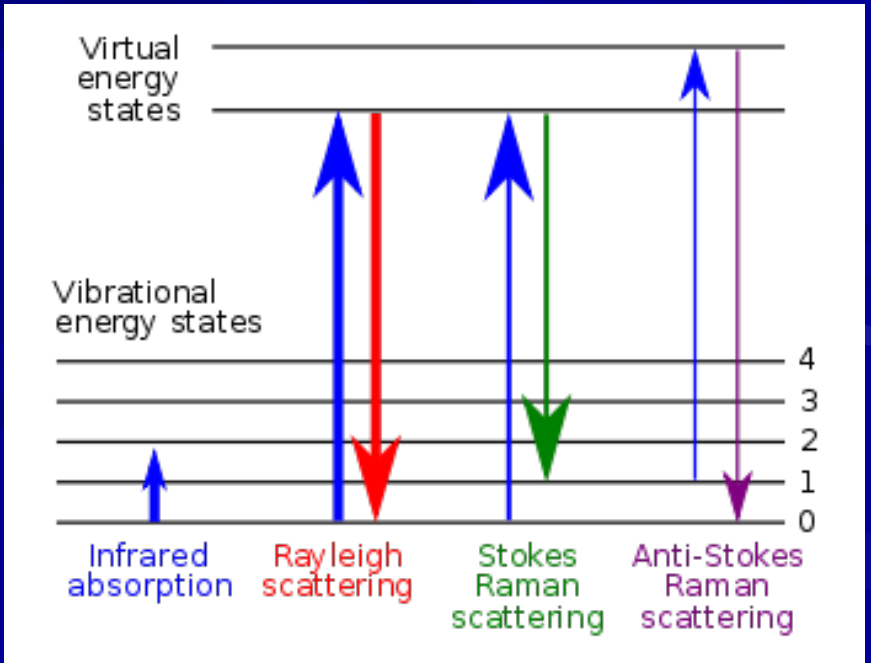


Reflectance spectroscopy and astrobiology - status

- Hasn’t really been intensively investigated for astrobiology
- Microbial spectra are almost too information-rich – many things can have similar spectra
- Doesn’t detect “life” directly – detects the presence of a wide range of organic molecules and bonding types
- Would probably work best in micro mode to get decent SNR (applies to most other techniques)
- Has worked very well for identifying suitable habitats

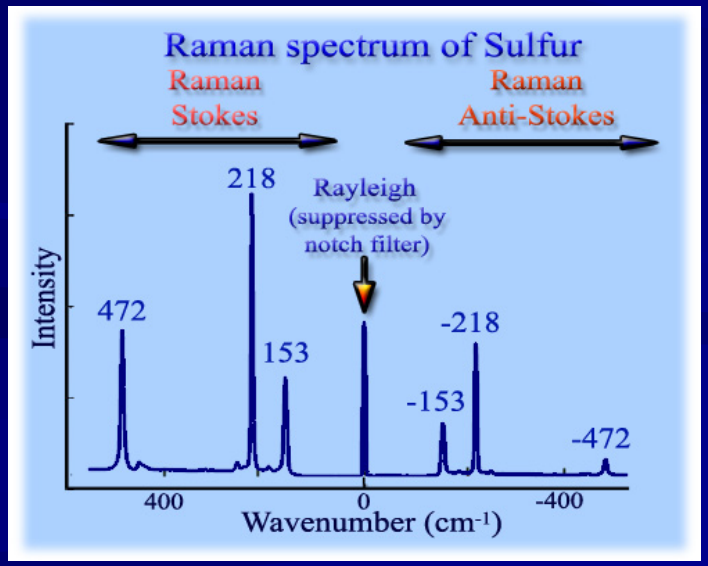
3. Raman spectroscopy

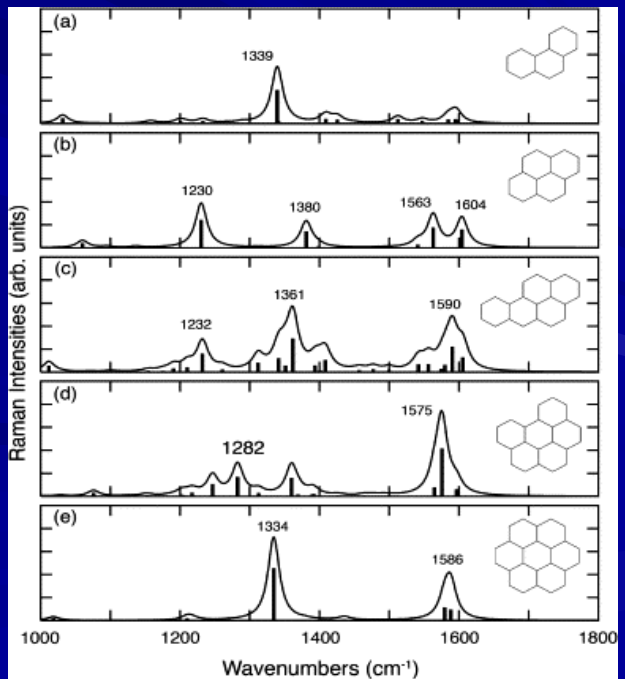
- Principle is sort of similar to reflectance. In Raman a molecule is excited to an intermediate excited state (like in reflectance), but the process involves the molecule emitting some excess energy because the starting and ending state are different (whatever!).



3.1. Raman spectroscopy

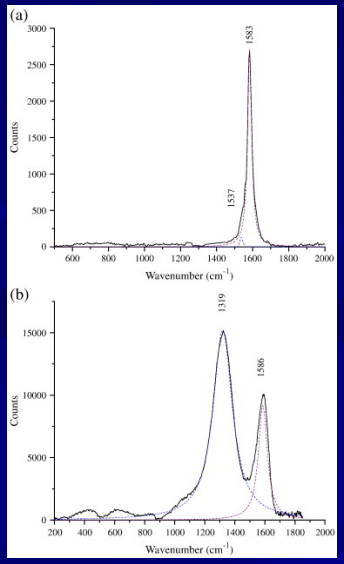
- Way weaker than reflectance/emittance
- But is complementary to reflectance. Therefore its good for homo-atom molecules, e.g.: O=O, C=C, S=S
- As a result Raman can effectively “see” through water
- Good for, you know, stuff like polycyclic aromatic hydrocarbons (PAHs), carbon-bearing materials with pi-bonds





3.2. Raman principles

- Usefulness of Raman spectrum will depend on how a target scatters/absorbs light. As a rule, longer wavelengths are better for organics, although really short ones are good too (WTF!)



UV (upper) and IR (lower) Raman spectra of graphitic material

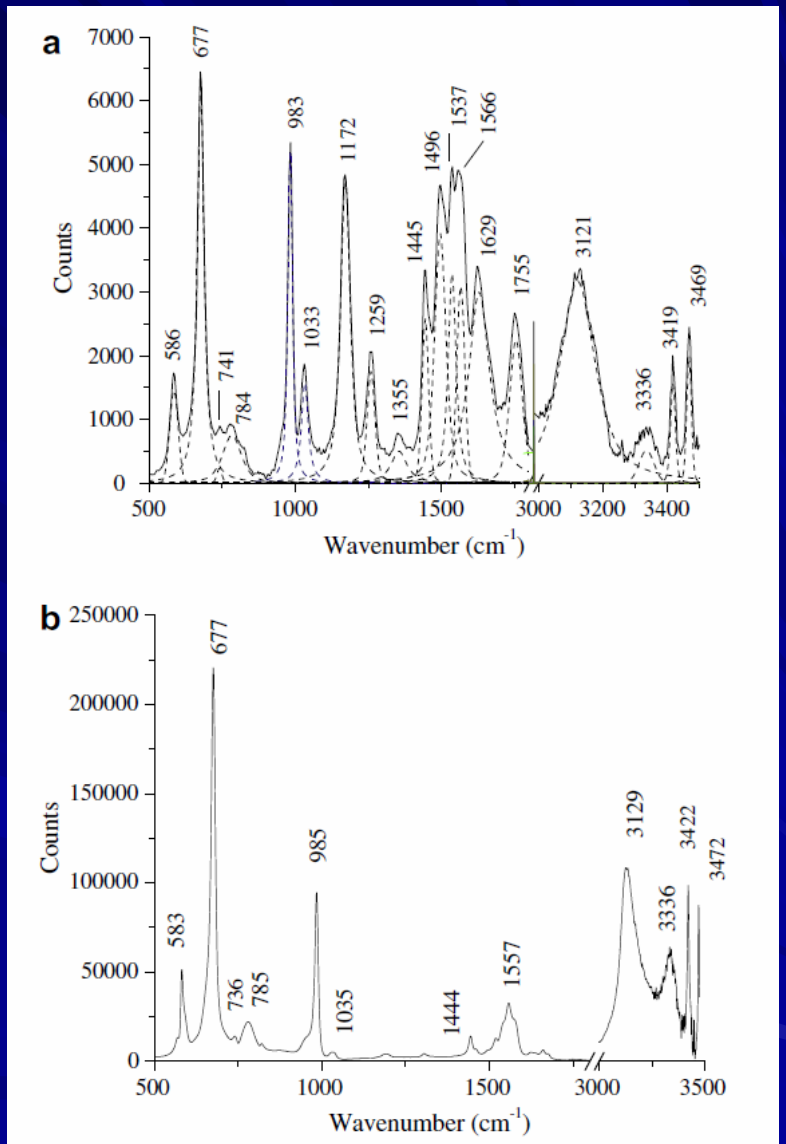


Fig. 3. (a) UV Raman spectra (244 nm) of melamine after offset and linear background (line) corrections. Integration time was 30 min, objective was UV 40× and laser power was 0.6 mW; (b) NIR Raman (785 nm) spectrum of melamine without background correction. Integration time was 20 s, objective was 50× and power was 3 mW.

3.3. Raman – extremophile example

Available online at www.sciencedirect.com
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Icarus 175 (2005) 372–381
ICARUS
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Raman spectroscopic analysis of cyanobacterial colonization of hydromagnesite, a putative martian extremophile

Howell G.M. Edwards [a,*], Caroline D. Moody [a], Emma M. Newton [a], Susana E. Jorge Villar [a,1], Michael J. Russell [b]

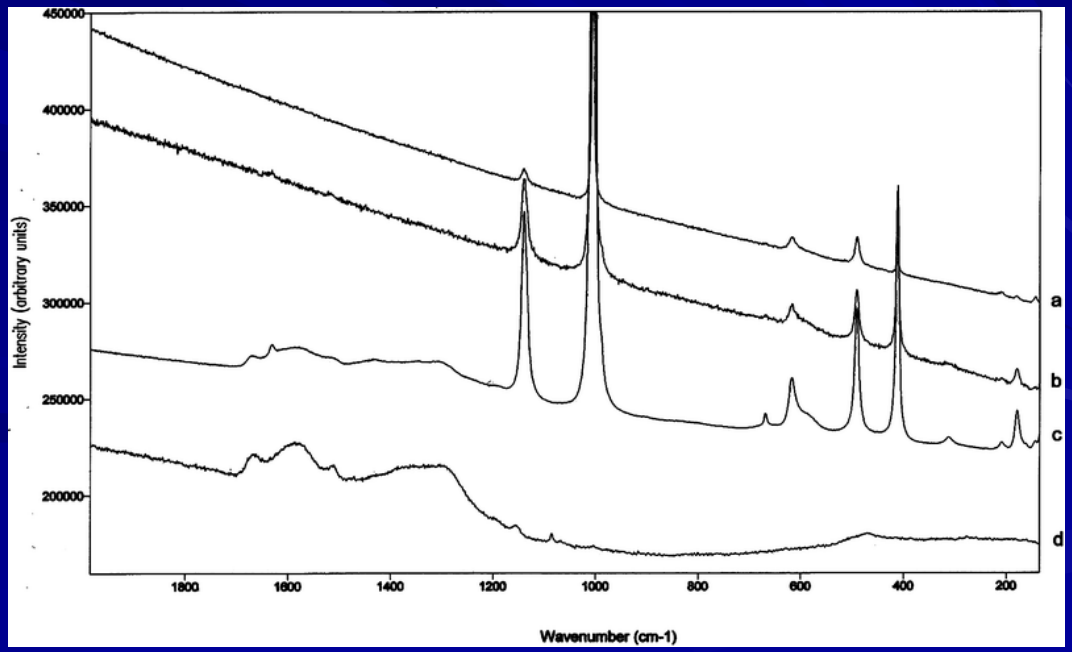


Fig. 4 Confocal Raman spectroscopic depth study of cyanobacterial colonies, halotrophic extremophiles in a gypsum host matrix; a, spectrum at the gypsum surface; b, spectrum at a position in the crystal about 1 mm below the surface; c, spectrum near the interface between the biological colony and the gypsum host; d, spectrum of the cyanobacterial colony about 3 mm below the surface of the gypsum host crystal. Excitation wavelength 514.5 nm, wavenumber range 100–2000 cm−1.

3.4. Raman and astrobiology - summary

- New techniques available that enable Raman in daylight, for targets tens of metres away, and at depth.
- Surface properties can greatly affect Raman signal
- No one wavelength will be best in all cases

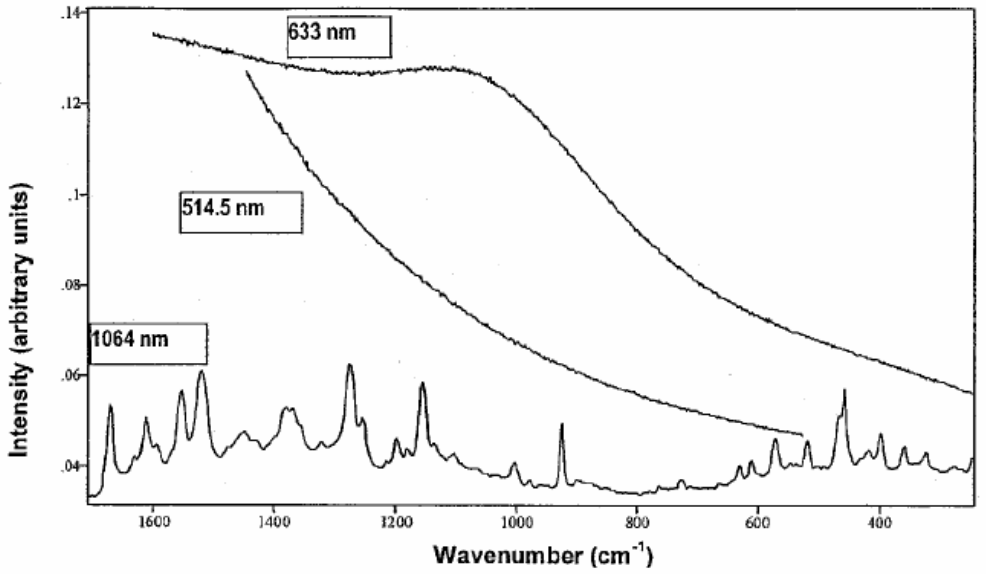


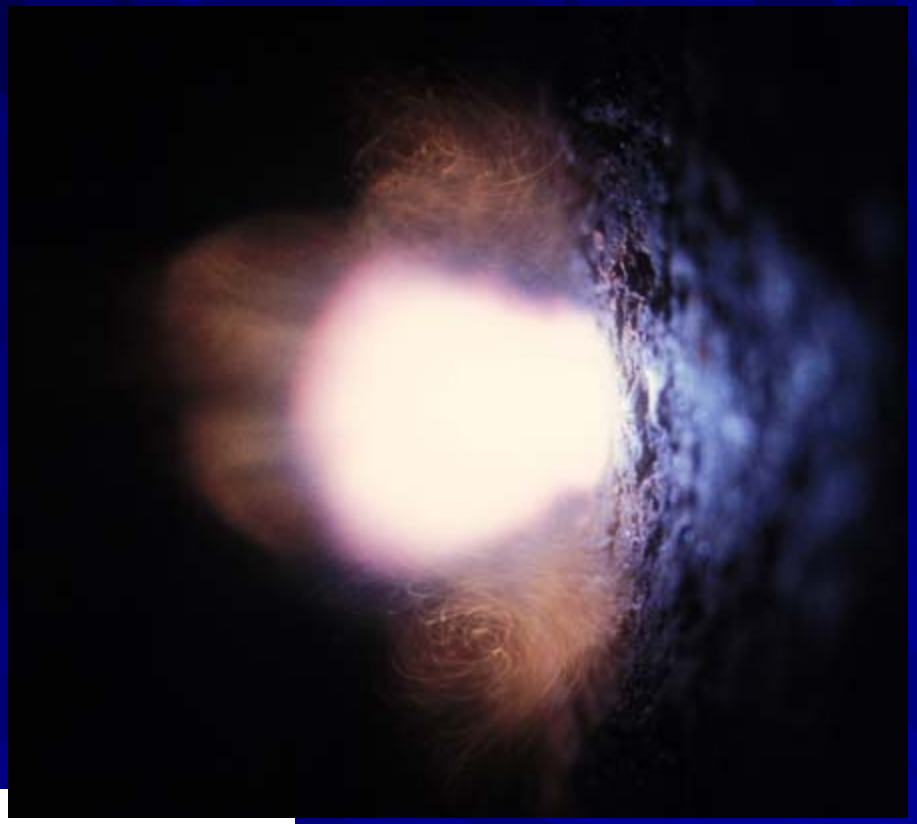
Figure 1. Raman spectral stack-plot of an Antarctic epilithic lichen, *Caloplaca saxicola*, with laser excitation at 514.5 (green) 633 (red) and 1064 nm (near infrared). Clearly, the vibrational band information quality is better with excitation in the near infrared, whilst onset of fluorescence emission swamps the Raman spectral bands in the visible.

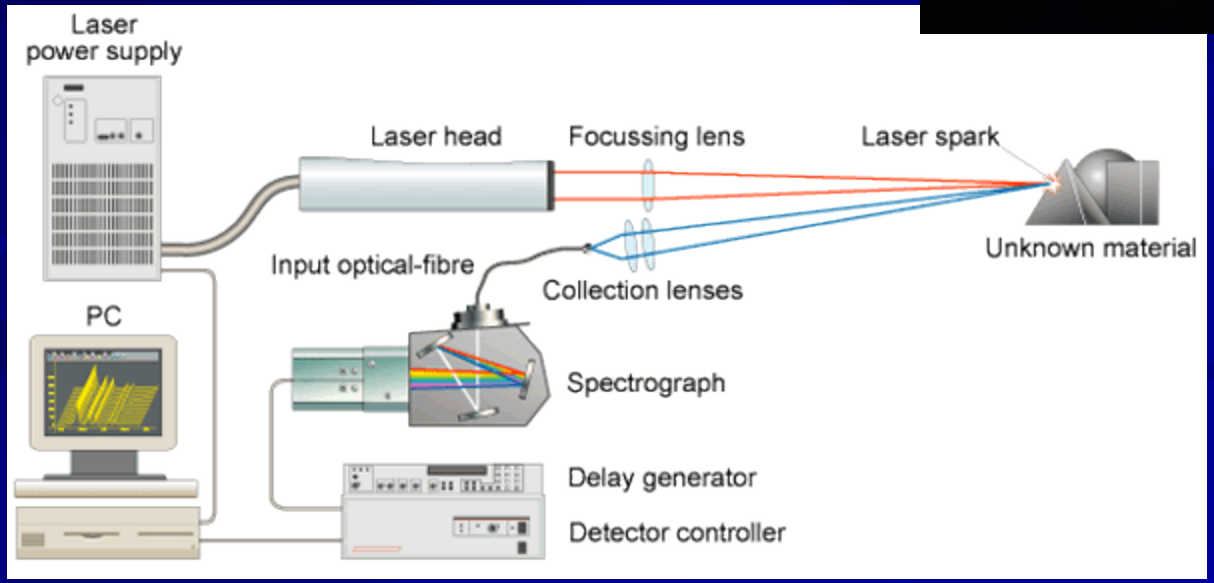
4. Laser-induced breakdown spectroscopy

- The concept:
  - Zap a target with a strong laser pulse – results in a plasma – atoms and electrons dissociate. Soon after, they recombine (seen as a brief flash of light). The recombination involves a loss of energy (as photons – emission lines)
  - The energy of recombination is specific to each element
  - Multiple lines are possible
  - The whole periodic table is potentially accessible

4. LIBS

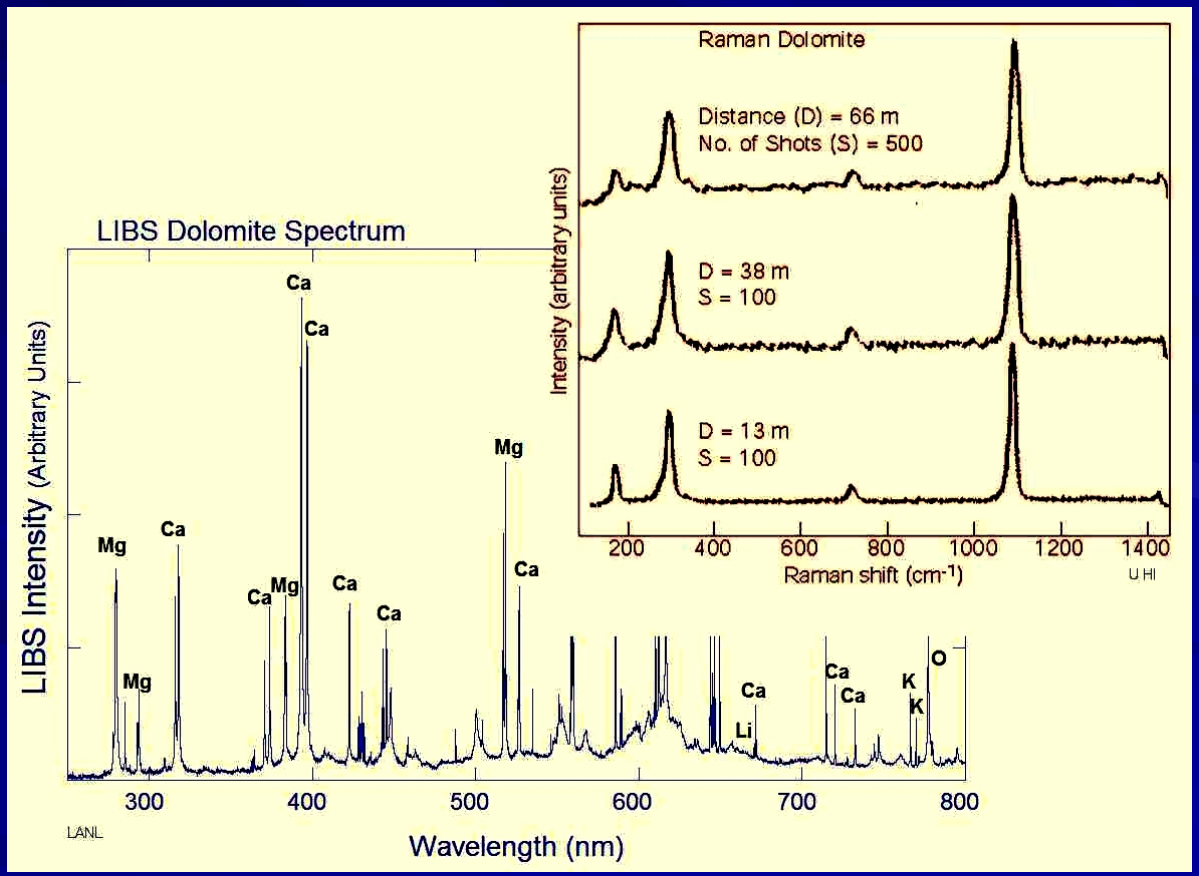
- Break up the light into constituent wavelengths





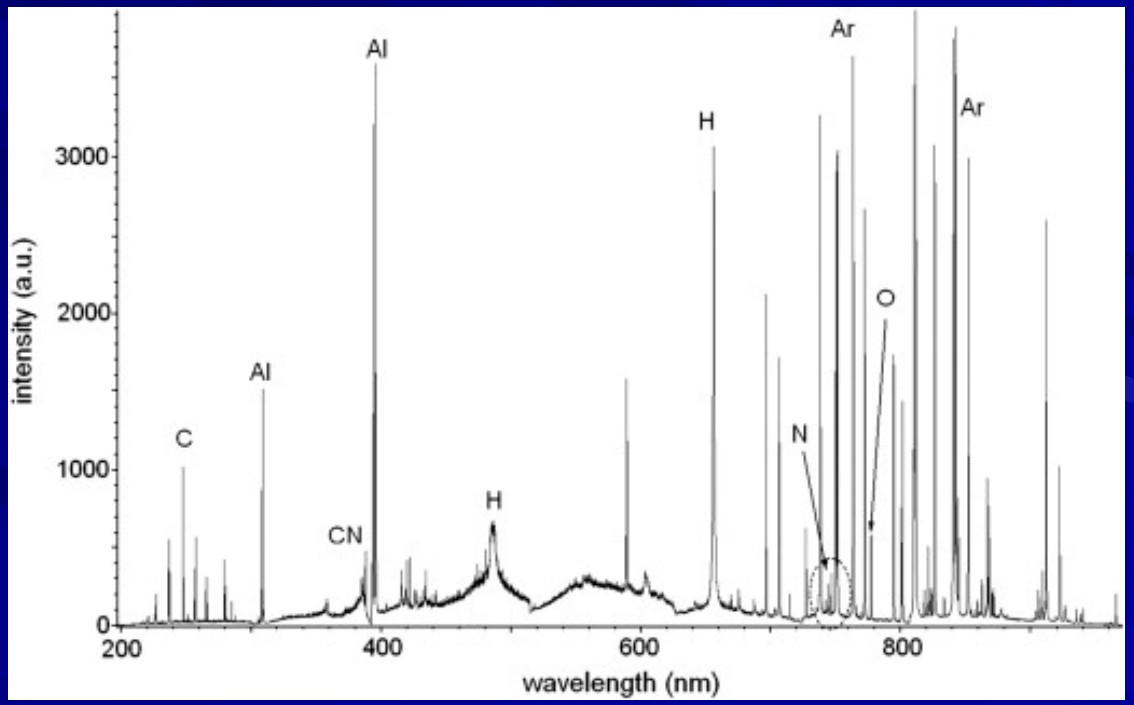
4. LIBS spectra

- Consist of a forest of lines – there are many ways in which ions and atoms recombine
- Getting quantitative data is tough



4.1. LIBS for astrobiology

- Still very much under development – e.g., detection limits, matrix effects
- Low Z atoms do have emission lines
- Can even get info on carbon bonding

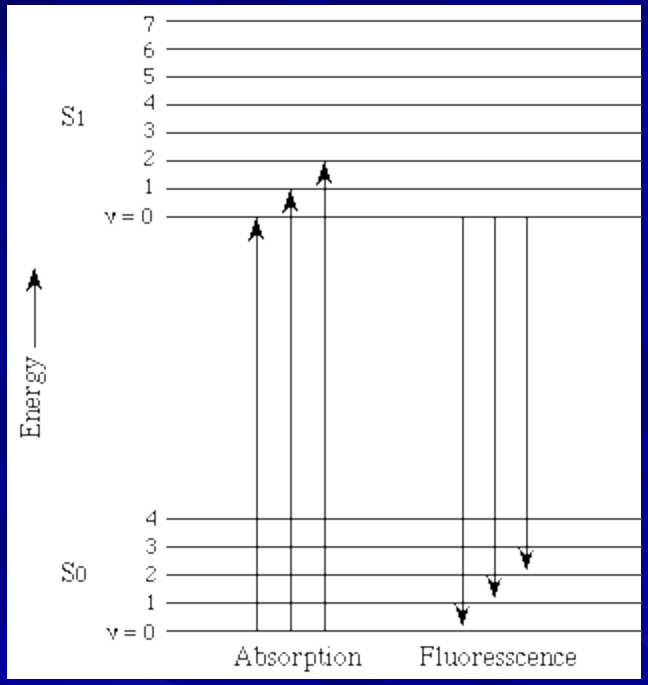


4.1. LIBS and astrobiology - status

- I don’t think anyone is actively investigating LIBS for extremophile detection and characterization (thesis time!)

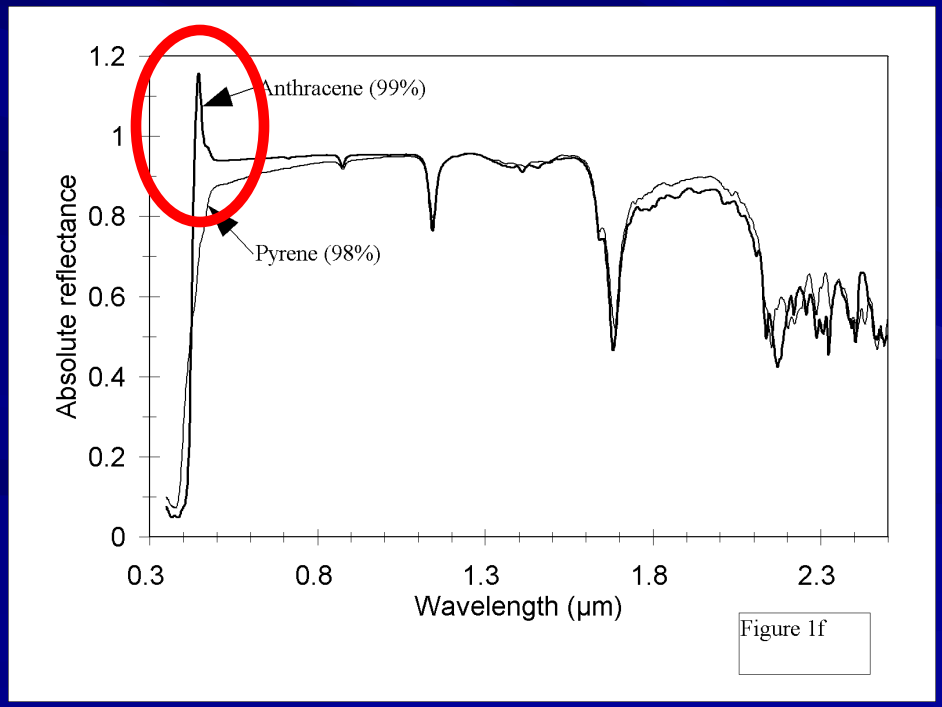
5. Fluorescence spectroscopy

- Works by exciting a molecule (again) which then decays to the ground state via one or more well-defined intermediate energy. The emitted light is always lower energy (higher wavelength) than the incident light
- To work well, need to hit a specific target with light of the right wavelength to boost it to an excited state.



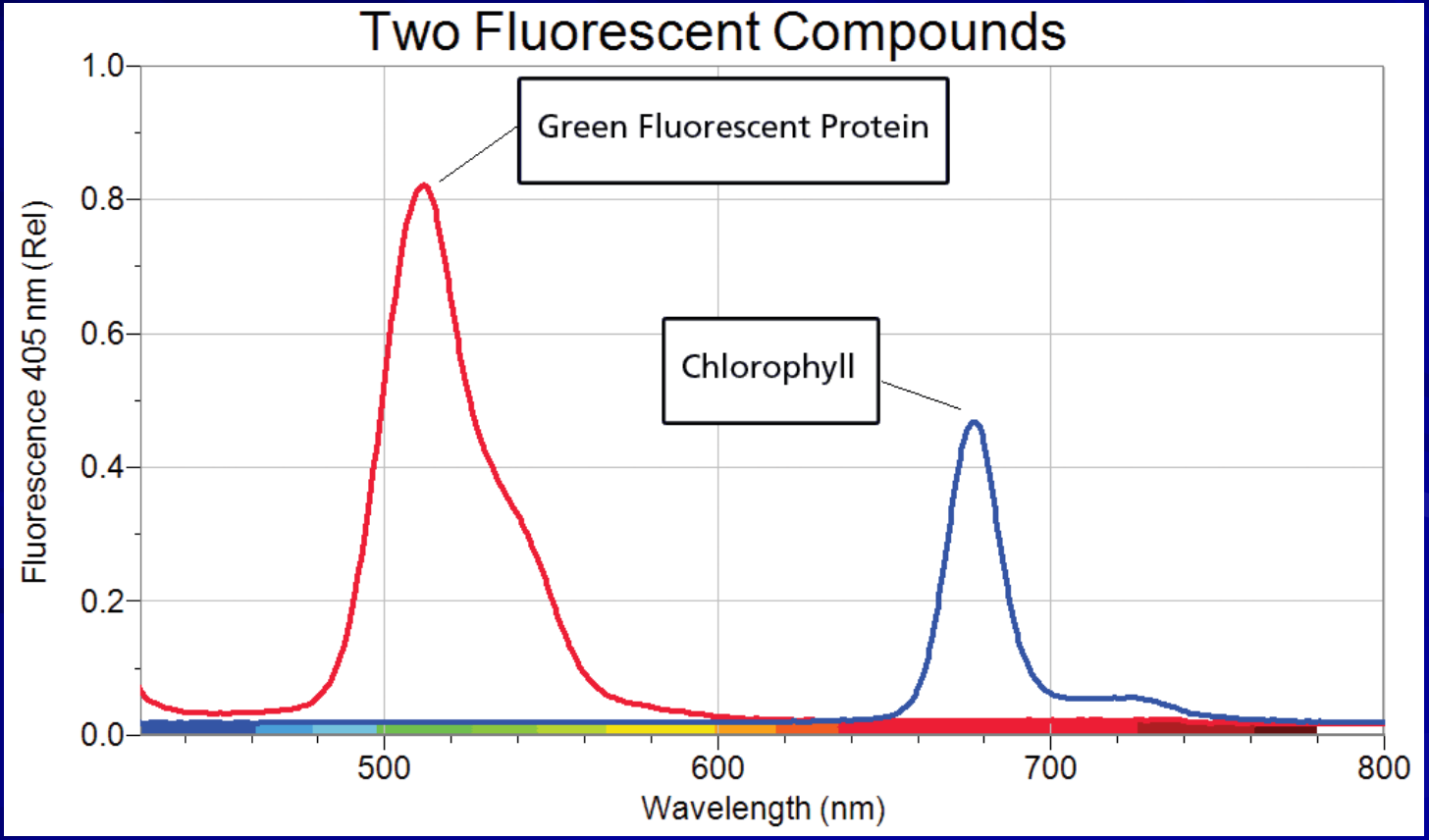
5. Fluorescence spectroscopy

- Here's an example. Anthracene strongly absorbs UV photons that are re-emitted at longer wavelength – see how the peak near 0.38 microns has >100% reflectance



5.1. Fluorescence spectroscopy and astrobiology

- Many common organic compounds have well-known fluorescence behaviour



ASTROBIOLOGY
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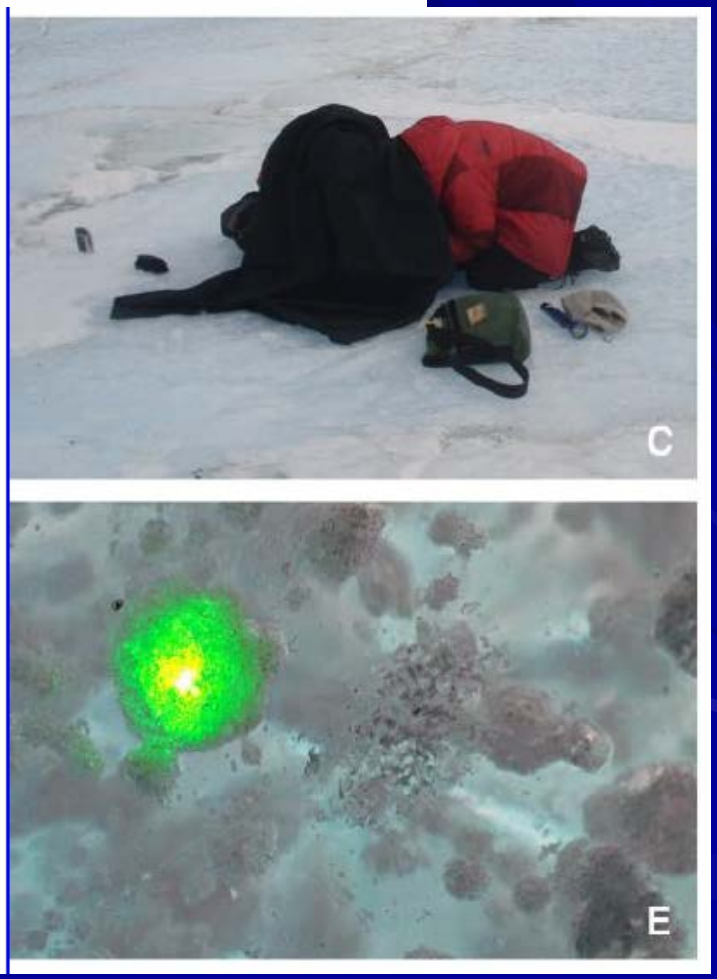
DOI: 10.1089/ast.2009.0351

Research Article

Laser-Induced Fluorescence Emission (L.I.F.E.): *In Situ* Nondestructive Detection of Microbial Life in the Ice Covers of Antarctic Lakes

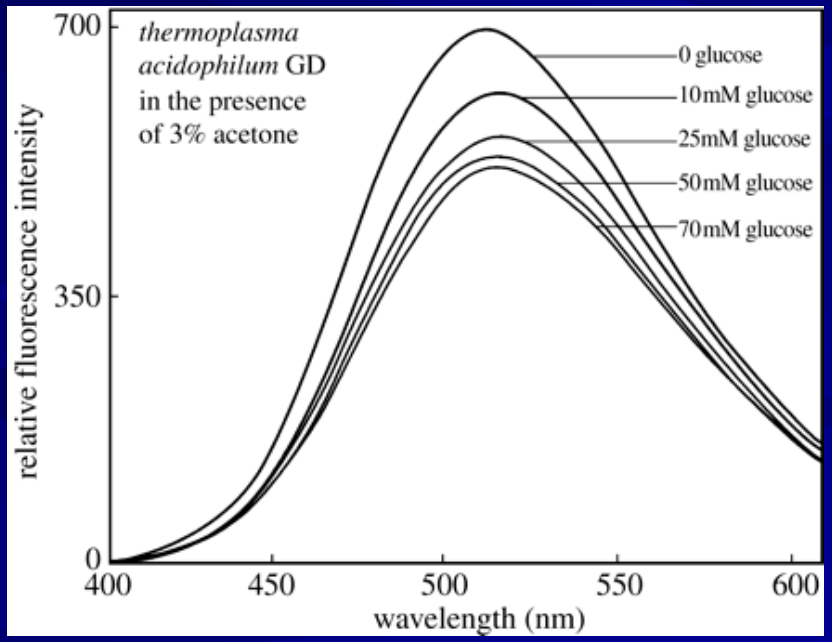
Michael C. Storrie-Lombardi[1] and Birgit Sattler[2]

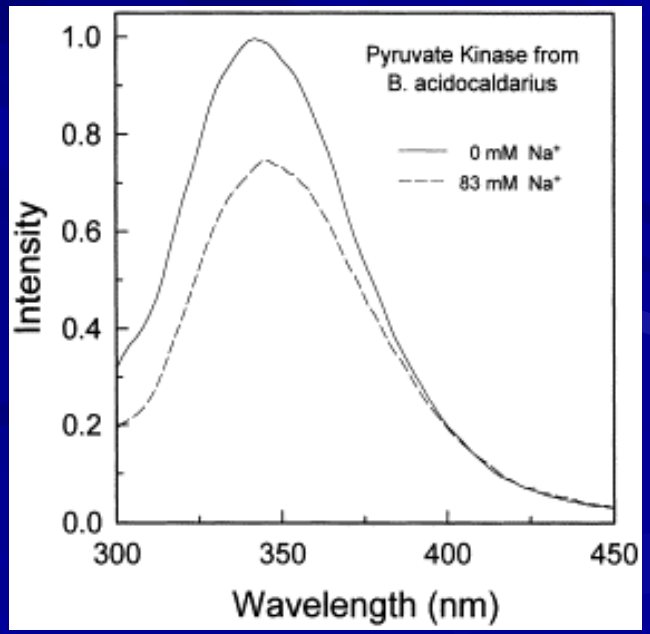
- Can take fluorescence to the individual critter level.
- Easy to do, cheap, light, robust – what's not to love?



5.1. Fluorescence spectroscopy and astrobiology

- There is a huge data base on how organic molecules fluoresce. Its cheap, light, robust, easy to do – what's not to love? Well……
  - Many minerals also fluoresce
  - Fluorescence peaks are generally broad and non-diagnostic – get a few overlapping peaks and things get ugly.





Optical spectroscopies - outlook

- The various optical spectroscopies are complementary
- Translating successes under ideal lab conditions to real world materials is tough
- None of these techniques will definitively detect life (unless something moves)
- Most can, and are being adapted for planetary missions
- Astrobiologists need to jump aboard and investigate how to exploit these instruments and maybe influence their design

Optical spectroscopies and astrobiology

- Astrobiologists need to jump aboard and:
  - Investigate how to exploit these instruments (they will fly – oh yes)
  - Maybe influence their design to be more bio-useful and less geologically-focused or find acceptable compromises
  - Figure out how specific we can get with any detections
  - Test these technologies at analogue sites
  - Test these technologies on all sorts of extremophiles

Other things to think about

- CSA has just completed development of a series of instruments for mounting on prototype rovers
- Students should:
  - Get familiar with these instruments
  - Think about how to use these techniques in their research
  - Think about how to use the actual instruments in their research
  - Think about how they can make use of the rovers/instruments on analogue missions

Astrobiologists….. **RISE UP!**