# Infrared and Raman spectroscopy for Earth and Planetary Sciences Eric Quirico – IPAG/UGA



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# The infrared and Raman ranges correspond to vibrational energies in molecules and solids





#### The ultimate quest of analyst: resolving space and frequency



Adapted from Hitchcock et al. 2002

Introducing Infrared and Raman micro-spectroscopy

- o I A little pint of theory
- o II Instrumentation and practical issues
- o III Examples of application

# Part I - THEORY



# **Born-Oppenheimer approximation**



## Let's start with the simplest model: the diatomic molecule

Decoupling of electronic, vibrationnal and rotational motions





#### **Oscillateur anharmonique**

$$E_p = \frac{1}{2}k(r - r_{eq})^2 + \sum_{i=3} \frac{1}{i!} \frac{\partial^i E_p}{\partial r^i} (r - r_{eq})^i$$
$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3$$



### How to excite a vibration ?

Absorption (IR) and Scattering (Raman) are efficient ways to excite vibrations and collect a signal that provides insights into the nature of chemical bond









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> 4 3 2

> > n



### **Some examples**



Table 3.2 Vibrational constants of diatomic molecules, cm<sup>-1</sup>

Molecule	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$
<sup>40</sup> Ar <sub>2</sub>	25.74		<u> </u>
<sup>138</sup> Ba <sup>16</sup> O	669.76	2.02	-0.003
<sup>12</sup> C <sup>16</sup> O	2169.81358	13.28831	0.010511
$^{1}H_{2}$	4401.21	121.33	0.812
<sup>1</sup> H <sup>35</sup> Cl	2990.946	52.8186	0.2243
$^{127}I_{2}$	214.50	0.614	
$^{127}I^{\bar{3}5}Cl$	384.29	1.501	
<sup>23</sup> Na <sup>35</sup> Cl	366.0	2.0	
<sup>23</sup> Na <sup>1</sup> H	1172.2	19.72	0.160
$^{23}Na_{2}$	159.12	0.7254	-0.00109
$^{14}N_{2}$	2358.57	14.32	-0.00226
<sup>14</sup> N <sup>16</sup> O	1904.20	14.075	0.011
<sup>16</sup> O <sub>2</sub>	1580.19	<b>11.98</b>	0.0474
<sup>16</sup> O <sup>1</sup> H	3737.76	84.881	0.540

Data taken from K. P. Huber and G. Herzberg, Molecular and Molecular Structure: Constants of Diatomic Molecules, Van Nostrand-Reinhold, New York, 1979.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

- v : frequency vibration
- $-\mu$  : reduced mass

C-C

C=C

C≡C

- **k** : bonding strength
- $m_A$  et  $m_B$ : masses of atoms A and B

		Liaison:	≡С-Н	=С-Н	-С-Н
1200 cm <sup>-1</sup> 1650 cm <sup>-1</sup>		Fréquence:	~3300 cm <sup>-1</sup>	$\sim 3100 \text{ cm}^{-1}$	$\sim 2900 \text{ cm}^{-1}$
	↑k	k (N.m <sup>-1</sup> ):	593	523	458
2150 cm <sup>-1</sup>		Type de liaison:	sp-s	sp <sup>2</sup> -s	sp <sup>3</sup> -s
		Longueur (Å):	1,08	1,10	1,12

$$\overline{\nu} \left[ cm^{-1} \right] = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

# $\mu$ dependency

Liaison	<b>⊽</b> (cm <sup>-1</sup> )	m <sub>2</sub> (g)	μ (g)	
С-Н	3000	1	0,923	1
C-C	1200	12	6,000	
C-O	1100	16	6,857	↑ <i>μ</i>
C-Cl	800	35,5	8,968	
C-Br	550	80	10,43	
C-I	~500	127	10,96	*

#### Line and Band



Transition between two levels: Lorentzian profil

$$L(\omega) = \frac{\gamma}{2\pi} \frac{1}{(\omega - \omega_0)^2 + \gamma^2 / 4}$$
  
$$\gamma = \gamma_{rad} + \gamma_{nonrad} + \gamma_{coll} + \dots$$



Intensity = strength of coupling

$$FWHM \propto \frac{1}{\gamma}$$

#### Absorption band

- ✓ Series of lines
- ✓ Distribution discrète (low P gas)
- ✓Continuum (liquid/solid)

$$E = \frac{h^2}{8\pi^2 I} J(J+1) + \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} (v + \frac{1}{2})$$

 $\Delta J=\pm 1$ 

#### 2 Series = Two branchs





#### Inhomogeneous broadening

Gas (Maxwellian distribution)

#### Heterogeneity in the solid

- Impurities
- defects





**Figure 8.2** The Voigt profile, formed by the convolution (8.29) of the Gaussian profile with the Lorentzian profile, effectively sums Lorentian profiles (solid curves) centered at all frequencies  $\omega'$ , weighted by the value of the Gaussian profile (dashed curve) at those frequencies.





$$I = I_0 e^{-\alpha x} = I_0 e^{-N\sigma}$$

 $\alpha$  absorption coefficient (cm<sup>-1</sup>) x thickness (cm) N column density (molecule.cm<sup>-2</sup>)  $\sigma$  absorption cross section (cm<sup>2</sup>.molecule<sup>-1</sup>)

## Solid CO



#### **Polyatomic molecules**

N atoms : 3N-6 or 3N-5 (linear) vibrations

Harmonic assumption: \* 3N-6 (5) Independant oscillators \* 3N-6 (5) Normal coordinates = lin. Comb. of atomic coordinates

$$\eta_{i} = \xi_{i} \sqrt{m_{i}}$$

$$\frac{d}{dt} (\dot{\eta}_{i}) + \sum_{j} b_{ij} \eta_{j} = 0$$

$$\eta_{i} = \sum_{j}^{3N} M_{ij} q_{j}$$

$$T = \frac{1}{2} \sum_{i}^{3N} \dot{\eta}_{i}^{2}$$

$$H = T + V = \sum_{i}^{3N-6} (\dot{Q}_{1}^{2} + \lambda_{i}Q_{i}^{2})$$
  
$$|\psi_{\text{vib}}(Q_{1}, \dots, Q_{3N-6})\rangle = \prod_{i}^{3N-6} N_{v_{i}}H_{v_{i}}(\zeta_{i})\exp(-\zeta_{i}^{2}/2)$$
  
$$\dot{Q}_{i} + \lambda_{i}Q_{i} = 0 \qquad i = 1, \dots, 3N$$
  
$$Q_{i} = Q_{i}^{0} \sin(t\sqrt{\lambda_{i}} + \delta)$$
  
$$E_{\text{vib}} = \sum_{i}^{3N-6} hv_{i}(v_{i} + \frac{1}{2})$$

**Polyatomic molecules** N atoms : 3N-6 or 3N-5 (linear) vibrations

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## $CH_4$ : ponctual group $T_d$



### Symmetry rules for IR activity

				Ta	ble 1:	Charac	ter table for $T_d$ I	point group
	$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
$v_1$	$A_1$	1	1	1	1	1		$x^2 + y^2 + z^2$
$v_2$	$A_2$	1	1	1	-1	-1		
	E	2	-1	2	0	0		$(2z^2-x^2-y^2,x^2-y^2)\\$
	$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$	
IR $V_{3,}$	$v_4 T_2$	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)



C <sub>2v</sub>	Е	C <sub>2</sub>	σ <sub>v</sub> (xz)	<b>σ</b> <sub>v</sub> , (yz)		
<b>A</b> <sub>1</sub>	1	1	1	1	z v <sub>1</sub> , v <sub>3</sub>	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	-1	R <sub>z</sub>	ху
B <sub>1</sub>	1	-1	1	-1	x, R <sub>y</sub>	xz
B <sub>2</sub>	1	-1	-1	1	y, R <sub>x</sub>	yz

#### Things gets complicated with increasing N



#### Things gets complicated with increasing N



#### Things gets complicated with increasing N

19 atoms => 51 vibrations modes Normal modes and frequencies not connected to atomic motions



# Molecular motion types

## Methylene : -CH<sub>2</sub>

symétrique

(~2853 cm<sup>-1</sup>)

asymétrique

élongation

(~2926 cm<sup>-1</sup>)

Protons are decoupled from the carbon backbone



Group vibrations and fingerprint regions

The spectral range is divided into regions of interests Bands are assigned *at first order* to a chemical bond



## **ANALYTICAL CHEMISTRY - INFRARED SPECTROSCOPY**

Commonly referred to as IR spectroscopy, this technique allows chemists to identify characteristic groups of atoms (functional groups) present in molecules.



Infrared frequencies make up a portion of the electromagnetic spectrum. If a range of infrared frequencies are shone through an organic compound, some of the frequencies are absorbed by the chemical bonds within the compound. Different chemical bonds absorb different frequencies of infrared radiation. There are a number of characteristic absorptions which allow functional groups (the parts of a compound which give it its particular reactivity) to be identified. This graphic shows a number of these absorptions.

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Lin-Vien (1991)





# Group vibrations and fingerprint regions

- A successful identification of species can be achieved for very simple mixtures
- For complex mixtures, a functional analysis can be achieved, but quantification remains an issue
- Absorption cross-sections are usually poorly known, and they are sensitive to the molecule surrounding
- Non-linearities blurr inverse-methods
- FTIR is a technique used along with an array of analytical tools

# Identification of simple molecules on planetary bodies



Emery et al. (2024)

Quirico et al. (1999)

# Coals and Kerogens

#### Bousige et al. (2016)



#### An example of very complex solid material

#### Phan et al. (2021)



# Coals and Kerogens

An example of a very complex solid material







# Coals and Kerogens

An example of a very complex solid material





Phan et al. (2021)

Integrated absorbance ratio A<sub>CH</sub>,/A<sub>CH</sub>

## Vibrational modes in solids

Solid = Giant molecule of ~6 10<sup>23</sup> atoms Vibrations propagate in the lattice as phonons

$$x(t) = Ae^{i(qx_n - \omega t)}$$


### Vibration propagation : vibron

### Translation : phonon

### *Hindered rotation : libration*



# **CO<sub>2</sub> : dispersion curves and VDOS**



# **Photon-phonon coupling**

Overtones and combinations modes reflect VDOS

### Momentum conservation

$$ec{k} = ec{q} = rac{2\pi}{\lambda} ec{n} \sim 0$$
 $u(ec{k} = ec{0})$ 
 $u_i(ec{k}) + 
u_j(-ec{k})$ 



### Static and dynamic effects

- STATIC=Symmetry of the molecule in the crystal is lower than in gas
- DYNAMIC=Phase and out-of-phase interactions of neighbouring vibrators



Figure III.3: Illustration des effets dits statique et dynamique. A) la bande  $v_5$  d'un cristal de  $CH_3I$ ; B) la même bande pour des molécules de  $CH_3I$  diluées à 10 % dans un cristal de  $CD_3I$  (d'après Poulet et Mathieu 1970).

#### Quirico et al. (1996)

### Fundamental modes SO<sub>2</sub>

Splitting LO-TO

#### Space group Aea2



<sup>a)</sup> Within the molecule, the orthogonal axes x and z lie in the molecular plane with the latter coincident with the molecular C<sub>2</sub> axis, y is normal to both.



Tableau III.1: Le diagramme de corrélation du cristal de SO2.

Figure III.4: Les bandes fondamentales  $v_1$  (a),  $v_2$  (b) et  $v_3$  (c). Ces spectres ont été effectués avec un échantillon polycristallin (couche mince) à une température d'environ 112 K. Pour les 3 modes, la composante de droite est due à l'isotope<sup>34</sup>S<sup>16</sup>O. Le profil des bandes est dû au dédoublement LO-TO.

### Overtone and combination modes in solid SO<sub>2</sub>







**Fig. 7.** The  $3v_1 + v_3$  and  $v_1 + 3v_3$  combination bands of solid SO<sub>2</sub> at 128 K. This spectrum was measured on a 1 cm thick polycrystal grown from the liquid phase. Arrows indicate the predicted dispersion width (four-phonon continuum). The two bands appear split of their respective continuum and are consequently bound states (biphonons)

### Carbonates

lonocovalent solids :

- vibrations of anions
- external modes of cations

### Aragonite: Pmcn



 $\frac{4 \text{ formular units}}{4 \text{ anions } CO_3^{2-}}$   $4 \text{ cations } Ca_2^+$  57 Vib/Lib + 3 T









#### Carteret et al. (2013)

TABLE II. Classification of the vibrational modes of aragonite. Symmetry is obtained from group theory analysis. IR and Raman polarization directions are indicated. External (lattice) and  $CO_3^{--}$  internal modes are characterized by very different frequencies, and are easily identified through graphical animation of the eigenvectors.

			<b>Optical Modes</b>				
Symmetry	IR activity	Raman activity	External	Internal	Total		
$\overline{A_g}$		$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	5	4	9		
$B_{1g}$		$lpha_{xy}$	4	2	6		
$B_{2g}$		$lpha_{\scriptscriptstyle XZ}$	5	4	9		
$B_{3g}$		$\alpha_{yz}$	4	2	6		
$A_u$			4	2	6		
$B_{1u}$	$\mathbb{E} \parallel c$		4	4	8		
$B_{2u}$	$\mathbb{E} \parallel b$		3	2	5		
<i>B</i> <sub>3<i>u</i></sub>	E    <i>a</i>		4	4	8		

 $\Gamma_{total} = 9A_g \oplus 6A_u \oplus 6B_{1g} \oplus 8B_{1u} \oplus 9B_{2g} \oplus 5B_{2u}$  $\oplus 6B_{3g} \oplus 8B_{3u}. = 57 \text{ optical vibration modes}$ 

TABLE III. Calculated (B3LYP) and experimental (fitted) IR active vibrational frequencies  $\nu$  (cm<sup>-1</sup>) and oscillator strengths *f* (adimensional and multiplied by 10<sup>3</sup>) along the *a*, *b*, and *c* axes ( $B_{3u}$ ,  $B_{2u}$ , and  $B_{1u}$  symmetry, respectively) of aragonite. Calculations were performed at the optimized cell volume. Experimental values were obtained through a best fit with the three-parameter Drude-Lorentz model.  $\delta \nu$  is the TO-LO splitting.  $\Delta \nu$ ,  $\Delta f$ , and  $\Delta \delta$  are the differences between calculated and experimental quantities.  $F = \sum_n f_n$  is the sum of the oscillator strengths,  $\Delta F = \sum_n |\Delta f_n|$  is the sum of the absolute differences between experimental and calculated oscillator strengths. Statistics are reported in Table V. The symbol # indicates a combination mode.

		ТО				LO			TO-LO				
		$v_{calc}$	ν <sub>exp</sub>	$\Delta \nu$	$f_{calc}$	$f_{exp}$	$\Delta f$	$v_{calc}$	ν <sub>exp</sub>	$\Delta \nu$	$\delta v_{calc}$	δν <sub>exp</sub>	$\Delta\delta$
a (B <sub>3u</sub> )	1	174.1	183.1	-9.0	91.8	60.4	31.40	174.6	183.3	-8.7	0.5	0.2	0.3
	2	210.1	207.8	2.3	3920.2	4105.6	-185.36	353.8	348.4	5.4	143.7	140.6	3.1
	3	269.1	259.2	9.9	62.4	77.4	-15.01	266.9	257.2	9.7	-2.2	-2.0	-0.2
	4	288.9	286.9	2.0	35.0	43.5	-8.53	287.0	284.6	2.4	-1.9	-2.3	0.4
	5	719.2	718.3	0.9	0.1	0.4	-0.26	719.2	718.4	0.8	0.0	0.1	-0.1
	#		843.6		•••	6.1							
	6	861.9	852.2	9.7	113.1	116.1	-2.98	886.7	876.7	10.0	24.8	24.5	0.3
	7	1092.9	1082.8	10.1	2.4	1.9	0.46	1093.6	1083.3	10.3	0.7	0.5	0.2
	8	1469.9			0.0			1469.9			0.0		
	$F\left[\Delta F ight]$				4225.0	4405.3	[244.0]						
b (B <sub>2u</sub> )	1	65.4	105.4	-40.0	6554.9	2228.3	4326.63	83.7	116.5	-32.8	18.2	11.1	7.1
	2	158.7	164.2	-5.5	62.1	53.4	8.66	158.9	164.2	-5.3	0.3	0.0	0.3
	3	198.0	219.9	-21.9	5838.5	4862.0	976.45	343.8	352.5	-8.7	145.8	132.6	13.2
	4	697.4	699.8	-2.4	5.2	6.7	-1.53	698.1	699.0	-0.9	0.7	-0.8	1.5
	5	1445.1	1444.5	0.6	467.1	458.0	9.08	1571.8	1561.0	10.8	126.7	116.5	10.2
	$F\left[\Delta F ight]$				12927.7	7608.4	[5322.4]						
$c\left(B_{1u}\right)$	1	147.3	144.4	2.9	16.2	59.3	-43.10	147.4	144.9	2.5	0.1	0.5	-0.4
	2	200.7	208.6	-7.9	2617.5	1829.6	787.87	218.4	221.3	-2.9	17.8	12.7	5.1
	3	245.5	249.5	-4.0	2286.7	2423.0	-136.31	359.7	364.2	-4.5	114.2	114.7	-0.5
	4	293.1	298.0	-4.9	7.0	164.9	-157.91	292.8	292.8	0.0	-0.2	-5.2	5.0
	5	712.2	712.4	-0.2	15.5	16.6	-1.12	714.2	714.4	-0.2	2.0	2.0	0.0
	6	913.1	908.8	4.3	0.1	0.2	-0.06	913.1	908.8	4.3	0.0	0.0	0.0
	7	1092.9	1082.8	10.1	1.3	1.1	0.21	1093.1	1082.9	10.2	0.2	0.1	0.1
	8	1474.1	1466.6	7.5	469.2	461.2	8.02	1602.9	1586.0	16.9	128.8	119.4	9.4
	$F\left[\Delta F ight]$				5413.5	4955.9	[1134.6]						



#### Chakrabarty and Mahapatra (1999)



# Part II - Instrumentation and practical issues

### FTIR spectroscopy



$$\tilde{I}(\delta) = \int_0^\infty I(\bar{\nu}) \cos^2(\pi \delta \bar{\nu}) d\bar{\nu} = \frac{1}{2} \int_0^\infty I(\bar{\nu}) (1 + \cos(2\pi \delta \bar{\nu})) d\bar{\nu}$$







Fig. 1.8 Series of apodization functions and their corresponding instrument line shape functions; in each case the equations representing the shapes of the apodization and ILS functions are given, together with the full width at half-height,  $\Delta v_{1/2}$ , and the amplitude of the largest side lobe, S, as a percentage of the maximum excursion. (a) Boxcar truncation; (b) trapezoidal; (c) triangular; (d) triangular squared; (e) Bessel; (f) cosine; (g) sinc<sup>2</sup>; (h) Gaussian apodization. (Reproduced from [5], by permission of the Optical Society of America; copyright © 1981.)

#### Griffiths and Haseth (2007) 2<sup>nd</sup> Edition

# Mono and FPA detectors for fast imaging



Focal Plane Array (FPA)-Detector

There are two separate optics within the microscope to optimize the homogeneity of the infrared and the visual light

The size of the FPA-Detector element is 2.56 x 256mm Using the 15x objective total measurement area corresponds to 2.56mm $15=177\mu m$ 

The size of each pixel is  $177\mu$ m\64 (number of pixels) =2.6µm (depending on the wavelenght)

#### **HYPERION 3000**



Improve spatial resolution and signal-to-noise ratio

# + source luminance (Csl Globar, synchrotron, tunable laser)+ objective diffraction



Theoretical spatial resolution is almost never reached for complex heterogeneous natural samples



50 µm





50 µm

FIG. 5. Transmission FT-IR imaging of three human hairs. Images based on the variation of (A) the amide II band and (B) the CH stretching band of hair; the color scale bars show the value of the integrated absorbance for each band. Image size is  $266 \times 266 \ \mu m^2$ . (C) The integrated absorbance profile along the line shown on image (A); blue diamonds and red triangles, respectively, represent the profile of amide II (1540 cm<sup>-1</sup>) and CH bending (1396 cm<sup>-1</sup>) of hair. (D) Visible image of the embedded hair sample. (E) The extracted spectra along the line indicated in (A) from the left of the line (top spectrum) to the right (bottom spectrum).

## ATR = Attenuated Total Reflectance spectroscopy



- Improve spatial resolution (factor 2-4)
- Spectra not strictly similar to transmission spectra

#### 10 µm



Distance/µm

15 the line (bottom spectrum) to the right (top spectrum).

# AFMIR = combined FTIR + AFM

- A new generation of instrument operating at ultra high spatial resolution (~40 nm)
- Real potential still to be tested
- Not easy to implement: developments in sample preparation
- Will be continously improved thanks to laser development





Dazzi et al. (2012) Applied Spectroscopy

# Sample preparation for IR: a critical issue

- ☑ Quantification
- ☑ Spectral quality
- ☑ Band saturation and signal-to-noise ratio



## Absorption and radiative transfert

- Solid sample must be thin enough (< tens of micrometers)
- Reflection/transmission at each dioptre => interferences



 ✓ Spectrum = f(n,k)
 ✓ Optical modeling required: radiative transfer and Krammers-Krönig algorithm

# Formation of thin films from vapor

### Cryogenic system for ices



### Evaporator for refractories





# Formation of thin films from vapor





- Control thickness and planeity/rugosity by interfgerometry (de 10-100 nm à ~ 100 μm)
- Controlled conditions of deposition and annealing (substrate, température, deposition rate)
- Monocrostalline or polycrystalline samples.
- Contamination (eau, CO2...).
- Index gradient possible for the first monolayers.



# Cristal growth from the liquid phase



#### Thickness range = $25-800 \ \mu m$







# Measurements on pellets





✓ Robust material (resistant to grinding)
 ✓ Scattering and water contamination
 ✓ Quantification difficult: require radiative transfert and scattering modeling
 ✓ No control on crystal orientation

# Ultramicrotomy

Standard thin section (30  $\mu$ m): limited to NIR in transmission, epoxy contamination.

Double-polishing : suitable for faint feature in NIR (e.g. structural OH)

```
✓ thins (~ 1 µm)✓ ultra-thin (20-200 nm)
```





✓ Epoxy vs Organic matter✓ Hard material = difficult
# Ultramicrotomy in sulfur



Figure 5. Conceptual diagrams of embedding processes in our protocol.

# Ultramicrotomy in sulfur







## **Pressing (soft samples)**

- ISO 7 clean room, under an ISO 5 laminar hood.
- Micromanipulation by hand







# MEB images (SE2)



Crushed on diamond window



#### Crushed on Germanium window



# **Part III - Applications**

## **III.1 - Geomaterials in the laboratory**







Organic matter



+

Water

# **Usual minerals**

Silicates	Tectosilicates Inosilicates Nesosilicates Phyllosilicates	Si polymorphs, Feldspaths, Amphiboles, pyroxens, Olivines, Garnets, Micas, Chlorites, serpentine,
Carbonates		
Sulfates		
Sulfides		
Phosphates		
Oxides/Hyd	roxides	

Merouane et al. (2014)

# Mineralogy of cometary grains



10 µm

5 kV

20 µm

5 kV





#### Linear combination of end-members

- 1. Fe and Mg end members of olivine (forsterite:  $Mg_2SiO_4$ and fayalite: Fe<sub>2</sub>SiO<sub>4</sub>, noted as Fo and Fa, respectively, in the following sections).
- 2. Mg end member and Ca–Mg solid solution of pyroxene (enstatite:  $MgSiO_3$  and diopside:  $CaMgSi_2O_6$  noted as En and Di, respectively, in the following sections).
- 3. Amorphous compounds of Fe and Mg olivine end members compositions and an amorphous compound of pyroxene Mg end member composition.

Table 3

Silicate Composition of Each Particle Given by Our Fitting Procedure

	-		•			
Particle	ol/(ol+px)	Mg/(Mg+Fe)	Ca/(Ca+Mg)	Amorphous Content		
L2021 C5	0.7	1	0	35%		
L2021 D7	0.1	1	0.6	0%		
L2021 Q3	1	0.95		0%		
L2036 AE3	0	1	0	0%		
L2036 AE4	1	0.45		0%		
L2036 AG1	0.15	1	0.025	80%		
L2071 E36	1	0.75		5%		
L2076 H1	0.3	1	0.075	0%		
L2079 J1	0.7	1	0	45%		
L2083 B7	0.95	1	0	0%		
L2083 E11	0.65	1	0	0%		
L2083 E15	0.35	1	0	0%		

## Mg-Rich Silicate Crystals in Comet Hale–Bopp: ISM Relics or Solar Nebula Condensates?



FIG. 1. Silicate features in Comet Hale–Bopp at four epochs, fitted with smooth curves (smoothed over ~0.24  $\mu$ m at all epochs except over ~0.48  $\mu$ m at 2.8 AU) using a least-squares algorithm (Bevington 1969). The silicate features are shown by the flux-to-continuum ratios (Hanner *et al.* 1994b), with continuum parameters from Wooden *et al.* (1999). The silicate features flux/cont are derived from the HIFOGS spectra on 1996 October 07–14 UT at 2.8 AU (preperihelion) (*heavy black line*), 1997 February 14–15 UT at 1.2 AU (preperihelion) (*heavy black line*), 1997 February 14–15 UT at 1.2 AU (preperihelion) (*heavy gray line*), 1997 April 11 UT at 0.93 AU (~perihelion) (*thin black line*), and June 24–25 UT at 1.7 AU (post-perihelion) (*dotted line*). The principal peaks of the crystalline ortho-pyroxene at 9.3 and 10.5  $\mu$ m and of crystalline olivine at 10.0, 11.2, and 11.8  $\mu$ m (Koike *et al.* 1993) are marked (*vertical hairlines*).



#### Emission ~ B(I,T)\*e(I)=B(I,T)\*abs(I)





#### THE INFRARED SPECTRUM OF COMET HALE-BOPP\*

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Figure 4. The SWS spectrum of C/1995 O1 (Hale-Bopp) and a modelled spectrum of forsterite (from a laboratory spectrum provided by W.-F. Thi and L. d'Hendecourt).

## **Probing water in geomaterials**











#### Hydroxyls and molecular water in clays





Kaolinite

#### Pyrophillite

Layer type	Interlayer	Group*	Subgroup	Species Chrysotile, lizardite, amesite			
1:1	None or H <sub>2</sub> O only	Serpentine-kaolin $x \sim 0$	Serpentines				
8 . 000	(Eds.), M	nwox8 .D bn	Kaolins	Kaolinite, dickite, nacrite, halloysite			
	None	Talc-pyrophyllite	Talcs	Talc, willemseite			
		x ~ 0	Pyrophyllites	Pyrophyllite, ferripyrophyllite			
	Hydrated exchangeable	Smectite x ~ 0.2-0.6	Saponites	Saponite, hectorite, sauconite, stevensite, etc.			
	cations		Montmorillonites	Montmorillonite, beidellite, nontronite, volkonskoite, etc.			
	Hydrated exchangeable cations	Vermiculite x ~ 0.6-0.9	Trioctahedral vermiculites Dioctahedral vermiculites	Trioctahedral vermiculite Dioctahedral vermiculite			
2:1	Non-hydrated	True mica	Trioctahedral true micas	Phlogopite, biotite, lepidolite			
	cations	$x \sim 0.5 - 1.0$	and the second s	zinnwaldite, annite, etc.			
			Dioctahedral true micas	Muscovite, illite, glauconite, tobelite, paragonite, etc.			
	Non-hydrated cations	Brittle mica $x \sim 2.0$	Trioctahedral brittle micas	Clintonite, bityite, anandite, kinoshitalite			
			Dioctahedral brittle micas	Margarite			
	Hydroxide sheet	Chlorite x variable	Trioctahedral chlorites	Clinochlore, chamosite, nimite, pennantite, baileychlore			
	a presi bornen		Dioctahedral chlorites	Donbassite			
			Di, trioctahedral chlorites	Cookeite, sudoite			



FIG. 15.3 (*left*). Hydroxyl absorption of A, talc; B, hectorite; C, saponite; D, phlogopite; E, biotite; F, biotite. The mica spectra were obtained from single flakes at normal (N) and 45° incidence (R). The spectra of hectorite and saponite correspond to anhydrous K-saturated specimens.

FIG. 15.4 (*centre*). Hydroxyl absorption of randomly oriented samples of A, pyrophyllite; B, beidellite; C, rectorite; D, muscovite or paragonite; E, margarite; F, Wyoming montmorillonite; G, Skyrvedalen montmorillonite; H, Woburn montmorillonite; J, nontronite and K, ferric celadonite. FIG. 15.5 (*right*). Hydroxyl absorption of A, kaolinite; B, dickite; C, nacrite; D, Pugu kaolin (disordered). R indicates randomly oriented specimens, and N films at normal incidence. Spectra (Figs 3, 4, 5) from Farmer and Russell (1964).

# OH cationic environment controls OH peak positions

TABLE 15.I. Band frequencies  $(cm^{-1})$  in the hydroxyl stretching region of the infrared spectrum of some synthetic talcs, from Wilkins and Ito (1967)

Talc composition	OH ion vibration frequency close to								
	Mg Mg Mg	Mg Mg R	Mg R R	RRR					
Mg100	3676.6	Star Star		31 12 12					
Mg84Ni16	3676.5	3661.9	3644.8	occab <u>ae</u> r					
Mg76 Ni24	3676.6	3662.3	3645.2	3624.1					
Mg52 Ni48	3676.5	3662.5	3645.9	3625.0					
Mg28 Ni77	3676.7	3662.9	3646.2	3625.9					
Mg1 Ni99			3646.9	3627 . 2					
Mg54 Co46	3677.4	3661.4	3643.3	3622.3					
Mg <sub>92</sub> Zn <sub>8</sub>	3676.6	3664.4	3649.7						
Mg86 Zn14	3676.8	3665.2	3651.6	3634.6					
Mg52 Fe48	3678.3	3663.5	3646.0	3624.2					
Mg92 Mn8	3677.1	3663.6	3650.0						
Mg55 Cu45	3676.0	3669.9	3663.7	3656.3					



FIG. 15.2. OH stretching vibrations of synthetic Mg–Ni talcs. 5-7.5 mg samples in KBr disks (from Wilkins and Ito, 1967).

## Cations in octahedral layers of micas

Easy to implement Probe only octahedric catrions bound to OH Whatever the cation (e.g. NMR, Fe)

#### Well-known standards

Sample Cation	Zavalye C (I)	69G (II)	31 (III)	B. Patom G (IV)	655 <b>G</b> (V)	Taiheisan C (VI)	E8/2 <b>G</b> (VII)	5/1 (VIII)	Oya C (IX)	933/3 (X)	132 (XI)	133G (XII)	
Si	3.96	3.94	3.94	3.46	3.64	3.72	3.65	3.69	3.99	3.88	3.96	3-84	
Al <sub>IV</sub> Fe <sup>3+</sup>	0.04	0.06	0.06	0.54	0.36	0-28	0-35	0-31	0.01	0·02 0·10	0-04	 0∙16	Substitution in T
Alvi	0.05	0.05	1.10	1.11	0.08	0.16	0.68	0.13	0.93	in a	1.4		
Fe <sup>3+</sup>	0.96	1.15	0.17	0.41	1.08	1.07	0.79	1.30	0.25	1.47	1.32	0.75	
Fe <sup>2+</sup>	0-26	0.36	0.07	0.13	0.12	0.14	0.10	0.07	0.44		0.07	1.05	In O layer
Mg	0.73	0.41	0.64	0.35	0.66	0.67	0.43	0.50	0.31	0.53	0.54	0.55	
K	0.89	0.83	0.91	0.74	0.90	0.82	0.78	0.78	0.73	0.43	0.65	0.59	
Na		0.01	0.07	0.01		0.18	0.01		0.18	0.08	0.02	0.03	Interfalier
Ca	0.10	0.03		0.06					0.02	0.02	0.01		interioliar
Mg				0.07				0.02		0.05			

Besson et al. Clay Minerals (1987) 22, 465-478 Slonimskaya et al. Clay Minerals (1986), 377-388



FIG. 3. Decomposition of the IR spectrum of leucophyllite 31.



FIG. 4. Decomposition of the IR spectrum of Bolshoi Patom glauconite.

Free parameters: ✓ Position ✓ FWHM ✓ Integrated intensity 600

00

FIG. 1. Decomposition of the IR spectrum of Zavalye celadonite.



FIG. 2. Decomposition of the IR spectrum of celadonite 69G.

Absorption coefficient similar for all components

Wave number (cm <sup>-1</sup> )	r Cation pair	Zavalye (I)	69G (II)	31 (III)	B. Patom (IV)	655 (V)	Taiheizan (VI)	E8/2 (VII)	5/1 (VIII)
3495	Fe <sup>2+</sup> Fe <sup>2+</sup>	hand <del>-</del> À	6.5	<u></u>	e en <del></del> triget				
3505	MgMg	9.1	3.0	2.9	and the second	8.4	9.9	(	5.0
3531*	$Fe^{2+}Fe^{3+}$ $Fe^{3+}Fe^{3+}$	30.0	49.8	3.2	20.2	28.0	30-1	14.9	35.9
3545	Fe <sup>3+</sup> Fe <sup>3+</sup>	ts, T <u>he</u> ab	3.6	i ir <u>tis</u> no	13 . <u>2 .</u> for s	4.3	diana <u>na</u> r kad	j	11.5
3560	Mg Fe <sup>3+</sup>	54.0	30.0	16.4	6.9	38.3	35.6	32.8	23.1
3580	Fe <sup>2+</sup> Al	2.6	ger <del></del> ord	1.7	8.1	6.8	11.4	7.6	8.9
3605	Mg Al	4.3	6.8	46.8	26.7	10.4	8.8	12.9	12.0
3620	Al Al	and the second second	1994)	12.8	22.6	3.2	3.3	27.6	3.6
3640	Al Al	1999 <u>109</u> 900	010 <u>5 01</u> 1	16.2	15.2	0.6	0.9	4.2	
χ²		1.55	0.65	0.23	0.29	0.12	0.75	1.01	0.17
(3528	Fe <sup>2+</sup> Fe <sup>3+</sup>	21.1	23.0	3.2	6.0	6.3	2.1	0.9	
* { 3534	Fe <sup>3+</sup> Fe <sup>3+</sup>	8.9	26.8	att day	14.2	21.7	28.0	14.0	35.9

TABLE 2. Correlations between OH stretching frequencies and octahedral cations to which the hydroxyl groups are coordinated, and integrated optical densities of IR band (%).

 $C_{\rm Al} = (2W_{\rm AlAl})_{\rm calc} + (W_{\rm AlFe^{2+}})_{\rm calc} + (W_{\rm AlFe^{3+}})_{\rm calc} + (W_{\rm AlMg})_{\rm calc}.$ 

W : Integrated absorbance of the Lorentzian component

Composition of octahedral layer is determined Combining with SE put constraints on composition of the tetrahedral layer

#### Insights into long and short range orders in extraterrestrial proto-serpentines

b



Organics

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200µm

hosphate Lith.

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#### Insights into long and short range orders in extraterrestrial proto-serpentines





Beck et al. (2014)

#### Fe/Mg ratio controls with and position of 3 µm OH feature



#### Water in Earth mantle: where and how much?



<sup>-&</sup>lt;u>hydrated mineals (phyllosilicates, amphiboles, ...)</u>

- nominally anhydrous minerals (olivines, pyroxenes, ringwoodite, ...)









Bournhonnet, Rapport stage M2R / dir. J. Ingrain Beamline SA5 - LURE (Orsay)

# Abundance estimation

Calibration with standards (hydrogen measured by mass spectrometry)





Model structure of humic acid (Stevenson 1982)

#### Characterization of fungal melanins and soil humic acids by chemical analysis and infrared spectroscopy

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Fig. 1. Infrared spectra of fungal melanins. A Melanins from fungal cells of Asperisporium caricae; B Melanins from fungal cells of Cladosporium oxysporum; C Melanin from culture medium of Pleurophragmium sp.; D Melanin from culture medium of Asperisporium caricae; E Melanin from fungal cells of Aspergillus sydowi



Figure 1. DRIFT spectra of the whole soil (a), of the HS-extracted soil (b) and of the oxidized soil (c) of the Chernosol.

#### Multi-variate statistical approaches

Estimate soil quality for ingeneering purposes



Fig. 6. Mid-infrared absorbance spectra for calibration (n=135) and validation (n=120) of soil samples after removal of the noisy part ( $<600 \text{ cm}^{-1}$ ) of the signal (spectra is shown in both wavenumbers (cm<sup>-1</sup>) and wavelength (nm) for easy reference, where [(10,000,000/wavenumbers)=wavelength)].
#### Table 1 Soil properties and methods.

Soil property	Method of determination	Reference
Air-dried moisture content ( <b>W</b> )	Gravimetric (%)	Islam et al. (2003)
Particle-size distribution	Hydrometer (%)	Gee and Bauder (1986)
tClay, tSi, tSa		
Exchangeable Ca (eCa), Mg (eMg)	1:10 soil-to-1.0 N KCL extraction followed by AAS $(cmol(+)kg^{-1})$	Shepherd and Walsh (2002)
Exchangeble Na (eNa)	1:10 soil-to-1.0 N KCL extraction followed by AES $(cmol(+) kg^{-1})$	Shepherd and
Exchangeable K (eK)	1:10 soil-to-modified Olsen solution extraction followed by AAS $(cmol(+)kg^{-1})$	Walsh (2002) Shepherd and
Cation exchange	Sum of $eCa + eMg + eNa + eK \ (cmol(+)kg^{-1})$	Shepherd and Walsh (2002)
ESP	Ratio [(eNa/CEC)*100] (%)	Viscarra Rossel et al. (2008)
Sodium-ion concentration	1:5 soil-to-water extract read on Na-ion electrode meter (Na5, mg kg $^{-1}$ )	Irvine and Reid (2001)
Soil organic carbon (SOC)	Dry combustion using CN analyzer (%)	Viscarra Rossel et al., 2008
Atterberg limits: LL, PL, LS	BSI BS: 1377 (%)	BSI (1975)
Plasticity index (PI)	Numeric difference ( $PI=LL-PL$ ) (%)	BSI (1975)
Coefficient of extensibility (COLE)	from LS data [(COLE=(Lm-Ld)/Ld)] (unit); where Lm=length moist soil (=140 mm), Ld=length dry soil (140–LS mm)	Igwe (2003)
Volumetric shrinkage (VS)	From COLE data, $VS = [(COLE + 1)^3 - 1]^* 100 (\%)$	Igwe (2003)
Activity number (A)	A=PI/tClay (%)	Fratta et al. (2007)



## III.2 Carbonaceous materials: the advantage of Raman spectroscopy



Bernier et al. (1997)

The fourth element in the universe is highly versatile







The fourth element in the universe is highly versatile





#### Raman features of carbon materials:

- G and D peaks in a VDOS (but named bands)
- Resonance effect: high sensitivity
- Dispersive bands (vary upon wavelength excitation)
- Semi-quantitative characterization

# Structural order of graphites, kerogens and coals



Tuinstra and Koenig (1970); Wopenka and Pasteris (1993)

## Thermometry in metasediments



**Fig. 1.** Geological map of the Schistes Lustrés unit, western Alps, with sample location and main isograds in pelites: *car*, carpholite; *cld*, chloritoid; *grt*, garnet. (modified after Beyssac *et al.*, 2002).

# Thermometry in metasediments



### Metamorphic grades



## Thermometry in metasediments



R2 ratio

# Very disordered carbon materials



FIG. 6. Schematic diagram of influences on the Raman spectra. A dotted arrow marks the indirect influence of the  $sp^3$  content on increasing G position.

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a} \qquad \frac{I(D)}{I(G)} = C'(\lambda)L_a^2$$

Ferrai et al. (2000, 2001)



#### Ferrari+2000

## Very disordered carbon materials



# Coals



- Raman spectra sensitive to weak structural variations
- TK70 relation does not hold

Celemen&Fang01; Ouirico+05: Jehlicka+03.08

# Coals



• Simple parameters trace the extent of heating : FWHM-D,  $I_D/I_G$ , ...

• No quantitative structural parameters

Kelemen and Fang 01; Jehlicka+03; Quirico+03, 05

# Thermal metamorphism of poorly ordered OM

Kouketsu et al. (2014)



**Fig. 1** Locations of the Kasuga, Daimonji, Shirataki, Kitagawa, Kure, and Nobeoka areas and distributions of the Ryoke, Mino-Tamba, Sambagawa, Chichibu, Shimanto, and Kurosegawa belts in Southwest Japan. Abbreviation: MTL, Median Tectonic Line.



# Thermal metamorphism of poorly ordered OM



Fig. 3 Flowchart for the peak fitting procedure used in this study.

# Thermal metamorphism of poorly ordered OM



 $T (^{\circ}C) = -2.15 (FWHM-D1) + 478$ (coefficient of determination  $R^2 = 0.970$ )

(Equation 1)

and

 $T (^{\circ}C) = -6.78 (FWHM-D2) + 535$ (R<sup>2</sup> = 0.968) (Equation 2)

# Low thermal metamorphism in primitive meteorites

## 151 chondrites / 112 with Raman features



- Reappraisal of petrologic types (PT)
- Identification of very primitive objects
- PT reflects peak temperature
- Insensitive to retromorphosis
- Weak dependance on fluid circulation



# More than heating

COALS



### **CHONDRITES**



# More than heating



- IOM remains O-rich  $\odot$
- Different structural pathways  $\odot$
- $\odot$
- Precursor memory(?), possibly metamorphic conditions Precursors accreted by different families are fairly similar  $\odot$

# CONCLUSIONS

- Infrared and Raman spectroscopy are versatile non-destructive techniques
- Insights into water and organic matter in geomaterials
- Nanometric scale is now achieved, bit still implementation and interpretation issues
- Remote sensing applications