Honey and wine

2D correlation spectroscopy

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24.02.2021

0 Outline

1 Outline

1 Experiment

- FTIR spectrometer
- mid-IR range
- ATR accessory
- liquid samples

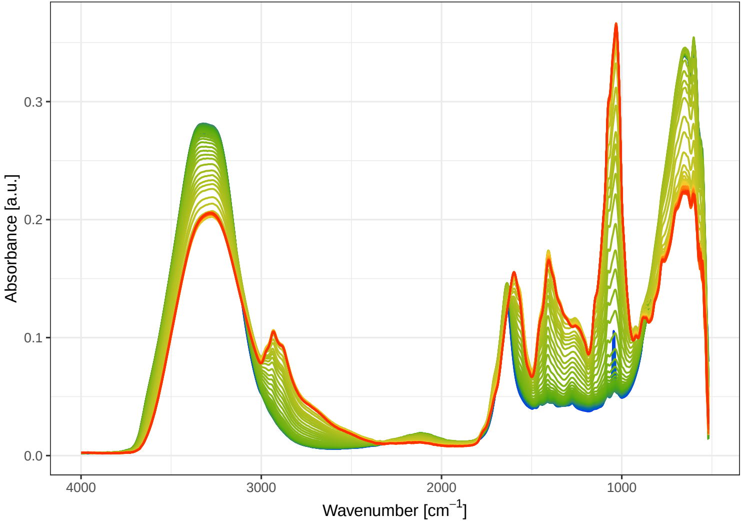
- macro-driven experiment
- sets of spectra with time-stamp in filename

1 Sample: Propolis

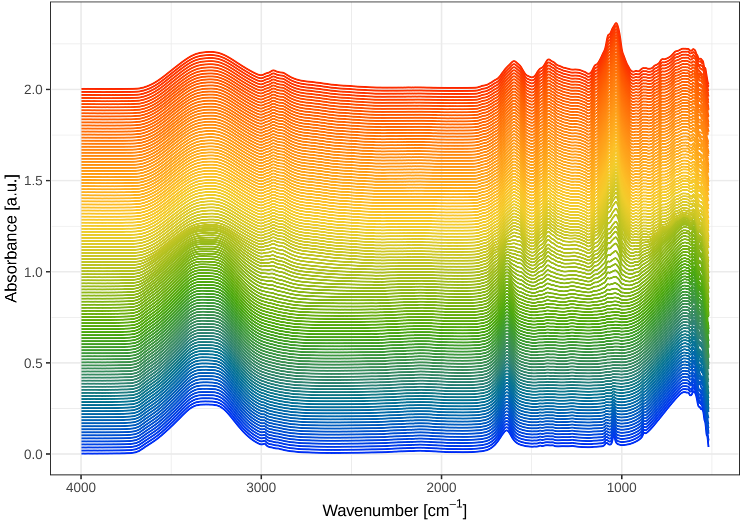
- derived from Greek to mean defense for *pro* and city or community for *polis*
- *bee glue* for sealing holes and cracks and for the reconstruction of the beehive and smoothing the inner surface of the beehive,preventing invasion by predators
- composed mainly of resin (50%), wax (30%), essential oils (10%), pollen (5%), and other organic compounds (5%) (phenolic compounds, esters, flavonoids, terpenes, beta-steroids, aromatic aldehydes, and alcohols)
- contains also important vitamins (B1, B2, B6, C and E) and useful minerals (Mg, Ca, K, Na, Cu, Zn, Mn and Fe)
- numerous applications in treating various diseases due to its antiseptic, anti-inflammatory, antioxidant, antibacterial, antimycotic, antifungal, antiulcer and anticancer

1. Introduction
2. Classic Visualization
   - All Spectra
   - Wavenumbers time dependence
3. Multivariate Statistics
4. Correlation Matrix
5. 2D Correlation Spectroscopy
6. Summary

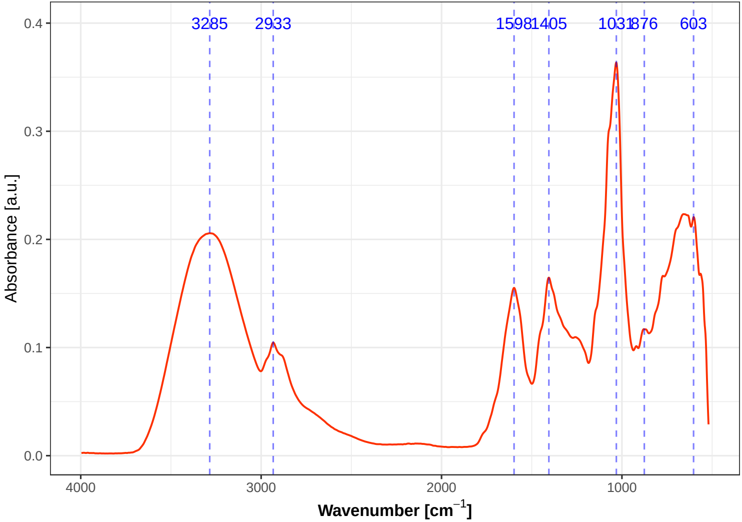
2 All spectra: from blue to red



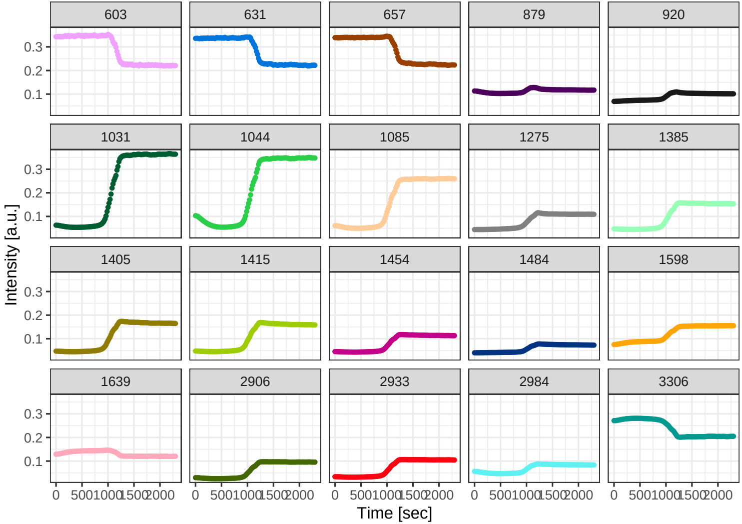
2 All spectra with shift



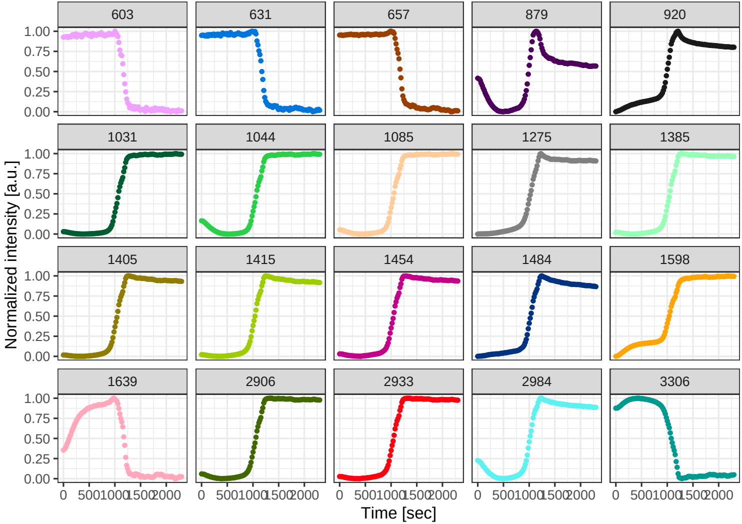
2 One spectrum



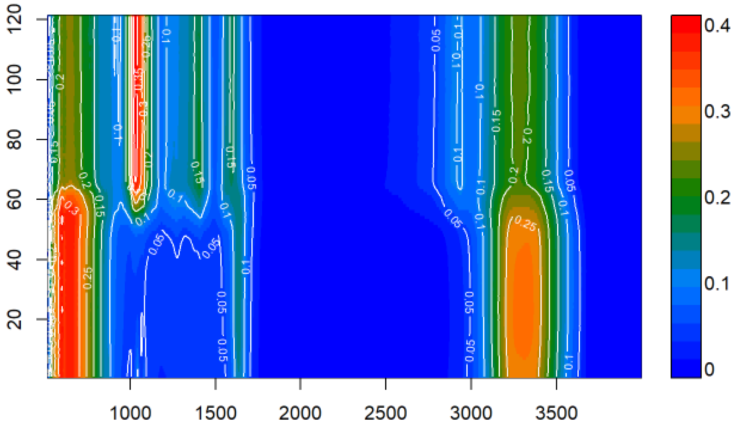
2 Raw Spectra



2 Normalized Spectra

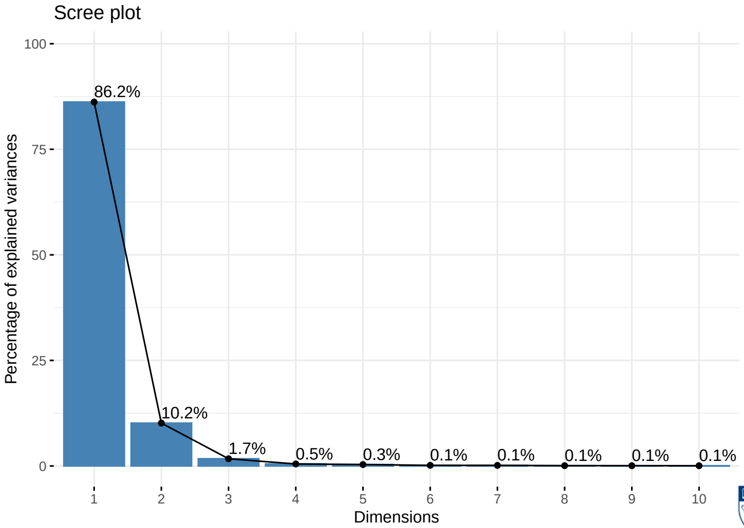


2 Level plot

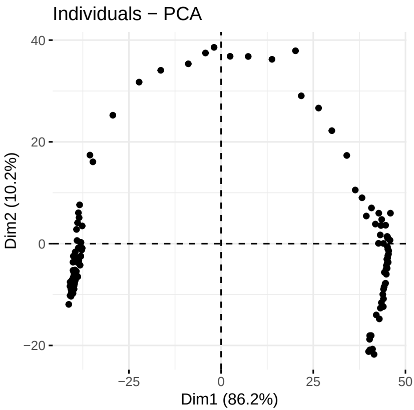


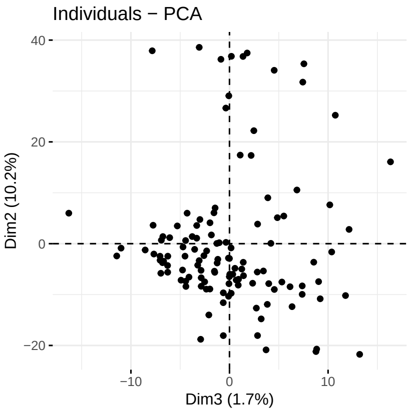
3 Outline

3 PCA Screeplot

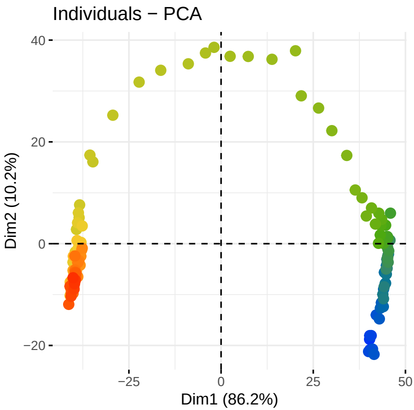


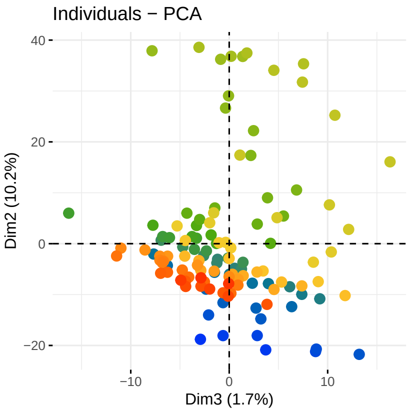
3 PC Scoreplots





3 PC Scoreplots with Colours





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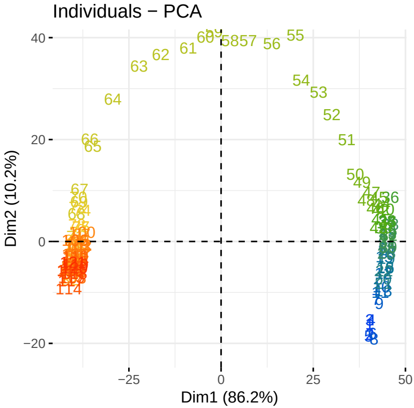
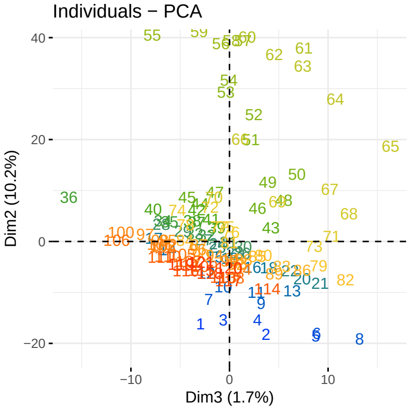
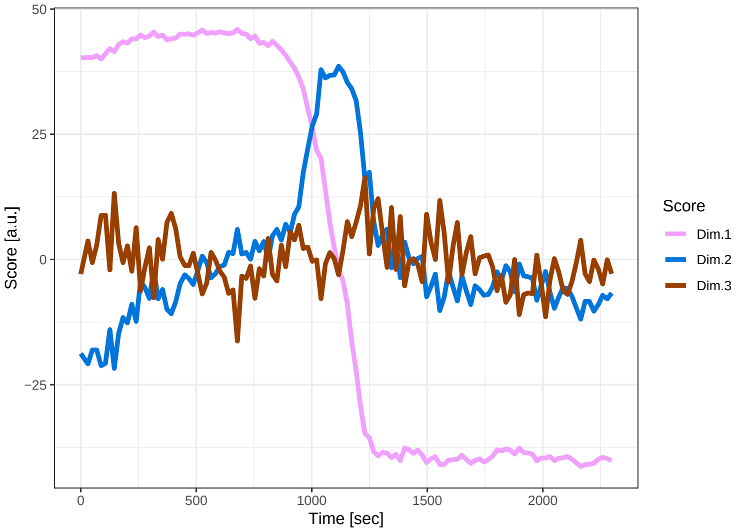
3 PC Scoreplots with Numbers

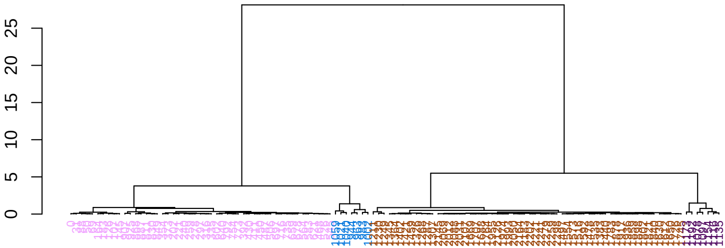




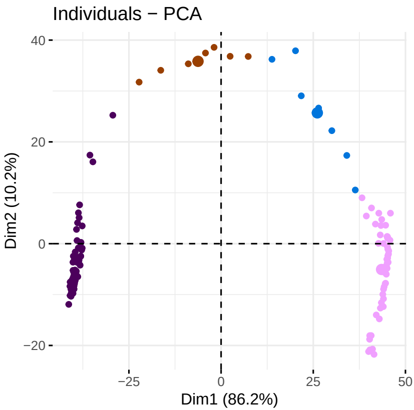
3 PC Scores changes in time

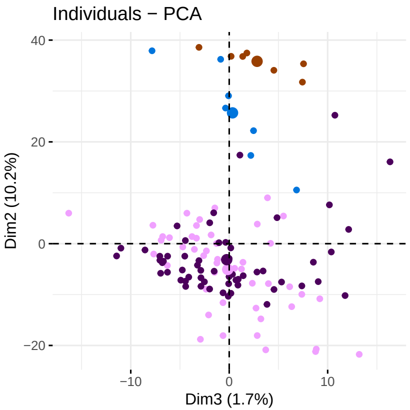


3 HCA Dendrogram 4 Clusters

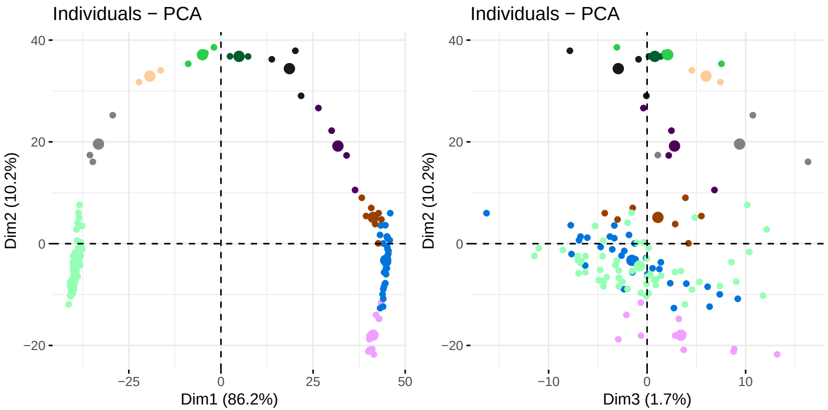


3 PCA Scoreplots with 4 Clusters Membership





3 PCA Scoreplots with 10 Clusters Membership



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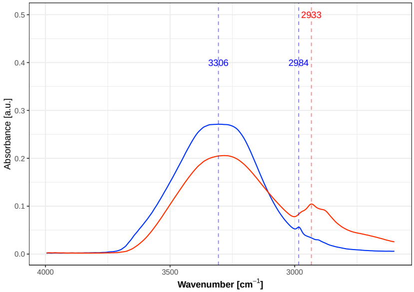
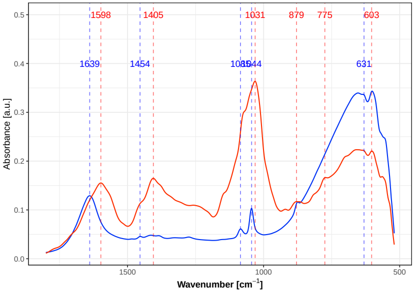
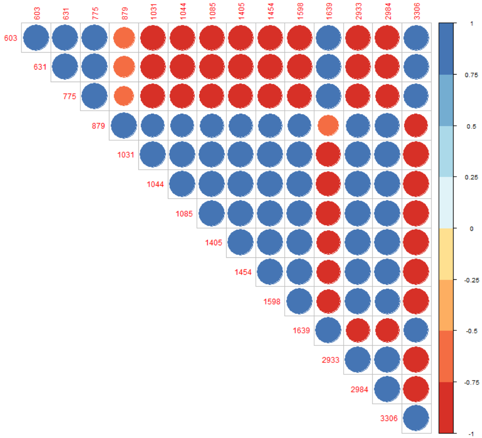
4 Outline

4 Spectra Inspection

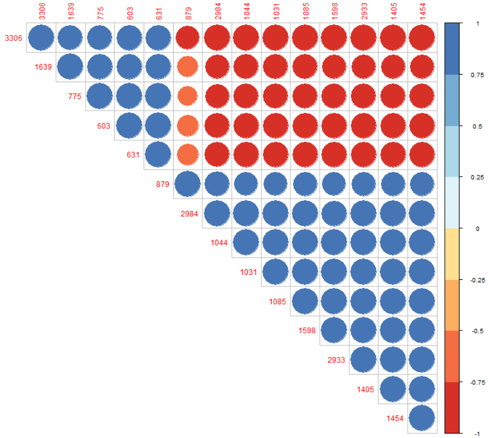




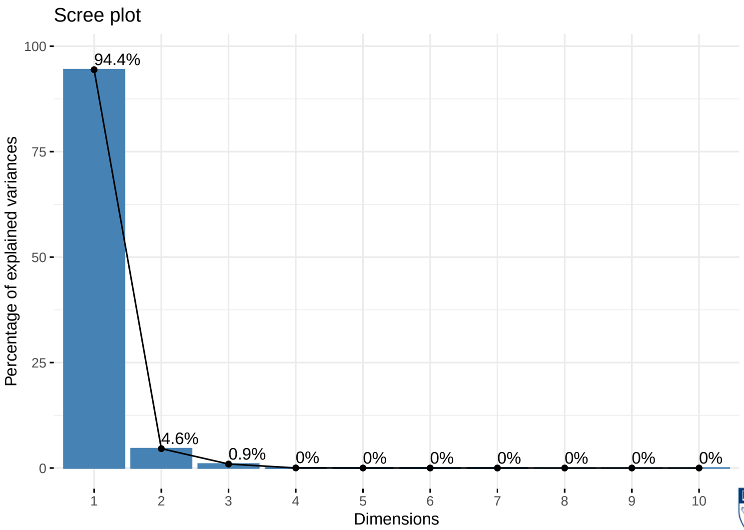
4 Correlation Matrix - Original Order



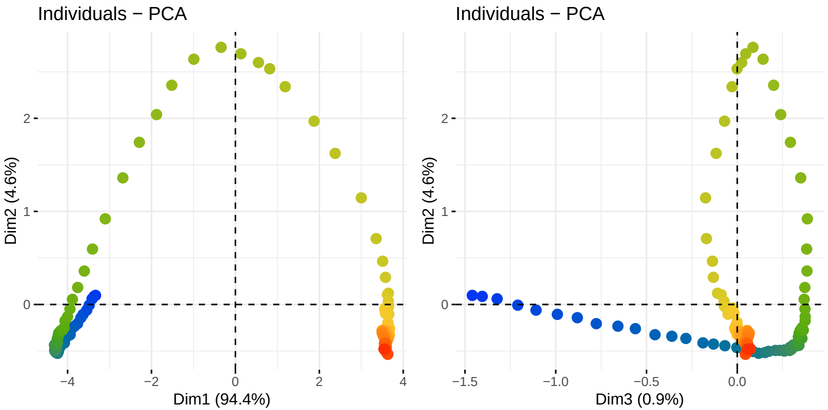
4 Correlation Matrix - Clustering Order



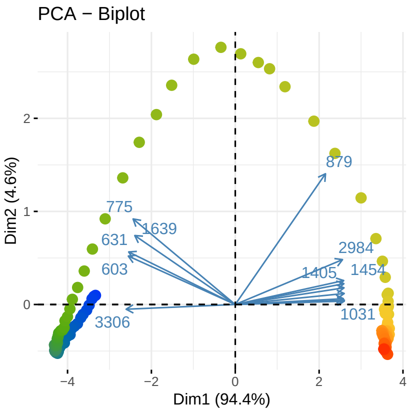
4 PCA on selected wavenumbers

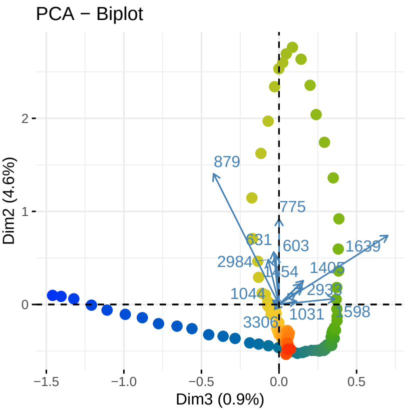


4 PCA Scoreplots with Colours



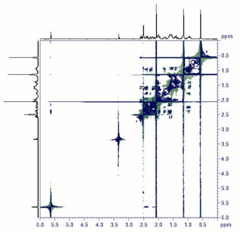
4 PCA Biplots





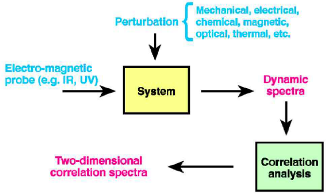
5 Some history

- 1971 Jean Jeener AMPERE Summer School Basko Polje (Yugoslavia)
- 1976 Richard Ernst first experimental demonstration of the technique
- 1986 Isao Noda sinusoidal perturbations based 2D spectroscopy
- 1993 generalized 2D correlation analysis based on Fourier transformation
- 2D correlation analysis is used for the interpretation of many types of spectroscopic data (including XRF, UV/VIS spectroscopy, fluorescence, infrared, and Raman spectra)



5 Idea

- mathematical technique used to study changes in measured signals
- Spectra measured with perturbation
  - time
  - temperature
  - pressure
  - incidence angle
  - magnetic field
  - position in space
- measured spectra show systematic variations that are processed with 2D correlation analysis for interpretation
- synchronous and asynchronous matrix



5 Applications

- determine the events that are occurring at the same time (in phase) and those events that are occurring at different times (out of phase)
- determine the sequence of spectral changes
- identify various inter- and intra-molecular interactions
- band assignments of reacting groups
- to detect correlations between spectra of different techniques, for example infrared spectroscopy and Raman spectroscopy

5 Foundation of 2D correlation spectroscopy

$$C_{\mathrm{auto}}(\tau) = \int_{-\infty}^{\infty} f^*(u) \cdot f(u+\tau) du \tag{1}$$

$$C_{\mathrm{cross}}(\tau) = \int_{-\infty}^{\infty} f^*(u) \cdot g(u+\tau) du \tag{2}$$

5 Dynamic spectra and reference spectrum

$$\widetilde{y}(\nu, t) = \begin{cases} y(\nu, t) - \overline{y}(\nu) & \text{for } T_{\min} \leq t \leq T_{\max} \\ 0 & \text{otherwise} \end{cases} \tag{3}$$

$$\overline{y}(\nu) = \frac{1}{T_{\max} - T_{\min}} \int_{T_{\min}}^{T_{\max}} y(\nu, t) dt \tag{4}$$

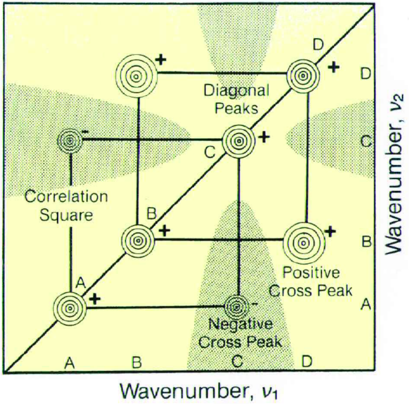
5 Complex cross-correlation function

$$\widetilde{Y}(\nu,\omega) = \mathcal{F}(\widetilde{y}(\nu,t)) = \int_{-\infty}^{\infty} \widetilde{y}(\nu,t) \cdot e^{-i\omega t} dt \tag{5}$$

$$\Phi(\nu_1,\nu_2) + i\Psi(\nu_1,\nu_2) = \frac{1}{2\pi(T_{\max} - T_{\min})} \int_{-\infty}^{\infty} \widetilde{Y}(\nu_1,\omega) \cdot \widetilde{Y}^*(\nu_2,\omega) d\omega \tag{6}$$

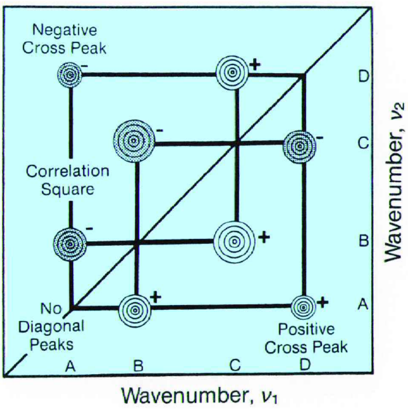
5 Synchronous Spectrum

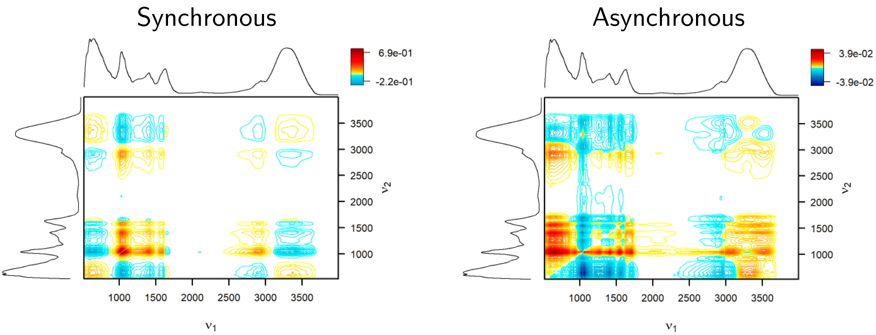
- peaks at diagonal - auto-correlation function
- magnitude of autopeaks (>0) - the overall intensity variation
- off-diagonal cross peaks - simultaneous changes of spectral intensities for two spectral variables
- the sign of synchronous cross peaks is positive if the intensities at two different spectral variables are either increasing or decreasing together



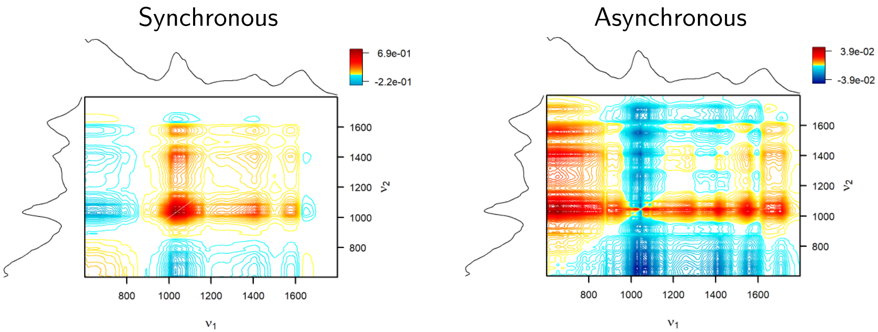
5 Asynchronous Spectrum

- antisymmetric with respect to the diagonal line
- asynchronous peak develops only if the intensities of two spectral features change out of phase (delayed or accelerated) with each other
- the sign of an asynchronous peak becomes positive if the intensity change at ν_1 occurs predominately before ν_2 in the sequential order of t

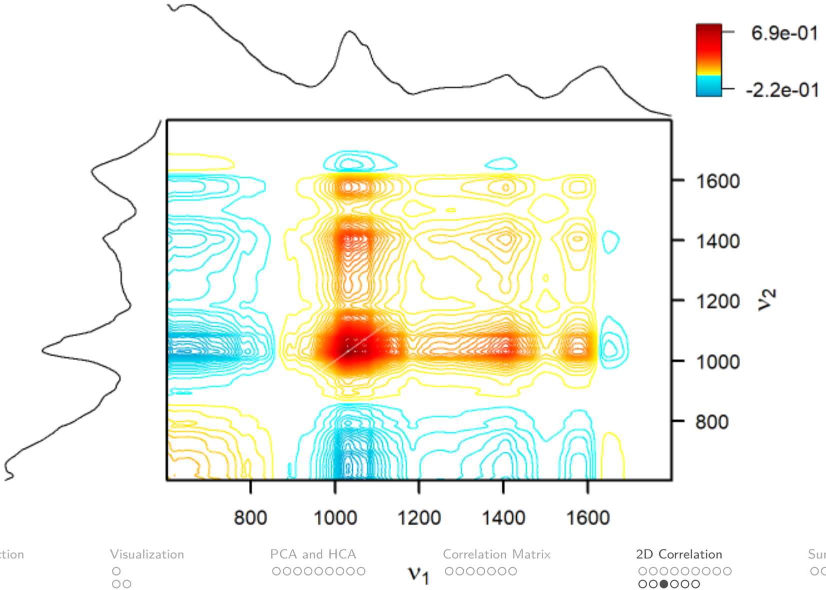



Synchronous
6.9e-01
-2.2e-01
3500
3000
2500
2000
1500
1000
1000 1500 2000 2500 3000 3500
ν_1
ν_2
Asynchronous
3.9e-02
-3.9e-02
3500
3000
2500
2000
1500
1000
1000 1500 2000 2500 3000 3500
ν_1
ν_2

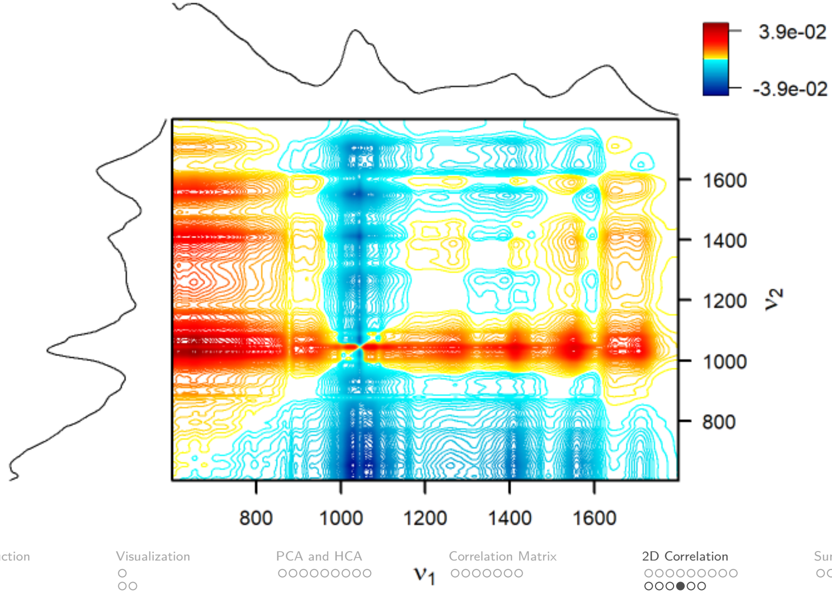
5 Close-up


Synchronous
6.9e-01
-2.2e-01
1600
1400
1200
1000
800
ν_2
800
1000
1200
1400
1600
ν_1
Asynchronous
3.9e-02
-3.9e-02
1600
1400
1200
1000
800
ν_2
800
1000
1200
1400
1600
ν_1

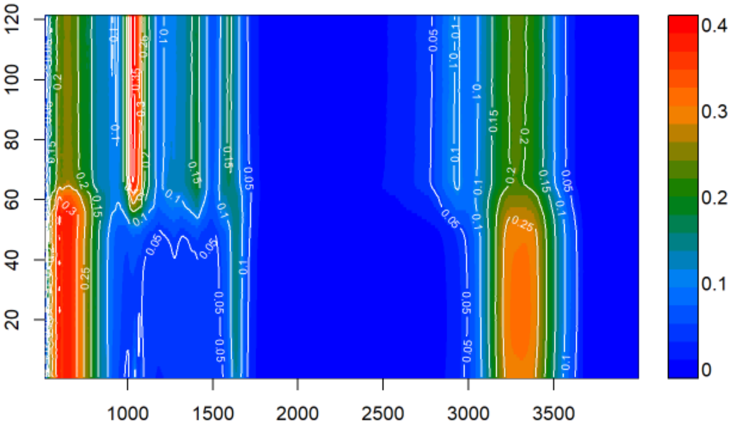
5 Close-up: Synchronous Only



5 Close-up: Asynchronous Only



5 Level plot



5 Software

Platform	Author
standalone software 2DShige	Shigeaki Morita (2005)
MATLAB	home-written scripts López- Díez et al(2005) Barton, de Haseth, and Himmelsbach (2006) Spegazzini, Siesler, and Ozaki (2012)
OPUS	Bruker Corporation (2016)
Origin	twoDCorrSpec.opx extensionOriginLab (2019)
R	package corr2D Geitner, Fritzsch, and Bocklitz (2019)
Python	package correlationAdam Hughes (2014)

6 Outline

- for the spectral datasets measured with external perturbation (time, temperature, pressure, pH, concentration, position in space) we can look for correlations
- dimension reduction is helpful in finding the important wavenumbers (energies, frequencies)
- 2D correlation analysis and investigation of synchronous and asynchronous matrices may help in finding relationships between spectral bands and clearly visualise the changes under the perturbation

6 References 1

1 Noda I (1986). "Two-Dimensional Infrared (2D IR) Spectroscopy." Bulletin of American Physical Society, 31, 520–524.

2 Noda I (1990). "Two-Dimensional Infrared (2D IR) Spectroscopy: Theory and Applications." Applied Spectroscopy, 44(4), 550–561.

3 Noda I (1993). "Generalized Two-Dimensional Correlation Method Applicable to Infrared, Raman, and Other Types of Spectroscopy." Applied Spectroscopy, 47(9), 1329–1336.

4 Czarnecki MA (1998). "Interpretation of Two-Dimensional Correlation Spectra: Science or Art?" Applied Spectroscopy, 52(12), 1583–1590.

5 Noda I, Dowrey AE, Marcott C, Story GM, Ozaki Y (2000). "Generalized Two-Dimensional Correlation Spectroscopy." Applied Spectroscopy, 54(7), 236–248.

6 Šašić S, Muszynski A, Ozaki Y (2000). "A New Possibility of the Generalized Two- Dimensional Correlation Spectroscopy. 1. Sample-Sample Correlation Spectroscopy." The Journal of Physical Chemistry A, 104(27), 6380–6387.

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7. Noda I (2003). "Two-Dimensional Correlation Analysis of Unevenly Spaced Spectral Data." Applied Spectroscopy, 57(8), 1049–1051.
8. Yu ZW, Liu J, Noda I (2003). "Effect of Noise on the Evaluation of Correlation Coefficients in Two-Dimensional Correlation Spectroscopy." Applied Spectroscopy, 57(12), 1605–1609.
9. Shinzawa H, Morita SI, Awa K, Okada M, Noda I, Ozaki Y, Sato H (2009). "Multiple Perturbation Two-Dimensional Correlation Analysis of Cellulose by Attenuated Total Reflection Infrared Spectroscopy." Applied Spectroscopy, 63(5), 501–506.
10. Spegazzini N, Siesler HW, Ozaki Y (2012). "Sequential Identification of Model Parameters by Derivative Double Two-Dimensional Correlation Spectroscopy and Calibration-Free Approach for Chemical Reaction Systems." Analytical Chemistry, 84(19), 8330–8339.
11. Geitner R, Fritzsch R, Bocklitz T (2019). "corr2D: Implementation of 2D Correlation Analysis in R." R package version 0.4.0, URL https://CRAN.R-project.org/package=corr2D.

Thank you!

Slides available at:
https://banas.netlify.app/talk/2021-02-24_2D_correlation/

6 2D correlation spectra based on the Hilbert Transform

$$\Phi(\nu_1, \nu_2) = \frac{1}{T_{\max} - T_{\min}} \int_{T_{\min}}^{T_{\max}} \widetilde{y}(\nu_1, t) \cdot \widetilde{y}(\nu_2, t) dt \tag{7}$$

$$\widetilde{z}(\nu_2, t) = \mathcal{H}(\widetilde{y}(\nu_2, t)) = \frac{1}{\pi} \quad PV \int_{-\infty}^{\infty} \frac{\widetilde{y}(\nu_2, t')}{t' - t} dt \tag{8}$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{T_{\max} - T_{\min}} \int_{T_{\min}}^{T_{\max}} \widetilde{y}(\nu_1, t) \cdot \widetilde{z}(\nu_2, t) dt \tag{9}$$

6 Equations 6

$$\Phi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{j=1}^{m} \widetilde{y}(\nu_1, t_j) \cdot \widetilde{y}(\nu_2, t_j) \tag{10}$$

$$\widetilde{z}(\nu_2, t_j) = \sum_{k=1}^{m} N_{jk} \cdot \widetilde{y}(\nu_2, t_k) \tag{11}$$

$$N_{jk} = \begin{cases} 0 & \text{if } j = k \\ \frac{1}{\pi(k-j)} & \text{otherwise} \end{cases} \tag{12}$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{j=1}^{m} \widetilde{y}(\nu_1, t_j) \cdot \widetilde{z}(\nu_2, t_j) \tag{13}$$