Accurate spectra of diluted solutions

Outline

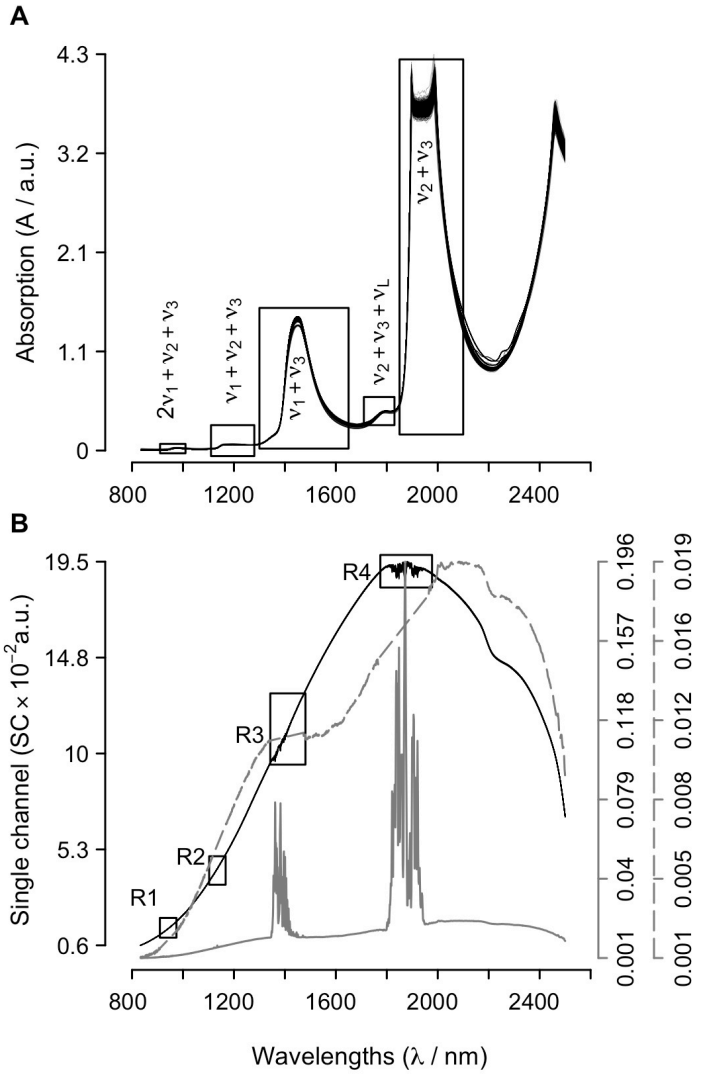
- Detrending with solvent subtraction
- Classical vs Proposed method
- Examples
- Future: more than (just) preprocessing?
- (*Anal. Chim. Acta*, 955, 86-97, 2017)

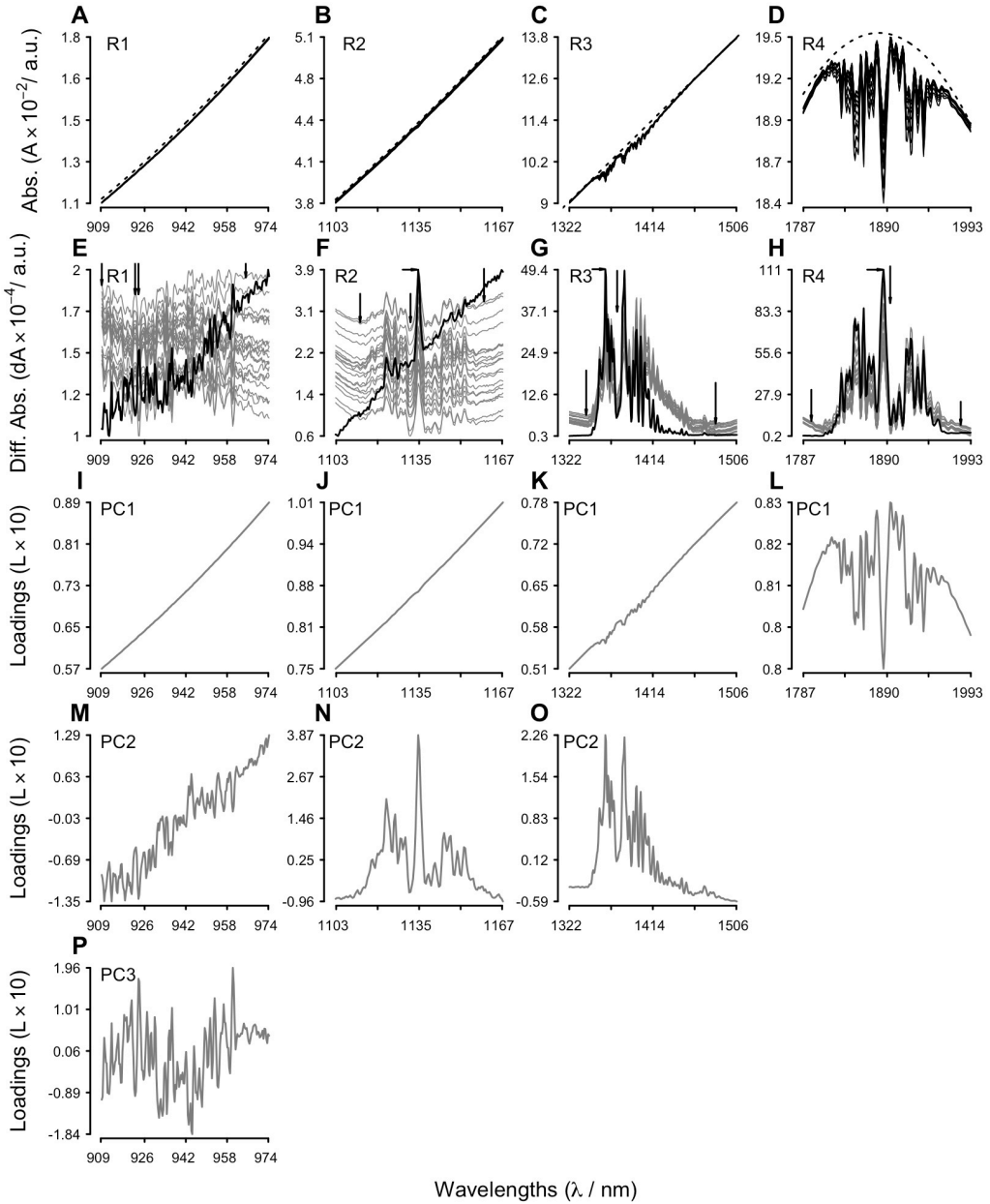
“Classical” subtraction

- Assumptions related to subtraction of averaged solvent spectrum:
  - Negligible baseline shifting
  - Normality
  - Controlled environmental condition
  - Sufficient band intensity

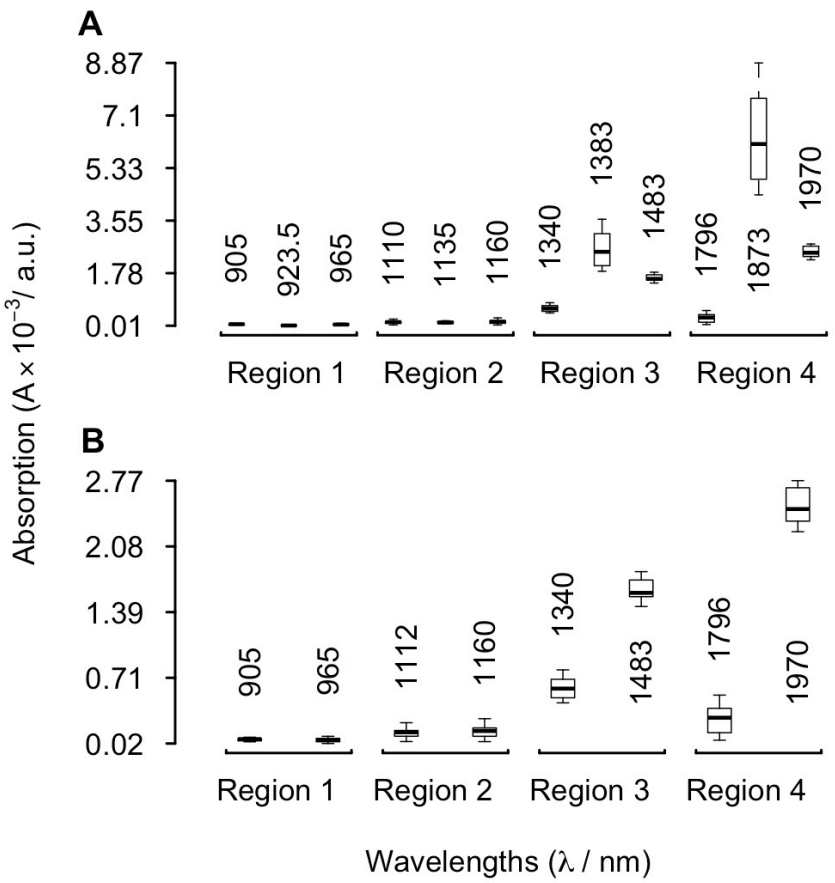
  are not entirely satisfied and obscure extraction of weak bands in diluted solutions, leaving SNR ratios essentially unchanged.

Baseline variability



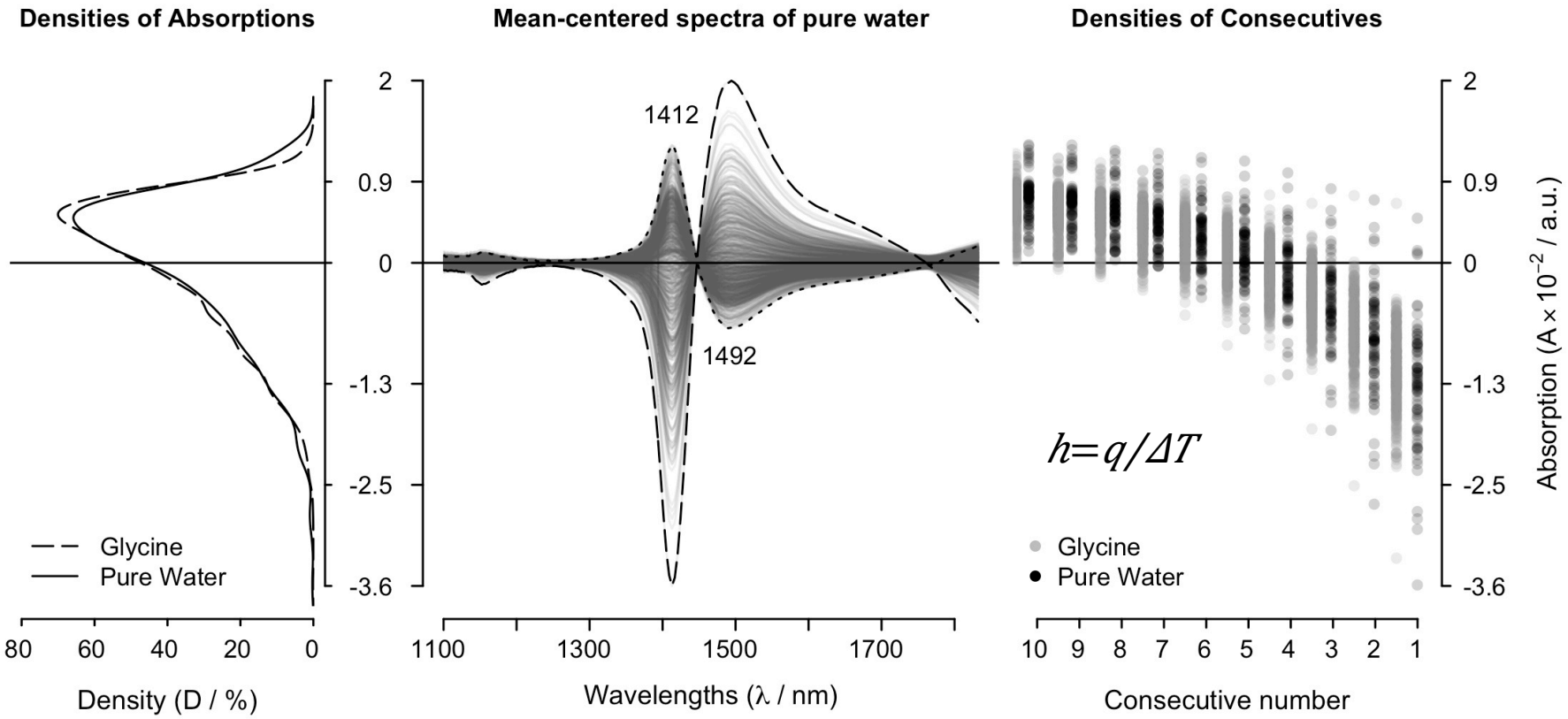


Baseline variability



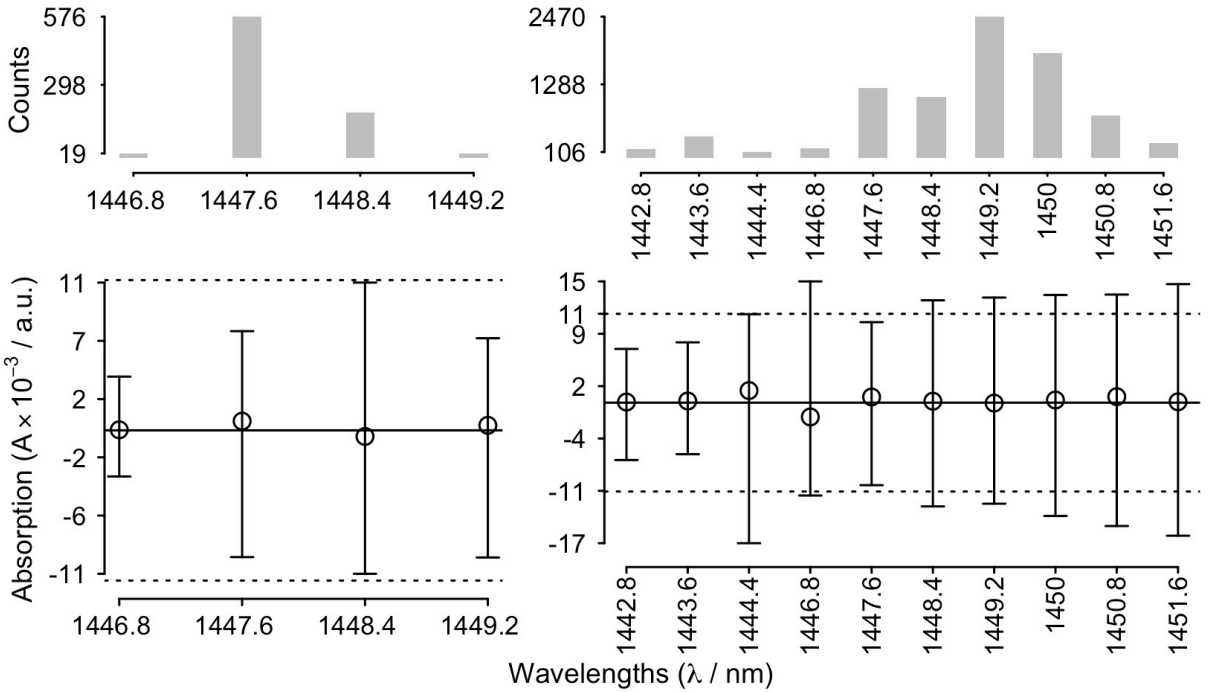
- Non-negligible (~10^{-4}):
  - Influences weaker bands more strongly (Regions 1&2: ~10^{-4}).
  - Insignificant for stronger bands (Regions 3&4: ~10^{-3} -10^{-2}).

Normality



- Shifting of consecutive spectra (non-linear heat transfer coefficient (h~1/T), right panel) skews Absorption densities (left panel) thus challenging normality & averaging of solvent spectra.

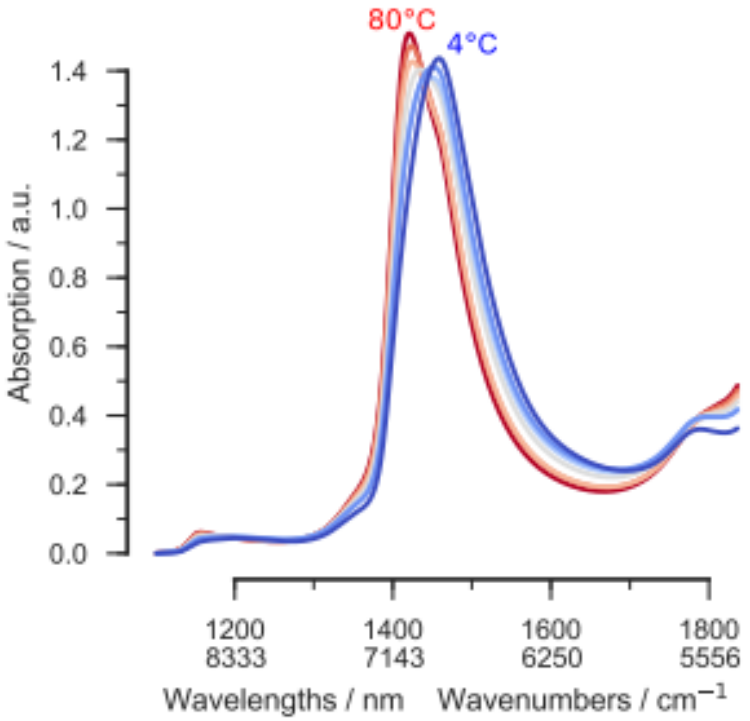
Normality



- Absorbance range (@1412nm) for pure water at different temperatures approaches values typical for band intensities in subtracted spectra (~10^{-3}-10^{-2}).

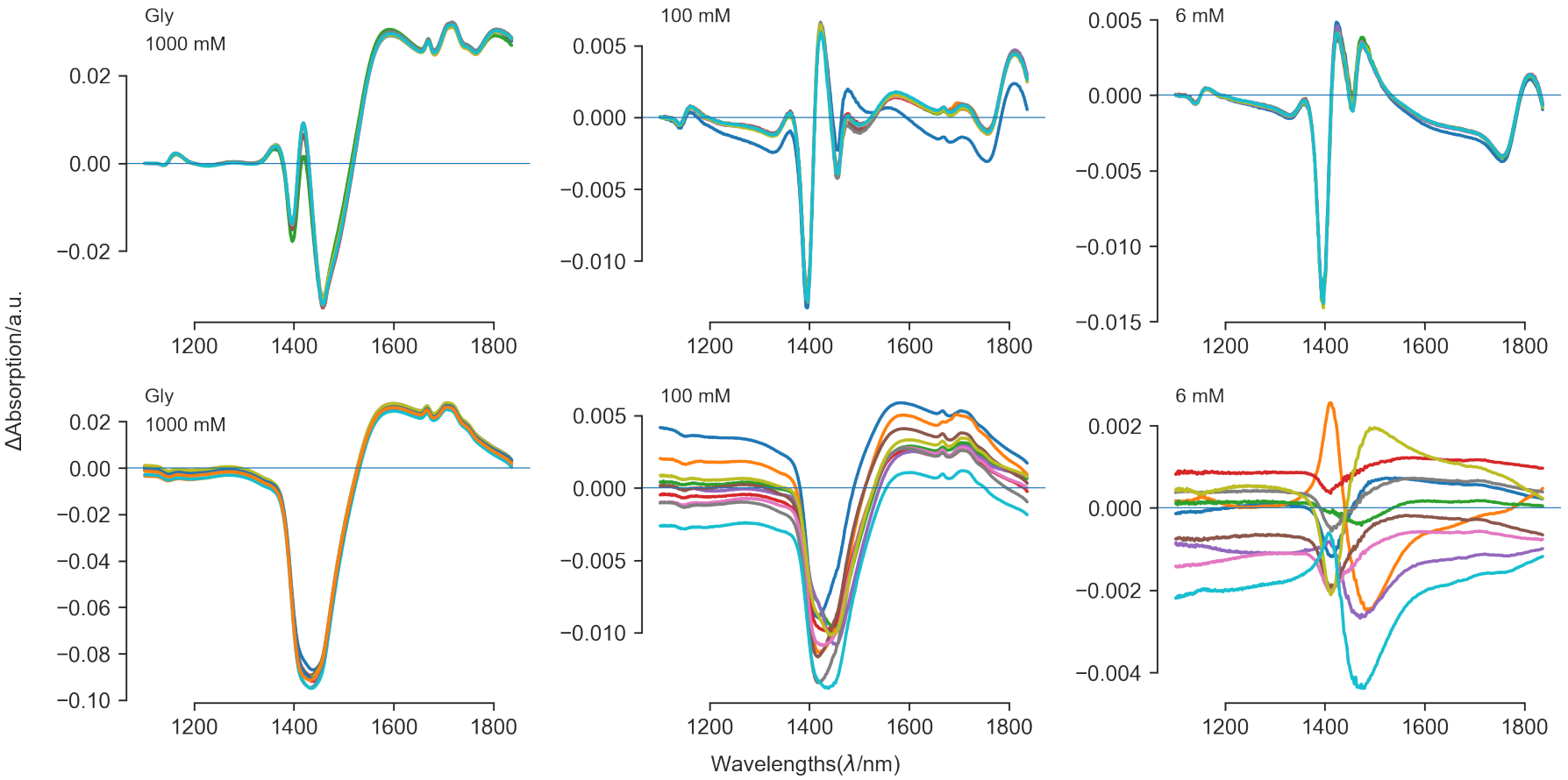
Proposed method

- Subtraction of the “closest” solvent spectrum
- Requirement: database of solvent spectra
- Solid samples?



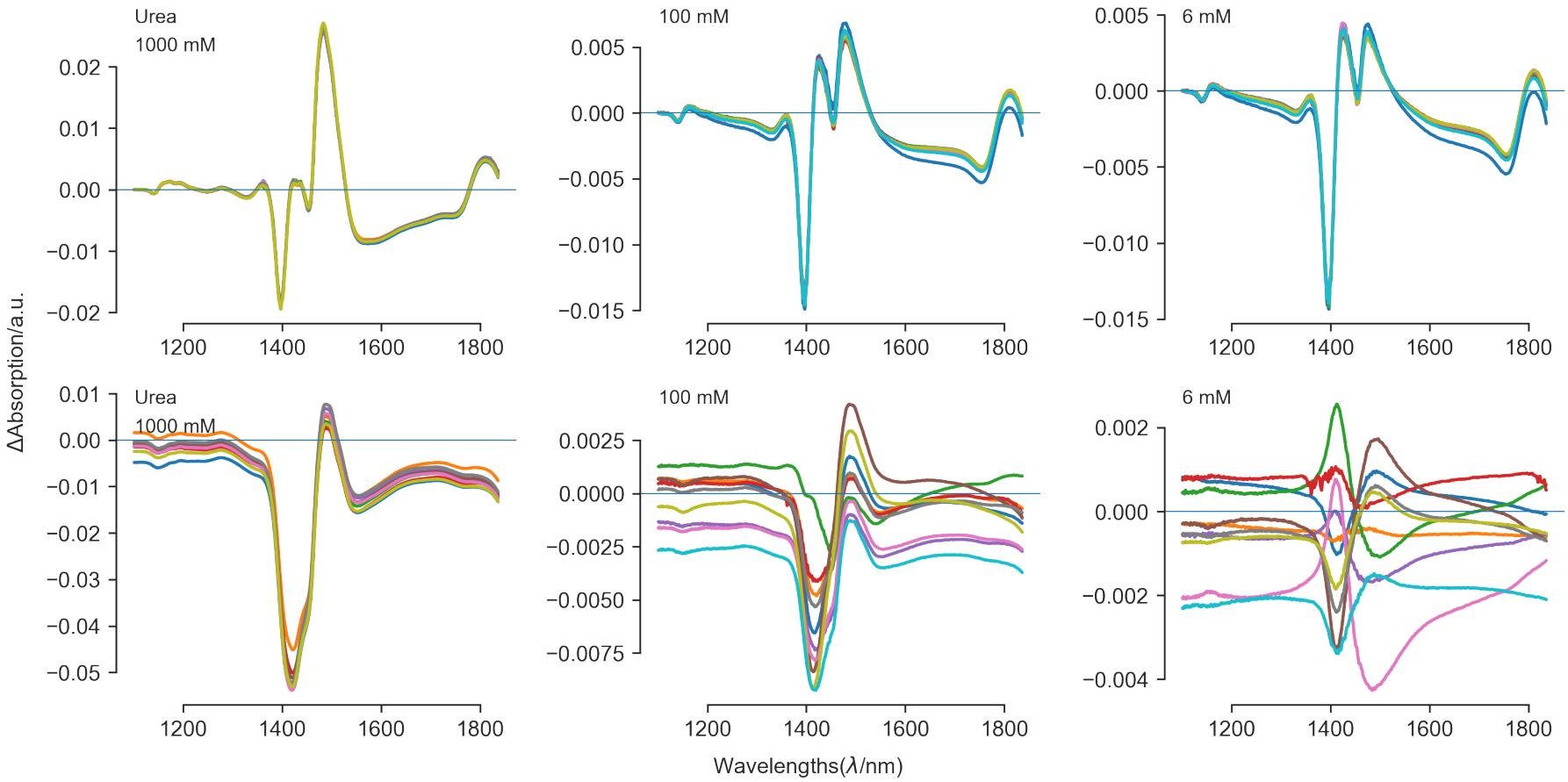
Examples (Glycine)

- 1st row: “closest” solvent spectrum subtracted.
- 2nd row: averaged solvent spectrum subtracted.



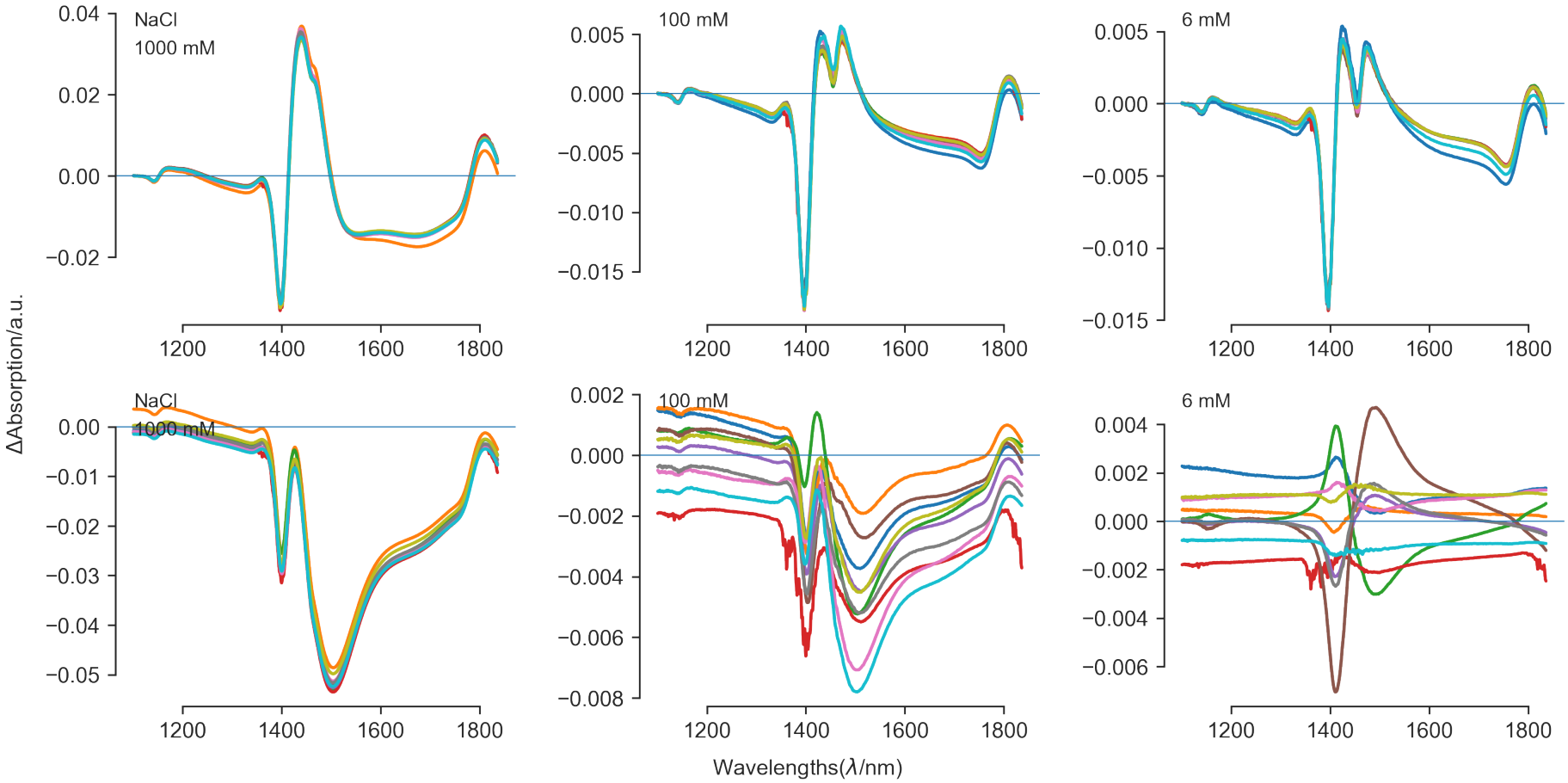
Examples (Urea)

- 1st row: “closest” solvent spectrum subtracted.
- 2nd row: averaged solvent spectrum subtracted.



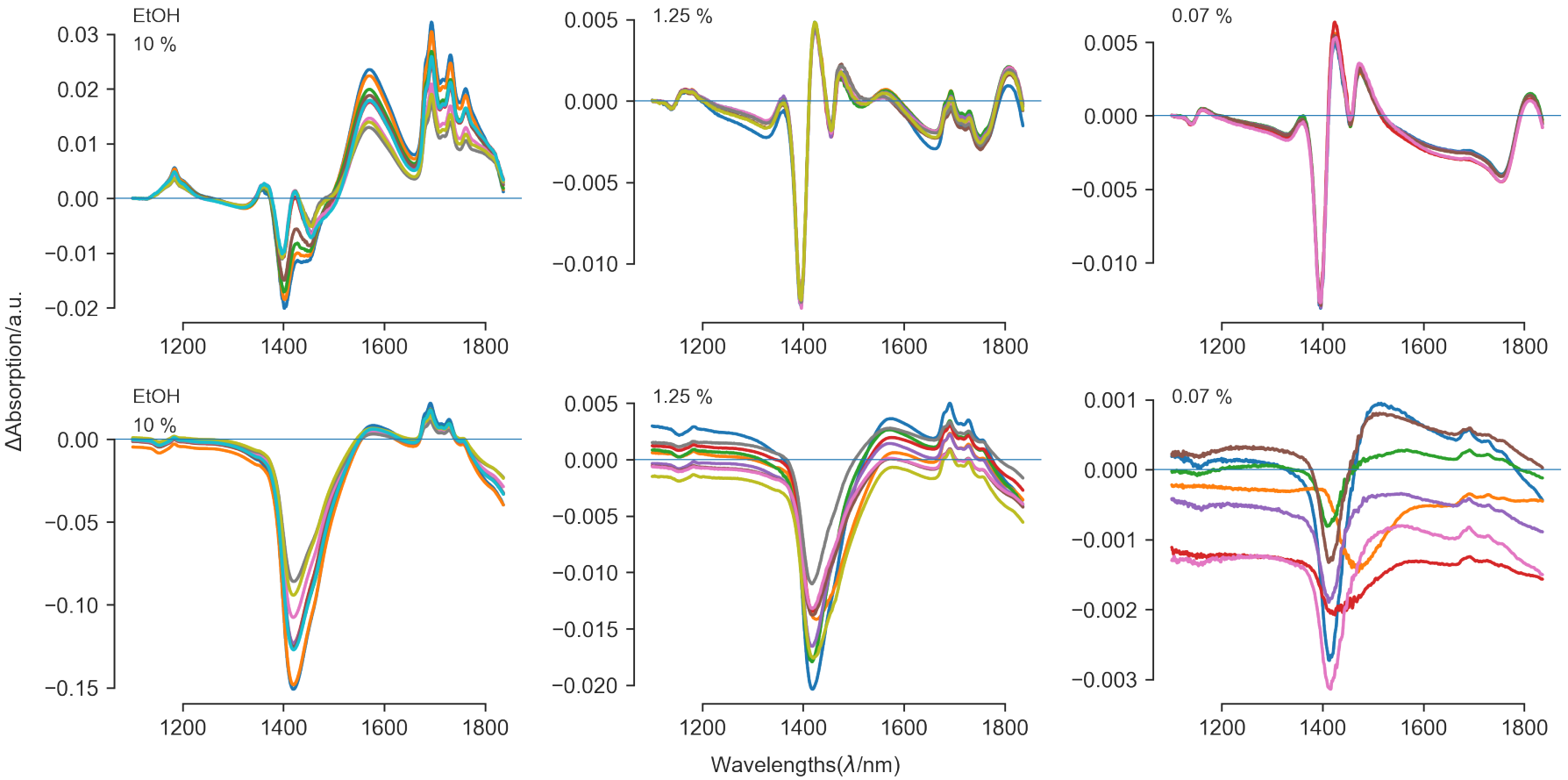
Examples (NaCl)

- 1st row: “closest” solvent spectrum subtracted.
- 2nd row: averaged solvent spectrum subtracted.

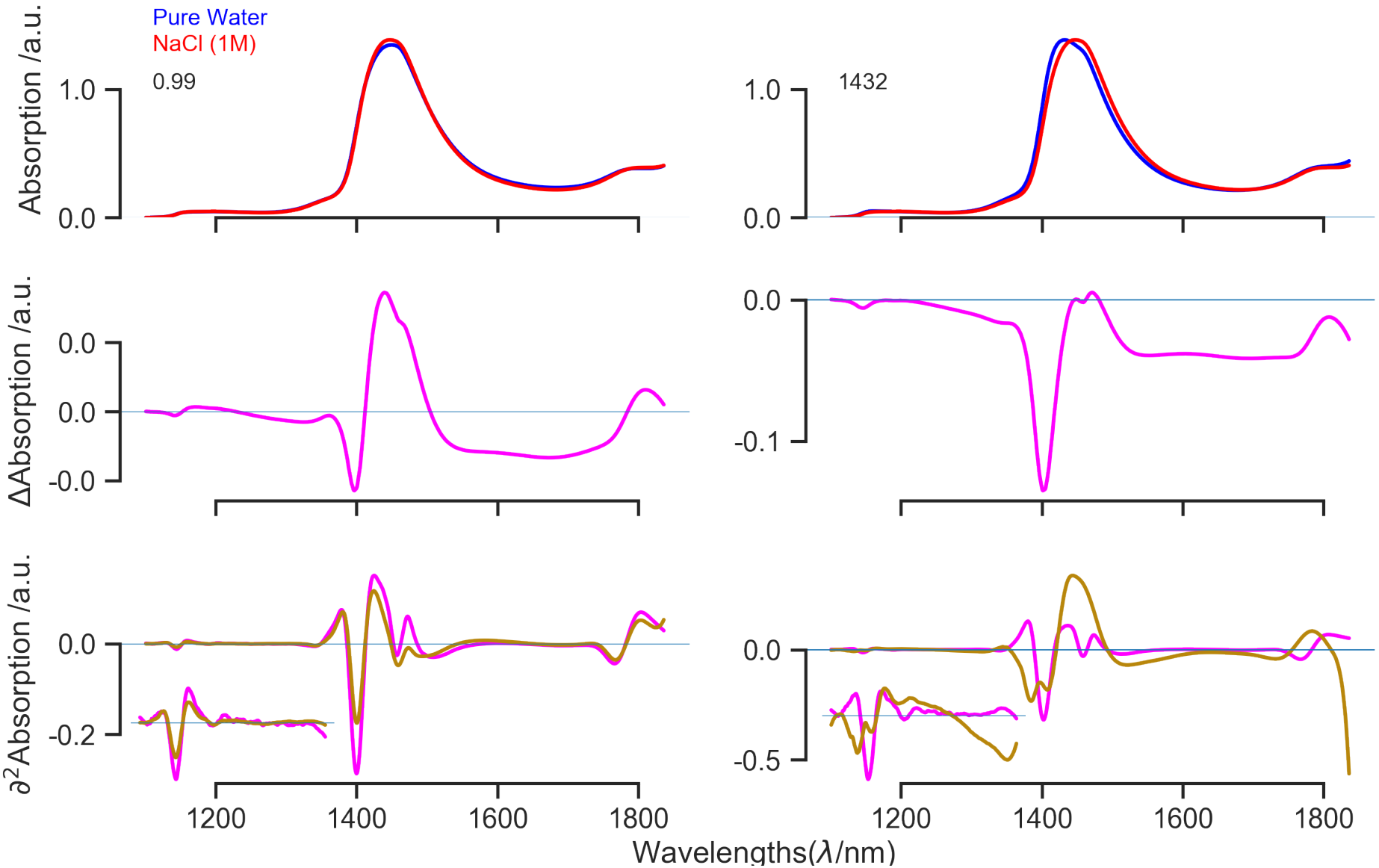


Examples (EtOH)

- 1st row: “closest” solvent spectrum subtracted.
- 2nd row: averaged solvent spectrum subtracted.



Scaling & Peak shifting

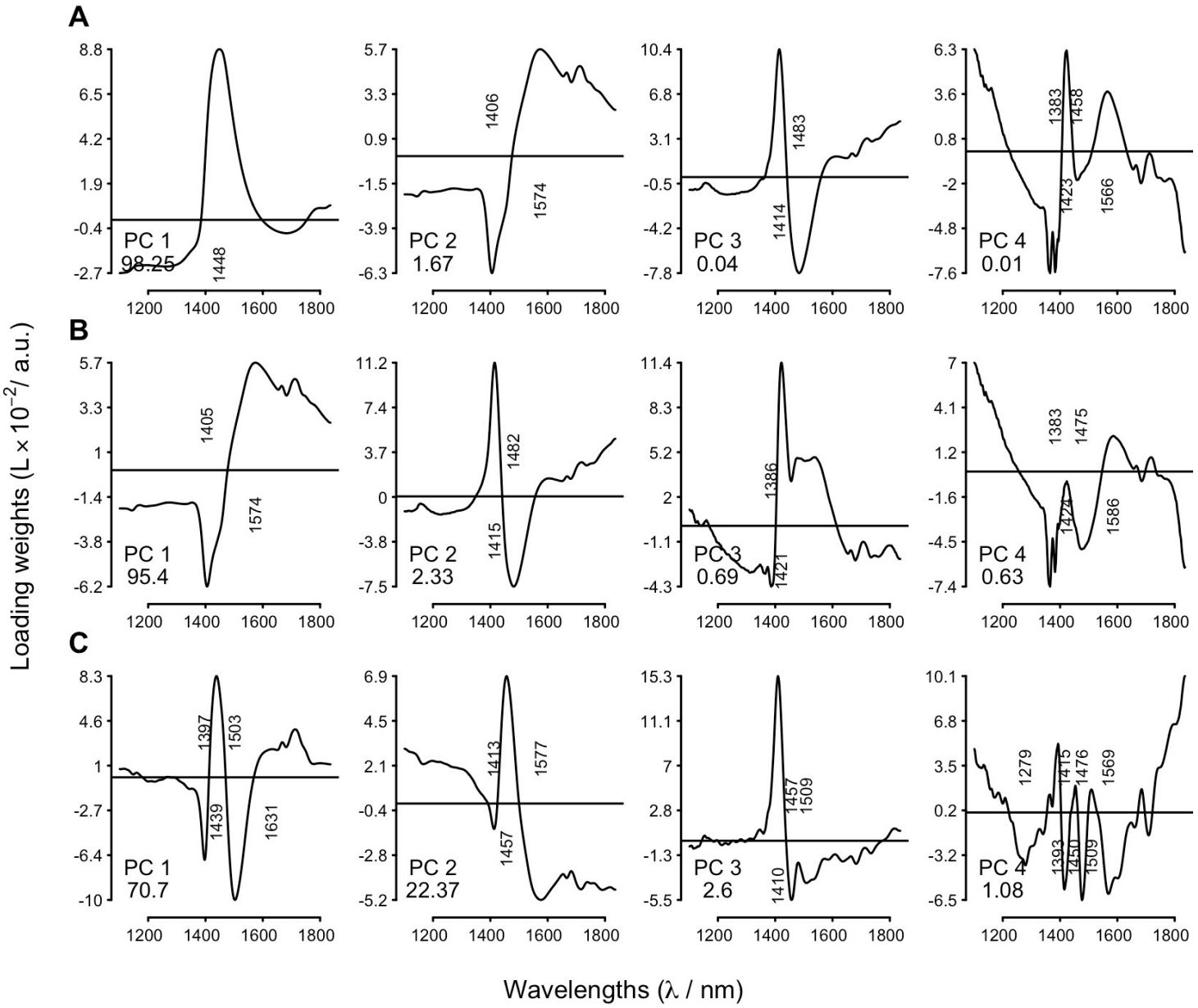


PCA (Loadings, Glycine @62mM)

A: Raw spectra

B: solvent (averaged) subtracted spectra

C: solvent (closest) subtracted spectra

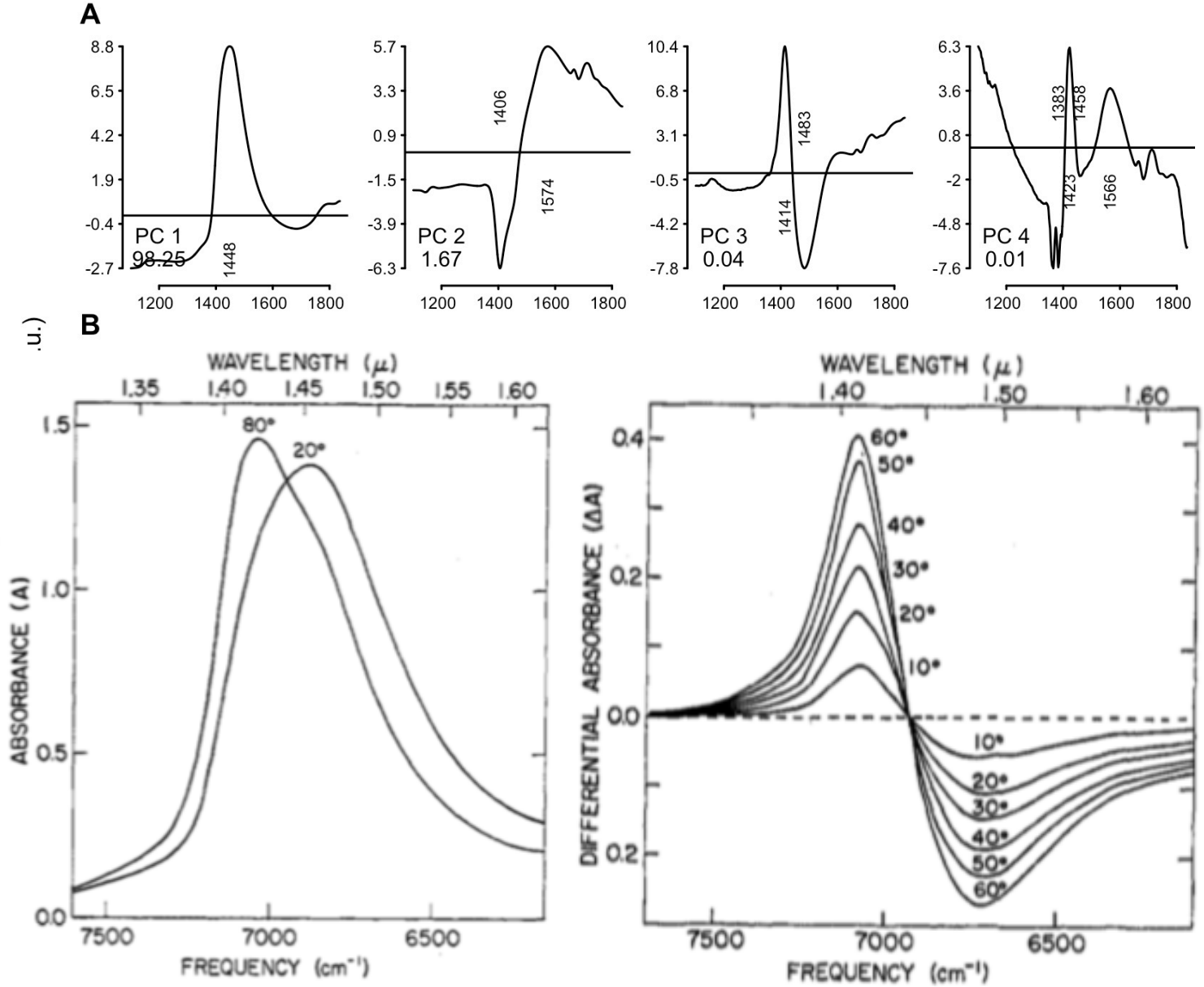


A: PC1 - averaged raw spectrum
PC2 - solvent displacement
PC3 - heat transfer (see next slide)
PC4- solute excited bands

B: PC1- averaged subtracted spectrum
PC2-heat transfer
PC3&4-solute excited bands 1&2

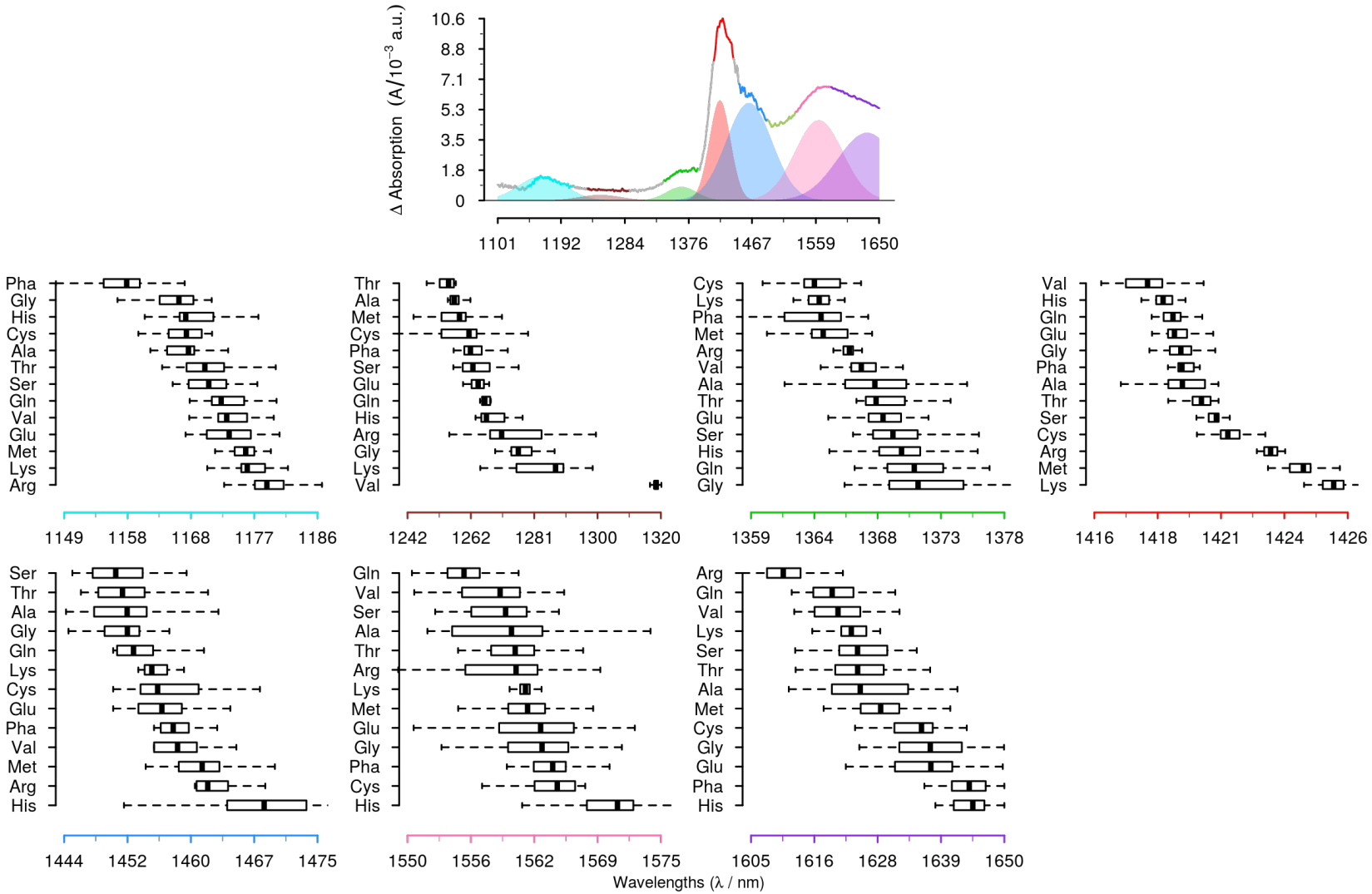
C: PC1-4-solute excited bands

PCA (Loadings, Glycine @62mM)

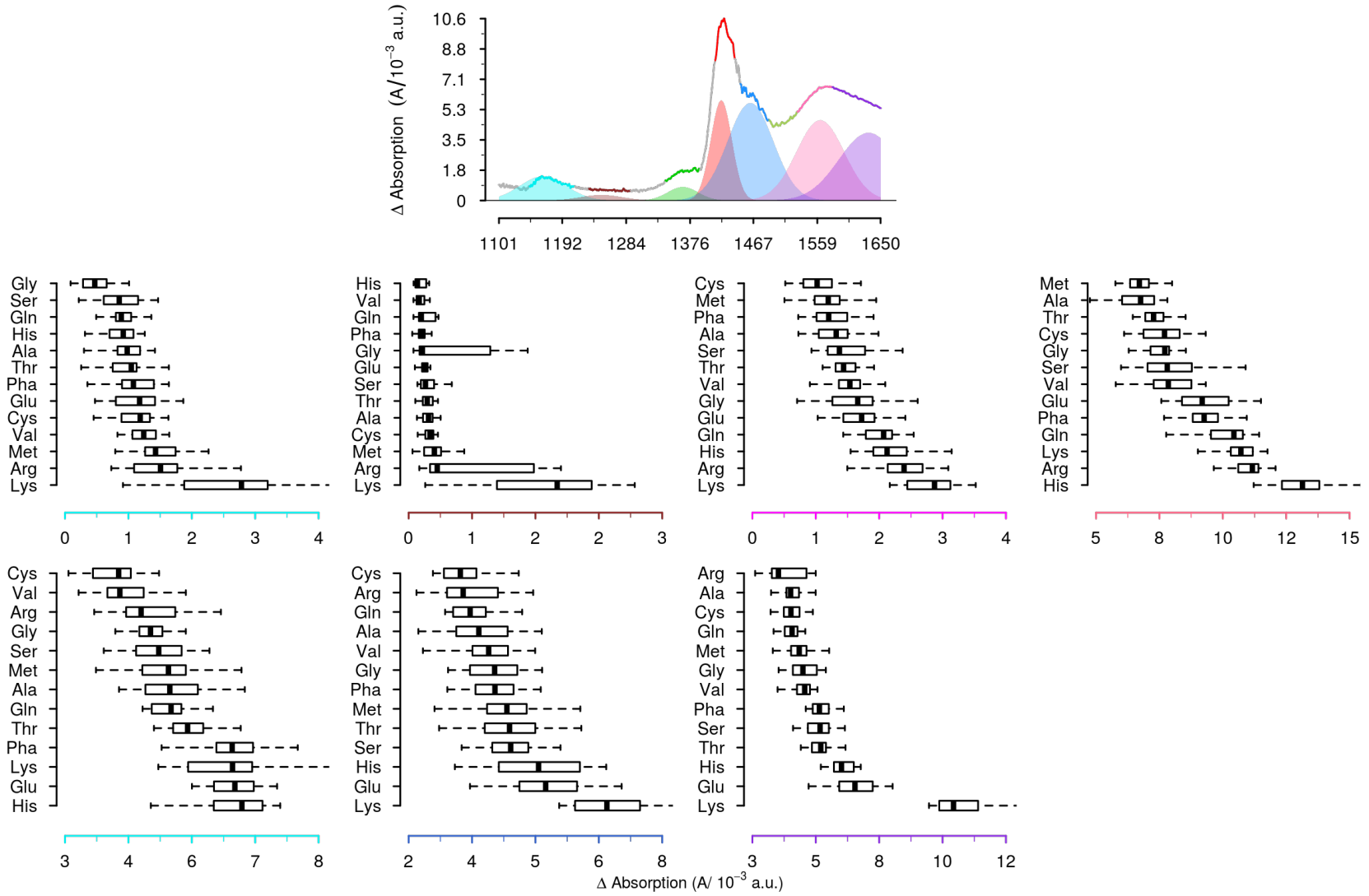


PC3 - heat transfer: spectral pattern of PC3 closely resembles mean centered spectra of temperature perturbed pure water spectra.

Examples (Amino-acids, wavel.)



Examples (Amino-acids, Abs.)



Future

- chemometrics → chemometrics
- Splitting of variance:
  - Chemical
  - Correlated
    - $Total_{Raw} = Solvent_{SC1} + (Solute_{SCx}) + Solute_{SC2}$
- Outlier reduction/detection
- Spectral Components

Second Circular

Aquaphotomics:

Exploring Water Molecule Systems in Nature

The 3rd International Symposium

December 2 – 6, 2018

Awaji Yumebutai International Conference Center
(Reception Hall B)

1 Yumebutai
Awaji City, Hyogo, Japan

http://conference.aquaphotomics.com

On Behalf of the Organizing Committee of the 3rd International Aquaphotomics Symposium:

WELCOME TO AQUAPHOTOMICS

The importance of water in biological systems has not been well explored and recognized. In recent years, along with the advancement of computer science, data analysis and new measurement technologies, water has been studied by scientists and researchers in a wide variety of disciplines. This new trend deserves special attention and effort to bring new findings and discoveries about water to a wider audience.

Aquaphotomics is a new "–omics" discipline coined by Professor Tsenkova from the Biomeasurement Technology Laboratory at the Faculty of Agriculture in Kobe University, Japan. The main objective of this new field is to understand the role of the water molecular system by monitoring water spectrum of bio– and aqueous systems under various perturbations. Aquaphotomics presents water spectrum as a holistic bio marker, which works as molecular mirror, epitomizing the respective system.

In October 2014, we organized the 1st International Symposium on Aquaphotomics as a part of Kobe University Symposium held at its European Office in Brussels, Belgium. Scientists from 11 countries, mainly in Europe, came with talks and posters. Since then, a 5-year EU project which includes Aquaphotomics was started at UC Dublin. On November 26 – 29 2016, the 2nd International Symposium was held at Kobe University in Japan. Researchers from around the world participated in the event and presented their research studies on Aquaphotomics. Workshops were organized to introduce new analysis techniques and open lectures were held to promote the importance of water science. This year, the 3rd Aquaphotomics International Symposium will be held on December 2 – 6 in the Awaji Yumebutai International Conference Center in Awaji, Japan. In the world of inter-disciplinary science and technology, understanding the role of water and how it works is of crucial importance. This will pave a new path for hardware and software development of new water measurement devices. New industry of big data management and analysis of spectral data coming out of in-vivo bio monitoring will be seen in food quality evaluation and biotechnology. New methods and instruments measuring changes in water structure directly related to disease diagnosis, understanding and prevention will lead to discoveries of new phenomena.

Thanks to the support of all the co-organizers of the Symposium, we have the ambition to establish a network of scientists from different disciplines learning about the water molecular matrix and its direct relation to system functionality, for the benefit of society.

Looking forward to welcome you all in the beautiful city of Awaji.

Chairperson
Roumiana Tsenkova