Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information

Observing Non-Classical Crystallisation Processes in Gypsum via Infrared Attenuated Total Reflectance Spectroscopy

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Materials and reagents

As solvents for crystallisation ultrapure water and deuterium oxide 99,9% (Deutero, Kastellaun) were used. For the precipitation of $CaSO_4 \cdot 2H_2O$, calcium chloride (Carl Roth, Karlsruhe) and sodium sulfate decahydrate (Merck, Darmstadt) were used. For cleaning and polishing of the measurement cell, tetrahydrofuran (Merck, Darmstadt) was applied without further purification.

Experimental procedure

For precipitation experiments, sample solutions of Ca^{2+} and SO_4^{2-} were prepared in D2O (99.9%), and in ultrapure water.

All measurements were repeated at least three times to ensure reproducibility. Sulfate (70 mMol/L) and calcium700 mMol/L, solutions were prepared in deuterium oxide and millipore water.

504 µL sulfate solution were sampled into the measurement cell. During the first scans, 56µL of calcium solution were injected into the sulfate solution. The resulting concentrations of $CaSO_4$-solution were 70 mMol/L. This basic procedure was identical in all measurements. The experiments are subdivided into two classes.

1 Closed conditions without disturbing the system under nitrogen atmosphere. This setup should prevent the evaporation and interaction with the environment during the measurement

2 Spike experiments: H_2O solutions were sampled onto the ATR diamond and the cell was closed until the reaction shows a stable state without any fast changes (approx. 30 minutes). Then D2O was spiked into the cell. D_2O was prepared using the same concentration of calcium and sulfate as the initial solution to avoid any dilution effects. (18 µL sulfate solution and 2 µL calcium solution). Spikes were injected in regular time intervals (30min).

Instrumentation:

As an FTIR-spectrometer, a Bruker Alpha (Bruker Optics, Ettlingen, Germany) was used equipped with a single-bounce diamond ATR module and a DLaTGS detector. A 3D-printed measurement cell, which was designed specifically for studying crystallisation processes was mounted onto the ATR system. (Figure S1). It has a capacity > 1 mL and can be flushed and sealed to perform precipitation experiments in a in a controlled nitrogen atmosphere. The polymer of choice for fabricating the cell was polylactic acid (PLA).
A PTFE foil was used for sealing the cell against the ATR top plate assembly. A lid was designed to seal

the compartment against the surrounding atmosphere. Furthermore, the surface of the cell was first incubated in THF steam and then polished with THF for minimizing the surface roughness and to prevent crystallization at the cell walls.

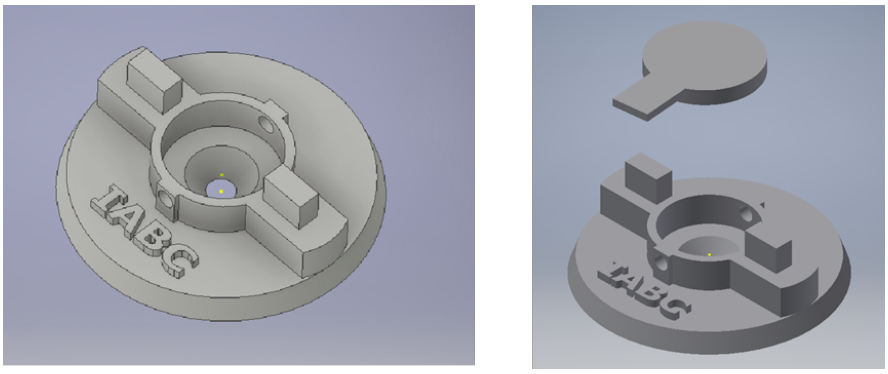


Figure S1: Sampling cell developed at IABC for mounting at the ATR accessory top plate.

Instrumental settings

The spectra were recorded from 4000 cm^{-1} to 400 cm^{-1}, with 64 averaged scans and a resolution of 2 cm^{-1}. This results in approximately two minutes per spectrum.

Total reflection X-ray fluorescence (TXRF) measurements

The calcium content of saturated gypsum solutions was measured via TXRF with a Bruker S2 Picofox (Bruker Ettlingen).
Saturated solutions were equilibrated in H_2O respectively D_2O for 3 Days. The solutions were centrifuged and the remaining solvents were diluted (1/100) and spiked with an internal Gallium standard. The mixtures were dropcasted (10 µl) on clean quartz-glass sample carriers, dried and measured with an exposure time of 100s. The whole procedure was repeated 3 times with 3 independent samples each, to ensure a high reproducibility.

Additional spectral information on precipitation experiments in pure water

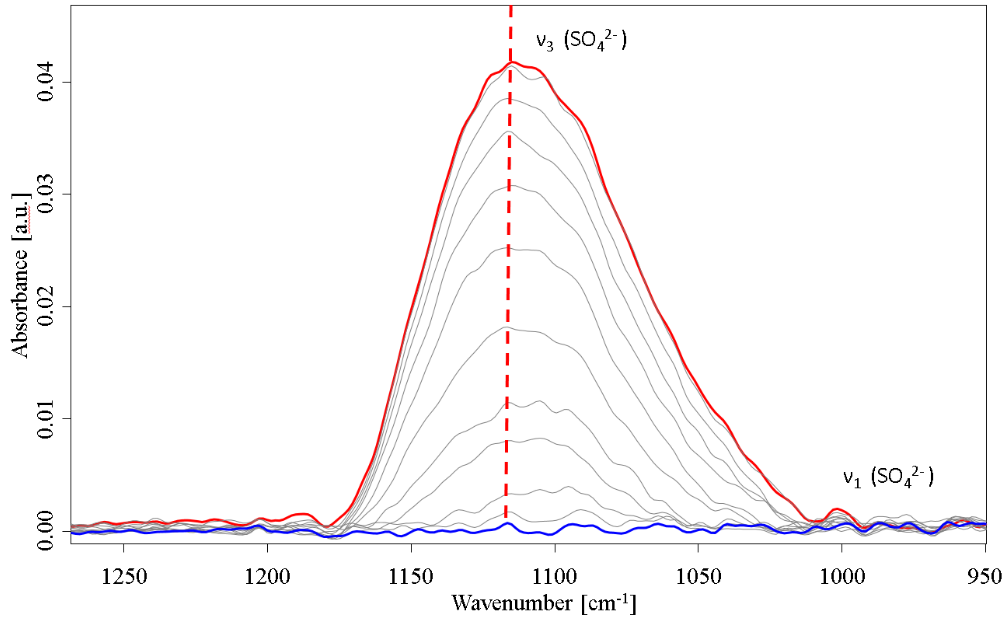


Figure S2: Zoom onto sulfate v_3 Band of Figure 1. Spectra were collected over a period of 16 h in the closed sample cell under nitrogen atmosphere. Blue: start at t_0; Red: end at t=16 h

Spectral behaviour upon time in precipitation experiments in pure D_2O

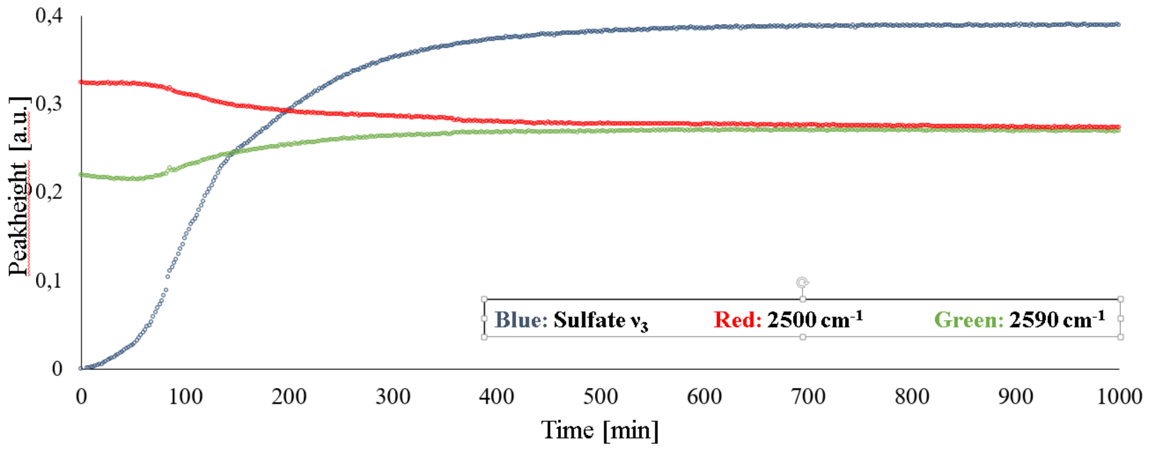


Figure S3: Evolution of the D_2O stretching vibrations at 2590 cm^{-1} and 2500 cm^{-1}, and of the sulphate v_3 mode derived from spectra of Figure 2. Spectra were collected over a period of approx. 16 h in under nitrogen atmosphere.

Infrared spectra and SEM images of dried gypsum samples

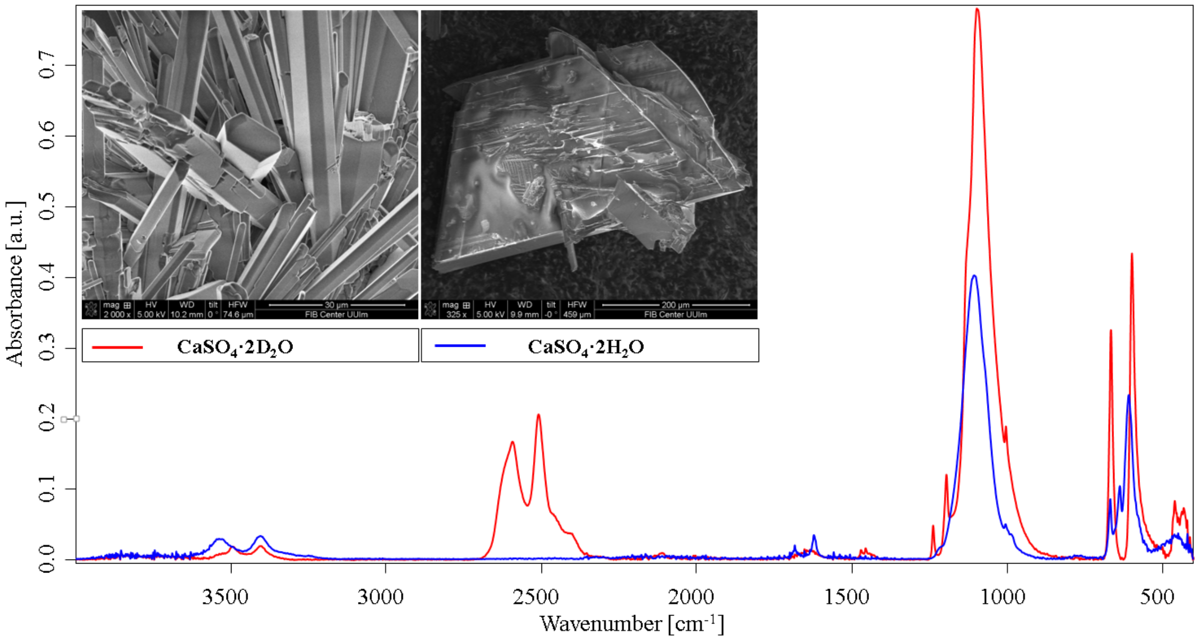


Figure S4: IR-ATR spectra of solid gypsum grown in D_2O (red), and in H_2O (blue) along with the corresponding SEM images of the obtained solids. Differences in total absorbance are ascribed to apparent contact pressure differences at the ATR crystal surface.

Band evolution as a function of time in spike experiments

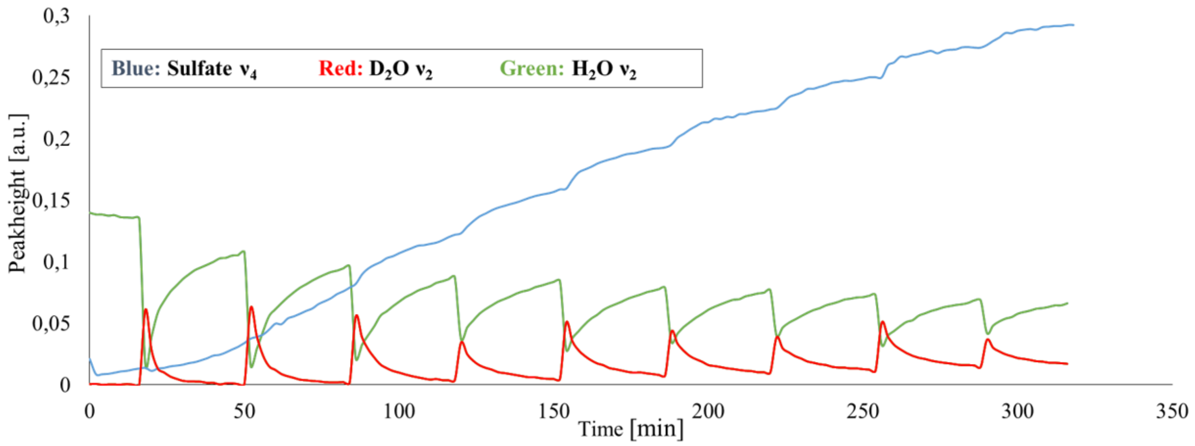
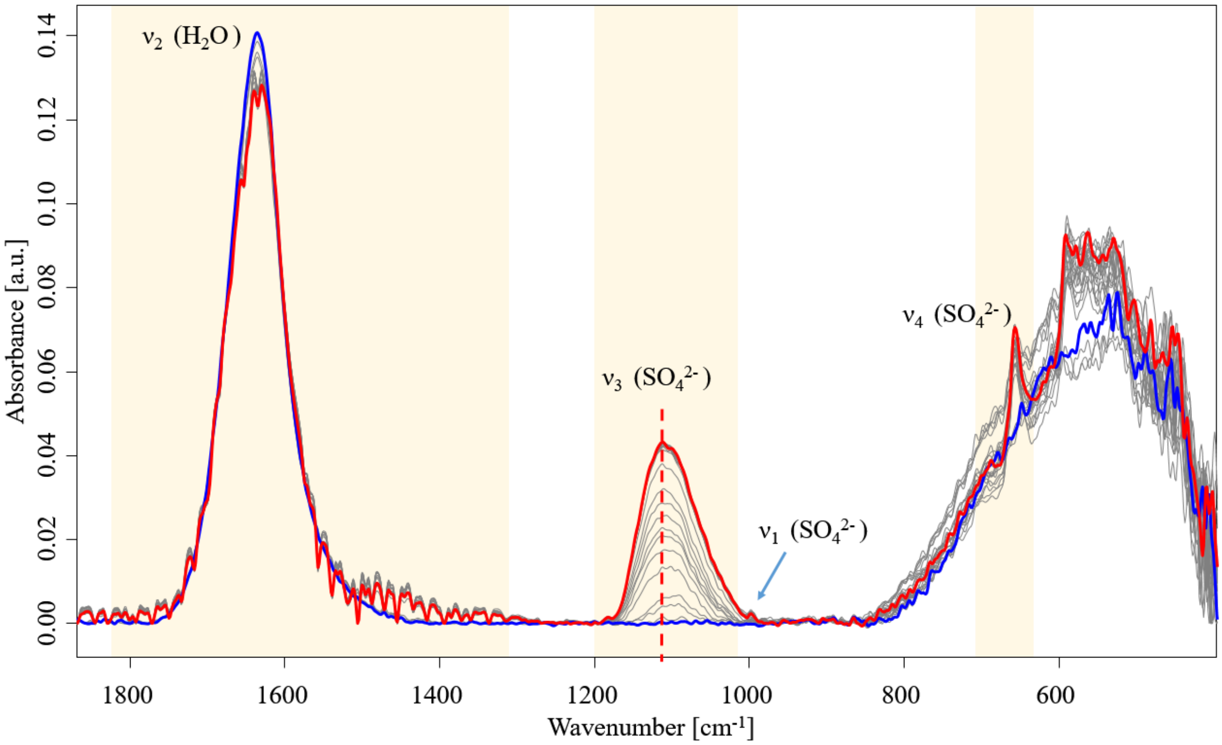


Figure S5: Extracted change of the D_2O ν_2 bending, H_2O ν_2 bending, and sulfate ν_3 vibration during spike experiments. Derived from spectra of Figure 3.

Full Size Figures

To improve the legibility of the figures from the text, they are enlarged and displayed as full size figures in this ESI-chapter.

Figure 1



Infrared spectra of an aqueous Ca^{2+} and SO_4^{2-} solution during crystallisation. Spectra were collected over a period of 16 h in the closed sample cell under nitrogen atmosphere. Blue: start at t_0; red: end at t = 16 h. For a detailed view of the ν_3 band, see ESI† Fig. S2. The dashed line highlights a shift of the $SO_4^{2-}\nu_3$ mode at 1105 cm^{-1} to higher wavenumbers.

Figure 2

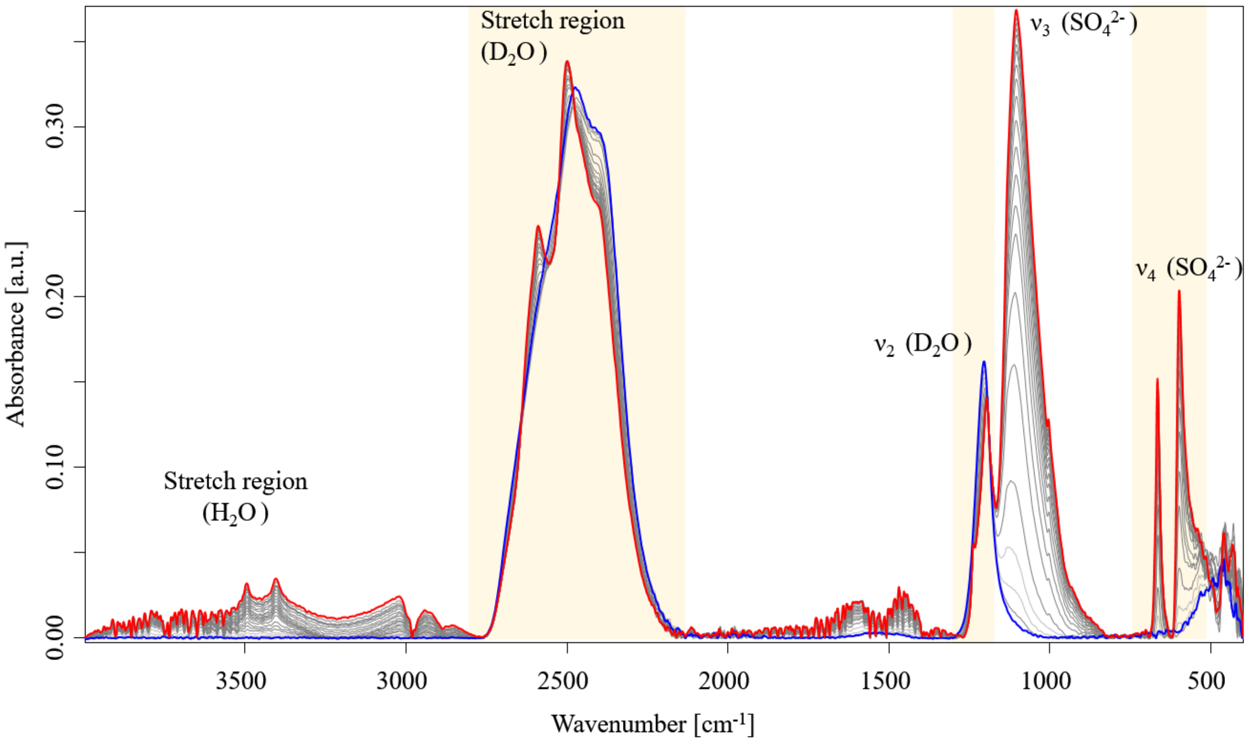


Fig. 2 IR-ATR spectra of a CaSO$_4$ solution in D$_2$O during crystallisation collected over a period of 16 h under nitrogen atmosphere. Evolution of the D$_2$O stretching vibrations and of the sulfate ν$_3$ mode, see ESI† Fig. S3.

Figure 3 a)

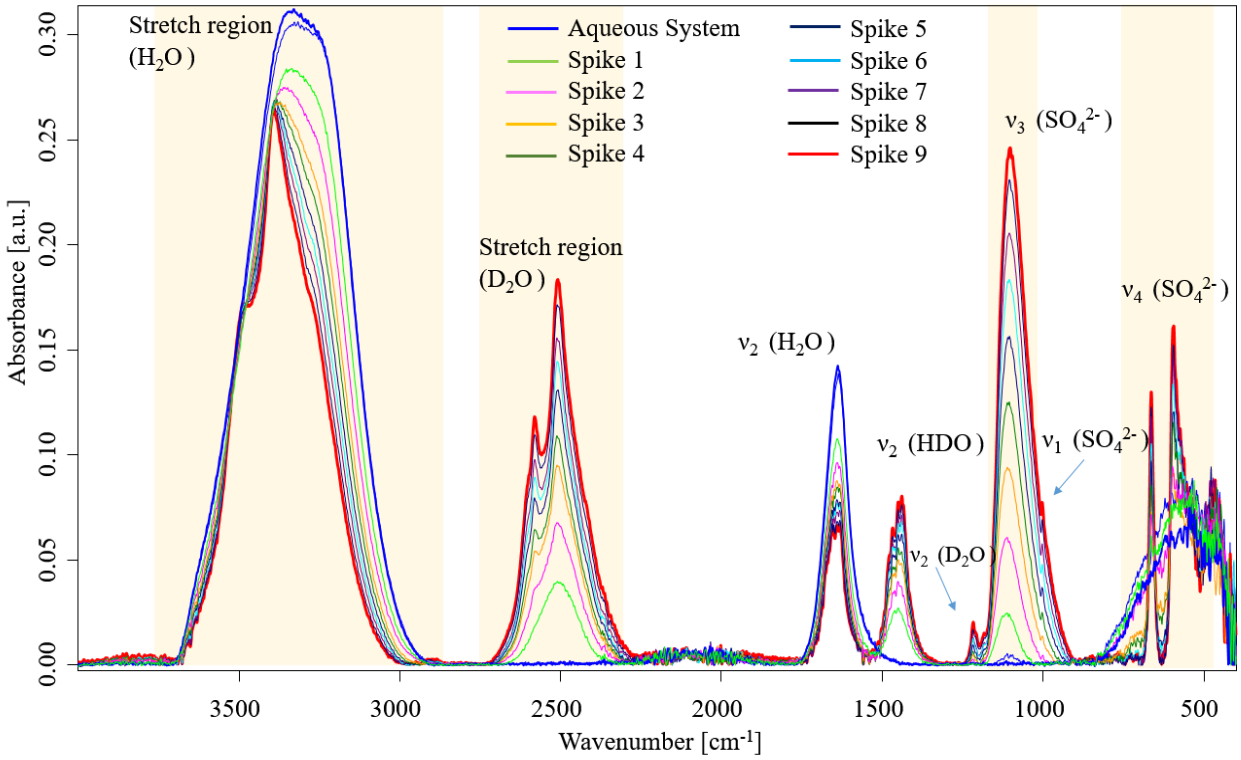


Figure 3 b)

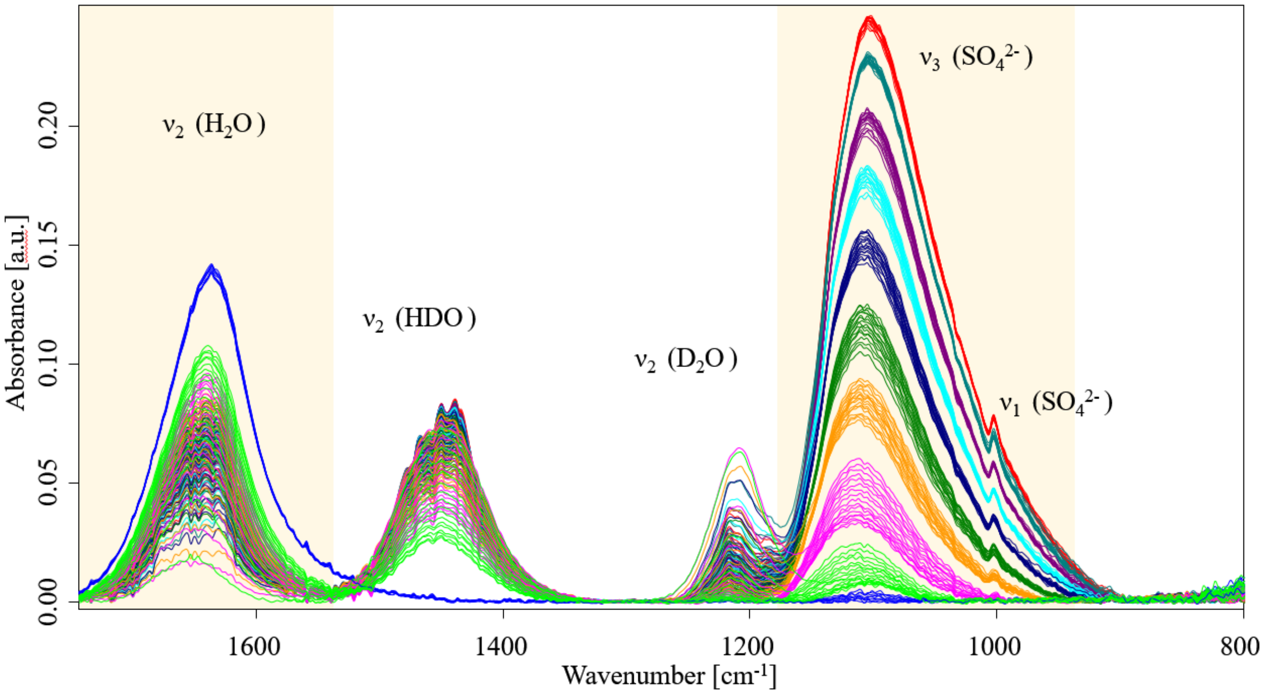


Fig. 3 a) IR-ATR spectra of aqueous $CaSO_4$ solution, which was spiked with D_2O in intervals of 30 min. Blue spectra: prior to spiking; red spectrum: last D_2O spike. b) Zoom onto the sulfate ν_3 band and water bending region. The spectral behaviour as a function of time is given in Fig. S5 within the ESI.†