The crystal orientation of THF clathrates in nano-confinement by *in-situ* polarized Raman spectroscopy

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1. Parameter used for calculation of melting point depression using Gibbs-Thomson equation

The general Gibbs-Thomson equation is given below.

$$\frac{\Delta T_m(r)}{T_{m,bulk}} = -\frac{2M}{\Delta H^{fus}\rho r}\gamma_{nl}cos\theta$$

Here, ρ is the crystal density, M is the molar mass, γ_{nl} is the surface tension between the crystal and the fluid surrounding it, θ is the interfacial angle between the condensed phase and the confined media on which it may have nucleated and ΔH^{fus} is the molar heat of fusion in bulk.

ρ = 916.61 kg/m^3 (273K)[(1)]

M = 378

γ_{nl} = 0.016 J/m^2[(1)]

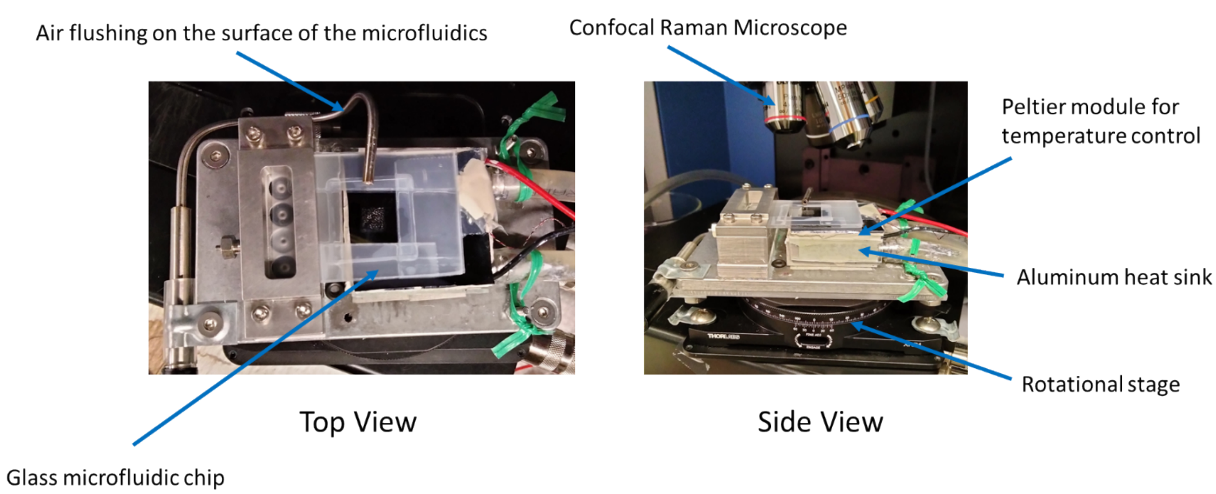
θ = 30.5° – 56.1° (experimentally determined)

ΔH^{fus} = 98.0 KJ/mol[(2)]

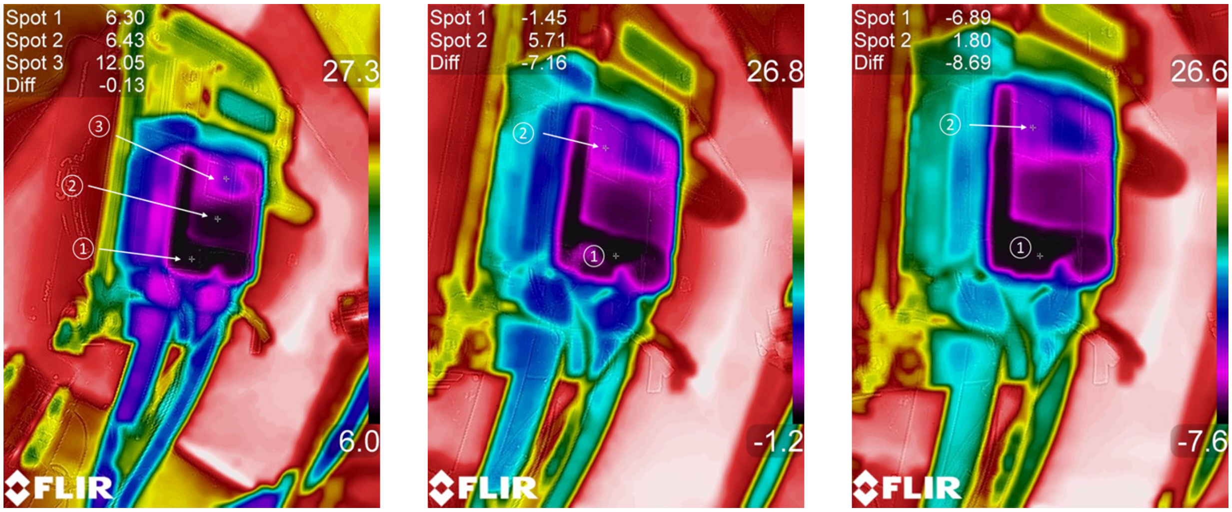
$T_{m,bulk}$ = 277.4 K[(2)]

r = 10, 20 nm (radius of the nanopores)

2. Image of experimental setup

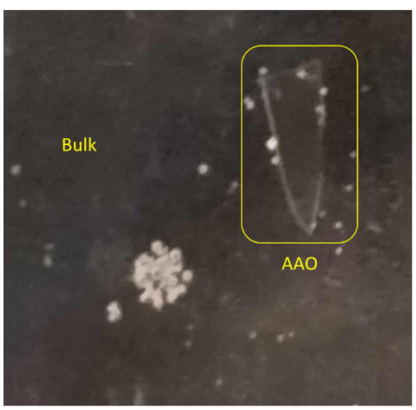


3. IR images for the temperature difference observed

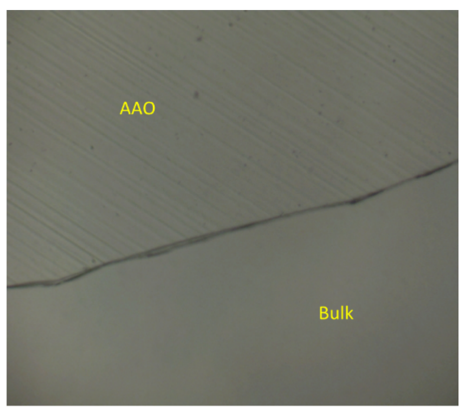


Here, spot 1 is the temperature of the peltier at the base of the glass microsystem
Spot 3 in the extreme left image and spot 2 in other two images on the right is the temperature inside the cavity where hydrates are formed. The temperature difference is due to the constant air flushing on the surface of the coverslip to avoid the moisture condensation.

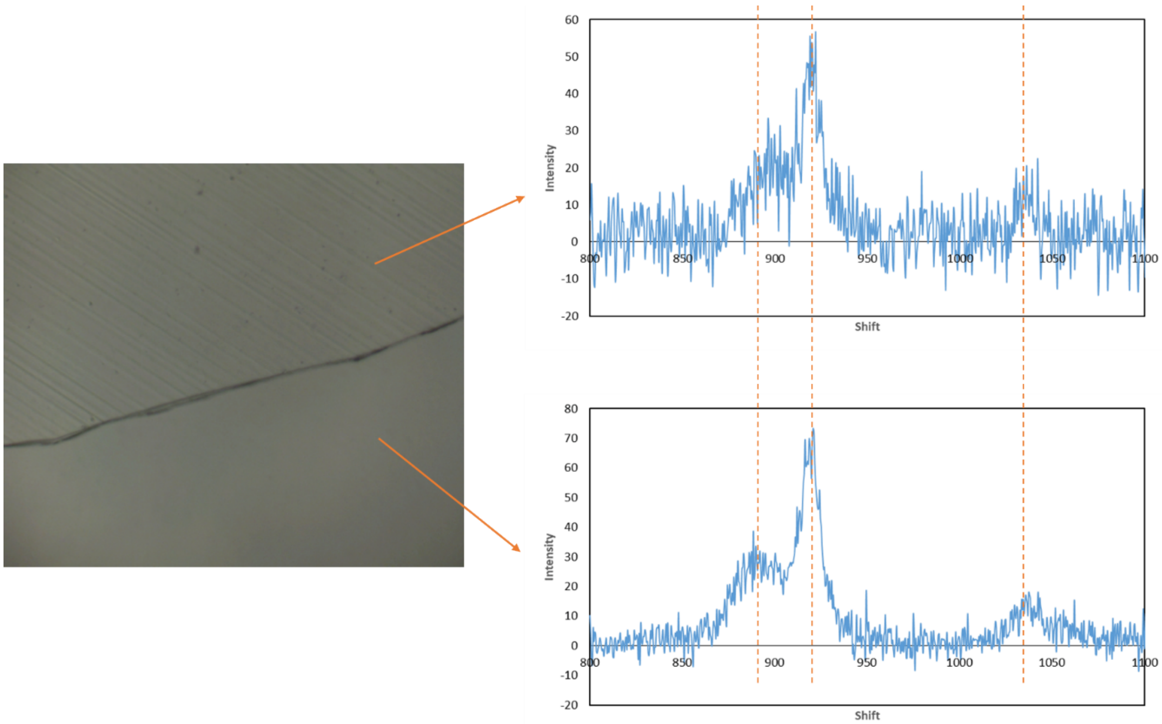
4. Images and spectra on Anodic Aluminum Oxide during experiments



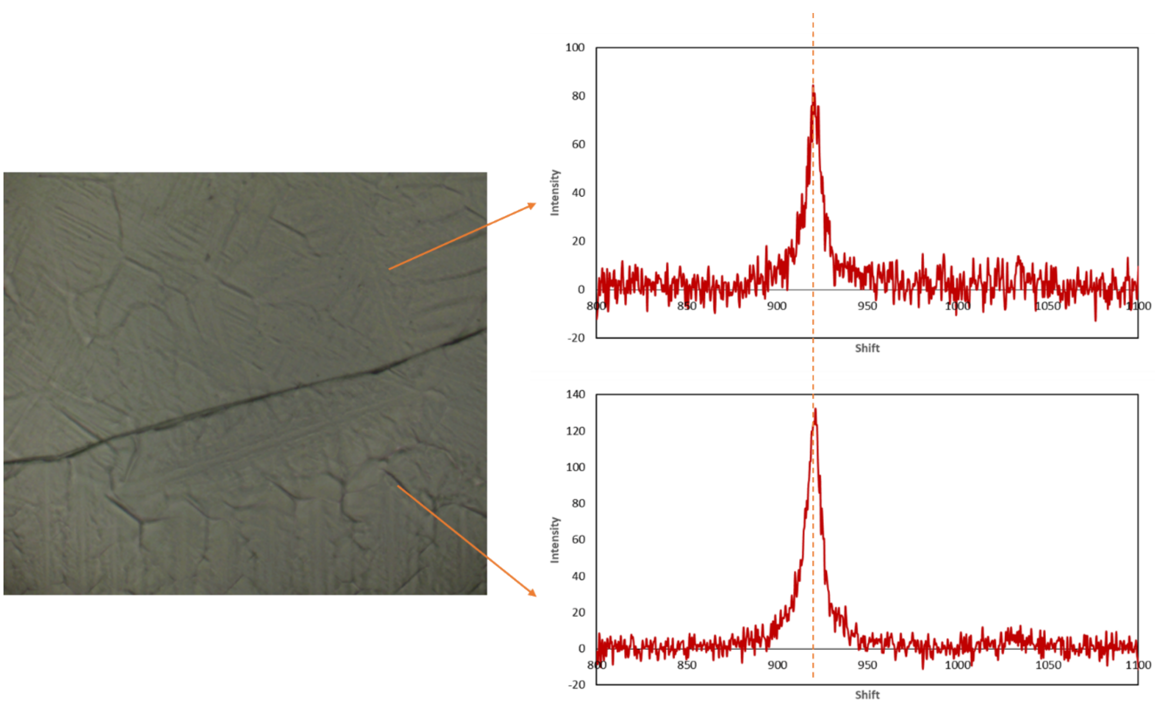
4x Objective



10x Objective

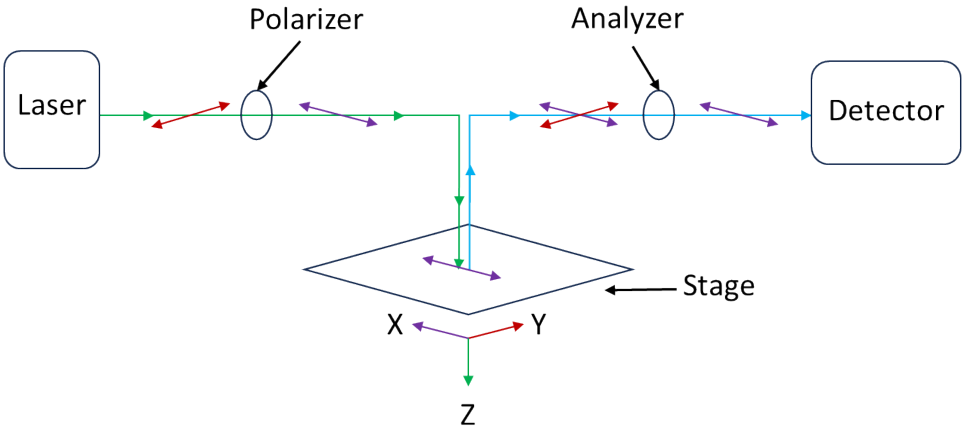


Spectra obtained for THF water mixrure in bulk and in AAO nanopores with 785nm laser at 100% ND filter and 50x objective (image shown is of 10x objective)

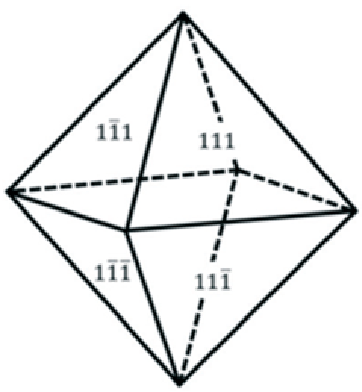


Spectra obtained for THF water mixrure in bulk and in AAO nanopores with 785nm laser at 100% ND filter and 50x objective (image shown is of 10x objective)

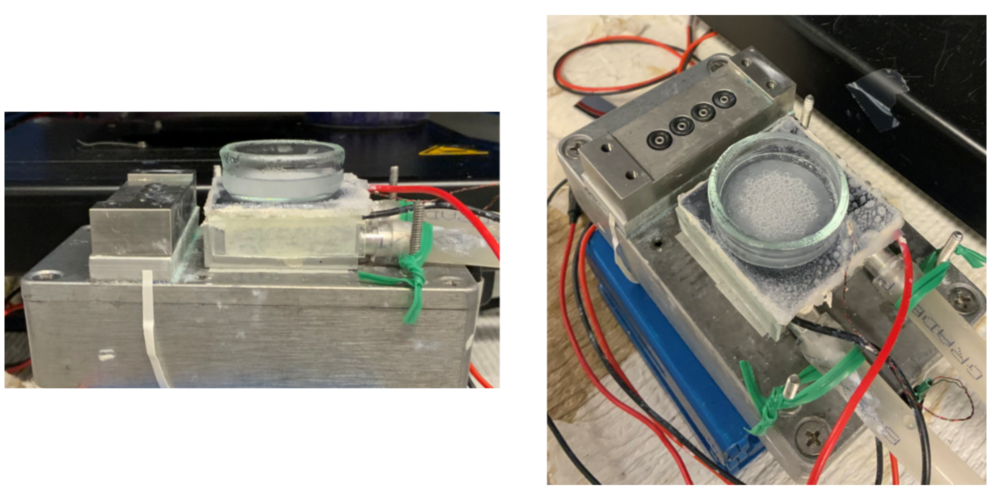
5. **Instrument configuration schematic for the rotational measurements (shown for the Z(XX)Z configuration**

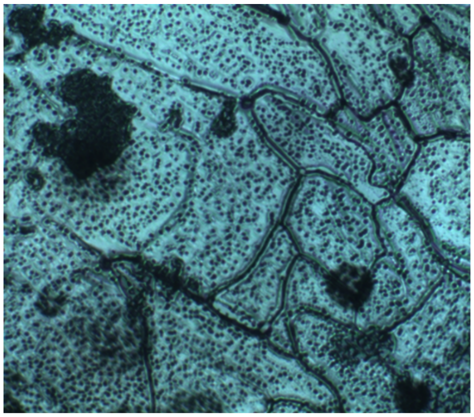


6. **THF hydrate octahedral crystals sketch**



7. **Single crystal formed in the petri dish for the measurement**





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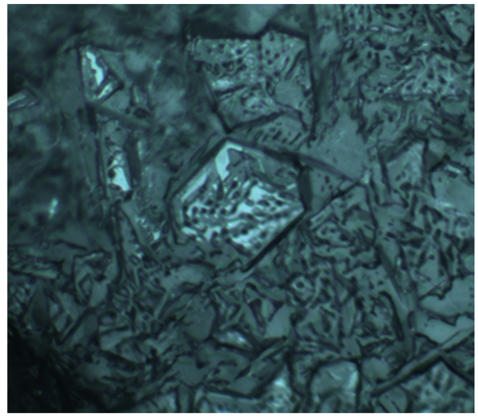
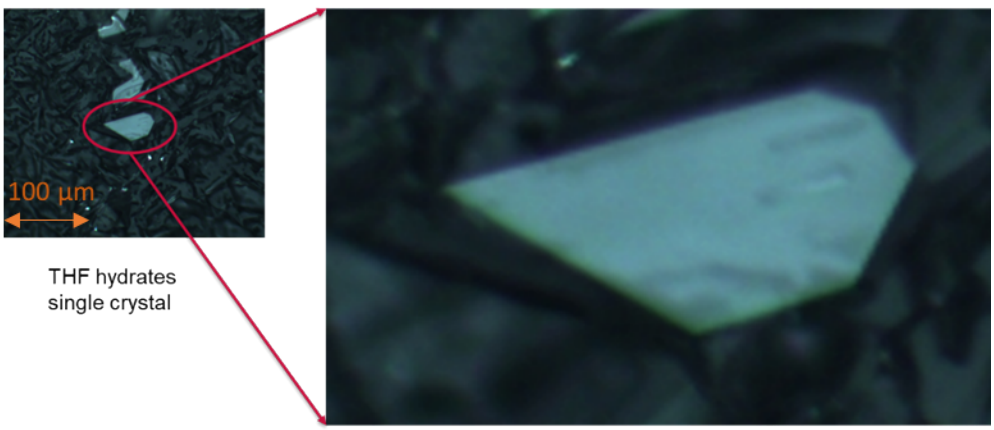
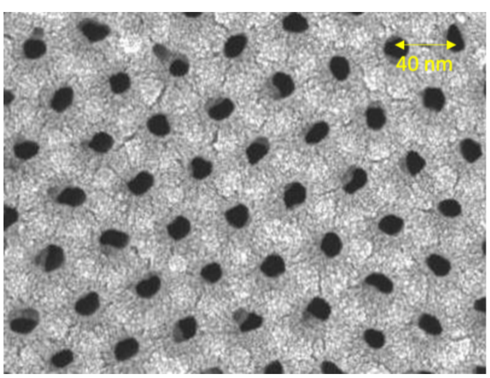
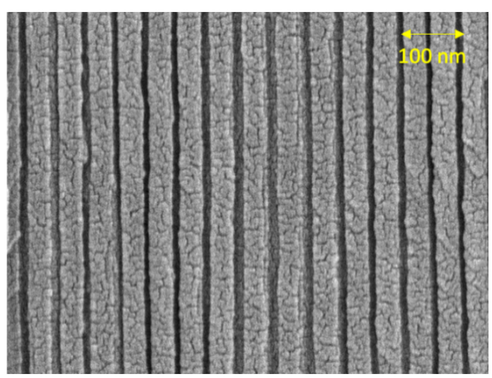


THF HYDRATES



8. **AAO wafers cylindrical pores (SEM images, InRedox LLC, USA)**





9. **Chemical safety and hazard information**

The tetrahydrofuran used has acute oral toxicity of 4 and is known to form explosive peroxides.

SDS information (https://www.sigmaaldrich.com/US/en/sds/SIAL/401757)

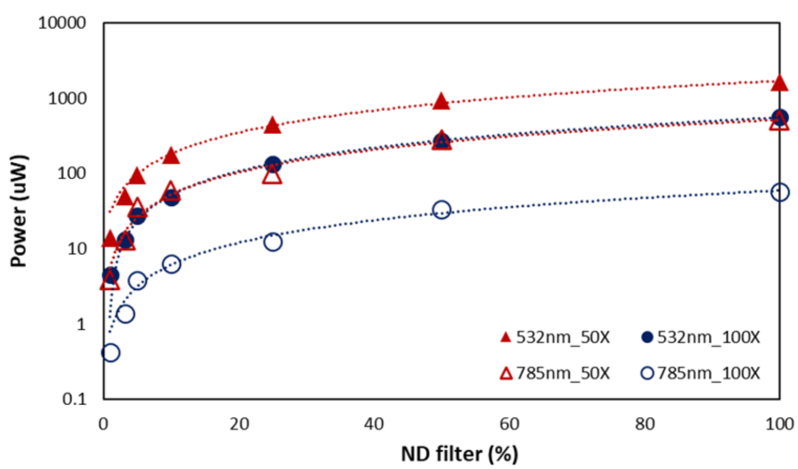
GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)

Flammable liquids (Category 2), H225

Acute toxicity, Oral (Category 4), H302
Eye irritation (Category 2A), H319
Carcinogenicity (Category 2), H351
Specific target organ toxicity - single exposure (Category 3), Respiratory system, Central nervous system, H335, H336

10. Laser power measurement

It is observed that the irradiation power depends on the selected microscope objective and the exposure (**Fig. 6**). The difference between the power values for the 532 nm laser and 785 nm is one order of magnitude. However, when switched to the 100x objective, the difference is more compared to the 50x as transmission values for the 100x objective are in the range of 200 – 700 nm. For the 785 nm laser, the transmission of the 100x objective was lower than 50x, the 50x objective was chosen over 100x. At this combination, angle-resolved experiments were performed in a test run to visually monitor the crystal deformation after each acquisition at a single location. Even after 20 acquisitions, crystal melting was not observed, and 50x objective and 100% ND filter values were kept constant for the rest of the experiment for data acquisition.



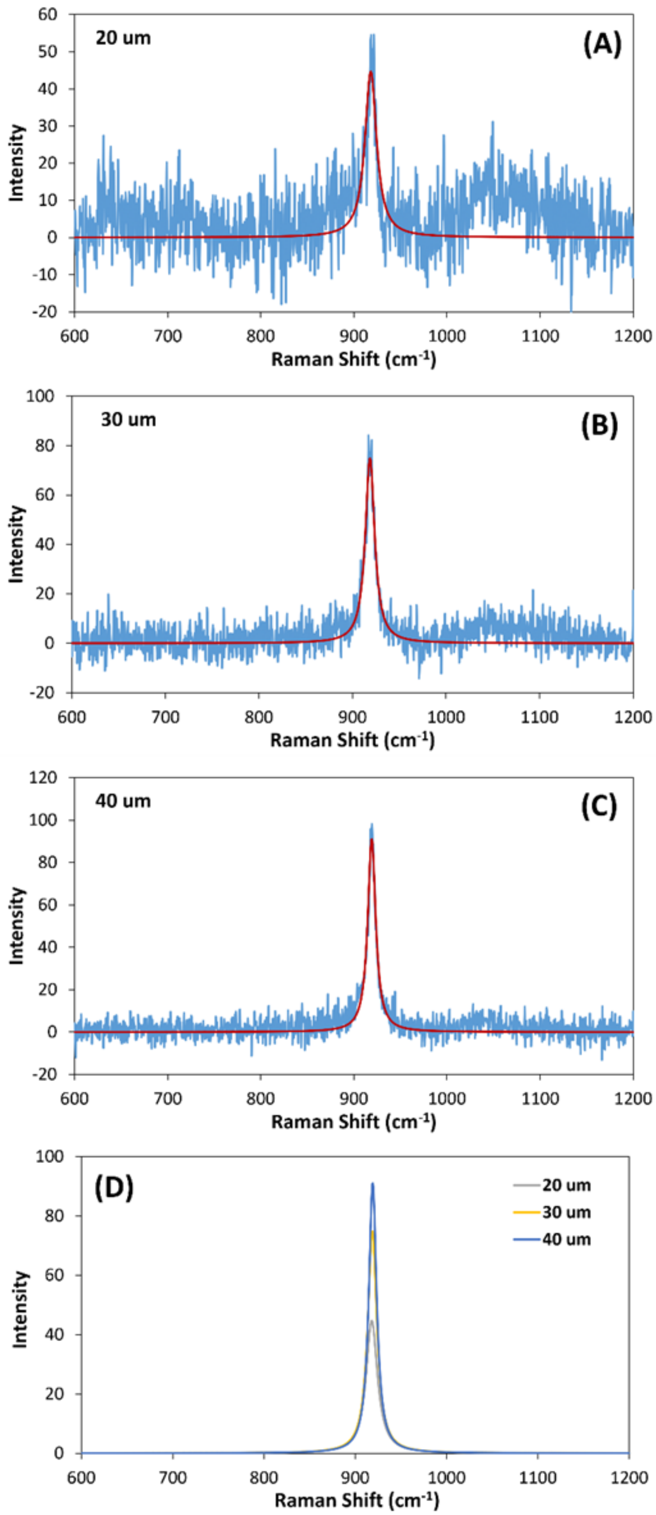
11. Raman signal acquisition depth

While acquired Raman spectra using a 785 nm laser in AAO nanopores is sufficient to distinguish between the THF water mixture and THF hydrates through identified distinct peaks, the signal resolution depends on the depth at which the spectrum is acquired. It has already been established that for AAO films, the reflectance value is proportional to the AAO film thickness and the interparticle distance. In one study, authors tested AAO films of 20 um thickness with varying interpore distance (pore density). They showed that the contribution of interpore distance in reflectance is significant compared to the film thickness75.

$$R_{max}=91.93-(7.38\times 10^{-5} \times Thickness)-(9.11\times 10^{-2} \times D_{int}) \quad (10)$$

Here, R_{max} is the maximum reflectance, D_{int} interpore distance, Thickness is the thickness of the AAO films. According to eqn. (10), maximum reflectivity is lower for lower pore density though the pore diameter is large. It has implications for the depth at which the signal can be acquired and the resolution obtained. However, the proposed relationship cannot be used because the Raman signal is the effect of light scattering. The depth at which the signal was acquired was determined experimentally for each experiment to get a good resolution to minimize the signal-to-noise ratio.

After confirmatory analysis, while switching to a 785 nm laser, the signal for the THF hydrates was acquired stepwise at every ten µm depth from the AAO surface (depth = 0 µm). The depth with the highest signal-to-noise ratio observed was selected for the angle-resolved measurement (Fig. 7).



References

1. Lee, J.; Yun, T.; Santamarina, J.; Ruppel, C., Observations related to tetrahydrofuran and methane hydrates for laboratory studies of hydrate-bearing sediments. *Geochemistry, Geophysics, Geosystems* **2007,** *8* (6).

2. Sharifi, H.; Yoneyama, A.; Takeya, S.; Ripmeester, J.; Englezos, P., Superheating clathrate hydrates for anomalous preservation. *The Journal of Physical Chemistry C* **2018,** *122* (30), 17019-17023.