TBAB semi-clathrates studied by Quasi Elastic Neutron Scattering (QENS) using Emu, the high resolution backscattering spectrometer at ANSTO

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Potential applications for gas hydrates include gas purification, water desalination, and CO_2 capture that is possibly combined with methane extraction [Sum, Xu, Mon]. All of these rely on the high selectivity of the guest molecule in gas hydrates. It has been shown, that the addition of TBAB (i.e. Tetra-n-butyl ammonium bromide) softens the thermodynamic conditions of formation without compromising the CO_2 selectivity [Li, Cha1], a substantial benefit in reducing the carbon output from existing fossil-fuel power plants. To gain a better understanding of the improved gas selectivity process, we studied the dynamics of CO_2- TBAB semi-clathrate hydrates particularly the libration of the butyl chains, and their interaction with CO_2 molecules via intermediary water molecules. . EMU, the neutron back-scattering spectrometer, with its energy resolution of 1μeV, is capable of measuring the slow dynamics of the relatively heavy and highly hydrogenous butyl chains of the TBAB cation.

[Sum] Sum, A.K., Koh, A.K., Sloan E.D., Ind. Eng. Chem. Res. 2009, 48, 7457-7465; [Xu] C.-G. Xu, X.-S. Li, RSC Adv. 4 (2014) 18301–18316; [Mon] Mondal M.K., Balsora H.K., Varshney P., Energy 46 (2012) 431–441; [Cha1] Chazallon B., Pirim, C., Chem. Eng. J., 2018, 342, 171-183 ; [Li] Li, X.-S., Zhan, H., Xu, C.-G., Zeng, Z.-Y., Lv, Q.-N., Yan, K.-F., Energy Fuels (2012), 26, 2518–2527

Carbon Capture and Storage (CCS)

Typical CO_2 concentration in gas mixtures (e.g. CO_2+N_2) released from industrial activities: **5-40%**

Reduce and control emission: CO_2 capture in post-combustion

1) CO_2 is extracted from flue gases by a "chemical solvent": Selective trapping on contact with CO_2
2) CO_2 is recovered from the solvent by heat regeneration
3) Storage and geological internment

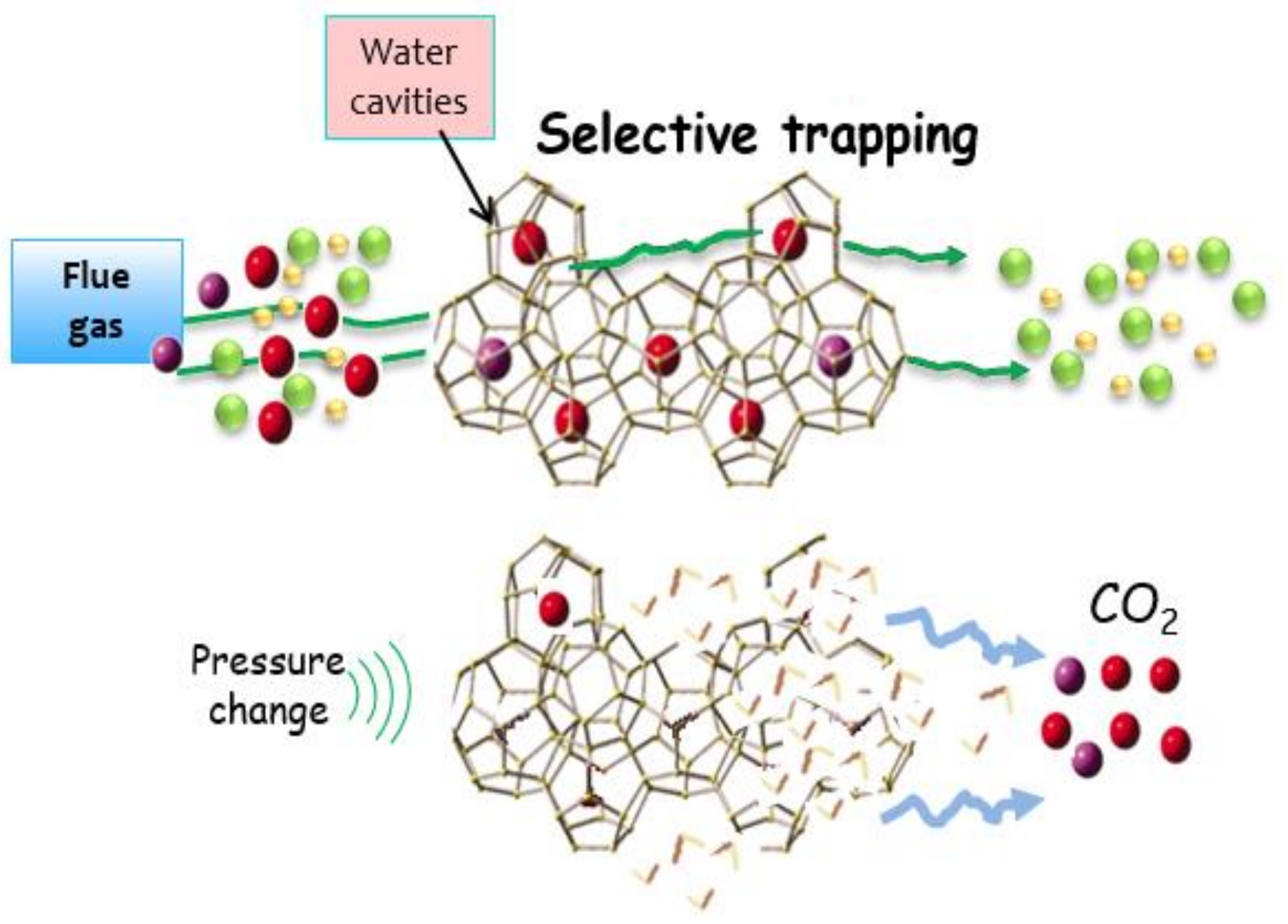
Advantage: Adapted to existing industrial plants

Drawbacks: Expensive and energy-intensive

→ CO_2 emission can be reduced by 80-90% for a modern power plant equipped with CCS technology (Metz et al., IPCC 2005)

Alternative: Gas separation by Hydrate formation

Spencer, U.S. Patent 5700311, 1997
Spencer U.S Patent 6106595, 2000
Spencer et al., U.S. Patent 6352576, 2002

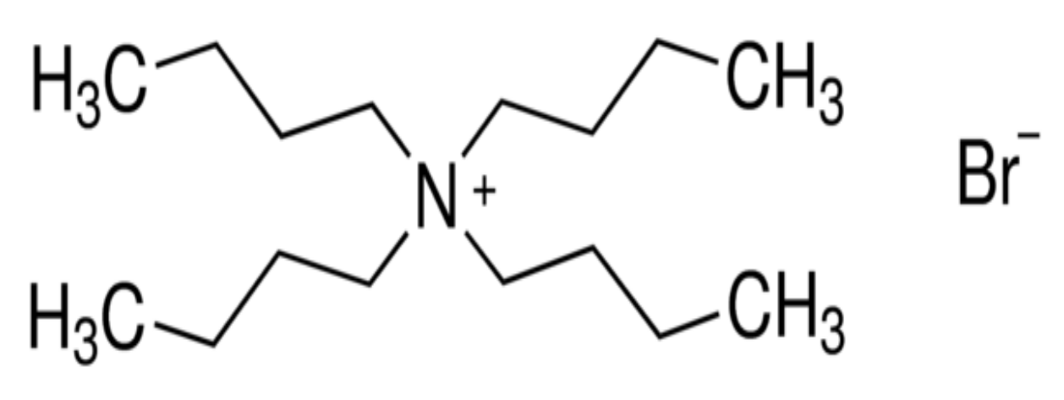


Requirements:
- cost-effective process
- mild thermodynamic conditions
- high selectivity of CO_2
- rapid hydrate formation high gas storage capacity

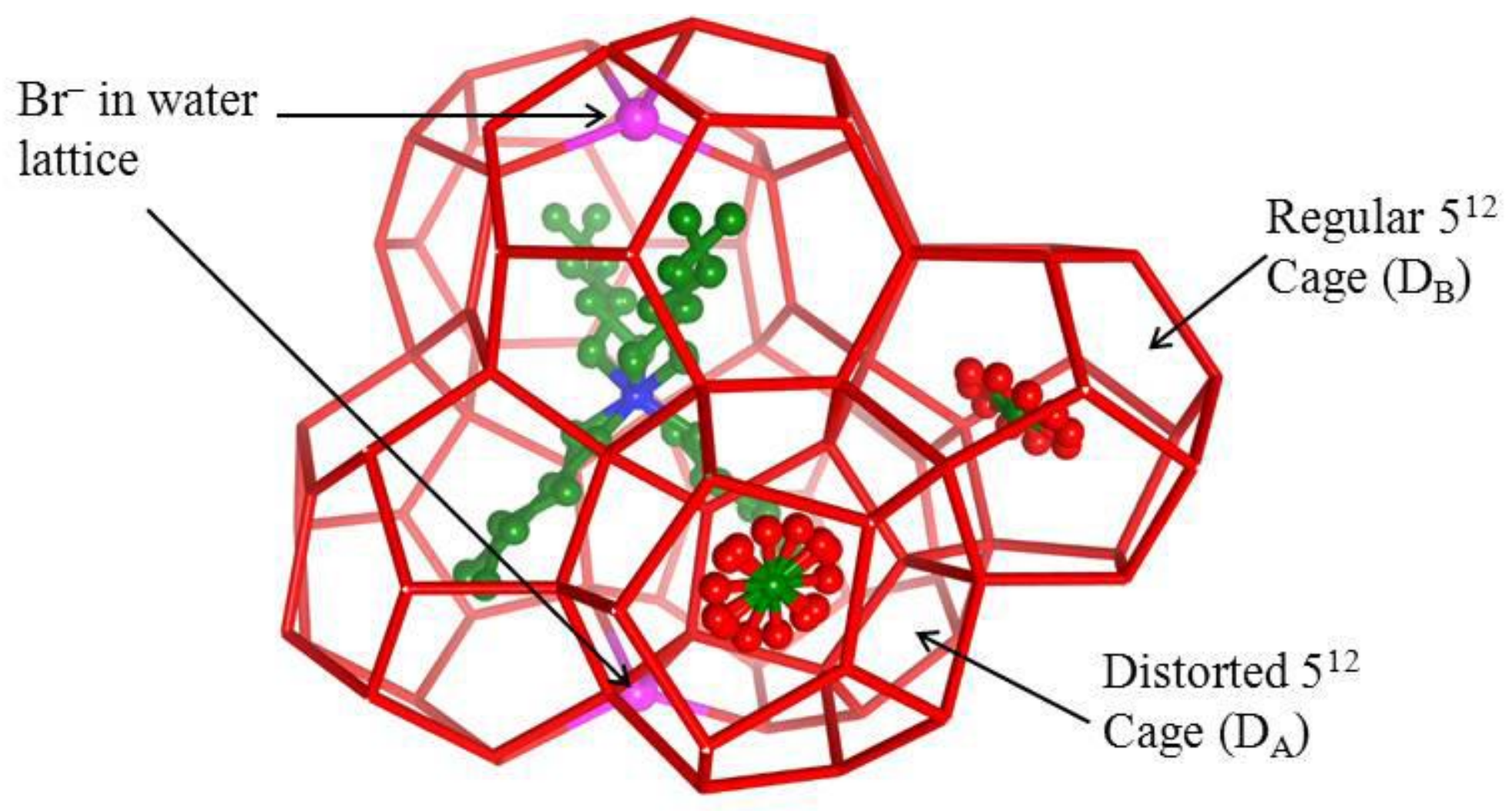
Efficiency improved by thermodynamic additives like TBAB salt

CO_2 semi-clathrate hydrate from TBAB

Salt additive:



Tetra-n-butyl ammonium bromide (TBAB).



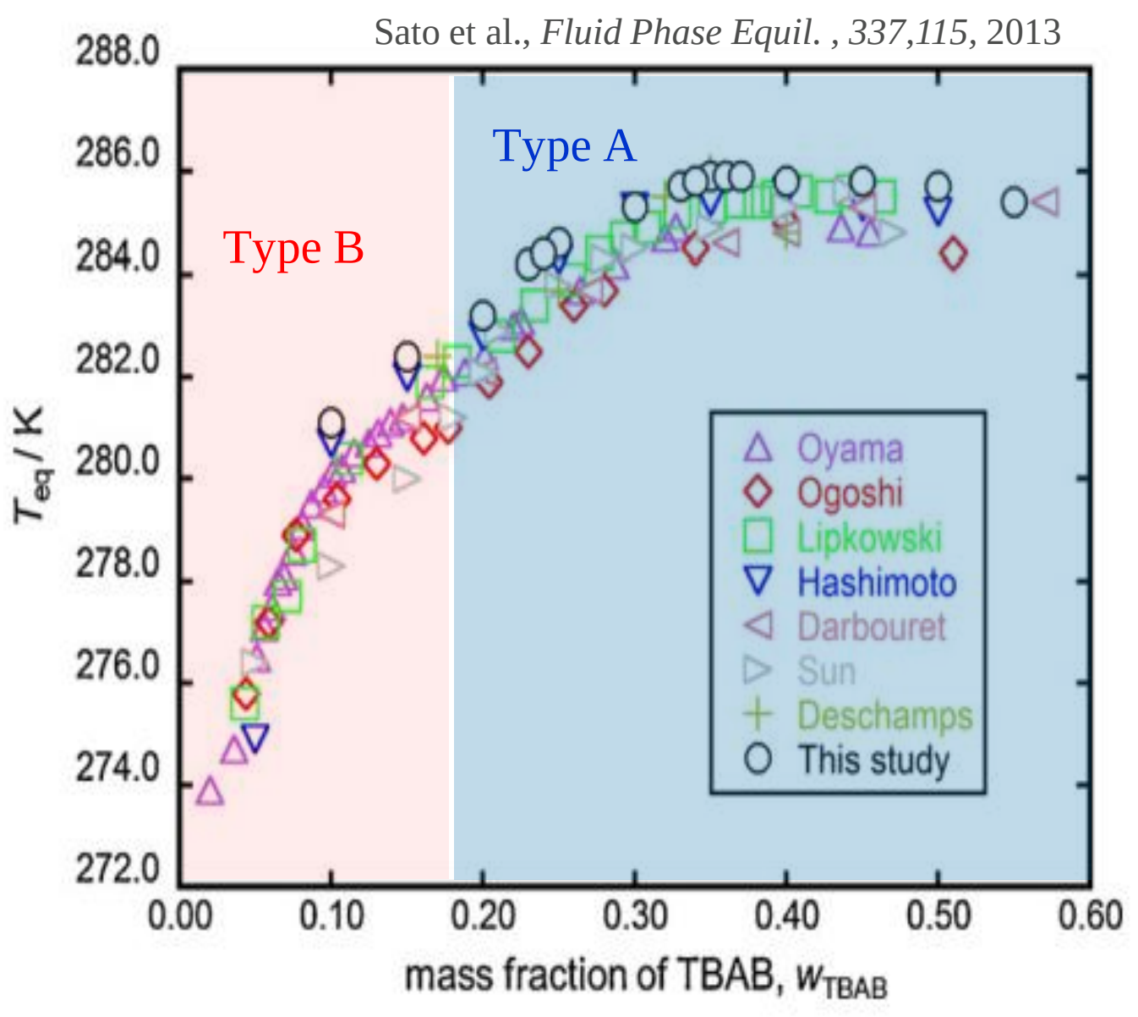
Selective CO_2 storage

Type	Tm	Hydrate Formula	Hydration Number	Space group	Unit cell a,b,c (Å)	H_2O cages	Max. CO_2 Storage
A	288 K	Bu_4NBr - $26H_2O$	26	P4/mmm (tetra.)	23.9, 23.9, 50.8	10 small, 2 medium, 2 large	8.8 wt% *
B	282 K	Bu_4NBr - $38H_2O$	38	Pmma (ortho.)	21.01, 12.6, 12.0	6 small, 2 medium, 2 large	11.6 wt%**

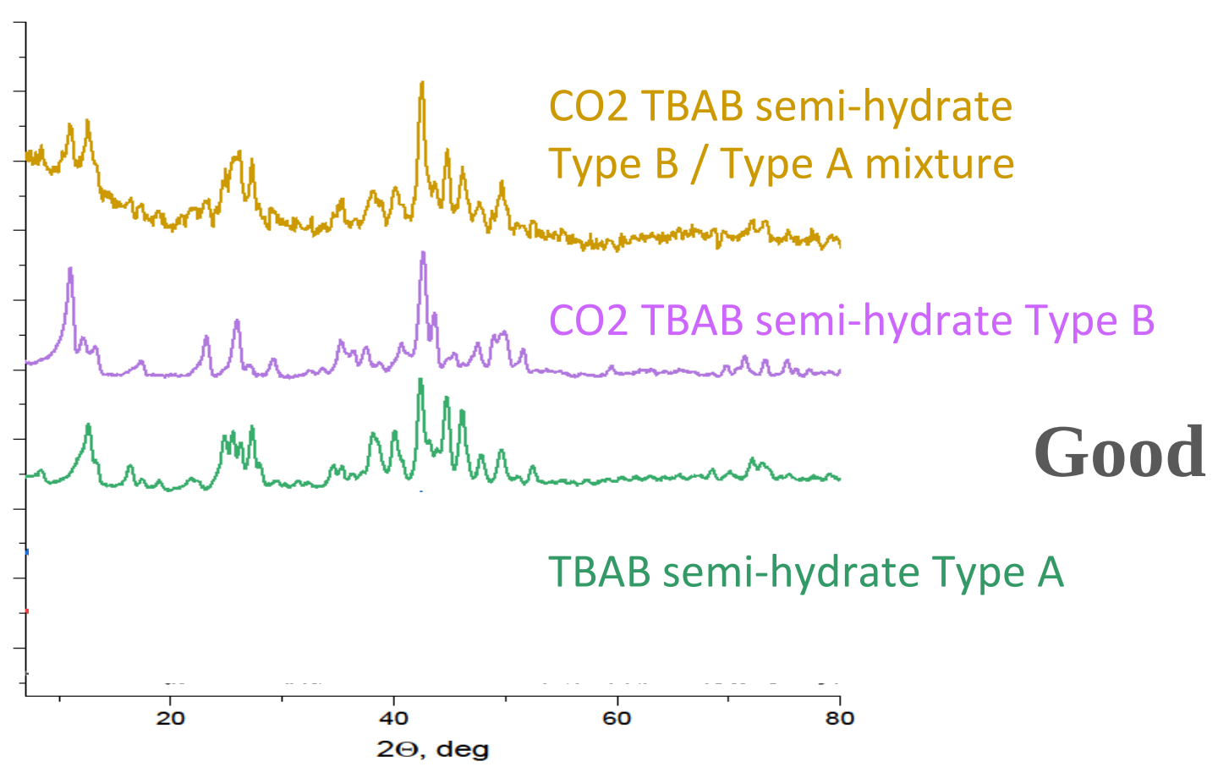
* Shimada et al., Acta. Cryst. 2005 ** Rodionova et al., J. Phys. Chem. 2013

Hydrate Preparation

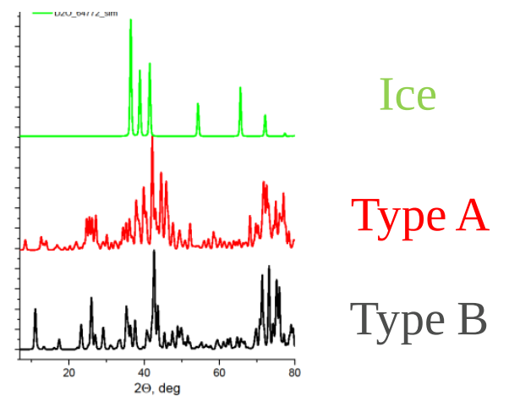
Sato et al., *Fluid Phase Equil.* , *337,115*, 2013



Phase diagram of TBAB hydrate



Calculated pattern



Good sample quality!

Neutron Powder Diffraction to characterise the various samples

The samples were synthesized by cooling a liquid solution of TBAB and D_2O to 258K with and without the introduction of CO_2 gas. A liquid solution containing 40 wt% TBAB results in Type A semi hydrate and 5 wt% TBAB in Type B.

Emu, high resolution backscattering spectrometer

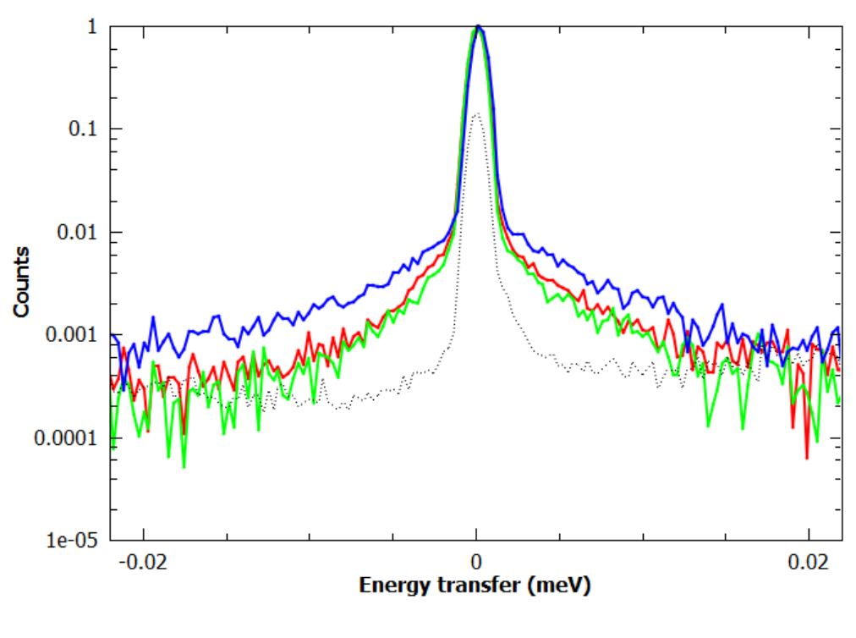
Highly sensitive to Hydrogen and suited to detect slow dynamics

… used to measure
- quasi-elastic (QENS) scattering
- motion of confined butyl chain of TBAB cation
- Temperature < 220K

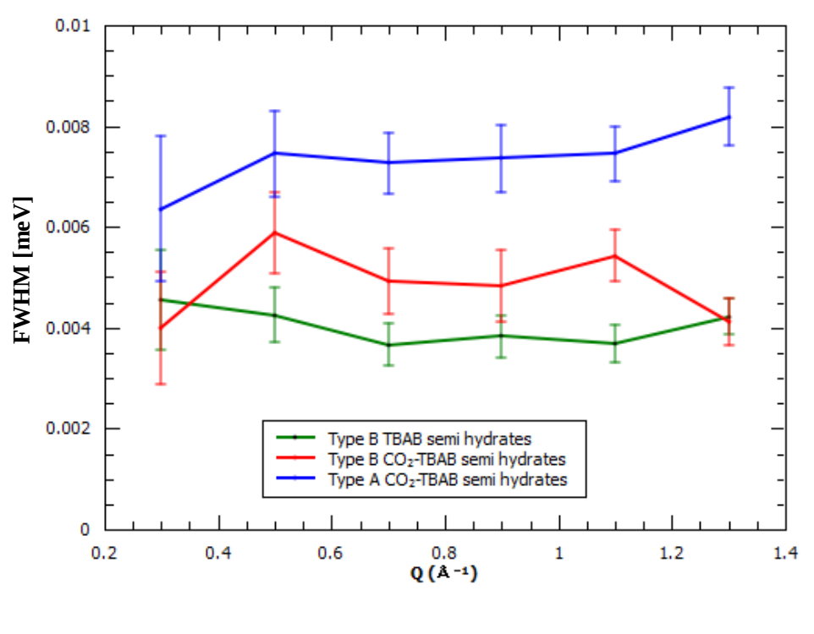
The scatter from the water framework was supressed exchanging H_2O for D_2O. The guest gas, CO_2, does not contribute to the inelastic signal due to its negligible incoherent scatter (i.e. no H atoms).

Quasi-elastic neutron scattering (QENS)

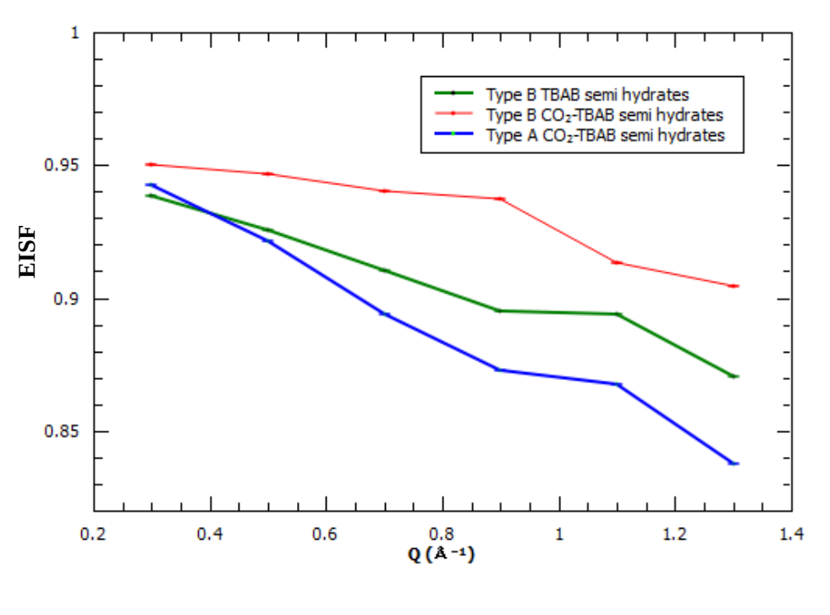
Blue: Type A CO_2-TBAB semi hydrates, Red: Type B CO_2-TBAB semi hydrates, Green: Type B TBAB semi hydrates, Grey: Vanadium/instrument resolution



QENS spectra at 193K
(sum of all Q-values)



FWHM Lorentzian fit at 193K



Elastic Incoherent Structure Factor (EISF) at 193K

Summary

- Dynamical processes for type A and type B semi-clathrates are different, probably due to differing occupations of the n-butyl chains in the water cages.
- The motion of the encaged butyl changes might be influenced by encaged CO_2 molecules.
- The Q-independent line width of the single Lorentzian fit implies a localized diffusive motion of the methyl groups
- Localized motions of Type A and Type B show different time scales.
- The calculated elastic incoherent structure factor (EISF) for type A and type B indicate different landscapes for the motion of the confined n-butyl chains.

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