Pressure-induced hydrogen formation and phase transitions in H_2S-THF clathrate hydrate

Selene BERNI (CNR-IFAC, Italy),
Demetrio SCELTA (LENS, Italy, CNR-ICCOM, Italy)
Milva CELLI (CNR-IFAC, Italy)
Milo AGATI (ESRF, France)
Katarzyna SKRZYNSKA (ESRF, France)
Leonardo DEL ROSSO (CNR-IFAC, Italy)

Abstract

Hydrogen-bearing compounds are attracting increasing attention because they provide valuable model systems to investigate the behaviour of hydrogen under extreme conditions, while also offering potential routes for hydrogen storage and release [1]. Among hydrogen-containing molecules, hydrogen sulfide (H_2S) is particularly appealing as it exhibits a remarkably rich high-pressure chemistry, such as molecular dissociation and the formation of hydrogen-rich hydrides, including phases exhibiting near-record superconducting critical temperatures [2].

In this framework, H_2S hydrates offer an unexplored platform to investigate how a hydrogen-bearing guest molecule interacts with a hydrogen-bonded host lattice under compression. Indeed, H_2S is known to form clathrate hydrates which are believed to play an important role in planetary environments by promoting the trapping of volatile species and thus influencing out-gassing processes [3]. However, despite their significance for the interiors of icy moons and satellites, the behaviour of H_2S hydrates has been studied exclusively at low pressure [4, 5, 6], while at pressures in the GPa range, typical of subduction processes and of the interiors of icy bodies, its chemistry remains unexplored.

We investigated the room temperature compression (0.1 -10 GPa) of the H_2S-THF clathrate hydrate (THF acts as a clathrate stabiliser) in membrane Diamond Anvil Cells (mDACs) using Raman spectroscopy and synchrotron x-ray diffraction, finding multiple phase transitions below 3 GPa. Beyond establishing the clathrate high-pressure stability field, we observed a pressure-induced decomposition associated with sulfur segregation and the direct formation of molecular hydrogen, which remains trapped within a hydrate phase. These remarkable findings provide new insights into the mechanisms of hydrogen generation and release from hydrogen-bearing compounds under extreme conditions, firmly establishing H_2S hydrates as a model system for studying pressure-driven hydrogen synthesis in molecular systems.

[1] Struzhkin, Viktor V., et al. "Hydrogen storage in molecular clathrates." *Chemical reviews* 107.10 (2007): 4133-4151.
[2] Goncharov, Alexander F., et al. "Hydrogen sulfide at high pressure: change in stoichiometry." *Physical Review B* 93.17 (2016): 174105.
[3] Lodders, Katharina, and Bruce Fegley. "Sulfur in the giant planets, their moons, and extrasolar gas giant planets." *The Role of Sulfur in Planetary Processes: from Cores to Atmospheres*. Cham: Springer Nature Switzerland, 2026. 1447-1516.
[4] Chazallon, Bertrand, et al. "A comparative Raman spectroscopic study of natural gas hydrates collected at different geological sites." *Chemical geology* 244.1-2 (2007): 175-185.
[5] Sun, Jiyue, et al. "Crystallization behavior of the hydrogen sulfide hydrate formed in microcapillaries." *ACS omega* 6.22 (2021): 14288-14297.
[6] Dartois, E., et al. "Hydrogen sulfide clathrate hydrate FTIR spectroscopy: A help gas for clathrate formation in the Solar System?." *Icarus* 220.2 (2012): 427-434.