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Dissolution of H₂-rich gas mixtures in brine under subsurface storage conditions: molecular simulations and thermodynamic modeling

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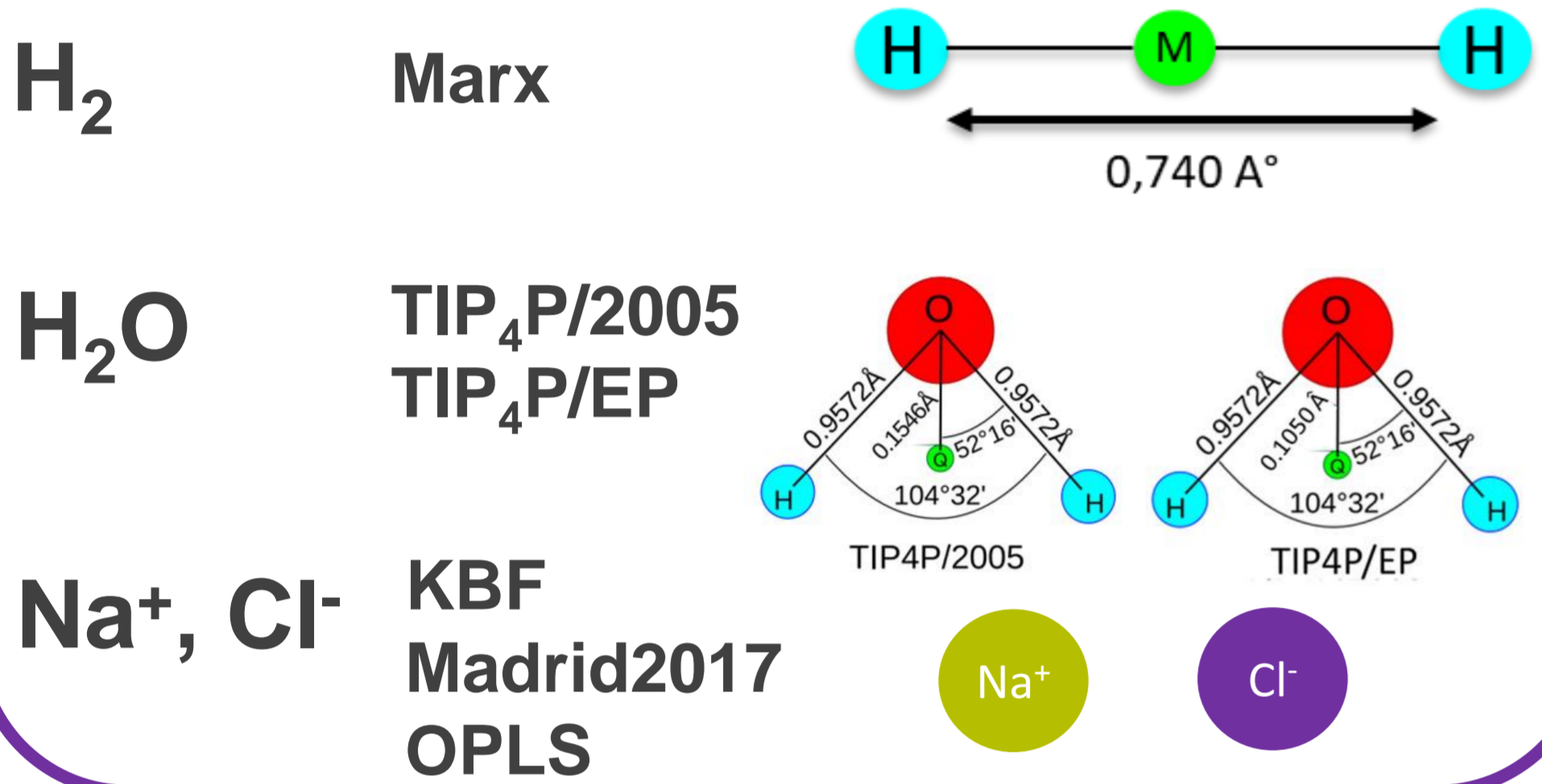
Context & Motivations

The storage of hydrogen in deep saline aquifers through Power-to-Gas process offer a great capacity and geographical availability for large-scale renewable energy storage. However, the contact between gas, brine, and rock can affect the mobility and stability of hydrogen and is not sufficiently documented at the time being. Thus, the accurate knowledge of thermophysical properties is required for the study and development of such infrastructure.

In this work, the first part focuses on the use of Monte Carlo simulations to predict H₂/brine solubility which is then validated against experimental data measured in this work. In the second part, literature data (CH₄/NaCl brine, CO₂/NaCl brine) and measured data (experiments + molecular simulations) are used to optimize thermodynamic models. It is shown that the developed thermodynamic model can be used to predict the vapor-liquid equilibria of H₂/NaCl brine and H₂/CH₄/CO₂/NaCl brine systems for underground H₂ storage and bio-methanation applications.

Monte Carlo Simulation

Selected models



Simulation details

Sampling method: Continuous Fractional Component Monte Carlo (CFCMC)

Ensemble: NPT ensemble

Mixing rules: Lorentz-Berthelot (LB)

Henry constant from molecular simulation

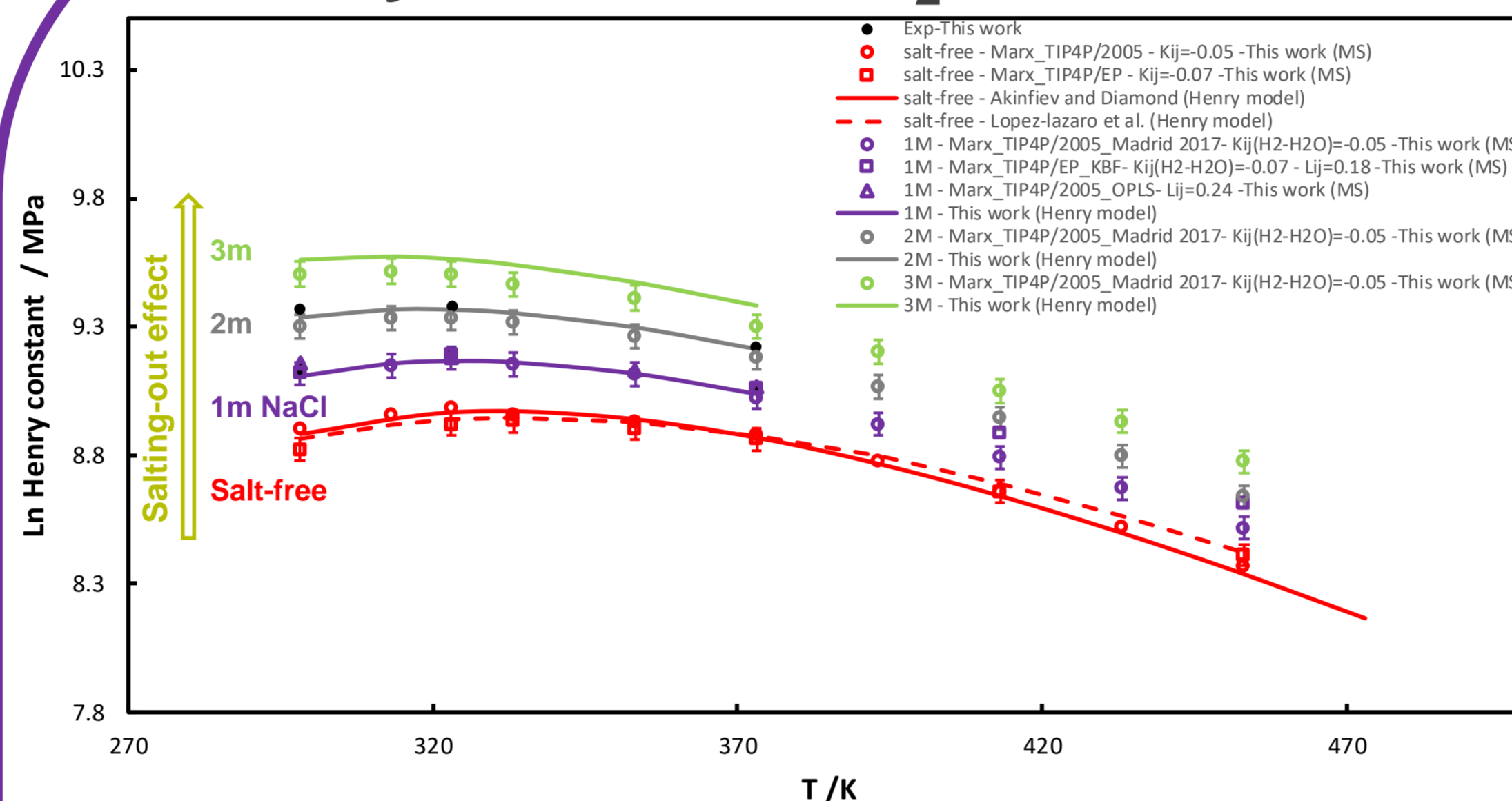
$$H_i = \rho k_B T \exp(\mu_i^{excess} / k_B T)$$

Molar composition

$$x_i(P, T, m_s) = \frac{y_i P \varphi_i}{H_i \gamma_i \exp\left(\frac{P - p_{sat, solvent}}{RT}\right)}$$

Simulation results

Henry constant of H₂ in NaCl brine

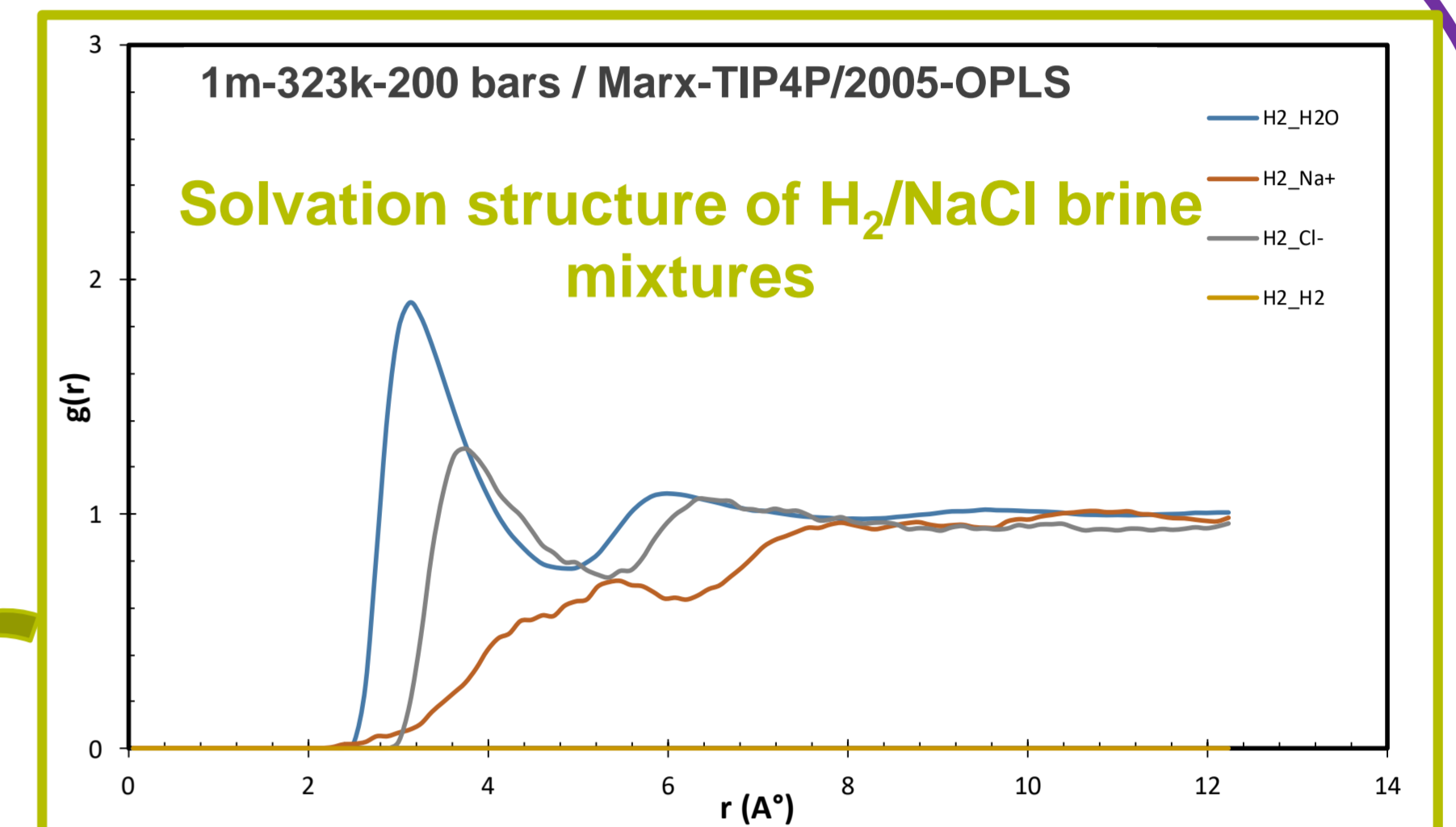


✓ **Excellent** representation of **H₂ solubility in NaCl brine** using three different models (Marx_TIP4P/2005_OPLS – Marx_TIP4P/EP_KBF-Marx_TIP4P/2005_Madrid).

✓ **The radial distribution function (RDF)** is used to evaluate the solvation structure of the H₂/brine mixtures which is shown to be **dominated** by the **H₂-H₂O** and **H₂-Cl⁻** interactions. **A constant BIP** on energy for H₂-H₂O and on volume for H₂-Cl⁻ are used to improve the quantification of the H₂ solubility in brine.

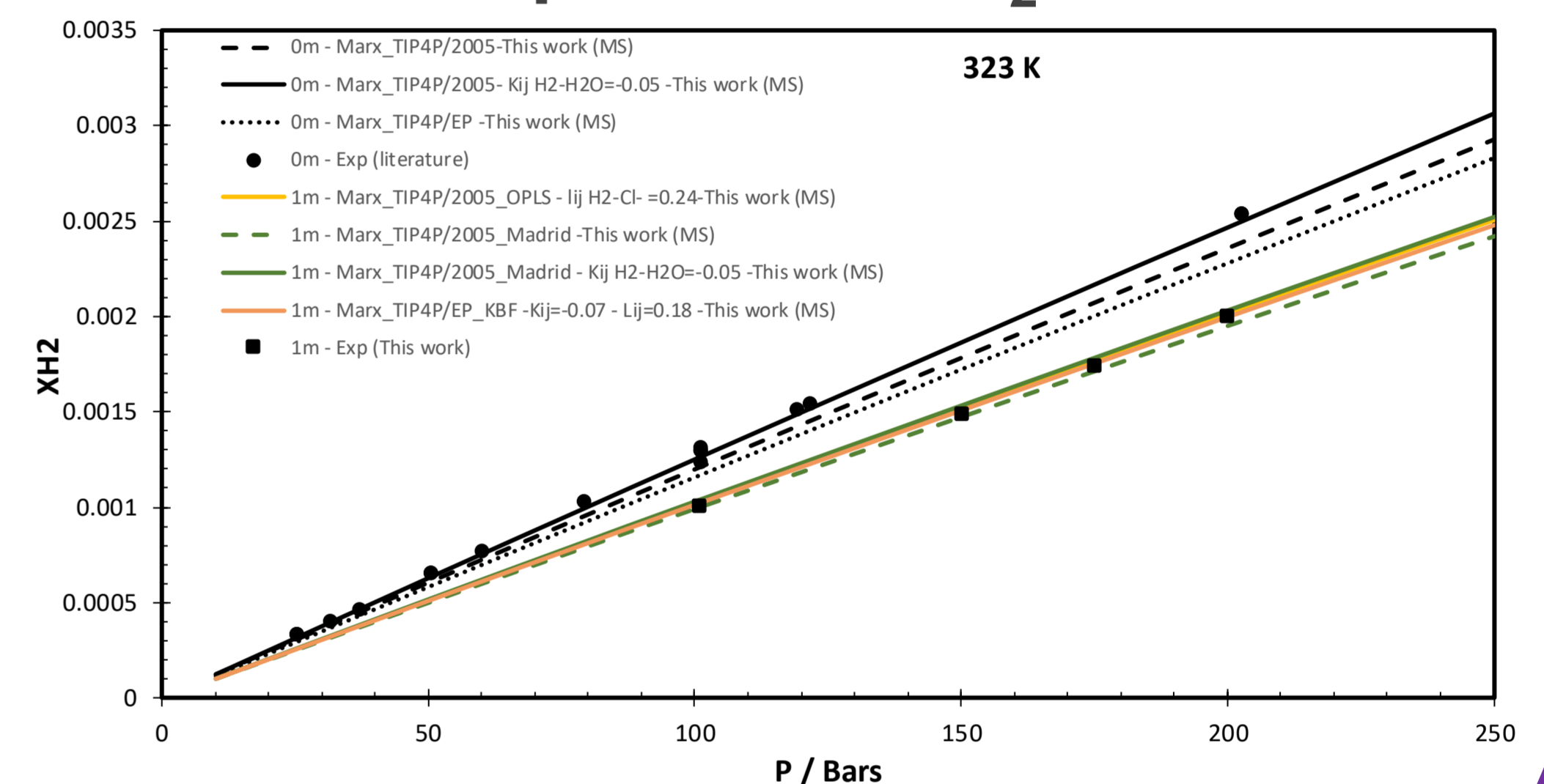
✓ Pseudo-data from molecular simulations can be produced under storage conditions in aquifers with temperatures ranging from **298.15 K to 453.15 K** and **NaCl molality up to 3 mol/kg_w**.

Radial distribution function (RDF) of H₂+H₂O+NaCl system



✓ **According to the RDF results, H₂-H₂O and H₂-Cl⁻ interactions are dominant!**

Molar composition of H₂ in NaCl brine



Thermodynamic Modeling

Selected models

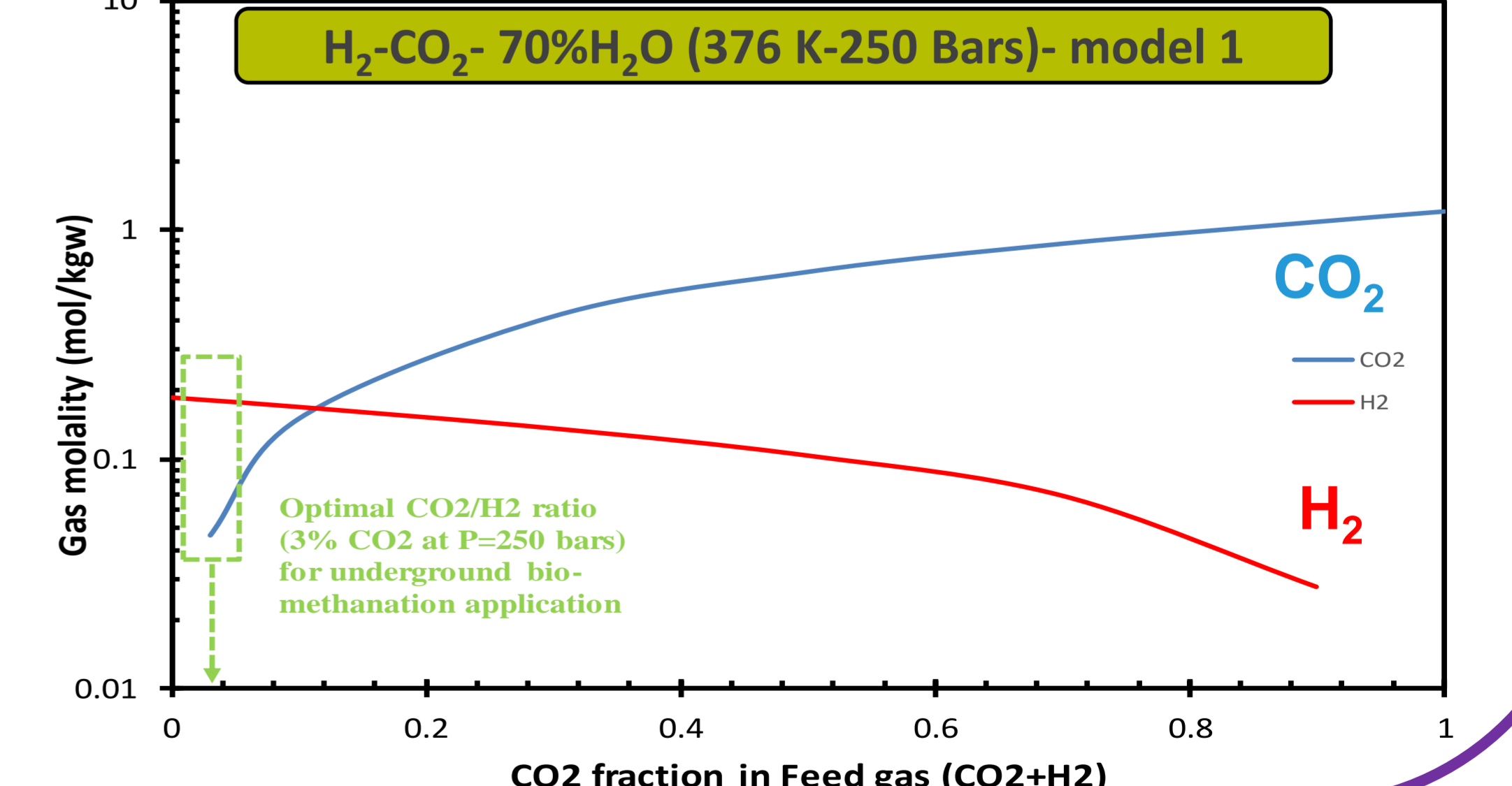
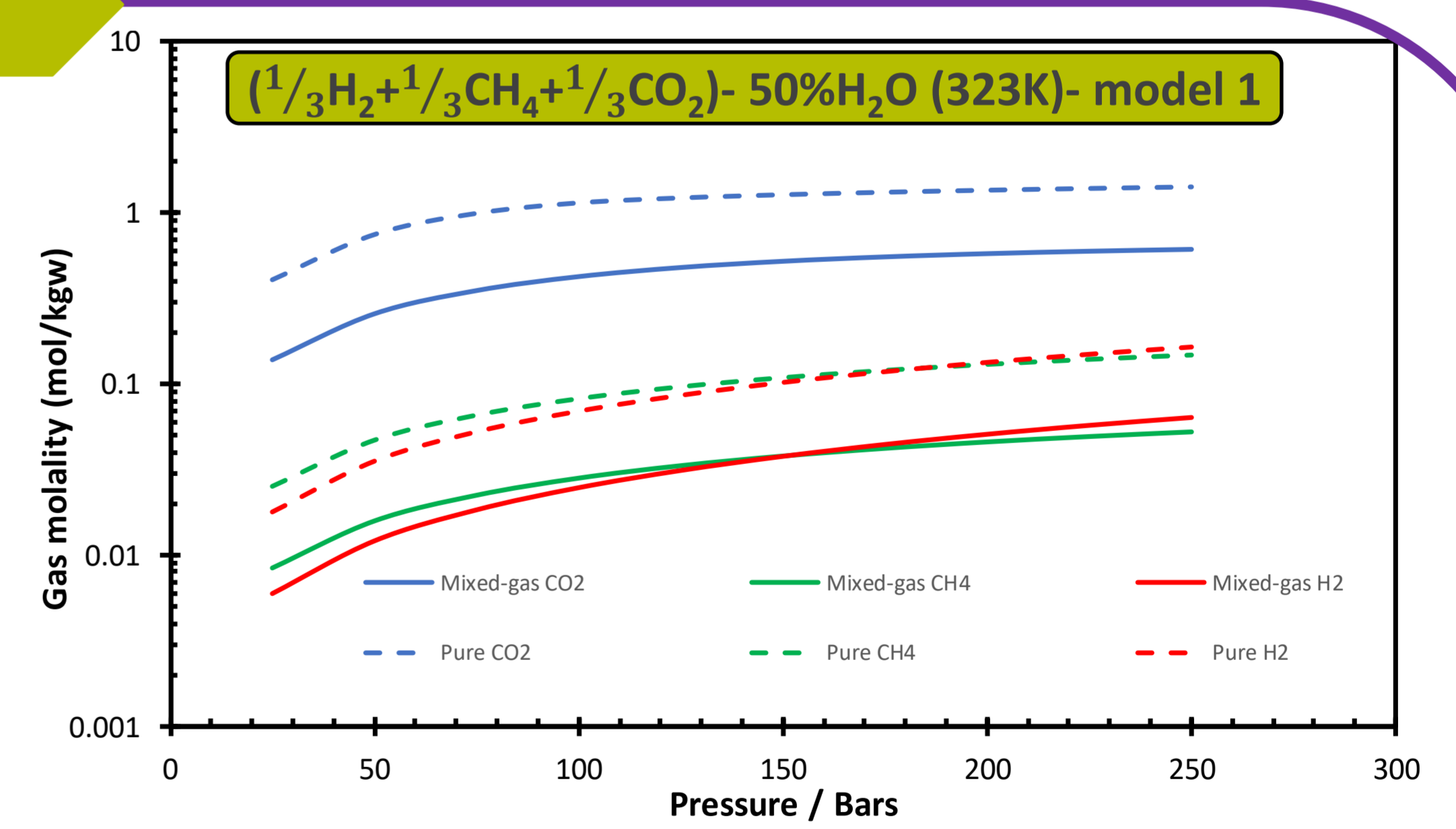
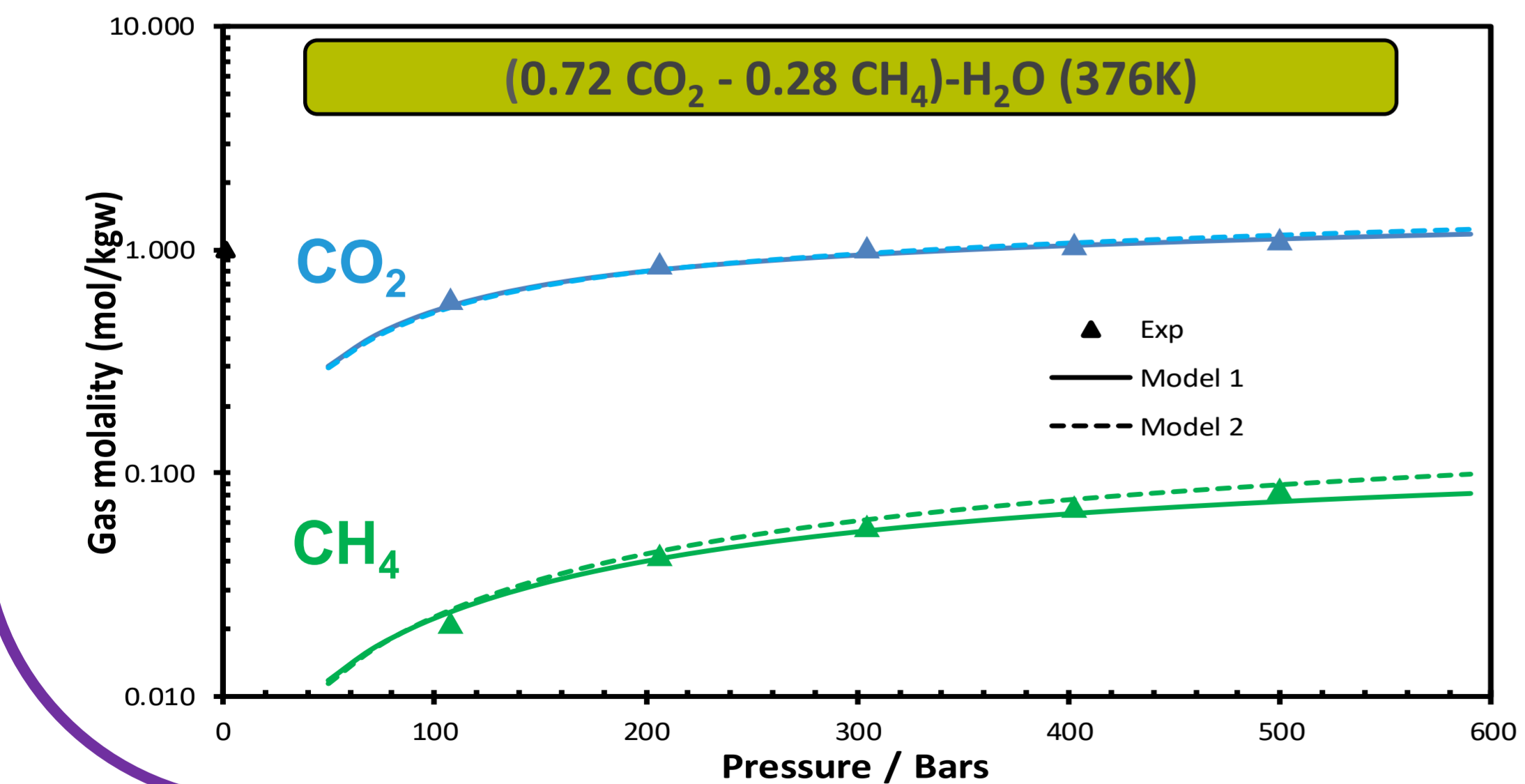
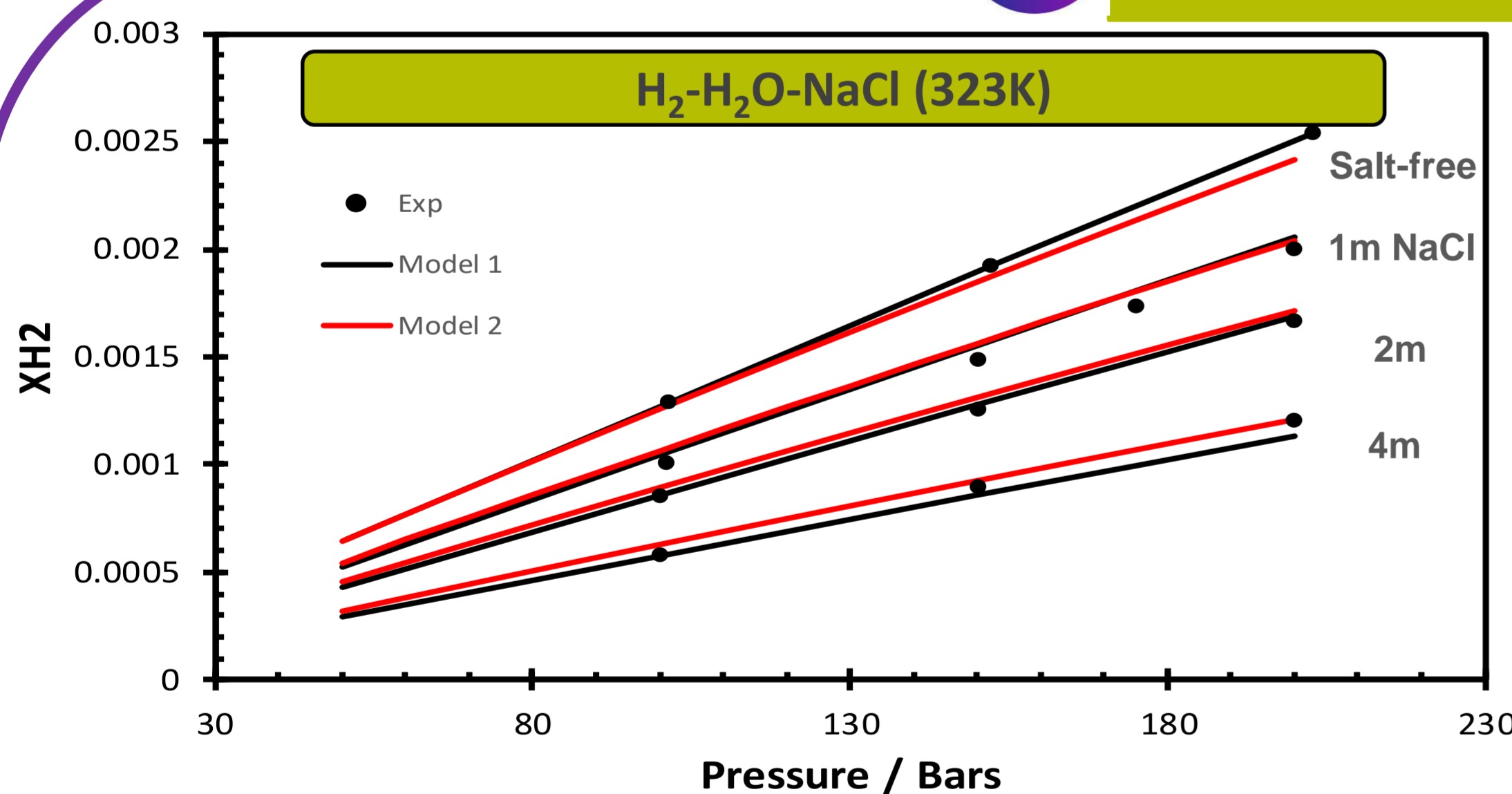
- **Model 1: Henry+γ/EoS model;**
- **Model 2: Søreide and Whitson EoS.**

✓ The parameters of both models are fitted on binary (gas/water) solubility data.

✓ The models **predict** the ternary **CO₂-CH₄-H₂O** system very well when **compared** with **literature experimental data**.

✓ The **co-solubility** of mixed-gas in the quaternary system **H₂-CH₄-CO₂-H₂O** is also **predicted** and **compared** with the single-gas (binary systems) solubilities.

✓ The ternary **H₂-CO₂-H₂O** system was also modeled to estimate the **optimal H₂/CO₂ ratio** for **underground bio-methanation** application.



Conclusions & Perspectives

- **Molecular simulation models** were **validated** and used to provide "pseudo-experimental" data. These data in addition to those from the literature for other gases (CH₄ and CO₂) were used to **optimize** the parameters of **the thermodynamic models (phi-phi and gamma-phi approaches)**.
- Finally, **the thermodynamic modeling** showed that **the optimal H₂/CO₂ ratio** for **underground bio-methanation** application is around **3% CO₂ (97% H₂)** to be injected (to have a stoichiometric ratio of 1:4).

Recording and References

