

Structure and vibrational spectroscopy of hydrogen clusters in hydrogen clathrate hydrate by molecular dynamics simulation and first-principles calculation

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Molecular modeling techniques are applied to elucidate the vibrational spectroscopy, and the molecular and electronic structure of encaged hydrogen molecules in hydrogen hydrate. Molecular-dynamics simulations, using empirical potentials, are performed to generate collections of the clathrate water cages of different hydrogen occupancies. The first-principles calculations, using Density Functional Theory with B3LYP hybrid density functionals for exchange and correlation, are carried out to optimize the structures and to calculate the Raman shift and activity. The Raman spectra of encaged hydrogen molecules are computed by a weighted moving average over a number of different structural configurations for each type of hydrogen occupancies. The results show that experimentally observed Raman peaks around 4120~4125 cm⁻¹ are from the hydrogen molecule singly occupied in the small cages, and those around 4125~4150 cm⁻¹ from those in the large cages with one to four hydrogen molecules. The Raman peaks of H₂ molecules in the doubly occupied small cages are expected to be around or above 4155 cm⁻¹, which has not been observed in experiment. This result could inspire new experiments for synthesizing hydrogen clathrate with higher hydrogen occupancy [1]. Additional molecular structural analysis shows that the hydrogen molecule singly-occupied in the small cages and those in the large cages are loosely encaged, while hydrogen molecules doubly-occupied in the small cage are tightly confined in the cages. Normal mode analysis shows that there is limited vibrational coupling for H₂ molecules in L¹⁻⁴ while a strong vibrational coupling is observed in S². The isovalue maps of total electron density and electrostatic potential suggest significant electron sharing between H₂ molecules and water molecules, and important interaction between hydrogen and water oxygen atoms.

[1] Wang, Lu & Ripmeester (2009) *Journal of American Chemical Society* **131**, 14132–14133.

Effect of brine on the TSR and generation of H₂S revealed by gold-tube simulation experiments

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In MgSO₄-nC₂₄ TSR system, compared to that in blank series, the H₂S yield was slightly increased with addition of montmorillonite (1.48 mg), and much more H₂S was available with addition of minor elemental sulfur (only 0.19 mg) which was consistent with previous studies [1]. Meanwhile, yield of H₂S was largely enhanced with addition of NaCl (3.0 mg). The MgSO₄-nC₂₄ TSR experiment with addition of different weight of NaCl furtherly illustrated that yield of H₂S was continuously increased even with addition of 6 mg NaCl.

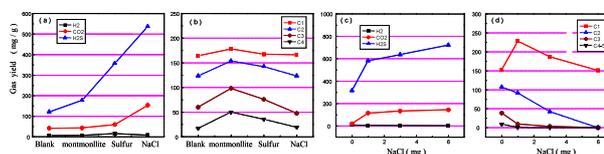


Figure 1: Gas yields in the gold-tube simulation experiment of magnesium sulfate and nC₂₄ under 420 °C and 50 MPa.

A very low solubility of CaSO₄ relative to higher solubility of Na₂SO₄ and MgSO₄ in pure water at room temperature, together with a sharply decreased trend of the solubility of CaSO₄ with increased temperature under 100 °C, may limited the imagination of anhydrite as an effective reactant for participation in TSR. However, most saline formation fluids are brine [2] and composed dominantly of Na, Ca and Cl and slightly enriched in Mg [3]. Moreover, at 100, 150 and 200 °C, the CaSO₄ solubility in NaCl solution (0.005~0.035 mol/kg H₂O) increased with increasing salinity at high NaCl concentrations up to halite saturation, and apparently larger than that in Na₂SO₄ (0.002~0.009 mol/kg H₂O) and K₂SO₄ (0.001~0.009 mol/kg H₂O) solution [4]. This indicates that solubility of anhydrite or gypsum can be greatly enlarged in brine solution in the real subsurface, thus, the possibility and rate of TSR from anhydrite under practical geological conditions can be greatly enhanced.

[1] Goldhaber & Orr (1995) *J. Am. Chem. Soc.* 412–425. [2] Carpenter, 1978. *Geol. Surv. Circular* **79**, 60–77. [3] Posey & Kyle (1988) *Chem. Geol.* **74**, 1–24. [4] Freyer & Voigt (2004) *GCA* **68**, 307–318.