Molecular dynamics simulation of high-pressure phases of CH4-CO2 mixed hydrate

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The molecular dynamics (MD) method was applied to CH4-CO2 mixed hydrates with the structures sII (cubic) and filled ice (orthorhombic), in order to reproduce and predict the compositional dependence of crystallographic and thermodynamic properties.

The following three patterns of sII mixed hydrate crystals were prepared for the simulation:
1) The CH4 is completely partitioned into S-cage, and CO2 into L-cage.
2) The CH4 and CO2 are evenly distributed to S- and L-cages (Disordered structure).
3) The CO2 is completely partitioned into S-cage, and CH4 into L-cage.
The system contains 192 gas molecules (= 128 in S-cage + 64 in L-cage) and 1088 H2O molecules. The interatomic potential model employed is an empirical one, which can reproduce the dielectric constant, diffusion coefficient, and density for H2O, the vibration spectrum, density, and structure for CH4 and CO2. The MD calculation was carried out under constant temperature and pressure conditions (P = 0.25 GPa, T = 100, 250, and 300 K).
The lattice parameter varies systematically with the CO2 concentration [= CO2 / (CH4 + CO2)] in S- and L-cages. The concentration of CO2 in S-cage largely affects the lattice parameter. Under low temperatures (100 and 250 K), there occurs a preferred orientation of CO2 molecules, which lowers the symmetry of the crystal from cubic to tetragonal. The structure with the enrichment of CO2 into L-cage is more stable than the disordered structure, where CH4 and CO2 are evenly distributed to both cages.

The system with filled ice structure employed in this study contains 64 gas molecules and 128 H2O molecules. (Filled ice structure has only a kind of site that can contain gas molecules.) The MD calculation was carried out under constant temperature and pressure conditions (P = 5 GPa, T = 100 and 250 K), with the same potential model as mentioned above.
This filled ice structure is maintained only with the CO2 concentration less than 20 %. In this range, the lattice parameters a, b, and c vary systematically with the CO2 concentration.