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First principles molecular dynamics study on filled ice hydrogen hydrate under pressure

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We present a study on the structural and vibrational properties of filled ice C2 hydrogen hydrate under compression by first principles molecular dynamics (FPMD). It is essential to note that the experimentally reported cubic Fd-3m (space group) C2 phase reflects the symmetry at high (room) temperature when the hydrogen bond network is disordered and the hydrogen molecules are orientationally disordered. In this sense, the ”cubic” symmetry would definitely be lowered at low temperature where the hydrogen bond network is ordered and the hydrogen molecules are aligned. Indeed, we found tetragonal symmetry (P41212 and Pna21 space group) in our FPMD at low temperature. This finding demonstrates that the thermal effects play an essential role in stabilizing the structure to appear as cubic below 40 GPa. We also observed an indication of transition to an unknown high pressure phase above 40 GPa which is consistent with the experimental findings. Moreover, we extend our efforts to determine the phase boundary line between hydrogen bond ordered (disordered) phases and the H2 rotation and non-rotation phases at a rough approximation. The vibrational frequencies are extracted from Fourier analysis of the MD trajectories, which are in good agreement with experimental data. Hydrogen bond is predicted to symmetrize below 60 GPa based on the analysis of O-H stretching frequencies and radial distribution function g(OH). In comparison with the pure ice VII, the hydrogen bond symmetrization pressure in C2 hydrogen hydrate is much lower as reduced by a factor two.

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