Isotope fractionations under super-cold conditions: A theoretical case study of Titan

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As the largest moon of Saturn, Titan has a thick atmosphere (146.7 kPa) mainly consists of N_2 and CH_4 with a extremely low surface temperature of 93.7 K, which is just above the triple-point of CH_4 (1 atm, 90.67 K).

Telescopic, orbital satellitic and *in-situ* observations have confirmed Titan has a complex atmosphere just like the Earth [1-5]. CH_4 is destroyed and converted to complex hydrocarbons irreversibly through photolysis in stratosphere and then form haze or transported downward and finally deposited on the ground. CH_4 on Titan behaves very similar with H_2O on Earth [4]. The CH_4 cycle on Titan is the key to understand not only the source and sink, but also a potential window for studying the inner part of Titan and even origin of extraterrestrial life.

Similar with hydrologic cycle research on Earth, the C and H isotopes can be the best solutions for this problem on Titan. However, all the processes driving isotope fractionations in Titan's atmosphere are happened under super-cold conditions. Low temperatures means more quantum effects and more complete spectroscopic model for molecules must be considered, such as quantum tunnelling effect for kinetic isotope effect (KIE), vibrational anharmonicity and so on.

By extending our previous developed theory and calculation methods [6] to liquids, solids and kinetic processes, we performed *ab-initio* calculations to determine the H and C isotope fractionations for both equilibrium and non-equilibrium processes under Titan's conditions. Such as the phase equilibria of ice, liquid and gas phases of CH_4, and the dissociation of CH_4 and recombination reactions of different radicals in Titan's stratosphere.

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