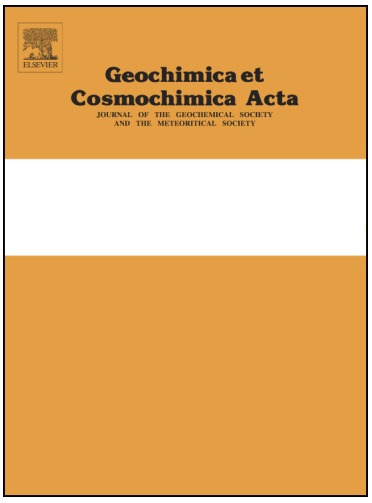


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# The theory of equilibrium isotope fractionations for gaseous molecules under super-cold conditions

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**Abstract**

It is necessary to build a proper theoretical method that can precisely describe isotope fractionation processes under super-cold (< 200 K) conditions, because there have been many isotopic data obtained in our solar system that are related to such processes. However, current methods of isotope fractionation calculation, i.e., the Bigeleisen-Mayer equation and its higher-order energy corrections, may not be applicable to super-cold conditions. Here, we have checked important assumptions and higher-order corrections that can affect isotope fractionations of gas-phase molecules under super-cold conditions and developed a new theoretical method for calculating equilibrium isotope fractionation factors. Compared with previous works, we have added three new corrections into our calculation, i.e., nuclear-spin weights for quantum mechanical rotation, correction for Born-Oppenheimer approximation (BOA), and inversion splitting effect for non-planar molecules such as $NH_3$. We further examined gaseous molecules of geochemistry and