

Computational Modeling of Equilibrium Nitrogen Isotope Fractionation for Hexamethylenetetramine ($C_6H_{12}N_4$) and Ammonium

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Chondrites appear to originate from asteroids that are remnants of solar system formation and planetary accretion processes in a low temperature environment. Chondrites contain both refractory and volatile components. The vast majority of volatile elements, carbon and nitrogen in carbonaceous chondrites, occur in the form of organic molecules. Chondrites are sedimentary rocks by nature and leads to controversy with respect to the origin of their organic molecules. Isotopic signatures provide the best evidence that one can use to try to constrain how organic molecules formed in chondrites. And, they have been widely used in cosmochemical studies. For example, nitrogen isotope ratios ($^{15}N/^{14}N$) have been utilized to identify normal and anomalous isotopic compositions in solar system materials. Ice experiments, with ice composed of water, methanol, and ammonia, have been also conducted to simulate the evolution of organic molecules in the cold interstellar medium. The main by-product (organic residues) of the ice experiments is hexamethylenetetramine ($C_6H_{12}N_4$) or HMT. Although HMT can be formed at the high temperature (greater than 200 K) and that HMT can act as a precursors of complex organic compounds, there are still large gaps in understanding how it acts in a molecular cloud environments versus the environment where chondritic organic molecules were formed. Theoretical studies have predicted that the ammonium ice becomes highly ^{15}N enriched in the coldest environments with temperatures less than 10 K. Thus, one could hypothesize that there would be ^{15}N -rich organics associated with HMT. However, the inner solar system had temperatures warmer than about 300 K, an environment that would lead to aqueous alteration on the chondritic parent bodies. Therefore, those ^{15}N -rich molecules would be modified by aqueous alterations as opposed to alteration in an icy environment. Importantly, HMT itself has not observed either by astronomical observation though perhaps due to difficulties of such measurements in chondritic materials or due to decomposition on the chondrite parent bodies. Also, the properties of HMT such as isotope equilibrium between HMT and ammonium solution are not well understood. Such knowledge is vital in order to assess the validity of HMT occurrence in chondritic parent bodies and the possibility of detecting remnant signatures of reaction products. One need to put constrains on the properties of HMT including the stiffness of its chemical bonding. In order to do this, we calculate isotope fractionations factors between HMT and ammonium to understand “normal” isotope compositions of HMT. We perform theoretical calculations of equilibrium isotopic fractionation in HMT by using harmonic approximation of partition functions, which is an established method in isotope geochemistry. In this project, we apply computational quantum chemistry methods to calculate N isotopic equilibrium fractionation factors for molecules utilizing the rigid rotor, harmonic, and anharmonic oscillator approximations. The calculations are performed by using the Gaussian09 program package on a personal computer. We use the Becke-3 parameter-Lee-Yang-Parr (B3LYP) hybrid density function theory (DFT) method and the B97-1 function as recommended by past studies. We use the most abundant isotopes 1H , ^{12}C , and ^{14}N to construct the isotopically “light” molecule to optimize the geometry and harmonic frequencies. Subsequently, we substitute a single ^{14}N for a ^{15}N in order to calculate the harmonic frequencies of the isotopically “heavy” molecule. Different basis sets gave significantly different results. We discuss the accuracy of individual calculations by comparing experimental results. We also discuss the possibility of nitrogen isotope fractionation due to pH and basicity of the dissolved compounds.

Keywords: HMT, Nitrogen isotopes, Chondrites, DFT