Frey et als. Photolytic control of the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling is a bold attempt to try an unravel some of the strange isotope effects observed in snow pack nitrate. These isotope effects are a combination of nitrate production in the atmosphere and post depositional processing by photo and phase chemistry. Frey et al. attempts to evaluate how post depositional processes would impact isotopes of nitrate. This is a very important concept because of on going work hoping to use ice core nitrate isotopes as a tracer of past oxidation chemistry in the atmosphere. But to do so requires deconvoluting the depositional effects, which is the aim of this paper. However, I think that there are some fundemtal flaws with some of their modeling assumptions that would need to be addressed before this manuscript can move forward. I have focused on these to the exclusion of the *in situ* data because I feel these issues require the most attention and might alter the authors interpretation of the field data. My comments are in italics.

EDIT: No experimental values for gas - solid - liquid equilibrium phase fractionation of nitric acid are currently available, but in analogy to the stable isotopes in water (H2O) one would expect net enrichment of both nitrogen and oxygen stable isotopes in the NO–3 fraction remaining in the snow phase.

Why would this be "expected" as detailed below this is not like the water case. For water it is the difference between the liquid phase bonding potential (intra-molecular...ie hydrogen bonding) relative to the free gas, this is not the case for HNO₃ which is likely controlled by degree of protonation as noted by the authors below

Since evaporation of HNO3 occurs in the molecular form (Sato et al., 2008), one might argue that the required recombination of NO-3 with a proton (Reaction R6) induces depletion

Correct

of the heavy oxygen isotopes in NO3- . This will be the case if O2N18O-H is energetically much favored over O2N16O-H. Incorrect, it is the equilibrium $O_2N^{18}O-H + N^{16}OO_2^- \leftarrow \rightarrow O_2N^{16}O-H + N^{18}OO_2^$ that must be considered, the authors are ignoring the anion isotope contribution.

As a first-order estimate we calculate shifts in the vibrational frequencies _ for the O-H (3550cm-1) and O-NO2 (647 cm-1) stretching modes in HNO3,g as a result of substituting 16O with 18O (Table 3). *There are no* ^{18}O *values in table 3*

Approximation of the heavier isotopologue using the known relationship between vibration frequencies and reduced masses of a harmonic oscillator (e.g. Criss, 20 1999) yields shifts of 1 cm–1 and 26 cm–1, for the O-H and O-NO2 stretching modes, respectively. This indicates that isotopic replacement increases mostly the N-O bond strength, whereas the impact on the O-H bond is negligible.

Incorrect. There are multiple frequency shifts for the single substituted ¹⁸O depending of which O atom the H is bonded to, the same for ¹⁵N, applying the SHO is not applicable to the whole molecule. see reference below.

Dissociation/recombination of HNO3 will therefore enrich the heavy oxygen isotopes in the ionic form.

Nope. The authors should see "Analysis of Isotope-effect calculations illustrated with exchange equilibria among oxynitrogen compounds." **Monse, Spindel. and Stern** in Isotope Effects in Chemical Processes. ACS Advances in Chemistry series #89 1969 This work shows the exact equilibrium constant of 1.0052(Table V) in favor of the ¹⁸O protonated form of HNO₃. Therefore the gas phase would be enriched in the authors model. 15N equilibrium can be calculated from data in this work.

quantum yield estimated for -30 C after Chu and Anastasio (2003) and the respective spectral UV absorptivity (Fig. 5a) yields 14NO-3 (15NO-3) photolysis rates j (j') of 7.65 (7.29)×10-8 s-1

The authors should note that the shape and intensity of the isotopologues absorption cross section is <u>assumed</u> to be identical and only blue/red shifted in this model. Actual cross sections of isotopologues may not be identical because of shape of the upper state dissociation curve, Frank-Condon overlap, and different probability widths of the ground state function (reflection principle).

Remainder of this section suffers from lack of ¹⁸O data. Authors should re write utilizing Monse. K^+ salt will induce shifts large compares to H^+

PHIFE can be applied to aqueous NO3 due to its continuous UV absorption spectrum (Chu and Anastasio, 2003) and lack of predissociation (Miller and Yung, 2000, and references therein).

It is not clear to me why the authors can justify this statement. Miller and Yung model suggested that the lack of pre-dissociation is ideal (direct dissociation), but that paper only discusses water isotopologues and no mention is made of the nitrate ion. The authors seem to be inferring that there is no pre-dissociation during nitrate photolysis. Im not an expert but I believe nitrate photolysis is initiated by a $\pi \rightarrow \pi^*$ or $n \rightarrow \pi$ transition to an excited state, this excited state can then decompose, react, or isomerize (ONOO). Is not that the definition of pre dissociation? Also the quantum yields are not 1. Based on Mack's review, the main photolysis product, NO_2 - has less than a 20% quantum yield and at the authors proposed wavelengths this yield drops to a few percent. and the minor products (OH, O3P) are trivial suggesting quenching of NO_3^-* is the important (Daniels et al showed total reaction yields is .15 and quenching is .85). Therefore the direct dissociation in PHIFE can not be applied to nitrate. The authors model would need to be modified to incorporate the isotope effects in the unimolecular decomposition and bimolecular reactions of the excited species and isotope effects of quenching (ie collsional frequency). This is likely why the data and the model are so far removed.

This may be beyond the scope of existing models and data, but that would be for the authors to decide.