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A Computational Approach to Studying the Vapor Pressure Isotope Effect for Sulfur Dioxide on Io

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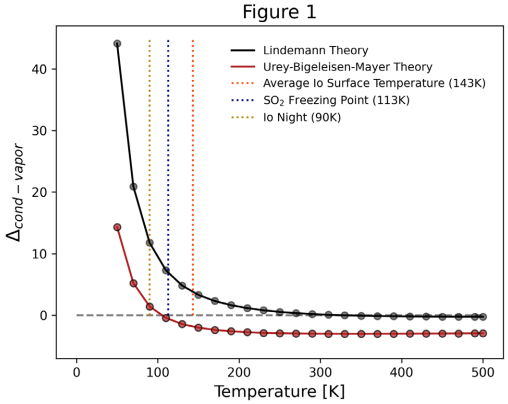
The stable isotopic compositions of planetary atmospheres and surface materials constrain the physico-chemical processes that they have undergone following their formation. Isotopic data is generated by telescopic, orbiter, lander and meteorite/returned sample analysis. However, interpreting these data often requires laboratory experiments that may be challenging to perform at relevant planetary conditions. Theory presents an alternate approach to understanding isotopic fractionations arising from chemical processes. Simple systems have been investigated using first-principles chemical physics models, at levels of theory ranging from simple approximations (*e.g.* [1-2]), to more recent Density Functional Theory and path-integral methods (*e.g.* [3]), which harness the complete scope of modern computational power.

In 2024, de Kleer and co-authors found that SO_2 in the Jovian moon Io's atmosphere is preferentially enriched in ^{34}S [4]. This observation can be explained by atmospheric escape from a gravitationally stratified atmosphere supplied by volcanic degassing and sustained by mixing between surface and interior planetary reservoirs [4]. However, Io's SO_2 atmosphere also undergoes a sublimation-condensation cycle that could either amplify or diminish the overall isotopic fractionation of atmospheric sulfur based on the vapor pressure isotope effect (VPIE).

This work computationally investigates the VPIE for SO_2 at Io-relevant temperatures. Vibrational modes for SO_2 isotopologues are calculated with Quantum ESPRESSO [5] and are translated into isotopic fractionations through partition function ratios. Varying complexities of theory predict $^{34}S/^{32}S$ VPIEs ranging from 0‰ to 10‰, largely dependent on the treatment of low-frequency lattice modes. Rayleigh distillation in Io's SO_2 meteorological cycle may further amplify these effects. These predictions complement the findings of de Kleer et al. (2024) and leave intact their conclusion that volcanic degassing, combined with atmospheric escape, occurred throughout Io's ~4-billion-year history. Future laboratory experiments will complement the computational results and allow for a closer interpretation of the range in model predicted VPIEs.

Figure 1



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