

**PHOTOCHEMISTRY OF VOLATILES IN THE SOLAR NEBULA.**

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**Introduction:** Photochemistry is a significant process and the driving force of many of the chemical reactions in the early solar nebula. Photochemical processes play a significant role in the early Earth and other planetary atmospheres and development and evolution of atmospheres. The volatile inventory of the solar system was acquired and evolved dynamically over millions of years or more and was subjected to photochemical processing. The volatile inventory and their evolution pattern are differing for inner solar system rocky planets and outer regions.

Photochemistry of oxygen bearing reservoirs, e.g., CO and H<sub>2</sub>O likely played an important role in determining the oxygen isotope map of inner solar system solids [1-3]. Oxygen enriched in heavier isotopes (<sup>17</sup>O and <sup>18</sup>O) could potentially be generated by photochemical processes at the outer nebula and may transferred to the inner nebula as water-ice and subsequently get incorporated into the rocks through fluid-rock interaction. Photochemistry also played a substantial role in the evolution of volatiles in the early Earth and photochemical evolution is an active process in the outer solar system bodies- within their thin atmospheres as well as in the ices of water, carbon dioxide, methane, and ammonia. The outer planets Uranus, Neptune, dwarf planet Pluto and some satellites (Titan, Triton, and Enceladus) have significant atmospheres and the compositions of these atmospheres are different from each other. Recent space missions have returned copious information about the atmospheres of these objects [4-6]. Records of photochemically evolving atmospheres are found in their isotopic signatures as complicated photochemical processes are isotope selective.

**Experimental:** In the past, we have investigated the isotope effects in the volatile elements while studying the vacuum ultra-violet (VUV) photodissociation processes in CO, N<sub>2</sub> and H<sub>2</sub>S (gases of nebular significance) and discovered that the isotope effect during photodissociation is highly quantum mechanically selective [1, 7-11]. Recently we have studied the VUV photodissociation of SO<sub>2</sub> for wavelength dependent sulfur isotopic fractionation, and UV photodissociation of NH<sub>3</sub> to determine the isotope effect in nitrogen and hydrogen. All VUV experiments are performed at the Advanced Light Source (ALS) synchrotron and the UV experiments were done at the UCSD laboratory using different lamps. VUV photodissociation of SO<sub>2</sub> shows a wavelength dependent isotope effect and is mass independent (e.g.,  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S} \neq 0$ ). UV photodissociation of NH<sub>3</sub> shows no wavelength dependency, however <sup>15</sup>N is fractionated by only a few tens of permil, whereas  $\delta\text{D}$  values are a few hundred permil enriched in the dissociation product. More experiments are underway with CH<sub>4</sub>.

**Conference Plan:** New results from the VUV experiments of SO<sub>2</sub> and UV experiments of NH<sub>3</sub> and CH<sub>4</sub> will be presented. A comprehensive picture of the evolution of the volatiles in the solar system, inner and outer nebula, based on the photochemical isotope data will be constructed and presented in the conference.

**References:** [1] S. Chakraborty *et al.* (2008) *Science* 321, 1328-1331. [2] J. R. Lyons, E. D. Young (2005) *Nature* 435, 317-320. [3] N. Sakamoto *et al.* (2007) *Science* 317, 231-233. [4] J. H. Waite *et al.* (2017) *Science* 356, 155-159. [5] K. Altwegg *et al.* (2015) *Science* 347. [6] B. D. Teolis *et al.* (2010) *Science* 330, 1813-1815. [7] S. Chakraborty *et al.* (2016) *The Journal of Chemical Physics* 145, 114302. [8] S. Chakraborty *et al.* (2014) *Proceedings of the National Academy of Sciences* 111, 14704-14709. [9] S. Chakraborty *et al.* (2013) *Proceedings of the National Academy of Sciences* 110, 17650-17655. [10] S. Chakraborty *et al.* (2012) *The Journal of Chemical Physics* 137, 024309-024312. [11] S. Chakraborty *et al.* (2009) *Science* 324, 4.