

HUGE ISOTOPIC EFFECT IN VUV PHOTODISSOCIATION OF N₂: IMPLICATIONS FOR METEORITE DATA. S. Chakraborty¹, Teresa L. Jackson¹, B. H. Muskatel², Musahid Ahmed³, R.D. Levine^{2,4} and M. H. Thiemens^{1*}, ¹University of California, San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Drive, La Jolla, CA 92093-0356 (subrata@ucsd.edu), ²The Fritz Haber Research Center, Hebrew University, Jerusalem 91904, Israel, ³Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, ⁴Department of Chemistry and Biochemistry, Crump Institute for Molecular Imaging, and Department of Molecular and Medical Pharmacology, University of California, Los Angeles, CA 90095.

Introduction: Nitrogen isotopic analyses (¹⁵N/¹⁴N) have been carried out in a variety of solar system objects, e.g., meteorites, giant planets to the rocky planets, interplanetary dust particles (IDPs) and cometary dust particles. Recently, the nitrogen isotopic composition of solar wind was measured from Genesis return samples [1, 2] and found to be ~ 400 ‰ lighter than the terrestrial composition.

The most abundant nitrogen bearing component in carbonaceous chondrites is organic matter [3]. Until now, the most extreme enrichments in ¹⁵N have been found in ‘hotspots’ (regions that are extremely isotopically enriched relative to the surrounding matter) in anhydrous cluster IDPs. The largest ¹⁵N enhancements detected in meteoritic ‘hotspots’ have ¹⁵N/¹⁴N enhancements of more than a factor of ~5 relative to the Earth (i.e. $\delta^{15}\text{N} > 4000\text{‰}$) [4]. Values up to 1500 ‰ have been observed in whole rock carbonaceous chondrites [5] and ~ 1000 ‰ have also been found in hotspots in IDPs and *Stardust* samples. In contrast, IOM (interstellar organic matter) from meteorites, whose parent bodies are in the asteroid belt, display bulk isotope anomalies that are relatively small compared to those in IDP hotspots [6].

The ¹⁵N excesses relative to the Earth's atmospheric value indicates that N-bearing volatiles in the solar nebula underwent important N isotopic fractionation at some stage of solar system formation. The N-isotopic composition in the Jovian planets and Titan have been modeled [7] and it was suggested that N₂ photolysis may explain the ¹⁵N enrichment observed in HCN for Titan's atmosphere, whereas, for Jupiter's atmosphere, NH₃ photolysis was prescribed. However, the processes active within the solar nebula which potentially modulate the isotopic composition of nitrogen are not clear and remain an open question. It is possible that self-shielding dominates N₂ photolysis and can play a leading role. The extreme range of isotopic variation observed in early solar system materials is interesting and requires mechanistic understanding. In this abstract, we present the wavelength dependent experimentally determined N-isotopic fractionations during VUV photolysis of N₂ using the ALS synchrotron. We also present the theoretical results of N-isotopic fractionation calculated at the experimental condition.

Experimental: VUV photolysis of N₂ was carried out in a differentially pumped reaction chamber described earlier [8]. The trapping of the product N-atoms is non-

trivial. A steady flow of high purity premix gas (N₂: H₂ = 50 : 50) was established in the reaction chamber at a pressure of 200 mtorr (column density ~ 4 x 10¹⁷ molecule/cm²). Photolysis of this gas mixture was carried out at ten different synchrotron bands (80 to 98 nm, FWHM = 2.2 nm) in twelve different experiments while keeping the column density constant. Except two experiments performed at room temperature, all other experiments are performed at dry-ice temperature (-78 °C). Photolytically produced atomic N was trapped as NH₃ and collected in sample tubes and analyzed at UCSD. Due to the lower gas phase rate constant of NH₃ formation reaction, the NH₃ yield was low and based on cross-section varied between 0.1 to 1.3 micromoles. N₂ was produced by pyrolysis (in presence of CuO) of NH₃ as described by [9]. Finally, N-isotopic composition of N₂ was measured using a Finnigan MAT 253 IRMS.

VUV photochemistry of N₂: The absorption bands of N₂ can be divided into two regimes; above 100 and below 100 nm. Above 100 nm, there are only a few absorption bands and below 100 nm there are several. Predissociation of N₂ occurs for photons < 100 nm [10] and is a good candidate for studying isotopologue selection. Since N₂ and CO are isoelectronic, there are many similarities in the spectra of these two molecules [11]. A large effect in oxygen isotopes has been measured for the indirect (accidental) predissociative states of CO (e.g., at 105.17 and 107.62 nm) [8, 12]. Likewise, several states are indirectly predissociative for N₂. As an example, the b¹Π state (accessible by 95.2 nm photons) indirectly predissociates via the C³Π state to the continuum of C³Π. A recent *ab-initio* theoretical study on isotope effects during photoexcitation of the N₂ molecule, displays a large isotope effect (thousands of permil) and is highly energy sensitive due to the coupling geometry of the potential energy surfaces [13].

Results and Discussion: The N-isotopic compositions measured for all ten synchrotron bands are shown in Figure 1. As the column densities are kept constant for all the experiments, the only variable is the wavelength (for a particular temperature) and wavelength dependent fractionation is measured. An unprecedented ¹⁵N enrichment is observed at a wavelength of 90 nm (111111 cm⁻¹). This particular wavelength zone is

quite unique because of strong electronic states crossings leading to perturbations as shown in Figure 2.

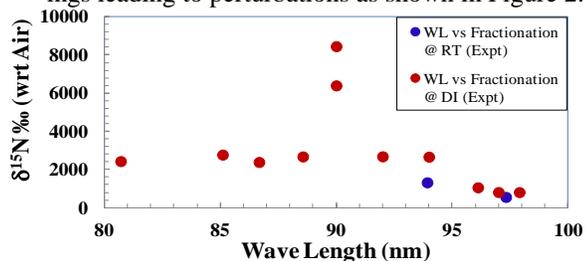


Figure 1. N-isotopic fractionations in VUV photodissociation of N_2 at dry-ice temperature (red) and room temperature (blue).

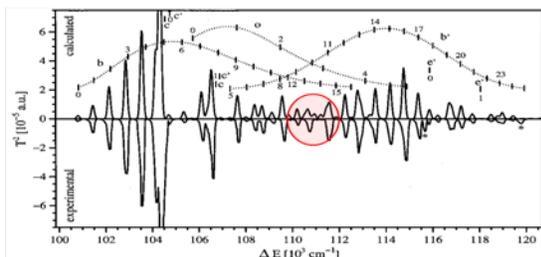


Figure 2. Experimental and calculated dipole strength distribution for N_2 (adopted from [14]). The largest ^{15}N fractionation (6400 ‰) measured in the wavelength region where strong strong perturbation occurs due to electronic states cross-overs.

An isotope self-shielding calculation have been performed using an *ab-initio* approach: by taking the diabatic potentials from [14] with states b, c, o, b', c', e' (of Π and Σ symmetries) and adding triplet Π states F, G, C, C' with their spin-orbit coupling to the singlets, a total 342 bound vibronic states in the Hamiltonian is obtained. The Hamiltonian is diagonalized to generate an adiabatic spectrum of the molecule, which shows good agreement with the experimental results [15]. This process was performed separately for three isotopologues of N_2 using a fixed rotational line widths of 4 cm^{-1} . Total absorption of each isotopologue was calculated incorporating the calculated cross-sections and experimental parameters using the Beer-Lambert law. The calculated isotope ratios are normalized to air isotope ratio to calculate δ -values as shown in Figure 3. When calculated the same using the available experimental linewidths [16], the calculated ^{15}N enrichments are about 4 to 5 times higher than the measured enrichments.

Though with fixed rotational line widths of 4 cm^{-1} , the calculated ^{15}N enrichments are comparable to the measured values, the wavelength dependent enrichment trend was not the same as that measured (Figure 1 and 3). Moreover, the measured peak enrichment at 90 nm was not observed in this calculation. The discrepancy in dipole strengths between experimental and

calculated (red circle in Figure 2) reflect the perturbation in the electronic states and the same may be the reason behind not observing the measured ^{15}N enrichment peak in the calculation.

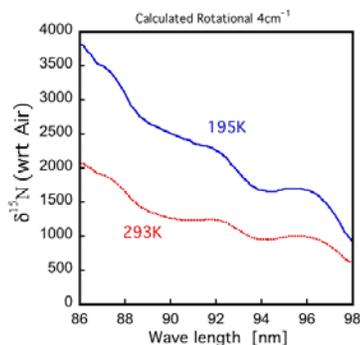


Figure 3. Calculated wavelength dependent N-isotope fractionation at two different temperatures (293 K (RT) and 195 K) keeping all other experimental parameters constant. The rotational line widths are fixed at 4 cm^{-1} for all cases in the calculation.

An important point is that VUV photodissociation is a potential mechanism in the solar nebula to generate unprecedented isotopic enrichment observed in meteorites. In the present experiment, the N-isotopic enrichments are stored in NH_3 , which represents a direct analog to the solar system. The enriched nitrogen could be trapped in NH_3 and serve as a precursor of the organic molecules as observed in IOMs.

Acknowledgement: We gratefully acknowledge support from Chemical Dynamics Beamline of ALS. The work is funded through NASA's Origins/Cosmochemistry program. MA and the ALS are supported by the Director, Office of Energy Res., U. S. Dept. of Energy (Contract No. DE-AC02-05CH11231).

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