

LOW TEMPERATURE (80K) VACUUM ULTRAVIOLET PHOTODISSOCIATION OF NITROGEN: ISOTOPIC FRACTIONATIONS AND SIGNIFICANCE FOR SOLAR NEBULAR CHEMISTRY. S. Chakraborty^{1*}, Teresa L. Jackson¹, Bruce Rude², Musahid Ahmed² and M. H. Thiemens¹, ¹University of California, San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Drive, La Jolla, CA 92093-0356 (subrata@ucsd.edu), ²Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720.

Introduction: Nitrogen isotopic analyses of meteorites, terrestrial planets, atmospheres of giant planets and their moons, solar wind, comets, and interplanetary dust particles advance understanding of volatile chemistry and prebiotic processes in the early solar system [1].

The isotopic inventory of nitrogen in astronomical environments is reasonably well known. The solar system was formed with an initial $^{15}\text{N}/^{14}\text{N}$ ratio acquired from parental molecular clouds from interstellar medium (ISM). The near-identical compositions measured in solar wind and the Jovian atmosphere ($\delta^{15}\text{N} \sim -400\text{‰}$) may indicate the formation of the gas giant with the initial solar system materials of the same N-isotopic composition. Bulk meteorite analysis exhibits a variation in the range of few hundred permil in $\delta^{15}\text{N}$ (wrt to air- N_2) [2-4] with occasional exceptionally high values (as well as range of variation) in some carbonaceous chondrites, stony-iron and iron meteorites. Conversely, extremely high ^{15}N enrichments are observed in meteoritic ‘hotspots’ (of $\sim 5000\text{‰}$ in some cases), interplanetary dust particles (IDPs), cometary samples (including that from Stardust mission) and, in insoluble organic matter (IOM) from meteorites [5-7].

Photochemically processed nitrogen within the solar nebula might be one of the sources of enriched ^{15}N (compared to the initial solar value) component. We recently reported a massive nitrogen isotopic fractionation in the vacuum ultraviolet (VUV) photodissociation of N_2 [8] performed at temperatures between ambient and dry ice ($\sim 200\text{K}$). Here we present new data on the N-isotopic composition in ammonia formed by VUV photodissociation of N_2 at 80K temperature. The new data will be discussed in light of the basic chemical physics and its significance to the solar system will be emphasized.

Experimental: VUV photolysis of N_2 was carried out in a differentially pumped reaction chamber, newly designed and built at the Advanced Light Source (ALS) to perform the photolysis experiments at temperatures close to 80K (by liquid nitrogen cooling system). A steady flow of high purity premixed gas ($\text{N}_2 : \text{H}_2 = 50 : 50$) was established in the reaction chamber at N_2 -partial pressure of 100 mtorr (column density: 5×10^{17} molecule/ cm^2). Photolysis of this gas mixture was carried out at nine different synchrotron bands between 85 to 95 nm. Photolytically produced atomic N was trapped as NH_3 and collected in sample tubes. Due to the lower gas phase rate constant of

NH_3 formation reaction, the NH_3 yield was low (~ 0.1 to 1.3 micromoles). N_2 was produced by pyrolysis (with CuO) of NH_3 and N-isotopic composition was measured using a Finnigan MAT 253 IRMS. The wavelength dependent N-isotopic compositions (Figure 1, top panel) measured at 80K are significantly different than that measured at the same wavelengths, but at higher temperatures (200 K and above, Figure 1, bottom panel).

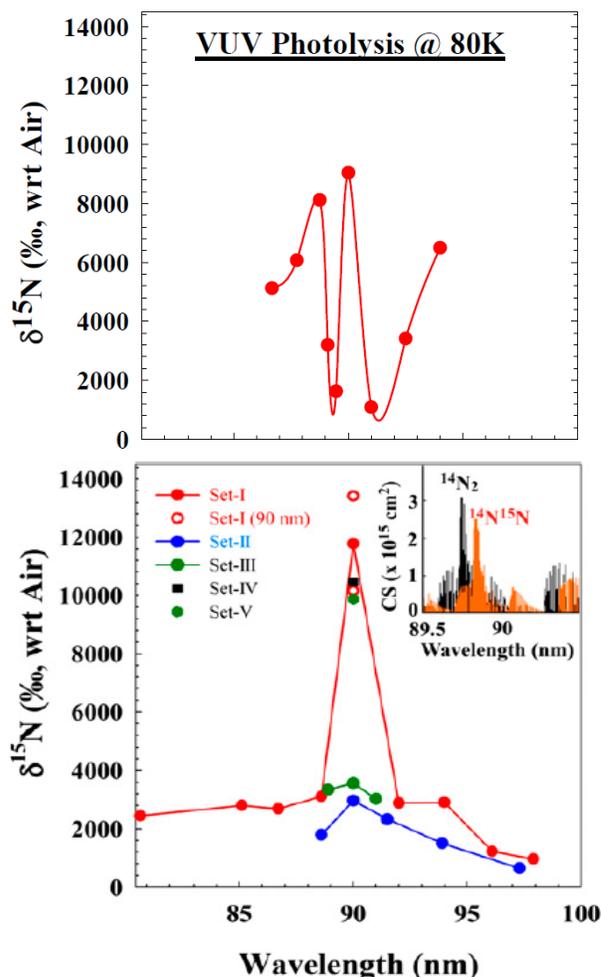


Figure 1. Measured nitrogen isotopic fractionation in VUV (81 to 98 nm) photodissociation of N_2 . Top: $\delta^{15}\text{N}$ measured at 80K temperature. Bottom: $\delta^{15}\text{N}$ measured at different temperatures between- 200K (Set-I) and 300K (Set-II) [8]. Though the fractionation profiles show peaks at 90nm for both the cases, however, multiple peaks exist for 80K profile depicting higher overall $\delta^{15}\text{N}$ values in the examined wavelength regime.

VUV photochemistry of N₂: N₂ absorbs photons through slightly broadened partly overlapping rovibrational lines of excited states in the VUV region and dissociates via a repulsive triplet state. Excitation of ground state N₂ molecules in the VUV yields several bound excited electronic singlet states with Σ and Π symmetries and, for each symmetry group, with two Rydberg and one valence state. As a consequence of interaction of Rydberg and valence states of both symmetries, perturbations are common. Spin-orbit coupling to triplet states, some of which are repulsive, leads to predissociation and accidental predissociation. The extensive electronic state couplings result in a wide range of lifetimes for predissociation and are a strong function of isotope masses and is highly sensitive to the excitation wavelength. It is suggested that the strongest isotope effect will occur in spectral regions where states of significantly different oscillator strengths are strongly mixed [9].

Discussion: The line absorption by N₂ is subject to shielding primarily by absorption of the more abundant ¹⁴N₂ isotopologue resulting in an enrichment of ¹⁵N in the dissociation product due to preferential absorption of rarer ¹⁴N¹⁵N and ¹⁵N¹⁵N isotopologues [10-11]. Isotopic fractionation based on self-shielding was calculated for the 200K experiments [8], which show higher enrichments compared to the measured values and suggested that the self-shielding might only be partly responsible for high ¹⁵N enrichments but more importantly an additional and massive isotope effect must be considered to explain the unprecedented enrichment peak at 90 nm. This particular wavelength zone is quite unique because of extensive state mixing in highly localized spectral regions leading to large scale perturbations.

The new 80K data firmly establishes the hypothesis that the perturbation dominated state mixing (through overlapping wavefunctions) dynamics determines which isotopologues preferentially dissociate. With lowering temperatures, the state mixing dynamics change dramatically in localized zones and hence, the measured fractionation. The self-shielding calculation does not show such drastic change in fractionation with temperature as compared in Figure 1 and hence inadequately reflects the dissociation process.

Connection to the Solar Nebula: The organic material in carbonaceous chondrites hosts the enriched ¹⁵N components, mostly as IOM. These macromolecular materials encompass condensed aromatics at their cores, connected by aliphatic and ether linkages and with various functional groups (e.g., nitrile, amine etc) attached, and are suggested to be of common origin [12]. Aromatic molecules (polycyclic aromatic hydrocarbons, PAHs) are ubiquitous in the ISM and are the

most common class of organic compounds in the universe in gas phase as well as in carbonaceous dust. When nitrogen replaces a carbon in the ring structure, it forms polycyclic aromatic nitrogen heterocycles (PANHs). Nucleobases, the essential building block for the origin of life, are PANHs and are a prebiotically significant component. It is possible that PANHs are formed inside the solar system by nitrogenation of PAHs [13]. The initiating step in these processes would be the production of highly enriched ¹⁵N from N₂ photodissociation (the integrated photochemical effect) as demonstrated in the present experiment at the outer edges of the disk where VUV was not opaque. This process may potentially generate ¹⁵N-enriched amine and nitrile group molecules from a ¹⁵N-rich atomic nitrogen pool as demonstrated here.

The ¹⁵N enrichments measured in meteorite organics perhaps originated through this photodissociation pathway, and this proposition would not simultaneously enrich D and ¹⁵N as observed in many cases. The largest isotope effects are observed as a consequence of the actual photodissociative process and not self shielding and must be accounted for in any successful model.

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