Photoselective isotope fractionation dynamics of N_2 with cosmo and atmospheric chemistry perspectives

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Abstract

Stable isotope ratio measurements provide valuable insights into a broad range of natural processes, from planetary atmospheres and climate to interstellar chemistry. Nitrogen, which has two stable isotopes, exhibits varying isotope ratios across the solar system. To model these observations the isotope fraction as a function of energy is essential. At the Advanced Light Source, we measured the photodissociation of molecular nitrogen (N_2) with vacuum UV photons where a single photon is sufficiently energetic to dissociate the strong bond. The nitrogen atoms produced are scavenged with H_2 to form ammonia, whose isotopic makeup is determined. Blending the experiments with dynamical computations that include the shielding of light, we examine the isotopic composition and electronic atomic states produced. The measured photodissociation of N_2 at a natural isotopic composition with a frequency broad light beam exceptionally strongly favors the formation of the heavier nitrogen isotope, ^{15}N. Computations concur and suggest that the maximum in the quantum yield reflects significant variations in the specific electronic quantum states of the product N atoms that have quite different reactivities. Our quantum computations show that at similar energies, photodissociation of $^{14}N^{14}N$ and $^{15}N^{14}N$ can lead to different product channels. The computed dynamics include extensive state-selective spin-orbit and non-adiabatic couplings affecting the light absorption and dissociation pathways that proceed via the triplet manifold of states. Our results are relevant for future exploration missions, both in situ and sample-return and for other molecules such as O_2 and CO.

Significance statement

Nitrogen is a common element in Earth's atmosphere and the broader galaxy, playing a central role in the formation of biomolecules. While molecular nitrogen (N_2) is exceptionally stable and chemically inert, photodissociation cleaves its strong triple bond, producing reactive nitrogen atoms in different electronic states with quite different reactivities. Our new vacuum ultraviolet (VUV) photolysis experiments, combined with theoretical modeling that includes the shielding of incident light, reveal an exceptionally strong mass dependence and non-statistical behavior in the photodissociation dynamics of different N_2 isotopologues. Integration of experimental results and dynamical computations demonstrate pronounced initial-state selectivity and product electronic-state specificity. Our results provide new insights into the mechanisms underlying the substantial enrichment of the ^{15}N isotope as observed in space.

Stable isotope ratios are powerful tracers of physical and chemical processes in planetary atmospheric and interstellar environments (1, 2). The distribution of isotopomers of compounds varies significantly across the solar system in space and time, showing that the molecular weight, as weighted by the fractions of the different isotopes, is not constant. Variations in the observed nitrogen isotope ratio ($^{15}N/^{14}N$) provide key insights into the evolution of planetary atmospheres, the origin of solar system volatile components and the chemical history of meteorites and comets (3-10). These isotopic signatures reflect specific formation and loss processes — especially photodissociation — that are often mass- and quantum-state dependent.

To better understand origins of the isotopic ratio variability, we investigate the wavelength- dependent dynamics of N_2 photodissociation using both new experimental measurements and quantum dynamical modeling. The study employs VUV photolysis of N_2 at the Advanced Light Source (ALS), with product nitrogen atoms trapped as NH_3 for isotopic analysis. This is integrated with state-of-the-art dynamical simulations that account for isotope-selective light shielding (11-13) (Full details of the light shielding computations are given in the SI). We show that the observed *extreme* isotopic fractionation arises from non- statistical dissociation dynamics—driven by specific electronic couplings and state-selective pathways—thus offering a compelling example of photoselective chemistry. Allowing for the shielding of light is necessary but as discussed quantitatively in the SI, the saturation of the absorption lines by the $^{14}N^{14}N$ molecules, unlike those by the much rarer $^{14}N^{15}N$, is not responsible for the effect. High-level quantum chemical computations of the relevant potentials and of their different selective couplings, which vary in magnitude are essential input to our demonstrations. While we focus on nitrogen, our framework is directly applicable to other molecules, such as CO, for which isotopic anomalies have been reported as significant in the early nebula (14, 15). These findings have implications for interpreting nitrogen isotope data in planetary environments, including Mars— especially for understanding Martian atmospheric chemistry, both at present and in the evolving early atmosphere—and for return samples from Mars and satellites.

The quantitative foundational considerations of isotope ratio measurements date back to a 1947 paper by Urey (16) detailing isotopic exchange equilibrium at high precision (17), (18). At present, an important area of application centers on isotope effects during photodissociation (1, 2). One of the best-known applications involves a mass- independent isotope effect in photodissociation of SO_2 in the Earth's earliest atmosphere between 3.8 and 2.2 billion years ago. Interpretation is limited by the lack of measurements or a theory for the energy-dependent isotopic fractionations of this molecule (19).

Photodissociation plays a particularly important role across space and time because its isotopic

selectivity is potentially far higher than that of other factors. Modeling across relevant wavelengths and predicting isotope effects is intrinsically challenging, but necessary as otherwise the Fractionations would need to be measured across a wide wavelength range which is not realistic in the UV region. In this paper, we report a combined measurement/modelling effort to resolve the contributing parameters in the photodissociation and their isotopic selectivity across the UV range. Molecular nitrogen is chosen as all isotopic parameters are well known. Co-development of a complete model for nitrogen will serve as a template for other molecules such as CO or those lacking measured fractionation factors for dissociation.

Cosmophotochemistry does differ from other branches of chemistry in that it is typically a high energy density process, often at low material density. Challenges lie in both the theoretical description of the elementary processes and of the simulation of gas low (20). The elementary dynamical pathways matter because almost always there is a maze of electronic states, see Figure 1, that are potentially relevant at the energies of interest and there is a range of coupling mechanisms of varying strengths among these states (21). Often, these couplings are individually mass dependent, and their effective strength depends also on the spacings of the potentials of the coupled states. As we discuss below, the electronic state of the nascent products can therefore be dynamically non-statistical and show initial wavelength dependence and considerable isotopic selectivity.

Nitrogen isotope measurements of extraterrestrial objects have been extensively reported. This includes interstellar molecular clouds and protostellar envelopes, and protoplanetary disks, all driven by the photolysis of N_2 (5, 22). Photolysis of nitrogen in extra-terrestrial environments is a precursor of organics observed in meteorites that have uncertain synthetic pathways (7-10). Isotopic measurements with knowledge of the isotope effects provide a way to model systems in greater detail. During the Viking landing, the nitrogen isotopic composition of the Martian atmosphere revealed a massive ^{15}N enrichment (23) first modeled by ref. (24) . The enrichment was suggested as arising from selective escape of ^{14}N vs ^{15}N following photolysis (25). A quantitative measure of the enrichment is $\delta^{15}N$, the fractional excess of $\delta^{15}N$ over the mean isotopic composition on Earth. Recently, the Curiosity Mars rover remeasured Mars nitrogen isotopic composition at $\delta^{15}N = 572$ ‰ , confirming Viking measurements (25) . As discussed, this may result from mass-dependent escape processes, although a cometary impact could also explain the enrichment as they contain high $\delta^{15}N$ values, between 600 and 1000 ‰ (25) . In models of the nitrogen isotopic evolution of Mars, there are requisite assumptions regarding the magnitude of the isotope fractionation in UV photodissociation of N_2. The present work could provide the theory and experiments needed to improve the models of Mars nitrogen evolution.

In a similar vein, at 100 km in the Earth's atmosphere the environment is such that there is no longer a Boltzmann distribution defining the interface of our atmosphere with space and atmospheric leakage to space occurs. Very little is known at the level of isotopic composition to quantify this distillation. This is a significant component, relevant to Earth's atmospheric evolution over time. There is expected photo related isotopic chemistry as suggested for photoproduced atomic oxygen (26). The only isotopic measurements of the mesosphere are from rocket-borne cryogenic whole-air samples where an O_2 anomaly was reported at 60 km (27). It is expected that nitrogen will have a large fractionation due to the observed strong isotope effect and higher absorption. These new data can allow improved modeling of what to expect and guide future sampling.

Experiment

The experiments were all done at the Advanced Light Source Synchrotron at the Lawrence Berkeley lab using the UV source available at the Chemical Dynamics line. Details are described also in refs (28-30). Below is a short outline noting those aspects that are new. A more complete account is in the supplementary materials, (SI), including a schematic of the experimental setup, Figure S1. As discussed in the SI, subsequent to (28, 29) we have greatly improved our protocol, and we also remove the blank correction uncertainty. Our final yields are one to two orders of magnitude higher.

In short, the experiments are a windowless, differentially pumped flow system with a high purity 50:50 N_2:H_2 mix inlet. The N_2 has natural isotopic composition. Photolysis occurs in the flow chamber maintained at liquid nitrogen temperature and total pressure of 250 mbar. The light beam has an asymmetric Gaussian profile as a function of frequency, Figure S4, and it is broad so as to generate enough products. The large frequency breadth of the incident light will mask any finer structure in the frequency dependence of the yields. Flow control was maintained with a new Baratron mass flow controller. Photolysis occurs in the 120 cm path length cell. Following N_2 photodissociation, reaction with H_2 produces NH_3 which traps on the cold chamber walls of the photocell. Tests were conducted to determine if there was any leakage of NH_3 past the photocell. No NH_3 was collected on a series of three liquid nitrogen traps past the photocell, and we assume 100% collection efficiency. When the UV source is shut down, the residual carrier gas is pumped away until the initial vacuum system pressure is attained. The liquid nitrogen is removed from the jacket and the product NH_3 is collected cryogenically, product amount measured and transferred to the sample tube. In these experiments, we determined in a series of tests, that complete removal of the NH_3 from the traps is achieved by heating of the traps for 40 minutes and a temperature above 100 °C. The photocell is also warmed with heat guns. NH_3 has a strong adhesion to stainless steel, and this is an essential step and increased our yield significantly (factor of ten). The

samples are returned to UCSD, and the NH_3 is converted by thermal decomposition at 910 °C for 6 hours. The product water is removed cryogenically, and nitrogen yield measured, and isotopes are determined on a Finigan MAT 253 IRMS. A new protocol of preparing the CuO was developed to completely remove nitrogen and argon trapped in the high-purity CuO solids. This allowed us to remove any significant blank that would require correction. Each sample is carefully analyzed for contaminants, especially CO. A set of NH_3 samples of known isotopic composition is analyzed to determine that the process is optimal. The new data protocol has amplified the yield and provided an enhanced sample-to-blank ratio such that correction is not needed. In summary, we report a rather large observed isotopic fractionation in a photodissociation reaction. The quantitative results as a function of the light beam mean frequency are shown in Table S1.

Theory

Our theoretical work shows how an exceptionally large isotopic fractionation can manifest itself in a chemical reaction. The computations indicate that an understanding of the intricate dynamics of the photodissociation of N_2 is needed for the interpretation of the measurements. It implies that the outcome is not statistical meaning that the isotopic fractionation does reflect the initial conditions. On the other hand, the need for detailed dynamics is useful because it shows that photo-selectivity can provide a probe of the environment. We further argue that our considerations apply to other molecules of astrochemical interest such as CO. We discuss the essence of the modeling and why and how it applies to other systems.

A key first step is the understanding of the excited states that are accessible by a one-photon transition from the electronic ground state to a neutral excited state. In N_2 and in most other examples, these are (quasi-) bound states, states that do have enough energy but that do not directly dissociate (30). Direct dissociation in N_2 requires an energy higher than 117,000 cm^{-1} and is typically competes with ionization. Extensive quantum chemical studies have well characterized these singlet electronic adiabatic states N_2, e.g., (31-36) and identified the vibronic states e.g., (31). The bound singlet vibronic states are spin-orbit very selectively coupled (37) to a large manifold of triplet electronic states, some of which are dissociative. Both non-adiabatic and spin-orbit terms couple the triplet states among themselves such that, eventually, but not statistically, the molecule exits on a dissociative channel. The available exit channels are identified in the potential energy curves as shown in Figure 1. Several potential energy curves for nuclear motion are highly anharmonic. The lowest exit channel can be populated from lower-lying states, accessed by spin-orbit coupling from the lowest singlet Π state.

We follow the quantum dynamics of the molecule from excitation to the exit (38) , see SI. Our computations show that different initial conditions in each isotopomer can result in exits via a different channel, Figure 2. The isotopic selectivity is mainly due to *similar initial conditions for different isotopomers resulting in different exit preferences*. In N_2 and for other molecules such as CO, different exit channels correspond to different electronic states of the product atoms.

These two complementary aspects of selectivity that we demonstrate in the computations are here suggested as the dynamical origin of the exceptionally large isotopic fractionation that is seen experimentally, Figure 2.

In the case of N_2 photodissociation experiments where the N atoms are scavenged by an excess of H_2, we consider that $N(^2D)$ atoms are more than ten times more reactive toward H_2 than $N(^2P)$ atoms (41-46) and in the computations we regard $N(^2P)$ as non-reactive. In the photodissociation of CO, carbon can exit on different electronic states. Only $O(^3P)$ atoms exit at lower energies and $O(^1D)$ atoms are produced at an energy above 94.12nm (47) . For N_2, the energy threshold for producing $N(^2P)$ atoms is slightly above 89.3 nm. Thus, our approach is relevant for meteorites and radio astronomy, and for modeling chemical reaction networks which include the large differences between atomic nitrogen states.

The observed and computed branching into different channels as a function of the initial state and isotope are shown in Figure 2 above and reported in Tables S3-S7 of the SI. It is seen to change dramatically with energy, and, in our interpretation, this difference in the decreasing yields of the much more reactive toward H_2 $N(^2D)$ atoms in the two isotopomers that is the cause of the drop in isotopic preference at higher energies. See also Figure S3 of the SI.

Results

Our experiment and computations, Figure 2, consistently report an exceptionally high, thousands of per mil, isotopic fractionation in the photodissociation of N_2 with a natural isotopic composition (0.364% $^{15}N^{14}N$). It is the higher most values reported (28). The precise number depends on the excitation energy, composition and density of the target gas, method of detection of products, and, in particular on the role of light shielding as discussed in detail in the SI. Computations reproduce and explain the observed smooth trends and provide an understanding on the contribution of dissociation dynamics to the high isotopic fractionation. As shown by the comparison with the experimental results in Figure 2, the modelling is consistent with both the large magnitude and overall shape as a function of the excitation energy. To accurately capture the observation, we incorporate in dynamical considerations that show a non- monotonic variation in the electronic states of the dissociated

atoms. The computed branching fractions of the different products, Figure 2(B), are in close agreement with recent molecular beam measurements for both the lighter and, separately, the heavier isotopomer (39, 40, 48). Combining the branching fractions with the absorption cross-section enables us to examine, as in Figure 3, dissociation to $N(^2D)$ and $N(^2P)$ products separately for each isotopomer. Their differences suggest a dominant role of dynamics in governing isotopic fractionation at higher energies. Our computed lifetimes for dissociation (21) are also quite different depending on the initially optically excited state (Σ or Π symmetry) and the two different isotopomers, see SI. It is remarkable that some initial states dissociate slowly, while others, adjacent in energy, dissociate rapidly. There can be considerable variation in the results on different physicochemical initial conditions, such as composition and column density as determined by the shielding of the incident light. Computations, see details in the SI, show reduced selectivity at lower pressures due to reduced self-shielding, Figure S3(D). The molecular hydrogen used in the experiment to scavenge nascent N atoms does not significantly absorb light in the spectral range of interest and has limited effect on the shielding computations, Figure S3(B). The central role of dynamics requires high-level quantum chemistry computations of the energetics and the non-adiabatic and the state-selective spin orbit couplings, Figures S5 and S6.

In the experiment the nascent N atoms are scavenged by the excess of H_2 that is added to the sample. The isotopic fractionation is in part due to the difference in the reactivity of the two different electronic states of the product N atoms, $N(^2D)$ and $N(^2P)$ towards H_2. In nature there can be other scavengers that are important. In the SI we provide rate constants for reactions of the electronically excited N atoms with other substrates. These often show a similar trend so possibly this difference in reactivity is not uncommon.

Beyond upper atmospheric chemistry, astrochemistry, and space physics, our results from contrasting the two isotopomers are relevant to the long-sought critical demonstration of photoselective chemistry (49). We explain and illustrate, using quantum dynamics and high- level quantum chemical computations, that there are two unique dynamical effects that give rise to the spectacularly high measured isotopic enrichment. First, even small variations in the light's wavelength can lead to different exit channels of the nascent products. This also results in considerable variations in the dissociation rate as a function of excitation wavelength. Second, *at similar wavelengths, two different isotopomers can lead to products exiting through different channels*. This is what laser scientists call highly non-statistical and state-selective chemistry—a long-sought goal that, using the isotopic preference, we conclusively demonstrate that we have achieved.

Perspective

The measured photodissociation enrichment in ^{15}N as a function of wavelength, with a downward trend above 90 nm, is attributed to dynamical effects. Two key mechanisms are identified by the computations: (1) the selective branching between exit channels, Figure 2 and (2) the more subtle role of the non-monotonic variation in individual linewidths, which at higher energies begin to significantly overlap. The linewidths affect both the shielding computations at higher energies and the absorption cross–sections themselves. Modeling requires accurate quantum dynamical simulations using state-of-the-art multireference potential energies and their state-dependent couplings. As the excitation energy rises, competition between different coupled exit channels-some leading to reactive N (^2D), leading to significantly less reactive N (^2P) increases in an isotope dependent manner, thereby modulating product N-atom reactivity. Our work shows that modeling can interpret novel experimental observations and account for the exceptionally high selectivity. Further progress requires accurate high-resolution UV spectra across entire UV bands, both measured and computed, to complement fractionation measurements. The complexity of the non-statistical dynamics and the role of light shielding, make such high-resolution work necessary for a detailed understanding of isotope enrichment in the higher-energy regime for nitrogen and for other cosmochemically relevant molecules such as CO. The massive range in isotopic composition may constrain models of meteoritic nitrogen. Samples from Earth's space-atmosphere interface, where N_2 photolysis occurs, would offer a compelling application.

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Figure legends

Fig. 1. Potential energy curves computed for the N_2 electronic states in the energy range 90,000–120,000 cm^{-1} (23). The black solid curve (singlets) are the states that can be VUV optically accessed by one photon from the ground electronic state. Triplet states are plotted as dashed lines, and quintets with dotted lines. The lowest dissociative exit channels are shown in blue and orange and are the two channels relevant in the energy range of this study, the range of neutral states accessed by a one photon transition from the ground state.

Fig. 2. (A) The experimental, red dots, and computed ^{15}N enrichment factor for a model that incorporates the primary dynamical effect namely that in the shaded blue area, at energies above 112,000 cm^{-1}, not all nascent N atoms are produced in the $N(^2D)$ electronic state, see Figure 1. The blue curve is a computation that assumes that only the $N(^2D)$ react with H_2 during the flow and considers the variable width of the spectral absorption lines. As discussed in considerable detail in the SI, the computed results in panel (A) above (blue line) and in Figure S3, include a spectral band-dependent line width. This lowers the computed curves in the intermediate energy region and results in closer agreement with the experimental enrichment factor (red line) than the results shown in Figure S2 that are computed with fixed width. (B) Measured at higher energies (see Table S1), black circles, branching fraction of nascent $N(^2D)$ atoms for the two isotopomers (39, 40) and the values, blue bars, computed by the dynamics. See Figure 3 for the separate cross sections to final states of the N atoms.

Fig. 3. Absorption cross-section (black) and cross-section to the two isotopomers. **(A)** Full measured energy range. The vertical black line $^1\Sigma^+$ state at 104,323 cm^{-1}, which has a high fluorescence yield. (B) shows and example where large isotopic shift causes overlap between $^{14}N_2$ and $^{14}N^{15}N$ bands of different nature. (C) shows an example of differing reactivities of the nascent product for $^{14}N_2$ and $^{14}N^{15}N$. **(B)** and **(C)** highlight spectral regions where dynamical input is essential, due both to difference in nascent product reactivity and natural linewidth. To compute isotopic fractionation, results are averaged over the broad spectral profile of the ALS light beam, see Figure S4 in the SI. The same computation accounts for the decrease in light intensity along the experimental path, see Figure S1. This shielding effect is included through using the standard Beer-Lambert law, see details in Section Shielding of the light beam in the SI.