

TEMPERATURE AND WAVELENGTH DEPENDENT OXYGEN ISOTOPIC FRACTIONATION IN THE VUV PHOTODISSOCIATION OF CO: IMPLICATIONS FOR THE SOLAR NEBULA. Subrata Chakraborty^{1*}, Ryan Davis¹, Musahid Ahmed², Teresa L. Jackson¹, and M. H. Thiemens¹, ¹Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0356 (subrata@ucsd.edu), ²Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720.

Introduction: A type isotopically selective photodissociation known as isotopic self-shielding of CO at vacuum ultraviolet (VUV) wavelengths has been invoked as a photochemical process in the solar nebular (or in interstellar molecular clouds) to explain the observed isotopically anomalous meteoritic oxygen isotopic compositions [1-3].

A large number of absorption bands exist for carbon monoxide (CO) in the VUV region: 91 – 108 nm [4]. All bands contribute towards CO photodissociation in the solar nebula to different extents. Experimental measurements of the low temperature isotopic fractionation throughout the entire VUV region are required to determine the oxygen isotope fractionation through CO photolysis in solar nebula to enhance our understanding of this process and to develop experimental measurement based models of oxygen isotopic evolution in the solar nebula. The oxygen isotopic fractionation due to VUV photodissociation of CO in some bands was previously reported [5, 6]. Subsequently, a large number of experiments have been carried out by scanning the undulator [7] at the Chemical Dynamics Beamline of the synchrotron facility at the ALS (which delivers photons in a wavelength window of ~ 2 nm with a flux of ~ $5 \times 10^{14} \text{ s}^{-1}$) to cover the entire VUV region with different pressure and temperatures. Here we report new results and discuss the implications for oxygen isotopes in the solar system.

Experiments and Results: We investigated the temperature and pressure dependent isotopic fractionation of CO photodissociation for the synchrotron bands centered at: 91.3, 92.6, 94.12, 97.03, 105.17, and 107.61 nm, which together cover the entire relevant VUV regime and energy surfaces. For these experiments we used the same experimental set-up previously reported [5]. The pressure range in these experiments were varied such a way that the column density changed by a full order of magnitude (~ 10^{17} to 10^{18} molecules/cm²). The upper limit of the pressure was set by the gas handling capacity of the differential pumping system designed for this experiment. The lower limit of the pressure was set by several constraints: amount of product gas (CO₂) required for isotopic analysis, and availability of beam-time at ALS. We observed that the relative fractionation between ¹⁷O and ¹⁸O (reflected in the slope value in the oxygen three-isotope plot) of product CO₂ depends on all the three factors: VUV wavelength, column density of CO,

and the temperature of the gas column. All these three parameters affect the isotopes in different ways. The variation of VUV wavelengths produce different slope values (in three-isotope oxygen plot) ranging from 0.55 to 1.3. For a particular wavelength and temperature, the column density variation only changes the magnitude of ¹⁷O and ¹⁸O fractionation, without changing their relative proportion. However, for a particular wavelength and pressure, the change in temperature not only alters the magnitude of ¹⁷O and ¹⁸O fractionation, but also the ratio between the minor isotopes. None of the results are consistent with self shielding.

Photochemistry: The synchrotron VUV bands excite CO to different excited electronic states which photodissociates following predissociation. A molecule predissociates with a certain probability when a bound electronic state couples to a continuous state. Coupling of a bound state to another intermediate bound state, which itself is predissociative may lead to electronic predissociation. Predissociation proceeds through coupling between intermediate states (Rydberg and repulsive), therefore, the geometry and nature of the coupling states make the predissociation process extremely energy sensitive and hence isotope selective [8]. A recent sophisticated *ab-initio* theoretical study on isotope effects during predissociation of the N₂ molecule (which is isoelectronic with CO, and hence there are a large number of similarities in the spectroscopic/dissociative nature among these two molecular system), displays a huge isotope effect (thousands of permil) during photolysis and is highly energy sensitive due to coupling geometry [9]. Though all the input parameters involved in the formation of the coupling matrix are mass dependent, due to coupling geometry the final products become mass independent in this calculation. The wavelength dependent isotope effect observed in the present experiment emerges from the isotope selective nature of predissociation, which result in different relative isotopic fractionation between ¹⁷O and ¹⁸O for different upper electronic states in the entire VUV region.

From the perspective of isotopic fractionation, among all the wavelength bands explored in these experiments, synchrotron bands centered at 105.1 and 107.6 nm are markedly different from the others, producing very high slope value (~1.3, in oxygen 3-isotope plot) and associated upper electronic state E¹Π with vibrational states v=0 and 1, respectively. As we have interpreted earlier [5], the upper electronic

state ($E^1\Pi$) of CO in VUV region show two leaky channels for dissociation corresponding to these vibrational states and likely to be isotope selective. The bound rydberg state $E^1\Pi$ is coupled to an intermediate bound state $k^3\Pi$ (via spin-orbit coupling), and leads to (accidental) predissociation near $J = 31$ and 9 for $^{12}\text{C}^{16}\text{O}$, respectively for the $v = 0$ and 1 states [10] and is a near resonance phenomenon. $k^3\Pi$ predissociates through a repulsive $^3\Pi$ state. The observed temperature dependency is the direct manifestation of the J -value dependency of the leaky channels.

Implications: Oxygen isotopes in the solar system is still an intriguing issue. The Genesis solar wind data [10] suggests the Sun to be on the meteoritic CAI line after several corrections and assumptions [11] with enrichment in ^{16}O . This is consistent with CAI's condensing from the residual gas of the solar reservoir if the correction factors and model assumptions are correct. The suggestion arises from the observation that chondrules evolve in the same trend line with depleted ^{16}O composition towards the value of the terrestrial planets. This may infer complete decoupling of Sun and rest of the nebula in the oxygen isotope space, with the nebula being enriched in ^{17}O and ^{18}O in such a way that the mixing line gives a slope of ~ 1 . The self-shielding models [2, 3] produce this slope during nebular CO photodissociation with the *assumption* that there is no isotope effect in the actual photodissociation. Our extensive experimental studies (see also the abstract on anomalous sulfur isotopes effect in VUV predissociation [12] of H_2S in this conference) and recent theoretical study [9] strongly suggest that this assumption is not valid and a strong dissociation dynamics dependent large isotope effect (sometime thousands of permil) is present during photodissociation (especially during predissociation). Therefore, CO photodissociation does not generate a slope 1 as assumed and model calculations are incomplete. However, using our complete data set (specially low temperature wavelength dependent data) an improved model can be developed to evaluate the isotopic composition of O-atom pool derived from CO photodissociation by the available VUV spectra in the solar nebula. Further uncertainty remains with the self-shielding model due to the other components of the model, namely, CO photodissociation in the surface layer within a constrained zone, conversion and preservation of anomalous O-atoms (CO photo dissociation derived) through water-ice, which is prone to UV photodestruction [13] in the nebula after formation, and transport of the anomaly to the inner disk from the disk midplane (~ 50 AU).

Recently, Dominguez [14] proposed an alternative model to generate ^{16}O depleted H_2O in the densed

molecular cloud via ozone-mediated reaction on the grain surface. Though this reaction pathway is well established, an isotopically anomalous ozone formation on the grain surface (similar to symmetry dependent gas phase reaction) needs laboratory demonstration. However, this proposition has several advantages over self-shielding model. This model can produce ^{16}O rich gaseous reservoir (Sun and CAI's) and ^{16}O poor water simultaneously and there is no issue related to transport of the anomaly as is for self-shielding model.

In conclusion, to date the CO photodissociation spectrum has been studied for isotopic fractionation. The effect of column density has been evaluated over an order of magnitude in pressure to look for shielding effects. There is no evidence in any experiment to date to support self shielding and, the data and new quantum chemical calculations show that the assumption of no isotopic fractionation during CO photolysis is not valid.

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