

WAVELENGTH DEPENDENT OXYGEN ISOTOPIC FRACTIONATION IN THE VUV PHOTODISSOCIATION OF CO: AN EARLY SOLAR SYSTEM PERSPECTIVE. 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: The oxygen isotopic fractionation in the vacuum ultraviolet (VUV) photodissociation of carbon monoxide (CO) was recently experimentally measured [1-2] to test the isotopic selectivity of photodissociation (isotopic self-shielding). The self-shielding mechanism was theoretically introduced as a photochemical process in the solar nebula [3-5] (and interstellar molecular clouds [6]) to explain the observed meteoritic oxygen isotopic compositions. The experimental results were the first measurements of the isotopic fractionation in CO photolysis. In this abstract we present new data and further address theoretical issues on previous experimental results. The direct relevance of this data set for the oxygen isotopic composition of the solar system is also discussed.

New CO Photodissociation Experiments and Results: The experimental apparatus and procedures are described in [1]. Using the same apparatus we carried out new CO photolysis experiments investigating the oxygen isotopic fractionation at a new synchrotron band centered at 92.6 nm at different column density regimes. The CO absorption bands explored (including the results from [1]) span the entire wavelength regime relevant for nebular CO photodissociation. A slope value in product CO₂ of 0.58 was obtained for the new synchrotron band, which is also inconsistent with self shielding predictions.

VUV Photochemistry of CO and Isotopic Fractionation: CO photodissociation occurs in the wavelength range ~ 92 to 107 nm through predissociation [7-8] though some CO absorption bands do not undergo direct predissociation. The bands at 105.17 and 107.61 nm predissociate indirectly via accidental predissociation [9-10]. It is known that predissociation creates a significant isotope effect [11] while direct predissociation is a mass dependent fractionation because the dissociation linewidths depend upon the reduced mass of the isotopologues [11]. For CO, predissociations proceed through spin-orbit coupling and the relative line width variation among different isotopologues does not result in preferential lighter isotope scission [11] consequently predissociation products are expected to be enriched in a mass-dependent way.

An anomalous isotope effect is observed in indirect predissociation, where the mass-dependence no longer holds [12] and, is a highly selective process. This is manifest in the measured linewidths for two different CO bands undergoing two varieties of dissociation

processes (C¹Σ⁺: predissociation; E¹Π: accidental predissociation) [13-14]. The isotopologue specific linewidths are significantly different and that should be seen in the photolytic isotopic fractionation.

To explore this, another synchrotron band was investigated in the present study (centered at 92.6 nm) which encompasses the CO absorption bands (91, 92.46, 92.58, and 93.57 nm) which undergo direct predissociation. The observed near mass-dependent slope value (~ 0.58) in product CO₂ with enriched δ¹⁷O and δ¹⁸O (relative to the initial CO composition) is consistent with the predissociation mechanism described above, and confirming theoretical models for the isotopic fractionation process, but not self shielding.

Results and Summary: The slope values measured for all five synchrotron bands used so far for CO photolysis show a wide range of values (δ¹⁷O/δ¹⁸O = 1.85, 1.68, 1.05, 0.6 and 0.58 for synchrotron bands centered at 107.61, 105.17, 97.03, 94.12, and 92.6 nm, respectively). Among these five synchrotron bands, bands at 105.17 and 107.61 nm encompass two specific CO absorption bands at their peak position. The upper electronic state of these two bands are E¹Π with vibrational states $v = 0$ and 1, respectively, that undergo indirect (accidental) predissociation via the perturbing bound surface k³Π. For these two states, the observed slope values are 1.68 and 1.85, respectively, which are significantly higher than the slope values measured for other synchrotron bands. As discussed, accidental predissociation is anomalous and is not mass-dependent as manifest by the anomalous linewidths [14] and the observed isotope effect in the photolysis product. Therefore, our measurements are consistent with the upper electronic state properties controlling dissociation mechanisms, but not self shielding.

A criticism of the data interpretation was that the slope values observed in these experiments for synchrotron bands 105.17 and 107.62 nm of 1.68 and 1.85, respectively [15] are due to optically thick ($\sigma \ell = \tau > 1$) C¹⁸O (e.g., C¹⁸O shielding) lines, an effect of high column densities used in the experiments. This argument is not consistent with the slope values observed for rest of the synchrotron bands, because the column density used in all other experiments are in the same range, or, with the measured experimental parameters. It was suggested that the wavelength dependent

dent slope value is expected in self-shielding using isotopologue specific absorption cross-sections [16-17] for different CO bands. This argument is weak as the relevant spectroscopic data are not available. As a theoretical test, the absorption cross-section values were superficially altered by [18] to attempt to match measured slope values for the different bands. This test requires an enormous and unrealistic difference (~ 40 to 50 %) in isotopologue specific absorption cross-sections, and differs significantly between bands. This hypothesis is inconsistent with other molecular system such as OCS, where isotopologue specific cross-section variation for a particular band vary less than a few percent thus, this test fails [19].

CO Photodissociation and Early Solar System:

Isotope self-shielding in CO was suggested as a mechanism to produce a ^{17}O , ^{18}O enriched reservoir in the solar nebula with a slope value of unity [4-5] to explain the meteoritic oxygen isotopic composition. The nebular self-shielding model succeeds only if a slope of unity in the oxygen reservoir is achieved through CO photolysis processes. A recent self-shielding model [20] shows that the slope value of unity in oxygen reservoir is possible through CO self-shielding, however, in this model the cross sectional constants for C^{17}O are taken as that of C^{18}O because spectroscopic data for C^{17}O is not available.

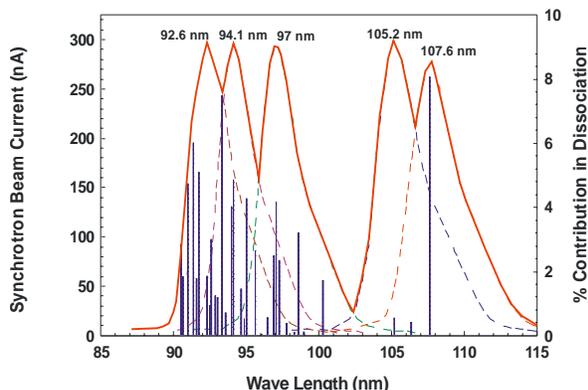


Figure 1. Schematic showing the VUV envelop covered by the entire study (red curve). The peaks correspond to the synchrotron band centers used in these experiments. The contribution in total photodissociation (%) by different CO major absorption bands (which are much narrower compared to the synchrotron bands) are shown by lines (dark blue). The contribution was calculated based on CO absorption cross-section of each band relative to total dissociation cross-section by all these bands taken as 100%. The dashed curves are to show the synchrotron band profiles.

The synchrotron bands used in the experiments are wide, with a FWHM ~ 2 nm and the bands collectively cover the entire VUV range required for CO photolysis as shown in Figure 1. The isotope data from all the synchrotron bands can be used to determine (through weighted averaging) the precise solar equivalent integrated slope value of the product oxygen. For simplicity, we divided five synchrotron bands in three groups based on their values: (a) 1.83 for 105.17 and 107.61 nm, (b) 1.05 for 97 nm, and (c) 0.58 for 94.12 and 92.6 nm. The dissociation contributions from each of these groups are 9.2, 14.0, and 76.8 %, respectively (the cut-off of each synchrotron band was taken based on FWHM of that band). The calculation yields an integrated slope value of 0.75 for the atomic oxygen reservoir generated by CO photodissociation in the solar nebula by VUV light, which is clearly not 1.0 as required by nebular self-shielding models. Therefore, self-shielding of CO in the solar nebula has no experimental support to explain the meteoritic oxygen isotopic composition. There are other shortcomings of the nebular self-shielding model as discussed in [21-22]; inappropriate slope value in CO photodissociation may be the most serious among them. The fundamental assumption that there is no isotope effect other than self shielding has been further tested and shown to fail.

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