EXPERIMENTAL TEST OF ISOTOPE SELF-SHIELDING IN VUV PHOTODISSOCIATION OF CO.

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Introduction: Isotopically selective photodissociation of CO has been invoked as a photochemical process in interstellar molecular clouds to explain the observed abundance variation of minor isotopomers of CO ($^{13}C^{16}O$, $^{12}C^{18}O$, $^{12}C^{17}O$) [1-3], a process known as isotopic self-shielding. Self-shielding of CO, the most abundant nebular oxygen bearing molecule, within the nebular disk has also been advocated as the source of isotopically anomalous oxygen in the solar reservoir and has been suggested as a mechanism for production of meteoritic oxygen isotopic compositions [4-6]. There have been no experiments that measure the relevant isotopic fractionation associated with VUV-CO photodissociation, a major limit on the models.

Eventual verification of models and continued development requires measurement of isotopic fractionation associated with specific quantum processes. Our laboratory is engaged in CO photochemistry experiments at the short wavelengths relevant to nebular photochemistry [7-9]. Here we present new oxygen isotope data of VUV photo-dissociation of CO through a series of CO photo-dissociation experiments at the Advanced Light Source (LBNL) synchrotron at Berkeley. The experiments demonstrate an anomalously enriched atomic oxygen reservoir is possible to be generated through CO photo-dissociation, but, *without requiring isotopic self shielding*.

Experiment: A windowless flow chamber with three-stages of differential pumping and two stainless steel spirals (frozen in LN_2) at the outlet was used at the chemical dynamic beamline (9.0.2) of the Advanced Light Source (ALS), Berkeley. Ultra high purity carbon monoxide was passed through a cylindrical reaction chamber at different pressures which effectively provide a differential shielding depth. VUV synchrotron photons (10^{16} photons/sec) from the beamline was aligned through three 3-mm apertures of the differential pumping sectors and passed through the reaction chamber. The photon wavelength of interest was selected by varying the undulator gap of the beamline.

During the photon irradiation (of a fixed column density CO for 7 to 15 hours), photodissociation produces C and O atoms with the O-atom recombining with CO to form CO_2 and was immediately collected in the spirals avoiding secondary photolysis. At the end of the exposure, the CO flow was stopped and the product CO_2 was collected in a sample tube cryogenically. At UCSD CO_2 was reacted with BrF_5 following

the conventional fluorination techniques. The liberated oxygen was purified via gas chromatography and measured in a dual inlet IRMS (Finnigan MAT 253) to determine the isotope ratios. Standard CO_2 samples of known isotopic composition and of the same size as the actual samples were measured as controls.

Results and Discussion: The oxygen isotopic composition of product CO_2 is heavily enriched compared to initial CO for all four different wavelengths: 107.61, 105.17, 97.02, 94.12 nm used in these experiments as shown in Figure 1. The extent of isotopic enrichment is of the order of a few thousands of per mil, depending upon experimental conditions (column density and exposure time). This extent of isotopic fractionation is one of the largest reported for any process.
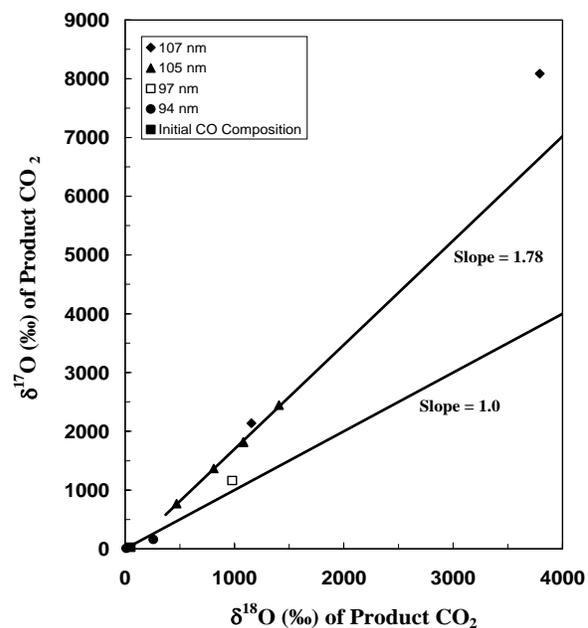

Figure 1. Oxygen isotopic composition of product CO_2 following CO dissociation (by VUV wavelengths) and subsequent recombination of product O-atom with CO. Except for photolysis at 94.12 nm, the products are all highly mass independent, exhibiting a strong wavelength dependent isotopic fractionation.

Except for photolysis at 94.12 nm, are highly mass independent, exhibiting a strong wavelength dependent isotopic fractionation. The same data are plotted in logarithmic scale in Figure 2.
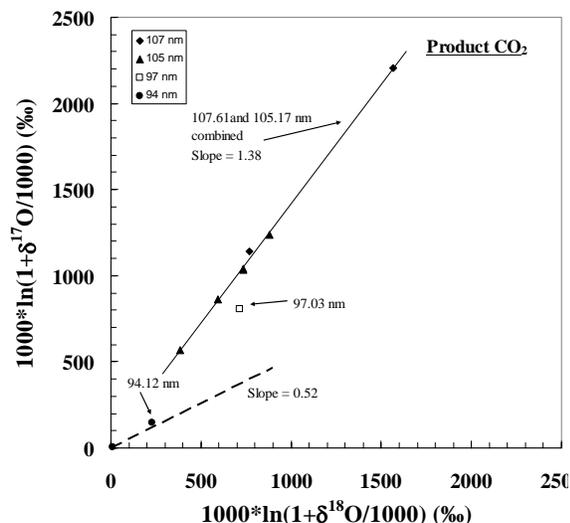
Figure 2. Oxygen isotopic composition of product CO_2 (same as Figure 1) are plotted in three-oxygen isotope space in logarithmic scale to accommodate the non-linearity in δ-scale for large δ-values.

It was anticipated previously that a *self-shielding* effect should be present at 105.17 nm (Band # 31 [6]) and 94.12 nm, whereas, there should be *no self-shielding effect* at 107.62 and 97.03 nm [10]. Moreover, a slope value of unity is expected in a three-isotope oxygen plot from self-shielding effect and can be calculated through photon absorption by different isotopomers. The results show, in contrast to this anticipation, a similar trend line with a slope value of 1.38 (with an intercept of 37 ‰) for 107.61 and 105.17 nm. The data for 97.03 nm lies close to 1.38 slope value (not shown in the figures), whereas, the data for 94.12 nm lie close to the mass dependent line (of Slope ½ in Figure 2). Therefore, the experimental results *do not show any effect of self-shielding*, rather the products displays a large fractionation, dependent on the wavelength of dissociating photons. Close examination of the potential energy curve depicts that the large fractionation at 107.62 and 105.17 nm is associated with an upper electronic state $E^1\Pi$, where a special predissociation effect, termed "accidental predissociation" occurs [11]. Photodissociation at 97.03 and 94.12 nm take place through different upper electronic states and thus results in a different kind of fractionation. Pandey and Bhattacharya [12] showed mass-independent effect in CO + O recombination reaction and the non-zero intercept in the trend line of 107.61 and 105.17 nm photolysis products (37 ‰ in Figure 2) can be accounted for by this process.

The elegant self-shielding model described by Lyons and Young [6] calculated the isotopic composition of water-ice in disk mid-plane arising from isotopic self shielding (using Band# 31). The model incorporated dust contribution, vertical transport and turbulent mixing, but, the isotopic effect due to CO photodissociation was not considered since it had not been measured. The present experiments demonstrate that photodissociation of CO produces a major isotopic fractionation (highly enriched and anomalous) and a similar highly enriched anomalously fractionated water-ice reservoir is possible as predicted by self-shielding effect, *only through CO photodissociation* and completely neglecting the self-shielding effect. Hence, the fractionation associated with CO photodissociation must be considered in any modeling effort to reconstruct the oxygen isotopic composition of nebular water in the early evolution of our solar system.

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