Introduction: Carbon is an important element in the evolution of prebiotic processes and is biologically significant in compounds with hydrogen, oxygen and nitrogen [1]. The isotope ratio for carbon (\(^{12}\text{C} / {^{13}\text{C}}\)) in the solar system is widely accepted to be 89 [2], which is greater than the local interstellar medium (ISM), where the value is taken to be 77. The \(^{12}\text{C} / {^{13}\text{C}}\) ratio at the galactic center is about 62 [3-4]. The galactic gradient is due to the higher star formation rate in the inner galaxy, where the fraction of \(^{13}\text{C}\) has been enhanced by the \(^{13}\text{C}\)-rich ejecta of evolved, intermediate-mass stars in the time since the formation of the solar system. The Sun formed approximately 1.9 kpc closer to the galactic center than its present location (7.94 kpc), presumably it would have formed in a region with a lower \(^{12}\text{C} / {^{13}\text{C}}\) ratio. The large difference between this value and the present solar system value of 89 indicates that the solar system must have become either significantly enriched in \(^{12}\text{C}\), or there was a significant depletion of \(^{13}\text{C}\). Apart from this enigmatic initial carbon isotopic composition of the solar system, the internal (within solar system) variation as shown in Figure 1 is equally daunting.

There are two mechanisms which known to alter carbon isotopes: fractionation through chemical isotope exchange and during photodissociation. It was shown through laboratory experiments that the most important isotope exchange reaction effecting isotopic ratios is: \(\text{H}^{12}\text{CO}^+ + {^{13}\text{CO}} \rightarrow \text{H}^{13}\text{CO}^+ + {^{12}\text{CO}} + \Delta E (= 9\text{K})\) and is effective at very low temperature [5]. In photodissociation part, isotope self-shielding during photodissociation of CO was considered [6]. Carbon isotopic fractionation in a photon dominated region was also studied with a chemical network along with self-shielding and assuming there is no isotope effect during photodissociation [7].

We have reported oxygen isotopic fractionation during CO photodissociation and showed that apart from self-shielding effect there are intrinsic isotope effects associated with photodissociation process, which lead to enormous isotopic fractionation that in fact dominate self shielding [8]. Subsequently, we have shown that the quantum mechanically governed isotope effect is common for the molecules, which follows predissociative pathways during dissociation, such as for N\(_2\) [9]. During these investigations it turned out that the isotope effects are quite localized in energy space and extremely difficult to calculate through any model. Thus, to construct any models for the solar nebula there is no resource except measurement of the wavelength dependent isotope effects. We recently investigated the carbon isotopic fractionation during vacuum ultraviolet (VUV) photodissociation of CO to begin to evaluate the wavelength dependency.

Here we present new data on the C-isotopic composition in carbon dioxide formed by VUV photodissociation of CO 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 CO 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 (CO: H\(_2\) = 50:50) was established in the reaction chamber at CO partial pressure of 100 mtorr (column density: 5 x \(10^{17}\) molecule/ cm\(^2\)). Photolysis of this gas mixture was carried out at three different synchrotron bands between 97 and 107 nm. Photolysis product CO\(_2\) was collected in sample tubes. Since it is known from our previous experiments that the oxygen isotopic composition of photoproduction CO\(_2\) is mass-independently fractionated [8], determination of carbon isotopic composition was bit tricky. At UCSD, the isotopologue ratios 45/44 and 46/44 of CO\(_2\) (from an ali-
quot of sample) was first measured after cryogenically drying the sample from the photochemically product water using a Finnigan MAT 253 IRMS. In the next step, the product CO$_2$ was equilibrated in the presence of CuO at 900 °C to erase any mass dependent oxygen isotopic composition and the equilibrated CO$_2$ was remeasured for the same isotopologue ratios. From the initial and final isotopologue ratios, $\delta^{13}$C, $\delta^{18}$O, and $\delta^{17}$O of photochemically produced CO$_2$ was determined.

**Results:** Figures 2 and 3 show the carbon and oxygen isotopic composition of the product CO$_2$. The oxygen isotopic composition of CO$_2$ is very different and more enriched from that reported earlier [8] for photodissociation at the same wavelengths at higher temperature (200 K). Interestingly, the slope values in oxygen three isotope plot are also different, where the reported slope values for 105 and 107 nm was 1.4 and a value of 1.0 for 97 nm thus requiring an extraordinary mass independent temperature dependence in the photolysis.

![Figure 2. Wavelength dependent carbon and oxygen isotopic fractionation in product CO$_2$. Along with oxygen isotopes, carbon isotopes are also significantly enriched.](image1)

**Discussion:** The line absorption by CO is subject to shielding primarily by absorption of the more abundant $^{12}$C$^{16}$O isotopologue resulting in an enrichment of $^{13}$C, $^{17}$O and $^{18}$O in the dissociation product due to preferential absorption of rarer isotopologues [6, 10]. Isotopic fractionation based on self-shielding models depend on cross-section and column density and does not show a large variation with temperature as measured and compared with reported measurements. 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 of temperatures, the state mixing dynamics change dramatically in localized zones and hence, the measured fractionation.

**Connection to the Solar Nebula:** Through a chemical fractionation model of IS clouds Langer et al. [10] was able to classify carbon bearing species into three families—CO, HCO$^+$, and the “carbon isotope pool”—with distinct isotopic behaviors [11]. The carbon bearing molecules such as HCN, CN, C$_2$, CH$_4$, C$_2$H$_4$ etc are the members of this pool. The measured carbon isotopic composition from the molecules of giant planets and comets, which show $^{13}$C enrichments compared to the terrestrial planets, belongs to this said pool. $^{15}$C enriched C atoms generated from CO photodissociation may potentially generate the carbon containing molecules of this pool and thus enriched in $^{13}$C. Photodissociation is an inevitable process in the solar nebula and that would generate isotopic enriched molecular pool and potentially can explain the observed (summarized in Figure 1) extreme variation measured in solar system bodies [12].

![Figure 3. Three isotope plot of oxygen showing the isotopic composition in CO$_2$ at different wavelengths. The isotopic enrichments in heavy oxygen isotopes are larger by a factor of >2 compared to the compositions measured at higher temperature (200K) photodissociation at the same wavelengths [8].](image2)

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**References:**