Introduction: To experimentally verify the so-called “CO self-shielding” model invoked to explain oxygen isotope distribution of the early solar system [1-8], we have started investigating the predissociation behavior of excited state \( E^1\Pi_{v=1} \) around 105.17 nm [9] of carbon monoxide (CO), by comparing the absorption efficiencies of \(^{12}\text{C}^{16}\text{O}, ^{12}\text{C}^{17}\text{O}, \) and \(^{12}\text{C}^{18}\text{O}\) in their excited states respectively. We previously reported our finding at the 2011 LPSC meeting regarding the excited state of CO before predissociation [9]. Here we further report the shielding effects and document its isotopic composition of atomic \(^{16}\text{O}, ^{17}\text{O} \) and \(^{18}\text{O}\) as fragments from CO’s predissociation. To our knowledge, this is the first direct isotopic measurement of photodissociation products in the specified vacuum ultraviolet (VUV) region including minor isotope \(^{17}\text{O}\).

Recent solar wind measurements from Genesis mission revealed that terrestrial planets are in general enriched in \(^{17}\text{O}\) and \(^{18}\text{O}\) compared to the Sun by ~6% [8], whereas \(^{15}\text{N}\) in enriched by 40% [10], a factor of ~7 difference. Clayton [11] has recently suggested that a possible solution to explain this large difference is due to the fact that predissociation products of \( \text{N}_2 \) is far more reactive (in excited states) than that of CO (in ground state). Generally atoms at excited states are more reactive in a metathesis reaction, such as \( \text{N} + \text{H}_2 \rightarrow \text{NH} + \text{H} \) and \( \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \). These are key steps, respectively, in “trapping” atomic dissociation products of \( \text{N}_2 \) and CO with huge isotopic effects after self-shielding [11]. It is well known that 50% of atomic nitrogen from \( \text{N}_2 \) predissociation from 90nm to 110nm are at excited states [12,13]. However, the quantitative studies of CO predissociation dynamics were rarely examined in detail in this wavelength region. It is generally assumed that the O from CO predissociation is at ground state \( \text{O}(^3\text{P}) \). We have recently showed for the first time that this is not the case [14]. Therefore, we have now started a systematic investigation to establish the branching ratios of all CO dissociation channels in the VUV region between 90-110 nm, using the time-slice velocity-map ion imaging technique [14]. Here in the second half of the abstract, we report our results to help explain the different rare isotope enrichment between N and O reported by the Genesis team [8, 10].

Experiment: Our experimental setup consists of two VUV laser systems, and a time-of-flight (TOF) mass spectrometer (Fig. 1). The ultra-high resolution VUV1 was shielded (absorbed) by CO with natural composition at different number densities. The attenuated VUV1 laser excited CO isotopologues in supersonic molecular beam to rovibrational states undergoing predissociation. To enhance detection on TOF-MS, isotopically labeled \(^{17}\text{O}\)- and \(^{18}\text{O}\)-enriched CO gas was used in the molecular beam chamber, while the “shielding” was done with a natural composition. Subsequently, with a 300 ns delay, the second VUV2 laser probes (ionizes) the atomic oxygen from CO predissociation. As VUV1 scans across the wavelength region of interest with high resolution, absorption and dissociation spectra of CO and O are taken respectively in real time.
We scanned the VUV\textsubscript{1} from 95082.0 to 95083.6, from 95055.8 to 95056.2, from 95031.65 to 95032.3 cm\textsuperscript{−1}, respectively, to excite \(^{12}\text{C}^{16}\text{O}, ^{12}\text{C}^{17}\text{O}, \text{and} ^{12}\text{C}^{18}\text{O}\) to Q branches in state \(E'\Pi \nu=1\). The VUV\textsubscript{2} is fixed to a strong autoionization line of atomic O (\(^3\text{P}\)) at 92.95 nm to ionize atomic oxygen with a technique of 1VUV+1UV ionization. By measuring oxygen intensity as a function of the photon energy of VUV\textsubscript{1} we obtained the rovibrational spectra of oxygen for the Q branches of \(^{12}\text{C}^{16}\text{O}, ^{12}\text{C}^{17}\text{O}, \text{and} ^{12}\text{C}^{18}\text{O}.\) Spectra were taken over the same VUV energy range under different shielding conditions. Intensities of \(^{16}\text{O}\) were attenuated by 5 to 99%. But intensities of \(^{17}\text{O}\) and \(^{18}\text{O}\) were almost not changed, suggesting no shielding for minor isotopologues of \(^{12}\text{C}^{16}\text{O}, ^{12}\text{C}^{17}\text{O}, \text{and} ^{12}\text{C}^{18}\text{O}.\)

**Results and Analysis:** Seven data points were reduced and shown in Fig. 2 in the three-oxygen-isotope plot. The temperature of the CO molecule beam was at 50K. Each of the data points represents a different shielding depth. The slope = 1.003 obtained by least square linear fitting agrees with the prediction of self-shielding model. Our result is at odds with a similar experiment for the same band by [15] using broadband synchrotron VUV light source at Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The discrepancy remains to be resolved by taking into account the details outlined in [16-18].

Our recent work [14] on atomic oxygen dissociated from some of the CO predissociation state in the 90-110 nm region contains one or both of ground O(\(^3\text{P}\)) and excited O(\(^1\text{D}\)) states. They are generated from different dissociation channels of one CO excited state. For example, each photoion ring in the image on the left of Fig. 3 represents one dissociation channel of CO at \(W'\Pi \nu=3\) (92.58 nm). The brightness of the ring illustrates the intensity of the channel. The curve on the right of Fig. 3 is reduced from the image, and shows the population of dissociation channels resulting in ground and excited O. We studied the branching ratio of CO dissociation channels for dissociation bands in the range of 90.5-95 nm. All bands at energies lower than 94 nm generate no excited O(\(^1\text{D}\)). Over all, CO dissociation generates 6.9% O(\(^1\text{D}\)), weighed by the predissociation cross section.

On the other hand, N\textsubscript{2} produces 50% excited N [12,13]. So, N(excited)% : O(excited) % = 7.2. This ratio may help to explain why the heavier isotope of N is more enriched than those of O in molecular compounds, as suggested by Clayton [11].

**Summary:** We completed the design and implementation of 2VUV-PDI-TOF-MS (Fig. 1). Using this unique apparatus, spectroscopic study of atomic oxygen isotopes as direct dissociation products of CO has been performed. The experimental results of state \(E'\Pi \nu=1\) of CO confirms the prediction of the self-shielded model. The new results also corroborate our previous finding with CO [9]. The ratio of O at ground state and excited state generated from CO pre-dissociation was measured with the time-slice velocity-map ion imaging technique. Only 6.9% excited O(\(^1\text{D}\)) is generated in the region of 90.5-110 nm. Comparing this result with 50% excited N generated from N\textsubscript{2} predissociation, we expect atomic oxygen to be less reactive than atomic N in “trapping reactions”. As a next step, we plan to expand the test on “self-shielding” model to cover other significant bands of CO predissociation.

**References:**

[9] Shi et al. (2011) 42\textsuperscript{th} *LPSC*, A2705.  