FURTHER TESTING OF "SELF-SHIELDING" MODEL FOR THE OXYGEN ISOTOPE EVOLUTION IN THE EARLY SOLAR NEBULA — ISOTOPE COMPOSITION OF ATOMIC OXYGEN FROM CO PRE-DISSOCIATION.
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Introduction: Inner solar system materials have distinct oxygen isotopic compositions, suggesting a large scale mixing between ^{16}O-rich and ^{16}O-poor reservoirs. Exactly how these reservoirs were first developed in the solar nebula has remained elusive ever since the discovery of the oxygen isotope anomalies in 1973 (1). Recently, building on earlier suggestions (2, 3) and well known astronomical observations (e.g. 4), an intriguing model known as carbon monoxide (CO) "self-shielding" was invoked (5-7) to explain the observed oxygen isotope anomalies in the early Solar System materials. The model is important in that the proposed mechanism and reaction pathways involve all major oxides in the early solar nebula (CO ~50%, H$_2$O ~33% and the rest as solid oxides of other elements ~17%) (8). According to the model, oxygen isotope anomalies were produced with CO, stored in H$_2$O, and reacted with dust, and discovered in meteorites today (5-7). The model has recently garnered observational support (9-12).

To experimentally verify the self-shielding model, we have started investigating the photopredissociation behavior of excited state $E^1\Pi$ v=1 around 105.17 nm (13) of carbon monoxide (CO), by comparing the absorption efficiencies of ^{12}C^{16}O, ^{12}C^{17}O, and ^{12}C^{18}O in their excited states respectively. According to (14), the integrated cross section of absorption and predissociation is close to unity. Therefore the absorption efficiencies ratios of isotopologues are analogous to the ratios of the products of the predissociation of ^{16}O, ^{17}O, ^{18}O. We have previously reported our finding at the 2011 LPSC meeting regarding the excited state of CO before predissociation (15). Here we further report the shielding effects and document its isotopic composition on CO's predissociation products: atomic ^{16}O, ^{17}O and ^{18}O. To our knowledge, no direct isotopic measurement of photodissociation products for the specified vacuum ultraviolet (VUV) region have been reported for minor isotopes such as ^{17}O.

Experiment: The experimental setup consists of two VUV laser systems, and a time of flight (TOF) spectrometer (Fig. 1). The ultra-high resolution VUV-1 is shielded (absorbed) by CO with natural composition at different number densities. The attenuated VUV-1 laser excites CO isotopologues in supersonic molecular beam to rovibrational states undergoing predissociation. To enhance time-of-flight mass spectrometer detection (TOF), isotopically labeled, ^{17}O- and ^{18}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 VUV-2 laser probes (ionizes) the atomic oxygen from CO predissociation. As VUV-1 scans across the wavelength region of interest with high resolution, absorption and dissociation spectra of CO and O are taken respectively in real time.
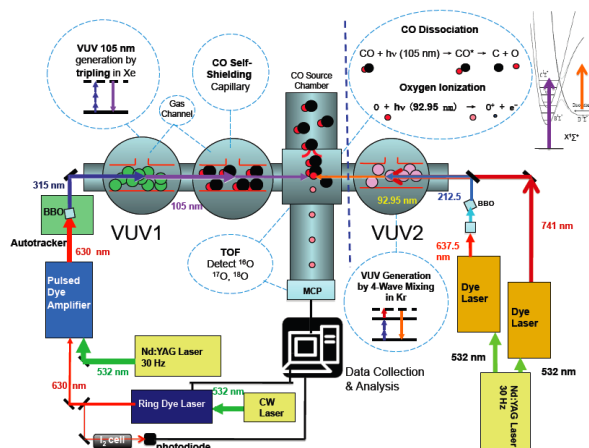

Fig. 1. Schematics of all-in-one setup for the CO self-shielding experiment, the ultra high-resolution two VUV laser photodissociation and photoionization time-of-flight mass spectrometer (2VUV-LPP-TOF-MS). Figure to the left of blue dotted line shows the schematics for probing CO* (excited radical) with one VUV laser, as reported earlier by us (15). With the new parts to the right of blue dotted line added, the complete set-up shows the schematics for probing O with two VUV lasers. The VUV light paths, after generation in the tripling or 4-wave mixing chamber, are windowless inside vacuum chamber. The CO and H$_2$ absorption (shielding region) and the CO photodissociation-photoionization region are located in partitioned differentially pumped vacuum chambers.

Results and Analysis: Fig. 2 shows the TOF mass spectra of atomic ^{16}O and ^{17}O as products of VUV-1-dissociation-VUV-2-ionization. The Q branches in state $E^1\Pi$ v=1 of ^{12}C^{16}O, ^{12}C^{17}O, and ^{12}C^{18}O are separated by more than 20 cm^{-1} from each other. Information on the predissociation behavior is obtained by directly detecting the atomic oxygen isotopes generated by CO predissociation. We scanned the VUV-1 from 95082.0 to 95083.6, from 95055.8 to 95056.2, from 95031.65 to 95032.3 cm^{-1}, respectively,

to excite CO to Q branches in state $E^1\Pi$ v=1. The VUV-2 is fixed to a strong autoionization line of atomic O (^{3}P) at 92.95 nm to ionize atomic oxygen. By measuring oxygen intensity as a function of the photon energy of VUV-1 we obtain the rovibrational spectra of oxygen for the Q branches of $^{12}C^{16}O$, $^{12}C^{17}O$, and $^{12}C^{18}O$, shown in Figure 3.
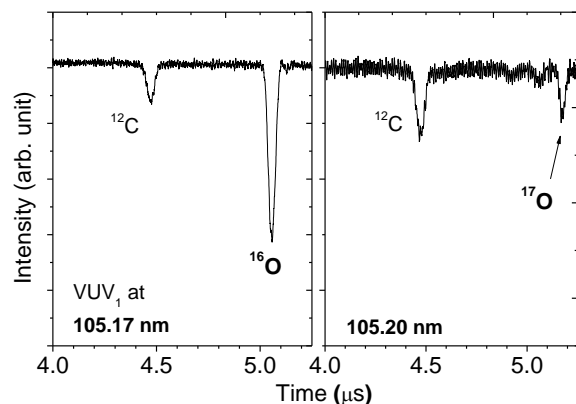

Fig 2. Time-of-flight spectrum of $^{16}O^+$ and $^{17}O^+$, full width at half maximum (FWHM)=80 ns. VUV-2 is fixed at 92.95 nm.

Spectra were taken over the same VUV energy range under different shielding conditions. In Fig. 3, black, blue, and red curves represent the dissociation efficiencies of CO as measured by atomic O with two shielding conditions and one without shielding, respectively. The part (a) of the figure shows the dissociation efficiency of the C^{16}O reduced by approximately 30% (blue) and 60% (black) compared to the unshielded spectrum (red). Under the same shielding conditions, the dissociation efficiencies of the C^{17}O and C^{18}O almost did not change, as shown by the overlapping of the black, blue and red curves of ^{17}O and ^{18}O in inset (b) and (c), illustrating no shielding for minor isotopologues of C^{17}O and C^{18}O.
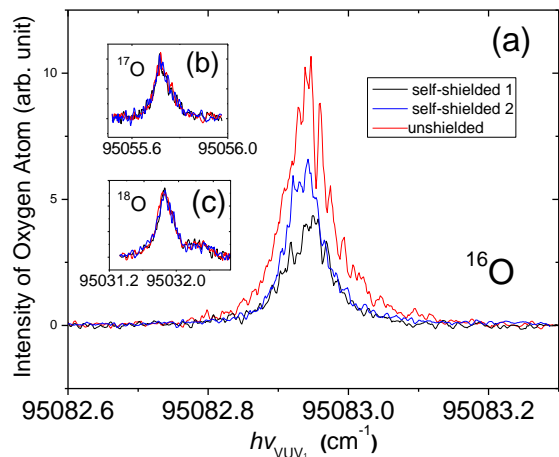

Fig. 3. Oxygen from the Q branches of (a) C^{16}O, (b) C^{17}O, and (c) C^{18}O predissociation.

We have obtained and reduced seven data points as shown below in Fig. 4 in three-oxygen-isotope plot.

The temperature of the CO molecule beam was at 160K. 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 theory. Our result is at odds with a similar experiment for the same band by (16) 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 (17,18,19).
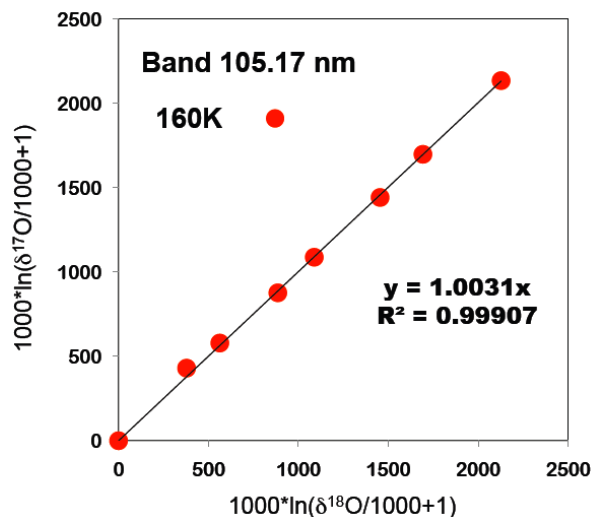

Fig. 4. Three-isotope plot of $^{12}C^{16}O$, $^{12}C^{17}O$, and $^{12}C^{18}O$ in Q ranch of $E^1\Pi$ v=1

Summary: We completed the design and implementation of 2VUV-LPP-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 $E^1\Pi$ v=1 of CO confirms the prediction of the self-shielded model. The new results also corroborate our previous finding with CO. As a next step, we plan to cool the molecular beam further and cover other significant bands of CO photopredissociation.

References: [1] Clayton et al. (1973) *Science,* 182, 485. [2] Thiemens & Heidenreich (1983) *Science* 219, 1073. [3] Navon & Wasserburg (1985) *EPSL* 73, 1. [4] Bally & Langer (1982) *ApJ.*, 255, 143. [5] Clayton (2002) *Nature* 415, 860. [6] Yurimoto & Kuramoto (2004) *Science* 305, 1763. [7] Lyons & Young (2005) *Nature* 435, 317. [8] Lodders (2003) *ApJ,* 591, 1220. [9] McKeegan et al. (2011) *Science,*332, 1528. [10] K. Hashizume, M. Chaussidon (2005) *Nature*, 434, 619. [11] Sakamoto et al. (2007) *Science*, 317, 231. [12] Hashizume et al. (2011) *Nature Geosci.* 4, 165. [13] W. Ubachs et al. (2000) *J. Chem. Phys.* 113, 547. [14] Letzelter et al. (1987) *Chem. Phys.* 114, 273. [15] Shi et al. (2011) 42nd LPSC, A2705. [16] Chakraborty et al. (2008) *Science*, 321, 1328. [17] Yin et al. (2009) *Science*, 324, 1516c. [18] Lyons et al. (2009) Science, 324, 1516a. [19] Federman and Young (2009) Science, 324, 1516b.