

TESTING “SELF-SHIELDING” MODEL WITH LABORATORY EXPERIMENT FOR THE OXYGEN ISOTOPE EVOLUTION IN THE EARLY SOLAR NEBULA — A PROGRESS REPORT. Xiaoyu Shi¹, Qing-Zhu Yin², Zhihong Luo¹, Huang Huang¹, Cheuk-Yiu Ng¹ ¹Department of Chemistry, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA (xyshi@ucdavis.edu; c yng@ucdavis.edu), ²Department of Geology, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA (qyin@ucdavis.edu).

Introduction: Inner solar system materials have distinct oxygen isotopic compositions, suggesting a large scale mixing between ¹⁶O-rich and ¹⁶O-poor reservoirs. Exactly how these reservoirs were developed in the first place 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” has been invoked (5-7) to explain the observed oxygen isotope anomalies in the early Solar System materials. The model has recently garnered observational supports (8-10). About half of the total oxygen in our solar system resides in CO, with another third in H₂O, and the rest is stored as oxides of other elements (11). The proposed mechanism is significant because it involves all of these major oxides. It is very important to verify the pathways experimentally.

We experimentally investigated the photopredissociation behavior of excited state $E^1\Pi v=1$ around 105.17 nm (12) of carbon monoxide (CO) with “self-shielding”, by comparing the absorption efficiencies of ¹²C¹⁶O, ¹²C¹⁷O, and ¹²C¹⁸O in their excited states respectively. The $E^1\Pi v=1$ band is thought to be responsible for the about 60% of self-shielding effect in CO (13). 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 ¹⁶O, ¹⁷O, ¹⁸O.

Experiment: The experimental setup (Figure 1) consists of a narrowband dye pulsed amplifier, seeded by the output of a continuous wave ring dye laser, pumped by a Nd:YAG laser. It provides wavelength tunable pulses of 6 ns duration and 100 mJ pulse energy. Vacuum ultraviolet (VUV) laser generated by frequency doubling the output of dye pulsed amplifier to UV in a BBO crystal and subsequently frequency tripling UV in a pulsed jet of Xenon gas. The VUV is absorbed by CO gas in a shielding capillary. The CO gas is supplied by a pulsed jet. We can easily adjust the number density in the capillary by regulating the backing pressure of the jet, to regulate the shielding strength. After the shielding (absorption), the residual of VUV crosses with the CO supersonic molecular beam, exciting CO molecules to the excited states, which undergo predissociation. The rovibrational spec-

troscopic study is performed in a differentially pumped windowless chamber using the technique of 1 VUV + 1 UV two-photon ionization. The resolution of VUV is about 0.0010 cm⁻¹. TOF mass spectra have been obtained for unshielded natural composition: ¹²C¹⁶O (99.76%), ¹²C¹⁷O (0.04%), and ¹²C¹⁸O (0.20%), as well as shielded composition. Figure 2 shows the TOF mass spectra of two less abundant isotopologues.

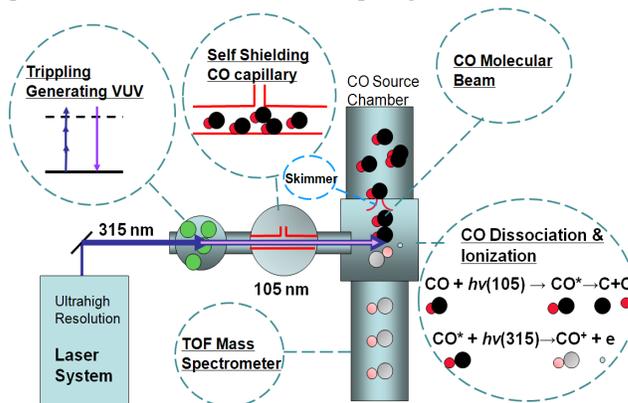


Figure 1. Schematic diagram of the windowless experimental configuration.

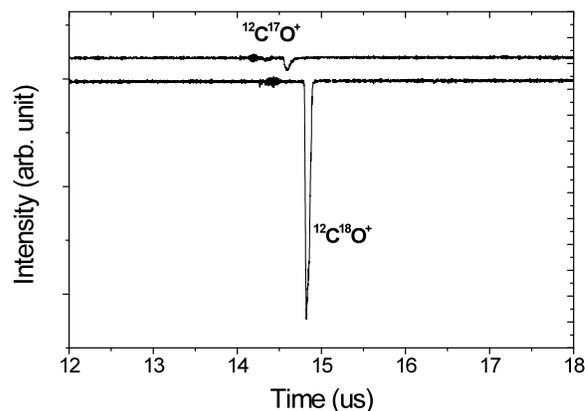


Figure 2. Time-of-flight spectrum of ¹²C¹⁷O⁺ and ¹²C¹⁸O⁺, full width at half maximum (FWHM) = 80 ns.

Results and Analysis: The Q branches in state $E^1\Pi v=1$ of ¹²C¹⁶O, ¹²C¹⁷O, and ¹²C¹⁸O are separated by more than 20 cm⁻¹ from each other. Information on the predissociation behavior is deduced from the large broadening of rotational states in Q branches. The lifetimes of excited ¹²C¹⁶O, ¹²C¹⁷O, and ¹²C¹⁸O are only several hundred of ps. We scanned the VUV from 95082.0 to 95083.6, from 95055.8 to 95056.2, from 95031.65 to 95032.3 cm⁻¹, respectively, to obtain the

rovibrational spectra for the Q branches of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$, shown in Figure 3. Spectra were taken over the same VUV energy range under different shielding conditions. In Figure 3, black, blue, and red curves represent the absorption efficiencies of CO with two shielding conditions and one without shielding, respectively. The part (a) of the figure shows the absorption efficiency of the C^{16}O reduced by approximately 40% (blue) and 70% (black) compared to the unshielded spectrum (red). Under the same shielding conditions, the absorption efficiencies of the C^{17}O and C^{18}O almost did not change, illustrated by the overlapping of the black, blue and red curves of isotopologues of C^{16}O , C^{17}O and C^{18}O in inset (b) and (c).

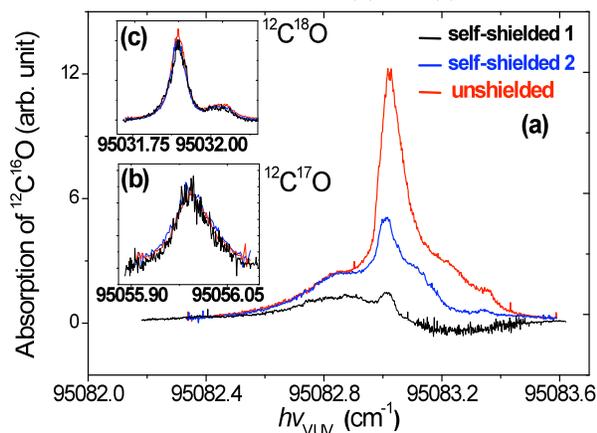


Figure 3. Q branches of (a) $^{12}\text{C}^{16}\text{O}$, (b) $^{12}\text{C}^{17}\text{O}$, and (c) $^{12}\text{C}^{18}\text{O}$, recorded with 1 VUV + 1 UV photonization.

We calculated the efficient number densities as a function of the pressure in the shielding chamber recorded by an ion gauge, with constant parameters of the experimental setup: the volume of the shielding chamber, volume of the shielding capillary, pumping speed of molecular turbo pumps, etc. In Figure 3, self-shielding condition 1 (black) represents shielding with an efficient number density (number density times path length) of 1.75×10^{17} molecules/cm²; and self-shielding condition 2 (blue) corresponds to an efficient number density of 6.37×10^{16} molecules/cm².

The temperature during photopredissociation of CO can be manipulated from 10 to 150 K to simulate settings in the solar nebula where self-shielding might occur (6-7). The temperature we used in present study was approximately 150 K. This could be lowered further if a cooling carrier gas (e.g. H₂, He) is doped in the molecular beam of CO. This has added advantage of mimicking “solar nebula” gas composition. The accurate temperature can be calibrated by comparing the calculated population of rotational states in Q branch with the real population of rotational states in the unshielded absorption spectra, which are the red curves in Figure 3.

As of this writing, we have obtained and reduced three data points as shown below in Figure 4, in three oxygen isotope plot. While the results agree with the prediction of self-shielding theory, it is premature to discuss the differences with similar experiments for the same band by (15) using broadband synchrotron VUV light source at Advanced Light Source at Lawrence Berkeley National Laboratory. We need to acquire more data points under the variable shielding depth. With three data points only, the uncertainty on the slope is large.

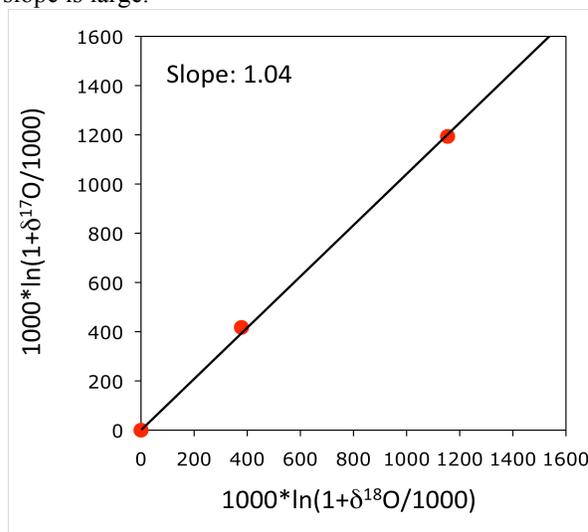


Figure 4. Three-isotope plot of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ in Q ranch of $E^1\Pi v=1$

Summary: The experimental results of state $E^1\Pi v=1$ of CO confirms the prediction of the self-shielded model. More shielding conditions will be tested to obtain more data points in the three-isotope plot for C^{16}O , C^{17}O , C^{18}O at 105.17 nm band. We will also vary the temperature of the molecular beam and cover other significant bands to CO photopredissociation. Our ultimate goal is to detect the direct products of the dissociation of CO (i.e. O and C) to confirm our results obtained for CO. For this purpose we are now building a second VUV photoionization laser to ionize ^{16}O , ^{17}O , ^{18}O and detect their cations using time of flight (TOF) spectrometry.

References: [1] R. N. Clayton et al. (1973) *Science*, 182, 485. [2] M. H. Thiemens & Heidenreich (1983) *Science* 219, 1073. [3] Navon & Wasserburg (1985) *EPSL* 73, 1. [4] J. Bally, W. D. 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] K. D. McKeegan et al. (2008) *LPSC XXXIX*, A2020. [9] K. Hashizume, M. Chaussidon (2005) *Nature*, 434, 619. [10] N. Sakamoto et al. (2007) *Science*, 317, 231. [11] K. Lodders (2003) *ApJ*, 591, 1220. [12] W. Ubachs et al. (2000) *J. Chem. Phys.* 113, 547. [13] van Dishoeck and Black (1988) *ApJ*. 334, 771. [14] C. Letzelter et al. (1987) *Chem. Phys.* 114, 273. [15] Chakraborty et al. (2008) *Science*, 321, 1328.