**TESTING "SELF-SHIELDING" MODEL WITH LABORATORY EXPERIMENT FOR THE OXYGEN ISOTOPE EVOLUTION IN THE EARLY SOLAR NEBULA.** Xiaoyu Shi[1], Qing-Zhu Yin[2], and Cheuk-Yiu Ng[1], [1]Department of Chemistry, University of California Davis, One Shields Avenue, Davis, CA 95616, USA (xyshi@ucdavis.edu; cyng@ucdavis.edu) , [2]Department of Geology, University of California Davis, One Shields Avenue, Davis, CA 95616, USA (yin@geology.ucdavis.edu).

**Introduction:** Inner solar system materials have distinct oxygen isotopic compositions, suggesting large scale mixing between $^{16}$O-rich and $^{16}$O-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 is significant in that the proposed mechanism and reaction pathways involve all major oxides in the early solar nebula (CO~50%, $H_2O$~33%, and the rest in oxides of other elements~17%) (8). According to the model, oxygen isotope anomalies were produced with CO, stored in $H_2O$ and reacted with dust, and discovered in meteorites today. Some of the predictions of the model have recently garnered observational supports (9-11).

We propose an experiment to directly confirm or refute if the carbon monoxide (CO) "self-shielding" mechanism would produce the expected mass independent oxygen isotope fractionation, and further test which temperature environment of the proposed astrophysical sites (5-7) may be most suitable to produce the observed oxygen isotope anomaly in the early Solar System materials.

**Experimental Setup**: The unique VUV laser photodissociation-photoionization mass spectrometry facilities at UC Davis [12] (see Fig. 1) will allow VUV photodissociation study of CO + hv (VUV) → C + O in the 90-110 nm region in a windowless environment. The ultrahigh-resolution VUV laser will make possible the selective excitation of individual predissociative rovibronic states of the $^{12}C^{16}O$, $^{12}C^{17}O$, $^{12}C^{18}O$, and $^{13}C^{16}O$ isotopomers. The resulting oxygen atoms ($^{18}O$, $^{17}O$, and $^{16}O$) and carbon atoms ($^{12}C$ and $^{13}C$) will be directly detected by photoionization using a second VUV laser, such that the oxygen isotopic composition due to CO photodissociation can be measured in situ by the time-of-flight (TOF) mass spectrometer.

The proposed experiment will be performed with an ultra-high resolution VUV laser sent across two separated molecular beams in sequence, the first one is for attenuation of light ("*shielding*") by CO absorption, and the second one is for fragmentation of CO by photodissociation (Fig. 2). Following photodissociation of CO, all isotopic photofragments will be detected simultaneously by another spatially overlapped but temporally slightly delayed photoionization VUV laser. Isotopic exchange reaction is prevented as no collision occurs during molecular beam free expansion.
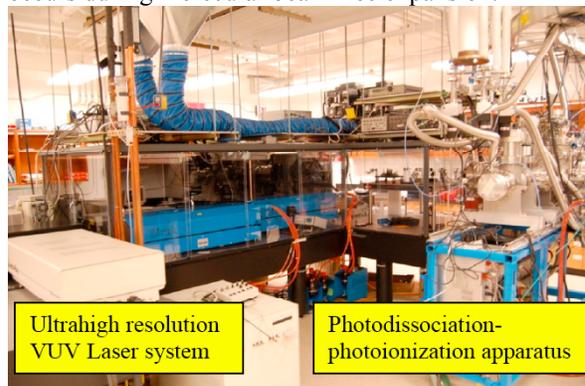


Fig. 1. The photograph showing the ultra-high resolution Vacuum Ultraviolet (VUV) laser photodissociation and photoionization apparatus in the laboratory of Chemistry Department at UC Davis. (Optical Bandwidth = 250 MHz, Intensity up to $10^{13}$ photons/pulse, Tuning range = 64-177 nm)
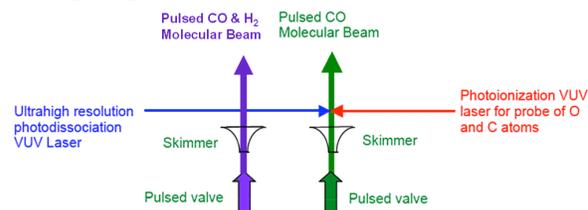


Fig. 2. All-in-one set up for the proposed CO self-shielding experiment. The VUV light paths are windowless. The CO & $H_2$ absorption and the CO photodissociation-photoionization region are located in partitioned differentially pumped vacuum chambers.

**Merits of Our Experimental Design:** Compared with the latest attempt of Thiemens' group at UC San Diego (13), in which a windowless flow tube at room temperature is used to test CO self-shielding at four fixed wavelengths of synchrotron light, our experiment has following merits:

1. Unmatched resolution and S/N ratio compared to synchrotron experiment. In the Chakraborty *et al.* (13) experiment, they set the monochromator at a wavelength bandwidth of 2.2 nm, or ≈2000 cm$^{-1}$ full-width at half-maximum (FWHM). The VUV beam profile centered at 105.17 nm and 107.61 nm would overlap. This could explain why the slopes derived from the

two wavelengths are identical (1.38 in their Fig. 1). A modern VUV laser has an optical resolution in the range of 0.1-0.008 cm$^{-1}$ (FWHM), which is several orders of magnitude higher than that used in the VUV synchrotron experiment of Chakraborty *et al.* (13). Since the high resolution offered by the VUV laser is needed to resolve the rotational absorption lines of CO in the VUV range of interest, the use of VUV laser should allow proper determination of the isotopic fractionation of oxygen atoms from CO self-shielding.

2. More relevant low temperature range of 10K-150K afforded by molecular beam technique. thus hypothesized astrophysical sites of CO self-shielding may be tested.

3. Isotopic exchange reaction is avoided in molecular beam environment. In Chakraborty *et al.* (13), Fig. 1 regression lines do not go through a zero intercept (initial starting composition) suggesting that the reaction (O+CO) at high temperature may alter the experimental results and complicate the interpretation of the data. In fact, it was shown by (14) that anomalous oxygen isotope enrichments in $CO_2$ could result from O+CO reaction alone, and the enrichment does not depend on the isotopic composition of O atom or the sources from which it is produced.

4. Coincident line shielding from $H_2$ on CO photodissociation will be included to simulate solar nebula composition.

5. In reporting their experimental data, Chakraborty *et al.* (13) should have summed up yields at different bands normalized by time integrated VUV photon fluence at different wavelength, and weighted by solar or interstellar VUV radiation field to get one oxygen isotopic composition. By varying the degree of "shielding" through changing gas cell pressure, a series of data points on the three oxygen isotope plot needs to be obtained to test the self-shielding hypothesis. Instead, they just plot raw data points measured for different bands.

**Controls on CO Photodissociation Temperature**: Since rotational energy spacing is in the range of thermal energy, rotational temperature is typically in equilibrium with translational temperature. The translational temperature of molecular beam can be described as: $T = T_o / (1 + M^2(\gamma-1)/2)$ where $T_0$ is source temperature, $\gamma = C_p/C_v$, $\gamma = 5/3$ for monoatomic and $\gamma = 7/5$ for diatomic,

$$M = Mach\# = \frac{V}{V_s} = \frac{mean\ flow\ speed\ of\ jet}{local\ speed\ of\ sound},$$

when $M > 1$, molecular beam becomes supersonic jet. Mean flow speed of jet is determined by: $\overline{V} = \sqrt{2C_p(T_0 - T)/m}$, where m is the mass of the molecule. The Mach# also depends on geometry of beam expansion condition: $Mach\# = A \bullet (D/d)^{\gamma-1}$ where A is constant, A=3.26 for monoatomic species, D is distance from nozzle, and d is diameter of nozzle orifice. At D=1cm distance away from nozzle and for orifice diameter of d=0.8mm, Mach# is about 17.6 for monoatomic molecule, and temperature is about T=2.8K. In practice, rotational temperature of CO molecular beam can be easily varied from 10K to 150K by varying beam expansion condition or using different carrier gas to vary the effective mass of the molecular beam, such as He, Ne, Ar, which typically does not participate in reaction.

**Estimation of Counting Rate:** A conservative signal-to-noise analysis shows that the VUV intensities of $10^{10}$-$10^{11}$ photons/pulse are already sufficient for the present proposed experiment to detect all O and C isotopic fragments from six CO isotopomers. Counting rate of atomic oxygen ion will be $I_O{}^+ = 611$ counts/pulse using:

$$I_{O^+} = \sigma_{CO \to O} \cdot \sigma_{O \to O^+} \cdot n_{CO} \cdot I_{Disso-VUV} \cdot I_{Ioniz-VUV} \cdot \ell \cdot \frac{4}{\pi d^2}$$

and counting rate of atomic carbon ion will be $I_C{}^+ = 3258$ counts/pulse using: $I_{C^+} = I_{O^+}(\sigma_{c \to c^+} / \sigma_{o \to o^+})$ Given abundance of oxygen and carbon isotopes, following isotopic ion counting rate are obtained using a 30Hz repetition rate VUV laser: $^{16}O^+ = $ 611/pulse x 99.76% x 30Hz = 18.3K counts/sec, $^{17}O^+ = $ 7.3 counts/sec, $^{18}O^+ = $ 36.7 counts/sec, $^{12}C^+ = $ 96.6K counts/sec, $^{13}C^+ = $ 1.0K counts/sec. The Multi-Channel Plate (MCP) ion detector typically has a noise level about 1~2 counts/min. Even for $^{17}O^+$, which has lowest counting rate, the signal-to-noise ratio will be:

S/N$_{17O+}$ = I$_{17O+}$ / I$_{noise}$ = 7.3 / 0.033 = 220,

which is sufficient for the proposed experiment.

**Conclusion:** Self-shielding may or may not ultimately explain the oxygen isotope anomalies for the early Solar System, but Chakraborty *et al.* (13) are far from disproving the case for self-shielding for the reasons outlined above. Much work remains to be done with the potential of the molecular beam technique combined with high resolution VUV laser in a windowless environment. Such experiments will shed new light on the oxygen isotope anomalies in the solar system known for over three decades but has defied consensus explanation as of today.

**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. Lodders (2003) *ApJ,* 591, 1220. [9] K. D. McKeegan et al. (2008) *LPSC XXXIX*, A2020. [10] K. Hashizume, M. Chaussidon (2005) *Nature*, 434, 619. [11] N. Sakamoto et al. (2007) *Science*, 317, 231. [12] C.-N. Ng (2002) *Annu. Rev. Phy. Chem* 53, 101. [13] S. Chakraborty et al. (2008) *Science*, 321, 1328. [14] A. Pandey, S. K. Bhattacharya, J. Chem. Phys., 124, 234301 (2006).