

We scanned the VUV₁ from 95082.0 to 95083.6, from 95055.8 to 95056.2, from 95031.65 to 95032.3 cm⁻¹, respectively, to excite ¹²C¹⁶O, ¹²C¹⁷O, and ¹²C¹⁸O to Q branches in state $E^1\Pi v=1$. The VUV₂ is fixed to a strong autoionization line of atomic O (³P) 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 VUV₁ we obtained the rovibrational spectra of oxygen for the Q branches of ¹²C¹⁶O, ¹²C¹⁷O, and ¹²C¹⁸O. Spectra were taken over the same VUV energy range under different shielding conditions. Intensities of ¹⁶O were attenuated by 5 to 99%. But intensities of ¹⁷O and ¹⁸O were almost not changed, suggesting no shielding for minor isotopologues of C¹⁷O and C¹⁸O.

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].

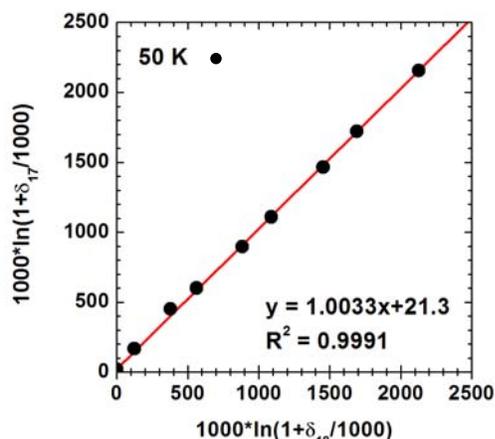


Fig. 2. Three-isotope plot of atomic ¹⁶O, ¹⁷O, ¹⁸O from predissociation of ¹²C¹⁶O, ¹²C¹⁷O, and ¹²C¹⁸O in Q ranch of $E^1\Pi v=1$. The molecular beam is at rotational temperature of 50K.

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(³P) and excited O(¹D) 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 $W^1\Pi v'=3$ (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(¹D). Over all, CO dissociation generates 6.9% O(¹D), weighed by the predissociation cross section.

On the other hand, N₂ 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]

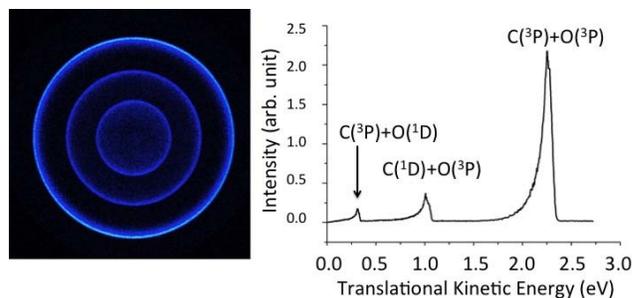


Figure 3. Left: Time-slice velocity-map ion image of CO at $W^1\Pi v'=3$ (92.58 nm) state. Each photoion ring represents a predissociation channel, whose brightness illustrates the intensity of the channel. Right: Reduced spectrum from the image. Each peak corresponds to a photoion ring.

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 $E^1\Pi v=1$ 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(¹D) is generated in the region of 90.5-110 nm. Comparing this result with 50% excited N generated from N₂ 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: [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] Lodders (2003) *ApJ*, 591, 1220. [8] McKeegan et al. (2011) *Science*, 332, 1528. [9] Shi et al. (2011) 42nd LPSC, A2705. [10] Marty B. et al. 2011. *Science* 332, 1533. [11] Clayton, R. N. (2011) 74th MetSoc, A.5010. [12] Walter et al, (1993) *J. Chem. Phys.* 99, 6421. [13] Buijsse et al, (1997) *J. Chem. Phys.* 107, 94475 [14] Gao, H. et al. (2011) *J. Chem. Phys.* 135, 221101. [15] Chakraborty et al. (2008) *Science*, 321, 1328. [16] Yin et al. (2009) *Science*, 324, 1516c. [17] Lyons et al. (2009) *Science*, 324, 1516a. [18] Federman and Young (2009) *Science*, 324, 1516b.