**OXYGEN ISOTOPIC FRACTIONATION IN VACUUM ULTRAVIOLET PHOTODISSOCIATION OF CO: LACK OF SELF-SHIELDING AND RELEVANCE TO THE EARLY SOLAR SYSTEM.**
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**Introduction:** Isotopically selective photodissociation of CO at vacuum ultraviolet (VUV) wavelengths has been invoked as a photochemical process in interstellar molecular clouds to explain the observed abundance variation of minor isotopologues of CO [1-2], a process known as isotopic self-shielding (SS). Isotopic SS of CO within the nebular disk has also been advocated as the source of isotopically anomalous oxygen in the solar reservoir and has been suggested as a mechanism for production of meteoritic oxygen isotopic compositions [3-6].

**Assumptions in the SS Models:** The SS models [1, 6 and references therein] have assumed the following: (i) the quantum yield of dissociation is unity (e.g., each photon absorption after light shielding leads to immediate dissociation), (ii) the oscillator strengths and predissociation probability for different isotopomers are same as those for $^{12}C^{16}O$ [1] (e.g., no isotope selectivity). Consequently, the isotope selectivity derives from only differential photon absorption and line saturation of the major isotopologue. This is incorporated into the various models through a parameter termed 'shielding function', which primarily depends on column densities of CO and $H_2$ [1, 6]. This readily yields a slope of unity in three-isotope oxygen space for the product atomic oxygen. Recently, spectroscopic studies show that the oscillator strengths and predissociation rates for different isotopologues of CO is different for a particular absorption band [7] and the photodissociation yield arises from the combination of: (i) band oscillator strength (*f*-value), and (ii) predissociation rate. Therefore, the basic assumptions of the SS models are invalid.

**Experimental Data Analysis:** Recently we published new oxygen isotope data from the VUV photodissociation of CO through a series of CO photodissociation experiments at the Advanced Light Source synchrotron [8], the only experimental tests of SS in CO. Four different synchrotron bands (s-bands) centered at 107.61, 105.17, 97.02, and 94.12 nm were used to photolyze CO of various column densities in different sets of experiment, and chosen such that $C^{16}O$ is optically thick ($\sigma cl = \tau > 1$) and the minor isotopologues are optically thin ($\tau \ll 1$). Results show that the product atomic oxygen is highly enriched and lies over regression line of various slope values in three-isotope oxygen space as shown in Figure 1.
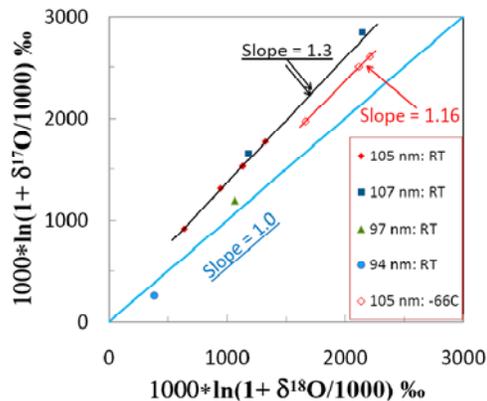


**Figure 1.** Oxygen isotopic composition of atomic oxygen produced by VUV photodissociation CO [8].

The s-bands are sufficiently wide (FWHM of ~ 2 nm) because of the synchrotron characteristics and more than one CO absorption feature contributes to the dissociation yield, but, are easily accounted for. Other than 105.17 nm CO bands, 106.31, 107.61 and 108.79 nm bands are also present within the measured s-band of 105.17 nm. The CO bands of 105.17, 106.31 and 108.79 nm are present within the 107.61 nm s-band (Figure 2); however the photon intensity available to these side bands is limited. Figure 2 shows the estimated contribution (%) of these side bands in the total dissociation yield.

SS or saturation of isotopologue specific line is only possible when the band heads of different isotopologues are separated. Based on available data [9], bands at 105.17 and 106.31 nm may self-shield, whereas 107.61 and 108.79 may not. It is estimated that for the 105.17 nm s-band ~ 66 % dissociation was potentially through the SS bands (105.17 and 106.31 nm) and only 34 % was through the non-SS bands (107.61 and 108.79 nm). In contrast, for 107.61 nm s-band, 78 % of dissociation occurs through non-SS bands. Therefore, 105.17 and 107.61 nm s-bands can be considered as potentially representative of SS and non-SS band, respectively. The isotope data show (Figure 1) that the products from these two s-bands fall in a same slope value of 1.3 and thus require the same physical process for both bands (SS and non-SS). This immediately rules out SS as a process and another process dominates CO in photolysis under astronomical environments.
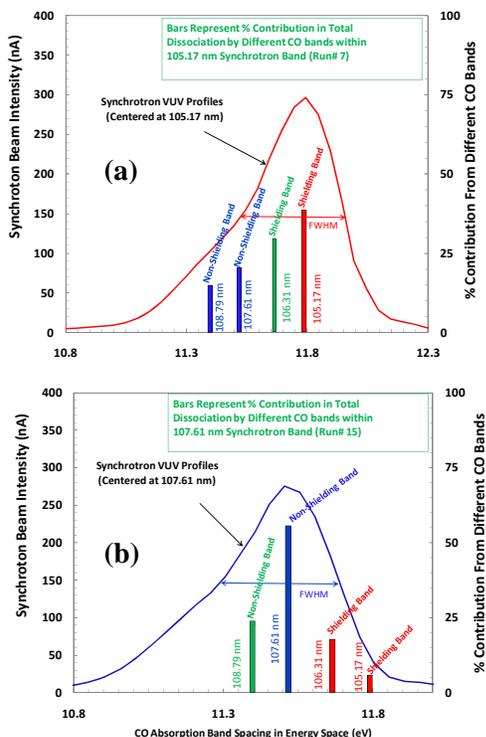
**Figure 2.** Synchrotron beam profile centered at (a) 105.17, and (b) 107.61 nm. A few CO absorption bands lie within each synchrotron bands. Bar represents (right axis) their relative contribution in dissociation yield (estimated based on $^{12}C^{16}O$).

**Accidental Predissociation in CO the Source of the Non-SS Isotope Effect:** A molecule predissociates with a certain probability when a bound electronic state couples to a continuous state. Coupling of a bound state to another intermediate bound state, which itself is predissociative may lead to electronic predissociation [10]. In the first case, all rotational (*J*-states) are affected, whereas, for the second case, predissociation may occur only through *J*-states that coincide with the *J*-states of the intermediate state. This creates a narrow leaky channel for dissociation. The upper electronic state ($E^1\Pi$) of CO in VUV region show two leaky channels for dissociation corresponding to $\nu = 0$ and 1 vibrational states, respectively. The bound rydberg state $E^1\Pi$ is coupled to an intermediate bound state $k^3\Pi$ (*via* spin-orbit coupling), and leads to (accidental) predissociation near $J = 31$ and 9 for $^{12}C^{16}O$, respectively for the $\nu = 0$ and 1 states [10] and is a near resonance phenomenon. $k^3\Pi$ predissociates though a repulsive $^3\Pi$ state. These two leaky channels related to vibrational states at 107.61 and 105.17 nm and likely to be isotope selective [11]. Therefore, isotope selectivity in photodissociation of CO does not result from

the simple photon absorption process as assumed by SS models [1, 6] rather follows a three-step isotope selectivity scheme as shown in Figure 3.
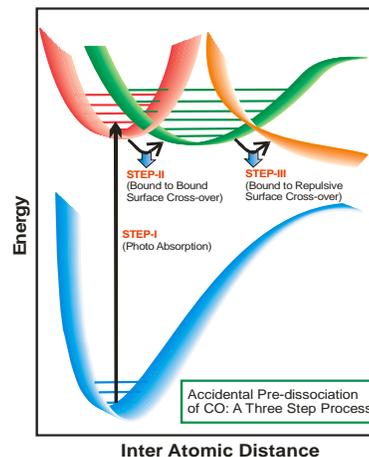


**Figure 3.** Schematic showing a three-step isotope selectivity dissociation scheme with absorption of light as step-I. Dissociation through a narrow leaky channel due to accidental predissociation as step-II and predissociation to the repulsive surface as step-III.

**Discussion:** The two leaky isotope selective dissociation channels may be responsible for the observed fractionation (the same slope value for 105.17 and 107.61 nm) and *not self-shielding*. Comparison of similar column density runs for 105.17 and 107.61 nm s-bands (Run# 3 and 14 in Table-1 of [8]) yield higher fractionation for 107.61 nm s-band provides another evidence that SS is not operative because 78 % dissociation yield comes from non-SS bands (107.61 and 108.79 nm together). Moreover, The lower slope value for -66 °C experiment at 105.17 nm s-band [8] may also be explained through the same *J*-sensitive accidental predissociation as it produce lower yield and do not scale with absorption cross-section, which is at least twice than that at room temperature [9]. Thus, all experiments do not support current SS models.

**References:** [1] van Dishoeck E. F. and Black J. H. (1988) *Astrophys J., 334*, 771–802. [2] Federman S. R. et al. (2003) *Astrophys J., 591,* 986-999. [3] Thiemens M. H. and Heidenreich J. E. (1983) *Science, 219*, 1073–1076. [4] Clayton R. N. (2002) *Nature, 415*, 860–861. [5] Yurimoto H. and Kuramoto K. (2004) *Science, 305*, 1763–1766. [6] Lyons J. R. and Young E. D. and (2005) *Nature, 435*, 317–320. [7] Eidelsberg M. et al. (2006) *Ap. J., 647*, 1543–1548. [8] Chakraborty S. et al. (2008) *Science, 321,* 1328–1331. [9] Eidelsberg M. et al. (1991) *Astron. Astrophys. Suppl., 90*, 231–282. [10] Cacciani P. et al. (1995) *J. Chem. Phys., 102*, 8308–8320. [11] Bhattacharya S. K. et al. (2000) *GRL, 27*, 1459–1462.