SIMULATION OF THE MASSIVE FRACTIONATION OBSERVED IN CO PHOTODISSOCIATION EXPERIMENTS. J. R. Lyons[1] and G. Stark[2]. [1]IGPP, University of California, Los Angeles, CA 90095 USA; jimlyons@ucla.edu. [2]Department of Physics, Wellesley College, Wellesley MA 02481 USA

Introduction: The observation of massive fractionation (~10,000 ‰) in CO_2 produced in laboratory CO photolysis experiments [1] provides a superb illustration of the process of self-shielding. Self-shielding results from the saturation of CO isotopologue absorption lines, and yields an abundance-dependent fractionation upon dissociation. Because $^{12}C^{16}O$ is ~ 500 times more abundant than $^{12}C^{18}O$, saturation of $^{12}C^{16}O$ lines occurs at much lower gas column densities than for the rare isotopologues, creating a region of ^{17}O and ^{18}O-enriched O atoms. CO self-shielding is essential to understanding the distribution of oxygen isotopes in the solar system [2],[3],[4]. For the experiments performed in [1] the typical column densities were ~ 10^{18} cm^{-2}, implying $^{12}C^{16}O$ optical depths > 1000 [5]. Thus, self-shielding was unavoidable in these experiments. In order to elucidate the origin of the large fractionations measured in [1], we have performed detailed modeling of the photolysis of the CO E(0) – X(0), E(1) – X(0), and C(1) – X(0) bands at 107.6, 105.17, and 106.3 nm, respectively. To the cross sections computed in [6] we have included the perturbation of the E(1) state by the k(6) triplet state using the formalism of [7].

Results: For simulation of the experiments at 105.17 nm, the model $\delta^{x}O'(CO_2)$ values are ~ 6,000-12,000 ‰ (comparable to measured values), but have a δ^{17}/δ^{18} slope ~ 1.05, lower than the measured value of 1.3. $\delta^{x}O'(CO_2)$ decrease with CO column density and become negligible when optical depth is << 1, as expected for a self-shielding effect. Low optical depth experiments are needed to confirm this result. The δ^{17}/δ^{18} slope can be accounted for by a 30% stronger band oscillator strength for $^{12}C^{17}O$ versus $^{12}C^{18}O$. However, we do not expect such large isotopic variation in band oscillator strengths, and doubt that this is a satisfactory explanation.

Simulation results [6] for the synchrotron beam at 107.61 nm (E(0) band) show that a slope ~ 1.4, comparable to the measured values, occurs at the highest column densities (as observed), but is not present at lower densities. It is important to note that self-shielding does occur in this band, contrary to the claims of [1]. The non-unity δ^{17}/δ^{18} slope arises from the pattern of closely overlapping lines among the isotopologue spectra.

Conclusions: The key results here are that massive fractionation is expected from self-shielding alone, and that the fractionation depends on wavelength. The δ^{17}/δ^{18} slope associated with CO photolysis must be determined from the summation over all CO bands for comparison with the CAI line (0.95-1.0).

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