EXPLORING $^{12}$CO/$^{13}$CO ICE-GAS FRACTIONATION THROUGH INTERSTELLAR ICE-ANALOG EXPERIMENTS. L. R. Smith¹, E. M. Panto¹, M. S. Gudipati², R. L. Smith¹,³,⁴, ¹Appalachian State University (smithlr2@appstate.edu), ²Jet Propulsion Lab, California Institute of Technology (Murthy.Gudipati@jpl.nasa.gov), ³NC Museum of Natural Sciences (rachel.smith@naturalsciences.org), ⁴UNC Chapel Hill.

Introduction: Understanding carbon chemistry in forming planetary systems is key toward establishing comprehensive evolutionary pathways for carbon in the formation of planets and prebiotic molecules. Carbon monoxide (CO) is a valuable tracer of this chemistry, from molecular clouds and envelopes, to protoplanetary disks. Observations of young stellar objects (YSOs) tracing a range of these protoplanetary reservoirs reveal an unexpected heterogeneity in the $[^{12}\text{C}]^{16}\text{O}/[^{12}\text{C}]^{18}\text{O}$ abundance ratio in forming systems close to the Sun (Galactocentric radius of ~8 kpc), with $[^{12}\text{CO}]/[^{13}\text{CO}]$ ranging from ~85 to 165 [1]. Comparison of the CO ice fraction ($[^{12}\text{CO}]_{\text{ice}}/[^{12}\text{CO}]_{\text{gas}} + [^{13}\text{CO}]_{\text{gas}}$) against the gas-phase $[^{13}\text{CO}]/[^{12}\text{CO}]$ suggests that CO ice-gas fractionation may play a role in the observed heterogeneity in YSOs ([1], Figure 1), and therefore could be an important driver in protoplanetary carbon chemistry.

It has been proposed that differences in the zero-point energies (ZPEs) between CO isotopologues could lead to significant preferential fractionation of the lighter isotopologues [2,3]. Toward exploring potential ZPE affects on the photodesorption of $^{12}$CO and $^{13}$CO as a possible explanation for the $[^{12}\text{CO}]/[^{13}\text{CO}]$ heterogeneity observed toward YSOs, we performed ice-analog experiments in the Ice Spectroscopy Laboratory at the Jet Propulsion Laboratory, under near-astrophysical conditions. We are currently investigating thermal desorption and photodesorption, phenomena thought to be important in the chemistry of protoplanetary ices [3,4,5].

Methods: Experiments were conducted under near-astrophysical temperatures (~10 to 35 K) and pressures (~10⁻⁷ to 10⁻⁹ mbar). The experimental setup is shown in Figure 2. CO ice was formed by first cooling the system to 20 K and depositing a natural abundance ($[^{12}\text{CO}]/[^{13}\text{CO}]$, 99:1) of CO gas at pressures ranging from 5×10⁻⁷ to 2×10⁻⁵ mbar, deposited for between 15 minutes and 72 hours, depending on the abundance of ice to be tested in each experiment. The gas in the system was monitored using a Residual Gas Analyzer (quadrupole mass spectrometer) to determine composition of the remaining gas in the vacuum, and a Fourier Transform Infrared Spectrometer (FTIR) was used to examine the composition and abundance of the components in the ice sample.

A sample spectrum of CO ice at 28 K is shown in Figure 3. A CO sublimation curve was derived as a benchmark for the thermal desorption and photodesorption...
Figure 3: Sample FTIR spectrum taken at 28 K, showing the four major CO isotopologues, $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, and $^{13}\text{C}^{17}\text{O}$.

Figure 4: Initial results from experiments establishing the CO sublimation point.

Results: Onset of sublimation for thin CO films (a few 100 nm) was above 28 K, with the first observable depletion of CO ice absorption at 28.5 K (Figure 4). In a separate experiment, it was observed that over a period of 5 hours when held at 28.5 K, the thin CO ice film completely sublimated, suggesting that under astronomical time scales, sublimation of CO could occur between 28 and 28.5 K. Initial photodesorption experiments. CO ice temperature was increased to 25 K, then to 27 K in 0.5 K intervals at a rate of 0.1 K/min, with spectra taken at each interval to measure changes in ice concentration. The ice temperature was increased in 0.1 K intervals until the ice completely sublimated. Any preferential isotopologue photodesorption was tested by exposing the CO ice to ionizing Lyman-$\alpha$ radiation (121.6 nm 10.2 V), with emission monitored using UV spectroscopy. Ice samples were irradiated until all of the ice was photodesorbed. During irradiation, ice and gas were monitored simultaneously to compare $[^{12}\text{CO}] / [^{13}\text{CO}]$ at constant intervals.

Figure 5: Preliminary results showing the evolution of integrated absorption intensities of $^{12}\text{CO}$, $^{13}\text{CO}$, and $^{12}\text{CO}$ overtone bands. The $^{12}\text{CO}$ fundamental curve is normalized with the overtone to be in the same scale. The $^{12}\text{CO}$ fundamental absorption was tested by exposing the CO ice to ionizing Lyman-$\alpha$ radiation (121.6 nm 10.2 V), with emission monitored using UV spectroscopy. Ice samples were irradiated until all of the ice was photodesorbed. During irradiation, ice and gas were monitored simultaneously to compare $[^{12}\text{CO}] / [^{13}\text{CO}]$ at constant intervals.

Conclusions and Future Work: Preliminary results from new CO ice-analog experiments under astrophysical conditions reveal a sublimation temperature of 28.5 K for thin CO ice films. Thus far, no preferential difference was found between $^{12}\text{CO}$ and $^{13}\text{CO}$ in photodesorption at 30 K. Experiments will be repeated in the coming months to verify results, and lower temperatures will be tested with interstellar ratios of $[^{12}\text{CO}] / [^{13}\text{CO}]$. Thermal desorption experiments will incorporate CO$_2$ and H$_2$O ices in relevant mixtures with CO to investigate the effects of various astrophysical mixtures on fractionation in CO reservoirs.

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