NEW ^{12}CO AND ^{13}CO BINDING ENERGY MEASUREMENTS: AN EXPLANATION FOR SYSTEMATIC TEMPERATURE DIFFERENCES OBSERVED IN COLD PROTOPLANETARY RESERVOIRS.

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Introduction: High-resolution spectroscopic observations of CO in absorption trace molecular gas along a single line of sight, enabling the precise derivation of molecular abundances of CO isotopologues, and integrated gas temperatures through the envelope and disk [e.g.,1-4]. Such data provide valuable insights into the evolution of young stellar objects (YSOs) in a range of protoplanetary environments, informing mysteries surrounding nebular processes such as CO self-shielding in the solar nebula [e.g.,3,5], supernova enrichment of the protostellar cloud [6], and potential influence of CO ice on the gas-phase reservoir at various stages of YSO evolution [4].

In addition to high-resolution astronomical observations, experiments under controlled astrophysical conditions are also important for understanding phenomena that could influence the formation of planets and prebiotic molecules. As part of our interdisciplinary study toward understanding protoplanetary processes in carbon reservoirs, precise sublimation temperatures and binding energies for $^{12}C^{16}O$ and $^{13}C^{16}O$ (heretofore, ^{12}CO and ^{13}CO) were carried out in the Ice Spectroscopy Lab at JPL [7]. These new results can now help explain the systematically lower temperatures observed for ^{13}CO vs. ^{12}CO in cold-gas regimes toward YSOs [2,4]. This trend in CO isotopologue temperature observations is one that we continue to observe with precision, but until now has defied explanation.

Methods: Astronomical observations. Using high spectral resolution on large ground-based telescopes, we observed CO in rovibrational absorption in the $M-$bands ($v = 1-0$) for optically thin ^{13}CO and $^{12}C^{18}O$, and $K-$bands ($v = 2-0$) for ^{12}CO, ensuring that all analyzed lines would have relatively similar optically thin depths. For comparison to low-mass YSOs observed with VLT-CRIRES ($R \sim 95,000$) [3,4], we began a survey of bright, massive YSOs across the Galaxy using Keck-NIRSPEC ($R \sim 25,000$) [8; R.L. Smith et al., in prep], and are currently using NASA's infrared research telescope facility (IRTF)-iSHELL ($R \sim 80,000$). Figure 1 shows sample spectra from our new iSHELL study. Following the methods in [3] for spectrally resolved CO lines, molecular column densities for each YSO were obtained by fitting each spectral line with a Gaussian and deriving optical depths using the mean line width from the $^{12}C^{18}O$ lines. Assuming a Boltzmann distribution, a rotational analysis was used to derive final total isotopologue column densities and integrated excitation temperatures, using one- or two-temperature models (Figure 2). Experiments: Precise binding energies (E_b) for ^{12}CO and ^{13}CO ices were obtained under astrophysical conditions (10 to 35 K; 10^{-7} to 10^{-9} mbar) in the Ice Spectroscopy Lab at JPL. Methods included a combination of *temperature programmed desorption* (TPD, following [9]) and a new procedure termed *temperature interval desorption* (TID) that ensures equilibration for a given temperature for pure ^{12}CO and ^{13}CO ices. Using the Arrhenius equation that connects the pre-exponential factor ($\nu_\circ$) and E_b, TPD experimental data were used to independently derive $\nu_\circ$ as a free parameter. TID experimental data were then used with the average $\nu_\circ$ from the TPD experiments to precisely determine final E_b values. Figure 3 shows one of the TPD experiments with pure ^{13}CO ice [7].

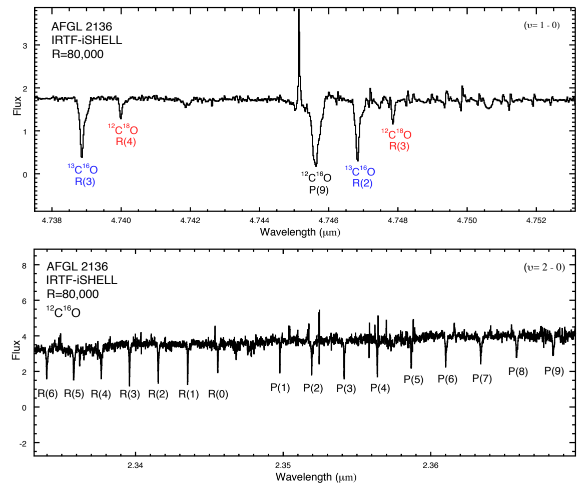

Figure 1: Portions of $M-$ (top) and $K-$ (bottom) band spectra of massive YSO AFGL 2136 observed at very high spectral resolution (IRTF-iSHELL, $R \sim 80,000$). Representative CO isotopologue lines are marked (Smith & Boogert, new data).

Results and Discussion: YSO cold gas-phase temperatures for ^{12}CO and ^{13}CO from our ongoing current observations and from the literature [2,4] are shown in Figure 4. For nearly all YSOs, integrated excitation temperatures for cold (5 to 57 K) CO regimes are found to be systematically lower for ^{13}CO than for ^{12}CO along the same line of sight. These temperature differences range from 0 to 23 K, with the majority of targets showing differences of 15 K or less. From the new experiments, precise binding energies are:

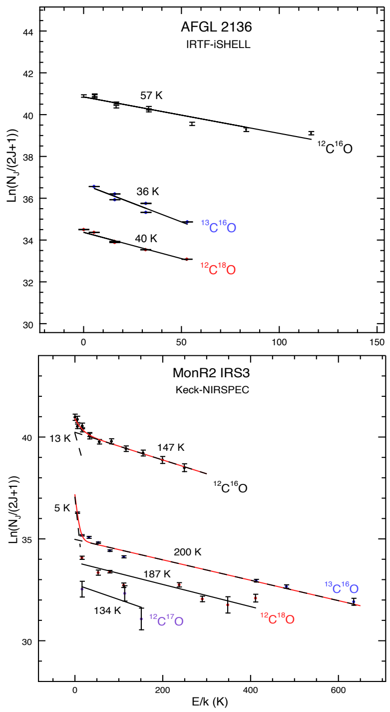

Figure 2: Two recent rotational analyses for massive YSOs AFGL 2136 (IRFT-iSHELL; R. L. Smith & Boogert, new data) and MonR2 IRS3 (Keck-NIRSPEC; Blake & R. L. Smith, new data). Single- and two-temperature fits are shown. Error bars are 1σ, E_J is the J^{th} rotational state energy, k is the Boltzmann constant.

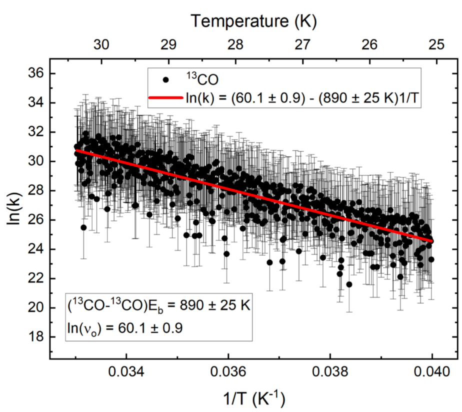

Figure 3: Arrhenius plot from one of the TPD experiments with ^{13}CO ice. The pre-exponential ($\nu_{\circ}$) was taken as a free parameter, resulting in a TPD-derived E_b = 890 $\pm$25 K [7].

(^{12}CO-^{12}CO)E_b = (833 $\pm$ 1 K) and (^{13}CO-^{13}CO)E_b = (848 $\pm$ 1 K), with an average $E_b \sim$ 840 K assumed for mixed ^{12}CO-^{13}CO ices. Also measured is a systematic 0.1 K sublimation temperature difference between ^{12}CO (28.9 K) and ^{13}CO (29.0 K). In astrophysical settings, these results support the assumption that ^{13}CO is more strongly bound in the ice phase than ^{12}CO [7]. Thus, for a given integrated temperature observation, less energy should be in the gas vs. the ice phase for ^{13}CO, and the lower temperatures

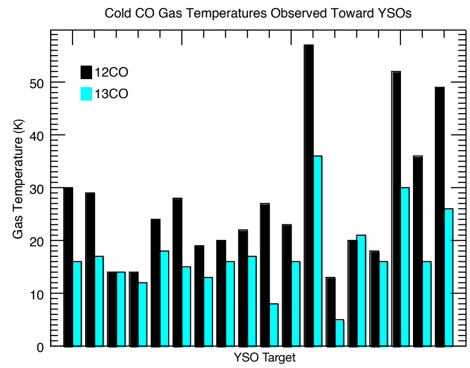

Figure 4: Compilation of integrated cold-regime ($<$ 60 K) ^{12}CO and ^{13}CO gas temperatures from our massive YSO IRTF-iSHELL and Keck-NIRSPEC data, and from Subaru-IRCS [2], and VLT-CRIRES for low-mass YSOs [4]. Each temperature pair represents a single YSO target.

we observe for ^{13}CO compared to ^{12}CO in cold gas-phase reservoirs may be at least partially explained by ^{13}CO requiring more energy than ^{12}CO to sublimate from the ice. Interestingly, at gas-phase temperatures $>\sim$ 90 K, this trend is observed to reverse in both massive and low-mass YSOs [2,4, R. L. Smith et al., new data] – a possible signature of varying chemical pathways for CO gas-phase reservoirs.

Conclusions: We report systematically lower ^{13}CO cold gas-phase temperatures as compared to ^{12}CO along a single sight line for nearly all YSOs observed at high spectral resolution, including in our current IRTF-iSHELL project. This trend can be explained, at least in part, by the new, precisely measured higher binding energy for ^{13}CO compared to ^{12}CO. This quantification of ^{13}CO being more tightly bound in the ice phase should be considered for models of CO processing along key chemical pathways for a range of YSOs and the solar nebula. Future observational testing will include astronomical strategies using large telescopes and high-resolution instruments for CO isotopologue detection at different energy transitions.

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