

WAVELENGTH DEPENDENT ISOTOPIC FRACTIONATION IN CO PHOTOLYSIS: EXPERIMENTAL FINDINGS RELEVANT TO THE SOLAR NEBULA.

Subrata Chakraborty¹, M. Ahmed² and M. H. Thiemens¹,
¹Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0356 (subrata@chem.ucsd.edu), ²Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720.

Introduction: Isotopically selective dissociation of CO (the most abundant nebular oxygen bearing molecule) is invoked as a significant photochemical process in interstellar molecular clouds [1-3] to explain the observed over abundance of minor isotopomers of CO ($^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{12}\text{C}^{17}\text{O}$). This process is known as isotopic self-shielding and has been suggested as a mechanism to explain the oxygen isotopic composition of meteoritic material [4-7]. There have been no experiments that measure the relevant isotopic fractionation factors associated with UV-CO photochemistry.

Our laboratory is engaged in CO photochemistry experiments at the short wavelengths relevant to nebular photochemistry [8-9]. Eventual verification of models and continued development requires measurement of isotopic fractionation factors associated with specific quantum processes. Here we present new data and discuss the potential importance and relevance of excited state photo-physics under nebular conditions.

Experiment: We have pursued CO photochemistry experiments in the laboratory at three different wavelengths centered at 107.6, 108.75 and 147.5 nm at the Advanced Light Source (ALS) of Lawrence Berkeley Laboratory's synchrotron facility with a maximum photon flux of 1×10^{16} photons/sec. This addresses the excited states $E^1\Pi$, $C^1\Sigma^+$ and $A^1\Pi$, respectively. A stainless steel photolysis chamber was designed and used for this purpose. The chamber was fitted with a LiF window (1 mm thick). The photolysis chamber was equipped with a Baratron capacitance manometer to monitor the inside gas pressure, three (each 10 inch long) cold fingers trap the condensable gases during photolysis. A manifold facilitates evacuating the chamber, introducing high-purity CO gas (of known isotopic composition) and hydrogen (in some cases), and extraction of the photolysis products. The length of the chamber varied from 90 to 120 cm to vary the optical path length during different experiments. At 108.75 nm two sets of photolysis experiments were carried out (photolysis duration of each experiment was 7 to 8 hours). The first one with pure CO (high purity, 99.995 %) and the second one with a mixture of H_2 and CO with varying ratio from 1.0 to 3.0 in different steps. At 147.5 nm, only pure CO Photolysis was carried out (with duration of 3 hours for each experiment). The CO column densities used in the experiments range from 10^{19} to 5×10^{20} mol/cm². In all the experiments, the product CO_2 was collected and ana-

lyzed for oxygen isotopes (^{17}O and ^{18}O) by CO_2 fluorination.

Results: Figure 1 shows the oxygen isotopic compositions of the product CO_2 in different experiments along with the initial and leftover CO compositions.

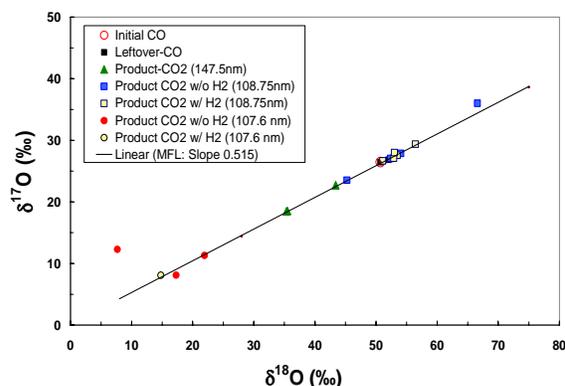
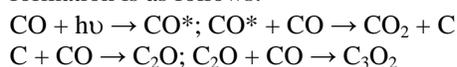


Figure 1. Oxygen isotopic composition of initial and residual CO and product CO_2 during CO photolysis at different wavelengths. Except one experiment at 107.6 nm (at initial CO pressure of 42 torr, which is much lower than the other experiments at the same wavelength), all data lie over the mass fractionation line (of slope 0.515).

CO Photochemistry: It is well known that CO is photodissociated by absorption of VUV photons on discrete lines [2]. The excited (Rydberg) states are mostly predissociated through the interaction with continuum states. In the wavelength region 90 to 110 nm, there are numerous strong absorption bands (a total number of 41 bands are identified and among them ~12 having integrated absorption cross section exceeding 10×10^{-18} cm² nm) [10-11]. Interestingly, in the above mentioned wavelength region, absorption in all the bands do not lead to (or insignificant) dissociation (e.g. band at 108.79 nm with an upper state $C^1\Sigma^+$ ($v=0$)).

For most of the bands, the lines for their corresponding isotope species are sufficiently shifted and thus the mutual shielding (by C^{16}O) is not effective. In the presence of hydrogen (as in the case of the solar nebula), the effective absorption spectra becomes more complex. Not only are a large number of band systems of CO shielded by the strong absorption of hydrogen, isotopically selective shielding of the lines renders the situation complex. All of the lines (corresponding to all the isotope species of CO) of a particular band system are not effected by hydrogen lines, rather hydro-

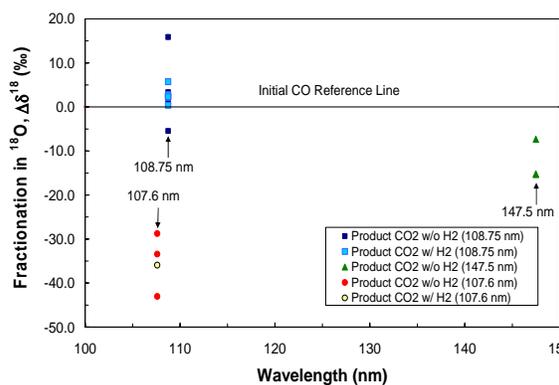
gen lines effect different lines of CO-isotopic species of different CO absorption band systems in a random way. For example, the band at 105.17 (with upper state $E^1\Pi$ ($v = 1$)) is suggested as being responsible for 58 % of $C^{18}O$ dissociation (with equal absorption and dissociation cross sections of $\sim 2.5 \times 10^{-18} \text{ cm}^2 \text{ nm}$) [2], where as there is no photodissociation of $C^{16}O$ at this band. The opposite is true for the band system at 107.6 nm (with upper state $E^1\Pi$ ($v = 0$) and absorption and dissociation cross sections $> 30 \times 10^{-18} \text{ cm}^2 \text{ nm}$). Other than these predissociative band systems below 110 nm, an absorption band system exists in the region of 120 to 160 nm (termed the 4th positive system ($A^1\Pi - X^1\Sigma^+$) with absorption cross section close to $3.0 \times 10^{-18} \text{ cm}^2 \text{ nm}$ and with no dissociation cross section [12]. These non-dissociative band systems are interesting, since, these lines are not shielded by hydrogen (as it is the case for the lines below 110 nm) and relatively moderate amounts of absorption occurs at these wavelengths without dissociation leading to the formation of CO^* (electronically excited CO). There are few studies over the photolysis product of CO and the proposed mechanism [13] for the product formation is as follows:



The main draw back of metastable state photochemistry is the radiative lifetime of the state involved. Mostly, metastable states have lifetimes in the range of ms to ns and thus may not be suitable for chemical reactions under nebular conditions. However, CO is an interesting molecule having strong singlet-triplet perturbation in the excited states [14] and serves as a model molecule to study intersystem crossing. The radiative transitions directly to the ground state are forbidden for most of the excited states [15]. It was shown that the lifetime of $a^3\Pi$ state is large (~ 3.7 ms) and, $X^1\Sigma^+ \leftarrow a^3\Pi$ transition is spin forbidden and thus it borrows intensity from the $X^1\Sigma^+ \leftarrow A^1\Pi$ transition due to an amount of $^1\Pi$ character in the $^3\Pi$ wavefunction [16]. This phenomenon of interaction with the neighboring triplet states increases the effective lifetime of the $A^1\Pi$ state, though its own lifetime is in the order of μs [17]. At present, there is no study for the $C^1\Sigma^+$ state, though one may plausibly assume the same extended lifetime for the $C^1\Sigma^+$ state since the nature of singlet-triplet interaction remains the same.

Discussion: In the present experiments, isotopic fractionation due to the absorption of three different energy photons (11.5, 11.4 and 8.4 eV) was measured. The fractionation in ^{18}O appears to be wavelength dependent. For 107.6 and 147.5 nm photons, the product CO_2 is depleted with respect to initial CO, though the

extent of fractionation is different (Figure 2). The direction of fractionation at 108.75 nm is opposite, i.e., the product CO_2 is enriched with respect to initial CO (Figure 2). The photo-chemical mechanisms at different wavelengths are different as described in the previous section. There is no photodissociation at 108.75 and 147.5 nm, though they display an opposite fractionation with respect to the initial CO. Photodissociation is possible only at 107.6 nm and it shows the highest fractionation at this wavelength (~ -30 to -40 % depending upon experimental condition). The presence of hydrogen at 107.6 and 108.75 nm experiments does not change the overall fractionation pattern.



photolysis at different wavelengths relative to initial CO composition.

Based on this wavelength dependent fractionation experiment, a more extensive study of fractionation for all wavelengths (where CO absorption take place) is needed for incorporation of this fractionation in nebular photochemical models that explain the oxygen isotopic composition of the early solar system.

References: [1] Bally J. and Langer W. D. (1982) *Astrophys. J.*, 255, 143-148. [2] van Dishoeck E. F. and Black J. H. (1988) *Astrophys J.*, 334, 771-802. [3] Federman S. R. et al. (2003) *Astrophys J.*, 591, 986-999. [4] Thiemens M. H. and Heidenreich III J. E. (1983) *Science*, 219, 1073-1075. [5] Clayton R. N. (2002) *Nature*, 415, 860-861. [6] Yurimoto H. and Kuramoto K. (2004) *Science*, 305, 1763-1766. [7] Lyons J. R. and Young E. D. (2005) *Nature*, 435, 317-320. [8] Chakraborty S. and Thiemens M.H. (2005) *LPS XXXVI*, Abstract #1113. [9] Chakraborty S. and Thiemens M.H. (2006) *LPS XXXVII*, Abstract #1436. [10] Letzelter C. et al. (1987) *Chem. Phys.*, 114, 273-288. [11] Eidelberg M. H. et al. (1992) *Astron. Astrophys.*, 269, 839-842. [12] Herzberg G. (1989) *Krieger Publishing Co.*, 452-453. [13] Okabe H. (1978) *Wiley-Interscience Publications*. [14] Provorov A. C. et al. (1977) *J. Chem. Phys.*, 67, 5393-5394. [15] Wells W. C. et al. (1973) *Phys. Rev A*, 8, 2463-2468. [16] Jongma R. T. et al. (1997) *J. Chem. Phys.*, 107, 7034-7040. [17] Strobl K. H. and Vidal C. R. (1986) *J. Chem. Phys.*, 86, 62-70.