

**PHOTOLYSIS OF CO AT LONG WAVELENGTHS: COMPARISON WITH LABORATORY EXPERIMENTS AND IMPLICATIONS FOR THE SOLAR NEBULA** J. R. Lyons<sup>1</sup>, G. Stark<sup>2</sup>, A. N. Heays<sup>3</sup>, P. L. Smith<sup>4</sup>, M. Eidelsberg<sup>5</sup>, S. R. Federman<sup>6</sup>, J. L. Lemaire<sup>5</sup>, L. Gavilan<sup>5</sup>, N. de Oliveira<sup>7</sup>, D. Joyeux<sup>7</sup>, and L. Nahon<sup>7</sup>, <sup>1</sup>School of Earth and Space Exploration, Arizona State University, 781 South Terrace Road, Tempe, AZ 85281, USA, jimlyons@asu.edu; <sup>2</sup>Department of Physics, Wellesley College, Wellesley, MA 02481, USA; <sup>3</sup>Leiden Observatory, Leiden University, PO Box 9513, 2300 RA Leiden, The Netherlands; <sup>4</sup>93 Pleasant Street, Watertown, MA 02472, USA; <sup>5</sup>Observatoire de Paris, 5 place Jules Janssen, F-92195 Meudon, France; <sup>6</sup>Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606, USA; <sup>7</sup>Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, BP 48, F-91192 Gif sur Yvette Cedex, France.

**Introduction:** CO isotopologues are used extensively as probes of the physical conditions of molecular clouds and protoplanetary disks. In cosmochemical studies of the solar system, accurate quantification of oxygen isotope fractionation during CO photolysis provides a key consistency test of the CO self-shielding hypothesis as the source of the CAI mixing line [1]. For these reasons, we have been performing high resolution absorption cross section measurements of 5 stable isotopologues of CO (<sup>13</sup>C<sup>17</sup>O the lone exception) using the VUV Fourier transform spectrometer (FTS) at the Soleil synchrotron. We have recently published greatly improved *f*-values (electric dipole oscillator strengths) for several dissociating bands of CO isotopologues from 105 to 108 nm [2]. These are the longest-wavelength dissociating bands for CO, and are particularly important for determining oxygen isotope fractionation in molecular clouds [3].

Laboratory photolysis experiments on natural abundance CO have found high <sup>17</sup>O and <sup>18</sup>O enrichment in product CO<sub>2</sub>, and  $\delta^{17}\text{O}/\delta^{18}\text{O}$  (logarithmic) slopes ranging from ~ 0.7 to 1.3 [4]. These results have been used to argue against a self-shielding origin for the CAI line, given the wavelength dependence of the isotope slopes. Model simulations of the experiments using synthesized line-by-line spectra were able to reproduce the magnitude of the isotope fractionation measured, and broadly reproduced slopes at shorter wavelengths (< 100 nm) [5]. However, the experimental slopes in the longer wavelength bands (105 and 107 nm) were both ~ 1.3, and the model simulations could reproduce these results only by assuming large isotopic variations in CO dissociation probabilities for the E(1) and E(0) bands, at 105.2 and 107.6 nm, respectively [5]. Measurements of isotopologue state lifetimes (from linewidths) [6] for the E(1) – X transition rule out this possibility for the E(1) band. Lifetime data is not available for the E(0) state, although we do not expect large (~ factor of 2) variations in dissociation probability with isotopologue for this state. (See [5] for further discussion.)

Here we evaluate fractionation in the long wavelength bands of CO using the most accurate spectra available [2]. Our objective is to understand the cause of the slopes seen in the long-wavelength photolysis experiments [4]. Reconciling the photolysis experiment results with model simulations is essential to confidently moving forward with models of oxygen isotope fractionation in astrochemical environments, especially the solar nebula.

**Spectra and photolysis model results:** Figure 1 shows computed spectra using *f*-values measured at Soleil [2]. The computation includes the weak interaction between the E<sup>1</sup>Π(1) and k<sup>3</sup>Π(6) states [6]. This interaction, suggested to be the source of the ~1.3 slope from the photolysis experiments [4], is most evident in the <sup>13</sup>C<sup>16</sup>O (1316) Q-branch (central peak), but is otherwise of negligible importance.

Corresponding optical depths are shown in Figure 2 for a CO (1216) column abundance of  $3 \times 10^{17} \text{ cm}^{-2}$ . (The column depths in [4] were ~ 1-11  $\times 10^{17} \text{ cm}^{-2}$  in a photocells of length 48-180 cm.) The very high optical depths of the 1216 line peaks produce the massive self-shielding-derived enrichment in <sup>17</sup>O and <sup>18</sup>O photo-products (O and CO<sub>2</sub>). The peaks of 1316 are also optically thick, as is the Q-branch of 1218. Self-shielding by 1218 implies a  $\delta^{17}\text{O}/\delta^{18}\text{O}$  slope > 1, qualitatively consistent with the photolysis experiments. The E(0) band at 107.6 nm is ~ 15 times stronger than E(1), and the optical depths are correspondingly higher.

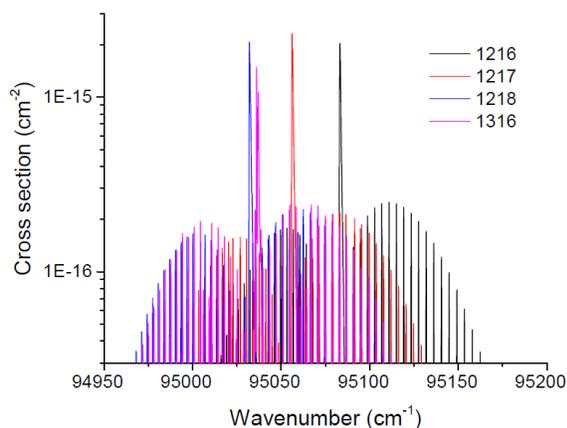
Photochemical modeling of the experiments is carried out with a 1-D time-dependent photochemical code [5]. Molecular diffusion along the axis of the photocell is accounted for, but the same value of diffusion coefficient is used for all masses. Zero-flux boundary conditions are enforced at the ends of the photocell, assumed to be 100 cm in length, and with a 1cm grid size. The ALS beam is incident at one side of the cell, with intensity values and beam shape taken from [4] (photon flux across beam is ~  $5 \times 10^{14} \text{ ph s}^{-1}$ ). CO<sub>2</sub>, CO<sup>18</sup>O, and CO<sup>17</sup>O are formed by the gas-phase reaction, O + CO → CO. This is a spin-forbidden 3-body reaction, with a rate ~  $1 \times 10^{-35} \text{ cm}^6 \text{ s}^{-1}$ . The loss time-

scale of O to CO<sub>2</sub> formation is  $\sim 10^3$  seconds, and the diffusion time for O along the photocell is  $\sim 10$  seconds. Thus, we expect that O atom isotopes are well mixed in the photocell, even though they are produced at different depths due to shielding effects.

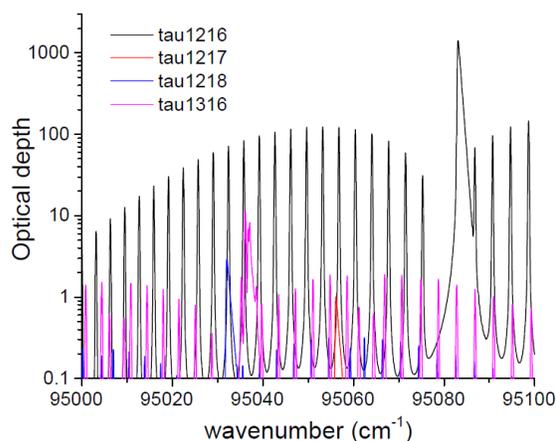
Model runs were made for several cases presented in [4]. A comparison of the experimental and model slopes is given in Tables 1 and 2, respectively. The experimental slopes (non-logarithmic) for CO<sub>2</sub> are 1.4-1.8, considerably higher than unity. The model slopes (Table 2) are initially high due to self-shielding by C<sup>18</sup>O, but quickly tend to near-unity values at times much shorter than the residence timescale for CO gas in the experiments. The model delta-values are higher than the experimental delta-values at 107.6 nm, possibly indicating too low a photon intensity in the model for these cases. So far, only an isotope dependence in the dissociation probabilities can explain the measured slopes, as discussed previously [5].

**Conclusions:** Model simulations of CO photolysis experiments [4] at long wavelengths cannot explain the high slopes measured, except by invoking isotopic differences in dissociation probabilities [5]. Processes not considered in the modeling include: 1) CO<sub>2</sub> photolysis prior to capture on the cold finger; 2) mass-dependent diffusion coefficients for gas in the photocell. The addition of these processes to the code is in progress.

**References:** [1] Clayton R. N. (2002) *Nature*, 415, 860-861. [2] Stark G. et al. (2014) *Astrophys. J.*, 788, art. 67. [3] van Dischoek E. F. and J. Black (1988) *Astrophys. J.*, 334, 771-802. [4] Chakraborty S. et al. (2012) *J. Phys. Chem.*, 137, 024309. [5] Lyons J. R. (2014) *MAPS*, 49, 373-393. [6] Ubachs W. et al. (2000), *J. Chem. Phys.*, 113, 547-560.



**Fig. 1** Cross sections for isotopologues of CO E(1) band as determined from measurements at the Soleil synchrotron (see Stark et al. 2014).



**Fig. 2** Optical depths for four isotopologues of CO E(1) band for an assumed column density of  $3 \times 10^{17}$  cm<sup>-2</sup>. Black curve shows the highly optically thick Q-branch of <sup>12</sup>C<sup>16</sup>O, and the Q-branches of the other isotopologues in a forest of 1216 P-branch lines. The Q-branch of 1316 is optically thick and is mostly unshielded by 1216.

Table 1. Several experimental results at 20 °C [4].

$\lambda$ , nm	$N_{\text{CO}}$ , cm <sup>-2</sup>	$t_{\text{CO}}$ , s	$\delta^{17}\text{CO}_2$	slope <sup>a</sup>
107.6	2.7E17	1.5E4	801	1.53
107.6	6.4E17	3.2E3	905	1.81
105.2	2.6E17	1.1E4	408	1.39
105.2	7.7E17	3.7E2	1810	1.68

<sup>a</sup>slope defined here as  $\delta^{17}\text{CO}_2 / \delta^{18}\text{CO}_2$  (not logarithmic)

Table 2. Model results at 300 K for 100 cm cell.

$\lambda$ , nm	$N_{\text{CO}}$ , cm <sup>-2</sup>	slope(0) <sup>a</sup>	$\delta^{17}\text{CO}_2$ <sup>b</sup>	slope <sup>b</sup>
107.6	3E17	1.52	1300,410	1.00
107.6	7E17	2.14	8400, 2400	0.98
105.2	3E17	1.12	1200, 340	0.99
105.2	7E17	1.30	8900, 210	1.00

<sup>a</sup>slope(0) =  $\delta^{17}\text{CO}_2 / \delta^{18}\text{CO}_2$  at  $t = 1\text{E-}4$  second.

<sup>b</sup> $\delta^{17}\text{CO}_2$  and slope at  $t = t_{\text{CO}}$  of corresponding row in Table 1, and for full VUV exposure ( $\sim 4\text{E}4$  seconds).