Supplementary Information

The Effect of CO Rotation from Shaped Pulse Polarization on Reactions that Form C₂

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Kinetics of $CO(a^3\Pi)$ Formation

The observation of Swan band emission is evidence for the formation of the $C_2(d^3\Pi_g)$ state following multiphoton absorption by CO with seven (or more) 800-nm photons. The CO $(a^3\Pi)$ state is considered to a likely reactant in C_2 formation reactions, based on studies on CO/He plasmas. The combined energy of seven 800-nm photons corresponds to excitation to CO $(B^1\Sigma^+)$. Here we consider the kinetics of $(B^1\Sigma^+)$ state relaxation by emission and collisional energy transfer that leads to formation of $CO(a^3\Pi)$. Fig. 1 shows the energy levels involved in the multiphoton excitation and subsequent relaxation of CO. If higher energy CO states are initially prepared in the multiphoton step, it is likely that they will relax even faster that the $(B^1\Sigma^+)$ state.



Figure 1. Energy level diagram for CO.

Multiphoton absorption and relaxation steps. Multiphoton absorption by the $CO(X^{1}\Sigma^{+})$ state leads to prompt formation of the CO $(B^{1}\Sigma^{+})$ state, shown in Eq. 1, based on the temporal profiles of the shaped pulses (Fig. 1 in main text).

$$CO(X^{1}\Sigma^{+}) + 7 (800 nm photons) \xrightarrow{prompt} CO(B^{1}\Sigma^{+})$$
 Multiphoton absorption (1)

The CO($B^1\Sigma^+$) state can relax by emission to the ($A^1\Pi$) or ($X^1\Sigma^+$) states, as in Eq. 2, or through collisions to the ($b^3\Sigma^+$) state, as in Eq. 3. The rate constant k_1 includes emission to both the *A* and *X* states.

$$CO(B^{1}\Sigma^{+}) \xrightarrow{k_{1}} CO(A^{1}\Pi \text{ or } X^{1}\Sigma^{+}) + photon \qquad \text{Emission (2)}$$

$$CO(B^{1}\Sigma^{+}) + M \xrightarrow{k_{2}} CO(b^{3}\Sigma^{+}) + M \qquad \text{Collisional quenching (3)}$$

The CO($b^{3}\Sigma^{+}$) state can relax by emission or by collisions to the ($a^{3}\Pi$) state, as in Eqs. 4 and 5.

$$CO(b^{3}\Sigma^{+}) \xrightarrow{k_{3}} CO(a^{3}\Pi) + photon$$

$$CO(b^{3}\Sigma^{+}) + M \xrightarrow{k_{4}} CO(a^{3}\Pi) + M$$
Triplet state quenching (5)

The rate constants are summarized in Table I.

Table I: Rate	constants for formati	on of the CO	$(a^3\Pi)$ state.

Rate constant	Value	Source
$k_1 = \frac{1}{\tau_A} + \frac{1}{\tau_X}$	$7.35 \times 10^8 s^{-1}$	$ au_A = 6.8 imes 10^{-8} s$; Ref. 1 $ au_X = 1.7 imes 10^{-8} s$; Ref. 2
k_2	$1.82 \times 10^{-10} \ cm^3 molecule^{-1} s^{-1}$	Ref. 1
k_3	$1.03 \times 10^7 s^{-1}$	Ref. 3
k_4	$1.01 \times 10^{-9} \ cm^3 molecule^{-1} s^{-1}$	Ref. 3

Kinetic equations. The kinetic equations are developed here for the formation of the CO $(a^3\Pi)$ state following multiphoton excitation to the $(B^1\Sigma^+)$ state. The following definitions are used in

the kinetic equations: $B \equiv CO(B^{1}\Sigma^{+})$, $A \equiv CO(A^{1}\Pi)$, $X \equiv CO(X^{1}\Sigma^{+})$, $b \equiv CO(b^{3}\Sigma^{+})$ and $a \equiv CO(a^{3}\Pi)$.

Under pseudo-first order conditions, the loss of $CO(B^{1}\Sigma^{+})$ is given by Eqs. 6 and 7.

$$\frac{d[B]}{dt} = -(k_1 + k_2[M])t$$
(6)

$$\frac{[B]}{[B]_0} = e^{-(k_1 + k_2[M])t}$$
(7)

The combined formation of $CO(A^{1}\Pi)$ and $CO(X^{1}\Sigma^{+})$ is given by Eqs. 8 and 9.

$$\frac{d([A]+[X])}{dt} = k_1[B] = k_1[B]_0 e^{-(k_1+k_2[M])t}$$
(8)

$$\frac{[A]+[X]}{[B]_0} = \frac{k_1[B]_0}{k_1+k_2[M]} \left(1 - e^{-(k_1+k_2[M])t}\right)$$
(9)

The formation and decay of of $CO(b^{3}\Sigma^{+})$ is given by Eqs. 10 and 11.

$$\frac{d[b]}{dt} = k_2[M][B] - (k_3 + k_4[M])[b]$$
(10)

$$\frac{[b]}{[B]_0} = \frac{k_2[M]}{k_3 + k_4[M] - k_2[M]} \left[e^{-(k_1 + k_2[M])t} - e^{-(k_3 + k_4[M])t} \right]$$
(11)

Finally, the appearance of $CO(a^3\Pi)$ is given by Eqs. 12 and 13.

$$\frac{d[a]}{dt} = (k_3 + k_4[M])[b]$$
(12)

$$\frac{[a]}{[B]_0} = \beta \left[(k_1 + k_2[M]) \left[1 - e^{-(k_3 + k_4[M])t} \right] - (k_3 + k_4[M]) \left[1 - e^{-(k_1 + k_2[M])t} \right] \right]$$
(13)

where

$$\beta = \frac{k_2[M]}{[(k_1 + k_2[M]) - (k_3 + k_4[M])](k_1 + k_2[M])}$$
(14)

Figure 2 shows the pressure dependent kinetics for [B], [A], [X], [b] and [a] using Eqs. 7, 9, 11 and 13 and the rate constants from Table I. The $(a^3\Pi)$ state number density increases with increasing pressure because of the collision energy transfer. The lifetime for appearance of the $(a^3\Pi)$ state decreases from 4.5 ns at 25 Torr to 1.5 ns at 100 Torr.



Figure 2. Time-dependent fractional populations of CO $B^{1}\Sigma^{+}(B)$, $A^{1}\Pi(A)$, $X^{1}\Sigma^{+}(X)$, $b^{3}\Sigma^{+}(b)$ and $a^{3}\Pi(a)$ for the four pressures used in our experiments. Formation of the $a^{3}\Pi$ state is enhanced at higher pressures shows the fractional populations for the CO states at 100 Torr pressure. The relaxation of the b state occurs readily at pressures of 25-100 Torr and is predominantly collision induced.

References:

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