

# Distribution of Internal States of CO from O (<sup>1</sup>D) + CO Determined with Time-Resolved Fourier Transform Spectroscopy

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Following collisions of O (<sup>1</sup>D) with CO, rotationally resolved emission spectra of CO ( $1 \leq v \leq 6$ ) in the spectral region 1800–2350  $\text{cm}^{-1}$  were detected with a step-scan Fourier transform spectrometer. O (<sup>1</sup>D) was produced by photolysis of O<sub>3</sub> with light from a KrF excimer laser at 248 nm. Upon irradiation of a flowing mixture of O<sub>3</sub> (0.016 Torr) and CO (0.058 Torr), emission of CO ( $v \leq 6$ ) increases with time, reaches a maximum  $\sim 10 \mu\text{s}$ . At the earliest applicable period (2–3  $\mu\text{s}$ ), the rotational distribution of CO is not Boltzmann; it may be approximately described with a bimodal distribution corresponding to temperatures  $\sim 8000$  and  $\sim 500$  K, with the proportion of these two components varying with the vibrational level. A short extrapolation from data in the period 2–6  $\mu\text{s}$  leads to a nascent rotational temperature of  $\sim 10170 \pm 600$  K for  $v = 1$  and  $\sim 1400 \pm 40$  K for  $v = 6$ , with an average rotational energy of  $33 \pm 6$   $\text{kJ mol}^{-1}$ . Absorption by CO ( $v = 0$ ) in the system interfered with population of low  $J$  levels of CO ( $v = 1$ ). The observed vibrational distribution of ( $v = 2$ ):( $v = 3$ ):( $v = 4$ ):( $v = 5$ ):( $v = 6$ ) = 1.00:0.64:0.51:0.32:0.16 corresponds to a vibrational temperature of  $6850 \pm 750$  K. An average vibrational energy of  $40 \pm 4$   $\text{kJ mol}^{-1}$  is derived based on the observed population of CO ( $2 \leq v \leq 6$ ) and estimates of the population of CO ( $v = 0, 1$ , and 7) by extrapolation. The observed rotational distributions of CO ( $1 \leq v \leq 3$ ) are consistent with results of previous experiments and trajectory calculations; data for CO ( $4 \leq v \leq 6$ ) are new.

## I. Introduction

The collisional quenching of O (<sup>1</sup>D) by small molecules is important in the atmospheric heat budget because it transfers the electronic energy to the vibrational energy of these species in the stratosphere.<sup>1,2</sup> The transfer from electronic to vibrational and rotational energy is of interest also for theoretical studies, especially when the process involves a spin-forbidden surface crossing that typically involves a long-lived collisional complex.<sup>3</sup>

The energy transfer of O (<sup>1</sup>D) to CO has been extensively investigated experimentally<sup>4–13</sup> and theoretically.<sup>14–16</sup> The rate coefficient of quenching for the reaction



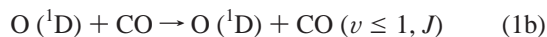
was determined to be in the range  $(5–7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>4,5,10</sup> The vibrational distribution of CO has been investigated using various methods. Lin and Shortridge probed the absorption of CO, produced from a mixture of O<sub>3</sub>, CO, and SF<sub>6</sub> subjected to flash photolysis with a cw CO laser, and reported a vibrational distribution of CO ( $v \leq 7$ ) represented by a Boltzmann distribution with a vibrational temperature of  $\sim 5580$  K.<sup>8</sup> Their further work yielded a vibrational distribution corresponding to  $T \cong 8000$  K and extended the measurements to four temperatures between 246 and 323 K; their observation

of nearly equal proportions of C<sup>16</sup>O and C<sup>18</sup>O from <sup>16</sup>O (<sup>1</sup>D) + C<sup>18</sup>O indicates that energy was completely randomized in the CO<sub>2</sub> complex before it dissociated.<sup>9</sup> Harding et al. investigated this process with time-resolved diode laser absorption spectroscopy; they determined the nascent population of CO ( $v = 0$ ) and reported a vibrational population of CO ( $0 \leq v \leq 4$ ) corresponding to a temperature  $\sim 5000$  K.<sup>11</sup> Abe et al. employed vacuum ultraviolet (VUV) laser-induced fluorescence (LIF) to probe the rotational and vibrational distributions of CO produced from reaction 1a.<sup>13</sup> They added  $\sim 2$  Torr of Ar to the mixture of O<sub>3</sub> and CO and probed CO at 5  $\mu\text{s}$  after laser irradiation to produce O (<sup>1</sup>D) so that rotational quenching ensured a Boltzmann rotational distribution at room temperature; the reported vibrational distribution of CO ( $v \leq 6$ ) corresponds to a temperature smaller than that reported by Shortridge and Lin.<sup>9</sup> The reported efficiencies for the transfer from electronic to vibrational energy, defined as the ratio of average vibrational energy of CO to the energy of O (<sup>1</sup>D) relative to O (<sup>3</sup>P), vary substantially, with values of 17 (ref 13), 21 (ref 6), 25 (ref 11), and 40% (ref 9).

Abe et al. made the only report on the rotational distribution of CO ( $v$ ); distributions were determined only for vibrational levels  $v \leq 3$  because of severe overlap of lines of CO ( $v \geq 4$ ) in their LIF spectrum.<sup>13</sup> Rotational distributions of CO ( $v = 2, 3$ ), which can result only from nonadiabatic collisions to form O (<sup>3</sup>P) + CO ( $v, J$ ), agree with trajectory calculations performed on a triplet potential-energy surface, whereas those of CO ( $v =$

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0, 1) show a significant contribution in the low- $J$  levels from the adiabatic process



The efficiency for the transfer from electronic to internal (rotational and vibrational) energy was reported to be 29% by Abe et al.<sup>13</sup> and 31% by Matsumi et al.<sup>12</sup>

To understand the dynamics of energy transfer, one must characterize the potential-energy surfaces of the electronic states involved. Only a few theoretical investigations are reported.<sup>17–21</sup> The  $\text{O} (^1\text{D}) + \text{CO} (X ^1\Sigma^+)$  channel correlates with an angular  $\text{CO}_2$   $^1\text{B}_2$  state that lies about 550 kJ mol<sup>-1</sup> above the ground state. There are three angular states,  $^1\text{A}_2$ ,  $^3\text{A}_2$ , and  $^3\text{B}_2$ , with energies less than that of the  $^1\text{B}_2$  state; all of them cross the  $^1\text{B}_2$  state. An accurate and balanced calculation of all states involved in the conical intersections remains a demanding task; only the parts near equilibrium geometries of these angular states are characterized.<sup>20</sup>

Experimental investigations on the dynamics of bimolecular reactions or collisional quenching require special attention because these processes need collisions to facilitate reaction, but in the same way collisional quenching of the products might become significant, hence modifying the nascent rotational distribution. In previous work, we have demonstrated that step-scan time-resolved Fourier transform spectroscopy (TR–FTS) is advantageous for studying the dynamics of bimolecular reactions because its multiplex capability allows probing of all states simultaneously, hence assisting understanding the effects of rotational quenching due to collisions.<sup>22,23</sup> Furthermore, TR–FTS has been demonstrated to cover more vibrational–rotational states than resonance-enhanced multiphoton ionization (REMPI) or VUV LIF in detecting HX ( $X = \text{F}, \text{Cl}, \text{and Br}$ )<sup>24–29</sup> and  $\text{CO}$ ,<sup>30,31</sup> because REMPI and VUV LIF detection was limited by the short lifetimes of the upper states. We report here an application of time-resolved Fourier transform spectroscopy to investigate the collisional excitation of CO by  $\text{O} (^1\text{D})$  and compare observed distributions of internal states of CO with those from previous reports; information on rotational distributions of CO ( $v = 4–6$ ) is new.

## II. Experiments

The apparatus employed to obtain step-scan time-resolved Fourier transform spectra has been described previously.<sup>26,32,33</sup> The size of the photolysis beam from a KrF laser at 248 nm (Lambda Physik, LPX 200) was  $\sim 2.5 \times 10 \text{ mm}^2$  at the detection center with a fluence  $\sim 200 \text{ mJ cm}^{-2}$ . We employed an InSb detector with a rise time of 0.7  $\mu\text{s}$ ; its transient signal was preamplified with a factor of  $10^5 \text{ V A}^{-1}$  (bandwidth 1.5 MHz), followed by further amplification with a factor of 200 (bandwidth 1 MHz) before being digitized with an external data-acquisition board (PAD1232, 12-bit ADC) at 50 ns resolution. Data were typically averaged over 60 laser pulses at each scan step; 7251 scan steps were performed to yield an interferogram resulting in a spectrum of resolution  $0.2 \text{ cm}^{-1}$  in the spectral region 1800–2350  $\text{cm}^{-1}$ . To improve the ratio of signal-to-noise ( $S/N$ ) of the spectrum, 20 consecutive time-resolved spectra were summed to yield spectra representing emission at intervals 1.0  $\mu\text{s}$ . The temporal response function of the instrument was determined using an IR laser beam as a source, as described previously.<sup>29</sup>

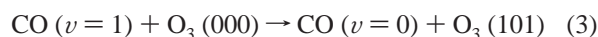
Ozone ( $\text{O}_3$ ) and CO were injected into the reaction chamber with varied partial pressures; to reduce collisional quenching of CO, a minimal pressure was used. For the understanding of

the effects of pressure, two sets of data were taken with  $P_{\text{CO}} = 0.058 \text{ Torr}$  and  $P_{\text{O}_3} = 0.016 \text{ Torr}$ , and with  $P_{\text{CO}} = 0.231 \text{ Torr}$  and  $P_{\text{O}_3} = 0.0686 \text{ Torr}$ . A large fraction of  $\text{O}_3$  was dissociated upon irradiation at 248 nm based on the reported absorption cross section of  $1.5 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$  for  $\text{O}_3$  at 248 nm.<sup>34</sup> Flow rates are  $F_{\text{O}_3} = 1.7–2.4 \text{ sccm}$  and  $F_{\text{CO}} = 6.3–8.1 \text{ sccm}$ ; sccm stands for  $\text{cm}^3$  per min under standard conditions (273 K and 760 Torr). Depletion of  $\text{O}_3$  after each laser pulse is not serious, as was indicated by the negligible change of the signal when we reduced the repetition rate of the photolysis laser from 23 to 12 Hz.

CO (Air Products, 99.9%) was used without purification except for degassing. Ozone was produced from  $\text{O}_2$  (Scott Specialty Gases, 99.995%) with an ozone generator (Polymetrics, model T-408), stored over silica gel at 196 K, and eluted from the trap with or without a small flow of He (Scott Specialty Gases, 99.999%). The partial pressure of  $\text{O}_3$  was determined by the absorption of Hg emission at 254 nm in a cell with length of 7.0 cm; the absorption cross section of  $\text{O}_3$  at 254 nm was taken to be  $1.15 \times 10^{-17} \text{ cm}^2$ .<sup>35</sup>

## III. Results and Discussion

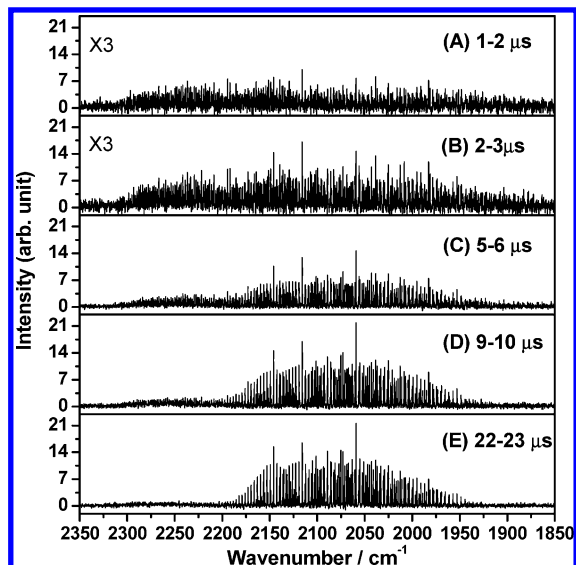
Collisional quenching of CO plays an important role in this system. Vibrational quenching of CO by itself or  $\text{O}_3$  is relatively slow:



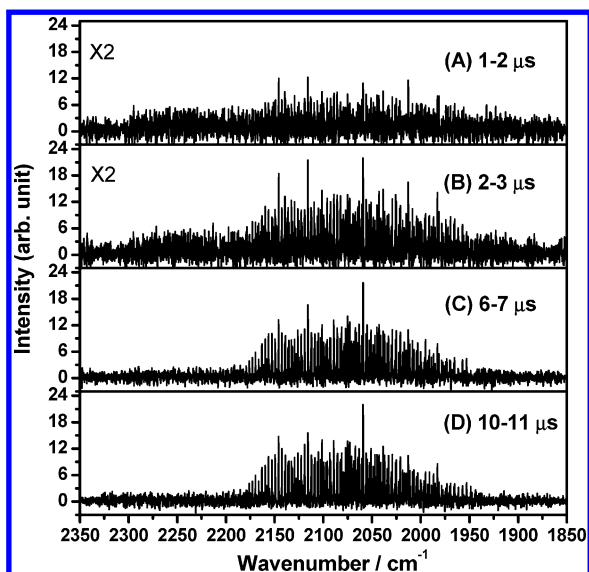
with  $k_2$  in the range  $(3–20) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $v = 2$  to 7,<sup>11,36,37</sup> and  $k_3 = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>11</sup> With both  $[\text{CO}]$  and  $[\text{O}_3]$  less than  $5 \times 10^{15} \text{ molecules cm}^{-3}$  ( $\sim 0.15 \text{ Torr}$  at 298 K), vibrational quenching of CO is less than 10% of the original population within 10  $\mu\text{s}$ . Rotational quenching is, however, much more rapid and must be taken into account. To maintain a nearly collisionless condition within a 3.0  $\mu\text{s}$  period, the pressures of the system were made as small as practicable while maintaining a satisfactory signal-to-noise ratio.

Figure 1 shows emission spectra of CO at a resolution of  $0.2 \text{ cm}^{-1}$ , recorded 1.0–2.0, 2.0–3.0, 5.0–6.0, 9.0–10.0, and 22–23  $\mu\text{s}$  after photolysis of a flowing mixture of  $\text{O}_3$  and CO with partial pressures of 0.016 and 0.058 Torr, respectively; eight spectra recorded under similar conditions were averaged to improve the ratio of signal-to-noise. The smaller intensity in periods 1.0–3.0  $\mu\text{s}$  reflects the small rate of production of internally excited CO; the signal attains a maximum near 10  $\mu\text{s}$ , followed by a slow decay. For comparison, Figure 2 shows emission spectra of CO recorded 1.0–2.0, 2.0–3.0, 6.0–7.0, and 10–11  $\mu\text{s}$  after 248 nm photolysis of a flowing mixture of  $\text{O}_3$  and CO with partial pressures of 0.0686 and 0.231 Torr, respectively. Rotational quenching is more severe in these spectra relative to those at low pressure. Hence, we chose the period 2–3  $\mu\text{s}$  in Figure 1 as a representative spectrum for analysis; under these conditions the ratio of signal-to-noise is satisfactory for quantitative analysis while the rotational quenching is still small.

An expanded partial spectrum of Figure 1B is shown in Figure 3. Assignments based on spectral parameters reported by Ogilvie et al.<sup>38</sup> are shown as stick diagrams; values of  $J'$  are indicated. The spectrum indicates that the  $0.2 \text{ cm}^{-1}$  resolution is adequate to resolve a large number of lines involving  $v = 1–6$ . The emission spectra in Figure 1 exhibit emission of CO with  $J'$  up to 68 and  $v'$  up to 6.



**Figure 1.** Infrared emission spectra of CO in spectral region 1850–2350  $\text{cm}^{-1}$  recorded at varied intervals upon photolysis of a flowing mixture of  $\text{O}_3$  (0.016 Torr) and CO (0.058 Torr) at 248 nm. (A) 1.0–2.0  $\mu\text{s}$ ; (B) 2.0–3.0  $\mu\text{s}$ ; (C) 5.0–6.0  $\mu\text{s}$ ; (D) 9.0–10.0  $\mu\text{s}$ ; (E) 22–23  $\mu\text{s}$ . Spectral resolution is 0.2  $\text{cm}^{-1}$ ; 60 laser pulses were averaged at each scan step of the interferometer. Eight spectra recorded under similar conditions were averaged.

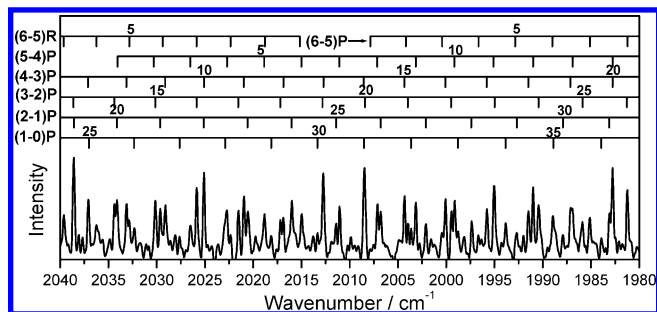


**Figure 2.** Infrared emission spectra of CO in spectral region 1850–2350  $\text{cm}^{-1}$  recorded at varied intervals upon photolysis of a flowing mixture of  $\text{O}_3$  (0.0686 Torr) and CO (0.231 Torr) at 248 nm. (A) 1.0–2.0  $\mu\text{s}$ ; (B) 2.0–3.0  $\mu\text{s}$ ; (C) 6.0–7.0  $\mu\text{s}$ ; (D) 10.0–11.0  $\mu\text{s}$ . Spectral resolution is 0.2  $\text{cm}^{-1}$ ; 60 laser pulses were averaged at each scan step of the interferometer.

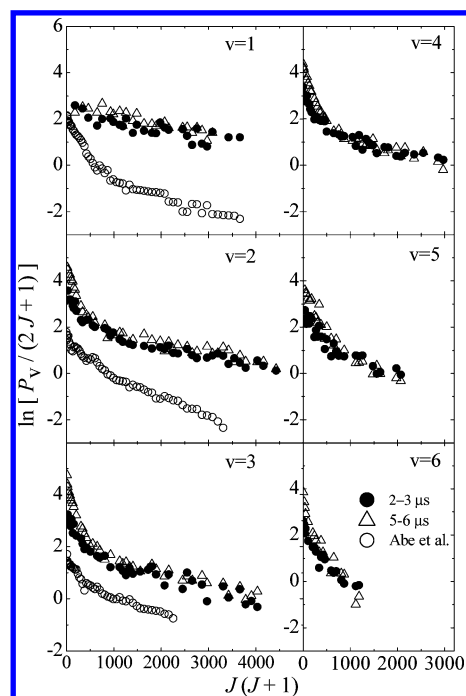
**1. Rotational Distribution of CO.** We calculated values of the Einstein A coefficient according to this formula,<sup>30</sup>

$$A_{v'J'}^{v''J''} = \frac{16\pi^3 \tilde{\nu}^3 |\mu| |\langle v'' | p(R) | v' \rangle|^2 (1 + C_{v'}^{v''} \iota + D_{v'}^{v''} \iota^2)}{3\epsilon_0 h (2J' + 1)} \quad (4)$$

in which  $\tilde{\nu}$  is the wavenumber of a transition from a vibration–rotational state ( $v'$ ,  $J'$ ) to another state ( $v''$ ,  $J''$ ),  $\iota = \frac{1}{2}[J'(J' + 1) - J''(J'' + 1)]$  is a running number depending on rotational quantum numbers  $J'$  and  $J''$ ,  $\langle v'' | p(R) | v' \rangle$  is a pure vibrational matrix element of electric dipolar moment between vibrational states  $v'$  and  $v''$ ,  $C_{v'}^{v''}$  and  $D_{v'}^{v''}$  are coefficients in the Herman–Wallis factor to take into account the rotational effect on the



**Figure 3.** Expanded view of partial infrared emission spectra of CO in Figure 1B, 2.0–3.0  $\mu\text{s}$ . Assignments are shown in stick diagrams.



**Figure 4.** Semilogarithmic plots of relative rotational populations of CO ( $v = 1-6$ ) upon photolysis of a flowing mixture of  $\text{O}_3$  (0.016 Torr) and CO (0.058 Torr) at 248 nm. Results of Abe et al.,<sup>13</sup> displaced vertically downward by two units for clarity, are also shown as  $\circ$ .

vibrational matrix element,<sup>39</sup> and  $\epsilon_0$  and  $h$  are fundamental constants. Each vibration–rotational line was normalized with the instrument response function, and divided by its respective Einstein coefficient to yield a relative population  $P_v(J')$ . Partially overlapped lines, such as  $J' = 22, 29, 39$  of CO ( $v' = 1$ ),  $J' = 7, 19, 22, 35$  of CO ( $v' = 2$ ),  $J' = 6, 15, 24, 32$  of CO ( $v' = 3$ ), and  $J' = 2, 14, 26$  of CO ( $v' = 4$ ), were deconvoluted to yield their intensities.

Semilogarithmic plots of  $P_v(J')/(2J' + 1)$  vs  $J'(J' + 1)$  for CO ( $v = 1-6$ ) produced from  $\text{O} (^1\text{D}) + \text{CO}$  at 2–3  $\mu\text{s}$  (marked  $\bullet$ ) and 5–6  $\mu\text{s}$  (marked  $\Delta$ ) are shown in Figure 4. These figures provide information on the extent of rotational quenching; quenching before 6  $\mu\text{s}$  is present but not serious, it affects slightly the low- $J$  distribution and requires only a small correction. For the period of 2–3  $\mu\text{s}$ , rotational distributions are not Boltzmann for CO ( $v = 2-5$ ), whereas those of CO ( $v = 1$ ) and CO ( $v = 6$ ) may be fitted with a Boltzmann distribution having rotational temperatures  $8380 \pm 1240$  K and  $1120 \pm 100$  K, respectively; unless specified, error limits listed in this paper represent one standard deviation in fitting. Rotational distributions of CO ( $v = 1-3$ ) reported by Abe et al.<sup>13</sup> (symbol  $\circ$ , displaced vertically downward for clarity) are shown also in Figure 4 for comparison. For CO ( $v = 3$ ), their results agree with ours satisfactorily except that our experiments

**TABLE 1: Fitted Rotational Temperature, Rotational Energy, and Vibrational Population of CO ( $\nu$ ) Recorded 2.0–3.0  $\mu\text{s}$  after Irradiation of a Flowing Mixture of  $\text{O}_3$  (0.016 Torr) and CO (0.058 Torr) at 248 nm**

$\nu$	$T_r/\text{K}$	$E_r(\nu)/\text{kJ mol}^{-1}$	vibr population
0			(0.372) <sup>d</sup>
1	8380 $\pm$ 1240 [10170 $\pm$ 610] <sup>b</sup>	36.3	0.977 <sup>c</sup> (0.236)
2	610 $\pm$ 70 <sup>a</sup> 7930 $\pm$ 540 [8800 $\pm$ 260]	28.1	1.000 (0.142)
3	580 $\pm$ 40 5870 $\pm$ 640 [7530 $\pm$ 490]	23.9	0.642 (0.091)
4	530 $\pm$ 50 5280 $\pm$ 670 [6610 $\pm$ 250]	21.6	0.510 (0.073)
5	500 $\pm$ 90 4450 $\pm$ 2000 [6290 $\pm$ 260]	13.5	0.322 (0.046)
6	1120 $\pm$ 100 [1490 $\pm$ 30] (390 $\pm$ 30) <sup>e</sup> (3390 $\pm$ 460) <sup>e</sup>	7.6	0.162 (0.023)
7			(0.017)
av		26.3 $\pm$ 3.6	

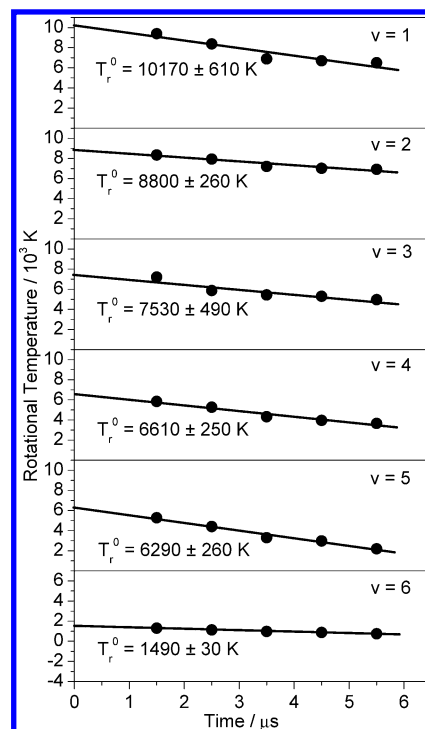
<sup>a</sup> Low- $J$  component of the bimodal distribution. <sup>b</sup> Rotational temperature extrapolated to  $t = 0$ ; only high- $J$  component was considered for  $\nu = 2-5$ . <sup>c</sup> Observed population relative to that of  $\nu = 2$ ; see text. <sup>d</sup> Normalized population with  $\nu = 0, 1$ , and  $\nu = 7$  predicted from Boltzmann distribution; see text. <sup>e</sup> Estimated by assuming a temperature of 3390 K for the high- $J$  component; see text.

extend observed  $J'$  to much larger values. In contrast, the distribution of CO ( $\nu = 1$ ) reported by Abe et al. shows a much greater population for  $J \leq 20$  than ours. Rotational distributions of CO ( $\nu = 4-6$ ) in this work are new. Although Abe et al. observed these vibrational levels, severe overlap of lines associated with these levels prevented them from undertaking further rotational analysis.

In our experiment, absorption of CO ( $\nu = 0$ ) in the system might interfere with measurements of the emission of CO ( $\nu = 1$ ) because the emission was collected with a multipass Welsh cell. For example, with a reported infrared absorption cross section of  $5.4 \times 10^{-17} \text{ cm}^2$  for the R line of CO ( $\nu'' = 0, J'' = 5$ ),<sup>40</sup> an estimated absorption length of 80 cm, a concentration of  $[\text{CO}] = 2.08 \times 10^{15} \text{ molecules cm}^{-3}$ , and a fraction of 8% of the total population for this level of CO at 298 K, a transmission of  $\sim 50\%$  is estimated. Hence, the population of the low- $J$  component of CO ( $\nu = 1$ ) determined in this work is unreliable and is not used. Correction for this absorption involves large uncertainties and is not recommended.

For convenience of description we fitted the rotational distributions of CO ( $\nu = 2-5$ ) with a double Boltzmann distribution function to derive the rotational temperature of high- $J$  and low- $J$  components. Results for  $t = 2.0-3.0 \mu\text{s}$  are listed in Table 1. For the high- $J$  component, the rotational temperature decreases with vibrational excitation. There is likely also an unresolved high- $J$  component in the observed distribution of CO ( $\nu = 6$ ) that overlaps with the low- $J$  component. If we employed an estimated rotational temperature of 3400 K for the high- $J$  component, we derived a rotational temperature of  $390 \pm 30 \text{ K}$  for the low- $J$  component, consistent with the decreasing trend.

Rotational temperatures of CO ( $\nu = 1$ ), CO ( $\nu = 6$ ), and the high- $J$  components of CO ( $2 \leq \nu \leq 5$ ) as a function of reaction period are shown in Figure 5. With a short extrapolation, we estimate the nascent rotational temperature to be  $10170 \pm 610$ ,  $8800 \pm 260$ ,  $7530 \pm 490$ ,  $6610 \pm 250$ ,  $6290 \pm 260$ , and  $1490 \pm 30 \text{ K}$  for CO ( $\nu = 1$ ) to CO ( $\nu = 6$ ), respectively, as listed in Table 1. The correction factors for rotational temperature at  $2-3 \mu\text{s}$  to derive nascent rotational temperature, taken as ratios



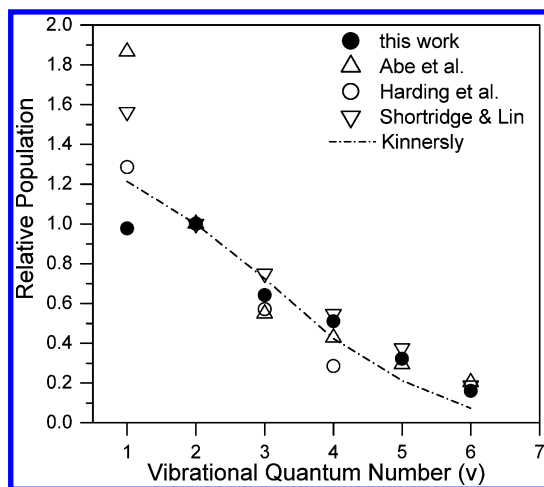
**Figure 5.** Rotational temperature of CO ( $\nu = 1-6$ ) as a function of time.

of extrapolated nascent temperature to observed rotational temperature at  $2-3 \mu\text{s}$ , are thus 1.21, 1.11, 1.28, 1.25, 1.41, and 1.33 for CO ( $\nu = 1$ ) to CO ( $\nu = 6$ ), respectively, and with an average of  $1.26 \pm 0.10$ . In contrast, the rotational temperature for CO ( $\nu = 1$ ) and CO ( $\nu = 6$ ) in the period  $1.0-3.0 \mu\text{s}$  under high pressure (shown in Figure 2) are  $870 \pm 120 \text{ K}$  and  $570 \pm 150 \text{ K}$ , respectively, indicating severe quenching under such conditions.

Rotational energies for each vibrational level,  $E_r(\nu)$ , obtained on summing a product of rotational energy and normalized population for each rotational level, are listed in Table 1. An average rotational energy  $E_r = 26 \pm 4 \text{ kJ mol}^{-1}$  for CO ( $\nu = 1-6$ ) observed  $2.0-3.0 \mu\text{s}$  after photolysis is derived on summing a product of vibrational population and associated  $E_r(\nu)$ ; the vibrational population is discussed in the next section. After applying a correction factor  $1.26 \pm 0.10$  for rotational quenching, we derive a nascent rotational energy of  $33 \pm 6 \text{ kJ mol}^{-1}$  based on observed data.

**2. Vibrational Distribution of CO.** Relative populations obtained on counting levels up to observed  $J_{\text{max}}$  in each vibrational level are indicated as  $\sum_J P_\nu(J)$ . For  $\nu = 1$ , we used extrapolated values for  $J \leq 20$  by assuming a Boltzmann distribution. We normalized values of  $\sum_J P_\nu(J)$  derived from the spectrum in Figure 1B for each vibrational state to yield a ratio of vibrational populations ( $\nu = 1$ ):( $\nu = 2$ ):( $\nu = 3$ ):( $\nu = 4$ ):( $\nu = 5$ ):( $\nu = 6$ ) =  $0.98:1.00:0.64:0.51:0.32:0.16$ . This distribution is plotted in Figure 6 and compared with that from previous reports. Because of possible errors in deriving the population of CO ( $\nu = 1$ ), we represent vibrational populations of CO ( $\nu$ ) relative to that of CO ( $\nu = 2$ ). The distribution of CO ( $\nu = 2-6$ ) corresponds to a vibrational temperature of  $6850 \pm 730 \text{ K}$ .

Vibrational distributions reported previously are compared with our results in Figure 6. Our results (symbol  $\bullet$ ) for CO ( $\nu \geq 2$ ) agree with those of Shorridge and Lin (symbol  $\nabla$ ),<sup>9</sup> who reported ( $\nu = 1$ ):( $\nu = 2$ ):( $\nu = 3$ ):( $\nu = 4$ ):( $\nu = 5$ ):( $\nu = 6$ ) =  $1.56:1.00:0.75:0.55:0.38:0.19$ . The distribution reported by



**Figure 6.** Comparison of relative vibrational distributions of CO from  $O(^1D) + CO$ . Key: (●) this work; (▽) Shortridge and Lin;<sup>9</sup> (Δ) Abe et al.;<sup>13</sup> (○) Harding et al.;<sup>11</sup> (dot-dash line) Kinnersly.<sup>15</sup>

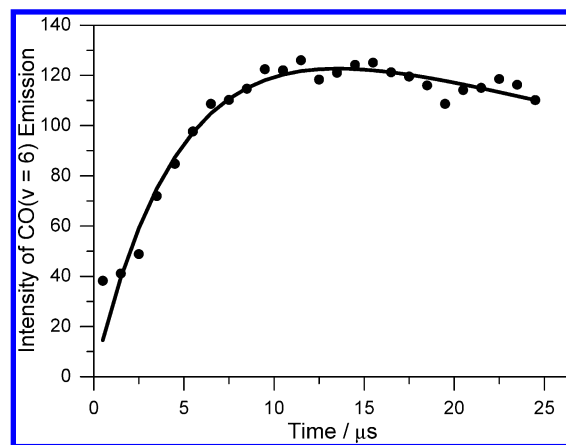
Harding et al. (symbol ○)<sup>11</sup> with  $(v=0):(v=1):(v=2):(v=3):(v=4) = 4.28:1.29:1.00:0.57:0.29$  corresponds to a smaller temperature. The ratio reported by Abe et al. (symbol Δ)<sup>13</sup> with  $(v=0):(v=1):(v=2):(v=3):(v=4):(v=5):(v=6) = 4.30:1.87:1.00:0.55:0.43:0.29:0.20$  also differs slightly from ours. The vibrational distribution predicted by Kinnersly using a classical collision complex model and potentials previously derived for  $C(^3P) + O_2(^3\Sigma_g^-)$ , agrees satisfactorily also with our observations, as shown with a dot-dash line in Figure 6.

Assuming a Boltzmann vibrational distribution, we estimate the population of  $v = 0, 1$ , and  $7$  relative to  $v = 2$  to be 2.62, 1.66, and 0.12, respectively. The vibrational distribution of CO normalized for  $v = 0-7$  is thus  $(v=0):(v=1):(v=2):(v=3):(v=4):(v=5):(v=6):(v=7) = 0.372:0.236:0.142:0.091:0.073:0.046:0.023:0.017$ , as shown in Table 1. The average vibrational energy of CO derived from our data is  $E_v = 40 \pm 4$  kJ mol<sup>-1</sup>. Our value is similar to values of  $42 \pm 3$  kJ mol<sup>-1</sup> reported by Shortridge and Lin<sup>9</sup> and  $37 \pm 3$  kJ mol<sup>-1</sup> by Abe et al.,<sup>13</sup> but much greater than the value of  $21 \pm 3$  kJ mol<sup>-1</sup> by Harding et al.<sup>11</sup>

The large extent of vibrational excitation can be rationalized according to a large variation in the bond lengths of the  $^3B_2$  state (and other angular states that might be involved) of  $CO_2$  relative to that of the ground state of CO. The bond length of these angular states is predicted to be in the range 1.25–1.26 Å,<sup>20</sup> whereas that of CO was determined to be 1.128 Å.<sup>38</sup>

**3. Temporal Profiles of Emission.** The total intensity of CO emission was derived by integration of all lines associated with CO in the spectrum. Emission of CO reaches a maximum at  $\sim 10$   $\mu s$ , followed by a slow decay; the data acquisition terminated at 24  $\mu s$  due to limitations of memory. This temporal profile is nearly identical to that recorded directly with the detector and an oscilloscope because CO is the only emitter. The temporal profile cannot be fitted with a simple function consisting of an exponential rise and an exponential decay because the rise and decay of many different vibrational levels of CO are involved.

The temporal evolution of emission of CO ( $v = 6$ ), the highest observable vibrational state, upon irradiation of a flowing mixture of  $O_3$  (0.016 Torr) and CO (0.058 Torr) at 248 nm is shown in Figure 7. We deconvoluted this profile with the instrument response function and modeled them with a mechanism consisting of formation and quenching of first order to derive a rate coefficient of formation  $k_f = (2.0 \pm 0.3) \times 10^5$



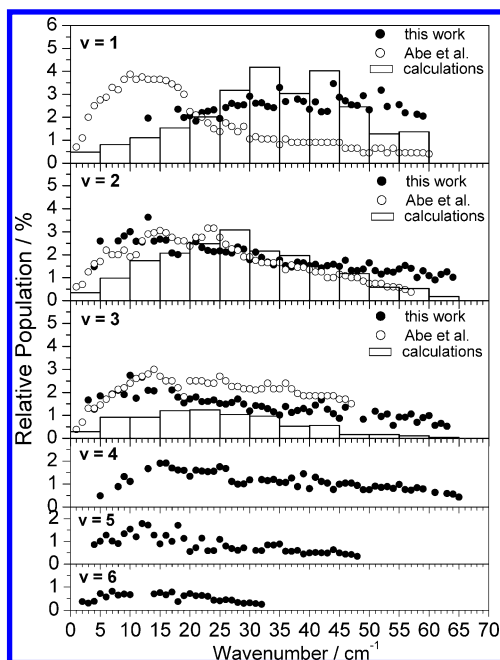
**Figure 7.** Temporal profiles of CO ( $v = 6$ ), shown as ●, upon photolysis of a flowing mixture of  $O_3$  (0.016 Torr) and CO (0.058 Torr) at 248 nm. The solid line represents a fitting to a simple rise and decay mechanism.

s<sup>-1</sup> and of quenching  $k_q = (1.7 \pm 0.7) \times 10^4$  s<sup>-1</sup> for CO. The slow rate of formation is consistent of a mechanism involving a long-lived adduct, as previously proposed. Using  $[CO] = 1.9 \times 10^{15}$  molecules cm<sup>-3</sup> and literature values of  $k_{1a} = (4-7) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,<sup>4,5,10</sup> we derive a pseudo-first-order rate coefficient  $k_{1a}^1 = (8-13) \times 10^4$  s<sup>-1</sup> for reaction 1a, slightly smaller than observed  $k_f$  in this work. The rate of quenching for CO ( $v = 6$ ) due to CO ( $v = 0$ ) was reported to be  $\sim 8.4 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,<sup>41,42</sup> corresponding to a pseudo-first-order rate coefficient of  $1.7 \times 10^3$  s<sup>-1</sup> under our experimental conditions, much smaller than observed  $k_q$ . This might indicate that quenching of CO ( $v = 6$ ) by  $O_3$  is much greater than by CO. The rate of quenching for this process is unreported, but is expected to be greater than  $k_3$  ( $2.0 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), quenching rate of CO ( $v = 1$ ) by  $O_3$ .<sup>11</sup>

**4. Comparison of Rotational Distribution with Trajectory Calculations.** Abe et al. predicted a rotational distribution of CO from reaction 1 with trajectory calculations.<sup>13</sup> Collisions of O ( $^1D$ ) with CO produce  $CO_2$  in its  $^1B_2$  state, which intersects with the  $^3B_2$  state of  $CO_2$ . All trajectories begin at the seam between the  $^1B_2$  and the  $^3B_2$  surfaces, which ranges from  $\theta = 100^\circ-130^\circ$  for the bending angle and  $R = 1.2-1.5$  Å for the bond length of the new C–O bond; the transition probability was assumed to be constant over this seam. The potential-energy surface was calculated with the MP2/6-31G\* method and fitted to an extended LEPS function by means of the least-squares method.

Figure 8 compares rotational distributions observed in this work (symbol ●) with those predicted with trajectory calculations (indicated with bars) and observed experimentally (symbol ○) with VUV LIF by Abe et al.;<sup>13</sup> experimental results were scaled to provide an effective overlap between  $J = 20-50$  for CO ( $v = 2$ ). The agreement for the rotational distribution of CO ( $v = 2, 3$ ) among both experiments and the calculation is satisfactory, whereas for CO ( $v = 1$ ) our result agrees with the calculation, but not with the experiment by Abe et al.<sup>13</sup> They attributed the excess population for CO ( $v = 1, 0 \leq J \leq 25$ ) to the adiabatic process, reaction 1b.

With the available kinetic energy, 33 kJ mol<sup>-1</sup>, of O ( $^1D$ ) from photolysis of  $O_3$  at 248 nm, only  $v \leq 1$  levels of CO can be populated from the adiabatic process. We are unable to observe the extra population for CO ( $v = 1, J \leq 20$ ) as reported by Abe et al.<sup>13</sup> partly because of the absorption by CO ( $v = 0$ ) and partly because of the kinetic energy of O ( $^1D$ ) might be partially thermalized in our system. The distribution of high- $J$



**Figure 8.** Comparison of rotational populations of CO ( $v = 1-6$ ) from O ( $^1D$ ) + CO. Key: (●) this work; (○) experiments from Abe et al.; (bars) trajectory calculations from Abe et al.<sup>13</sup>

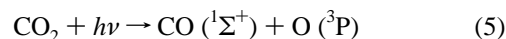
levels of CO ( $v = 1$ ) observed in this work agrees with trajectory calculations much better than that of Abe et al. Similar results of enhanced low- $J$  component of CO ( $v = 0$ ) were also reported by Abe et al., but we are unable to probe the population of CO ( $v = 0$ ) with our technique.

Elastic collisions with no exchange of atoms and inelastic collisions with exchange of oxygen atoms were distinguished in the trajectory calculations; the former has more contributions to production of CO ( $v = 0$  and 1), whereas the latter has more contributions to production of CO ( $v = 2$  and 3).<sup>13</sup> The elastic collisions tend to provide increased rotational excitation. We are unable to distinguish these two processes in this work; isotopic experiments are infeasible in our experiments using rapidly flowing gases. Observed bimodal distribution is consistent with the general picture predicted with previous trajectory calculations: inelastic collisions produce smaller rotational excitation but greater vibrational excitation, whereas the elastic collisions produce greater rotational excitation but smaller vibrational excitation.

Previous trajectory calculations take into account only the  $^3B_2$  potential-energy surface. According to quantum-chemical calculations, the  $^3A_2$  and  $^1A_2$  surfaces might also play a role.<sup>20</sup> The  $^1B_2$  state crosses the  $^3B_2$  and  $^3A_2$  states at distinctly different angles ( $\sim 92$  and  $109^\circ$  at  $R = 2.35$  Bohr) and the equilibrium angles for  $^3B_2$  and  $^3A_2$  states ( $118.5$  and  $127.4^\circ$ ) also vary substantially. If CO<sub>2</sub> adduct dissociates via these two states, the rotational distribution of CO might be distinctively different. Our observed non-Boltzmann (bimodal) distribution of CO is also consistent with a model that reaction 1a is associated with two or more dissociation paths. More sophisticated calculations are needed to enhance the understanding of the dynamics of these energy transfer processes and to compare with our experimental results.

**5. Comparison of Energy Transfer.** Stolow and Lee,<sup>43</sup> and later Lu et al.<sup>44</sup> investigated the photodissociation dynamics of CO<sub>2</sub> at 157 nm using photofragmentation translational spectroscopy; the latter authors employed direct VUV ionization with synchrotron radiation for detection. An average translational

energy was estimated to be  $\sim 150$  kJ mol<sup>-1</sup> based on their reported distribution of translational energy for the minor channel ( $\sim 4\%$ )



Given the excess energy of 230 kJ mol<sup>-1</sup> for reaction 5 upon 157 nm photodissociation, the internal energy of CO is estimated to be  $\sim 80$  kJ mol<sup>-1</sup>. The energy of CO<sub>2</sub> excited with light at 157 nm is only  $\sim 10$  kJ mol<sup>-1</sup> greater than the O ( $^1D$ ) + CO system upon photolysis of a mixture of O<sub>3</sub> and CO at 248 nm. The value of 80 kJ mol<sup>-1</sup> estimated for the internal energy of CO produced from photolysis of CO<sub>2</sub> at 157 nm in the molecular beam is similar to the value that we determined for reaction 1a:  $33 \pm 6$  kJ mol<sup>-1</sup> for rotation and  $40 \pm 4$  kJ mol<sup>-1</sup> for vibration.

The efficiency for E-V energy transfer determined in this work is  $40/(190) = \sim 21\%$ ; the initial translational energy of O ( $^1D$ ) was not taken into account. This value is similar to values 17% by Abe et al.<sup>13</sup> and 21% reported by Shortridge and Lin,<sup>9</sup> but greater than values 11% derived from the vibrational distribution reported by Harding et al.<sup>11</sup> Harding et al. reported an efficiency of  $25 \pm 5\%$  based on their measurements of the total number of CO ( $v = 1$ ) produced after collision with O ( $^1D$ ), with the quenching of CO by O<sub>3</sub> taken into account. The efficiency for the transfer of electronic to internal energy determined in this work, 38%, greater than values (29–31%) reported previously by Abe et al.<sup>13</sup> and Matsumi et al.<sup>12</sup>

#### IV. Conclusion

Rotationally resolved emission of CO up to  $v = 6$  and  $J = 68$  is observed upon photolysis of a flowing mixture of O<sub>3</sub> and CO at 248 nm; internally excited CO is produced via collisions of O ( $^1D$ ) and CO. The average rotational energy of  $33 \pm 6$  kJ mol<sup>-1</sup> and vibrational energy of  $40 \pm 4$  kJ mol<sup>-1</sup> for CO indicate that a substantial fraction of available energy is partitioned into the internal energy of CO, with  $f_r \cong 0.17 \pm 0.03$  and  $f_v \cong 0.21 \pm 0.02$ . Rotational distributions of CO ( $v = 2, 3$ ) agree with previous experiments and trajectory calculations by Abe et al.<sup>13</sup> Rotational distributions of CO ( $v = 4-6$ ) are new; they exhibit less rotational excitation than those in CO ( $v = 1-3$ ).

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