

Infrared radiative decay constants for the vibrational levels of CO($a^3\Pi$)

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The decay of the CO($a^3\Pi$, $v' = 0-3$) levels have been studied in a flowing-afterglow apparatus. The vibrational distribution was monitored by observing the CO($a^3\Pi-X^1\Sigma^+$) emission intensity. The results were interpreted to obtain 52.5, 77, and 178 sec^{-1} for the infrared radiative decay constants for the $v' = 1, 2,$ and 3 vibrational levels of CO($a^3\Pi$). The data also establish that the upper limit to the rate constant for vibrational relaxation of CO(a) by collision with He is $\leq 6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, corresponding to a collision probability of $\leq 1.5 \times 10^{-7}$.

INTRODUCTION

The radiative lifetime of the first-excited state of carbon monoxide, the $a^3\Pi$ state, has been the subject of numerous investigations.¹⁻⁶ Theoretical calculations by James^{5,6} have shown that the lifetime is a function of the quantum numbers J and Ω . An experimental confirmation of this calculation has been provided by Johnson⁷ and by Johnson and Van Dyck.⁸ Under conditions such that the rotational and multiplet levels are at thermal (300 °K) equilibrium, the electronic lifetime ($v' = 0$) given by Lawrence,^{1(a)} 7.5 msec, is the currently accepted value. Recently, Wicke and Klemperer⁹ have calculated the radiative transition probabilities for infrared emission from the $v' = 1-5$ levels and found that these lifetimes are comparable to the lifetime for the electronic transition. Thus, the vibrational populations of the CO($a^3\Pi$) state will change as a function of time because of infrared radiative decay.

The present work reports the time evolution (0-11 msec) of the relative vibrational populations of the $v' = 0-3$ levels of CO($a^3\Pi$). The experiments were done in a flowing-afterglow apparatus with helium carrier gas. The results confirm that electronic and vibrational radiative decay are in competition. In addition to obtaining the infrared radiative decay constants, an upper limit to the rate of vibrational relaxation of CO(a) in He was obtained from the data. The CO(a) was produced by the reaction He(2^3S) with CO₂ followed by electron recombination with CO₂(X). This system has been shown^{10,11} to be a clean and efficient source for study of CO($a^3\Pi$).

EXPERIMENTAL

The experiments were performed in a flowing-afterglow apparatus in which metastable He(2^3S) atoms were generated in a hollow-cathode discharge (400 V, 5mA) employing tantalum electrodes. The procedure was the same as described previously¹⁰ except for the design of the tubular reactor. The reactor (25 mm in diameter) had three observation windows which were 28, 108, and 188 mm from the end of the coaxial reagent inlet. This reactor permitted observation of the initial mixing zone (28 mm window) and observation of CO(a) at times up to 11 msec after observation. The observation time was varied by changing the distance from the flame terminus to the observation window, and by

changing the bulk velocity of the flowing helium. The latter was accomplished by throttling the pump. Computations are based upon the plug-flow approximation to obtain contact times.

Air Products' helium was passed through traps, placed both on the high and low pressure sides of the metering valve, which were at 77 °K and were packed with activated molecular sieve (5-A). The CO₂ (Matheson) was purified via bulb-to-bulb distillation and diluted (~10/1 in He) prior to use. Impurities, especially N₂ and H₂O, were very low as monitored by the N₂($B-X$) and OH($A-X$) emissions, which are excited from interactions with He(2^3S). The experiments were done at room temperature (~300 °K).

The CO($a^3\Pi-X^1\Sigma^+$) emission was observed with a 0.75 m Jarrell-Ash monochromator which was fitted with a cooled EMI 9558QA photomultiplier and a photon-counting rate meter. The detection system was carefully calibrated for wavelength response. The $\Delta v = -3$ and $\Delta v = -4$ sequences were observed for $v' = 0-3$ at all three windows. The vibrational band intensities were assumed to be proportional to the heights of the bands. These intensities were corrected for wavelength response and then converted to relative populations using Nicholls' Franck-Condon factors.¹² The time evolution of the fractional populations ($v' = 0-3$), as observed from the $\Delta v = -3$ sequence, is presented in Fig. 1. The data in Fig. 1 were taken over a range of pressure between 1 and 15 torr. The data for the $\Delta v = -3$ sequence are preferred because the signal-to-noise ratio is approximately a factor of 3 better than for the $\Delta v = -4$ sequence.

RESULTS

The results presented by James^{5,6} and by Wicke and Klemperer⁹ show that the lifetime of CO(a) is a strong function of v' , J' , and Ω . Since our experiments are in the pressure range 1-15 torr, the J' and Ω dependence will not be important because rapid relaxation will maintain Boltzmann populations. However, the decay plots of the vibrational levels shown in Fig. 2 clearly have larger slopes for the higher v' levels. This demonstrates a variation in lifetime with vibrational level. The results of Fig. 2 have been analyzed by the kinetic scheme described below.

The production of CO(a) in the He(2^3S) + CO₂ system

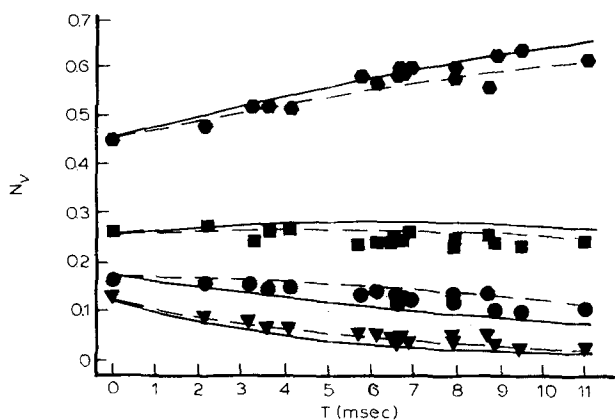
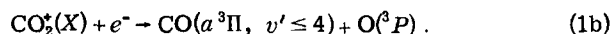
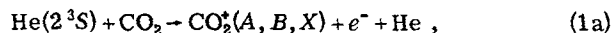
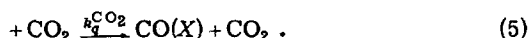
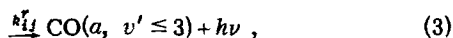
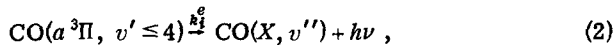


FIG. 1. The time evolution of the fractional populations N_v of CO (*a*) as observed from the $v = -3$ sequence. The symbols \bullet , \blacksquare , \bullet , and \blacktriangledown represent $v' = 0, 1, 2$, and 3 , respectively. As discussed in the text, the data were taken at various total pressures. The solid lines are the kinetic modeling results obtained when using the rate coefficients for infrared transitions calculated by Wicke and Klemperer⁹ and the rate coefficients for electronic transitions calculated from Eq. (9). The dashed line indicates the kinetic modeling when the rate coefficients for infrared transitions are those derived from Fig. 2 and partitioned according to the calculations of Wicke and Klemperer.⁹

is believed to proceed via $\text{CO}_2^* + e^-$ recombination¹⁰



The important decay processes for CO(*a*³Π) under our experimental conditions are summarized in the following equations:



In these equations k_i^e is the transition probability for radiation connecting the *a*³Π state with the ground state, k_{ij}^r is the transition probability for radiative transitions between the vibrational levels of the *a*³Π state, k_w is the rate constant for deactivation of CO(*a*³Π) by collisions with the reactor walls, and $k_q^{\text{CO}_2}$ is the rate constant for quenching CO(*a*) by CO₂. For our experimental conditions it is not necessary to include collision-induced electronic quenching or vibrational relaxation by He. This was demonstrated by observing that the fractional populations at a given window were invariant with He pressure from 1–15 torr. The fractional populations also show no correlation with [CO₂] for the concentration range used here. The following differential equation is obtained from the above processes:

$$\begin{aligned} d[\text{CO}^*, v_i]/dt = & \sum_{j=i+1}^{j_{\max}} k_{ij}^r [\text{CO}^*, v_j] \\ & - \left(k_i^e + \sum_{j=0}^{j-1} k_{ij}^r + k_w + k_q^{\text{CO}_2} [\text{CO}_2] \right) [\text{CO}^*, v_i]. \end{aligned} \quad (6)$$

This equation as it stands cannot be solved analytically. However, if the approximation is made that $\sum_{j=i+1}^{j_{\max}} k_{ij}^r [\text{CO}^*, v_j] \ll R_i [\text{CO}^*, v_i]$, where R_i is the sum of the four loss processes in Eq. (6), then the variables may be separated to yield

$$\ln \frac{[\text{CO}^*, v_i]}{[\text{CO}^*, v_i]^0} = - (k_i^r + k_i^e + k_w + k_q^{\text{CO}_2} [\text{CO}_2]) t, \quad (7)$$

where $\sum_{j=0}^{i-1} k_{ij}^r$ has been replaced by k_i^r . The population in state v_i can be compared with that in state $v = 0$ to obtain

$$\ln \frac{[\text{CO}^*, v_i]}{[\text{CO}^*, v=0]} = \ln \frac{[\text{CO}^*, v_i]^0}{[\text{CO}^*, v=0]^0} - [k_i^r + (k_i^e - k_0^e)] t, \quad (8)$$

where the reasonable assumption has been made that k_w and $k_q^{\text{CO}_2}$ are independent of vibrational energy level.¹⁰ Electronic energy is quenched with unit probability in wall collisions; therefore, differences in wall removal rates will depend only on the rate of diffusion to the walls of the reaction vessel. The diffusion rates will not vary significantly with a vibrational level in a given electronic state, especially since the [CO] is too low for energy exchange to be important.¹³ According to Eq. (8), a negative slope should result from a plot of $\ln[\text{CO}^*, v_i/\text{CO}^*, v=0]$ vs time. This slope is the sum of the two radiative-loss rate coefficients of level v_i minus the rate coefficient for the electronic transition from level $v = 0$. Figure 2 shows that the expected linear relationship is indeed followed and the slopes and intercepts from these plots are tabulated in Table I. The form of the experimental results gives some credence to our initial assumption made in obtaining Eq. (7), i.e., radiative-cascade processes which populate level v_i may be neglected with respect to other loss processes. As further support of this assumption, we note that $k_w = D_0/\Lambda^2 p$, where D_0 is the diffusion coefficient of CO*(*a*) in He, Λ^2 the characteristic diffusion length, and p the pressure. The diffusion coefficient for CO(*a*) in He at 300 °K is $\sim 660 \text{ cm}^2 \text{ sec}^{-1}$ at 1 torr,¹¹

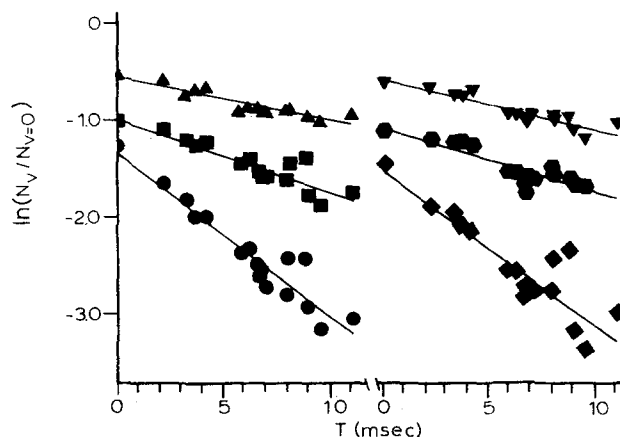


FIG. 2. The experimental data plotted according to Eq. (8). To clarify the results for the $\Delta v = -3$ and $\Delta v = -4$ sequences the data are plotted separately. The $\Delta v = -3$ sequence is denoted by \blacktriangle — $\ln(N_{v=1}/N_{v=0})$, \blacksquare — $\ln(N_{v=2}/N_{v=0})$, and \bullet — $\ln(N_{v=3}/N_{v=0})$ and the $\Delta v = -4$ sequence by \blacktriangledown — $\ln(N_{v=1}/N_{v=0})$, \bullet — $\ln(N_{v=2}/N_{v=0})$, and \blacklozenge — $\ln(N_{v=3}/N_{v=0})$. The solid lines are plots of the least squares best fits.

TABLE I. Slope and intercept values of Fig. 2.

Vibrational level	$\Delta v = -3$ sequence		$\Delta v = -4$ sequence	
	Slope (sec ⁻¹)	Intercept ^a	Slope (sec ⁻¹)	Intercept ^a
1	-40.5 ± 3.7	-0.58 ± 0.03	-51.3 ± 2.9	-0.60 ± 0.04
2	-76.2 ± 5.7	-0.99 ± 0.04	-65.4 ± 5.7	-1.09 ± 0.04
3	-167.9 ± 9.3	-1.33 ± 0.07	-154.4 ± 12.7	-1.57 ± 0.09

^aThese intercepts also are the logarithm of the ratios of relative vibrational populations produced from Reaction (1b). The normalized distribution ($v' = 0-3$) is 0.46 : 0.26 : 0.17 : 0.11, which corresponds to a temperature of 5150°K.

and $\Lambda^2 = r_0^2 / (2.4)^2$ ($r_0 = 1.25$ cm, the flow tube radius); thus, $k_w \sim 2.4 \times 10^3$ sec⁻¹ at 1 torr. Since the radiative-rate coefficients are at most 100–200 sec⁻¹, a major contribution to the decay of CO($a^3\Pi$) arises from diffusion to the wall even at a pressure of 10 torr. Furthermore, the concentration of CO₂ varied from $\sim 3 \times 10^{12}$ to 5×10^{13} molecule cm⁻³. Since¹⁰ $k_q^{CO_2} = 2 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹, the pseudo-first-order removal of CO($a^3\Pi$) by CO₂ will range between 60 and 1000 sec⁻¹, the higher figure being approached at higher reactor pressures. Therefore, as wall quenching becomes slower, quenching by CO₂ becomes more rapid, thus maintaining an overall rapid decay rate of CO*($a^3\Pi$) over the full range of pressures.

According to Eq. (8), the slopes from Fig. 2 will give k_i^e directly, if the rate coefficients for electronic transitions are the same for all vibrational levels. Lawrence and Seitel¹⁴ have measured absorption oscillator strengths from $v'' = 0$ of the ground state of CO to $v' = 0-5$ of CO($a^3\Pi$), and rate coefficients for the electronic transitions from CO($a^3\Pi$, $v' = 0-5$) can be obtained from these oscillator strengths, Franck-Condon factors,¹² and⁶

$$k_{v'}^e = \sum_{v''} \frac{A_{v''v'}}{6} = \frac{8\pi^2 e^2}{6m_e c} \frac{f_{v''v'}}{\bar{\nu}_{v''v'}} \left(\sum_{v''} \bar{\nu}_{v''v'}^2 q_{v''v'} \right). \quad (9)$$

The factor of 6 is based upon the assumption of equal population in the various sub levels of CO($a^3\Pi$). The other assumption in Eq. (9) is that of a constant transition moment. The intensity data from our laboratory for the v'' progressions from levels $v' = 0-3$, together with Nichols' Franck-Condon factors show that this assumption is satisfactory. Calculations based upon Eq. (9) give $k_i^e = 135.6, 130.1, 129.5, 120.7$ sec⁻¹ for $i = 0-3$, respectively. The lifetime calculated from k_0^e is 7.37 msec, which is in excellent agreement with the accepted value for the lifetime of CO($a^3\Pi$, $v' = 0$), 7.5 msec.³

If the calculated values for k_i^e are used with the overall decay rate constants obtained from an average (weighted by the inverse of the standard deviation) of the decay slopes of Fig. 2, values for k_i^e of $52.5 \pm 30\%$, $77 \pm 22\%$, and $178 \pm 17\%$ sec⁻¹ are obtained for vibrational levels 1–3, respectively. The lifetime values are summarized in Table II. These numbers can be compared with Wicke and Klemperer's⁹ calculated values of 57, 129, and 213 sec⁻¹ again for $v' = 1-3$. The agreement for $v' = 1$ and 3 is good, the discrepancy for $v' = 2$ is larger than expected.

As an alternative method of analysis, the data, as plotted in Fig. 1, were compared to computed results which were obtained by numerically integrating the differential rate equations using a fourth-order Runge Kutta algorithm. Calculations using the k_i^e values from Eq. (9) and the values of k_{ij}^r , as given by Wicke and Klemperer are compared to results using the experimental k_i^e values. This analysis incorporated the reasonable assumption that the rate constants for wall removal and electronic quenching by CO₂ are equal for all vibrational levels. This assumption should mean that the time evolution of the fractional populations is independent of the value $k_w + k_q^{CO_2}$. This point was checked by doing two calculations, one using $k_w + k_q^{CO_2} = 0$ and the other using $k_w + k_q^{CO_2} = 1.8 \times 10^3$ sec⁻¹; these calculations gave identical results for the time evolution of the fractional populations. The slopes of ln[CO(a , $v' = 0-3$)] vs t plots for these two calculations differed by the value of $k_w + k_q^{CO_2}$. The calculated results for $k_w + k_q^{CO_2} = 1.8 \times 10^3$ sec⁻¹ gave linear semilog plots of [CO(a , $v' = 0-3$)] vs time, supporting the method used in the previous analysis. The calculated time evolution of the fractional populations are compared to the data in Fig. 1. The important point to note is that there are *no free parameters* in this fit. An additional kinetic modeling calculation was done using values of k_i^e , which were derived in the following manner: the values of k_i^e as obtained from Eq. (8) were partitioned according to the calculations of Wicke and Klemperer.⁹ The results of these calculations are presented in Fig. 1. There is reasonable agreement between these data and the previous kinetic modeling results. Unfortunately, the calculations give no indication as to the source of the discrepancy in Table II for $v' = 2$.

The experimental data and the kinetic model results indicate that vibrational relaxation was negligible for all of the experimental conditions. The upper limit to the collision probability for vibrational relaxation by He can be estimated by assuming that a 10% change in the vibrational distribution would have been observable. Using the integrated pseudo-first-order rate expression to represent vibrational relaxation, the upper limit can be deduced from the experiment with the longest contact time and highest pressure. At the third window and under throttled conditions $t = 10.8$ msec. To be on the conservative side, we used 5 torr rather than 15 torr; setting $N_w/N_v^0 = 0.9$ gives $k = 6.1 \times 10^{-17}$ cm³ molecule⁻¹ sec⁻¹ for these conditions. The hard sphere bimolec-

 TABLE II. Summary of lifetimes for CO($a^3\Pi$, $v' = 0-3$).

Vibrational level	τ^e (msec)		τ^r (msec)
	Eq. (9)	This work ^a	
0	7.37		
1	7.69	19.0 ± 5.9	17.3
2	7.72	13.1 ± 2.9	7.8
3	8.28	5.6 ± 1.0	4.7

^aAverage values from the $\Delta v = -3$ and $\Delta v = -4$ sequences.

^bCalculated by Wicke and Klemperer.⁹

ular rate constant is $4.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 300 °K for molecular diameters of 2.6 Å and 3.6 Å for He and CO, respectively; thus, $P_{v',v'-1}^{\text{He}} \leq 1.5 \times 10^{-7}$. Apparently the vibrational relaxation of CO(*a*) by He resembles CO(*X*) rather than CO(*A*) or CO*(*A*) for which the transition probabilities are 0.1 to 0.01.^{15,16}

CONCLUSION

The temporal variation of the relative populations of CO(*a*³Π, *v*'=0–3) was studied in a flowing-afterglow apparatus from 0–11 msec. The data were analyzed to obtain average lifetimes for the infrared radiative transitions of the *v*'=1–3 levels. Our experimental values, which are in accord with the recent calculations of Wicke and Klemperer,⁹ show that for *v*'=3 [and presumably for the higher vibrational levels of CO(*a*³Π)] the infrared lifetimes are shorter than the lifetimes for the electronic transitions. The vibrational relaxation of CO(*a*³Π) by helium is slow with $k \leq 6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

Dr. Brian Wicke (TRW, Redondo Beach, CA) has pointed out that a better fit of his calculated infrared decay rate constants to our experimental data may be obtained by adjusting slightly the relative vibrational level populations at zero time to 0.44, 0.24, 0.19 and 0.14 for *v*'=0, 1, 2, and 3, respectively. These values are consistent with the present results to within the error limits (~10%). The discrepancy in decay rate constants for *v*'=2 may arise from the approximation involved in deriving Eq. 7. We wish to thank Dr. Wicke for his comments.

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