Vibrational energy transfer in CO from 100 to 300 °K*†

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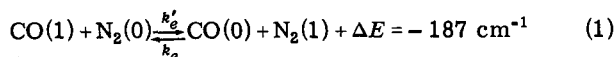
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The laser fluorescence method, whereby CO molecules are optically pumped from the vibrational level $v = 0$ to the $v = 1$ state by frequency-doubled pulses from a CO_2 laser, has been used to determine vibrational energy transfer rate coefficients for CO. Rates for the V-V exchange processes $CO(0) + N_2(1) \rightarrow CO(1) + N_2(0)$ and $CO(1) + CO(1) \rightarrow CO(0) + CO(2)$, and for the deactivation of CO by H_2 have been measured in the range $100°K \leq T \leq 300°K$. The probability of energy transfer from N_2 to CO decreases slightly as T decreases in this range, while the probability of the CO–CO V-V process is approximately proportional to T^{-1}. Rate coefficients were also measured at $T = 297°K$ for the deactivation of CO(1) by the polyatomic molecules CH_4, C_2H_4, C_2H_6, HCOOH, CH_3COOH, CH_3CHO, CH_3OH, C_2H_5OH, H_2O, D_2O, H_2S, and C_4H_{10}.
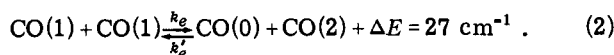
INTRODUCTION

Vibrational energy transfer in CO has been the subject of recent attention[1-8], in part because of the crucial role that vibrational energy transfer rates play in determining the operating characteristics of CO lasers, in part because of the occurrence of vibrationally excited CO in combustion processes, and in part because several new experimental techniques[2,3,6-8] have greatly facilitated determination of such rates. We have used the laser-excited vibrational fluorescence technique, whereby CO molecules are optically pumped from the $v = 0$ to $v = 1$ state with frequency-doubled pulses from a CO_2 TEA laser, to determine rate constants for the V-V transfers:

$$CO(1) + N_2(0) \underset{k_e}{\overset{k_e'}{\rightleftharpoons}} CO(0) + N_2(1) + \Delta E = -187 \text{ cm}^{-1} \qquad (1)$$

and

$$CO(1) + CO(1) \underset{k_e'}{\overset{k_e}{\rightleftharpoons}} CO(0) + CO(2) + \Delta E = 27 \text{ cm}^{-1} . \qquad (2)$$

The rate coefficients for reactions (1) and (2), which are of importance in understanding the performance of CO lasers, have been determined in the usual operating temperature range of CO lasers, $100°K \leq T \leq 300°K$. The probability of deactivation of CO($v = 1$) by hydrogen has also been measured in this temperature range. Because of the possible importance of vibrational activation and deactivation in combustion processes, the rates of deactivation of CO($v = 1$) by the series of polyatomic molecules methane, ethylene, ethane, formic acid, acetic acid, acetaldehyde, methanol, ethanol, H_2O, D_2O, hydrogen sulfide, and butane have been measured at room temperature.

EXPERIMENTAL

The general technique of laser-excited vibrational fluorescence has been discussed at length[9,10] and will not be reviewed here. Our particular experimental apparatus was used previously to determine room temperature rate constants for vibrationally excited CO[3] and NO.[11] References 3 and 11 discuss all relevant details not given below.

A stainless steel fluorescence cell 3 cm in diameter and 8 cm long with three brazed sapphire windows (laser entrance and exit windows, plus one perpendicular fluo-

rescence viewing port) was used for the low temperature measurements. Cooling was provided by flowing cold He gas through copper cooling coils soldered to the outside of the fluorescence cell. To thermally isolate the three cell windows, Pyrex tubing was glued to the cell windows and a sapphire window attached to the opposite (room temperature) end of the Pyrex tube. Thermally insulating foam tape was wrapped around the entire assembly. All of the four calibrated thermocouples attached to the cell walls always read within ±5 °K of the mean temperature reported in the results. Better agreement, of course, was achieved near room temperature. Temperature drift during any given measurement was less than 1 °K.

For the measurements at $T = 297$ °K of the deactivation rate of CO(1) by polyatomic molecules, the Pyrex cell used earlier[3,11] was again employed. For the substances in liquid phase at room temperature, a Pyrex sidearm containing the liquid was attached to the cell. After thorough degassing of the liquid, the pressure of its vapor in the cell was determined either by direct measurement with a capacitance manometer or by immersing the sidearm in a fixed temperature bath and using the vapor pressure vs temperature curves. Results obtained using these two different methods of pressure determination were in reasonable agreement, that
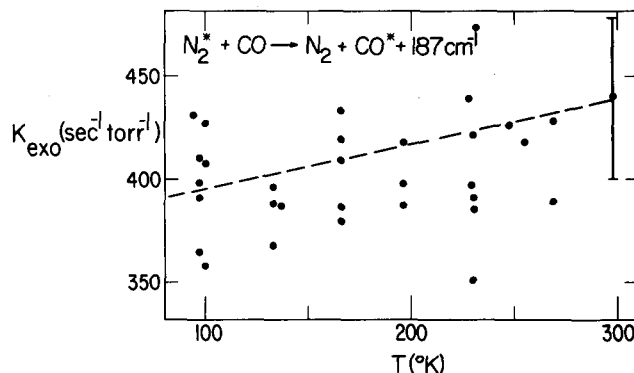

FIG. 1. Rate constant as a function of temperature for the exothermic transfer of vibrational energy from $N_2(1)$ to CO(0). Each data point represents a measurement on a different N_2–CO gas sample. The point at $T = 297$ °K is from Ref. 3.
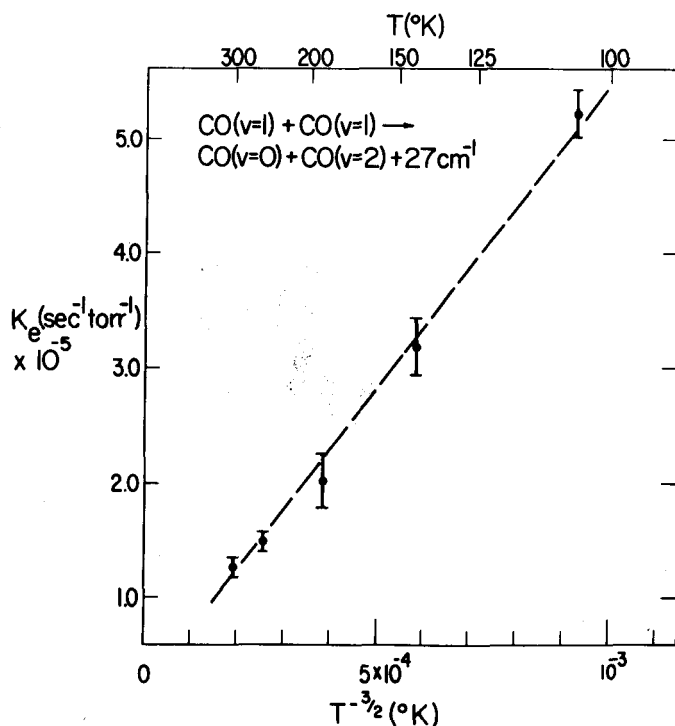
FIG. 2. Rate constant as a function of temperature for the CO V-V pumping process [Eq. (2) of text] in the exothermic direction. Each data point is the average result of the rate constants determined from several samples at different pressures at each temperature. The error bars are one standard deviation in the data. The point at $T = 297$ °K is from Ref. 3.

is any systematic difference between data with the two methods was much less than the statistical variation of individual measurements. Data were obtained as a function of the time that the gas mixture was in the cell in order to further guard against the systematic errors which may arise in determining the true pressure of
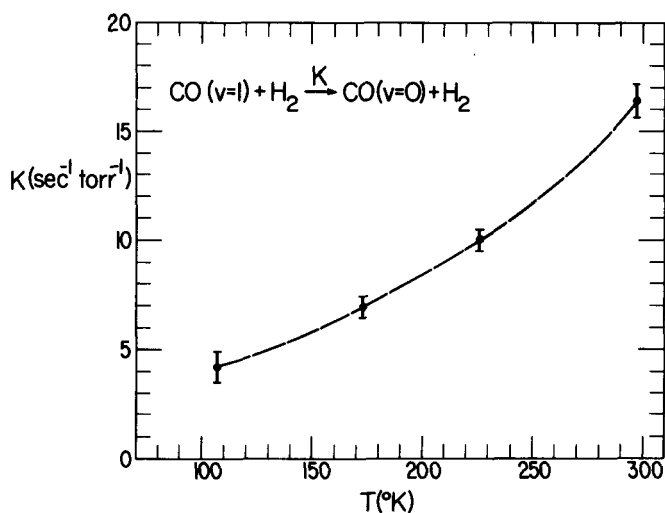

FIG. 3. Rate constant for the deactivation of CO($v = 1$) by normal hydrogen. Each data point is the average result of the rate constants determined from several samples at different pressures at each temperature. The error bars are one standard deviation in the data. The point at $T = 297$ °K is from Ref. 3.

these condensible vapors.

Measurements of the deactivation time τ, made over a pressure range factor, p_{max}/p_{min} of at least 10 and sometimes as much as 100 for a particular polyatomic species, were consistent with $\tau \propto p^{-1}$ in all cases.

The gases used and the impurities (in parts per million) or purity (in percent) claimed by the manufacturers are: CO, research grade ($H_2 < 5$, $O_2 < 20$, $Ar < 20$, $N_2 < 1000$, $CO_2 < 10$, dewpoint < -80 °F, hydrocarbons < 2); $N_2(\geq 99.998\%)Ar(\geq 99.9995\%)$; $He(H_2 < 0.05$, $CH_4 < 0.005$, $H_2O = 0.2$, $N_2 = 0.09$, $CO_2 = 0.02$, $O_2 < 0.1$, total < 1.3); $H_2(O_2 < 1$, $N_2 < 5$, hydrocarbons < 0.5, dewpoint $= -90$ °F); $CH_4(\geq 99.98\%)$; $C_2H_4(\geq 99.5\%)$; $C_2H_6(\geq 99\%)$; $C_4H_{10}(\geq 99.5\%)$; $H_2S(\geq 99.5\%)$. The H_2S was additionally purified by freezing out the H_2S at liquid nitrogen temperature under vacuum in order to remove any decomposed gas. The liquids were rated $CH_3OH(> 99\%)$; $C_2H_5OH(> 99\%)$; $D_2O(> 99.8\%$ isotopic purity); HCOOH(anhydrous $\geq 99\%$); $CH_3CHO(\geq 99\%)$; $CH_3COOH(\geq 99.7\%)$.

The fluorescence decay traces were single exponen-

TABLE I. Rate constants and probabilities for deactivation of CO($v = 1$) by polyatomic molecules, $T = 297 \pm 1$ °K.

Molecule	Deactivation rate constant (sec^{-1} torr^{-1})	Deactivation[a] probability per collision $\times 10^4$
H_2O	6400 ± 1600[b]	7.8
D_2O	440 ± 60	0.55
H_2S	650 ± 60	0.75
CH_4	297 ± 20[c]	0.26
HCOOH	11700 ± 1700	13.9
CH_3OH	5900 ± 1400	6.5
C_2H_6	3200 ± 300	2.9
CH_3CHO	4700 ± 300	4.8
C_2H_5OH	5900 ± 600	5.9
C_2H_4	3800 ± 250	3.6
CH_3COOH	20000 ± 3600	20.8
C_4H_{10}	6400 ± 300	5.4

[a]Deactivation cross sections, $\sigma(cm^{-2})$, are related to the rate constant (sec^{-1} torr^{-1}) by $\sigma = k\sqrt{\mu}/\times 1.227 \times 10^{-22}$, where μ is the collision reduced mass in atomic mass units. The probability per collision is σ(for deactivation) divided by a hard sphere cross section which has here been estimated from data for the Lennard–Jones potential compiled in J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), Tables I-A, p. 1110 and supplement p. 1212. The hard sphere cross section for H_2O is based on data for the Stockmayer Potential in Table 8.6-1, p. 599 and the value for D_2O is assumed identical. The hard sphere cross section for HCOOH is assumed identical to CH_3OH and those of CH_3CHO and CH_3COOH are assumed equal to C_2H_5OH.
[b]The error bars give the extremes of measured values and hence represent a conservative claim to accuracy.
[c]Reference 8 reports 293 ± 14 for this rate constant.

TABLE II. Deactivation of $CO(v=1)$ by gases at various temperatures.

T (°K)	P_{CO} (torr)	P_{GAS} (torr)	τ (μsec)
		H_2	
226	1.57	96.4	99.4
	2.32	211	49.3
	2.95	500	20.8
	3.36	150	63.8
173	3.09	671	21.2
	1.16	91.7	152
	2.68	412	33.9
	6.22	197	82.5
107	6.08	74.2	377
	1.91	314	86.2
	2.58	854	22.0
	3.30	516	43.6
	3.84	211	121
		He	
246	0.548	128	14.1
	0.112	106	62.5
	0.300	124	26
	0.208	148	37.2
188	0.507	141	12.1
	0.275	113	21.5
	0.122	117	46.9
	0.301	128	24.1
	0.301	350	20.2
	0.410	108	13.5
	0.410	303	13.6
143	0.440	110	8.51
	0.218	112	17.4
	0.348	104	12.5
	0.504	100	8.55
105	0.306	21.2	9.07
	0.179	19.6	14.9
	0.250	22.3	11.5
		N_2	
269	5.05	298	20[a]
	9.15	25.8	135
255	3.39	271	24
247	8.80	77.2	66
230	7.83	316	22
	5.71	16.1	260
	6.04	61.6	100
	7.44	324	21.4
	4.74	34.5	160
	4.14	80.5	87
196	6.40	313	27.4
	6.27	29.0	186
	4.98	74.0	104
166	6.36	355	31.5
	4.77	29.3	240
	6.28	81.6	115
	6.19	189	55
	6.73	439	25
138	4.85	331	48.8
		N_2	
133	3.48	43.3	274
	3.54	106	141
	2.92	469	41

TABLE II (Continued)

T (°K)	P_{CO} (torr)	P_{GAS} (torr)	τ (μsec)
100	8.70	·323	75
	8.21	102	180
	5.50	337	85
96	6.74	498	65
	4.07	100	260
	5.16	204	140
	7.96	404	72
	3.09	457	78

[a]The relaxation times τ listed for the $CO-N_2$ mixtures are for the fast $V-V$ relaxation process denoted λ_1 in Ref. 12.

tials except for mixtures of CO and N_2 where the $CO(v=1)$ fluorescence decayed as the sum of two exponentials, the characteristic time constant of the faster decay being at least a hundred times less than the time constant of the slower decay. Analysis of these data has been discussed at great length.[3,8-12] Fluorescence from the $CO(v=2)$ state was monitored by blocking the fluorescence from the $v=1$ state with a 3 cm long filter cell filled with one atmosphere of cold CO gas. The fluorescence from the $v=2$ state first rose then decayed at a much slower rate. The relation between the fluorescence rise time and k'_e for process (2) has also been discussed.[3,11,13] In determination of this latter rate constant, very dilute mixtures of CO in He or Ar (typically CO = 0.5 torr, He = 300 torr where one torr = 133.3 Nm^{-2}) were used. In the determination of k_e for process (1), mixtures of CO and N_2 with the mole fraction of CO, X_{co} in the range $0.003 \le X_{co} \le 0.3$ were used. All fast relaxation times τ for $CO-N_2$ mixtures obeyed the relation

$$\tau^{-1} = k'_e P_{N_2} + k_e P_{CO} \tag{3}$$

as expected from previous observations.[3,9-12] The ratio of fast to slow fluorescence signal heights, S, also followed the expected relation given by Eqs. (19) and (26) of Ref. 12.

RESULTS

Figure 1 shows the results for vibrational energy transfer between CO(1) and $N_2(0)$. The rate constant k_e was determined from the data via Eq. (3). The energy transfer in the exothermic direction is seen to be almost independent of temperature in the range 100 °K $\le T \le$ 300 °K. Figure 2 shows the results for the CO $V-V$ pumping rate [Eq. (2)]. The rate constant k'_e was determined[3] from $k'_e = (P_{CO}\tau)^{-1}$ and $k_e/k'_e = \exp(27 \text{ cm}^{-1}/kT)$. The rate coefficient k_e is approximately proportional to $T^{-3/2}$, and the transfer probability per collision to T^{-1}. The rate constant for deactivation of CO $(v=1)$ by normal H_2 is shown in Fig. 3. The deactivation probability decreases by a factor of 7 in the region 100 °K $\le T \le$ 300 °K.

Table I gives the room temperature deactivation rate constants and probabilities for the polyatomic collision partners.

TABLE III. Measurements of deactivation of CO($v=1$) by various gases.

$\tau_{\mu sec}$	P_{torr}	P_{CO}	P_{buffer}
	H$_2$O		Ar
440	0.34	3.25	0
800	0.24	3.21	0
140	1.2	3.36	0
145	1.2	3.36	0
240	0.58	3.36	0
320	0.46	3.36	0
8.5	18.2	4.41	248
33.0	4.6	4.24	233
	H$_2$S		Ar
6.3	209	4.6	0
96	16.5	2.74	233
200	7.34	2.34	242
485	2.99	1.89	251
14	102	3.86	0
28	50.3	3.68	249
63.5	25.2	4.45	249
160	10.6	3.84	251
400	5.16	2.48	237
	CH$_4$		Ar
375	8.6	2.52	230
200	16.1	7.1	224
85	40.5	1.7	209
41	76.6	3.4	175
22	162.	4.0	0
10.5	317	7.3	0
35.3	102	1.3	0
15.8	211	1.3	0
8.1	375	1.3	0
35.2	99.1	5.7	0
17.7	202	5.7	0
9.1	391	5.7	0
	C$_2$H$_4$		Ar
58	4.52	1.8	252
12	20.9	6.4	252
160	1.56	1.67	254
95	3.02	1.9	242
7.5	35.3	8.4	208
37.5	6.5	1.39	255
24.	11.2	4.15	226
	C$_2$H$_6$		Ar
230	1.21	1.65	236
115	2.58	1.37	274
10.2	31.2	5.23	251
18.5	16.3	3.45	236
27	11.1	3.18	262
69	4.4	4.08	278
	HCOOH		Ar
7.82	9.47	3.8	348
156.	0.54	4.16	0
33.	2.75	3.21	0
12.2	5.55	5.25	0
92.2	0.90	4.09	0
	CH$_3$OH		
375	0.455	3.90	0
164	0.98	2.73	0
26	5.45	3.62	0
15.7	14.0	4.1	0
75.	2.36	3.8	0

TABLE III (Continued)

$\tau_{\mu sec}$	P_{torr}	P_{CO}	P_{buffer}
	C$_2$H$_5$OH		He
11.5	15.5	3.5	340
47	4.37	3.83	0
360	0.43	3.38	0
170	1.00	3.5	0
	CH$_3$COOH		He
56	1.06	3.5	0
55	1.06	3.5	400
109	.52	3.6	384
10.4	5.23	3.9	383
20.6	2.12	3.7	390
137	0.29	3.3	325
150	0.35	3.9	0
	CH$_3$CHO		
278	0.735	4.39	0
74.0	2.71	4.5	0
18.7	11.4	3.8	0
43	5.55	3.3	0
148	1.46	3.0	0
572	0.378	2.5	0
	C$_4$H$_{10}$		
14.9	10.3	4.18	0
141	1.07	4.04	0
34.7	4.56	3.88	0
74.5	2.01	4.27	0
17.6	8.99	1.03	0
	D$_2$O		Ar
489	5.15	3.85	0
1820	1.26	3.04	337
680	3.67	2.81	312
175	13.8	3.50	321
354	6.70	3.50	302
220	9.47	3.71	0
1260	1.49	3.73	0

DISCUSSION

Probabilities for essentially resonant $V-V$ processes generally have been observed[12] to decrease as T^{-1} [i.e., k(sec^{-1} torr^{-1}) has been found to be linear with $T^{-3/2}$], so the data shown in Fig. 2 are not surprising. By using a gain/absorption technique to probe CO(v) populations excited by a pulsed electric discharge, Smith and Wittig[2] derived probabilities for

$$CO(0) + CO(v) \rightarrow CO(1) + CO(v-1) - \Delta E,$$

$4 \leq v \leq 10$, in the range $100\,°K \leq T \leq 300\,°K$. Since ΔE(cm^{-1}) = $27(v-1)$, the energy defect ranges from 81 to 243 cm^{-1} for their measurements. Smith and Wittig found that for all the levels $4 \leq v \leq 10$, the probability for $V-V$ transfer in the exothermic direction was a factor of 1.6 to 2 higher at $T=100\,°K$ than at $T=300\,°K$. If the collision diameter (3.763 Å) used in Ref. 2 is assumed, our data for the $v=2$ state give a probability $P \approx 0.035$ at $T=100\,°K$ and $P=0.013$ at $T=300\,°K$. The results given in Fig. 5 of Ref. 2 extrapolate smoothly back to these values of P for the case $v=2$.

The probability for $V-V$ exchange from N$_2$(1) to CO(0) decreases by about 60% in the region $T=300\,°K$ to $T=100\,°K$. This mild temperature dependence is ex-

pected by analogy to similar measurements on CO–CO exchange and $V-V$ transfer from $CO_2(00\,°1)$ to diatomics.[11] The importance of the various molecular parameters (ΔE, rotational constants, collision reduced mass, attractive and repulsive forces) in causing $V-V$ transfer has been discussed in many recent theoretical papers.[14] The rates for deactivation of CO(1) by H_2 (Fig. 3) are in complete agreement with the original work of Miller and Millikan.[1]

Deactivation rates of $CO(v=1)$ by the organic molecules listed in Table III are a factor of 10–20 slower than corresponding deactivation rates of the $CO_2(00\,°1)$ level[15] by the same molecules [the CO(1) is 2143 cm^{-1} and the $CO_2(00\,°1)$ is 2350 cm^{-1} above the ground state]. For both CO and CO_2, C_2H_6 is a factor of 13 more efficient than CH_4 at deactivating the respective molecular levels. However, for CO_2 there are a number of possible final states, other than the ground state [i.e., $CO_2(nm^l0)$] while for CO essentially the entire 2143 cm^{-1} of energy must be taken up by the vibrations (or rotations) of the collision partner. Since the internal states of the polyatomic collision partners are not determined, no information is available as to which combination of $V \rightarrow V$, R processes cause the deactivation of the CO(1). H_2O is 10 times as efficient as D_2O at deactivating CO, but only 0.5 times as efficient as D_2O at deactivating $CO_2(00\,°1)$.[16] The importance of a $V-V$ process for the CO_2 deactivation, but apparently not for the CO, is clearly indicated, since deuterated molecules are less efficient than the normal hydrogenated species at causing vibration to rotation energy transfer.[16,17]

ACKNOWLEDGMENTS

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