

Rate of population of CO(v) in a CS₂/O₂ flame^a

A. A. Vetter and F. E. C. Culick

Daniel and Florence Guggenheim Jet Propulsion Center, California Institute of Technology, Pasadena, California 91125

(Received 8 September 1976)

The rate of vibrational population of carbon monoxide in a steady CS₂/O₂ flame has been determined from CO overtone emission. A steady-state analysis indicates that, for a flame, the fifteenth vibrational level has the largest rate of population.

I. INTRODUCTION

The reaction between carbon monosulfide and atomic oxygen,



is interesting because the product carbon monoxide is formed very vibrationally excited with little or no CO formed in the lower vibrational levels. This chemically formed population inversion is the basis of many lasers.^{1,2} The distribution of vibrational energy in CO from this reaction has an inverted population and has a maximum production at the twelfth or thirteenth vibrational level.³⁻⁹ These relative rates of population were determined with low gas temperatures and different gas compositions than are found in the CS₂/O₂ flame laser.

In this paper, a technique is developed for using the intensity of CO emission to deduce the relative rates of population of the vibrational levels in a CS₂/O₂ free-standing flame. The first step is to determine the relative steady-state vibrational population of CO in the flame from the overtone bands of spontaneous emission.¹⁰ The relative rates of formation of CO(v), R_v , are then obtained from the relative steady-state populations, N_v , by solving the conservation equations for the populations CO(v) under steady-state conditions.¹¹ The case of a free-standing flame requires modifications of the analyses for the more idealized cases to which these techniques have been applied successfully in the past. These modifications are developed here and are applied to experimental data obtained from a small CS₂/O₂ flame; this flame is a scaled-down version of a free-standing flame laser.

II. TECHNIQUE

The steady-state populations of vibrationally-excited carbon monoxide are estimated from the intensity of the overtone emission,¹²

$$N_v \propto \frac{I_{v,v-2}}{A_{v,v-2} \nu_{v,v-2}}, \quad (2)$$

where N_v is the relative steady-state population of CO(v), $I_{v,v-2}$ is the relative intensity of the emission from CO(v) to CO($v-2$), $A_{v,v-2}$ is the spontaneous emission (Einstein) coefficient for the transition from CO(v) to CO($v-2$).

^aThis work was supported partly by Caltech funds and by AFOSR contract 74-2674. The Division of Engineering and Applied Science of the California Institute of Technology provided funds for computations.

The values of $I_{v,v-2}$ are obtained experimentally from the overtone spectra after correcting for optical system characteristics. The $I_{v,v-2}$ can be taken as the maximum intensity from each band or the integrated intensity of each band⁷; since the peak intensity method has been shown to be as effective as other techniques,⁷ this method was used. The steady-state analysis of the species conservation equation yields the relation for R_v in terms of N_v ,^{7,11}

$$R_v = \sum_{n=1}^v A_{v,v-n} N_v - \sum_{n=1}^{v_{\max}} A_{v+n,v} N_{v+n} + \sum_{q=1}^v \left(\sum_{n=1}^q K_{v,v-n}^q c X_q N_v - \sum_{n=1}^{v_{\max}} K_{v+n,v}^q c X_q N_{v+n} \right) + (K_w + K_p) N_v, \quad (3)$$

where R_v is the relative rate of population of CO(v) from all reactions; v_{\max} is the highest vibrational level of CO under consideration; $K_{v,v-n}^q$ is the n -quantum deactivation rate between species q and CO(v); c is the concentration of the gases; X_q is the mole fraction of species q ; K_w is the rate of deactivation of CO(v) at the walls; K_p is the rate of removal of CO(v) from the zone from which intensities are obtained.

This relation is derived from a homogeneous macroscopic control volume where the residence time of a molecule is large compared to the deactivation time and all production in the v -level occurs in this volume. This method is particularly useful when the residence time is large compared to the half-life for radiative decay, as the spontaneous emission coefficients are more accurately known than the other coefficients of Eq. (3). Note that Eq. (3) is not dependent on the absolute rate of reaction of Eq. (1).

Some simplifications are required in order to handle Eq. (3). Since multiquanta $V-V$ or $V-T$ transfers have a low probability, only single quantum exchanges will be considered. Due to the small spontaneous emission coefficients for many quanta emission, emission of only the fundamental and overtone bands will be considered. Since the CS₂/O₂ flame is free of wall influence except near the flame holder, the rate of deactivation by the walls, K_w , can be ignored. After use of these three assumptions, the relations of Eq. (3) can be put in the form

$$R_v = (A_{v,v-1} + A_{v,v-2}) N_v - A_{v+1,v} N_{v+1} - A_{v+2,v} N_{v+2} + c \sum_q X_q (K_{v,v-1}^q N_v - K_{v+1,v}^q N_{v+1}) + K_p N_v. \quad (4)$$

Because of the high temperatures and added cold CO

TABLE I. Flame conditions for overtone emission measurements.

Case	Total flowrates (m mol s ⁻¹)	O ₂ /CS ₂ mole ratio	CO/O ₂ mole ratio	Pressure (k Pa)	Boltzmann fit (K)	Estimated gas speed (m s ⁻¹)	Estimated gas temp (K)
1	2.7	6	0	1.4	10540	3.4	2100
2	2.7	7	0	1.4	10090	2.9	2000
3	2.7	5	0	1.3	11010	4.1	2200
4	2.7	4	0	1.2	11790	6.7	2300
5	2.7	3.5	0	1.2	11590	9.0	2350
6	2.7	5	0.13	1.3	10660	3.6	2130
7	2.2	5	0.34	1.3	9379	3.0	2030
8	3.0	10	0	2.1	9230	1.4	1700

which occur in the flame laser, two additional considerations are required. The rate of convection of CO(v) into the control volume, to which Eq. (3) applies, must be considered. This is due to the significant thermal contribution to the lower vibrational levels. The convection term can be represented by subtraction of the term

$$K_p N_v^I \quad (5)$$

from the right hand side of Eq. (4); the superscript I indicates the relative population of CO(v) in the gas which is input to the control volume. The other consideration is anharmonic pumping. The single quantum $V-V$ exchanges can be represented by addition of the term

$$c \sum_q X_q (K_{v,v+1}^q N_v - K_{v-1,v}^q N_{v-1}) \quad (6)$$

to the right hand side of Eq. (4). After these two contributions are included, Eq. (4) becomes

$$R_v = (A_{v,v-1} + A_{v,v-2}) N_v - A_{v+1,v} N_{v+1} - A_{v+2,v} N_{v+2} + c \sum_q X_q [(K_{v,v+1}^q + K_{v,v+1}^q) N_v - K_{v+1,v}^q N_{v+1} - K_{v-1,v}^q N_{v-1}] + K_p (N_v - N_v^I). \quad (7)$$

The sum over the species can be significantly reduced because contributions from only a few molecules dominate the contributions from the others.

III. EXPERIMENTAL ARRANGEMENT

The premixed two-dimensional flame stands off a 3×100 mm slot burner. Gaseous carbon disulfide, evaporated from a liquid reservoir, and oxygen are premixed in a chamber which is upstream of the burner. Carbon monoxide is added to the CS₂ line when the flame is run with some additional cold CO. The products are removed through a liquid nitrogen trap to a 7.5×10^{-3} m³ s⁻¹ vacuum pump. The flame was ignited with a 15 kV, 60 Hz electric discharge between the burner and exhaust port; after ignition the discharge is turned off, leaving a free-standing flame.

The viewing ports consist of two NaCl flats mounted past either end of the flame. The emission is chopped at 263 Hz before entering a McPherson 2051 monochromator with a 150 lines per mm grating blazed at 4 μ m. Detection is with a PbS cell and a Princeton Applied Research HR-8 lock-in amplifier. A gold-plated mirror is placed on the far side of the optical axis and a BaF₂ lens is placed on the near side.

IV. EXPERIMENTAL DATA

Intensities of overtone spectra were recorded for the $v=2-0$ to $v=20-18$ transitions under eight different flow conditions. The flow conditions for these eight cases are given in Table I. The relative populations of CO(2) to CO(19) for these cases were determined by reduction according to Eq. (3), after correction for characteristics of the optical system. The relative populations, as illustrated for case 6 in Fig. 1, indicate the highly nonequilibrium nature of the CO(v) which is expected for a free-standing CS₂/O₂ flame.¹⁰ Also plotted on Fig. 1 is an approximation to the Boltzmann distribution, normalized to CO(2), for the adiabatic flame temperature¹³ of 2680 K. A least-squares fit of the relative populations to a Boltzmann distribution yields a vibrational temperature of 10 660 K for case 6; the other cases yield least-squares fit temperatures from 9230 K to 11 790 K. The population distribution in the flame does not represent a Treanor distribution¹⁴; meaningful least-squares fits to the Treanor distribution could not be obtained for any of the cases. The shape of the curve presented in Fig. 1 is explained by population of the upper levels of CO, combined with $V-V$ exchange between the upper and lower levels of CO and between all CO levels and other molecules. The combined effects of

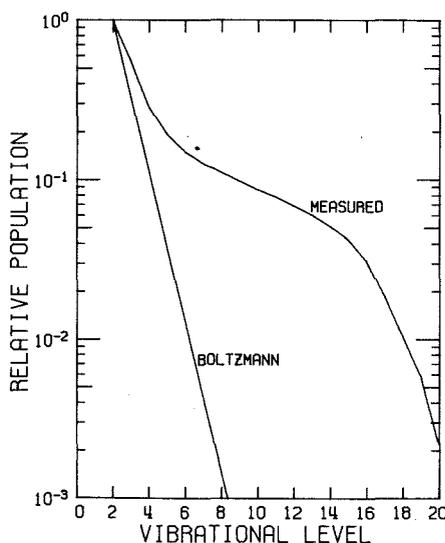


FIG. 1. The measured relative population in the flame for case 6. The Boltzmann distribution corresponds to the calculated flame temperature.

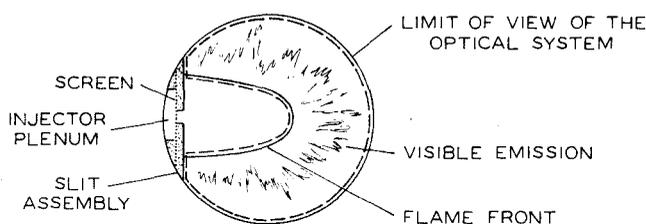


FIG. 2. Schematic view of the cross section of the flame as seen by the optical system. The dashed section represents the chosen control volume.

the $V-V$ exchanges spread the vibrational populations with the majority of the excited CO cascading downward and some pumped to higher v levels.

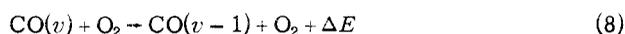
These data were obtained from a flame which is optically thin, so that the effects of absorption and stimulated emission can be neglected. However, all other conditions for a flame laser were maintained. A population inversion was not observed under the conditions which are reported here because the instrumentation was not arranged to provide sufficient spatial resolution.

V. RATE OF POPULATION OF CO(v)

The rate of population of the vibrational levels of CO by chemical means is estimated using Eq. (7). The control volume considered corresponded to the region of flame from which the emission was observed; that includes the region, as shown schematically in Fig. 2, in which flame reactions predominate, i.e., the flame front, to the limit of the optical system. The results are independent of the volume chosen; any volume which has no reaction producing excited CO contributes no errors. The region in which the majority of CO is produced is expected to be quite small; the gas temperature and composition are close to the equilibrium values immediately downstream of this region.¹⁵ Thus, the assumption of homogeneity of the gas phase for the derivation of Eq. (7) may not be grossly violated.

There were a few more approximations made in order to calculate the R_v from the N_v . The amount of CO(v) produced in the control volume is assumed to be much larger than that flowing in, so that the N_v^I can be ignored for the upper levels. The temperature, which is listed in Table I, is estimated from theoretical calculations.¹⁵ The rate of pumping, K_p , is chosen as the inverse of the residence time in the control volume, which in turn is estimated as the gas velocity of the hot region divided by the estimated flame thickness of 6 mm. The gas velocity listed in Table I, is estimated from the experimentally determined flame speed,¹⁵ extended by theoretical calculations for high O_2/CS_2 ratio, and the conservation of mass for a cylindrically expanding gas.

The three species O_2 , CO(0), and CO(1) were considered to have the predominant influence on the collisional process. The rates of vibrational deactivation by molecular oxygen by the collisional process



were estimated by the assumption of a functional depend-

ence for the rate of deactivation which is exponential with respect to the absolute value of the energy defect, ΔE , and proportional to the CO vibrational level, v ,

$$K_{v,v-1}^{O_2} \propto v \exp(-|\Delta E|) \quad (9)$$

These rates were normalized to the experimental rate of $1.3 \times 10^4 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the $v=12$ to 11 transition¹¹ with empirical constant of $3/(kT)$ for the coefficient in the exponential.¹¹ The rates for deactivation by CO(0) and CO(1) and activation by CO(1) were calculated from theoretical rates,¹⁶ which consider both long and short range interactions, normalized to experimental data for the $v=4$ to 3 rate of $1.2 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for deactivation by CO(0).¹¹ Although SO_2 is a product of CS_2/O_2 combustion, deactivation by SO_2 was not taken into consideration because the rate for $V-V$ and $V-T$ deactivation of CO is small.¹⁷ The $V-V$ energy defect for CS_2 and CO is only slightly larger than for O_2 and CO, so that CS_2 should be an efficient deactivator of CO. However for the lean flames which are considered here, the CS_2 mole fraction is very small in the region from which emissions were taken (i.e., downstream of the flame front). Deactivation of CO(v) by COS is very efficient¹¹ and COS is formed in CS_2/O_2 flames. However for lean flames in which the COS oxidizes, the mole fraction is very small in the region of interest.

The mole fraction of O_2 was estimated by assuming that the reactions to form CO went to completion. The mole fractions of CO(0) and CO(1) were estimated by assuming a thermal distribution for these two levels with the gas temperature used for the contribution from added CO and Boltzmann extrapolation from the lower vibrational levels, e.g., $v=2$ through 4 in Fig. 1, for the chemically formed CO.

The relative rates of population, R_v , were calculated from the populations, N_v , for the eight cases. The rates of population for $v=7$ through 18 were normalized to determine the fractional contribution within these levels. Each case had a peak in R_v for either $v=14$, 15, or 16. The means and standard deviations of these rates, which ideally are independent of the flow conditions, are given in Fig. 3. These data indicate that there is a maximum rate of production for $v=15$. This is two levels higher than expected from the experimental results obtained by others under different experimental conditions. The results reported here are compared with an unweighted average of the data from seven previous results for room temperature³⁻⁹ in Fig. 4.

The rate of production of CO(v) measured in the flame is the combined result of all reactions which produce carbon monoxide. The predominant reaction is that between carbon monosulfide and atomic oxygen, but the reaction



is also an important source of CO. This makes significant contributions into the lower vibrational levels¹⁸ and has been successfully used to explain the difference found by other experimenters for the distribution into the lower vibrational levels.¹⁹ The relatively large rate of population for the lower vibrational levels, which is

not expected from previous experimental³⁻⁹ or theoretical²⁰ work is then explained by contributions from reactions other than Eq. (1). Since the ancillary reactions are not known to produce highly excited CO, the distribution obtained for the upper vibrational levels is attributed to Eq. (1).

There are six processes which were considered in the calculation of R_v from Eq. (7): spontaneous emission, fluid mechanical transport, deactivation by molecular oxygen, deactivation by CO(0), deactivation by CO(1), and anharmonic pumping by CO(1). For the cases with high O₂/CS₂ ratio there is a large excess of O₂ in the flame; consequently, deactivation by O₂ is the largest contribution to the right-hand side of Eq. (7). For the cases closer to stoichiometric, the CO(*v*) mole fractions increase while the O₂ mole fraction decrease so that the contributions from CO(0) and CO(1) become more important.

As an example, for the cases treated, the net contribution to R_{15} , due to O₂, i.e., depopulation of CO(15) by collision with O₂ minus the rate of populating CO(15) due to O₂/CO(16) collisions, averages 43.6% of the net contributions for all six processes. The next most important contribution is from CO(0) which averages 33.0% for the eight cases. The average net contribution from deactivation and anharmonic pumping by CO(1) is 19.2%. The average transport and spontaneous emission contributions are 3.8% and 0.4%, respectively. The V-V processes dominate the calculation; therefore the results are dependent upon the theoretical models and rate constants.

In order to determine the sensitivity of the results to the V-V exchange rates, the rate constants for deactivation and anharmonic pumping by CO and deactivation by O₂ were increased and decreased by a factor of 2, one at a time. The values of R_v were calculated and

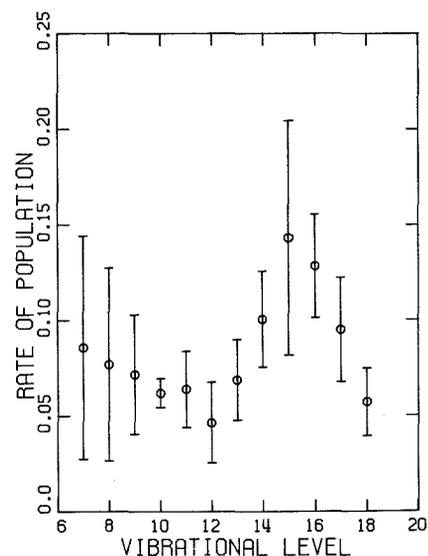


FIG. 3. The relative rates of population of CO(*v*) from a composite of eight cases. The rates were normalized so that the sum over the levels shown is equal to one. The mean is shown with one standard deviation error bars.

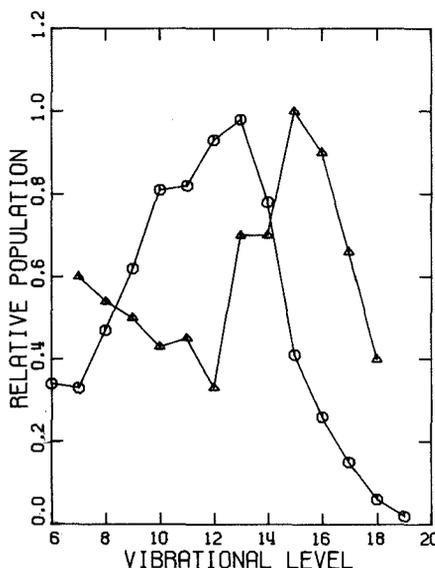


FIG. 4. The relative rates of population of CO(*v*) from this work (triangular symbols) compared to an average of previous experiments for room temperature (octagonal symbols).

averaged as before. The results of these calculations are displayed in Table II along with the results for the nominal case. The qualitative aspect remains the same, i.e., the maximum rate of population is for CO(15).

VI. ENERGETIC FEASIBILITY

The heat of reaction for the reaction CS + O → CO + S is -310.9 kJ mol⁻¹ at 300 K and increases by -2.0 kJ mol⁻¹ at 2000 K when the heat of formation of 230.12 kJ mol⁻¹²¹ for CS is employed. Comparing that energy with the vibrational levels of CO,²² the maximum vibrational level of CO which should result from this reaction is 12. The true heat of formation of CS is probably around 40-65 kJ mol⁻¹ larger,²³⁻²⁵ which would allow CO to be formed in the fifteenth vibrational level. These arguments are based on the assumption that the carbon monosulfide is at vibrational equilibrium.

In the CS₂/O₂ flame laser the predominant source of CS is the reaction

TABLE II. Rate of population of CO(*v*) with different V-V rates.

V	Nominal (Fig. 3)	$K_{v,v-1}^{CO_2}$		$K_{v,v-1}^{CO}$ and $K_{v,v-1}^{CO}$	
		$X_{\frac{1}{2}}$	X2	$X_{\frac{1}{2}}$	X2
7	8.6	10.7	6.0	6.4	10.5
8	7.7	9.4	5.6	6.0	9.2
9	7.2	8.6	5.4	5.7	8.5
10	6.2	7.4	4.7	5.1	7.2
11	6.4	7.3	5.2	5.5	7.1
12	4.7	5.5	3.5	3.8	5.3
13	6.9	7.2	6.4	6.5	7.2
14	10.0	9.6	10.6	10.5	9.7
15	14.3	12.4	16.6	16.1	12.6
16	12.8	10.5	15.9	15.3	10.8
17	9.5	7.4	12.3	11.8	7.6
18	5.7	4.2	7.7	7.4	4.3



The CS produced from Eq. (11) has a significant population in at least the first three vibrationally-excited levels²⁶ with 26% of the total reaction energy in the vibrational energy of the products. An independent measurement of the translational energy of the products indicates that a maximum of 10% of the reaction energy goes into translational energy.^{27,28} The harmonic constant and first anharmonic constant for the CS molecule²¹ indicate that for the first three vibrational levels of CS, each vibrational quantum can increase the maximum energetically possible CO vibrational level by one. Thus, the CO molecule can be formed excited to the 18th vibrational level.

VII. SUMMARY

The rate of population of CO by chemical means in a steady, premixed CS₂/O₂ flame has been determined by combining the average population of CO(v), obtained experimentally, with theoretical extrapolations for the rates of vibrational energy transfer in a steady-state analysis. The vibrational population of carbon monoxide has been determined from the spontaneous emission intensity of the overtone bands. These data indicate a maximum rate of population of CO(v) for the fifteenth vibrational level. Since the results are dependent upon the theoretical models chosen, the validity of this result depends on the accuracy of the models.

¹S. J. Arnold and H. Rojasca, *Appl. Opt.* **12**, 169 (1973).

²C. E. Wiswall, D. P. Ames, and T. J. Menne, *IEEE J. Quantum Electron.* **9**, 181 (1973).

³S. Tsuchiya, N. Nielson, and S. H. Bauer, *J. Phys. Chem.* **77**, 2455 (1973).

⁴G. Hancock, C. Morley, and I. W. M. Smith, *Chem. Phys. Lett.* **12**, 193 (1971).

⁵T. H. Powell and J. D. Kelley, *J. Chem. Phys.* **60**, 2191 (1974).

⁶N. Djeu, *J. Chem. Phys.* **60**, 4109 (1974).

⁷G. Hancock, R. A. Ridley, and I. W. M. Smith, *Trans. Faraday Soc.* **68**, 2117 (1972).

⁸K. D. Foster, *J. Chem. Phys.* **57**, 2451 (1972).

⁹K. D. Foster and G. H. Kimbell, *Symp. Int. Combust. Proc.* **14**, 203-210 (1973).

¹⁰K. D. Foster and G. H. Kimbell, *J. Chem. Phys.* **53**, 2539 (1970).

¹¹G. Hancock and I. W. M. Smith, *Appl. Opt.* **10**, 1827 (1971).

¹²G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), 2nd ed., p. 127.

¹³S. Gordon and B. J. McBride, *NASA Spec. Publ.* 273 (1971).

¹⁴C. E. Treanor, J. W. Rich, and R. C. Rehm, *J. Chem. Phys.* **48**, 1798 (1968).

¹⁵A. A. Vetter, Ph.D. Thesis, California Institute of Technology, 1975.

¹⁶S. D. Rockwood, *et al.*, *IEEE J. Quantum Electron.* **9**, 120 (1973).

¹⁷J. K. Hancock, D. F. Starr, and W. H. Green, *J. Chem. Phys.* **61**, 3017 (1974).

¹⁸J. W. Hudgens, J. T. Gleaves, and J. D. McDonald, *J. Chem. Phys.* **64**, 2528 (1976).

¹⁹J. D. Kelley, *Chem. Phys. Lett.* **41**, 7 (1976).

²⁰M. Shapiro and U. Halavee, *Chem. Phys. Lett.* **40**, 387 (1976).

²¹D. R. Stull and H. Prophet, *Natl. Stand. Ref. Data Natl. Bur. Stand. Circular* 37 (1971).

²²P. H. Krupenie, *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. Circular* 5 (1966).

²³V. H. Dibeler and J. A. Walker, *J. Opt. Soc. Am.* **57**, 1007 (1967).

²⁴H. Okabe, *J. Chem. Phys.* **56**, 4381 (1972).

²⁵D. L. Hildbrand, *Chem. Phys. Lett.* **15**, 379 (1972).

²⁶I. W. M. Smith, *Discuss. Faraday Soc.* **44**, 194 (1967).

²⁷P. L. Moore, P. N. Clough, and J. Geddes, *Chem. Phys. Lett.* **17**, 608 (1972).

²⁸J. Geddes, P. N. Clough, and P. L. Moore, *J. Chem. Phys.* **61**, 2145 (1974).