

Electron collision quenching of CO(v) chemiluminescence in CS₂/O₂ and CS₂/O₂/N₂O flames

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Chemiluminescence from vibrationally excited carbon monoxide formed by the reaction $\text{CS} + \text{O} \rightarrow \text{CO}(v) + \text{S}$ was observed in CS₂/O₂ and CS₂/O₂/N₂O flames to which an electric discharge was applied. Although the total amount of chemiluminescence increased with increasing discharge current probably due to enhanced reaction rates as a result of radical formation, the vibrational distribution was quenched, becoming thermal in character. The thermalization is attributed to superelastic electron collisions [$e + \text{CO}(v) \rightarrow e + \text{CO}(v-1)$]. The technique demonstrates a sensitive method for detecting collisional transfers between excited states by separating the perturbation (electron collisions) from the initial excitation mechanism (chemical reactions).

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I. INTRODUCTION

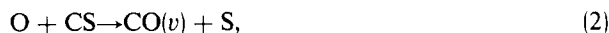
Electron impact cross sections for the excitation of the first eight vibrational levels of CO from the ground state have been measured¹ and treated theoretically.² Electron impact cross sections for transitions between higher vibrational states have been computed³ but no experimental measurements of them have been reported. In electrically excited CO lasers, the initial density of states with $v > 1$ is small and even after subsequent excitation remains small compared to the ground state. Hence electron excitation between highly excited states is difficult to detect and difficult to separate from excitation from the ground state. This is not the case in a CO flame where chemical reactions create vibrationally excited carbon monoxide and additives such as N₂O can help produce total (instead of partial) inversions. A large fraction of the CO is in excited states and electron impact transfers between excited states can be more easily seen.

In this paper we report observations of CO vibrational distributions in CS₂/O₂ and CS₂/O₂/N₂O flames in the presence of an electric discharge. A transverse electric discharge was applied to argon-buffered, low-pressure (5–20 Torr) flames. Vibrational distributions of CO(v) were calculated by observing first-overtone spontaneous emission. Severe perturbations of the CO vibrational distribution were detected as a result of applying the discharge. This technique separates the perturbation (electron collisions) from the dominant excitation mechanism (chemical reactions). The sensitivity of this approach is large compared to techniques which rely on the same method for both the initial excitation and subsequent perturbation.

The basis of the carbon monoxide flame laser is the reaction sequence^{4–6}



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The CO emerges from the reaction with a distribution of vibrational states peaked at $v \approx 12$, and with a maximum value of $v \approx 20$.^{7–9} The source of atomic oxygen is either reactions (3) and (4) or thermal dissociation of molecular oxygen requiring flame temperatures in excess of 1000 °C. The high temperature not only dissociates oxygen but also thermalizes the distribution of CO vibrational levels. Therefore, in flame lasers the oxygen is often dissociated prior to mixing in order to lower the temperature and increase laser power.¹⁰ N₂O is sometimes used as an additive in CS₂/O₂ flames in order to enhance the inversion. The VV relaxation rate of CO with N₂O is larger for the lower vibrational levels than the upper levels.¹¹ Therefore the lower vibrational levels are quenched more rapidly than the upper levels and an inversion results.

II. EXPERIMENTAL APPARATUS AND RESULTS

The experimental setup is shown in Fig. 1. The gases were regulated by standard rotameters and premixed in a plenum behind a porous plate feeding a 2 × 20 cm slot burner. The burner was mounted on an adjustable stage in an aluminum vacuum chamber which was evacuated through a LN₂ cold trap by a mechanical pump. First-overtone spontaneous emission from excited CO was observed through sapphire windows flushed with argon to prevent contamination. The burner was positioned to maximize the detectable emission. The emission was chopped, focused on the slits of a 1-m monochromator, and synchronously detected with a PbS detector and a lock-in amplifier. Spectra were displayed on a strip chart recorder. The discharge electrodes were 6.4-mm-o.d. stainless steel rods 25 cm long, separated by 3 cm and mounted on a separate movable stage. The power supply was a commercial regulated device. The burner and vacuum

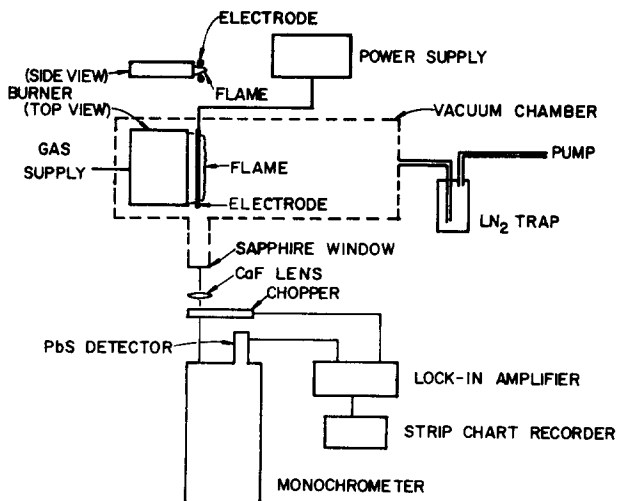


FIG. 1. Diagram showing a top view of the experimental setup. A side view of the burner displaying the placement of the electrodes relative to the burners is shown above the chamber.

chamber were ungrounded and allowed to float. The discharge operated in the negative glow regime.

In CS_2/O_2 flames, total inversions of the CO vibrational levels were not observed but the distributions were non-Boltzmann. When the discharge was applied, the CO vibrational distribution was thermalized towards a Boltzmann (see Fig. 2). As the discharge current was increased, the distribution became more thermal in nature. In addition to a change in the vibrational distribution, the total spontaneous emission intensity, calculated by integrating the first-overtone signal, increased with increasing discharge current. The flame temperature, calculated by fitting the rotational distribution of $\text{CO}(v=2)$ to a Boltzmann distribution, also increased with increasing discharge current (see Fig. 3).

The increase in total emission intensity could be due to electron impact dissociation of CS_2 which enables the pumping reaction [Eq. (2)] to proceed directly. The CS-S bond is the weakest bond of the molecules participating in the flame reaction sequence [Eqs. (1-4)] and therefore is the most likely molecule to be dissociated in the discharge. Atomic oxygen can also be produced by electron impact dissociation of O_2 , whose dissociation energy is the smallest of the diatomic molecules involved. The increase in gas temperature is probably due to discharge energy deposited in the gas, and the increase in enthalpy as a result of the higher reaction rate. Visual observations of the flame front indicated that the flame speed increased as the discharge current increased. This is consistent with the increase in flame temperature¹² and an increase in reaction rates.¹³

The increase in gas temperature certainly contributed to thermalizing the vibrational levels. At higher temperatures, the ratio of endothermic to exothermic CO-CO VV collisions and the probability of VT collisions are larger, both of which quench the distribution. The observed increase in temperature, though, is insufficient to account for the observed thermalization of the vibration distribution. This conclusion is the result of a calculation we performed similar to that previously reported in Ref. 14 in which the rate of population of $\text{CO}(v)$ is computed. The computation is briefly described in the following.

III. THE RATE OF POPULATION OF $\text{CO}(v)$ INCLUDING THE EFFECTS OF ELECTRON COLLISIONS

The rate of population of $\text{CO}(v)$, R_v , is defined as the rate at which $\text{CO}(v)$ is created by chemical reactions. The

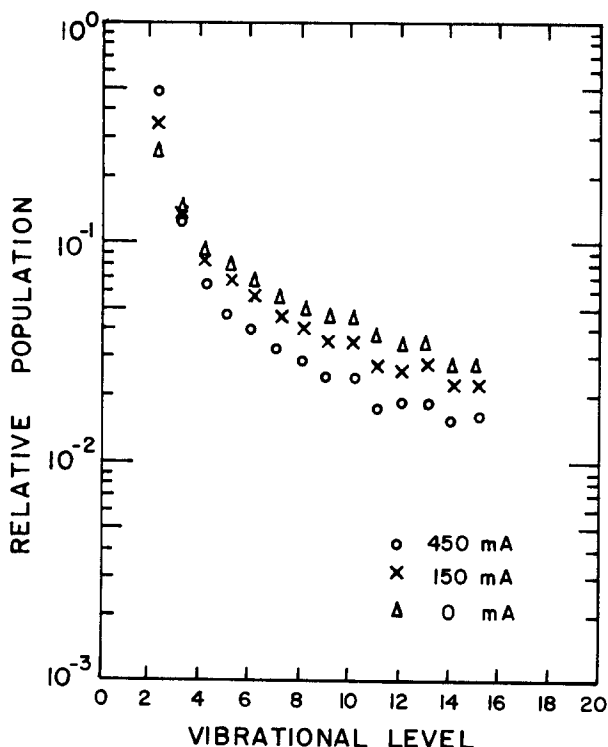


FIG. 2. Relative populations of $\text{CO}(v)$ in a CS_2/O_2 premixed flame as a function of discharge current. The chamber pressure was 5.1 Torr. Flow rates were 0.14 mmole/sec of CS_2 and 2.00 mmole/sec of O_2 .

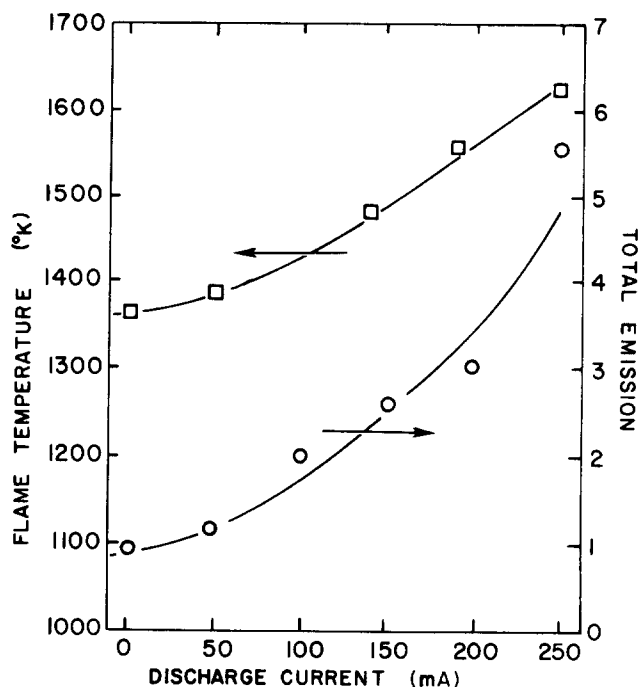


FIG. 3. Total first-overtone emission of $\text{CO}(v)$ and flame temperature for the conditions of Fig. 2.

observed densities of CO (v) must be corrected for nonchemical processes to obtain the rate of population. In a given control volume,

$$R_v = (A_{v,v-1} + A_{v,v-2})N_v - A_{v+1,v}N_{v+1} - A_{v+2}N_{v+2} + C \sum_q x_q (k_{v,v-1}^q + k_{v,v+1}^q)N_v - k_{v+1,v}^q N_{v+1} - k_{v-1}^q N_{v-1} + k_p(N_v - N_v^I) + R_v^{ex}, \quad (5)$$

where N_v is the observed population of CO (v), $A_{v,v'}$ is the spontaneous emission coefficient for $v \rightarrow v'$, C is the gas concentration, x_q is the mole fraction of species q , and $k_{v,v-n}^q$ is the n quantum deactivation of CO (v) by species q . The parameter k_p is a convection term accounting for the difference in CO (v) flowing into (N_v^I) and out of (N_v) the control volume. The rate of population due to external perturbations, such as the applied electric field, is R_v^{ex} . The terms $k_{v,v-n}^q$ are temperature dependent. With the assumptions detailed in Ref. 14, we calculated R_v in the absence of the discharge (i.e., $R_v^{ex} = 0$). These values serve as the unperturbed reference. We repeated the calculation using the gas temperature and N_v observed while the discharge was on and obtained new R_v . By subtracting the reference R_v from the new values, the change in the rate of population as a result of the discharge (R_v^{ex}) is obtained.

With smoothed experimental values, a typical example of the calculation of R_v^{ex} is shown in Fig. 4. In the presence of the discharge the rate of population of the first few vibrational levels is increased while that of $v > 2$ is decreased. This decrease is largest for $v \approx 5$ and is smaller for $v \approx 5$. The effect increases with increasing current density. We attribute this

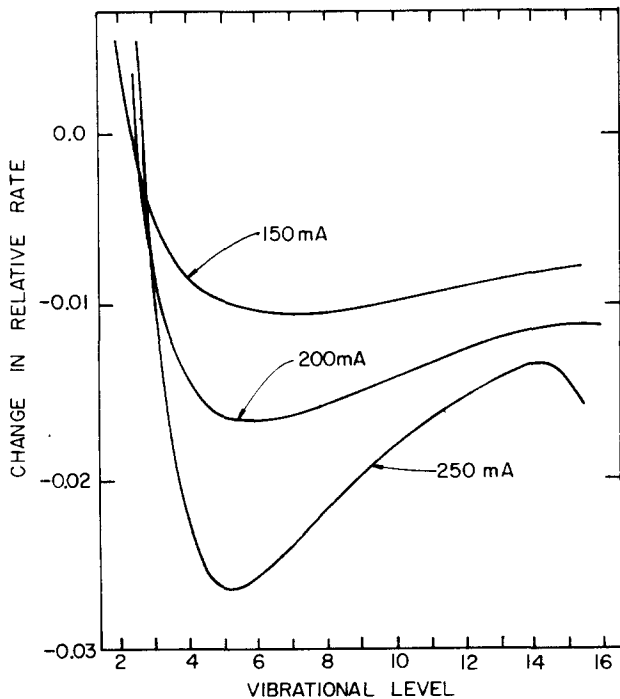


FIG. 4. Change in the relative rate of population of CO (v) as a function of discharge current. The change is defined as $R_v(I=0) - R_v(I)$, where I is the value of the discharge current and $\sum_v R_v = 1$.

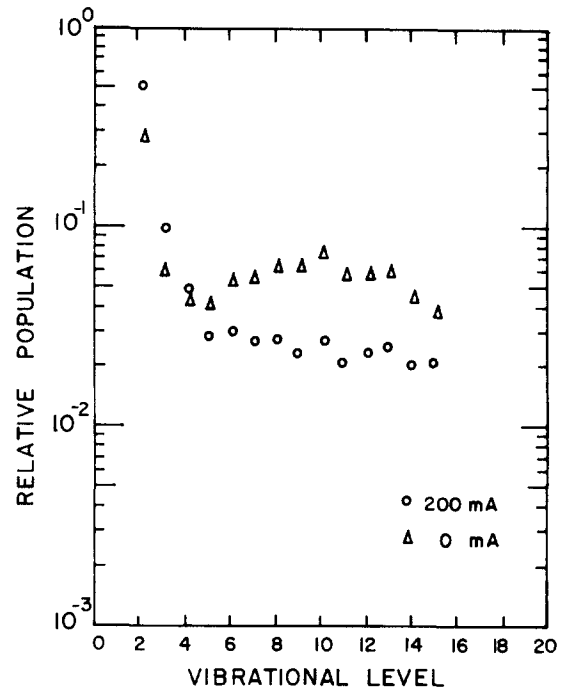


FIG. 5. Relative populations of CO (v) in a CS₂/O₂/N₂O premixed flame in the absence and presence of a discharge. The chamber pressure was 5.1 Torr. Flow rates were 0.14 mmole/sec of CS₂, 2.00 mmole/sec of O₂, and 0.37 mmole/sec of N₂O.

change in the rate of population to superelastic electron collisions. Successive superelastic collisions cause a downward cascade of CO (v) which populates the lowest levels at the expense of the upper levels. The measured electron impact cross sections for CO ($v=0$) \rightarrow CO ($v < 8$) decreases with increasing vibrational levels.¹ Therefore the rates of superelastic relaxation to the ground state (the inverse reaction) also decrease for increasing v . If only $v=0 \rightarrow v=v'$, $v' < 8$ electron impact reactions were important, superelastic collisions would relax the lower levels at a higher rate than the upper levels. This would invert the distribution in a similar manner as does adding N₂O. Clearly this is not the case. Hence a cascade of CO (v) from higher states to lower states caused by superelastic electron collisions between excited states can explain the observed rates.

An estimate for the superelastic electron collision rate can be obtained. With the assumption of steady-state conditions and that collisions of CO (v) with CO ($v=0$) are the dominant gas kinetic quenching mechanisms, then

$$k_{v,v-1}^e n_e [\text{CO}(v)] \approx \alpha k_{v,v-1}^{\text{CO}(v=0)} [\text{CO}(v=0)] [\text{CO}(v)], \quad (6)$$

where $k_{v,v-1}^e$ is the electron relaxation rate, n_e is the electron density, and α is the fractional change in CO (v) due to electron collisions. In the lean flames being discussed here, all of the CS₂ reacts to form CO so that the density of CO ($v=0$) is approximately equal to the input density of CS₂. The rates $k_{v,v-1}^{\text{CO}(v=0)}$ are tabulated¹¹ and α is measured experimentally. The electron density can be estimated from the relationship $I = n_e v_d e$, where I is the discharge current density, v_d is the drift velocity¹⁵ and e is the electronic charge. Solving for $k_{v,v-1}^e$, we obtain values of $\approx 10^{-11}$ cm³/sec which agree with the reported theoretical values.^{2,3}

IV. CS₂/O₂/N₂O FLAMES

Similar results were obtained in CS₂/O₂/N₂O flames. With N₂O as an additive, the CO (*v*) distribution was inverted. When adding the discharge this inversion is severely quenched (see Fig. 5). The quenching increases with increasing discharge current. Because of the relatively small NO-N bond energy, it is unclear how much of the thermalization is due to superelastic electron collisions and how much might be due to the dissociation of N₂O. For gas temperatures greater than 1000 °K, the dissociative attachment reaction $e + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$ is particularly important. The rate for this reaction increases exponentially for electron energies less than 2 eV as the gas temperature increases, and could contribute to a significant depletion of N₂O.¹⁶ Because the magnitude of the quenching in CS₂/O₂/N₂O mixtures is large as compared to CS₂/O₂ flames, a large fraction of the quenching is probably due to the dissociation of N₂O.

V. CONCLUDING REMARKS

In conclusion, vibrational populations of CO (*v*) were observed in CS₂/O₂ and CS₂/O₂/N₂O flames in the presence of an electric discharge. The non-Boltzmann CO (*v*) distributions were thermalized by the electric discharge. The thermalization increased with increasing discharge current at a rate exceeding the value one would calculate by the increase in gas temperature alone. The thermalization is attributed to superelastic electron collisions by which molecules cascade to lower vibrational levels by successive electron collisions. The effect is particularly severe in CS₂/O₂/N₂O flames where the products of dissociation of N₂O are probably also a major contributing factor. By separating the perturbation

from the initial excitation mechanism, we were able to directly observe electron collision transfers between excited states of CO. The method has potential application for detecting collisional transfer between excited states in other systems where chemical reactions form vibrationally or electronically excited products.

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