Chemical Physics Letters 659 (2016) 112–116

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Highly vibrationally excited CO generated in a low-temperature chemical reaction between carbon vapor and molecular oxygen

E. Jans, K. Frederickson, M. Yurkovich, B. Musci, J.W. Rich, I.V. Adamovich *

Michael A. Chaszeyka Nonequilibrium Thermodynamics Laboratory, Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH 43210, United States

ARTICLE INFO

Article history:
Received 1 June 2016
In final form 6 July 2016
Available online 7 July 2016

ABSTRACT

A chemical flow reactor is used to study the vibrational population distribution of CO produced by a reaction between carbon vapor generated in an arc discharge and molecular oxygen. The results demonstrate formation of highly vibrationally excited CO, up to vibrational level v = 14, at low temperatures, T = 400–450 K, with population inversion at v = 4–7, in a collision-dominated environment, 15–20 Torr. The average vibrational energy per CO molecule formed by the reaction is 0.6–1.2 eV/molecule, which corresponds to 10–20% of reaction enthalpy. The results show feasibility of development of a new CO chemical laser using carbon vapor and oxygen as reactants.

1. Introduction

Exothermic chemical reactions are commonly used for extraction of energy, where reactants are chemically converted to lower energy products and the excess chemical energy is converted to work. Chemical lasers utilize these types of chemical reactions, where chemical energy is stored in internal modes of the products and is then extracted through the stimulated emission process producing laser power. Recent theoretical and experimental studies of the exothermic reaction of atomic carbon and molecular oxygen have suggested that a significant fraction of the excess chemical energy (up to ~30%) is stored in the vibrational mode of the carbon monoxide product. These results suggest a potential development of a chemical carbon monoxide laser based on this reaction.

Electric discharge excited CO lasers possess a number of desirable qualities including high power and high efficiency. First demonstrated by Patel [1] and Osgood and Eppers [2], carbon monoxide lasers emit in the mid-infrared spectral band and have been reported to operate with efficiencies as large as 50% [3] and powers up to 200 kW [4]. The reported optimal performance was achieved using electric discharges operated at cryogenic temperatures. Laser gain is established on ro-vibrational transitions within the ground electronic state of the CO molecule by rapid vibration-to-vibration (V-V) quanta exchange among molecules in vibrationally excited levels initially populated by electron impact in the discharge. This V-V exchange process was first described by Treanor et al. [5] who explained the kinetics which result in a highly non-Boltzmann vibrational distribution among vibrational levels of molecules in low-temperature environments. It was shown by Rich [6] to cause the partial population inversions between ro-vibrational levels and laser gain along P-branch lines in the high power CO laser.

Current versions of chemical carbon monoxide lasers, specifically, those based on the reaction of carbon disulfide and molecular oxygen, present similar characteristics to the electric discharge type, i.e., they both show laser gain on the higher, more anharmonic, vibrational band components. The dominant CO product of $CS_2 + O$ and $CS + O$ reactions contains several vibrational quanta [7], with peak population in v = 12 [8]. A major benefit of this system is the formation of total population inversions among the lower vibrational levels, resulting in greater gain across more ro-vibrational transitions, including R-branch lines. Carbon disulfide, however, is a highly toxic compound and more costly than the common allotropes of carbon, such as graphite, making it a less desirable precursor. A novel chemical carbon monoxide laser based on the gas-phase reaction between atomic carbon vapor and molecular oxygen would exhibit numerous advantages over the current chemical or electric discharge carbon monoxide lasers. High power and efficiency would be achievable due to the relatively slow vibration-to-translation (V-T) and vibration-to-rotation (V-R) quanta loss, which is a characteristic property of carbon monoxide, and higher gain associated with the total population inversions found in chemical lasers could also be achieved. Finally, complications of using carbon disulfide would be removed by implementing the use of graphite or amorphous carbon as the carbon source in the reaction.

---

* Corresponding author.
E-mail address: adamovich.1@osu.edu (I.V. Adamovich).

http://dx.doi.org/10.1016/j.cplett.2016.07.016
0009-2614/

Molecular dynamics simulations have predicted one of the dominant products of this reaction would be vibrationally excited CO in the ground electronic state. The heat of reaction

$$C(^3P) + O_2\left(X^3\sum\nolimits_g^-\right) \rightarrow CO\left(X^1\sum\nolimits^+, v\right) + O(^3P), \qquad (1)$$

$\Delta H = -132.6$ kcal/mol (5.75 eV), is sufficiently large to populate a number of excited vibrational levels (CO vibrational quantum is approximately 0.26 eV). Subsequent crossed molecular beam experiments confirmed that the CO product is vibrationally excited. These results also demonstrate total population inversion over the first five vibrational levels. Higher vibrational levels could not be observed due to spectral bandwidth limitations of the laser probe. The objective of the present work is to detect vibrationally excited CO product of a chemical reaction between carbon sublimation products and oxygen, at pressures and temperatures suitable for development of a chemical CO laser.

2. Experimental

The oxidation of carbon vapor generated in an arc discharge in argon buffer was studied in a custom-made flowing chemical reactor, shown schematically in Fig. 1. The reactor consists of a six-arm cross stainless steel cells and a 1″ diameter observation cell, the first cell housing a DC arc discharge electrode assembly, and the other used for *in situ* spectroscopic diagnostics. The arc discharge cell arms are 2″ in diameter. Two of the arms are used to provide access for the arc discharge electrode mounts. The powered electrode is a tungsten rod ¼″ in diameter, and the grounded electrode is an amorphous carbon rod 2 mm in diameter, attached to vacuum-sealed electrode mounts. During the operation, the gap between the electrodes is controlled by a computer controlled stepper motor (Haydon Kerk 43HGJ-05-A01), coupled to the adjustable grounded electrode mount. Two other arms are used for inlet argon buffer gas flow through a ½″ diameter quartz tube extending into the arc discharge cell, and for exit of carbon electrode sublimation products, through a 2.5″ to 1″ diameter glass adapter 5 cm long connected to the observation cell, as shown in Fig. 1. The distance between the buffer gas inlet flow tube and the arc discharge electrodes is approximately 1 cm. The buffer flow entrains the carbon vapor products, to minimize their accumulation in the arc discharge cell. The pressure in the cell is 15–20 Torr, and the argon buffer flow rate is varied in the range of 2–12 slm.

The electrodes are powered by a 100 V, 150 A DC power supply. The arc discharge is initiated by advancing the grounded electrode toward the powered electrode until they were brought in contact with each other, after which the grounded electrode is retreated by ~1–2 mm, while the discharge is maintained. In the present work, the discharge is operated at 20 V and 35 A, for durations of 60 s. During operation, the gap between the electrodes somewhat increases, by up to ~1–2 mm, due to carbon sublimation from the grounded electrode. However, this moderate increase of the electrode gap did not terminate the discharge, such that advancing of the grounded electrode during the operation was not necessary. A flow of vapor-phase carbon products generated in the arc discharge is entrained by the Ar buffer flow into the observation cell 40 cm long, with CaF_2 windows attached to the flanges at both ends (see Fig. 1). This provides optical access for *in situ* infrared absorption and emission measurements.

A flow of oxygen or 20% O_2/Ar mixture is injected into the observation cell tube in the direction opposite to that of the carbon vapor – argon buffer flow, as shown in Fig. 1, at a flow rate of ~100 sccm. The reaction products exit the observation cell near the opposite end, such that the optical axis is parallel to the exit flow. For absorption measurements, emission from a calibrated blackbody source (InfraRed Industries Inc. Model 563), maintained at a temperature of 1000 °C, was focused into the absorption cell using a pair of off-axis parabolic mirrors, as shown in Fig. 1, and directed into the emission port of a Bruker IFS/66s Fourier Transform Infrared (FTIR) spectrometer by another pair of mirrors, to detect the products of carbon vapor reaction with oxygen. The optical path length for these measurements is 40 cm. The same signal collection was used for infrared emission measurements from the observation cell, to detect vibrationally excited states of the reaction products. For emission measurements, the blackbody source was blocked, and the FTIR was focused approximately in the center of the observation cell, 15 cm from injection of carbon vapor/argon and oxygen flows. In the present experiments, the FTIR was operated at spectral resolution of 0.25 cm^{-1}, averaging 50 scans during the 30 s arc discharge operation time.

3. Results and discussion

Fig. 2 shows FTIR fundamental emission spectrum from the observation cell, taken during the carbon arc discharge operation and counterflow injection of oxygen into the observation cell, as

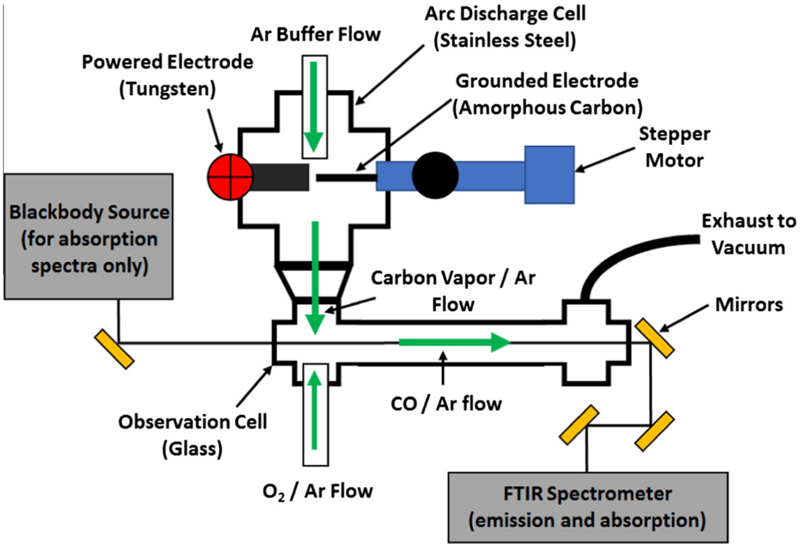

Fig. 1. Schematic of the experimental setup for CO generation by a chemical reaction between carbon vapor and oxygen.