THE OHIO STATE UNIVERSITY

Non-Equilibrium Thermodynamics Laboratory

Vibrationally Excited Carbon Monoxide Produced via a Chemical Reaction between Carbon Vapor and Oxygen

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Overview

1. Motivation and Background
2. Carbon Arc Reactor / CO production
3. Vibrationally Non-equilibrium Quasi-1D Model
4. Experimental Results and Comparison to Predictions
5. Future Work

Motivation and Background

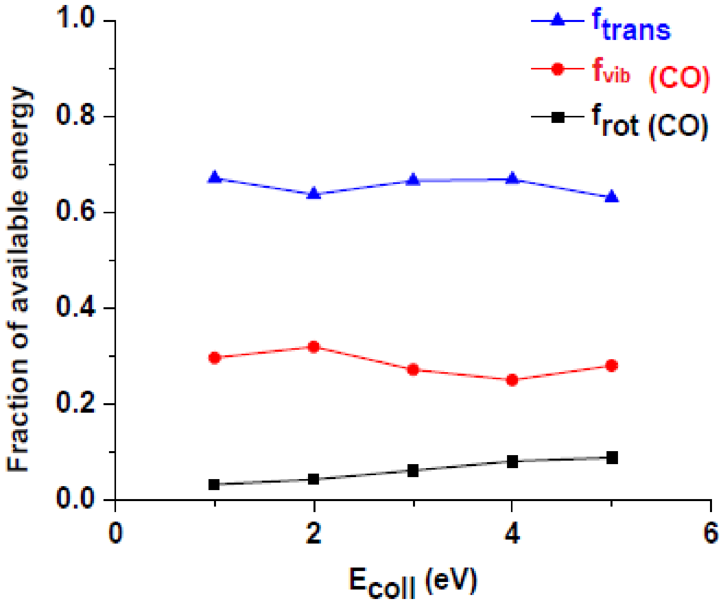
Motivation: Development of a CO laser from a chemical reaction for the generation of electricity onboard using photovoltaic cells a hypersonic vehicle.

Approach: Entrain external flow (O_2 / N_2) and react with an on-board propellant:

$$C + O_2 \rightarrow CO(v > 0) + O \rightarrow CO \text{ lasing}$$

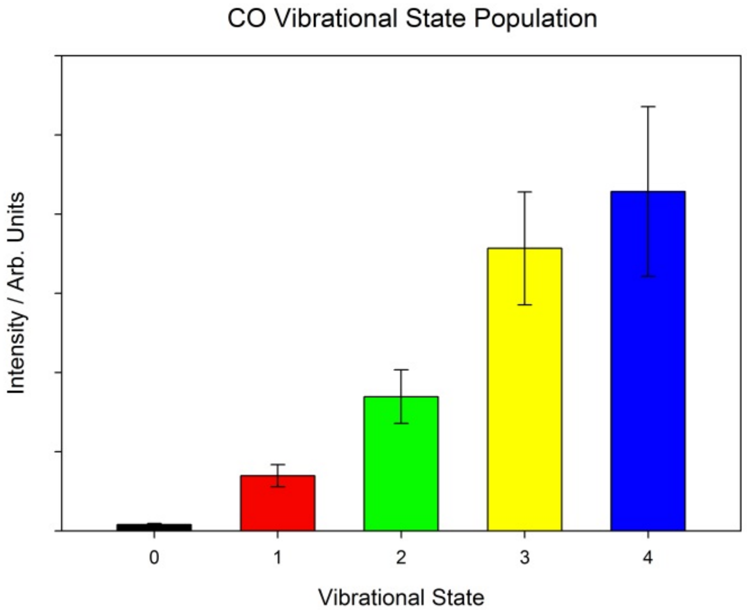
$$\Delta H = -5.72 \frac{eV}{molecule} \quad (-132.6 \frac{kcal}{mol})$$

Theory (G. Schatz)



- predicts 30% of reaction energy goes into vibrational mode.

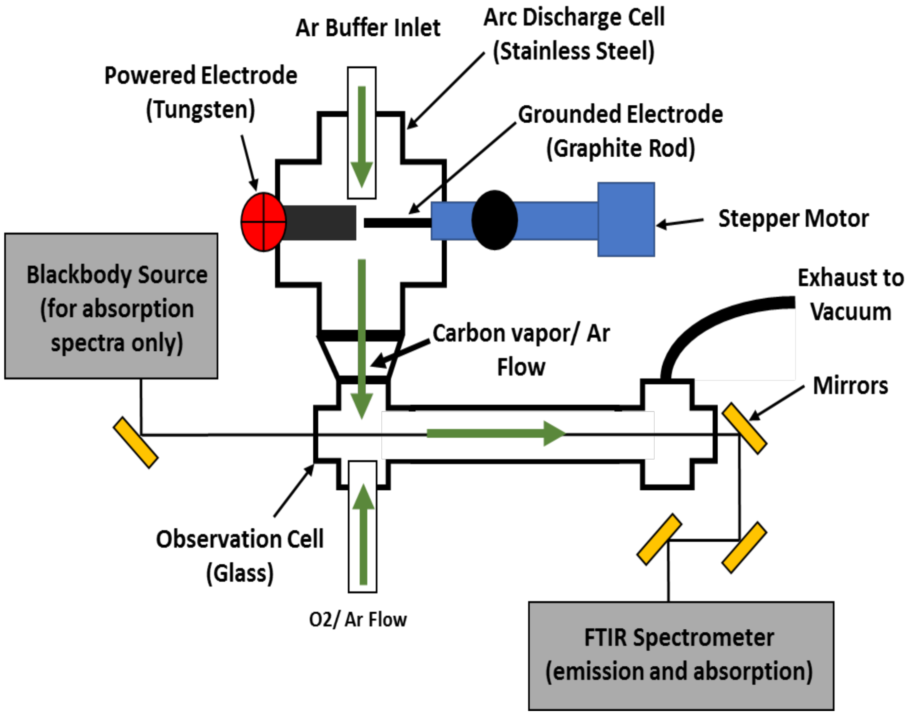
Experimental (T. Minton)

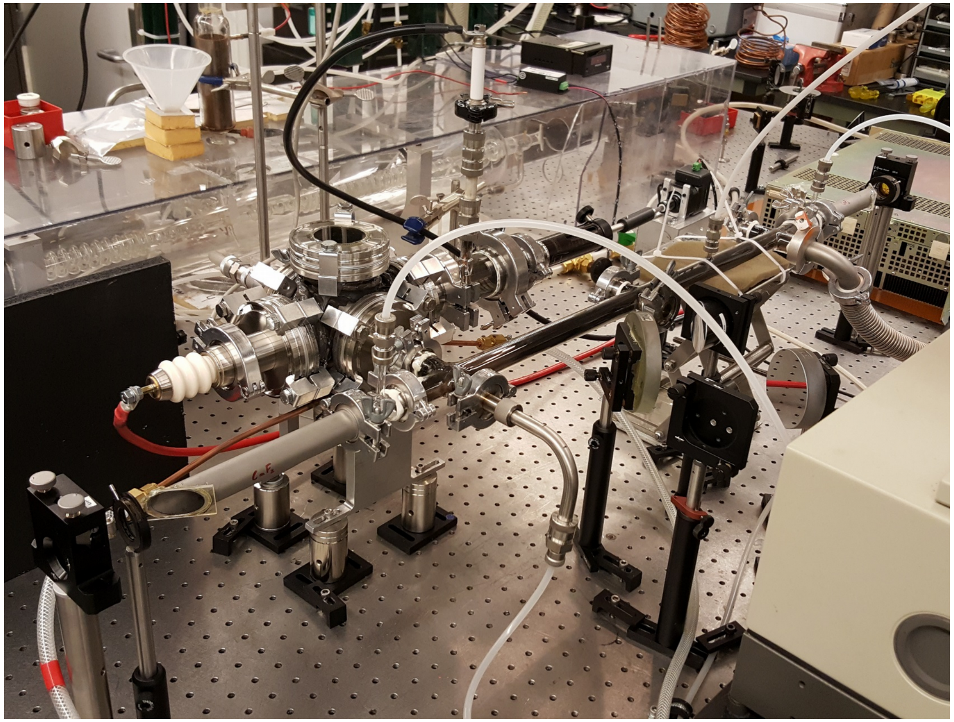


- Crossed beam 3+1 REMPI showed total population inversion

Chemical flow reactor:
carbon vapor / CO generation

Experimental setup





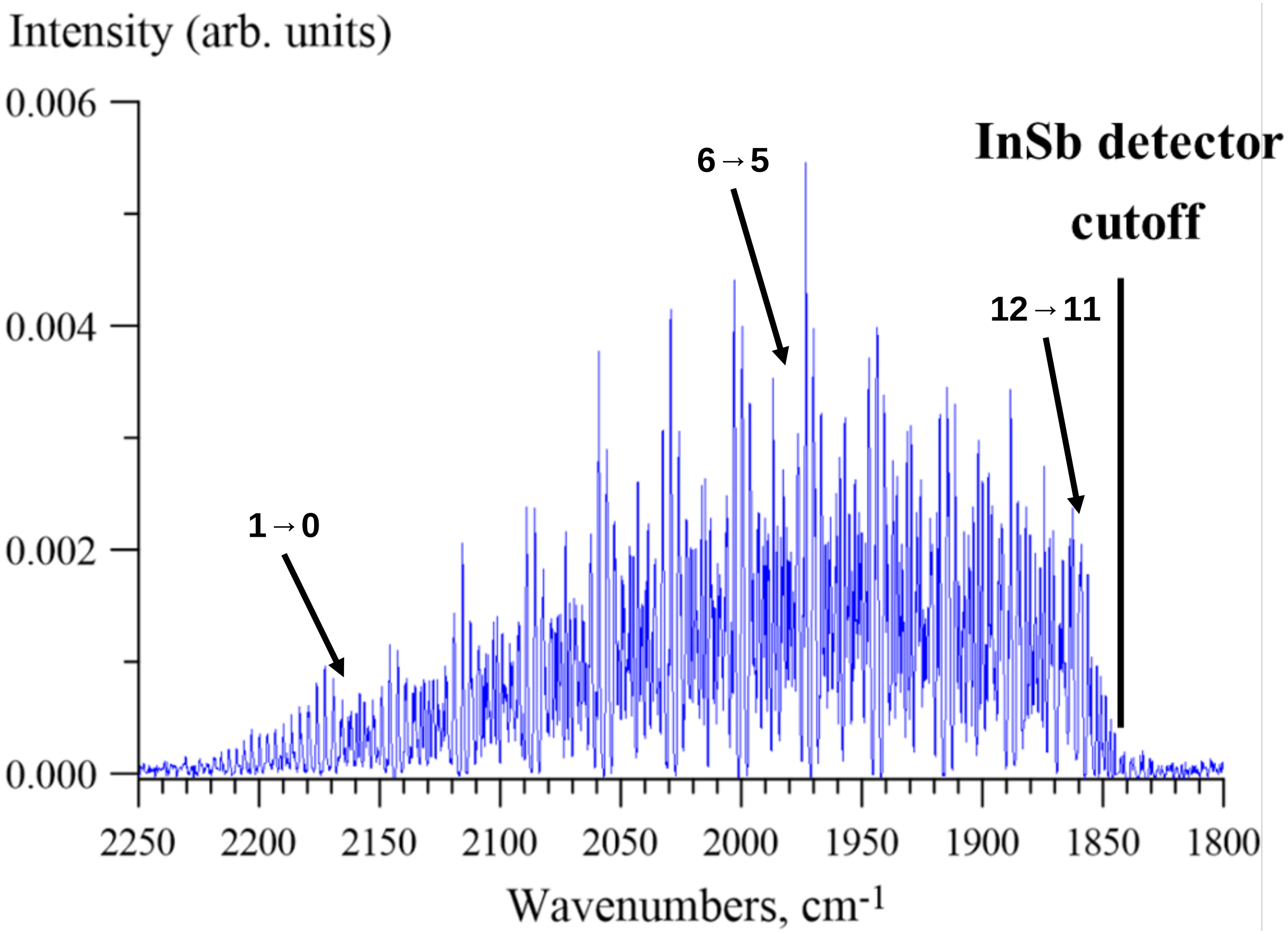
- Grounded electrode: Graphite
- High voltage electrode: Tungsten
- Arc conditions : 20 V, 40 A

- 20 Torr (Ar with 1-10% O_2)
- Observation cell 30 cm long
- 10-30 ms residence time

Model Description

- Quasi-1D flow reactor at 20 Torr and flow rate/dimensions matching experiment
  - Initial mixture: 90% Ar, 10% O_2 trace C
  - Konnov Combustion Mechanism
- $C + O_2 \rightarrow CO(v > 0) + O$ assumed to produce Gaussian vibrational distribution centered at v=8 (to match 30% of reaction energy from Schatz)
- State specific vibrational kinetics for CO and O_2 including:
  - Vibration-to-vibration transfer: CO-CO, CO-O_2, O_2-O_2
  - Vibrational-translational relaxation by CO, O_2, Ar, O
- Concentrations of C used as adjustable parameters

CO product measurements:
in situ FTIR emission

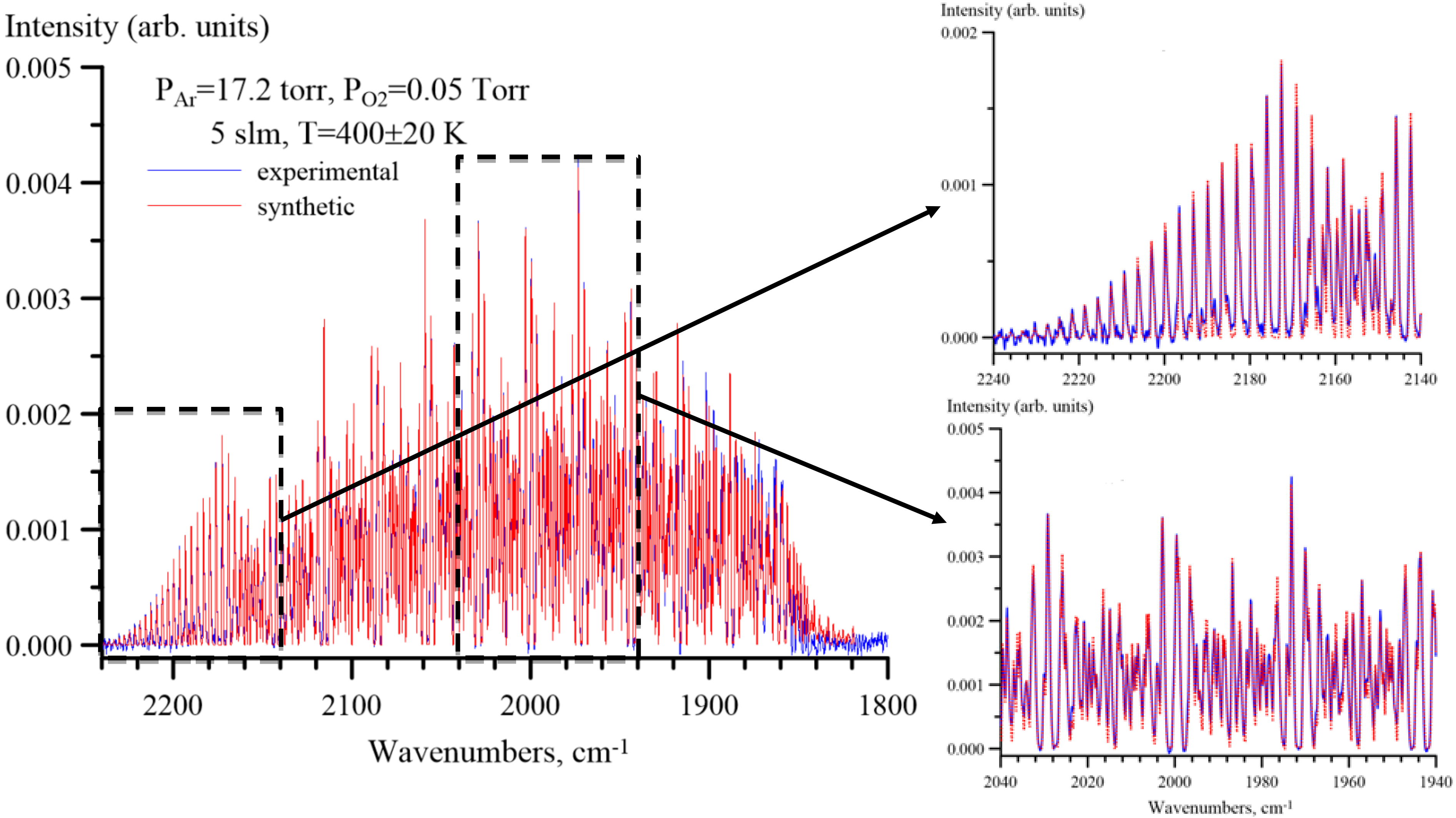


Ar Buffer
Total Pressure: 19.4 Torr
(0.2 Torr of O_2)

P_{CO} ≈ 10 mtorr
(from absorption Measurements)

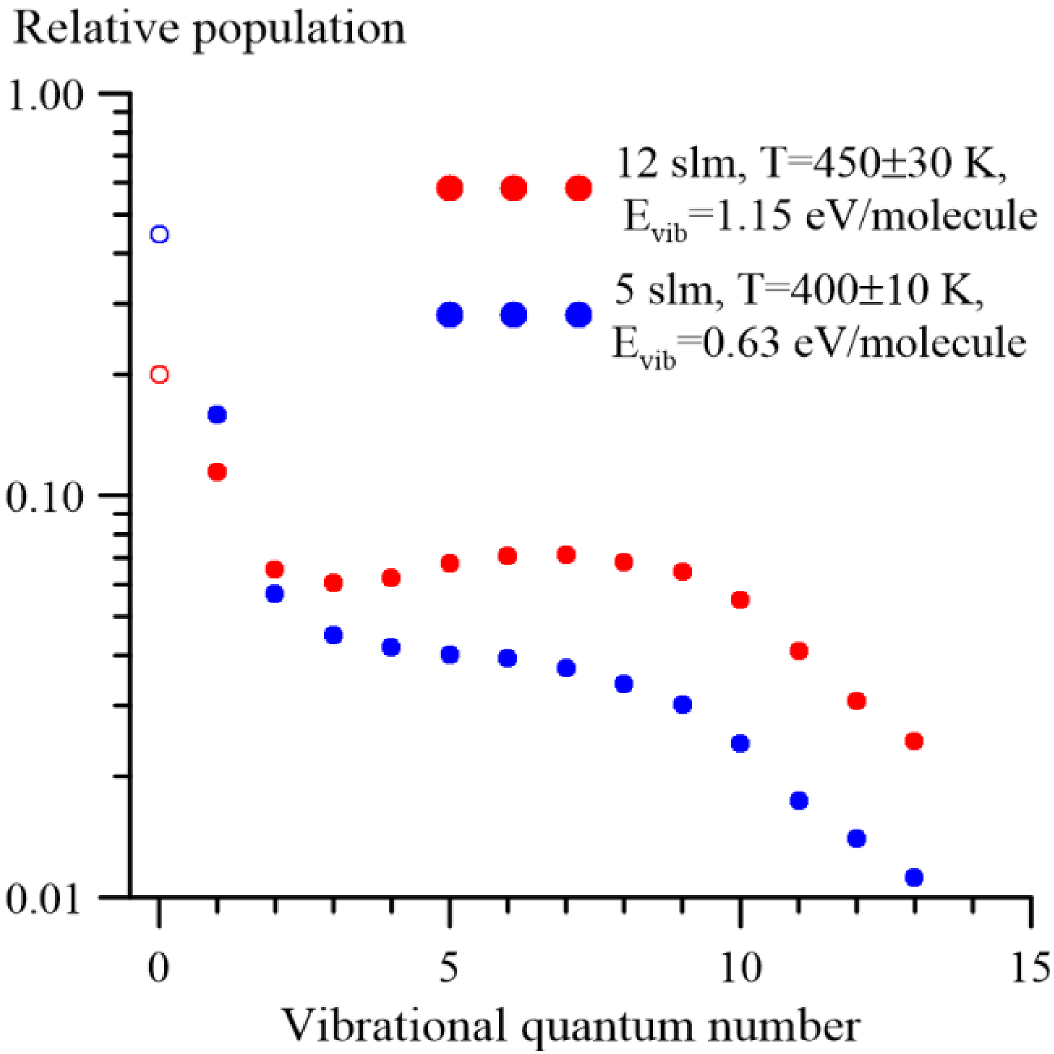
- **Evidence of strong vibrational non-equilibrium observed**
- **No observed CO_2**

CO Vibrational Population Inference



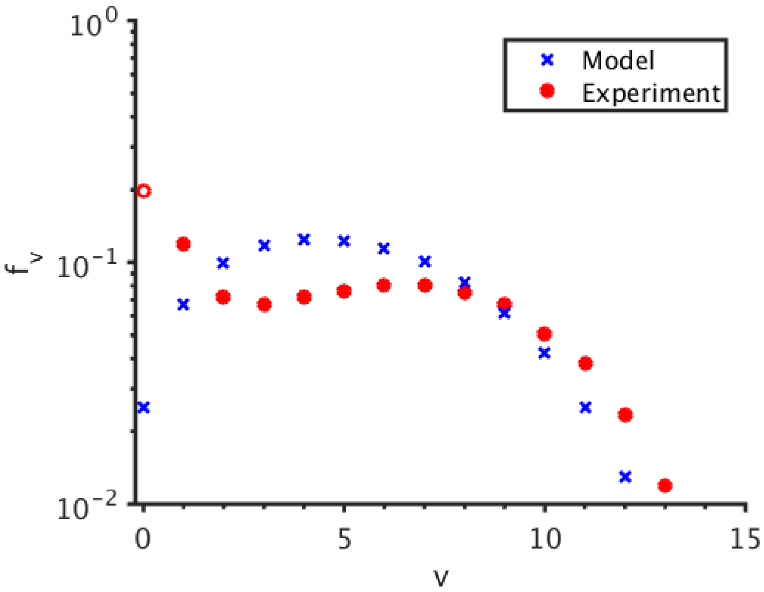
- Best fit synthetic spectrum used for inferring CO vibrational populations
- Close-up comparison of experimental and synthetic spectra

CO Vibrational Distribution Function



- Absolute vibrational population inversion detected among CO(v=4-7)
- Vibrational energy per CO molecule: ~ 1.2 eV/molecule (~ 20% of the heat of reaction)
- 12 slm is optimal flow rate for system

Comparison of predicted and measured VDF

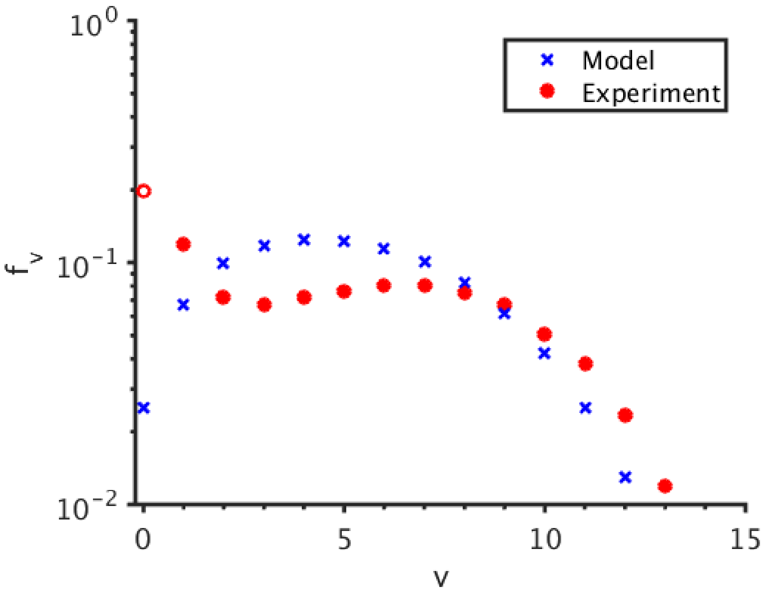


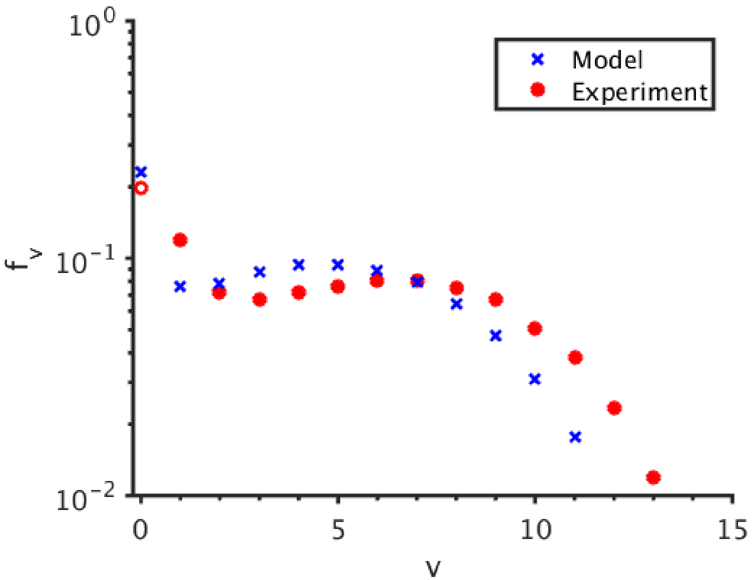
T_0 = 450K
1.6 mTorr of CO produced

Not enough time for vibrational kinetics to produce trend at v<3 in experiment

Implies some CO is produced by another reaction in v=0

Comparison of predicted and measured VDF





T_0 = 450K
1.6 mTorr of CO produced

Not enough time for vibrational kinetics to produce trend at v<3 in experiment

Implies some CO is produced by another reaction in v=0

Added another reaction that results in CO(v=0)

T_0 = 450K
1.6 mTorr of CO produced
2:1 ratio between vibrationally "live" reaction and "dead" reaction

Peak predicted gain: 0.06%/cm on v=7,J=10 → v=6,J=11

Summary and Future Work

- Demonstrated production of highly vibrationally excited CO by a chemical reaction between carbon vapor and molecular oxygen in collisionally dominated environment

- Kinetic modeling results in good agreement with experiment, showing likely second reaction producing vibrationally “dead” CO

Future Work

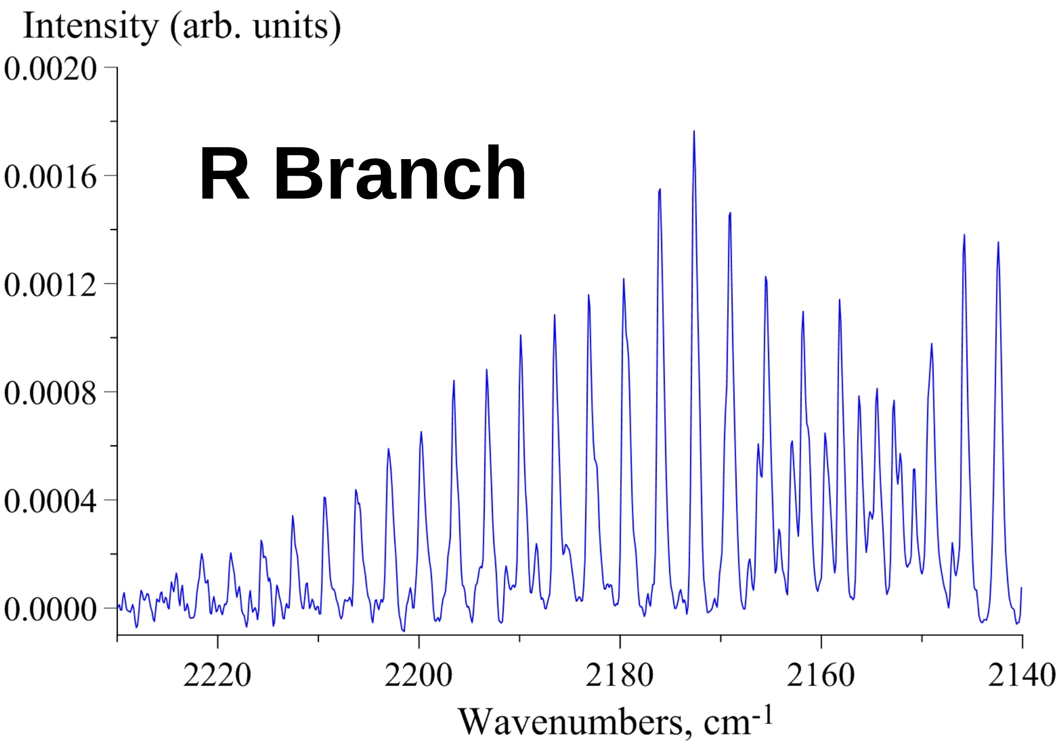
- Evaluate carbon arc products via mass spectrometry
- Create tabletop chemical CO laser using $C+O_2 \rightarrow CO(v) +O$ reaction

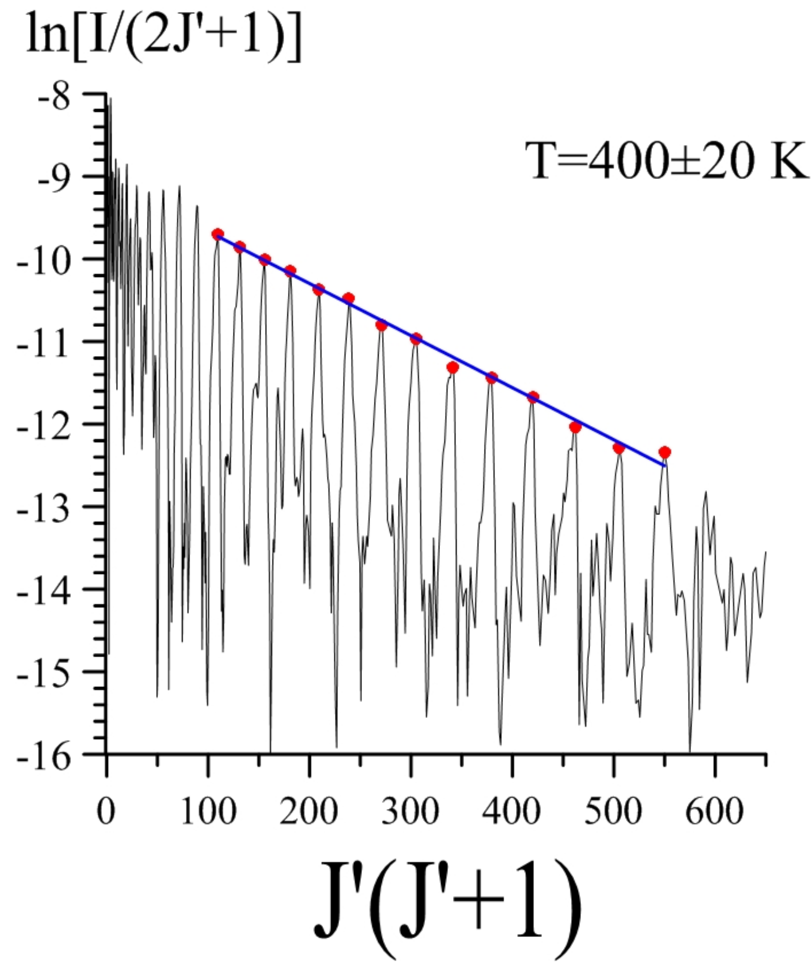
Acknowledgments

- Lockheed Martin Corporation (technical monitor Dr. Luke Uribarri)
- Michael A. Chaszeyka gift

Questions?

CO product measurements: Temperature Inference

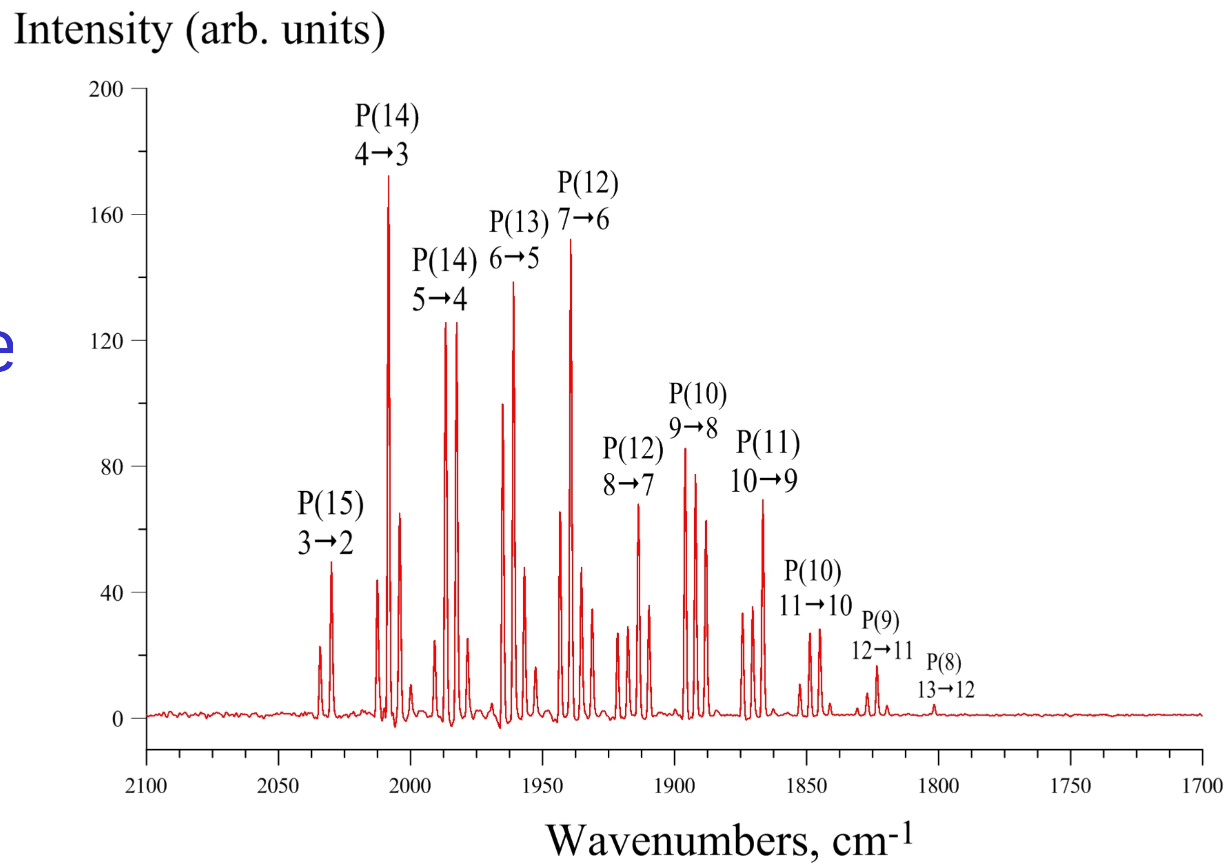




- **Lasing from optically pumped CO was previously demonstrated at temperatures up to T=500 K (Ivanov et al, Laser Physics, 2013)**

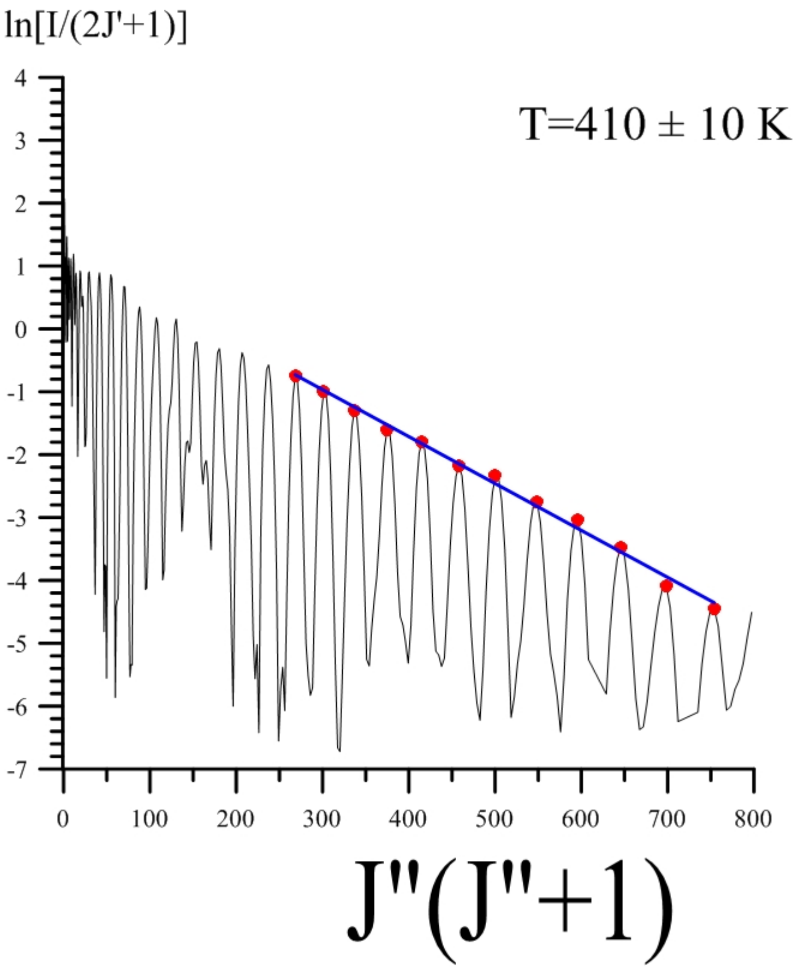
Laser Spectra: CO-He-O_2

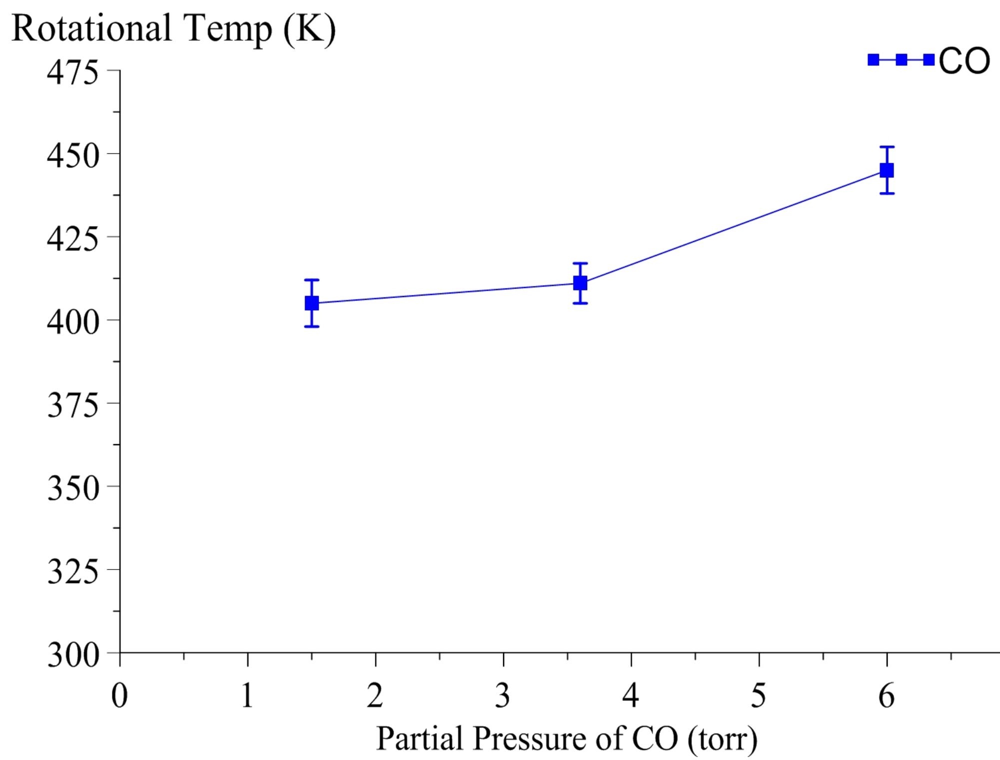
- 97 Torr He
- 3.1 Torr CO
- 3.3 Torr O_2
- 2000 W discharge power



- Disappearance of many vibrational-rotational transitions
- Consistent with significant power reduction
- Power: 1.84 W (measured), Model predicted no lasing

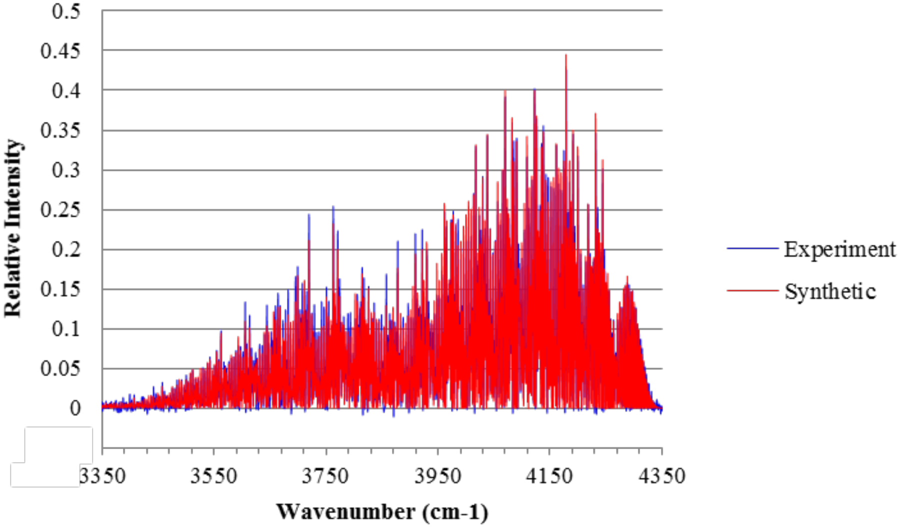
Rotational Temperatures

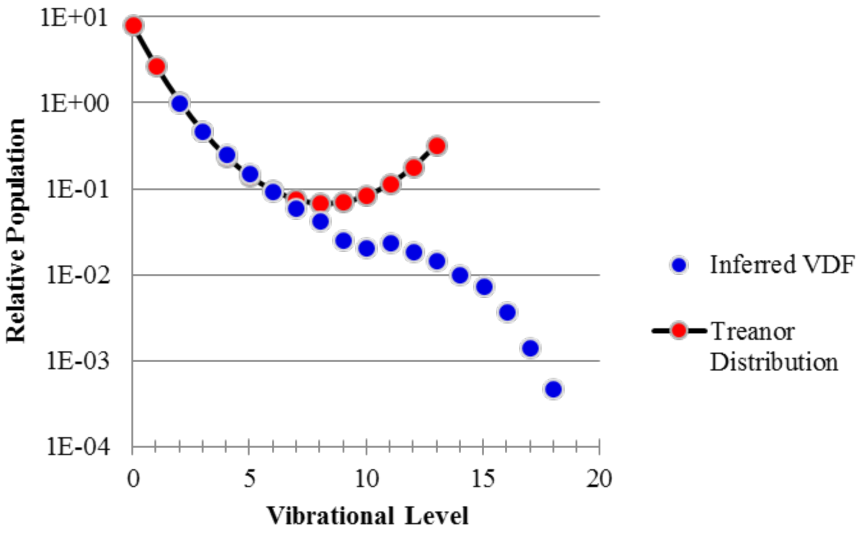


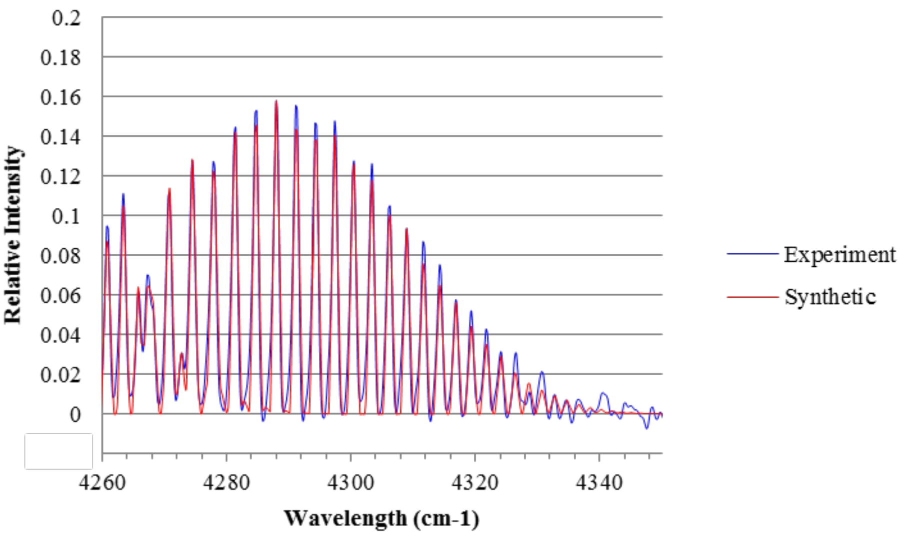


- RF power = 2000 W
- Temperature inference avoids self-absorption

VDF Inference

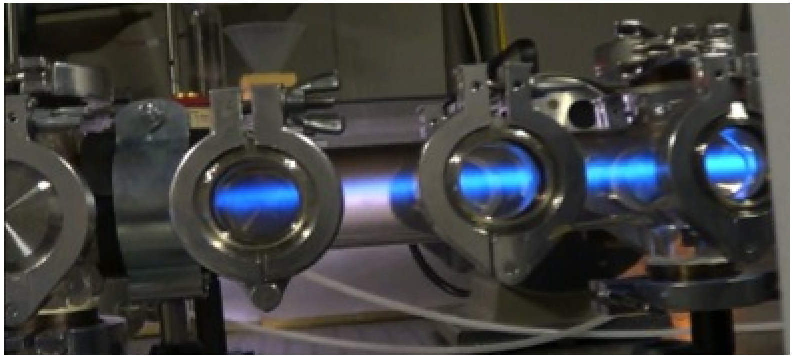






- Overtone region of CO emission spectra are compared with synthetic spectra to infer vibrational populations for V ≥ 2 (left)
- Treanor distribution is fit to the first several vibrational populations and used to infer V=1 and V=0 populations (right)

Recent Results (2013): Experimental demonstration of high-temperature lasing in CO

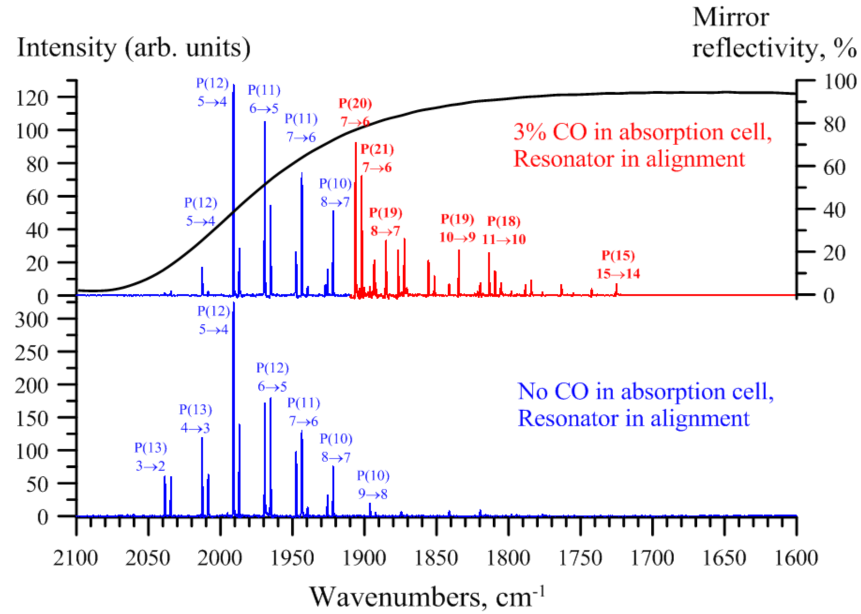


Optically pumped laser cell

Glow is from vibrationally excited flowing CO, reacting to form C_2, emitting on Swan bands

CO in absorption cell excited by a CO pump laser. The cell has mirrors to extract laser power. The cell lases efficiently at temperature up to T=500 K.
Laser output powers and spectral line details are in very good agreement with kinetic modeling predictions

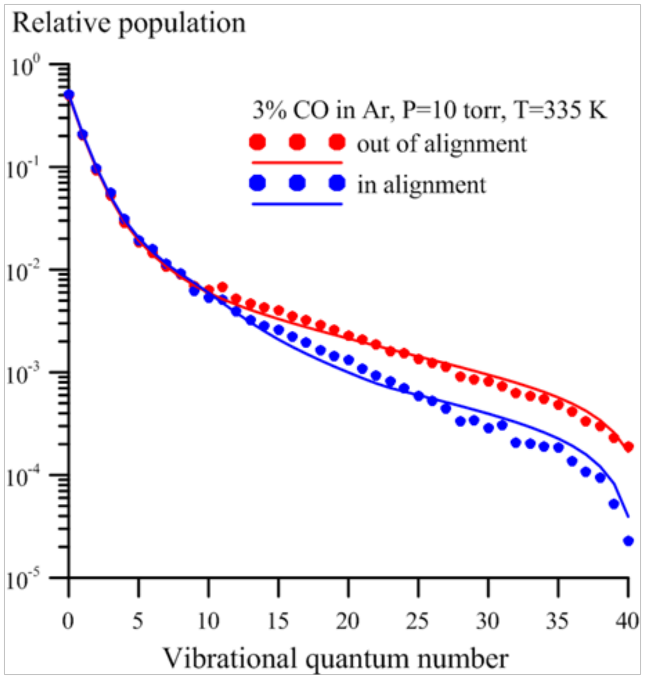
Ivanov et al, Laser Physics, 2013

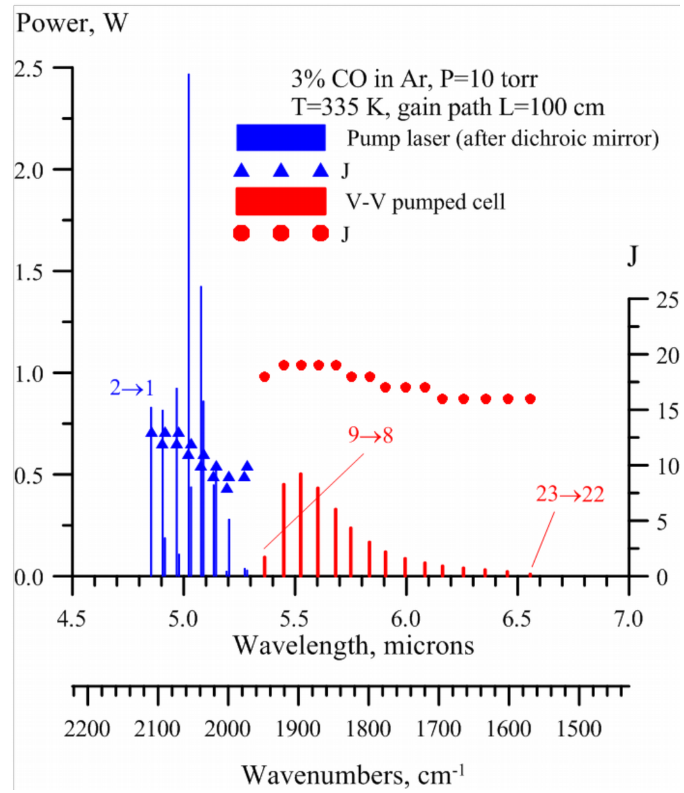


Laser output spectrum from the optically pumped cell

Top: red spectrum shows each laser line coming from the cell, and reflectivity of the cell mirrors (black).
Bottom: spectrum of the pump laser (blue).
Additional output lines, in red, are produced in the vibrationally energized CO in the cell. Efficiency is several percent, up to 400 K; spectra are in good agreement with kinetic modeling predictions

Recent Results (2013): Comparison with kinetic modeling calculations





CO VDFs with resonator in and out of alignment. Reduction of CO(v) populations due to stimulated emission is apparent.

Predicted pump CO laser spectrum (blue) and optically pumped laser spectrum (red).
Predicted conversion efficiency 28% (7-14% in experiment, strongly depends on mirror alignment / resonator losses)

Ivanov et al, Laser Physics, 2013