Cold Molecular Plasmas with Extreme Vibrational Mode Nonequilibrium

By

Igor Adamovich, Evgeny Ivanov, Walter Lempert, Munetake Nishihara and J. William Rich

The Michael A. Chaszeyka
Nonequilibrium Thermodynamics Laboratories
Dept. of Mechanical Engineering
The Ohio State University

Princeton University
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Nature of extreme vibrational mode excitation of small molecules in cold, weakly ionized plasmas.

Environments studied here are either absorption cells pumped by laser radiation, or electric glow discharges.

Focus on vibrationally excited carbon monoxide and novel carbon chemistry.

Types of Reactions:
- Associative Ionization of CO
- Vibration-to-Electronic Mode Energy Transfer
- Boudouard Disproportionation of CO to form CO₂ and free carbon
- Direct Dissociation of CO to form C and O²

Some applications:
- $^{13}$C, $^{14}$C isotope enrichment
- Synthesis of single-walled carbon nanotubes
- The “dissociation” of CO in high temperature gas environments
Each peak is from a successive vibrational state, $v$, ground state signal on the right. The time delay between the pump and probe pulse is (a) 150 ns, (b) 1 μs, (c) 5 μs, (d) 10 μs.
Schematic of Experimental Setup: Optical Pumping of IR-Active Molecules

UV–Vis

CO, ...

Ar

Step–Scan FT–IR

CO laser

POWER METER

to pump
Extreme Vibrational Up-Pumping of CO in Reaction Cell

\[ \nu' = 21 - \nu'' = 18 \]

\[ T_{\nu}(\text{CO}) = 3100 \text{ K} \]

\[ T_{\text{rot-trans}} = 530 \text{ K} \]
V-V Pumping in the Asymmetric Stretch Mode of CO₂

Optically Pumped Cell, CO₂/CO Mixture:

A glow discharge in a CO₂/N₂/He mixture
Nonequilibrium Vibrational Distribution Function

CO laser

V-V

V-T

Ionization:
CO(v)+CO(w) → (CO)₂⁺ + e⁻

V-E:
CO(X¹Σ, v~40)+M→CO(A¹Π)+M

Chem. Reactions:
CO(v)+CO(w)→CO₂+C

T = 600 K

Tv = 3300 K

2 Torr CO, 100 Torr Ar,
CO laser power 10 W c.w.
Associative Ionization in Optically Pumped Plasmas I

\[
\text{CO}(v) + \text{CO}(w) \rightarrow (\text{CO})_2^+ + e^- , \ E_v + E_w > E_{\text{ion}}
\]

Thomson discharge

Microwave absorption

Electron production rate:
\[
k_{\text{ion}} \sim 10^{-13} \ \text{cm}^3/\text{s}
\]

Electron density:
\[
n_e \approx 10^{11} \ \text{cm}^{-3}
\]
Associative Ionization in Optically Pumped Plasmas II
Formation of Heavy Positive Ions, (CO)$_2$C$_n$
Electron-Mediated V-E Energy Transfer
Low-Energy Electrons Mediate Excitation of Electronically Excited Radiating Species from Metastable “Dark” States

Process demonstrated for
- CO 4th positive system
- NO $\gamma$ band
- CN violet system
- $C_2$ Swan band

$\text{ionization fraction: } \frac{n_e}{N} \approx 10^{-9} - 10^{-7}$

free $e^-$ present in flow

e$^- \text{ removed by } V = 500V$
The Boudouard disproportionation:
\[ \text{CO(v)} + \text{CO(w)} \rightarrow \text{CO}_2 + \text{C}, \]
occurs in gas phase and with enhanced rate on surfaces.

The free carbon produced is rapidly consumed in various reaction channels:

\[ \text{C} + \text{CO} \rightarrow \text{C}_2\text{O} \]
\[ \text{C}_2 + \text{CO} \rightarrow \text{C}_3\text{O}_2 \]

polymeric forms precipitate out

\[ \text{C} + \text{C} + \text{M} \rightarrow \text{C}_2 + \text{M} \]

On various metal catalysts, the carbon can form single-walled carbon nanotubes (SWCNT)
The carbon products can be isotopically enriched in $^{13}\text{C}$
Carbon monoxide gas laser

Infrared Radiation

CaF$_2$ lens

Off axis parabolic mirror

Overtone Filter

Chopper wheel

Monochromator

Lockin Amplifier

Computer

InSb Detector

Flow to Vacuum pump

Absorption cell

Continuous Flow reactor

Ar

CO

He

Fourier transform spectrometer
Experimental $^{(12}\text{CO})$ and calculated $^{(12}\text{CO}$ and $^{13}\text{CO})$ vibrational distribution functions.

CO fraction in CO-Ar 13%, $^{13}\text{CO}$ fraction in CO 8%, $P=100$ Torr.
Vibrational Distribution Function

Fractional population vs.
Vibrational quantum number

\[ n_v = n_o e^{-\gamma} \exp \left( \frac{-E_v}{k_B T} \right) \]

\[ \gamma = \left( \frac{E_1}{k_B \theta_1} \right) - \frac{E_1}{k_B T} \]

Treanor, Rich and Rehm

\[ \text{CO(v) + CO(w) } \rightarrow \text{ CO}_2 + C \]
Measured Global Rate for CO(v) + CO(w) → CO₂ + C

$k_{\text{overall}} \text{ [cm}^3/\text{sec}]$

as a Function of Helium Partial Pressure

- [CO] = 12 Torr
- [CO] = 6.4 Torr
- Average for [CO]=12 Torr
- Exponential fit
- Calculated from Statistical Theory
Vibrational State Dependence of Disproportionation Rates and Isotope Enrichment of CO₂ Products

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![Graph with vibrational state dependence of disproportionation rates and isotope enrichment of CO₂ products.](image-url)
Boudouard Disproportion at Low Temperature: Surface-Catalyzed Reaction of Vibrationally Excited CO

Dimensions of the Automobile monolith used in the catalytic experiments

- **Automobile Catalyst**
- **Copper Oxide**
- **Blank**

Top View

- Length ~ 1-1+1/4 in
- Width ~ 1/4-1/2 in

Side View

- Height ~ 1/2-1/4 in
- d=1 mm
Enhancement of Vibrationally Pumped Disproportionation by Heterogeneous Catalysis

Carbon Dioxide Produced as a Function of Helium for the Gas Phase and Copper Oxide Surface

![Graph showing carbon dioxide production as a function of helium partial pressure](image-url)
Carbon Nanotube Synthesis from CO

R. Smalley et al.: equilibrium high pressure, high temperature process using CO with trace amounts of Fe(CO)$_5$

CO Disproportionation Reaction

$\text{CO(v)} + \text{CO(w)} \rightarrow \text{CO}_2 + \text{C}$

$E_v + E_w \geq 5.5 \text{ eV}$

low gas kinetic temperature

$n \cdot \text{C} \xrightarrow{\text{Ni,Fe catalyst}} \text{carbon nanotubes}$
Single-Walled Carbon Nanotubes Synthesized in Optically Pumped CO Plasmas

Plasma Conditions
CO: 50 Torr
Ar: 50 Torr
Fe(CO)$_5$, Ni(CO)$_4$:
several ppm
Laser Power: 18 W
T: 1200 K
Thermal Dissociation Rate from Shock Tubes

CO + M $\rightarrow$ C + O + M or CO + CO $\rightarrow$ C + CO$_2$ ?

$k = 1.33 \times 10^{15} \times T^{-5.5} \exp(-1.29 \times 10^5 / T) \text{ [cm}^3/\text{sec}]$

$E_a = 11 \text{ ev}$

$k = 1.1 \times 10^{-11} \times T^{-1/2} \exp(-6.9 \times 10^5 / T) \text{ [cm}^3/\text{sec}]$

$E_a = 6 \text{ ev}$
Summary

- Preparation of vibrationally-excited mixtures of small chemical reactants (diatomics, triatomics) in high density, cold plasma environments is possible

- Preparation can be by electric discharges, optical absorption by laser irradiation (IR, Raman)

- Excitation to chemically reactive states in thermally cold environments is achieved
  - Methods are mode-selective and are selective to a small range of excited quantum states

- Novel chemical syntheses are possible

- Demonstrated here:
  - Gas-phase CO disproportionation preparing free carbon; enhanced disproportionation reaction on cold catalytic surfaces
  - $^{13}$C, $^{14}$C isotope separation
  - Single-wall carbon nanotube synthesis at low temperature
  - Mechanism of high temperature CO “dissociation”
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Summary and Conclusions: Gas Phase

Thermal (shock tube) data for \( \text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M} \)

\[ k = 8E38T^{5.5} \exp(-1.2E5/T) \text{ [cm}^3\text{/sec-mole]} \]

\( \text{Ea}=7.2 \text{ ev, no pre-exponential} \)

\( \text{CO(v)} + \text{CO(w)} \rightarrow \text{CO}_2 + \text{C} \)
Experimental and Results: Cryogenic Liquid Phase

Carbon Monoxide Overtone Emission Spectrum
in Liquid Argon
for Different Nitrogen Concentrations

Intensity [-]

2e+6
2e+6
1e+6
5e+5
0
2000 2500 3000 3500 4000 4500
Wavelength [nm]
Molecular Nitrogen Fundamental in Liquid Argon
as a Function of Nitrogen Concentration

- \([N_2] = 50\) Torr
- \([N_2] = 100\) Torr
- \([N_2] = 200\) Torr
- \([N_2] = 400\) Torr
- \([N_2] = 500\) Torr
- \([N_2] = 600\) Torr
- \([N_2] = 700\) Torr
- \([N_2] = 1000\) Torr

Increasing \(N_2\)

\(N_2\) band center

\(CO_2\) \(v^3\)
Experimental and Results: Cryogenic Liquid Phase

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**CO/Ar/N₂**

- **Experiment**
- **Kinetic Modeling**

**Wavelength, nm**

**Relative population**

- **C¹³O¹⁶**
- **C¹³O¹⁸**
- **N¹⁴N¹⁴**

**Vibrational quantum number**

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10 20 30 40 45

1E-5 1E-4 1E-3 1E-2 1E-1 1E+0
Experimental and Results: Cryogenic Liquid Phase

Carbon Monoxide Overtone Spectra
with $^{14}_N\text{N}_2$ and $^{15}_N\text{N}_2$ in Liquid Argon

![Graph showing carbon monoxide overtone spectra with different nitrogen isotopes and varying pressures.](image-url)
Experimental and Results: Cryogenic Liquid Phase

Carbon Monoxide Overtone Emission Spectrum
in Liquid Nitrogen
for Different Carbon Monoxide Concentrations

- \([\text{CO}] = 1 \text{ Torr}\)
- \([\text{CO}] = 2 \text{ Torr}\)
- \([\text{CO}] = 5 \text{ Torr}\)

Nitrogen fundamental

Intensity [-]

Wavelength [nm]
**KEY RESULTS**

- Measured the specific reaction rate of the Boudouard reaction in cold CO plasmas
- Shown the enhancement of the Boudouard reaction by vibrational mode excitation in gas phase and on solid surfaces
- Shown a correlation between the reaction rates of the Boudouard reaction and energy in the higher vibrational states of the reactant
- In liquid phase: Observed the nitrogen fundamental in emission
  - Observed CO to N$_2$ energy transfer
  - High densities induce dipole moment

**FUTURE STUDIES**

- Investigate the influence on amount of CO reactant on the rate
  - Redo experimental setup to use FTIR to measure CO overtone
  - Vary the CO concentrations and power loading

- Investigate the influence of the e- on the carbon dioxide production
  - Occurring through CO(a$^3\pi$) state?
  - Population of CO(A$^1\pi$) state decreases with e- removal