Molecular Energy Transfer Processes in Nonequilibrium Hypersonic Flows

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Research backgrounds of students and post-docs: Mechanical Engineering, Aerospace Engineering, Electrical Engineering, Chemical Physics, Physical Chemistry, Physics
Previous state of the art

I. Lack of laboratory scale, long run time, multiple runs per day, nonequilibrium flow facilities
   • Limits amount of flow characterization data, slows down development of diagnostics

II. Lack of non-intrusive, high frame rate, portable diagnostics of high-speed nonequilibrium flows
   • Prevents spatially and time-resolved characterization of flow parameters, in particular state-specific measurements and kinetic model validation

III. Lack of predictive, physics-based, state-to-state molecular energy transfer rates and kinetic models
   • Use of simplified semi-empirical models, lack of confidence in modeling predictions
I. Development of a Nonequilibrium Flow Wind Tunnel

• Plenum pressure $P_0=0.5-1.0$ bar, steady-state run time 5-10 s
• Strong vibrational nonequilibrium generated in plenum ($T=500$ K, $T_v=2000$ K)
• Nonequilibrium flow in test section, Mach number $M=3-5$
• Used for characterization of nonequilibrium flow field by laser diagnostics
  • $P_s$ CARS for $T$ and $T_v$ in plenum, Mach 5 free stream, and behind Mach 5 shock
  • 10 kHz NO PLIF for 2-dimensional temperature distribution in nonequilibrium flow behind Mach 5 shock
  • 500 kHz NO$_2$ / NO MTV for velocity field in flow over Mach 5 shock
Nonequilibrium Flow Wind Tunnel

- Plenum pressure $P_0 = 0.5$-1.0 bar
- Steady-state run time 5-10 s, ~100 runs a day
- Strong vibrational nonequilibrium sustained by a diffuse electric discharge in plenum
- Interchangeable nozzle inserts, test section Mach number $M=3$-5
- Well characterized flow (US3D)
- Ample access for laser diagnostics
N\textsubscript{2} vibrational CARS spectra in plenum
• N\textsubscript{2}(ν=0-3) vibrational bands are detected
• Temperature inferred from rotational band structure
• T\textsubscript{V} = 2000 K, T\textsubscript{rot} = 450 K (nitrogen);
• T\textsubscript{V} = 800 K, T\textsubscript{rot} = 600 K (nitrogen with CO\textsubscript{2} added)
• Strong vibrational nonequilibrium at steady state
• Varied by adding relaxers such as NO, H\textsubscript{2}, CO\textsubscript{2}
Mach 5 Test Section: 500 kHz Flow Tagging Velocimetry*

- "Tag" beam: $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} $ ("painting" an invisible NO line in the flow), 355 nm
- "Interrogate" sheet: NO PLIF imaging ("lighting up" the invisible lines), 226 nm
- Inferring 2-D flow velocity field in shock layer. Free stream velocity $v = 719 \pm 10$ m/s

*Using OSU pulse burst laser
Nonequilibrium Mach 5 Flow Characterization: Free Stream and Shock Layer

Shock in Front of a Cylinder Model

Temperature distribution:
10 kHz NO PLIF (top), CFD (bottom)

Vibrational Temperature: Ps CARS

• $T_{\text{rot}}$, $T_v$ distributions behind shock are measured
• “Frozen” flow behind Mach 5 bow shock: N$_2$ vibrational relaxation very slow

$T_{\text{max}} = 500$ K
• Higher static pressure: CO$_2$ injection accelerates N$_2$ vibrational relaxation
• This results in gas temperature and pressure rise, pushing shear layer up
• 2-D N$_2$ vibrational temperature distribution measured in shear layer
• Effect observed only when N$_2$ is vibrationally excited
• At $T > T_v$, effect would be reversed (vibrational relaxation would reduce T)
Impact

• Robust, laboratory scale experimental platform for detailed studies of nonequilibrium hypersonic flows
• Essential for development and testing of laser diagnostics
• Straightforward generation of nonequilibrium high-pressure flows
• Detailed characterization of nonequilibrium flow in plenum, free stream, and Mach 5 shock layer
• Effect of accelerated vibrational relaxation on Mach 3 shear layer is detected and quantified
• Effect may be observed behind oblique shocks, in base flows in hypersonic flight
Challenges

• Effect of vibrational relaxation on high-speed flow field needs to be quantified at well characterized flow conditions, compared with nonequilibrium flow code predictions

• Time-accurate effect of vibrational relaxation on shock stand-off distance: high frame rate NO PLIF

• Development of high frame rate CARS (CARS data so far are obtained at 10 Hz)

• 10 Hz CARS limitation: although 10-100 laser shots used for 1-10 s wind tunnel run time, only one laser shot per run is used at short run time facilities

• Development of Cavity Ring Down Spectroscopy diagnostic, to measure “dark” states (non-radiating metastable species) in the flow, N$_2$(A$^3\Sigma$) and O$_2$(a$^1\Delta$)

• These states are critical for quantifying UV emission behind the shock, O$_2$ dissociation kinetics
II. Development of Laser Diagnostics of High-Speed Flows

• OSU pulse burst laser / high frame rate flow imaging system
  • Custom built Nd:YAG laser outputs “bursts” of 10-30 high energy, ns duration pulses at rep rate of up to 1 MHz (1 μs apart)
  • Pulse energy ~100 mJ (@1064 nm) at 1 MHz to ~500 mJ at 10 kHz
  • Tunable UV output generated by Optical Parametric Oscillator (OPO), in combination with sum frequency mixing
  • Planar Laser Induced Fluorescence (PLIF) imaging captured with high frame rate cameras
  • At OSU, used for 10 kHz NO PLIF and 500 kHz Molecular Tagging Velocimetry

• The laser is portable, traveled to take data at hypersonic flow facilities at NASA LaRC and CUBRC
Pulse Burst Laser / Flow Imaging System

Low energy, 1064 nm fiber laser pulses undergo 5 stages of amplification, frequency tripled to pump narrow linewidth OPO.

Typical 1 MHz laser pulse trains

1064 nm (100 mJ/pulse) | 226 nm for NO LIF (0.4 mJ/pulse)
NO PLIF at NASA LaRC Mach 10 Wind Tunnel

- Multiple sets of 500 kHz NO PLIF imaging of a Mach 10 boundary layer after a cylindrical trip, Re = 1.7 - 6.2 million / m
- Flow ranges from laminar to highly transitional, with instabilities and corkscrew vortices identified

Re = 1.7\cdot10^6 / m

Re = 6.2\cdot10^6 / m
NO PLIF at CUBRC 48” Shock Tunnel

- Free stream flow: nitrogen, Mach 9, run time 10 ms
- 10 kHz NO PLIF images of NO-seeded He jet injected into a model supersonic combustor
- Data quantify jet penetration depth and mixing with the main flow
Impact

• OSU pulse-burst laser: portable diagnostics for high frame rate characterization of nonequilibrium flows (~10 data sets per ~1 ms run)

• Diagnostics development, “shake-down”, and testing made possible by using the OSU laboratory scale nonequilibrium flow wind tunnel

• 500 kHz imaging of Mach 10 laminar and transitional boundary layer at NASA LaRC

• 10 kHz imaging of injection into a model supersonic flow combustor at CUBRC

• 500 kHz Mach 5 flow velocimetry at OSU
Challenges

• Development of portable, high frame rate CARS diagnostics, using the OSU pulse burst laser combined with a broadband OPO

• All previous CARS data are obtained at 10 Hz, such that only a single laser shot per run can be used at short run time test facilities.

• Use of high frame rate CARS will increase rate of data acquisition by an order of magnitude (~10-20 data sets for each ~1 ms run)

• Major technical challenge: monitoring and quantifying shot-to-shot variation of the Stokes beam spectral profile. This is critical for quantitative high frame rate CARS measurements.

• Operating the OSU nonequilibrium wind tunnel and the existing 10 Hz CARS setup is essential for development of this diagnostic.
III. Development of Molecular Energy Transfer / Nonequilibrium Air Chemistry Models

• Forced Harmonic Oscillator – Coupled Rotation model: physics-based, state-specific, close-coupled vibrational-rotational-translational (V-R-T) rates

• Coupled R-T / V-T energy transfer is critical near molecular dissociation limit

• 3-D molecular collisions

• Coupling among multiple vibrational levels, coupling between vibrational and rotational energy transfer

• Multi-quantum V-R-T rates predicted at high collision energies (temperatures)

• Good agreement with computer trajectory calculations for accurate potential energy surfaces

• Coordinated model development, experimental work, and validation in the same laboratory
Comparison with Trajectory Calculations: $P_{VRT}(v, j_0 \rightarrow w, j)$ and $P_{VT}(v \rightarrow w)$ for Nitrogen

- Good agreement with 3-D computer trajectory calculations for an accurate potential energy surface
- Analytic rate expressions: straightforward incorporation into existing nonequilibrium NS and DSMC codes
- Physics-based, predictive analysis of energy transfer and nonequilibrium chemistry behind strong shocks
Comparison with State-Specific Vibrational Energy Transfer Measurements in Air Plasma

- Pulsed air excitation in a diffuse filament, ~100 ns pulse discharge, P=100 Torr
- Experimental data: ps CARS (N₂ vibrational level populations), ns LIF and TALIF (NO, O, N number densities)
- Good agreement between data and modeling predictions for time-resolved N₂(v=0-8) vibrational level populations, vibrational temperature, gas temperature, and [N], [O], [NO]
Impact

• Straightforward incorporation of the model into nonequilibrium flow codes (Candler 1997; Boyd and Josyula 2011; Levin 2012; Schwartzentruber 2014; Gimelshein and Wysong 2018)

• Physics-based analysis of energy transfer and nonequilibrium chemistry at strongly nonequilibrium conditions

• Straightforward analysis of the molecular Potential Energy Surface (PES) effect on the energy transfer rates

• Complementing higher-fidelity, accurate PES, adiabatic / nonadiabatic trajectory calculations
Challenges

- High-fidelity, accurate PES, state-specific vibrational energy transfer and dissociation models have been developed recently (U. Minnesota, U. Michigan)

- Model validation data, specifically for state-specific dissociation rates, are scarce to nonexistent

- Need relevant experimental data obtained at well characterized conditions
Ongoing and Future Research - I

- What are the state-specific rates of O$_2$ dissociation behind strong shocks (above M~6)? O$_2$ dissociation drives high-temperature nonequilibrium air chemistry, UV and IR emission behind the shock.

- How can recent high-fidelity predictions of these rates (Boyd et al. 2015) be validated? State-specific measurements of O$_2$(v) and ground state O atoms in shock tubes are extremely challenging.

- Approach: simultaneous time-resolved measurements of O atoms and O$_2$(v) in recombining O atom - Ar buffer mixture, at well characterized conditions, obtaining dissociation rates from detailed balance:

\[
O_2(v) + M \overset{k_D(v\rightarrow,T)}{\underset{k_R(\rightarrow,v,T)}{\leftrightarrow}} O + O + M \quad \text{with} \quad k_D(v \rightarrow, T) = k_R(\rightarrow v, T) \cdot \frac{n_O^2(T)}{n_{O_2(v)}(T)}
\]
State-Specific Measurements of O atoms and O\textsubscript{2}(v) During Recombination

- O\textsubscript{2}-Ar excitation by a uniform ns pulse discharge burst (~100 pulses at 100 kHz), at P=0.5-1.0 atm, T\textsubscript{0}=500 K
- Complete dissociation of O\textsubscript{2} by electron impact, partial pressure of O atoms ~ 1 Torr
- Time-resolved measurements of O atoms (ps TALIF) and O\textsubscript{2}(v) (ps LIF) during O + O recombination
- Comparison with modeling predictions, validating state-of-the-art dissociation model (U. Michigan)
Ongoing and Future Research - II

- What is the effect of metastable (“dark”) molecular states on UV radiation from strong shocks (M=8-11)?

- Modeling predictions: NO UV radiation (γ bands) is due to energy transfer from metastable excited nitrogen, \( N_2(A^3\Sigma) \) (Wurster 1991, Treanor 1993)

\[
N_2(A^3\Sigma, w) + NO(X^2\Pi) \rightarrow N_2(X^1\Sigma) + NO(A^2\Sigma) \\
NO(A^2\Sigma) \rightarrow NO(X^2\Pi) + h\nu
\]

- Approach: generate \( N_2(A^3\Sigma) \) in an electric discharge in wind tunnel plenum

![Wind tunnel experiment](image)

![UV emission graph](image)

NO UV emission behind a normal shock in air \( u_s=3.86 \text{ km/s} \)
**N$_2$(A$^3$Σ) and NO measurements in Mach 5 Flow**

- Generate N$_2$(A$^3$Σ) in uniform ns pulse discharge burst in wind tunnel plenum
- Seed the flow with NO (in plenum or in supersonic flow section)
- Measure N$_2$(A) and NO(X) in a Mach 5 flow: CRDS, NO PLIF
- Image NO(A→X) UV emission (γ bands), quantify energy transfer from N$_2$(A) to NO(A)
- Generate data at well characterized flow conditions, compare with NO UV emission predictions by nonequilibrium flow codes

NO injected upstream from a cylinder model

NO PLIF

NO(A→X) emission
Cavity Ring Down Spectroscopy Diagnostics for $N_2(A^3\Sigma)$ Measurements in the Flow

- $N_2(A^3\Sigma)$ generated in uniform nitrogen plasma in CRDS cavity by a ns pulse discharge burst
- Absorption of a laser pulse is measured in the cavity with 99.99% reflectivity mirrors
- Absorption path ~ 2 km, very high sensitivity $N_2(A,v=0-2)$ measurements after the burst

\[
\frac{I}{I_o} = \exp \left(-\frac{t}{\tau}\right) \quad [N_2(A^3\Sigma)] = \frac{1}{c\sigma_{abs}} \left(\frac{1}{\tau} - \frac{1}{\tau_{empty}}\right)
\]
Results So Far: $N_2(A^3\Sigma, v=0-2)$ in Nitrogen Plasma*

- $N_2(A^3\Sigma)$ generated in uniform nitrogen plasma in CRDS cavity by a ns pulse discharge burst
- Absolute, time-resolved $N_2(A,v=0-2)$ after the burst measured by CRDS
- $N_2(A^3\Sigma)$ decay time is very long ($\sim 1$ ms), will survive from plenum to Mach 5 test section
- Measurements in Mach 5 CRDS cavity are underway

*Rao Prize, 73rd International Symposium on Molecular Spectroscopy, 2018
Related Work Originated from these Projects
(supported by Lockheed Martin SkunkWorks)

• Development of a novel supersonic flow chemical laser for electrical power generation on board of a hypersonic air vehicle
  • Ablation of carbon from a high-temperature surface in a hypersonic air flow
  • Reaction of C vapor with O$_2$ in the flow, generation of highly vibrationally excited CO
  • Creating population inversion, coupling out power in a CO laser resonator
  • CO lasers: scalable up to MW output power
  • Electrical power generation by photovoltaic conversion of laser power

• Approach to demonstrate feasibility in the lab
  • Carbon powder vaporized in a high temperature, inductively coupled plasma
  • Carbon vapor injected into airflow, reacts with O$_2$ in the flow: C + O$_2$ → CO(v) + O
  • Demonstrate population inversion in CO product
  • Demonstrate laser action in a supersonic flow
Generation of C Vapor and Vibrationally Excited CO for a Novel Chemical Laser

- Micron size carbon particles seeded in Ar vaporized in the plasma
- Carbon vapor injected into airflow, reacts with O₂ in the flow: C + O₂ → CO(v) + O
- CO product: total vibration population inversion, coupling out laser power is feasible
Goal: Demonstrate Lasing in a Supersonic Flow

- Generate carbon vapor in a high-temperature plasma, inject into airflow in plenum
- Carbon vapor reacts with $O_2$ in the flow: $C + O_2 \rightarrow CO(v) + O$
- Couple laser power in transverse supersonic flow resonator
- Supersonic flow laser infrastructure available in the lab
SUMMARY

• Development, operation, and instrumentation of a nonequilibrium flow wind tunnel, quantification of effect of vibrational relaxation on high-speed flow field
• Development of ps and ns CARS diagnostics to characterize vibrational nonequilibrium in the flow
• Development of pulse-burst laser / flow imaging system: portable diagnostics for high frame rate characterization of high-speed nonequilibrium flows
• Use of the pulse-burst laser for 500 kHz Mach 5 flow velocimetry at OSU, 500 kHz imaging of Mach 10 transitional boundary layer at NASA LaRC, 10 kHz imaging of flow in a model supersonic combustor in the 48” tunnel at CUBRC
• Development of close-coupled, state-specific vibrational-rotational-translational (V-R-T) rates for nonequilibrium NS and DSMC flow codes; models used extensively in the field
• Coordinated development of kinetic models, relevant experimental work, and model validation
• On-going work: state-specific measurements of nonequilibrium molecular dissociation, for validation of recently developed high-fidelity models
• On-going work: state-specific measurements of energy transfer from “dark” molecular states on UV radiation behind strong shocks
• On-going related work (support by Lockheed Martin SkunkWorks): development of a novel supersonic flow chemical laser for electrical power generation on board of a hypersonic air vehicle