Experimental characterization of energy transfer in nonequilibrium plasmas and high-speed flows using optical diagnostics


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The NETL Group

- 3 faculty (appointments in Mechanical and Aerospace Engineering, Chemical Physics, and Chemistry)
- ~15 graduate students, post-docs, visiting scholars. Backgrounds in engineering, physical chemistry, plasma physics
Objectives / Outline

- Obtain experimental data on molecular energy transfer mechanisms / rates to enable predictive modeling of high-speed nonequilibrium flow fields
- Develop instrumentation to measure temperature, vibrational populations, species concentrations: high frame rate NO PLIF, high frame rate NO$_2$ MTV, psec CARS, TALIF, Thomson scattering
- Demonstrate use of such instrumentation to obtain data in short duration hypersonic flow facilities (shock tunnels)
- Develop methods of actively influencing flow field energy storage, energy transfer, and aerodynamic control
- **Test bed I:** a small scale Mach 5 nonequilibrium flow wind tunnel, with vibrational energy of air species loaded by an electric discharge in plenum, controlled by adding relaxer species downstream
- **Test bed II:** nsec pulse, point-to-point, filament discharge loading vibrational energy in quiescent N$_2$ or air
- **Kinetic modeling:** do we really understand energy transfer mechanisms involved?
Test Bed I: Mach 5 Nonequilibrium Flow Wind Tunnel
Operating Conditions

- Mach 5, steady state run time 5-10 seconds, $P_0=0.5$-1.0 atm  (M~0.25 flow in plenum)
- Supersonic test section: 4 cm x 4 cm cross section, flow over a 5 mm cylinder model, 4 optical access windows for optical diagnostics
- Sustaining nonequilibrium flows: vibrational energy loading by nanosecond pulser / DC sustainer discharge in plenum
- Discharge power up to ~ 3 kW, power density ~ 300 W/cm$^3$
- Controlling vibrational disequilibrium: injection of V-V / V-T relaxers ($O_2$, NO, CO$_2$, H$_2$) downstream of discharge / upstream of the throat

Nishihara et al., AIAA J., 2012
Previous work: 500 kHz NO PLIF and Molecular Tagging Velocimetry in Mach 5 wind tunnel (equilibrium flow)

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**NO\textsubscript{2} MTV Method**

Tag: \[ \text{NO}_{2} + hv \rightarrow \text{NO} + \text{O} \]

Interrogate: NO PLIF Imaging

**Free Stream Results**

\[ \bar{V} = 719 \text{ m/s}, \quad \sigma_{\bar{V}} = 10 \text{ m/s} \]

Nsec Pulse Discharge: Large-Volume Diffuse Ionization

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Nishihara et al., AIAA J., 2012

Nitrogen, $P_0 = 300$ Torr, $v = 100$ kHz, no DC electrodes

Nitrogen, $P_0 = 650$ Torr, $v = 100$ kHz, no DC electrodes

Nitrogen, $P_0 = 300$ Torr, $v = 100$ kHz, no DC electrodes

Nitrogen, $P_0 = 350$ Torr, $v = 100$ kHz, $1000^{th}$ pulse, 5-μsec camera gate

Nitrogen, $P_0 = 300$ Torr, $v=100$ kHz, DC electrodes not powered

0.1 sec after beginning of burst (i.e. pulse # 10,000)

Pulse energy 4.5 mJ/pulse

Average nsec pulser power 450 W
Energy Addition: DC Sustainer Discharge
(overlapped with nsec pulse discharge in nozzle plenum)

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Nitrogen, $P_0 = 350$ Torr, $\nu = 100$ kHz:

- Plasma does not fully decay between nsec pulses
- Linear current rise with voltage: non-self-sustained DC discharge
- DC sustainer discharge stable up to 3 kW ($U_{PS}=3.5$ kV)
- $T_0=400$ K ($N_2$ emission), $T_{v0}=1800$ K (estimated)

$U_{PS} = 2$ kV, $U = U_{PS} - IR = 1.5$ kV

Current [A]

![Graph showing current and voltage relationships with different UPS voltages.](image)

Nishihara et al., AIAA J., 2012
Life before CARS: 2-line NO PLIF thermometry in Mach 5 flow over a cylinder model

Rotational temperature distribution without discharge in plenum. Nitrogen, $P_0=370$ torr + 0.3 torr NO.

Rotational temperature distribution with pulsed/DC discharge in plenum ($\nu=100$ kHz, $U_{PS}=4.5$ kV).

What is $T_v(N_2)$?

Nishihara et al., AIAA J., 2012
Coherent Anti-Stokes Raman Scattering (CARS) Spectroscopy – Basic Principles

CARS four wave mixing process can be thought of as two 2-photon processes:

1. Pump/Stokes photons induces a coherent (i.e. phased) oscillating polarization
   For N₂ vibrational CARS, a 532 nm pump requires a 607 nm Stokes beam

2. Probe photon induces anti-Stokes Raman scattering, coherent in the phase matching direction

\[ I_{\text{CARS}} \propto I_{\text{pump}} \cdot I_{\text{Stokes}} \cdot I_{\text{probe}} \cdot n^2 \]

Psec CARS: higher signal-to-noise (single-shot spectra possible), sub-nsec time resolution, no optical window damage
CARS Diagnostics in Mach 5 Nonequilibrium Wind Tunnel

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Tunnel Plenum

Optical access

Flow

Nsec Pulser Electrodes

DC Sustainer Electrodes

Optical Access

Injector

Main flow (N₂)

DC electrodes

Pulser electrodes

Laser Propagation

Top View

Side View
Collinear CARS Schematic:
Measuring $N_2(X,v)$ populations in wind tunnel plenum

Montello et al, AIAA J., 2012
Broadband Dye Laser (“Stokes”) Spectrum: Simultaneous access to multiple vibrational states

Broadband dye laser spectral profile, with necessary Stokes frequencies superimposed: enough bandwidth to probe several levels simultaneously

<table>
<thead>
<tr>
<th>Transition</th>
<th>Raman Shift [cm(^{-1})]</th>
<th>Stokes wavelength [nm]</th>
<th>Anti-Stokes wavelength [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 1</td>
<td>2330.7</td>
<td>607.3</td>
<td>473.3</td>
</tr>
<tr>
<td>1 – 2</td>
<td>2301.8</td>
<td>606.2</td>
<td>474.0</td>
</tr>
<tr>
<td>2 – 3</td>
<td>2272.9</td>
<td>605.2</td>
<td>474.6</td>
</tr>
<tr>
<td>3 – 4</td>
<td>2244.0</td>
<td>604.1</td>
<td>475.3</td>
</tr>
<tr>
<td>4 – 5</td>
<td>2215.1</td>
<td>603.1</td>
<td>475.9</td>
</tr>
</tbody>
</table>

\[
\frac{E_v}{\hbar} = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2
\]

\[
\frac{\Delta E_v}{\hbar} = \omega_e - 2\omega_e x_e (v + \frac{1}{2})
\]

Vibrational energy of a diatomic molecule (ignoring rotation)

For \( N_2 \):
\[
\omega_e = 2359.61 \text{ cm}^{-1}
\]
\[
\omega_e x_e = 14.456 \text{ cm}^{-1}
\]
Single-Shot $N_2$ CARS spectra in 300 Torr $N_2$: Pulser Alone vs. Pulser/Sustainer

Montello et al, AIAA J., 2012
• Varied laser delay timing to map out temporal evolution of $T_v(N_2)$
• $T_v(N_2)$ was observed to directly follow DC sustainer current profile

• Low $T_v$ system threshold $\sim 800-1000$ K observed (corresponds to nsec pulser excitation w/o DC sustainer)
• Threshold can be improved by reducing non-resonant background

Montello et al, AIAA J., 2012
Schematic of USED-CARS Experimental Arrangement

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[Diagram showing experimental setup with labels for various components such as Spectrometer, Short-Pass Filter, 100mm Lens, Beam Dump, Relays Lens Magnification System, Camera, Pump / Probe beam, 0.75 m, CARS signal, Nd:YAG, Broadband Dye Laser, Test section, Phase-matching, k_A, k_P, k_S, In, Out, AS, k]
Rotational / Vibrational CARS Spectra: Pulser-Sustainer Discharge – with / without relaxant injection

20-shot average spectra, $P_0=300$ Torr:
Pure $N_2$ and $N_2$ with 1 Torr $CO_2$ partial pressure

With Sandia CARSFIT synthetic spectrum
$T_{fit} = 322\pm10$ K.
Pulser-Sustainer Discharge: Effects of V-V / V-T Relaxer Injection

300 Torr total mixture pressure
Injection of CO₂, NO, H₂, O₂ and N₂

No effect of O₂ addition on Tᵥ (N₂) due to slow N₂-O₂ V-V energy transfer

Eᵥib (N₂) + Eₜrans/rot (all species) ~ const
(no vib. energy storage in relaxer species)

Characteristic relaxation times (from kinetic rates – τᵥᵥ ~ 1/kᵥᵥn_add):
1 Torr CO₂ (V-V) ~ 70 μsec
5 Torr NO (V-V) ~ 2 msec
10 Torr H₂ (V-T) ~ 6 msec
60 Torr O₂ (V-V) ~ 17 msec

Flow residence time ~ 2 msec
Schematic of 2-D CARS measurements in Mach 5 flow (XZ-resolution)

5 mm diameter x 7.5 mm long quartz cylinder model attached to 2 mm stainless steel support rod, creates bow shock in the Mach 5 flow

Two translation stages combined with pitch/catch optical arms offers positioning in the X and Z dimensions
CARS Spectra in Mach 5 Flow

(a) 8-shot averages - freestream ($P=1.2$ Torr, $T \sim 50$ K) and behind the shock ($P \sim 30$ Torr, $T \sim 300$ K) -- Plasma OFF

(b) 10-shot average, supersonic freestream -- Pulser-sustainer discharge

(c) 10-shot average, behind the bow shock -- Pulser-sustainer discharge

Change in number density indicates shock stand-off distance of 1.0 mm

Data collected within 300 μm of model surface

No detectable $N_2$ relaxation behind the shock
Test Bed II: Diffuse Filament Nsec Pulse Discharge between two bare metal spherical electrodes

Use of small (a few mm diameter), bare spherical electrodes increases power loading (~0.3 eV/molecule/pulse at P=100 Torr, coupled pulse energy ~15 mJ) AND creates plasma large enough to be easily probed by CARS

N₂, 100 Torr
“low current” regime

Air, 100 Torr
“high current” regime
BOX-CARS, broadband dye mixture: better spatial resolution, access to more vibrational levels


95% of signal generated over ~0.5 mm
Characterization of discharge filament size:
\( \text{N}_2 \) in “low current” regime \((U_{\text{DC}}=430 \text{ V})\)

Voltage, current, power, and energy for “low current” pulse discharge in \( \text{N}_2 \) (430 V DC)

Spatial scan of \( T_v(\text{N}_2) \) across the discharge filament, consistent with ICCD measurements, FWHM ~2 mm

ICCD image of discharge filament

FWHM ~2mm
Air: images and waveforms in “high current” regime 
\((U_{DC}=486 \, V)\)

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Compression waves formed by “rapid” heating, on sub-acoustic time scale

From known initial temperature & pressure, voltage, current, and filament diameter \(\rightarrow\)

Reduced electric field \((E/N)\) and electron density for kinetic modeling
Typical CARS Spectra, 100 Torr N₂
(Normalized to v=0, corrected for dye laser spectral profile)

100 laser “shot” averaged spectra vs. time after rising edge of current pulse

Vibrational level populations inference: least squares fitting to Voigt line shape
RHS terms represent vibrational quantum state change by the following processes:

El. Imp.: inelastic electron impact processes by free electrons
VT, VV: vibration-to-translation/rotation relaxation, vibration-to-vibration energy exchange
VE: electronic-vibration energy transfer during collisional quenching
V-Chem: vibrational – chemistry coupling for vibrationally enhanced reactions such as
\[ \text{N}_2(v) + \text{O} \rightarrow \text{NO} + \text{N}, \quad \text{O}_2(v) + \text{N} \rightarrow \text{NO} + \text{O} \]

• Rotational and translational modes are in equilibrium at a gas kinetic temperature
• Single vibrational quantum change processes dominate at low temperatures involved
• Significant body of theory and experimental validation data for the rates used
• Master equation coupled to Boltzmann equation for EEDF, species concentrations equations
• Nonequilibrium air plasma chemistry, excited electronic states kinetics are included
• Model validated using CARS $T_v(\text{N}_2)$ measurements in plane-to-plane nsec pulse discharge

Montello et al, AIAA Paper 2012-3180
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Air, “high current” regime: number of vibrational quanta per molecule vs. time

Average number of vibrational quanta per molecule ($N_{\text{quanta}}$):

$$N_{\text{quanta}} = \sum_{v=0}^{9} v f_v$$

- Significant increase of number of vib. quanta per molecule after the pulse (a factor of 2)

- At variance with the model, which predicts $N_{\text{quanta}} = \text{const}$ after the pulse (V-V exchange conserves quanta)
Air, “high current” regime: \(N_2(X,v)\) vibrational level populations vs. time

The VDF evolution can be divided into 3 phases:

1. **Initial appearance and growth of all vibrational levels** observed \((\Delta t \sim 100 \text{ nsec} – 1 \text{ \mu sec})\)

2. **Steady growth of low vibrational levels** \((v \sim 1-3)\) observed, while higher levels remain nearly constant \((\Delta t \sim 1 \text{ \mu sec} – 100 \text{ \mu sec})\)

3. **Vibrational energy decay:** V-T relaxation (by O atoms) and diffusion \((\Delta t \sim 100 \text{ \mu sec} – 10 \text{ msec})\)
Air: time evolution of $N_2(v=0-3)$

- $T_{v=01}(N_2)$ rise is primarily due to $N_2-N_2$ V-V exchange during relaxation: $v=0$, $w \rightarrow v=1$, $w-1$

- Master equation model captures early VDF dynamics well: vibrational excitation by electron impact is modeled accurately

- As time evolves, $v=0$, 1 level populations are well predicted by model; higher level populations ($v=2,3$) are significantly underestimated. $T_{v=01}(N_2)$ is not a good metric.
Results in nitrogen are even more dramatic!

- $N_{\text{quanta}}$ rise after the pulse by a factor of 4
- $N_2(v=1-8)$ rise after the pulse by up to a factor of 5
- Not reproduced by the model
Rotational Temperature Measurements

100-shot accumulation spectrum in “cold” 100 torr air, with Sandia CARSFIT best fit synthetic spectrum.

Histogram plot from measuring and fitting 80 such spectra.

95% confidence interval ~ ± 9 K.
Rotational Temperature Results, Energy Balance

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- Both in N\textsubscript{2} and air, model overpredicts “rapid” heating, likely N\textsubscript{2}(A,B,C,a) + M → N\textsubscript{2}(X,v) + M (E-V processes)
- Energy stored in low N\textsubscript{2}(X,v) underpredicted, especially in N\textsubscript{2}
- Results suggest additional energy transfer into N\textsubscript{2}(X,v) after the pulse: E-V processes?
- In air, also model underpredicts “slow” heating (absent in N\textsubscript{2}), likely V-T relaxation by O: N\textsubscript{2}(X,v) + O → N\textsubscript{2}(X,v-1) + O
Effect of electronic-to-vibrational (E-V) energy coupling on energy balance in nsec pulse filament discharge in N$_2$

$$N_2(C) + N_2(X) \rightarrow N_2(B) + N_2(X, \nu)$$
$$N_2(A) + N_2(A) \rightarrow N_2(B, C) + N_2(X, \nu)$$

$$k(\rightarrow \nu) = k(T) \frac{\exp(-\alpha \nu)}{\alpha}$$

$$\overline{\varepsilon}_{vib} = \sum_{\nu} \varepsilon(\nu) k(\rightarrow \nu) / k(T)$$

$\alpha$ – adjustable parameter controlling percentage of energy defect into vibrational mode, $\overline{\varepsilon}_{vib}$

Solid lines: no energy into $N_2(X, \nu)$ during $N_2(A, B, C, a)$ quenching
Dashed and Dash-dotted lines: 100% or 50% of energy defect into $N_2(X, \nu)$

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Dashed and Dash-dotted lines: 100% or 50% of energy defect into $N_2(X, \nu)$
50% energy defect into $N_2(X,v)$ during $N_2^*$ quenching: better agreement between measured and predicted $N_2(v)$

VDF dynamics at short time delays ($\Delta t \sim 0.1 - 1 \mu\text{sec}$) is still not reproduced well
Here is why these kinetics are important: NS DBD actuator on a cylinder model in a Mach 5 flow

Cylinder model / NS DBD plasma actuator
- Immersed electrode inside 6 mm quartz tube
- Exposed electrode: 1-3 mm wide copper strip

Schlieren image
Top view
5 mm diameter model
Stand-off distance 1.2 mm

NO PLIF image
Nitrogen, \( P_0 = 0.5 \text{ atm} \)

Plasma span \( \sim 1 \text{ cm} \), test section width 4 cm
\( T_R = 340 \pm 30 \text{ K}, \Delta T = 50 \text{ K} \) (\( \text{N}_2 \) emission spectra)

Nishihara et al, Phys. Fluids, 2011
Phase-locked schlieren images of bow shock perturbations

Air, $P_0=370$ torr

- Nsec discharge pulse: $t=0 \ \mu s$
- Compression wave formation: $t=1 \ \mu s$
- Wave propagation upstream: $t=1.0-2.5 \ \mu s$
- Compression wave reaches bow shock: $t=3 \ \mu s$
- Shock stand-off distance increase (up to 25%): $t=3-5 \ \mu s$
- Shock stand-off distance decreases: $t=7-17 \ \mu s$

Repetitive shock perturbation if pulses repeated every 10 $\mu$s (at 100 kHz)

Nishihara et al, Phys. Fluids, 2011
Summary

Psec, broadband CARS:
• Significant new advance in characterization of nonequilibrium flows: $T_{\text{rot}}$ and $N_2(X,v)$ with high spatial ($\sim 50 \times 500 \, \mu\text{m}$) and time ($\sim 1 \, \text{nsec}$) resolution
• Detailed new insight into kinetics of vibrational and electronic energy transfer, coupling to flow field

Experiments in Mach 5 nonequilibrium wind tunnel:
• Steady-state, vibrationally nonequilibrium flows generated in stable, high-pressure nsec pulser / DC sustainer discharge in plenum
• CARS measurements of $T_v(N_2)$, $N_2(X,v)$, and $T_{\text{rot}}$ in nozzle plenum, with and without adding vibrational energy relaxers
• Spatially resolved CARS measurements of $T_v(N_2)$ in Mach 5 free stream flow and in bow shock layer; no detectable relaxation in the shock layer

Experiments in single pulse, point-to-point (high power loading) nsec discharge:
• Significant energy loading (up to $\sim 0.3 \, \text{eV/molecule/pulse}$)
• Spatially- and time-resolved $N_2$ VDF and $T_{\text{rot}}$ indicates “feeding” of $N_2$ vibrations, e.g. $N_2(A) + N_2(A) \rightarrow N_2(C) + N_2(X,v)$, $\sim 10-100 \, \mu\text{s}$ AFTER $\sim 100 \, \text{ns}$ discharge pulse
Future work

• Elucidate mechanisms of coupling between microscopic molecular energy transfer and macroscopic flow parameters

  (a) “rapid” (sub-acoustic time scale) heating → compression wave formation

  (b) vibrational energy transfer from “storage” to “relaxer” species, their subsequent relaxation → modulation of energy fluctuations spectra?

• Coupling between “rapid” heating kinetics and amplitude of compression waves: straightforward mechanism for high-amplitude, high bandwidth flow perturbations

• Possible coupling between rapid N₂-CO₂ V-V energy transfer / CO₂ V-T relaxation and amplification of acoustic perturbations (reverse of ultrasound absorption in molecular gases). Can this process be used to trigger flow acoustic instabilities?
Acknowledgements

AFOSR Hypersonics program (Dr. John Schmisseur, technical manager)

DOE Low-Temperature Plasma Science Center

National Science Foundation

Sukesh Roy: generous help with psec CARS

Nikolai Popov: many discussions of kinetics of molecular energy transfer

RGD28 organizing committee, Ingrid Wysong, Andrew Ketsdever