Control of vibrational distribution functions in nonequilibrium molecular plasmas and high-speed flows

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Abstract
The control of the vibrational distribution of nitrogen by energy transfer to CO$_2$ is studied in two closely related experiments. In the first experiment, the time-resolved N$_2$(v = 0–3) vibrational level populations and temperature in the afterglow of a diffuse filament nanosecond pulse discharge are measured using broadband coherent anti-Stokes Raman spectroscopy. The rotational–translational temperature in the afterglow is inferred from the partially rotationally resolved structure of the N$_2$(v = 0) band. The measurements are performed in nitrogen, dry air, and their mixtures with CO$_2$. N$_2$ vibrational excitation in the discharge occurs by electron impact, with subsequent vibration–vibration (V–V) energy transfer within the N$_2$ vibrational manifold, vibration–translation (V–T) relaxation, and near-resonance V–V$'$ energy transfer from the N$_2$ to CO$_2$ asymmetric stretch vibrational mode. The results show that rapid V–V$'$ energy transfer to CO$_2$, followed by collisional intramolecular energy redistribution to the symmetric stretch and bending modes of CO$_2$ and their V–T relaxation, accelerate the net rate of energy thermalization and temperature increase in the afterglow. In the second experiment, injection of CO$_2$ into a supersonic flow of vibrationally excited nitrogen demonstrates the effect of accelerated vibrational relaxation on a supersonic shear layer. The nitrogen flow is vibrationally excited in a repetitive nanosecond pulse/DC sustainer electric discharge in the plenum of a nonequilibrium flow supersonic wind tunnel. A transient pressure increase as well as an upward displacement of the shear layer between the supersonic N$_2$ flow and the subsonic CO$_2$ injection flow are detected when the source of N$_2$ vibrational excitation is turned on. CO$_2$ injection leads to the reduction of the N$_2$ vibrational temperature in the shear layer, demonstrating that its displacement is caused by accelerated N$_2$ vibrational relaxation by CO$_2$, which produces a static temperature and a pressure increase in the test section. This demonstrates the significant potential of accelerated vibrational relaxation for nonequilibrium flow control, by injection of rapid ‘relaxer’ species at a desired location, resulting in the rapid thermalization of vibrational energy in nitrogen and air flows, and producing a significant effect on the flow field.

Keywords: vibrational relaxation, nonequilibrium flow, CARS, nanosecond pulse discharge

(Some figures may appear in colour only in the online journal)
1. Introduction

Vibrational relaxation is one of the main processes controlling the kinetics of internal energy thermalization, pressure distribution, and heat transfer in high-speed nonequilibrium flows. The use of coupling between the relaxation of vibrational energy modes and the perturbations of macroscopic flow parameters may have significant potential for high-speed flow field manipulation. At this time, our understanding of the coupling between the relaxation of energy stored in the internal energy modes of molecules, macroscopic flow energy spectra, and the mean flow field remains incomplete. For example, the effect of rapid thermalization of internal energy on a sub-acoustic time scale, which generates high-amplitude, high bandwidth pressure perturbations, has been quantified only recently [1–6]. However, the effect of this relatively straightforward coupling mechanism on the high-speed flow appears to be understood only qualitatively, with limited predictive capability. Recent experimental results also point to the existence of other coupling mechanisms between the excitation/relaxation of internal energy modes and the flow energy spectrum, such as the delay of turbulent transition in hypersonic boundary layer flows caused by vibrational relaxation of CO2 [7], or turbulence intensity reduction in low Reynolds number flows, when the relaxation time of nitrogen vibrationally excited in an RF discharge matches the turbulence decay time [8]. However, detailed experimental data isolating and quantifying these mechanisms are not available. This requires measurements of key parameters of nonequilibrium, vibrationally relaxing, chemically reacting flows in a relatively simple flow geometry, which lends itself to detailed optical diagnostics.

Recent experiments at Ohio State University [1, 4] provide new insight into the coupling of molecular energy transfer and fluid mechanics. In this work, the kinetics of the addition of nonequilibrium energy to internal molecular modes in air on a nanosecond time scale, with subsequent energy transfer among different energy modes on nanosecond to millisecond time scales, has been studied using picosecond coherent anti-Stokes Raman spectroscopy (CARS). The measurements were conducted in point-to-point, nanosecond pulse, diffuse filament discharges in quiescent nitrogen and dry air. The results yield direct, quantitative evidence of transient ‘rapid’ heating of the gas on a sub-acoustic time scale (i.e. the time scale for propagation of pressure perturbations). Kinetic modeling analysis of these results [4, 5] demonstrates that this occurs during the collisional quenching of electronically excited N2 molecules. These results also isolate significant ‘slow’ heating in air, on a time scale much longer compared to the acoustic time scale, which is nearly completely absent in nitrogen. Kinetic modeling calculations demonstrate that this phenomenon is caused by the vibration–translation (V–T) relaxation of nitrogen by O atoms. In contrast, V–T relaxation in pure nitrogen is quite slow, such that the ‘slow’ temperature increase does not occur.

These processes affect energy transfer in nonequilibrium flows on widely different time scales, from hundreds of nanoseconds to hundreds of microseconds, producing a two-fold effect. First, as discussed above, energy thermalization on a sub-acoustic time scale (‘rapid’ localized heating) produces high-amplitude pressure perturbations (compression waves), which can be generated repeatedly by varying the discharge pulse repetition rate. Second, energy stored in the vibrational mode of nitrogen in the ground electronic state, N2(X^3Σ_g,v) is not thermalized sufficiently rapidly to contribute to compression wave formation. However, energy transfer from vibrationally excited N2 to the vibrational modes of CO2, by rapid near-resonance vibration–vibration (V–V') energy exchange, may well accelerate the temperature increase and possibly affect high-frequency acoustic perturbations because of relatively rapid V–T relaxation of CO2.

Recently, characterization of vibrationally nonequilibrium flows generated in a Mach 5 nonequilibrium plasma wind tunnel [9] was performed using picosecond CARS [10, 11]. Briefly, vibrationally excited nitrogen flow was generated by an electric discharge sustained in the plenum of a laboratory scale blow down wind tunnel. Vibrational nonequilibrium in the flow was controlled by injecting species that accelerate the vibrational relaxation of nitrogen, such as CO2, NO, and H2, into the flow downstream of the discharge section. Also, injecting O2 into excited nitrogen flow generated vibrationally nonequilibrium synthetic air flow. After the injector, the nonequilibrium flow expanded through a nozzle with the area ratio corresponding to Mach 5. At the nozzle exit, a cylinder model was placed in the flow to generate a bow shock. Measurements of N2 vibrational temperature, T_v(N2), in the wind tunnel plenum showed that, as expected, injection of efficient V–T relaxer species into the flow excited in the discharge resulted in N2 vibrational relaxation and a rotational–translational temperature increase, controlling the vibrational nonequilibrium in the flow.

However, N2 vibrational temperature measurements in the supersonic test section (both in the freestream and behind the bow shock ahead of the cylinder model) demonstrated that the vibrationally excited flow remains nearly frozen, with only a ~10% reduction in T_v(N2) relative to the values measured in plenum. Basically, due to the short flow residence time in the test section and the low static pressure behind the shock (approximately an order of magnitude lower compared to the plenum pressure), N2 vibrational energy relaxation remained slow, even with CO2 injection in the plenum. Thus, despite the V–V' energy transfer from N2 to CO2 and subsequent V–T relaxation of CO2 being very rapid, the N2 vibrational energy relaxation on the flow residence time scale remained insignificant. In the present work, the flow geometry in the test section has been modified to increase the nonequilibrium flow residence time in the test section, and to study the effect of N2 vibrational relaxation on the supersonic flow under conditions where the vibrational relaxation time and the flow residence time are comparable. The effect of adding CO2 to a vibrationally nonequilibrium supersonic flow of nitrogen is quantified by measurements in a supersonic shear/mixing layer.

The main objective of the present work is to identify, isolate, and quantify a specific mechanism of flow field manipulation via targeted loading and storage of energy in internal molecular modes, its subsequent transport with the flow to the desired location, and forced energy coupling to the flow in a controlled way. This approach is fundamentally different from
the use of ‘plasma actuators’ which, in spite of their rapid development over the last years remain essentially ‘local’ flow forcing devices. Basically, their use requires placing and powering actuator electrodes at a certain location in the flow, which may not be amenable to such modifications. On the other hand, the present energy loading/transport/coupling approach may well circumvent this difficulty. The effect of accelerated vibrational relaxation on the flow may be used to generate high-amplitude perturbations in the boundary layer, shear layer, and shock wave/boundary layer interaction flows. These perturbations may have a stabilizing or destabilizing effect on the flow, depending on the ratio of the vibrational temperature and translational–rotational temperature, which determines whether vibrational relaxation results in a flow temperature increase or decrease. Quantitative studies of the effect of vibrational relaxation on high-speed flow fields would help to determine the feasibility of this approach for the active aerodynamic control of high-speed flows.

2. Experimental details

2.1. Diffuse filament nanosecond pulse discharge cell

A schematic of a diffuse filament nanosecond pulse discharge used in the first experiment of the present study is shown in figure 1. The discharge is sustained between two spherical electrodes 7 mm in diameter, made of copper, placed 8 mm apart. The electrodes are attached to copper tubes 1/4” in diameter and 16 mm long, with an inside diameter of 3 mm, and held by a U-shaped bracket machined of Macor ceramic. A 1 mm diameter hole is drilled through each electrode, along the centerline, and the electrodes are aligned to allow optical access for the pump and Stokes laser beams, as well as for the CARS signal beam, as shown in figure 1. The electrode assembly is placed inside a six-arm cross glass cell, with two 3” diameter BK-7 glass windows providing optical access for the laser beams, two 2” fused silica windows used to take plasma emission images, and two 1” flanges for high-voltage electrode feedthroughs. The cell is mounted on a 3D translation stage, used for alignment of the electrodes along the laser beams. The cell is equipped with two 1/4” diameter ports for the gas flow inlet and exit. The experiments are performed in nitrogen, dry air, and their mixtures with 10% CO₂. A pressure of 100 Torr and a total flow rate through the cell of 1.2 slm. The flow velocity through the cell, estimated from the flow rate and the cell arm cross sectional area, is approximately 4 cm s⁻¹. Gases are delivered to the cell from high-pressure cylinders, with CO₂ mixed with nitrogen or dry air approximately 3 m upstream of the cell. The flow through the cell is maintained by a vacuum pump. The flow rates are measured by mass flow controllers, Omega FMA 2308 (N₂ and air) and Sierra Smart Trak 2 series 100 (CO₂). The leak rate of the cell is approximately 6 Torr h⁻¹, such that the estimated flow impurity level (oxygen and water vapor) is ~10 ppm. The discharge electrodes are connected to the feedthroughs, and powered by a custom-built, externally triggered, high-voltage pulse generator, used in our previous work [4]. In the present experiments, the pulser generates an alternating polarity pulse sequence with a peak voltage of approximately 10 kV, a full width at half maximum (FWHM) pulse duration of about 100 ns, and a pulse repetition rate of 60 Hz. The pulse voltage and current are measured by a high-voltage probe (Tektronix P6015) and a current probe (Pearson 2877). High-voltage pulses generate a diffuse filament pulsed discharge between the electrodes, approximately 3 mm in diameter, with the laser beams directed along the centerline of the filament, as shown in figure 1. The use of this approach greatly enhances the CARS signal, which provides a significant advantage in probing excited environments with relatively low spatial gradients of parameters in the direction of the laser beams.

2.2. CARS diagnostics

The broadband CARS diagnostic used in the present work is essentially the same as in [12], where it is discussed in greater detail. Briefly, 90% of the second harmonic output of an externally triggered Nd:YAG laser (Surelite, SLIII-10, pulse energy up to 400 mJ, linewidth 0.4 cm⁻¹) is used to pump a custom-built broadband dye laser, which generates the Stokes beam with a FWHM of 3 nm, centered at 605 nm. The rest of the Nd:YAG laser output is used as the CARS pump/probe beam. The pulse energies of the pump/probe and the Stokes beams are 6.7 mJ and 2.3 mJ, respectively. The two beams are combined using a delay line and dichroic mirrors, and focused in the test section by an f = 150 mm lens, in a collinear phase matching geometry. The length of the probe volume (i.e. the region where over 90% of the CARS signal is generated), measured by translating a microscope.
2.3. Nonequilibrium flow supersonic wind tunnel

A schematic of the nonequilibrium flow supersonic wind tunnel [9], used in the second experiment in the present study is shown in figure 2. In the present work, the wind tunnel is operated in nitrogen, at a plenum pressure of $P_0 = 300$ Torr, a mass flow rate of $6\, g\, s^{-1}$, and a steady-state run time of several seconds. The dimensions of a rectangular cross section plenum/electric discharge section are 0.5 cm in height, 4 cm in width, and 4 cm in length in the flow direction. Two pairs of electrodes in the plenum are used to sustain a combination of two electric discharges fully overlapping in space. The first is a transverse, nanosecond pulse duration, repetitively pulsed discharge sustained between two planar copper electrodes flush mounted in the top and bottom plenum walls, and covered by alumina ceramic dielectric plates. The electrodes are powered by a high-voltage nanosecond pulse generator (FID GmbH 60-100MC4), which generates $\sim 25\, kV$ peak voltage, $\sim 10\, ns$ duration pulses, operated at a pulse repetition rate of $100\, kHz$. This discharge, operated at a very low duty cycle ($\sim 1/1000$), is used to produce ionization in a high-pressure flow. The second is a transverse (spanwise) DC discharge sustained between two copper plate electrodes in the side walls of the plenum. The DC electrodes are connected to a high-current DC power supply (Glassman, 5 kV, 2 A), in series with a 1 kΩ ballast resistor and a high-voltage switch (Behlke HTS 80-03), controlled by a delay generator and used to turn the DC voltage on and off and to synchronize the timing of data acquisition. The DC discharge is operated at a significantly lower voltage (below breakdown), such that it does not produce ionization in the flow until the nanosecond pulse discharge is turned on. The DC discharge is used for energy loading into the flow, with ionization produced by the pulsed discharge. The peak voltages and distances between the electrodes are $\sim 25\, kV$ and 0.5 cm for the pulsed discharge, and 3 kV and 3 cm for the DC discharge, such that the estimated peak reduced electric fields differ by over an order of magnitude, $(E/N)_{peak} \sim 500\, Td$ for the pulsed discharge and $(E/N)_{peak} \sim 10\, Td$ for the DC discharge at $P_0 = 300$ Torr (1 $Td = 10^{-17}\, V\cdot cm^2$). Thus, the pulsed discharge produces ionization efficiently, while a major fraction of input power in the DC discharge (up to $\sim 80$–$90\%$ [14]) is stored in the vibrational mode of nitrogen. Due to the extremely long $N_2$ V–T relaxation time at near room temperature, $\sim 1\, atm\cdot s$ [15], the use of this approach generates strongly vibrationally excited nitrogen flow at low translational/rotational temperatures.

Downstream of the discharge section, the flow expands through a 2D converging–diverging nozzle, as shown in figure 2. The top wall of the nozzle is contoured, with the throat located 14 cm downstream of the discharge section, and the planar bottom wall is followed by an expansion

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To vacuum

Static pressure port

Schematic of the nonequilibrium flow supersonic wind tunnel. Shear layer expansion angle, $\theta$, is labeled in the figure.

Figure 2.
corner 6 cm downstream of the throat. Downstream of the nozzle exit/expansion corner, the top wall diverges at a constant angle of 4°. The flow cross sectional areas at the throat and at the nozzle exit are 0.2 cm × 4 cm and 0.65 cm × 4 cm, respectively. The design Mach number at the nozzle exit is Mach 2.7, which corresponds to the estimated supersonic flow residence time in the 2.5 cm long flow region downstream of the expansion corner, probed by CARS, of \( \tau_{\text{res}} \approx 50 \mu s \). A subsonic flow of nitrogen, CO\(_2\), or a CO\(_2\)–N\(_2\) mixture, is injected (‘bleeding’) into the test section through a rectangular slot in the back step, 0.9 cm high and 3 cm wide, with the corners rounded. This is done to generate a shear layer between the main supersonic flow expanding through the nozzle and the subsonic injection flow, to mix the relaxer species flow with the nitrogen flow excited in the discharge in plenum. At the expansion corner, the main supersonic flow undergoes a Prandtl–Meyer expansion until the static pressure matches the pressure in the subsonic flow in the wake behind the back step, and then goes through an oblique lip shock at the end of the wake (see figure 2). The pressure in the flow behind the back step is monitored using a static pressure tap in the bottom wall approximately 1 cm downstream of the back step, as shown in figure 2, using a differential pressure sensor (Honeywell 162PC01D) with a custom-made signal conditioner, at a sampling rate of 25 kHz. Both the main flow and the injection flow are supplied from gas cylinders through solenoid valves. Rectangular, 3″ × 2″, UV-grade fused silica optical windows are flush mounted in the side walls of the supersonic section for schlieren imaging and CARS diagnostics. The schlieren imaging system uses a pulsed diode laser (Power Technology Inc., LDCU12/A088, 30 W peak power at 850 nm, pulse width 100 ns) as a light source and a standard dual-field-lens alignment. The schlieren images, sampled at 220 Hz, are digitized by a framing camera (Basler, acA2000-340kmNIR) with 2048 × 1088 pixels on the NIR-enhanced CMOS sensor and 8-bit intensity resolution.

3. Results and discussion

3.1. Diffuse filament nanosecond pulse discharge

Figure 3 plots the positive polarity pulse discharge voltage, current, and coupled energy waveforms in air (left) and a 10% CO\(_2\)–air mixture (right). It can be seen that in both cases, the pulse peak voltage is approximately 9–10 kV, the peak current is about 40 A, and the energy coupled to the plasma is approximately 8 mJ/pulse. During breakdown, the applied voltage drops by about 1 kV when the discharge current begins to rise. The FWHM current pulse duration is approximately 100 ns. The positive polarity waveforms taken in nitrogen and in 10% CO\(_2\)–N\(_2\) mixture are very similar to those in air and in 10% CO\(_2\)–air mixture. As expected, negative polarity pulse waveforms in all four gas mixtures are close to the positive polarity waveforms, as shown in figure 3, since the electrode assembly is symmetric. Figure 4 shows images of broadband plasma emission generated in four different gas mixtures, two for positive polarity pulses and two for negative polarity pulses. All the images in figure 4 are 100-pulse averages taken using a 100 ns camera gate incorporating the entire discharge current pulse, with the high-voltage electrode on the left. It can be seen that in all four cases the plasma filament is diffuse, with a diameter of approximately \( d = 2–3 \) mm. In N\(_2\) and N\(_2\)–CO\(_2\), the glow near the negative polarity electrode (the cathode of the pulsed DC discharge) is clearly visible. In all four cases, the plasma emission intensity along the filament centerline is somewhat lower, due to the 1 mm laser beam access holes in the electrodes (see section 2.1).

Figure 5 plots broadband N\(_2\) CARS spectra taken at three different delay times after the discharge pulse in nitrogen. In all present measurements, the reference time, \( t = 0 \), is the moment when the discharge current begins to increase (see figure 3). At \( t = 4 \mu s \) after the pulse, N\(_2\)(\( v = 0–4 \)) vibrational bands can be clearly identified. At \( t = 800 \mu s \), the \( v = 4 \) band is no longer detectable, although the \( v = 1–3 \)
Band signal increases considerably. Finally, at $t = 4$ ms, only the signal from $v = 0$–2 bands can be detected. Figure 6(a) compares two N$_2$ CARS spectra ($v = 0$ band) taken in a 10% CO$_2$–N$_2$ mixture at different delay times after the discharge pulse, $t = 4$ µs and $t = 180$ µs. It can be seen that at the longer delay time the rotational structure of the band is much more pronounced, and individual rotational levels can be identified, suggesting a higher rotational–translational temperature. Figure 6(b) compares the experimental spectrum taken in nitrogen 800 µs after the discharge pulse and the best fit synthetic (CARSFIT) spectrum. Under these conditions, the rotational–translational temperature inferred is $T = 590 \pm 65$ K, with the uncertainty defined as the temperature range where the least squares error calculated by CARSFIT is within 20% of the minimum value, which corresponds to the best fit temperature.

Figure 7 plots the N$_2(v = 0$–3) vibrational level relative populations, $f_v$, inferred from the CARS spectra, such as shown in figure 5. It can be seen that N$_2(v = 1, 2)$ populations steadily increase from $t = 4$ µs to $t \sim 1$ ms, before decaying on a millisecond time scale. This behavior has also been observed in previous studies of nanosecond pulse discharges in nitrogen and air [1, 16]. Master equation kinetic modeling calculations [5] have demonstrated that this initial N$_2$ vibrational excitation by electron impact during the discharge pulse,

\[
N_2(v = 0) + e \rightarrow N_2(w > 0) + e,
\]

creates a markedly bi-modal ‘nascent’ vibrational distribution [1, 16, 17]. After this, the N$_2$ vibrational level populations at $w \geq 2$ are redistributed by the ‘downward’ V–V exchange,

\[
N_2(v = 0) + N_2(w) \rightarrow N_2(v = 1) + N_2(w - 1),
\]

with the room temperature rate coefficient for $w = 1$ of $k_{VV} = 1.56 \times 10^{-14}$ cm$^3$ s$^{-1}$ [18], which reduces the populations of $w \geq 2$ and increases the population of $v = 1$. From the data of figure 7, the estimated characteristic time for N$_2$–N$_2$ V–V exchange for $w = 2$ is $\tau_{VV} \sim 1/[2k_{VV} \cdot n(N_2) \cdot f_2(f_1)] \approx 50$ µs. The decay of vibrational level populations in nitrogen at $t > 1$ ms is dominated by the radial diffusion of vibrationally excited molecules out of the plasma filament, with the characteristic time of $\tau_{\text{diff}} \sim [(d/2)^2/2.3D] \sim 1$–3 ms. The characteristic time for V–T self-relaxation of nitrogen under the present conditions is estimated to be in the order of $\tau_{\text{VT}} (N_2-N_2) \sim 10$ s [15], much longer compared to the radial diffusion time.
scale. Even in the presence of ~10 ppm of oxygen, estimated from the cell leak rate, the V–T relaxation time of nitrogen by trace amounts of O atoms,
\[ \text{N}_2(v) + \text{O} \rightarrow \text{N}_2(v-1) + \text{O}, \]
is estimated to be on the order of \( \tau_{\text{V-T}}(\text{N}_2-O) \sim 1/[k_{\text{V-T}}(\text{N}_2-O) \cdot n(\text{O})] \sim 10 \text{ s} \) [19].

The effect of the \( v = 1 \) population increase due to the downward V–V exchange after the discharge pulse is also readily apparent from figure 8, which plots the ‘first level’ \( \text{N}_2 \) vibrational temperature,
\[ T_v = \frac{E_{10}}{\ln \left( \frac{f_0}{f_1} \right)}, \]

where \( E_{10} = 3353 \text{ K} \) is the energy difference between vibrational levels \( v = 0 \) and \( v = 1 \), and \( f_0 \) and \( f_1 \) are their relative populations, respectively. It can be seen that the \( \text{N}_2 \) vibrational temperature increases from \( T_v \approx 1600 \text{ K} \) at \( t = 2 \mu\text{s} \) to \( T_v \approx 2700 \text{ K} \) at \( t = 800 \mu\text{s} \), before decreasing at \( t > 1 \text{ ms} \). From figure 8, it is also apparent that adding 10% \( \text{CO}_2 \) to nitrogen results in a much more rapid \( \text{N}_2 \) vibrational relaxation, on the time scale of \( \tau_{\text{V-V}}(\text{N}_2) \sim 50–100 \mu\text{s} \). Note that at these conditions, the characteristic time for rapid near-resonance V–V’ energy transfer from the \( \text{N}_2 \) to \( \text{CO}_2 \) asymmetric stretch mode (\( \nu_3 \)),

Figure 6. (a) \( \text{N}_2(v = 0) \) band CARS spectra taken in a 10% \( \text{CO}_2-\text{N}_2 \) mixture at 100 Torr, at two different delay times after the discharge pulse; (b) comparison of the experimental spectrum and the best fit synthetic (CARSFIT) spectrum used for rotational temperature inference, in nitrogen, 800 \( \mu\text{s} \) after the discharge pulse.

Figure 7. Time-resolved \( \text{N}_2(v = 0–3) \) relative populations after the discharge pulse in nitrogen at 100 Torr, inferred from the CARS spectra.

Figure 8. Time-resolved ‘first’ level \( \text{N}_2 \) vibrational temperature after the discharge pulse in nitrogen and in 10% \( \text{CO}_2-\text{N}_2 \) mixture at 100 Torr, inferred from the CARS spectra.
N\(_2\)\((v = 1) + \text{CO}_2(000) \leftrightarrow \text{N}_2(v = 0) + \text{CO}_2(001)\), \(k_{\text{v-v}} = 5 \times 10^{-13}\ \text{cm}^3\ \text{s}^{-1}\) \(\text{[20]}\), is an order of magnitude smaller, \(\tau_{\text{v-v}} \approx 1/k_{\text{v-v}} \cdot m(\text{CO}_2) \approx 5\ \mu\text{s}\). This suggests that the net rate of vibrational energy relaxation is controlled by collisional intramolecular \(\text{CO}_2\) energy re-distribution from the asymmetric stretch to symmetric stretch \((v_1)\) and bending \((v_2)\) modes,

\[
\text{CO}_2(010) + M \leftrightarrow \text{CO}_2(100, 020, 010) + M, \quad (6)
\]

followed by rapid \(\text{V} \rightarrow \text{T}\) relaxation of the bending mode,

\[
\text{CO}_2(010) + M \rightarrow \text{CO}_2(000) + M, \quad (7)
\]

where \(M = \text{CO}_2, \text{N}_2\). Based on \(\text{CO}_2(v_2)\) \(\text{V} \rightarrow \text{T}\) relaxation rates from the literature \([20]\), the estimated \(\text{CO}_2\) vibrational energy relaxation rate is \(\tau_{\text{VT}}(\text{CO}_2, M) \approx 200\ \mu\text{s}\), consistent with the present observations.

Figure 9 plots the rotational–translational temperatures after the discharge pulse in nitrogen and in the 10% \(\text{CO}_2\)–\(\text{N}_2\) mixture, inferred from the rotational structure of \(\text{N}_2(v = 0)\) band CARS spectra using best fit synthetic CARSFIT spectra, as shown in figure 6(b). It can be seen that in nitrogen, the temperature remains nearly flat (within experimental uncertainty), \(T \approx 550 \pm 50\) K, at \(t = 4\)–\(400\ \mu\text{s}\), after which it slowly decays to \(T \approx 500\) K at \(t = 10\) ms, most likely due to radial diffusion out of the filament. In a 10% \(\text{CO}_2\)–\(\text{N}_2\) mixture, the temperature starts from a somewhat lower baseline, \(T \approx 450\) K, and exhibits a well-pronounced steady rise at \(t = 4\)–\(400\ \mu\text{s}\), which appears to accelerate at \(t > 80\ \mu\text{s}\), and peaks at \(T \approx 670\) K. The rapid temperature rise in \(\text{CO}_2\)–\(\text{N}_2\), on the time scale of \(t \sim 100\ \mu\text{s}\), is consistent with the time scale of \(\text{CO}_2\) bending mode \(\text{V} \rightarrow \text{T}\) relaxation (see equation (7)), which is likely to control the net rate of \(\text{N}_2\) vibrational energy relaxation rate in the presence of \(\text{CO}_2\). Relatively high temperatures measured at short delay times after the discharge pulse, \(T \approx 570\) K in \(\text{N}_2\) and \(T \approx 470\) K in \(\text{CO}_2\)–\(\text{N}_2\) at \(t = 2\ \mu\text{s}\) (see figure 9), may be due to residual heating of the relatively slow flow in the cell by previous discharge pulses, as well as due to ‘rapid heating’ processes occurring on sub-microsecond time scales, which are not resolved in \(\text{N}_2\) and \(\text{CO}_2\)–\(\text{N}_2\) but detected in air and \(\text{CO}_2\)–air, as discussed below.

Figure 10 plots the ‘first level’ \(\text{N}_2\) vibrational temperature versus time delay after the discharge pulse in air and in 10% \(\text{CO}_2\)–air mixture. Some of the trends observed in air, such as the vibrational temperature increase from the value at the end of the discharge pulse, \(T_e \approx 1100\) K at \(t = 200\) ns, to \(T_e \approx 1900\) K at \(t = 200\ \mu\text{s}\), are similar to the results in nitrogen (see figure 8). As shown by kinetic modeling calculations \([4]\), this behavior is also controlled by the downward \(\text{N}_2\)–\(\text{N}_2\) \(\text{V} \rightarrow \text{V}\) exchange of equation (2). However, both the initial and the peak values of the vibrational temperature are significantly lower compared to the results obtained in nitrogen. Since the pulse peak voltage, current, and coupled energy waveforms in nitrogen and air are very close, this indicates a lower discharge energy fraction going to \(\text{N}_2\) vibrational excitation by electron impact in air, compared to nitrogen. Also, the vibrational temperature decay after the discharge pulse in air begins sooner, at \(t = 200\ \mu\text{s}\) compared to \(t = 800\ \mu\text{s}\) in nitrogen (compare figures 8 and 10). As shown in kinetic modeling calculations \([5]\), vibrational relaxation in a nanosecond pulse discharge in air is controlled by \(\text{N}_2\) relaxation by \(\text{O}\) atoms (see equation (3)), produced primarily during collisional quenching of electronically excited \(\text{N}_2\) molecules (generated by electron impact during the discharge pulse) by molecular oxygen,

\[
\text{N}_2(\text{A}^3\Sigma, \text{B}^1\Pi, \text{C}^1\Pi, \text{a}^1\Sigma, \ldots) + \text{O}_2 \rightarrow \text{N}_2 + \text{O} + \text{O}. \quad (8)
\]

Although in the present work the \(\text{O}\) atom number density has not been measured, the kinetic model used in \([5]\) is in good agreement both with \(\text{O}\) atom number density and with \(\text{N}_2\)
vibrational level populations measured in our previous work [21], providing confidence in the model predictions. Adding 10% CO2 to air results in rapid N2 relaxation, on the time scale \( t = 50–200 \mu s \) (see figure 10), similar to the results in CO2–N2 plotted in figure 8. The similarity between these data sets suggests that in both cases rapid vibrational relaxation of nitrogen is caused by near-resonance V–V' energy transfer from the N2 to CO2 asymmetric stretch mode (see equation (5)), followed by collisional intramolecular vibrational energy re-distribution in CO2 and V–T relaxation of the CO2 bending mode (see equations (6) and (7)).

Figure 11, which plots rotational–translational temperatures after the discharge pulse in air and in 10% CO2–air mixture at 100 Torr, indicates that the kinetics of energy thermalization over a wide range of time scales after the discharge pulse, \( t = 100 \text{ ns}–10 \text{ ms} \), is somewhat more complex compared to the results obtained in nitrogen and in 10% CO2–N2 mixture, plotted in figure 9. Specifically, the results clearly indicate a well-defined ‘rapid’ temperature increase on the time scale of \( t \approx 0.1–1 \mu s \) (shorter compared to the acoustic time scale of \( t_{\text{acous}} \approx d^2/2a \approx 2–3 \mu s \), where \( a \approx 0.5 \text{ mm} \mu s^{-1} \) is the speed of sound at \( T \approx 500 \text{ K} \)). This effect is observed both in air (heating from \( T \approx 510 \text{ K} \) to \( T \approx 660 \text{ K} \)) and in CO2–air (heating from \( T \approx 490 \text{ K} \) to \( T \approx 570 \text{ K} \)). These results are consistent with our previous temperature measurements in nanosecond pulse discharges in nitrogen, and their mixtures with CO2, air, and with kinetic modeling calculations [5], which show that rapid heating in air is dominated by the quenching of electronically excited N2 molecules by molecular oxygen (see equation (8)), on the same time scale of \( t \approx 0.1–1 \mu s \). In the present measurements in nitrogen and CO2–N2, this effect has not been detected, both because the ‘rapid’ heating in nitrogen is considerably slower [1], and since the N2\(_2\) (\( v = 0 \)) vibrational band in the CARS spectra at \( t < 2 \mu s \) was saturated.

At \( t \approx 1–6 \mu s \), the measurement results indicate a temperature drop, to \( T \approx 500 \text{ K} \) in air and to \( T \approx 470 \text{ K} \) in CO2–air (see figure 11). This effect has not been observed in our previous measurements in nanosecond pulse filament discharges but has been detected in a pin-to-plane nanosecond pulse discharge in [22], where it was shown to be most strongly pronounced near the pin electrode. This rapid temperature decrease is likely to be caused by near-adiabatic gas-dynamic expansion of the filament heated on a sub-acoustic time scale, predicted previously by kinetic modeling calculations [5], although with lower magnitude compared to rapid heating, \( \Delta T_{\text{cool}} \approx 50 \text{ K} \) versus \( \Delta T_{\text{heat}} \approx 200 \text{ K} \). Indeed, the magnitude of rapid cooling during near-adiabatic filament expansion is expected to be lower compared to the rapid nearly constant volume heating,

\[
\frac{\Delta T_{\text{cool}}}{T_0} = \left( \frac{\Delta P}{P_0} + 1 \right)^{\gamma - 1} - 1 = \left( \frac{\Delta T_{\text{heat}}}{T_0} + 1 \right)^{\gamma - 1} - 1, \tag{9}
\]

which gives \( \Delta T_{\text{cool}} = 47 \text{ K} \) for \( \Delta T_{\text{heat}} = 200 \text{ K} \), \( T_0 = 300 \text{ K} \), and \( \gamma = 1.4 \). A more significant temperature decrease under the present conditions may be caused by additional compression of the centerline region of the filament during the rapid heating stage, at \( t \approx 0.1–1 \mu s \), due to its nearly annular structure evident from plasma emission images (see figure 4), followed by expansion in a cylindrical shape rarefaction wave. It is unlikely, however, that rapid cooling may be enhanced by the in-flow of colder gas near the electrodes, as suggested in [22] based on the results of spatially resolved measurements, since in the present experiments it occurs on a microsecond time scale.

The more gradual temperature increase in air, on the time scale \( t = 6–600 \mu s \), evident from figure 11, is qualitatively consistent with our previous measurements and kinetic modeling calculations [1, 5], and is due to energy release during V–T relaxation of nitrogen by O atoms (see (3)), generated during N2 quenching by oxygen (see (8)). Finally, the temperature decrease at \( t > 1 \text{ ms} \) is due to radial diffusion, similar to nitrogen (see figure 9). In the 10% CO2–air mixture, the data indicate a well-pronounced steady temperature increase at \( t = 20–200 \mu s \), from \( T \approx 470 \text{ K} \) to \( T \approx 760 \text{ K} \) at a much faster rate compared to air. Compared to N2 vibrational temperature reduction at these conditions (at \( t = 50–200 \mu s \), see figure 10), it is apparent that heating on this time scale is caused by nitrogen vibrational energy transfer to CO2, followed by CO2 V–T relaxation, similar to the results in the CO2–N2 mixture.

Summarizing the results of CARS measurements in diffuse filament nanosecond pulse discharges in nitrogen, air, and their mixtures with CO2, it can be concluded that adding CO2 to nitrogen or air results in accelerated vibrational relaxation of nitrogen and a resultant temperature rise of the mixture, with the characteristic time of net relaxation/thermalization process of \( P_{\text{CO2}} \cdot \tau_{\text{relax}} \approx 1 \text{ ms} \cdot \text{Torr} \). This suggests that adding CO2 to nonequilibrium compressible flows of nitrogen or air may significantly change the temperature and pressure distributions in the flow, as well as the velocity field. This effect will be illustrated in section 3.2.
In ambient atmospheric pressure air without CO\textsubscript{2} addition, the effect of vibrational relaxation by carbon dioxide, studied in the present work, is likely to be fairly insignificant due to low CO\textsubscript{2} partial pressure, \( P_{\text{CO}_2} \sim 0.2 \) Torr (i.e. \( \tau_{\text{relax}} \sim 5 \) ms). However, the same qualitative effect of accelerated N\textsubscript{2} vibrational relaxation and energy thermalization is likely to be generated due to the presence of water vapor (up to \( P_{\text{H}_2\text{O}} \sim 20 \) Torr at \( T \sim 300 \) K, with the estimated relaxation time of \( \tau_{\text{relax}} \sim 0.5 \) ms [23]). Possible implications of this effect for plasma flow controls are discussed in section 4.

3.2. The effect of vibrational relaxation on the supersonic shear layer

Figure 12(a) plots the current and voltage of the DC discharge sustained in nitrogen in the wind tunnel plenum, at plenum pressure of \( P_0 = 300 \) Torr and a nanosecond pulse discharge repetition rate of 100 kHz. Under these conditions, the nanosecond pulse discharge peak voltage and pulse duration are approximately 25 kV and 10 ns, with an energy coupled per pulse of approximately 5 mJ/pulse (a time-averaged nanosecond discharge power of 500 W) [9]. It can be seen that the DC current rapidly increases after every high-voltage pulse and gradually decays between the pulses. The time-averaged DC discharge power coupled to the flow at these conditions is 2.3 kW. Figure 12(b) plots the DC discharge voltage and current at a low time resolution, during ten DC discharge pulses of 70 ms duration each, generated at 5 Hz during the same wind tunnel run. It can be seen that the DC current variation pulse-to-pulse is within \( \pm 10\% \).

Our previous picosecond CARS measurements in the wind tunnel plenum, taken under similar conditions, showed that the vibrational and rotational–translational temperatures of nitrogen flow at the discharge exit are \( T_v = 2000 \pm 100 \) K and \( T_r = 450 \pm 15 \) K, respectively [10].

To detect the effect of the rapid relaxer (CO\textsubscript{2}) injection on the parameters of the vibrationally excited N\textsubscript{2} flow in the supersonic test section, the time-resolved static pressure was measured at the bottom wall of the test section for different 20\% CO\textsubscript{2}–N\textsubscript{2} mixture injection flow rates [24]. The pressure was measured with the discharge turned off and on. In all runs, the DC sustainer discharge was turned on for 45 ms and its power was kept the same, 1.6 kW. Pressure traces measured during these runs, \( P_{\text{on}} \), normalized by their respective baseline values before the discharge initiation, \( P_{\text{off}} \), are plotted in figure 13. Spurious spikes at \( t = 0, 10 \) ms, 45 ms, and 60 ms are due to electromagnetic interference noise generated when the repetitively pulsed nanosecond discharge and the DC discharge are turned on and off, as labeled in the figure. As can be seen, the static pressure increase during the run becomes more pronounced as the CO\textsubscript{2}–N\textsubscript{2} mixture injection flow rate (i.e. CO\textsubscript{2} partial pressure in the test section) is increased, due to the additional heat released during vibrational relaxation of nitrogen flow accelerated by CO\textsubscript{2}, as measured in the diffuse filament nanosecond pulse discharge (see figures 8 and 9). In contrast, no measurable pressure increase is detected when pure nitrogen is injected into the test section. In this case, the...
The shear layer during N2 vibrational relaxation accelerated in the bottom part of the test section, due to heat released in rather than by vibrational relaxation. The pressure increase of energy relaxation in the test section is controlled by mixing. This suggests that under the present conditions, the net rate of baseline static pressures of \( P \approx 20\% \). The time lag between the DC sustainer discharge initiation and the beginning of the static pressure increase, for baseline static pressures of \( P_{\text{off}} = 9-14 \) Torr (\( \approx 6-7 \) ms), is significantly longer compared to the N2–CO2 vibrational relaxation/energy thermalization time at these conditions, which is estimated to be \( \tau_{\text{relax}} \approx 0.3-0.5 \) ms (see figures 8 and 9). This suggests that under the present conditions, the net rate of energy relaxation in the test section is controlled by mixing rather than by vibrational relaxation. The pressure increase in the bottom part of the test section, due to heat released in the shear layer during N2 vibrational relaxation accelerated by CO2, indicates that the expansion of the main flow at the back step corner becomes less significant, to match the higher pressure behind the back step. To verify this, the dependence of the shear layer expansion angle \( \theta \) (see figure 2) on the peak bottom wall static pressure has been measured at the same CO2–N2 injection flow rate (i.e. same baseline static pressure of \( P_{\text{off}} = 8 \) Torr and same baseline shear layer angle of \( \theta_{\text{off}} = 8^\circ \)), for different DC discharge powers, 1.35–2.3 kW [24]. Figure 14 plots the shear layer expansion angle \( \theta \) versus peak static pressure ratio during the run, \( P_{\text{on}}/P_{\text{off}} \). It can be seen that the expansion angle is reduced significantly as the discharge power (labeled in the figure), and consequently the peak static pressure during the run, are increased. This effect is illustrated further in figure 15, taken from [12], which compares schlieren images of the vibrationally excited N2 flow in the wind tunnel test section in two sets of conditions: (a) with N2 injection and (b) with 20% CO2–N2 mixture injection. In both cases, the injection flow pressure, measured before the discharge was turned on, is \( P_{\text{off}} = 8 \) Torr. In the case of non-excited N2 injection into vibrationally excited N2 flow, the shear layer expansion angle remains the same, \( \theta_{\text{on}} = 8^\circ \). In the second case, it can be seen that injection of the CO2–N2 mixture into vibrationally excited N2 flow results in significant reduction of the shear layer expansion angle, to \( \theta_{\text{on}} = 0^\circ \), as well as in considerable weakening of the expansion wave at the back step corner. Transient reduction of the shear layer expansion angle, and its subsequent return to the baseline position (i.e. forced shear layer ‘flapping’ as the DC sustainer discharge was turned on and off repeatedly at 5 Hz, as illustrated in figure 12), was also observed during the run.

Finally, the effect of N2 vibrational relaxation accelerated by CO2 addition, quantified by the time-resolved CARS measurements discussed in section 3.1, on the flow field in the supersonic test section has been confirmed by recent CARS N2 vibrational temperature measurements [12]. Figure 16, taken from [12], plots a 2D N2 vibrational temperature distribution measured with pure CO2 injection through the back step, interpolated from measurements at different axial and transverse locations indicated by dots. It can be seen that the vibrational temperature in the free stream remains nearly uniform. CO2 injection begins to affect the vibrationally excited N2 flow approximately 1 cm downstream of the expansion corner (at \( x = 1 \) cm), with CO2–N2 mixing occurring downstream of this location in the growing shear layer (see figures 2 and 15). At \( x = 2 \) cm, the extent of the mixing/shear layer becomes sufficiently large to resolve the N2 vibrational temperature spatial distribution. The transverse distribution of N2 vibrational temperature at \( x = 2 \) cm, with and without injection of CO2 through the back step, is also shown in figure 16. In these measurements, CO2 injection pressure with the DC sustainer discharge turned off was \( P_{\text{off}} = 7 \) Torr, and the shear layer expansion angle during its injection into vibrationally excited N2 flow (measured with the discharge turned on) was \( \theta_{\text{on}} = 0^\circ \), such that the flow field was very close to the schlieren image in figure 15(b), taken with 20% CO2–N2 mixture injection. The peak N2 vibrational temperature measured at this axial location is \( T_v = 1900 \) K. From figure 16, it can be seen that N2 vibrational temperatures with and without CO2 injection, measured at transverse locations \( y \geq 2 \) mm (\( y = 0 \) corresponds to the height of the expansion corner) are very close to each other. However, at \( 0 < y < 2 \) mm, the N2 vibrational temperature with CO2 injection is considerably decreased, to near the detection limit of approximately 1200 K, indicated by a dashed line in the figure. Without CO2 injection, however, the N2 vibrational temperature profile remains nearly flat, varying in the range \( T_v(N_2) = 1700–1800 \) K.
4. Summary

Control of the vibrational distribution of nitrogen by rapid energy transfer to CO$_2$ is studied in two closely related experiments. In the first experiment, time-resolved N$_2$(v = 0–3) vibrational level populations and temperature in the afterglow of a diffuse filament nanosecond pulse discharge are measured using broadband CARS. Rotational–translational temperature in the afterglow is inferred from the partially rotationally resolved structure of the N$_2$(v = 0) band. The measurements were performed in nitrogen, dry air, and their mixtures with CO$_2$. The nitrogen vibrational excitation in the discharge occurs by electron impact, with subsequent V–V energy transfer within the N$_2$ vibrational manifold, V–T relaxation, and near-resonance V–V$'$ energy transfer from N$_2$ to CO$_2$ asymmetric stretch vibrational mode. The results show that rapid V–V$'$ energy transfer to CO$_2$, followed by collisional intramolecular energy redistribution to the symmetric stretch and bending modes of CO$_2$ and their V–T relaxation, considerably accelerate the net rate of energy thermalization and temperature increase in the afterglow.

In the second experiment, injection of CO$_2$ into a flow of vibrationally excited nitrogen is used to demonstrate the effect of vibrational relaxation on a supersonic shear layer. The nitrogen flow is vibrationally excited in a repetitive nanosecond pulse discharge combined with a DC discharge in the plenum of a nonequilibrium flow supersonic wind tunnel, at a low rotational–translational temperature. Time-resolved static pressure measurements in the test section demonstrate a significant transient rise of static pressure, detected when a CO$_2$–N$_2$ mixture is injected into the vibrationally excited flow (i.e. when the electric discharge in plenum is turned on). The pressure returns to the baseline value when the discharge is turned off. The peak static pressure increase is proportional to the CO$_2$ injection flow rate and the discharge power. In contrast, no static pressure change is detected when pure nitrogen is injected into the test section while the discharge was turned on and off. These results suggest that shear layer displacement is caused by rapid N$_2$ vibrational relaxation by CO$_2$ in the shear layer, producing static temperature and static pressure increases in the supersonic test section. Flow schlieren images taken under these conditions are consistent with this suggestion. Specifically, they detect significant upward displacement of the shear layer. No shear layer displacement is detected when pure N$_2$ is injected into the nitrogen flow excited in the discharge in the plenum. Also, no shear layer displacement is detected when the electric discharge in the plenum is turned off, with or without CO$_2$ injection in the supersonic test section. Thus, these measurements also indicate that the
observed changes in the flow field are caused by rapid vibrational relaxation of $\text{N}_2$ by $\text{CO}_2$. This conclusion is confirmed by measurements of the $\text{N}_2$ vibrational temperature distribution in the shear layer by CARS [12], demonstrating that $\text{CO}_2$ injection results in its significant reduction.

The present results show that significant amounts of vibrational energy can be stored in nonequilibrium nitrogen and air flows, and released at a desired location, using local injection of rapid ‘relaxer’ species such as $\text{CO}_2$ or hydrocarbons, producing a significant effect on the high-speed flow. Modulated flow perturbations over a wide frequency range can also be produced using this approach, by repetitive pulsing of electric discharge loading energy into the $\text{N}_2$ vibrational mode. Finally, it is possible that the direction of this effect may be reversed under conditions in which the vibrational temperature is lower than the rotational–translational temperature, as occurs in the shock layer [25]. In this case, accelerating vibrational relaxation would result in a more rapid translational temperature reduction.

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References


