Vibrationally excited NO tagging by NO(A^2Σ^+) fluorescence and quenching for simultaneous velocimetry and thermometry in gaseous flows

Rodrigo Sánchez-González,1 Rodney D. W. Bowserox,2 and Simon W. North1**

1Department of Chemistry, Texas A&M University, 3012 TAMU, College Station, Texas 77842, USA
2Department of Aerospace Engineering, Texas A&M University 3141 TAMU, College Station, Texas 77842, USA
*Corresponding author: swnorth@tamu.edu

Received February 27, 2014; revised March 28, 2014; accepted March 28, 2014; posted April 1, 2014 (Doc. ID 206745); published April 30, 2014

We present measurements demonstrating simultaneous determination of velocity and temperature using a variant of the Vibrationally Excited Nitric Oxide Monitoring (VENOM) technique that does not employ NOx. The variant is based on tagging by electronic excitation of NO in the A^2Σ^+ → X^2Π(0) band and subsequent formation of vibrationally excited NO(A^2Π) by spontaneous emission and collisional quenching. Planar sequential laser-induced fluorescence imaging of the nascent NO(A^2Π, v′ = 1) was used to obtain spatially resolved average streamwise velocity and rotational/translational temperature. The temperature determination using this approach extends the applicability of the VENOM technique to low-density, high-speed flows, where slow thermalization of the tagged molecules represents a limiting factor. © 2014 Optical Society of America

Numerous flowfields relevant to combustion and hypersonics are strongly affected by nonequilibrium effects, and their study requires techniques capable of quantifying and correlating fluctuations in velocity and scalar distributions. The Vibrationally Excited Nitric Oxide Monitoring (VENOM) technique has previously been proven as a viable nonintrusive diagnostic to obtain instantaneous 2D velocity and temperature maps simultaneously in gaseous flowfields [1,2]. The VENOM technique employs NO(v′′ = 1) arising from NO2 photodissociation as a molecular tag. This represents an improvement over the NO fluorescence velocimetry technique that employs sequential fluorescence imaging after a single excitation event, requiring displacements to occur within the NO fluorescence lifetime [3]. The use of NO flow tagging resulting from NO2 photodissociation permits measurements in an extended range of flow velocities and quenching conditions since the NO photo-product tag is depleted only through slow recombination reactions, diffusion and mixing, and in the case of the NO(v′′ = 1), by slow vibrational relaxation. Molecular tagging using NO2 photolysis has been demonstrated in a variety of flowfields [4–8].

The NO2 photolysis approach also enables the simultaneous determination of temperature, similar to the femtosecond laser electronic excitation tagging technique of Miles and co-workers [2], by tuning the two “read” lasers to probe different rotational states. The first demonstration of a simultaneous two-component velocity and temperature measurement utilizing vibrationally excited nitric oxide [NO(v′′ = 1)] originating from photolysis of NO2 as a tag reported two-component velocity and temperature determinations within 5% and 9%, respectively, of results from computational fluid dynamics (CFD) simulations for most regions of an underexpanded jet [1]. However, the experimental temperature determination exceeded CFD predictions in the low-density regions, a result of using a rotationally excited photoproduct to obtain rotational/translational temperature information via the two-line thermometry technique. A subsequent experimental study established the insufficient collisional relaxation of the nascent NO photoproducts as the source of temperature overestimation under low number density conditions, persisting even with “write”–“probe” pulse time delays up to 2 μs [2]. It was also shown that the photolysis of NO2 can result in thermal perturbation of the flow when high fractions of seeded NO2 are combined with high-photolysis laser powers [2,10].

In this Letter, we present a new tagging method that preserves the velocimetry advantages of the original VENOM technique, overcoming the short fluorescence lifetime of NO in highly quenching environments and providing discrimination from background NO. Additionally, this new tagging method mitigates the possibility of thermal disturbance. Furthermore, the choice of seeding NO over NO2 increases the compatibility of the VENOM technique with facilities where the use of NO2 could be problematic due to condensation.

The performance evaluation of the proposed tagging technique was carried out in a flow test facility that has been previously described [11] using a 1 mm diameter sonic orifice operated continuously. We have employed the underexpanded jet flowfield for demonstration measurements given its challenging wide range of density, velocity, and temperature conditions, which overlap with the conditions encountered in cold hypersonic flows, where the VENOM technique is expected to provide valuable characterization information. A mixture of 10% NO in N2 at a stagnation temperature of 294 K and pressure of 60 kPa expanded through the nozzle into the main chamber maintained at a pressure of 253 Pa, resulting in a jet pressure ratio of 237.

The VENOM set-up used in these experiments are composed of two identical planar laser induced fluorescence (PLIF) laser systems that have been described in detail.
Fluorescence images resulting from excitation by the “read” laser were captured using a PI-MAX4 ICCD camera perpendicular to the laser sheets and fitted with a CERCO 100 mm $f$/2.8 UV lens and extension rings, using a gate width of 30 ns. For instantaneous measurements, two sequential read lasers and two cameras would be required. The “write” laser system was tuned to excite the $R_1 + Q_{31}$ bandhead of the $A^2\Sigma^+ (v' = 0) \leftarrow X^2\Pi_{1/2} (v'' = 0)$ band near 226 nm, which includes rotational levels with $J = 1.5$, 2.5, and 3.5. “Writing” an excitation pattern of vertical lines along the centerline of the flow by being sent through an evenly spaced aluminum mesh. The “read” laser system was sequentially tuned to probe the $R_1 + Q_{31}$ (1.5) and the $R_1 + Q_{31}$ (8.5) lines in the $A^2\Sigma^+_{1/2} (v' = 1) \leftarrow X^2\Pi_{1/2} (v'' = 1)$ band with time delays of 1.2 and 1.6 $\mu$s after the “write” laser, respectively. The time delays used between the probe laser pulses are chosen to permit sufficient grid displacement for an accurate velocity determination. This line selection has previously proven to result in acceptable signal-to-noise levels across the entire flowfield [1], while maximizing the energy difference between the two probed rotational states to achieve sensitive two-line thermometry measurements.

A raw fluorescence image pair is shown in Fig. 1. The flow, as shown, is from left to right and the 200-shot average images have a spatial resolution of 54 pixel/mm, displaying a field of view of $19 \times 19$ mm. The temperature effect on the Boltzmann populations of the probed states is clearly revealed upstream of the Mach disk. In addition, the $J = 1.5$ image shows lower fluorescence intensity downstream of the Mach disk due to low population of this state, and both images show an overall decreased fluorescence signal downstream of the Mach disk due to quenching, which is attributable to the relatively high levels of seeded NO. We have estimated fluorescence lifetimes of the order of the camera gate in this region. Based on calculations of the tagging efficiency using experimental factors, we estimate that resulting signal-to-noise levels are comparable to those obtained by NO$_2$ photolysis tagging. In fact, the experimental signal-to-noise levels range from 4 to 115 in the $J = 1.5$ image and from 1 to 85 in the $J = 8.5$ image, which are similar to or higher than those observed in previous NO$_2$ photolysis VENOM measurements in the underexpanded jet [1]. A comprehensive error analysis of VENOM measurements has previously been performed [2,10], where errors are estimated as a function of signal-to-noise. Both images were used to obtain an average streamwise velocity map by following a 1D fluorescence intensity pattern cross-correlation routine [11]. The resulting streamwise velocity profile along the centerline is shown in Fig. 2 (top panel), and is in good agreement with CFD predictions. The results are also comparable to previous reports of streamwise velocity determinations under similar conditions [1,8,12]. Although we do not report full-frame, two-component velocity maps, such measurements have been previously performed in the same flowfield [1,8], and only require “writing” horizontal grid lines to form intersections by an additional excitation laser or by power splitting of one single “write” laser.

Following electronic excitation by the “write” laser, the $A^2\Sigma^+$ state molecules will return to the ground $X^2\Pi$ state via either fluorescence or collisional quenching. The vibrational distribution of NO($X^2\Pi$) arising from $A^2\Sigma^+$ state fluorescence follows Franck–Condon dominated vibrational transition probabilities which favor low-$v''$ states, peaking at $v'' = 1$ with 0.28 fractional yield [13]. A recent experimental study reported the nascent vibrational distribution of NO($X^2\Pi$) produced by both fluorescence and collisional self-quenching of NO($A^2\Sigma^+, v' = 0$) [14]. Several studies have examined the role of reactive quenching of NO($A^2\Sigma^+$) [15,16], resulting in some cases in vibrational selectivity of the nascent distributions [16] or overall losses of the electronic ground state recovery due to NO reaction [15]. However, for the particular case of quenching by NO, reactive quenching is not significant, and the resulting NO($X^2\Pi$) vibrational distribution is approximately statistical [14].

The relevant ranges of pressure and temperature across the centerline of the underexpanded jet used were captured using a PI-MAX4 ICCD camera parallel to the laser sheets and fitted with a CERCO 100 mm $f$/2.8 UV lens and extension rings, using a gate width of 30 ns. For instantaneous measurements, two sequential read lasers and two cameras were required. The “write” laser system was tuned to excite the $R_1 + Q_{31}$ bandhead of the $A^2\Sigma^+ (v' = 0) \leftarrow X^2\Pi_{1/2} (v'' = 0)$ band near 226 nm, which includes rotational levels with $J = 1.5$, 2.5, and 3.5. “Writing” an excitation pattern of vertical lines along the centerline of the flow by being sent through an evenly spaced aluminum mesh. The “read” laser system was sequentially tuned to probe the $R_1 + Q_{31}$ (1.5) and the $R_1 + Q_{31}$ (8.5) lines in the $A^2\Sigma^+_{1/2} (v' = 1) \leftarrow X^2\Pi_{1/2} (v'' = 1)$ band with time delays of 1.2 and 1.6 $\mu$s after the “write” laser, respectively. The time delays used between the probe laser pulses are chosen to permit sufficient grid displacement for an accurate velocity determination. This line selection has previously proven to result in acceptable signal-to-noise levels across the entire flowfield [1], while maximizing the energy difference between the two probed rotational states to achieve sensitive two-line thermometry measurements.

A raw fluorescence image pair is shown in Fig. 1. The flow, as shown, is from left to right and the 200-shot average images have a spatial resolution of 54 pixel/mm, displaying a field of view of $19 \times 19$ mm. The temperature effect on the Boltzmann populations of the probed states is clearly revealed upstream of the Mach disk. In addition, the $J = 1.5$ image shows lower fluorescence intensity downstream of the Mach disk due to low population of this state, and both images show an overall decreased fluorescence signal downstream of the Mach disk due to quenching, which is attributable to the relatively high levels of seeded NO. We have estimated fluorescence lifetimes of the order of the camera gate in this region. Based on calculations of the tagging efficiency using experimental factors, we estimate that resulting signal-to-noise levels are comparable to those obtained by NO$_2$ photolysis tagging. In fact, the experimental signal-to-noise levels range from 4 to 115 in the $J = 1.5$ image and from 1 to 85 in the $J = 8.5$ image, which are similar to or higher than those observed in previous NO$_2$ photolysis VENOM measurements in the underexpanded jet [1]. A comprehensive error analysis of VENOM measurements has previously been performed [2,10], where errors are estimated as a function of signal-to-noise. Both images were used to obtain an average streamwise velocity map by following a 1D fluorescence intensity pattern cross-correlation routine [11]. The resulting streamwise velocity profile along the centerline is shown in Fig. 2 (top panel), and is in good agreement with CFD predictions. The results are also comparable to previous reports of streamwise velocity determinations under similar conditions [1,8,12]. Although we do not report full-frame, two-component velocity maps, such measurements have been previously performed in the same flowfield [1,8], and only require “writing” horizontal grid lines to form intersections by an additional excitation laser or by power splitting of one single “write” laser.

Following electronic excitation by the “write” laser, the $A^2\Sigma^+$ state molecules will return to the ground $X^2\Pi$ state via either fluorescence or collisional quenching. The vibrational distribution of NO($X^2\Pi$) arising from $A^2\Sigma^+$ state fluorescence follows Franck–Condon dominated vibrational transition probabilities which favor low-$v''$ states, peaking at $v'' = 1$ with 0.28 fractional yield [13]. A recent experimental study reported the nascent vibrational distribution of NO($X^2\Pi$) produced by both fluorescence and collisional self-quenching of NO($A^2\Sigma^+, v' = 0$) [14]. Several studies have examined the role of reactive quenching of NO($A^2\Sigma^+$) [15,16], resulting in some cases in vibrational selectivity of the nascent distributions [16] or overall losses of the electronic ground state recovery due to NO reaction [15]. However, for the particular case of quenching by NO, reactive quenching is not significant, and the resulting NO($X^2\Pi$) vibrational distribution is approximately statistical [14].

The relevant ranges of pressure and temperature across the centerline of the underexpanded jet used
in the present experiments are shown in Figs. 2 and 3, following CFD simulations described previously [8]. The gas undergoes a gradual expansion along the centerline, characterized by acceleration to hypersonic velocities and a drop in pressure and temperature. This expansion is terminated by sudden recompression at the Mach disk, where the pressure and temperature exhibit a rapid rise.

Using the CFD temperature and pressure conditions, the NO(\(^{X^2}\Pi; v'' = 1\)) total recovery quantum yields following tagging can be estimated for both fluorescence and collisional self-quenching, and are shown in Fig. 3 (bottom panel). The NO(\(^{A^2}\Sigma^+; v' = 0\)) radiative rate of 5.19 \times 10^4 \, \text{s}^{-1} is well established [17]. The collisional quenching rate is temperature dependent and we have used a collision complex formation power-law model, based on measurements by Settersten et al. [18], to model the self-quenching cross sections along the underexpanded jet centerline. The quenching due to collisions with \(N_2\) has been neglected, since the quenching cross sections are several orders of magnitude smaller than those of NO [18–20]. Assuming a statistical distribution of the nascent electronic ground state distribution \([14]\), the fraction of the NO(\(^{A^2}\Sigma^+\)) excited species which yield (\(^{X^2}\Pi, v'' = 1\)) available for VENOM probing can be calculated, and is shown in Fig. 3 (bottom panel). This calculation assumes a weak excitation by the tagging laser in order to obtain an estimate of the maximum fraction of NO(\(^{X^2}\Pi, v'' = 1\)) resulting from collisional quenching. Strong excitation by the tagging laser would deplete the initial NO(\(^{X^2}\Pi, v'' = 0\)) population that resides in low rotational states for the lowest temperature regions of the flow since the laser is tuned to excite at the bandhead. If depletion occurs, the nascent \(^{X^2}\Pi(v'' = 1)\) distribution will be dominated by fluorescence. Rotational-level independence of collisional quenching of the \(^{A^2}\Sigma^+(v' = 0)\) state of NO has been previously established [19,21], and thus the calculated recovery yields do not require rotational resolution. As observed in Fig. 3 (bottom panel), the overall fractional yield of NO(\(^{X^2}\Pi, v'' = 1\)) ranges from 0.11 in the highest-pressure region of the flowfield at the nozzle exit, where collisional quenching dominates, up to 0.28 in the lowest-pressure region of the flow before the Mach disk, where fluorescence is dominant, approximately 9 mm from the nozzle exit.

Although the experimental velocity determinations are discrete and are limited to the location of the tagged lines, as observed in Fig. 2 (top panel), the utilization of the aluminum mesh to “write” the grid lines results in a modulation of the excitation pattern that allows a continuous, full-frame temperature determination. The velocity measurement provides enough information to dewarp the second time-delayed fluorescence image, resulting in fluorescence intensity ratios that correspond to identical flow elements for temperature measurement. The temperature measurement associated with velocity determination using the VENOM technique utilizes two-line thermometry and thus requires a thermalized rotational distribution in the probed NO(\(^{X^2}\Pi, v'' = 1\)) state that reflects the true local flow temperature. The initial rotational distribution in the \(^{A^2}\Sigma^+(v = 0)\) state generated by the “write” laser beam reflects the selective excitation of a small range of low-J transitions associated with the bandhead. Following electronic excitation by the “write” laser, the NO(\(^{A^2}\Sigma^+)\) state molecules undergo rotational energy transfer (RET) by collision. RET coefficients of NO(\(^{A^2}\Sigma^+, v' = 0\) and \(v' = 1\)) with ground state NO and \(N_2\) have been measured by Ebata et al. [22]. These rates suggest that rotational thermalization in the \(^{A^2}\Sigma^+\) state should occur within tens of nanosecond at pressures of a few hundred Pa. Rotational thermalization in the NO(\(^{X^2}\Pi, v''\)) states formed by both fluorescence and quenching is completed within the time delay required between the “write” and “read” lasers to perform a VENOM experiment. This time delay is usually at least a few hundreds of nanosecond at a few hundred Pa for high-speed flows [1,2].

Figure 2 (bottom panel) shows the temperature profile along the underexpanded jet centerline calculated from the experimental images, using the temperature-dependent local fluorescence ratio \(R_{12} = C_{12}[2I' + 1]/(2I'' + 1)] \exp(-\Delta E_{12}/kT)\), where the calibration constant \(C_{12}\) was determined from a fluorescence ratio obtained in the cell under static conditions at 267 Pa and 294 K, using the same gas composition as the test gas. The resulting temperature profile shows an agreement within 5%–20% when compared to the CFD simulation. The largest discrepancies, observed as temperature oscillations in Fig. 2, occur between 5 and 7 mm from the nozzle exit due to imperfect dewarping of the second time-delayed fluorescence image. The overall temperature measurement, however, follows the predicted temperature profile even in the lowest-density regions.
of the flow, where the NO₃ photolysis approach resulted in temperature overestimations larger than 100 K [1].

This variant of the VENOM tagging approach shows more rapid rotational thermalization, with only a few collisions required due to the favored population of low rotational states induced by the “write” laser. This contrasts with NO₂ photolysis tagging, which requires significantly more collisions, and hence longer times, to reach the local temperature due to the much hotter (900 K) nascent rotational distribution [2,23]. When measuring low temperatures, as is the case in high-speed cold flows, probing low-J states to estimate temperature is also advantageous due to the increased RET rates at low-J values that favor quick thermalization. The NO₂ photolysis approach also requires more careful control of NO₂ seed fractions and photolysis laser power to minimize thermal perturbation of the flow, while this disadvantage is mitigated with the present VENOM tagging approach. The new VENOM variant does not have such limitations, making it more broadly applicable. Since this technique does not require NO₂, it is better suited to measurements in facilities where NO₂ seeding is problematic.

References
