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Long-lived nitric oxide molecular tagging velocimetry with 1 + 1 REMPI

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The successful demonstration of long-lived nitric oxide (NO) fluorescence for molecular tagging velocimetry (MTV) measurements is described in this Letter. Using 1 + 1 resonance-enhanced multiphoton ionization (REMPI) of NO at a wavelength near 226 nm, targeting the overlapping $Q_1(7)$ and $Q_{21}(7)$ lines of the A–X (0, 0) electronic system, the lifetime of the NO MTV signal was observed to be approximately 8.6 µs within a 100-Torr cell containing 2% NO in nitrogen. This is in stark contrast to the commonly reported single photon NO fluorescence, which has a much shorter calculated lifetime of approximately 43 ns at this pressure and NO volume fraction. While the shorter lifetime fluorescence can be useful for molecular tagging velocimetry with single laser excitation within very high-speed flows at some thermodynamic conditions, the longer lived fluorescence shows the potential for an order of magnitude more accurate and precise velocimetry, particularly within lower speed regions of hypersonic flow fields such as wakes and boundary layers. The physical mechanism responsible for the generation of this long-lived signal is detailed. Furthermore, the effectiveness of this technique is showcased in a high-speed jet flow, where it is employed for precise flow velocity measurements.

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Molecular tagging velocimetry (MTV) [1–4], as a powerful and accurate flow velocity measurement technique, has been widely applied for subsonic to hypersonic flow velocity measurements. Compared with other particle-based velocimetry techniques, MTV techniques usually apply gas or molecular seeding and thereby reduce the potential to induce wind tunnel contamination. MTV has also gained favorability over the more traditional PIV (particle imaging velocimetry) due to the elimination of particle lag effects in high Mach number and low-density flows. Such lag effects act like a low pass filter for fluctuations and result in the inability to see small scale turbulent features [5]. Another advantage of MTV techniques is their tendency to necessitate lower per-pulse laser energies when compared to unseeded techniques, such as the Rayleigh scattering imaging or Raman scattering imaging [6].

A common variant of MTV is to employ two laser beams for its operation. The first laser beam, known as the "write" laser, is used to excite tracer molecules to their excited states, effectively "tagging" them. These tagged molecules are subsequently transported by the fluid flow. To obtain the velocity information, a second laser beam, referred to as the "read" laser, is employed to re-excite the tagged molecules, generating a laser-induced fluorescence (LIF) signal. The displacement of the tagged gas (Δx) is determined by capturing two consecutive images at a known time interval (Δt). These images are then utilized to calculate the velocity [4,7–9]. However, it is worth noting that the "write" and "read" laser beams often have different excitation wavelengths, which can complicate the experimental process. This reliance on two laser systems for several MTV methods further adds to the complexity.

Therefore, a preferred approach is to employ MTV with single laser excitation. For instance, the use of nitric oxide (NO) molecules in MTV techniques for flow velocity determination has been explored [2,4]. However, NO possesses a natural decay lifetime within 200 ns for most practical flowfields, making it suitable for time intervals of a few hundred nanoseconds before the acquisition of the "read" image. While this is well-suited for measuring displacement in high-speed (often hypersonic) flows, the precision of the measurement is reduced within lower speed regions of such high-speed flows such as wakes. Using relatively longer time delays, such as a few microseconds, to create larger displacements has the trade-off with the NO fluorescence signal becoming too weak for reliable detection due to the relatively short lifetime. Additional challenges also arise at relatively higher pressure regions of supersonic and hypersonic flows, such as post-shock regions at higher Reynolds number conditions, where the NO laser-induced fluorescence signal lifetime becomes very short, thereby inhibiting a precise velocity measurement.

In recent years, several novel MTV techniques have emerged, including femtosecond-laser electronic-excitation tagging (FLEET) [10,11], picosecond laser electronic-excitation tagging (PLEET) [12,13], and selective two-photon absorptive resonance femtosecond-laser electronic-excitation tagging (STARFLEET) [14,15]. These methods employ a single, high-intensity laser beam to dissociate nitrogen molecules

into N atoms, with the subsequent recombination generating excited nitrogen molecules that fluoresce at visible wavelengths. Notably, although the nitrogen fluorescence has a brief lifetime of less than 100 ns, the recombination process itself takes a more extended period, approximately ~20 µs [12]. Consequently, this process yields long-lived N_2 fluorescence signals suitable for MTV measurements.

Another technique, krypton tagging velocimetry (KTV), encompasses both a two-beam mechanism [9] and a single-beam mechanism [16]. The single-beam KTV technique bears resemblance to FLEET/PLEET techniques. It entails the use of a high-intensity laser pulse to ionize krypton molecules, thereby generating long-lived fluorescence signals via electron reattachment. Recent KTV experiments [17] have revealed that the ionization of Kr is a pivotal process for generating long-lived signals through the resonance-enhanced multiphoton ionization (REMPI) procedure. However, ionizing krypton molecules presents a challenge, as it requires a laser wavelength of 212 nm for Kr resonant excitation, with the ionization necessitating three photons at this specific wavelength [17]. This, in turn, demands exceedingly high laser intensities to simultaneously excite the same molecule with three photons. Building upon previous experiences [7,16,17], it is established that Kr ionization necessitates around ~2 mJ per pulse at 212 nm with a 200-mm focus lens. Consequently, in laboratory-scale jet flows, a focus lens with a short 200-mm focal length is generally employed to achieve efficient three-photon excitation. However, the feasibility of this short-lens technique is limited in larger ground test facilities, as focal lengths near 1 m are typically needed for large-scale facilities. In such instances, laser pulses with much higher energy are required but are currently unattainable. Although prior efforts have endeavored to substitute the requisite third photon with a 355-nm photon, it remains evident that three-photon ionization poses a substantial challenge for flow tagging in large facilities due to the elevated laser energy demands associated with nanosecond pulses, especially when considering the potential damage to windows and wind tunnel models [7,16,17].

Considering the advantages of a simplified single-beam MTV using a molecule ionization or dissociation mechanism and recognizing the constraints of employing short focal lengths in large wind tunnels, we sought to identify a molecule that requires only two photons for ionization or dissociation instead of three photons. In pursuit of this goal, an examination of common gaseous tracer molecules within the NIST database was conducted, ultimately leading to the selection of NO, which is a free radical. This choice was informed by the fact that a frequently employed excitation wavelength of 226 nm is commonly used in NO planar laser-induced fluorescence (PLIF) [18,19] and MTV [2,4] measurements. Notably, the ionization energy of NO stands at a mere 9.26 eV (compared to krypton's ionization energy of 14.0 eV), with a dissociation energy of 6.45 eV. In contrast, a single photon at 226 nm carries an energy of 5.49 eV. Consequently, 1 + 1 REMPI of NO readily facilitates its ionization or photodissociation and also lowers the required pulse energy/intensity [7].

In this paper, the successful demonstration of 1 + 1 REMPI of NO is presented, along with the measurement of its lifetime under two different pressure conditions. Furthermore, the feasibility of long-lived NO MTV measurements for flow velocity determination is showcased, particularly in the context of cold high-speed jet flows.

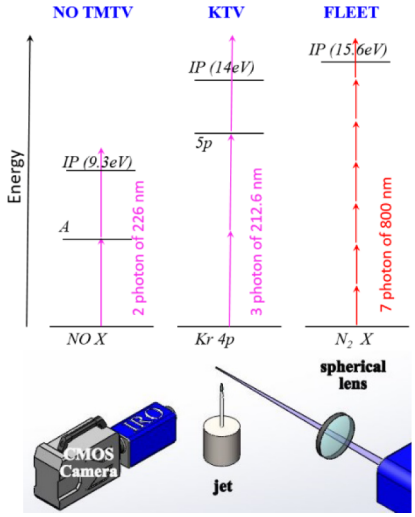

Fig. 1. Schematic of NO MTV with 1 + 1 REMPI energy levels (top) and experimental setup (bottom).

A burst-mode laser-pumped optical parametric oscillator (OPO) system was employed to generate the NO excitation wavelength at 226.22 nm (in vacuum), to target the overlapping NO $Q_1(7)$ and $Q_{21}(7)$ lines. These laser and OPO system have previously been used in several NO planar laser-induced fluorescence (PLIF) endeavors [17,20]. The laser pulse energy was approximately ~1 mJ per pulse in the injection-seeded configuration and was focused through a spherical lens onto a small jet flow (jet diameter of ~5 mm), as depicted in Fig. 1. The jet flow comprises 300 ppm of NO seeded in N_2 from a premixed gas cylinder. The laser beam was focused at H/D = 1 outside the jet. The regulator pressure was adjusted between 20 and 60 psi to create different jet flow speeds. For safety reasons, there is an NO detector and exhaust system in place. In the context of MTV with 1 + 1 REMPI, for signal intensity verification, several different focusing lenses were used including 100, 200, and 500 mm. As an alternative to the jet flow, an NO cell filled with 2% NO in 100 Torr of N_2 was employed for lifetime measurements. The phenomenon of long-lived NO MTV was previously observed during our NO single-photon MTV experiment [21] but was not reported in the previous work. The burst-mode laser was operated at a repetition-rate of 100 kHz in the previous setup, and therefore, the time interval between consecutive laser pulses was only 10 µs. While the long-lived fluorescence signal was successfully detected in that experiment, characterizing the lifetime was difficult due to the relatively short time interval, as the decay time exceeded 10 µs at some conditions. To more appropriately capture the long-lived signal decay lifetime of the NO MTV with 1 + 1 REMPI, the burst-mode laser and the OPO system were adjusted to operate at 2 kHz. This extended time interval of 500 µs at this repetition-rate was determined to be sufficiently large to record the entire NO MTV long-lived signal decay.

A high-speed camera (Photron SA-Z) equipped with an intensifier (LaVision IRO) and a UV camera lens (Cerco 50 mm $f/2.8$) was employed for NO fluorescence imaging detection. The spatial resolution of the camera system was approximately ~50 µm per pixel. The intensifier gain was set at 50%, and a gate width of 500 ns was used for signal collection. The camera and intensifier operated at a repetition-rate of 500 kHz, resulting in a time

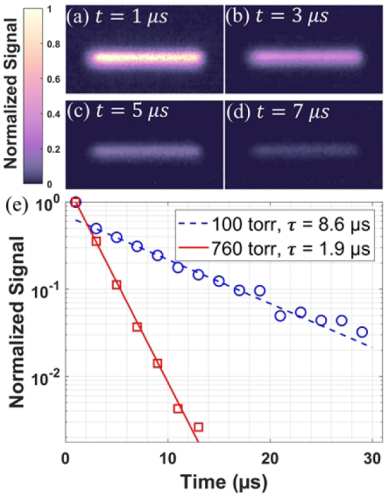

Fig. 2. Image sequence of NO MTV with 1 + 1 REMPI (top) and the signal decay with different pressures (bottom). The MTV lifetime is ~8.6 μs for 2% NO in N_2 at 100 Torr and 1.9 μs for 300 ppm NO in N_2 at 760 Torr in nitrogen.

interval of 2 μs in-between images. The first image was captured at 1 μs after the laser pulse to prevent interference with the NO single-photon fluorescence signal, which completely dissipated within a few hundred nanoseconds due to its short lifetime. Consequently, all of the recorded fluorescence signals in the images can be attributed to the two-photon process.

Figure 2 presents an illustrative sequence of NO MTV images acquired in a very slow jet flow. Even though the intensifier gain was set at 50%, the signal intensity at a 1 μs delay after the 1-mJ laser pulse is nearly saturated (registering at approximately ~4000 counts on the 12-bit camera). For 300 ppm NO at 760 Torr and shown on the left panel of Fig. 2, the signal-to-noise ratio (SNR) declines to approximately ~20:1 at a 7 μs delay time. The right panel in Fig. 2 compares NO MTV signal decay lifetimes for two different conditions: 100 Torr with 2% NO and 760 Torr with 300 ppm NO. The fitted lifetime is approximately ~8.6 μs for the 100 Torr case and decreases to approximately ~1.9 μs for the 760 Torr case. Single-photon LIF lifetime calculations at these conditions correspond to 43 ns for the 100 Torr with 2% NO condition and 124 ns for the 760 Torr with 300 ppm NO condition. At such conditions, the MTV with single-photon excitation cannot be easily performed for practical flow fields due to the short displacements corresponding to the very short lifetimes. Although two-laser techniques may be applied at such conditions to perform a velocity measurement, the 1 + 1 REMPI MTV method described here greatly simplifies the experimental approach.

Figure 3 displays sample images of the NO MTV with 1 + 1 REMPI signal along with a comparison of signal decays using various focusing lenses. As previously mentioned, lenses with focal lengths of 100, 200, and 500 mm were utilized for this evaluation. Given the natural potential utility of this technique for velocimetry measurements within large wind tunnels, the evaluation of longer focal length lenses is relevant to assess the measurement feasibility for large-scale testing facilities. Although no noticeable differences were observed in the lifetime of the NO MTV signal, it is surprising to note that the NO MTV signal exhibits greater signal strength with longer focal length lenses. This phenomenon serves as evidence that the NO

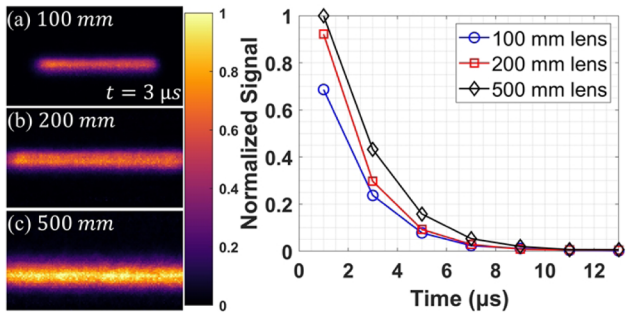

Fig. 3. NO MTV signal images with three different focusing lenses (left) and the signal decays (right). The line thicknesses are different for the three lenses due to the different focusing.

MTV process does not necessarily requires high-energy laser pulses. Using a longer focal length lens, such as the 500 mm one, likely results in a larger beam waist, which may lead to thicker probe volumes as seen in Fig. 3(c). While we typically used a laser pulse energy of approximately ~1 mJ per pulse, the long-lived NO MTV signal was successfully observed even with a pulse energy of only 0.2 mJ per pulse when using a 200-mm lens.

Both the burst-mode laser and the OPO system were injection-seeded for this experiment, resulting in an exceptionally narrow linewidth of approximately ~300 MHz at the OPO signal output wavelength of 624 nm [18]. Very high spectral intensities are therefore used for the measurements described thus far. The OPO output linewidth expands to approximately ~1 nm (equivalent to ~25 cm^{-1}) without injection seeding. The effects of the seeding versus non-seeding on NO MTV signals have also been explored in the current work. In the absence of OPO seeding, the MTV signal is roughly one-third of the signal observed with seeding when using a 500-mm lens; the measured 226 nm laser energy is also approximately one-third without seeding. Consequently it appears that the NO MTV signal remains roughly consistent on a per laser energy basis, whether under seeding or non-seeding conditions. Notably the NO MTV signal even shows a slight improvement without seeding for the shorter focusing lenses of 100 and 200 mm. Considering the additional costs and complexities of a seeding laser system, the potential to perform this measurement without injection seeding is a benefit.

The emission wavelength of REMPI MTV is crucial for understanding the underlying physical mechanism. Both KTV and FLEET/PLEET rely on a REMPI mechanism involving multiphoton ionization or dissociation. In FLEET, the emission originates from the N_2 B → A transition within the visible wavelength range. In the NO experiment, two potential physical mechanisms are considered. The first involves multiphoton processes ionizing or dissociating NO molecules, generating free electrons or atoms. These then recombine to form excited NO molecules, producing long-lived signals. The second mechanism involves NO ionization generating free electrons, which interact with nitrogen, leading to N_2 ionization/dissociation and recombination, producing emissions at a different wavelength. To differentiate between these mechanisms, it is crucial to determine the REMPI MTV emission wavelengths. NO emission ranges from approximately 226 to 300 nm, while nitrogen's falls within 500 to 800 nm. Using a 355-nm long-wavelength-pass filter (Semrock LP02-355RE-50), we did not detect NO MTV signals, ruling out the second mechanism. A

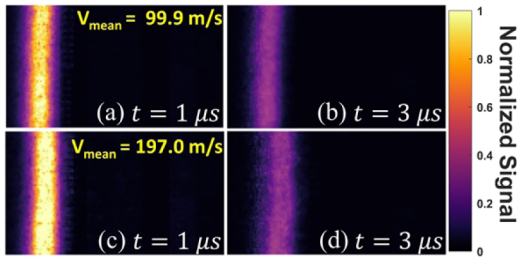

Fig. 4. Instantaneous NO REMPI MTV image sequences with different flow velocities. The laser energy is ~1 mJ/pulse.

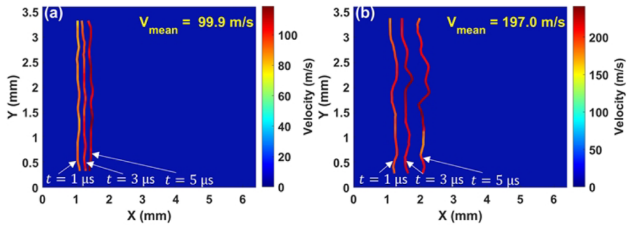

Fig. 5. Derived instantaneous flow velocity profiles based on NO REMPI MTV measurements.

300–340 nm bandpass filter (Semrock FF02-320/40–50) yielded similar results, indicating that all fluorescence signals in this technique originated from the NO fluorescence (the first mechanism). Thus, the correct REMPI MTV mechanism involves the REMPI process of NO molecules, leading to ionization or dissociation, with a significantly longer duration (a few microseconds) compared to the natural NO fluorescence (typically within 200 ns). No observed nitrogen or NO–N_2 energy transfer is involved in this process.

Figure 4 illustrates three examples of NO MTV for practical applications involving flow velocimetry measurements. As previously mentioned, 300 ppm of NO in nitrogen is used as the test gas with a jet diameter of approximately 5 mm. Two flow velocities are examined here of 100 and 200 m/s. While a sequence of images was captured at different delay times, this figure only shows two consecutive images with delay times of 1 and 3 μs for brevity.

The Gaussian curve fitting was used to determine the peak positions on a row-wise basis, and the displacement between two consecutive images was calculated. The flow velocity profiles were generated after a 5-point smoothing for refinement. Figure 5 presents two distinct velocity profiles at delay times of 1, 3, and 5 μs for each image. A color scale is used to denote the local flow velocities. The well-defined central jet flow, consisting of NO in nitrogen, is prominently visible. Mixed layers of the jet with ambient air, characterized by relatively weaker signals at the upper and lower edges, are also clearly discernible. The flow velocity measurement uncertainty is ~1–2%.

In summary, we successfully demonstrated the long-lived NO MTV with the 1 + 1 REMPI method employing a single laser beam. NO MTV with only two photons offers advantages over processes requiring three or more photons, such as KTV or FLEET. Additionally, this approach demands significantly less laser pulse energies. We measured the REMPI MTV fluorescence lifetime under various pressures and have proposed an underlying mechanism based on experimental evidence. We believe that the observed REMPI MTV signal originates from NO fluorescence rather than nitrogen emission. The technique was demonstrated in jet flows for velocimetry and has broad applicability for both reacting and non-reacting flow velocity measurements. As this paper was being prepared, we learned that the group at TAMU also discovered a similar phenomenon based on a released pre-print [22] at the time of this manuscript submission.

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Disclosures. The authors declare no conflicts of interest.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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