Exp Fluids (2014) 55:1791
DOI 10.1007/s00348-014-1791-8

LETTER

Multi-photon molecular tagging velocimetry with femtosecond excitation (FemtoMTV)

Shahram Pouya · Alexander Van Rhijn · Marcos Dantus · Manoochehr Koochesfahani

Received: 29 May 2014 / Revised: 30 June 2014 / Accepted: 9 July 2014

Abstract We present results for first molecular tagging velocimetry (MTV) measurements in water under resonant femtosecond excitation/emission process of a phosphorescent supramolecule. Both two-photon and three-photon absorption processes are examined, and the feasibility of measurements is demonstrated by single component velocimetry in a simple jet flow. The new capabilities enabled by FemtoMTV include elimination of the need for short wavelength UV excitation source and UV optical access in flow facilities, and potential for high rep-rate flow imaging.

Many of the current optical diagnostics utilized in fluid flow imaging rely on linear, single-photon excitation processes. This includes laser-induced fluorescence (LIF) techniques employed for tracer concentration/mixing measurements and temperature mapping, particle image velocimetry (PIV), and several implementations of molecular tagging velocimetry (MTV). A notable exception is coherent anti-stokes Raman spectroscopy (CARS), a multi-photon process which is utilized in combustion diagnostics for temperature and species selective concentration measurements (Begley et al. 1974; Goss et al. 1983), and its single-beam implementation using sub-10 fs pulses (Roy et al. 2009).

In MTV, long lifetime tracers are created from molecules that are either premixed or naturally present in the flowing medium using excitation by photons of appropriate wavelength (Koochesfahani and Nocera 2007). Typically, a pulsed laser is used to "tag" the regions of interest, and those tagged regions are interrogated at two successive times within the lifetime of the tracer. The measured Lagrangian displacement vector provides the estimate of the velocity vector. Nonlinear two-photon excitation methods have already been utilized for tagging purposes in some MTV schemes based on photodissociation using conventional nanosecond pulsed lasers; e.g., see several examples given in Koochesfahani and Nocera 2007 and more recent work described in Balla (2013). Multi-photon excitation of fluorescence/phosphorescence requires very high local instantaneous intensity, typically achieved with the short pulse width of ultrafast (femtosecond) lasers, to give an appreciable probability for simultaneous multi-photon absorption by a dye molecule.

Advances in ultrafast lasers have led to the development of numerous nonlinear optical spectroscopic methods, and the introduction of automated pulse compression methods has made a number of these approaches practical for applications outside the laboratory of ultrafast laser experts (Lozovoy et al. 2004; Dela Cruz et al. 2004). An ultrafast femtosecond pulsed laser was recently used for MTV in air, using the high photon flux of the femtosecond laser to photodissociate nitrogen in a nonresonant process (Michael et al. 2011). The intensity in these measurements was approximately 10^{14} W/cm^2, high enough to cause ionization in air. In this article, we demonstrate the feasibility of using multi-photon excitation by ultrafast femtosecond lasers for in situ MTV measurement of velocity in aqueous flow. We will also show some of the advantages that ultrafast lasers can provide to fluid flow studies compared to traditional single-photon methods.

S. Pouya · M. Koochesfahani (✉)
Department of Mechanical Engineering, Michigan State University, East Lansing, MI 48824, USA
e-mail: koochesf@egr.msu.edu

A. Van Rhijn · M. Dantus
Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA

Published online: 17 July 2014

The work described here takes advantage of the water-soluble phosphorescent supramolecule (1-BrNp·Mβ-CD·ROH), whose properties and utilization have been previously described elsewhere (Koochesfahani and Nocera 2007; Gendrich et al. 1997; Hu et al. 2006). This MTV triplex tracer has an absorption that peaks near 280 nm, with practically zero absorption beyond 325 nm. As a result, the lasers used for tagging purposes have traditionally been UV sources, e.g., 308 nm of Excimer laser or 266 nm of quadrupled Nd:YAG, therefore, also requiring UV optical access in the flow facility test section. Figure 1 shows the emission spectrum of the MTV triplex after conventional single-photon absorption/excitation at 280 nm (Hu et al. 2006). The emission spectrum exhibits fluorescence centered at around 328 nm and significantly red-shifted phosphorescence peaked at around 525 nm. These single-photon processes also have nonlinear multi-photon counterparts, where the simultaneous absorption of multiple lower energy photons enables excitation of a molecule to a higher energy state, similar to the absorption of a single high-energy photon. The phosphorescence emission spectrum of the MTV triplex through a two-photon absorption of a 400 nm ultrashort femtosecond laser pulse is also shown in Fig. 1 and is seen to be quite similar to its single-photon excitation counterpart. It is important to note that the femtosecond laser excitation wavelength (400 nm) is completely outside the (single-photon) absorption band of the triplex. Therefore, it suffers no attenuation by the tracer as it propagates through the solution. Furthermore, there is no longer a need for UV optical access.

The experimental setup for our femtosecond excitation MTV measurements consisted of a small water channel (Fig. 2) with a test section dimension of 150 mm (L) × 50 mm (H) × 50 mm (W) made of Plexiglas. The flow was created using a 9 V DC pump that fed the channel through a 10:1 contraction chamber with flow management to ensure an undisturbed uniform flow entering the test section. A second pump created a jet flow through a glass tube with an inside diameter of 3 mm that was placed roughly at the channel mid-plane. The jet flow speed was controlled by a manual valve placed after the secondary pump. The test section was covered by a 3-mm-thick Plexiglas plate (to demonstrate excitation beam access through flow facility Plexiglas walls). A quartz plate with thickness of 6 mm was attached to a section of this plate to create contact with the water free surface at the beam entry point to ensure small waves on the free surface did not alter the beam profile in the measurement domain. Although this secondary plate could have been made of Plexiglas as well, quartz was used to reduce the beam attenuation and also allow measurements with UV sources for comparison.

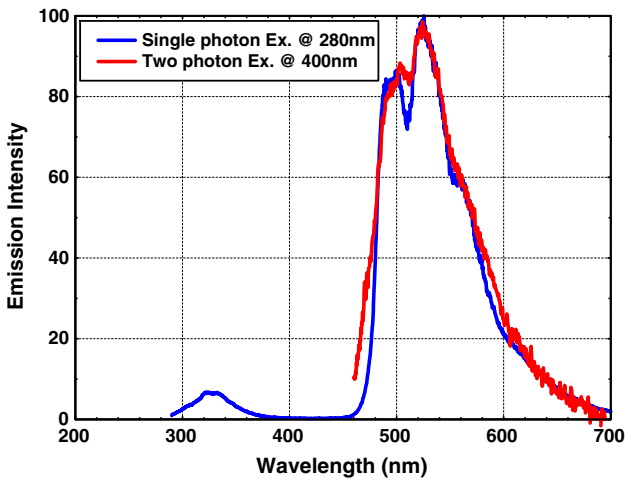

Fig. 1 Emission spectra for MTV triplex excited by 280 nm (single-photon) (Hu et al. 2006) and 400 nm (two-photon) wavelengths

The ultrafast femtosecond laser used here was a regeneratively amplified Ti:Sapphire laser (Spectra Physics, Spitfire), which was pumped by a Ti:Sapphire oscillator (KM-Labs). The amplified output had pulse energy of about 700 μJ and a wavelength centered at 800 nm, and pulse duration of about 50 fs. The amplifier could be configured to run at 1 kHz or any integer division thereof. The output from the amplifier was attenuated to approximately 500 μJ using a neutral density filter and focused onto a BBO crystal using a 100-mm-focal-length lens for upconverting the 800 nm laser pulses to 400 nm pulses through second harmonic generation (SHG). Because the SHG crystal thickness was not optimized for maximum output, we obtained only about 30 μJ per pulse at 400 nm. We stretched the pump pulses to avoid damaging the crystal and ended with pulse duration of about 200 fs. The MTV tracer concentration was about twenty times higher than that typically used in order to counteract the low pulse energy. The 400 nm beam was collimated by a 200-mm-focal-length lens and focused into the test section using a 30-mm-focal-length lens. A 12-bit, 1,280 × 1,024 pixel resolution, ICCD camera (Dicam Pro, PCO-Tech) was used to record images of tagged molecules, using a 105-mm Nikon lens without any optical filter. The camera was synchronized to the laser via a delay generator (DG535, Stanford Research Systems Inc.). The laser was pulsed at 100 Hz, while the camera was triggered once for every 10 pulses of the laser within a prescribed time delay.

For the particular results reported here, the jet speed was adjusted to be about 53 cm/s and the water channel speed was negligibly small. Instantaneous and average MTV image pairs of the region tagged by the femtosecond laser beam are shown in Fig. 3. The images show the expected displacement of the tagged molecules by the jet flow when comparing early time (top) and later time (bottom) images.

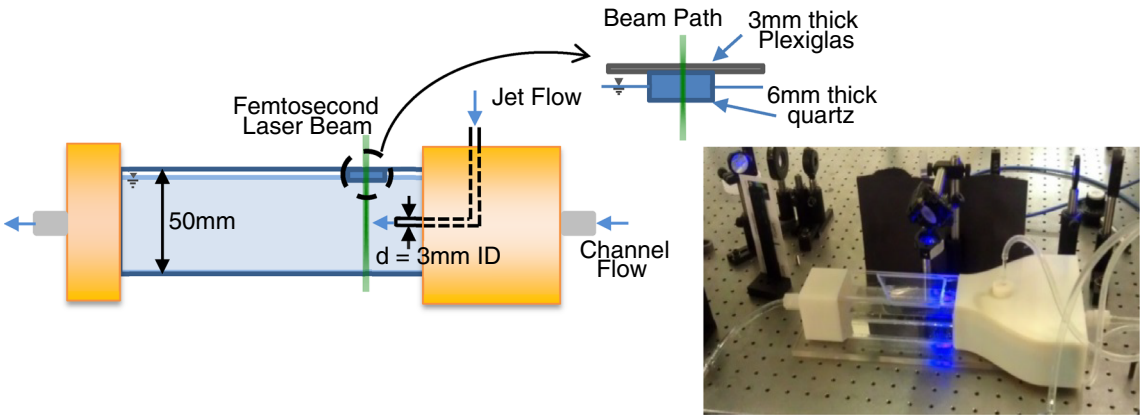

Fig. 2 Experimental setup for FemtoMTV measurements

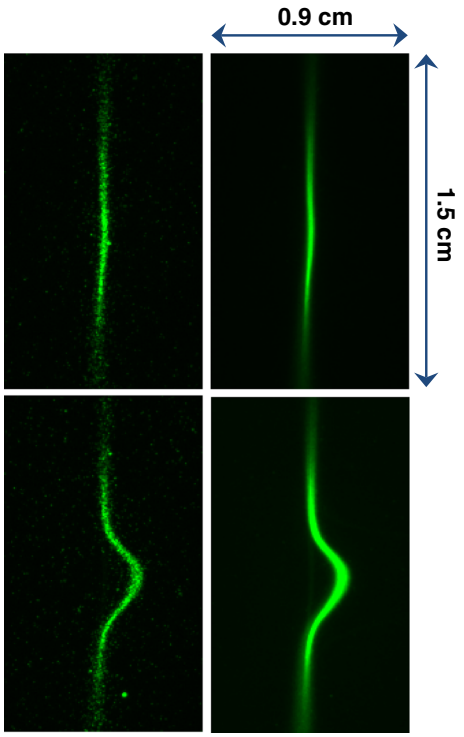

Fig. 3 Sample instantaneous (*left*) and average (*right*) MTV image pairs of jet flow ($x/d = 4$) with two-photon excitation. *Top* 100 μs after laser pulse (400 μs exposure), *bottom* 2.6 ms delay after first image (800 μs exposure)

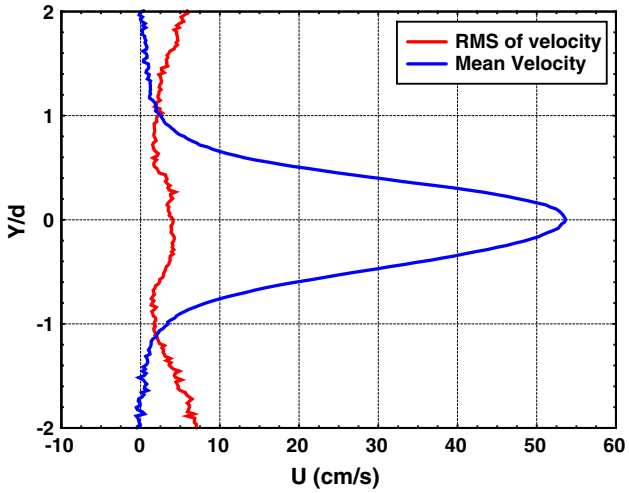

Fig. 4 Mean and RMS of jet flow velocity measured by MTV using two-photon excitation ($x/d = 4$)

The resulting mean and fluctuating velocity profiles in Fig. 4 are based on an ensemble of 256 instantaneous realizations obtained from a spatial correlation process (Gendrich and Koochesfahani 1996) applied to the instantaneous image pairs on a row-by-row basis. The mean profile depicts the expected jet profile. The rms profile, however, shows an increasing value outside the jet core, an artifact caused by the low signal-to-noise ratio of instantaneous images away from the focal point of the laser beam, which compromises the accuracy of instantaneous velocity estimates. The accuracy of the instantaneous velocity measurements in the current setup can be estimated by considering the lowest rms fluctuation measured at the edge of the jet, where the local velocity approaches zero. After taking into account the low-frequency velocity fluctuation introduced by the pump, the sub-pixel accuracy for determining the displacement of the tagged line was estimated to be about 0.25 pixel. For comparison, the peak jet velocity resulted in a displacement of about 23 pixels.

This experiment clearly shows that nonlinear multi-photon excitation works quite effectively for this MTV tracer. We can confirm the absorption/emission of MTV triplex is indeed a two-photon process by monitoring the emission intensity versus the laser energy over a small portion of the tagged region selected in Fig. 3. Results depicted in Fig. 5 demonstrate the quadratic dependence of emission intensity on laser excitation power due to the two-

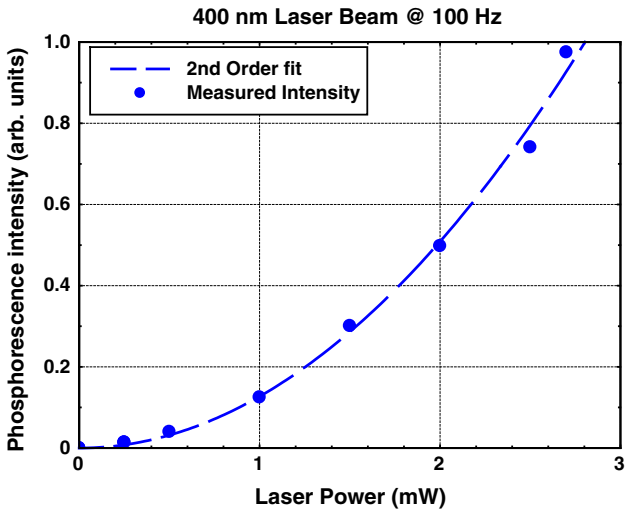

Fig. 5 Energy dependence of phosphorescence intensity of MTV triplex with two-photon excitation

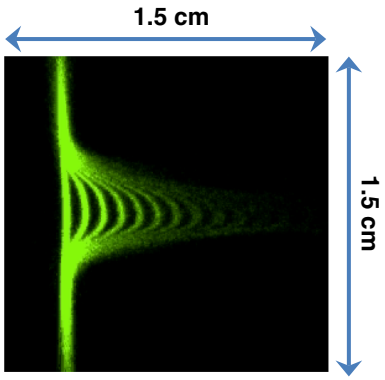

Fig. 6 Single frame illustrating kHz tagging by the femtosecond laser. Part of a time series video obtained at 10 frames/s

photon nature of the process. These results also point to the very large increase in image signal-to-noise ratio that is expected by increasing the energy of the excitation beam.

An exciting opportunity that now presents itself is the possibility for high rep-rate MTV imaging since modern near-IR lasers used for multi-photon excitation are also high rep-rate sources. We show in Fig. 6 an example of high rep-rate tagging using the same femtosecond laser as before, but now operating at 1 kHz. The 400-nm laser beam tagged the tracer molecules at location $x/d = 4$ downstream of the jet exit. The fluid tagged lines were created at a rate of 1 kHz (i.e., 1 ms apart), which then convected downstream by the fluid velocity field. Owing to the several millisecond lifetime of the tagged phosphorescent molecules, the Lagrangian displacement of several lines could be imaged all at the same time; about 9–10 lines are measureable in Fig. 6, each having been created 1 ms earlier by the femtosecond laser. The camera used here was not able to image the evolution of the tagged regions at kHz rate due to its frame rate limitation. Instead, we acquired a movie sequence at 10 frame/s, one frame of which is shown in Fig. 6. Employing a camera with kHz frame rate capability would allow the interrogation of the flow dynamics at high rate.

The feasibility of three-photon excitation was also considered using the original 800-nm infrared wavelength of the femtosecond laser. This wavelength is even higher than the phosphorescence emission range of the MTV triplex being studied here (see Fig. 1), and any excitation would only happen through simultaneous three-photon absorption with equivalent wavelength of 267 nm (i.e., a third of 800 nm). Results (not shown here) did show three-photon absorption, and phosphorescence emission and successful MTV measurements were, in fact, carried out in the same jet flow described here. Several limitations were noted, however. Despite strong absorption of the triplex at 267 nm, due to the low probability of three-photon process, the phosphorescence intensity was weak and recovering high-quality instantaneous data from low signal-to-noise images was challenging (extracting the mean velocity did not pose a challenge). Furthermore, the laser beam was observed to expand rapidly after focusing in water, which considerably limited the portion of the beam that could be used for spatially resolved measurements. This effect is believed to be due to the Kerr-induced self-focusing of the femtosecond laser pulse where the high intensity of the beam causes a local intensity-dependent variation of the refractive index, leading to a lens effect.

In conclusion, we have demonstrated the feasibility of using femtosecond pulse of ultrafast infrared lasers to effectively excite the water-soluble phosphorescent triplex for MTV measurement. While three-photon excitation posed challenges that require further scrutiny and improvement, two-photon absorption rendered high signal-to-noise images for successful MTV measurements. Nonlinear multi-photon excitation holds great promise for improvements in MTV techniques. It removes one of the constraints in the use of MTV, the need for short wavelength UV lasers to excite molecular tags and UV optical access in flow facilities. It also offers the opportunity for MTV flow imaging at high repetition rates. Due to the very low pulse energy in these proof-of-concept experiments, reliable data could be obtained over about 1.2 cm or more for the mean velocity and over about 6 mm for the rms velocity. We expect at least a factor of 10 increase in pulse energy by using an optimized SHG with better efficiency. Using a longer focal-length lens, this would allow an increase in the Rayleigh range of laser beam by a factor of 10, while keeping the same intensity (per unit area) as the current experiments. So, line tagging over lengths in the range 6–10 cm should be readily feasible.

Acknowledgments This work was supported by the Air Force Office of Scientific Research, Grant number FA9550-13-1-0034 (Drs. Enrique Parra and Douglas Smith, Program Managers).

References

Balla RJ (2013) Iodine tagging velocimetry in a Mach 10 wake. AIAA J 51(7):1783–1785

Begley RF, Harvey AB, Byer RL (1974) Coherent anti-Stokes Raman spectroscopy. Appl Phys Lett 25(7):387–390

Dela Cruz JM, Pastrick I, Comstock M, Lozovoy VV, Dantus M (2004) Use of coherent control methods through scattering biological tissue to achieve functional imaging. Proc Natl Acad Sci U S A 101(49):16996–17001

Gendrich CP, Koochesfahani MM (1996) A spatial correlation technique for estimating velocity fields using molecular tagging velocimetry (MTV). Exp Fluids 22(1):67–77

Gendrich CP, Koochesfahani MM, Nocera DG (1997) Molecular tagging velocimetry and other novel application of a new phosphorescent supramolecule. Exp Fluids 23:361–372

Goss LP, Trump DD, MacDonald BG, Switzer GL (1983) 10-Hz coherent anti-Stokes Raman spectroscopy apparatus for turbulent combustion studies. Rev Sci Instrum 54(5):563–571

Hu H, Lum C, Koochesfahani MM (2006) Molecular tagging thermometry with adjustable temperature sensitivity. Exp Fluids 40(5):753–763

Koochesfahani M, Nocera DG (2007) Molecular tagging velocimetry. In: Foss J, Tropea C, Yarin A (eds) Handbook of experimental fluid mechanics, vol 5.4. Springer-Verlag, Berlin

Lozovoy VV, Pastirk I, Dantus M (2004) Multiphoton intrapulse interference 4; characterization and compensation of the spectral phase of ultrashort laser pulses. Opt Lett 29(7):775–777

Michael JB, Edwards MR, Dogariu A, Miles RB (2011) Femtosecond laser electronic excitation tagging for quantitative velocity imaging in air. Appl Opt 50(26):5158–5162

Roy S, Wrzesinski P, Pestov P, Gunaratne T, Dantus M, Gord JR (2009) Single-beam coherent anti-Stokes Raman scattering (CARS) spectroscopy of N2 using a shaped 7-fs laser pulse. Appl Phys Lett 95(7):074102 (3 pages)