Humidity measurement in air using filament-induced nitrogen monohydride fluorescence spectroscopy

Shuai Yuan,1,2 Tiejun Wang,2,3 Peifen Lu,1 See Leang Chin,2,a) and Heping Zeng1,4,b)

1State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, China
2Centre d’Optique, Photonique et Laser (COPL) and Département de physique, de génie physique et d’optique, Université Laval, Québec, Québec G1V 0A6, Canada
3State Key Laboratory of High Field Laser Physics, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China
4Shanghai Key Laboratory of Modern Optical System, Engineering Research Center of Optical Instrument and System, Ministry of Education, School of Optical-Electrical and Computer Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

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Strong fluorescence emissions from nitrogen monohydride (NH) free radical at 336 nm were observed in air, when water vapor was present in a 400 nm femtosecond laser filament. The generated NH radical is ascribed to chemical reaction between nitrogen and water vapor during laser filamentation. The backscattered fluorescence from NH shows an exponential increase with increasing filament length, indicating amplified spontaneous emission. The fluorescence intensity of NH was found to be linearly dependent on the relative humidity around the filament region, and a record of NH fluorescence detection at 2 m was achieved, which opens up the possibility for remote humidity measurements. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867267]

Femtosecond laser filamentation1,2 which originates from a dynamic equilibrium between Kerr self-focusing and defocusing by the self-generated plasma produced by multiphoton/tunnel ionization of air molecules has attracted a lot of scientific interests.1–5 Intensity clamping inside the filament produces a self-stabilized high peak intensity of \( \sim 5 \times 10^{13} \text{W/cm}^2 \), which can benefit a lot of nonlinear effects, such as plasma grating,6,7 photodissociation,8–10 and forward and backward lasing.9–12 Inside the filament, most molecules undergo multiphoton/tunneling ionization and fragmentation, which excite the ions and fragment molecules into excited states, resulting in the collision and recombination of these highly excited fragments.13–15 Since the filament can be targeted at a long distance by adjusting the initial laser parameters, such as beam diameter, divergence, and pulse duration,1–5 remote sensing by filament induced breakdown spectroscopy has been demonstrated.16,17

Kasparian et al.17 have observed highly resolved atmospheric absorption spectrum from an altitude of 4.5 km, which opens the opportunity for aerosols identification in the atmosphere. Filamentation-assisted water condensation has been observed both in a cloud chamber and in the atmosphere.17–19 For atmospheric physics, relative humidity is particularly important, because of its relevance to the changes of state of water content in air, which is also the key parameter for predicting the weather. Remote humidity measurement would indicate the water condensation condition in the atmosphere, which will help us to understand the detailed physics in cloud formation or even lightning control.20 Most recently, by Wang et al.,21 the absolute humidity was measured in air using filament-induced fluorescence spectroscopy. However, in that work21 the humidity was calibrated by using the 308.9 nm fluorescence line from hydroxyl (OH) radical arising from laser induced dissociation of water vapor. The fluorescence from 308.9 nm is rather weak (two orders of magnitude weaker than nitrogen \( \text{(N}_2 \) ) fluorescence at 337.0 nm), and hence cannot be easily detected meters away.

In this work, strong fluorescence emissions from nitrogen monohydride (NH) free radical at 336 nm were found in air, by applying water vapor into an intense blue (400 nm) filament. A method based on femtosecond laser filaments induced chemical reaction is proposed to measure the relative humidity in air. The experimental results show that the fluorescence from NH free radicals is linearly dependent on the relative humidity in air. Besides, the amplified spontaneous emission (ASE) of NH radical in the backward direction was observed, which can extend the technique for remote fluorescence measurement.

The experiments were done by using a 8 mJ/50 fs, 1 kHz Ti:Sapphire (800 nm) laser beam. The schematic of the experimental setup is illustrated in Fig. 1(a). The laser beam passed through a 100-μm-thick beta-barium borate (BBO) crystal for second harmonic generation and was reflected by two dichroic mirrors (M1 and M2, with a high reflectivity of 99% at 400 nm and high transmission of 90% at 800 nm) to filter out the remaining 800 nm pulses. After that, the beam was focused by a lens of 30 cm focal length. The pulse energy at 400 nm is 1.8 mJ (measured after M2). A 3.5-cm-long filament was created. A beaker with open area of 10 cm in diameter was placed 6 mm under the filament. The beaker was fully filled with distilled water, which was used to change the relative humidity around the filament region. The water temperature was controllable by a heating plate underneath. The fluorescence from the side was collected at a distance of 50 cm from the filament by an imaging system of 4 fused silica lenses and sent to an intensified charge-coupled device (ICCD) gated spectrometer (Andor Mechelle M5000) through a fiber coupler. All the results shown in this paper are averaged over 600 000 laser shots.

a)Electronic mail: slchin@phy.ulaval.ca
b)Electronic mail: hpaeng@phy.ecnu.edu.cn
Fluorescence at 336 nm was observed as shown in Fig. 1(b). The signal became stronger when the water was heated from 20°C to 62°C. The fluorescence was identified as NH radiation from $A^3\Pi \rightarrow X^3\Sigma^-$, with the typical fluorescence from molecular N$_2$ at 337 nm also observed as shown in Fig. 1(b). The structure of the NH spectral line is similar to that reported in Ref. 13, when filaments interact with a flame. Here, the NH radicals might be ascribed to the complicated recombination process of the dissociated N$_2$ and water vapor molecules. When the water temperature increases, the water vapor concentration goes higher so that the NH fluorescence gets stronger. Especially at 62°C, the intensity of NH fluorescence at 336 nm is even stronger than that of N$_2$ fluorescence at 337 nm. “Clean” spectrum of NH was even found when the fluorescence was collected at a distance of 2 m from the filament, with water temperature at 43°C and larger mirror for fluorescence collection [see Fig. 1(c)].

In order to have a detailed physical picture of the filament-induced chemical reaction, the NH fluorescence in the backward and side directions were measured with the gated-ICCD spectrometer under different input pump pulse energies. The beam was focused by another focusing lens of 37 cm. The fluorescence from the side was measured by using the setup in Fig. 1(a). For detecting the backward fluorescence, one piece of dichroic mirror (fused silica, highly reflect (HR) 95% at 266 nm) with 70% transmission at 400 nm and partially reflecting at 334 nm–339 nm was installed right after the mirror M2 in Fig. 1(a) with 45° to the beam path, in order to transmit the 400 nm pump while reflecting the backward emitted fluorescence from the filament at 45° incidence.

![Diagram of experimental setup](image)

**FIG. 1.** (a) Schematic layout of experimental setup. Typical spectra in the range of 334–339 nm for filament-induced fluorescence of NH in air, with fluorescence collected at a distance of 50 cm (b) and 2 m (c) from the filament.

![Diagram of fluorescence intensity](image)

**FIG. 2.** The fluorescence intensity of NH at 336 nm versus the filament length. The fluorescence is measured in backward (a) and side (b) direction. The laser beam is focused by an external focusing lens ($f = 37$ cm). The polarization property of the fluorescence in backward and side direction is shown in (c) and (d), respectively.
angle. A UG11 filter was also employed after the dichroic mirror to filter out the blue scattering from the surface of the mirror. The fluorescence was collected with a fused-silica lens with 8 cm focal length and then sent to the ICCD-gated spectrometer. The water temperature was fixed at 43 °C and the distance between the filament and the water surface was at 6 mm. We used a CCD to image the filament for measuring the filament length. The result is shown in Figs. 2(a) and 2(b). In Fig. 2(a), the backward emitted NH fluorescence increases exponentially as the filament length increases, while in Fig. 2(b), the NH fluorescence from the side has a linear dependence with the filament length. If the NH fluorescence cannot see any gain effect along the filament, NH fluorescence emission detected in the backward and side directions should give similar results. However, in our experiment, the on-axis backward NH fluorescence signal increases much faster (increase exponentially) with the filament length than the one detected from the side (increase linearly). This indicates amplified spontaneous emission. By assuming that the intensity inside the filament is uniform because of intensity clamping, the gain coefficient \( g \) over the filament is obtained by fitting the experimental curve in Fig. 2(a) with \( (e^{gL} - 1)/g \) to get \( g = 0.556 \text{ cm}^{-1} \). We note that the value of gain from our measurement (0.556 cm\(^{-1}\)) from NH and that from Ref. 23 (0.300(3) cm\(^{-1}\)) from N\(_2\) for fluorescence measured at 357 nm are not comparable. The excised atomic nitrogen (N\(^*\)) is essential for generating highly excited nitrogen monohydride radical (NH\(^*\)), but there is no evidence that fragment N\(^*\) is only from direct dissociation of excised molecular nitrogen (N\(_2\)*). For instance, it is possible that N\(_2\) molecule is dissociated into the fragment of atomic nitrogen (N) in ground state. After that the ground state fragment N is excited into N\(^*\) by laser field or by collision. The polarization of the fluorescence from the backward and side direction is measured by rotating a polarizer placed just before the head of the fiber which couples to the ICCD. Both of them are randomly polarized as shown in Figs. 2(c) and 2(d). The isotropic polarization and the difference between the gain in backward and side directions provide strong evidences for ASE lasing.

In this sense, the ASE lasing testifies that the NH free radical, the product of filament-induced chemical reaction, is in an excited state and the population is inverted. Therefore, the translation of NH \( A^1\Pi \rightarrow X^3\Sigma^- \) gives strong radiation at 336 nm, which can be used for the humidity measurement based on filament-induced spectroscopy since the fluorescence intensity from NH is dependent on the relative humidity. To calibrate the relative humidity, in Fig. 3(a), the fluorescence intensities of NH at 336 nm and N\(_2\) at 337 nm were measured by varying the water temperature from 20 °C to 66 °C. The distance between the filament and the water surface was 6 mm. By increasing the water temperature, the NH fluorescence increases linearly, while the N\(_2\) fluorescence keeps roughly constant. As a reference for humidity calibration, a hygrometer was fixed 6 mm above the water surface. The relative humidity was recorded by changing the water temperature and linearly fitted in Fig. 3(b). By combining the experimental curve in Fig. 3(a) and the reference in Fig. 3(b), we obtain the relative humidity as a function of NH fluorescence (Fig. 3(c)). The relative humidity is linearly proportional to the fluorescence signal of NH free radical. This result provides a significant way to measure relative humidity by monitoring NH fluorescence from filament-induced chemical reaction.

Thus, it is reasonable to conclude that the high intensity laser filament induced the dissociation of the nitrogen and water molecules. After that the collision of the highly excited fragments generates the excited NH free radical with population inversion. The strong emission at 336 nm occurs; it is sensitive to the number of water molecules in air. Besides, lasing action in NH radical means once we increase the length of the gain medium by increasing input pulse energy, it is expected to achieve stronger emission at 336 nm in backward direction. Remote humidity calibration needs to avoid influence from nonlinear dependence of NH fluorescence upon filament length. For this purpose, the fluorescence could be calibrated at a large angle, e.g., at 45° from backward direction. The strong fluorescence emission at 336 nm works as an effective approach for calibrating the humidity, even remotely.

In summary, strong fluorescence emissions from NH free radical at 336 nm were observed in air. The fluorescence signal intensity is linearly dependent on the relative humidity around the filament region. The results reported in the paper not only give a further understanding of the filament-induced chemical reaction in air but also opens up possibilities to monitor the relative humidity remotely. The detailed underlying physics for the NH generation though filamentation awaits to be explored.

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