Field measurements suggest the mechanism of laser-assisted water condensation

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Because of the potential impact on agriculture and other key human activities, efforts have been dedicated to the local control of precipitation. The most common approach consists of dispersing small particles of dry ice, silver iodide, or other salts in the atmosphere. Here we show, using field experiments conducted under various atmospheric conditions, that laser filaments can induce water condensation and fast droplet growth up to several µm in diameter in the atmosphere as soon as the relative humidity exceeds 70%. We propose that this effect relies mainly on photochemical formation of p.p.m.-range concentrations of hygroscopic HNO₃, allowing efficient binary HNO₃–H₂O condensation in the laser filaments. Thermodynamic, as well as kinetic, numerical modelling based on this scenario semiquantitatively reproduces the experimental results, suggesting that particle stabilization by HNO₃ has a substantial role in the laser-induced condensation.
Owing to their impact on key human activities like agriculture, strong efforts have been dedicated in the last 70 years to seed clouds by dispersing small particles of dry ice, AgI, or other salts in the atmosphere. However, the efficiency of these techniques is still debated\(^1\). Recently, self-guided ionized filaments\(^2\), generated by ultrashort laser pulses, have been proposed as an alternative approach to trigger water condensation\(^3\).

Laser filaments are self-sustained light structures of typically 100\(\mu\)m diameter and up to hundreds of meters in length, widely extending the traditional linear diffraction limit. Their formation stems from an intensity-dependent refractive index modification of the propagation medium, known as the Kerr effect, and is due to third-order nonlinear polarization of the medium. It results in self-focusing of the beam, until the intensity rises sufficiently for ionizing the air. The self-generated plasma\(^4\) and/or negative higher order Kerr effect\(^5\) balance the self-focusing, resulting in self-guided propagation. Filaments convey an intensity as high as \(5 \times 10^{13} \text{W cm}^{-2}\) over long distances\(^6\), ionizing and photo-oxidising\(^7\) the air. Both of these effects could be expected to assist water condensation. However, the Thomson process\(^8\),\(^9\)\(^10\), triggered by charges and typical of the Wilson chamber\(^11\), is irrelevant to the atmosphere because it requires supersaturation\(^12\)\(^13\)\(^14\). Furthermore, we recently observed that laser-induced condensation and electron densities have different behaviours as a function of the incident laser power\(^15\).

Here, on the basis of field experiments performed under various atmospheric conditions, we show that laser filaments can induce water condensation and droplet growth up to several \(\mu\)m in diameter in the atmosphere as soon as the relative humidity (RH) exceeds 70%. We propose that the local photochemical formation of p.p.m.-range concentrations of hygroscopic HNO\(_2\) substantially contributes to this effect by enabling efficient binary HNO\(_2\)–H\(_2\)O condensation in the laser filaments. Thermodynamic as well as kinetic numerical modelling supports this interpretation. These results offer key information to optimize the water condensation process.

**Results**

**Laser-induced rise of particle density.** We investigated atmospheric water condensation initiated by the Teramobile mobile femtosecond–Terawatt laser system\(^16\) operating continuously and generating \(\sim 10\) filaments over typically 15–20m. We shielded the latter from wind by an open chamber and sampled the aerosols alternatively at 2 cm distance from the filaments and in background atmospheric conditions. Comparing the corresponding particle densities clearly evidences the laser-induced increase of the particle number in each size class, even far below water vapour saturation (Fig. 1a–d). The most spectacular effect is observed on nanoparticles of \(\sim 25\)\(\mu\)m diameter. For example, at 75% RH, the nanoparticle density typically increased by \(5 \times 10^{13} \text{cm}^{-3}\) (3–6 times the background concentration), while 10\(\mu\)m particles increased by a few particles per litre (up to 30% of background). Note that these are averaged values over the volume of the protection chamber, that is, after dilution by a factor of 200–400 as compared with the active filament volume (see below). As a result, the size distribution is shifted to the larger sizes (Fig. 1e), evidencing the laser-induced growth of the particles. Furthermore, these particles do not re-evaporate significantly. For example, 25-nm-diameter particles have been observed to last over at least 20 min, limited by the diffusion out of the measurement chamber (see blue line in Fig. 2c).

**Influence of atmospheric conditions.** Atmospheric conditions have specific and contrasted influence on the laser-assisted yield of different particle sizes. As illustrated in Figure 3, RH is positively correlated with the generation of particles below 400 nm, and negatively correlated above, whereas the opposite correlations are observed in the case of temperature. Conversely, water vapour volume mixing ratio (VMR) is anticorrelated with particles under 500 nm, positively correlated with particles above 3 \(\mu\)m, and uncorrelated with the generation of particles in the 600 nm–3 \(\mu\)m range.

This contrasted behaviour defines three size ranges. The first one regards nanoparticles (25 nm median diameter, as compared with

![Figure 1](image-url)
55 nm in the background), the concentration of which is increased by the laser in all conditions encountered during the campaign. Their increase is positively correlated with both relative and absolute humidity (Fig. 4a,c), and negatively correlated with temperature (Fig. 4a). Particles in the 230–400 nm range feature a second regime. The effect of the laser on their concentration decreases with increasing absolute humidity (Fig. 4f) and temperature (Fig. 4d). Conversely, it is negligible below 50% RH, and increases when RH rises up to 100% (Fig. 4e). The dependences vanish for diameters close to 500 nm (Fig. 4g,h,i), and reverse above, defining the third regime (Fig. 4j,k,l). Note, however, that the increase of micrometer-sized particles rises again when approaching 100% RH.

**Trace gas measurements.** Typical O$_3$ and NO$_2$ concentrations were, respectively, 200 p.p.b. and 25 p.p.b. in the open chamber, when the laser was operating, independent of the temperature and humidity (Fig. 2a,b). Considering the diffusion of the gases in the chamber and through its openings, the dilution factor between the filament volume and the chamber amounts to 200–400. The measured concentrations are therefore in line with laboratory results, as expected resulting in a HNO$_3$ concentration in the p.p.m. range or above inside the filaments. Figure 2c displays the decay time of these gases, as well as of nanoparticles, after the laser is switched off. The comparable time constants for gases and particles suggests that the decay is mostly governed by dilution through the chamber apertures and owing to the airflow induced by the air sampling of the aerosol and gas sensors. The ozone concentration decreases to its background level in 10 min, faster than the nanoparticles (20 min) while NO$_2$ exhibits a retarded effect typical of a secondary product generated by the oxidation of NO by ozone, which also speeds up the decay of the latter. The same behaviour was observed reproducibly over more than 30 experimental realizations.

NO$_3^-$ contents in laser-induced particles. As displayed in Figure 5, ionic chromatography of laser-induced particles impacted on filters reveals high concentrations of HNO$_3$ detected as dissolved NO$_3^-$ ions, regardless of the particle size. This concentration is one to two orders of magnitude above that of SO$_4^{2-}$ ions in the same particles. Smaller amounts of NO$_3^-$ ions are also detected.

**Discussion**

The three different regimes observed for nanoparticles, sub-micronic, and micrometric particles suggest the following condensation mechanism. The laser initiates particle nucleation or activates pre-existing nanometer-sized particles. This nucleation from the gas phase may occur via multicomponent nucleation of sulphuric acid, although it is beyond the scope of the present work in which no data is available on particles smaller than 25 nm. It results in the accumulation of ~25 nm particles inside the filaments. Such particles can grow, if the RH is sufficient to ensure their stability. Once they reach ~500 nm, their subsequent evolution is expectedly limited by diffusion of water molecules, which may explain why the growth of these particles requires high VMR, hence higher temperature, as illustrated by the correlation of both these parameters with bigger particles. On the other hand, the depletion of the humidity by the water uptake results in the negative correlation between RH and these micrometric particles.

This scenario requires a highly efficient stabilizing mechanism to prevent the particles from re-evaporating well below 100% RH. This mechanism may be provided by the strong impact of the laser filaments on the local chemical composition of the atmosphere.
In particular, the estimated HNO$_3$ concentration inside laser filaments is typically 1,000 times the p.p.b. levels at which the highly hygroscopic HNO$_3$ is known to stabilize water droplets in the atmosphere slightly below 100% RH (ref. 20). We can therefore expect efficient stabilization at much lower RH through binary HNO$_3$–H$_2$O condensation.

The dilution factor of 200–400 between the filament active volume (~10 filaments of 100µm typical diameter) and the protection chamber leads us to estimate that ~2×10$^3$ cm$^{-3}$ nanoparticles, and some 10$^6$cm$^{-3}$ microparticles are generated in the filaments by each laser shot. Notice that up to 10$^4$ ozone molecules (8×10$^{-11}$ g) and 2.5×10$^{10}$ NO$_2$ molecules (2×10$^{-11}$ g) are available for each nanoparticle. Consequently, even larger particle sizes (several micrometers) could be stabilized by the resulting HNO$_3$. These concentrations are therefore compatible with a pathway based on the binary condensation of HNO$_3$–H$_2$O particles.

We performed numerical simulations to evaluate to what extent this binary HNO$_3$–H$_2$O condensation model can explain the experimental data. Figure 6a displays the resulting Köhler plot, that is, the equilibrium RH over the ternary HNO$_3$–H$_2$O–NH$_3$NO$_3$ droplet surface, as a function of its diameter, in conditions representative of those encountered within the laser filaments. Water-vapour uptake dominates evaporation, if the RH is higher than its equilibrium value, that is, for conditions above the curve. This value decreases down to 75% RH for a HNO$_3$ concentration of 4 p.p.m., allowing droplets from several tens of nm to a few µm to grow at RH well below 100% and to shift towards the right of the plot until they reach an ascending branch of the Köhler curve at several µm, consistent with the experimental data. This effect persists over the whole range of temperatures encountered in the experiment, although its effectiveness significantly decreases at rising temperatures. In particular, a higher humidity is required to stabilize the particles in warmer
air. We checked that the condensation germs had no impact on the Köhler plots of particles above 80 nm, where the salt core is largely diluted (compare dotted and solid lines on Fig. 6a), so that our results can be expected to be also representative of situations with other nucleation germs implying for example, electric charges or sulphur compounds.

A 15 nm salt core stabilizes the smaller particles, as shown by the positive slope of the Köhler curves for diameters below 40 nm (see solid curves on Fig. 6a). This positive slope, which arrests the growth of the particles, constitutes a growth barrier if the RH is below the local maximum of the Köhler curve, and could therefore explain the median diameter of 25 nm observed by the nanoparticle counter, irrespective of the RH. Because RH influences the height of the Köhler maximum, and therefore the droplet capability to step over it, the Köhler plots provide a reasonable interpretation of the positive correlation between RH and the generation of particles of several hundreds of nm (Fig. 4e), as well as the rise of the generation of micrometer-sized particles at RH close to 100% (Fig. 4k).

Similar results are obtained over the whole range of temperatures encountered during our campaign (2–36°C). The calculated effect of the laser decreases with increasing temperature, in agreement with the observations previously made in the real atmosphere, from remote sounding of the atmosphere strongly modified by the laser. They form stable micro- or even nanometric particles, even at RH as low as 70%. These nanoparticles grow in particular by condensing water vapour and HNO₃ from the atmosphere strongly modified by the laser. They form stable micrometer-sized particles that persist over at least 20 min, demonstrating that the condensation is not transient during the laser pulse, but rather a process allowing the particle growth to stable micrometer-sized droplets. Numerical modelling based on binary HNO₃–H₂O condensation semi-quantitatively reproduces the experimental results, although it neglects any contribution of sulphuric acid, the laser-released charges, or the activation pre-existing condensation nuclei. The simulations predict fast particle growth, their stability at low RH, and the influence of the atmospheric conditions, which confirms the substantial contribution of binary HNO₃–H₂O condensation in the laser filaments. Although further work is needed to characterize the nucleation of new particles, these results provide a semi-quantitative interpretation to the laser-induced condensation and define favourable atmospheric conditions for laser-assisted condensation and provide a theoretical understanding for this phenomenon. As a consequence, they open the way to applications in the real atmosphere, from remote sounding of the atmosphere to laser-based rainmaking or rain prevention.

**Methods**

**Experimental conditions.** Experiments were performed in 28 runs, for a total of 133 hours of records from fall 2009 to spring 2010 on the bank of the Rhône River.
close to Geneva (46°12’ North, 6°5’ East, 380 m above sea level). This location was chosen to get the benefit from the relatively warm water flow from the Lake of Geneva acting as a heat buffer, locally increasing the RH. As detailed in Figure 7, data were acquired in a wide variety of atmospheric conditions: RH from 35 to 100%, temperature between 2 and 36 °C. Furthermore, experiments at all times of the day and the night ensured that both phases of increase and decrease of temperature and RH have been recorded.

**Experimental setup.** The experimental setup is depicted schematically in Figure 8. Water condensation was initiated by the Teramobile mobile femtosecond-Terawatt laser system. The laser was operated continuously and provided up to (160 mJ pulses of 240 fs unchirped duration at a central wavelength of 800 nm and a repetition rate of 10 Hz. The beam was expanded to 10 cm diameter and slightly focused (~15 m of horizontal propagation 1.2 m above ground, the beam generated some 1.107) coupled with a nanoparticle sensor (Grimm Nanocheck). The former sampled inside the chamber, at 2 cm distance from the filaments. Their size distribution was obtained by measuring the count median diameter of nanoparticles between 25 and 300 nm by measuring the particle charge, showing that the measurement of the nanoparticles is not inferred from both visual observation on a screen and the emission of a shockwave (~10 filaments), f ~ 20 m, running in the vicinity of our setup had minimal influence on our results; however, for safety, we disregarded the corresponding data in the analysis of our results.

**Chemical analysis of aerosol particles.** We characterized the chemical composition of the aerosols produced in the laser filaments by aspirating them at a flow of 1.21 min−1 during 2 h of continuous laser operation and impacting them on poly-cryogel membrane filters (Nuclepore Track-Etch) with 1.1 μm, 50 nm, or 15 nm pore sizes. Reference samples were collected without laser. Soluble particles were then dissolved by immersing the filters for 15 h in HPLC-grade water, including 15 min in an ultrasonic bath. The anions dissolved in the resulting solutions were analysed by an ionic chromatograph (ICS 3000).

**Trace gas measurements.** The influence of the atmospheric conditions on the generation of the precursors of HNO3, namely NO, NO2, and ozone, was investigated by recording the gas concentrations in the protection chamber around the filament. Standard analysers monitored the concentration of O3 (UV Photometric Analyser Model 49, Thermo Environmental Instruments, featuring a reaction time of 20 s) as well as NOx and NO (Chemiluminescent nitrogen oxides analyser AC 31 M, Environment S.A., 15 s reaction time) in the vicinity of the filaments.

**Modelling of particle stability.** We modelled the droplet stability within the size range accessible to our experimental system, that is, above 25 nm in diameter, leaving the initial particle nucleation beyond the scope of the present work. We adapted the extended Köhler theory to handle the multi-p.p.m. concentrations of HNO3 generated by laser filaments as well as the full experimental range of RH. The Köhler theory describes the equilibriums between evaporation and condensation of both water vapour and HNO3. It explicitly takes into account the Kelvin effect, which substantially shifts the equilibrium between evaporation and condensation because of the curvature-dependent surface energy. We neglected charge effects as well as species left in excited states in the plasma, and considered the condensational growth of a monodisperse cloud of spherical binary HNO3–H2O droplets. Within this framework, the composition- and curvature-dependent partial vapor pressure at equilibrium are expressed as:

\[ p_{v,j}(T, m_j) = p_{o,j}(T, m_j) \exp \left( \frac{\sigma(T, m_j) v_j(T, m_j)}{k_B T D_p(T, m_j)} \right) \]

where \( k_B \) is Boltzmann’s constant, \( T \) denotes the temperature, and \( p_{o,j} \) is the partial vapour pressure of species \( j \) (that is, H2O or HNO3). The partial molecular volumes \( v_j \) and the partial masses \( m_j \) of the considered species in the liquid phase by using the thermodynamic E-AIM model of the thermodynamic E-AIM model [http://aim.aim.aim.ai/aim/aim.php] \(^{15,16} \). The index \( j \) denotes the dependence on all involved species. Optionally, the droplets were doped with a NH4NO3, core accounting for typical nucleation gera\(^{30,31} \). For given salt core and water masses, we determined the equilibrium partition of HNO3 between the gas and liquid phases, in a closed system (that is for a fixed number of HNO3 and H2O molecules determined in the initial conditions). Equation (1) was then used to determine the equilibrium water vapour pressure over the corresponding droplet, defining the corresponding point in the Köhler plot.

**Kinetic modelling of particle growth.** The kinetic modelling of the droplet growth relies on the implementation of the full Kulmala model, in which we suppressed the assumption of near-saturation ambient vapour pressures owing to the low RH to handle, together with high HNO3 concentrations in the gas phase. Mass and heat transfers between a given spherical droplet and the atmosphere are described by the classical transition regime equations, including corrections for molecular
diffusivities and thermal conductivity. These corrections extend the applicability to droplet sizes approaching the thermal molecular mean free path.

\[
\frac{\text{dm}}{\text{dT}} = 2\pi D(T)M_\text{d}P(T, m_j) \left( \left( \frac{\rho_\text{sat}(T)}{\rho_\text{atm}} \right) \exp \left( \frac{\Delta v(T) \cdot m_j}{k_\text{B}T \cdot D(T, m_j)} \right) \right)
\]

(2)

\[
\frac{\text{dT}}{\text{dt}} = \sum_i q_i(T_i \cdot \text{d}m_i / \text{dT} - 2\pi D(T, m_j) \left( \left( \frac{\rho_\text{sat}(T)}{\rho_\text{atm}} \right) \exp \left( \frac{\Delta v(T) \cdot m_j}{k_\text{B}T \cdot D(T, m_j)} \right) \right) \cdot c_{\text{cond}}(T) \cdot s_i m_i
\]

(3)

Here, \( R \) is the universal gas constant, \( T \), the background temperature, \( T_j \) the droplet temperature, \( k_\text{B} \) the thermal conductivity of air, \( \epsilon_\text{d} \) the specific heat capacity of the liquid phase. \( D \) denotes the diffusivity of species \( i \) in air, \( M_i \) its molar mass, \( q_i \) its latent heat of condensation from the mixed solution. In these expressions, heating of the atmosphere by the laser has been neglected, because it is known to keep below a few degrees\(^\circ\). \( f(Kn, \alpha) \) is the Fuchs-Sutugin correction factor\(^\circ\)

\[
f(Kn, \alpha) = \frac{0.75\alpha(1 + Kn)}{Kn + 0.282Kn^2 + 0.75\alpha}
\]

(4)

where \( Kn \) is the Knudsen number\(^\circ\) (that is, the ratio of the molecular mean free path to the droplet radius). The mass and thermal accommodation coefficients \( \alpha_\text{m} \) and \( \alpha_\text{c} \) describe non-unity sticking probability of molecules of species \( i \) impinging the particle surface, and imperfect thermal coupling due to gas kinetic effects, respectively. We set them to unity, following the recommendation of Laaksonen et al. in the context of growth rate modelling\(^\circ\). The specific heat capacity \( c_\text{d} \) of the liquid phase is approximated by that of pure water, whereas the thermal conductivity of the atmosphere is approximated as that of pure air\(^\circ\). The effective latent heats of evaporation \( q_i \) depend on the particle composition due to the exothermic dissolution of gaseous HNO\(_3\). They are obtained from the equilibrium vapour pressures calculated with the F-AIM model, using the Clausius–Clapeyron equation:

\[
q_i(T, m_j) = \frac{RT^2}{} \cdot \rho_{\text{sat}, i}(T, m_j) \cdot M_i \cdot c_{\text{sat}, i}(T, m_j) \cdot \Delta T
\]

(5)

Using this expression neglects the distortion of the saturation vapour pressures due to the Kelvin effect, which however causes a relative change of the latent heats remaining below \( \sim 1\% \) even for droplet diameters as small as 10\( \text{nm} \)(ref. 35). Finally, owing to the low total condensed mass per air volume (typically 0.1\% for a droplet density of 1.000\( \text{cm}^{-3} \) and 1\( \text{µm} \) diameter), we neglect the impact of the latent heats of condensation and evaporation on the temperature of the reservoir.

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