

Supporting Information

Correlating droplet size with temperature changes in electrospray source by optical methods.

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Deoxygenation protocol for [Ru(bpy)₃]²⁺ solution:

Step 1: Degas the sample during 25-30 min with Ultrasonic Baths device in degas mode (Fisher Scientific)

Step 2: Bubble with Nitrogen for 5-10 min

Step 3: Degas the sample (closed container) during 25-30 min with ultrasound device (degas mode)

Step 4: Bubble with Nitrogen for 5-10 min & Take off solution with a syringe (to avoid any contact with atmosphere)

Step 5: Under inert atmosphere, fill up the airtight thermos-regulated cell (to avoid any contact with atmosphere)

Step 6: Close the airtight cell for measurement.

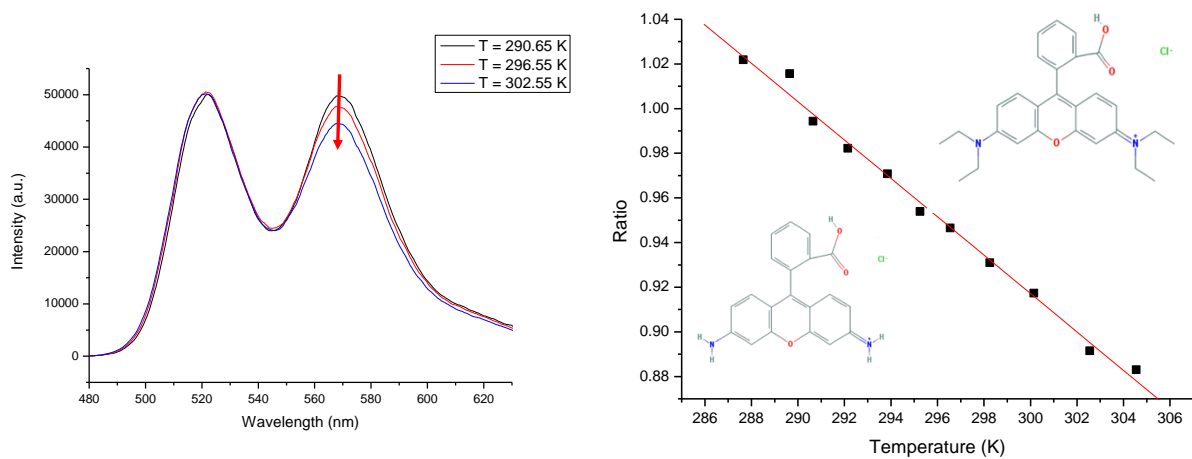


Fig S1 : Left. Fluorescence spectra of a mixture of Rhodamine 110 ($\lambda_{max} = 523$ nm) and Rhodamine B ($\lambda_{max} = 567$ nm) in Methanol at different temperatures. Right. Calibration curve showing the ratio $I_{max}^{RhB} / I_{max}^{Rh110}$ versus the temperature. Linear regression $Y = A + B \cdot X$; $R = -0.996$; $A = 3.49588 \pm 0.07452$; $B = -0.0086 \pm 0.00025$. Inset: Chemical Structure of (bottom) Rhodamine 110 and (top) Rhodamine B.

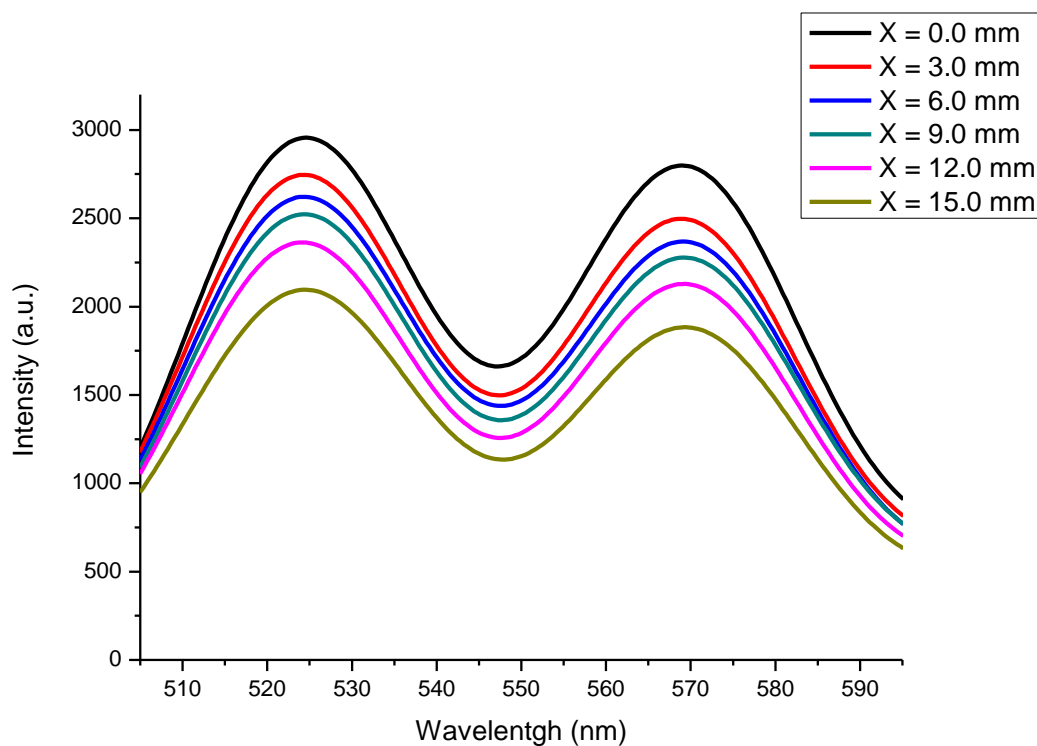


Fig. S2 : Fluorescence spectra of a mixture of Rhodamine 110 at 0.2 μ M and Rhodamine B at 2 μ M in methanol (SGT = 423 K, SGF = 3 L/min) at several positions for axial temperature profiles through the center of the spray.

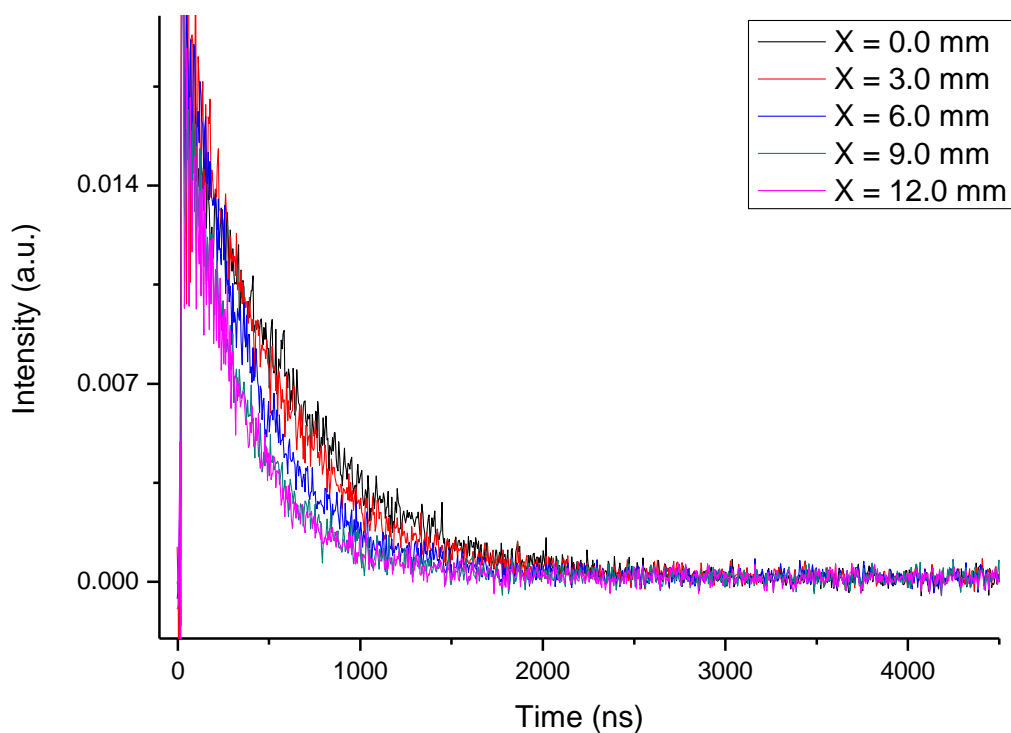


Fig. S3 : Typical Fluorescence decay of a solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ at 0.1 mM in methanol (SGT = 423 K, SGF = 3 L/min) at several positions for axial temperature profiles through the center of the spray.

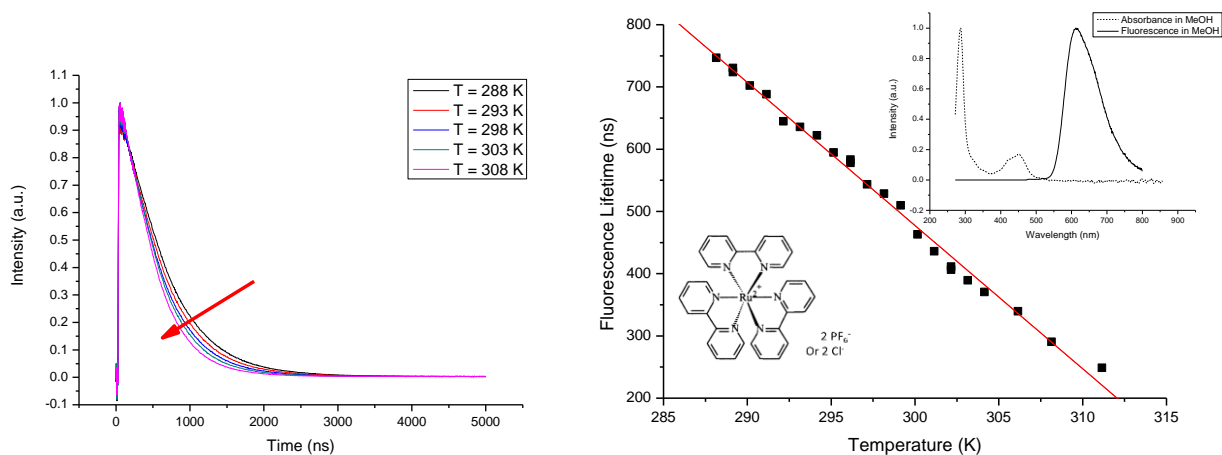


Fig S4 : Left. Fluorescence decay of a solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ in Methanol for different temperatures. Right. Calibration curves showing the fluorescence lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ in methanol versus the temperature. Linear regression: $Y = A + B \cdot X$; $R = -0.996$; $A = 7379.7955 \pm 142.8738$; $B = -23.00829 \pm 0.48099$

Inset : (top) absorbance and fluorescence spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bottom) Chemical Structure of $[\text{Ru}(\text{bpy})_3]^{2+}$

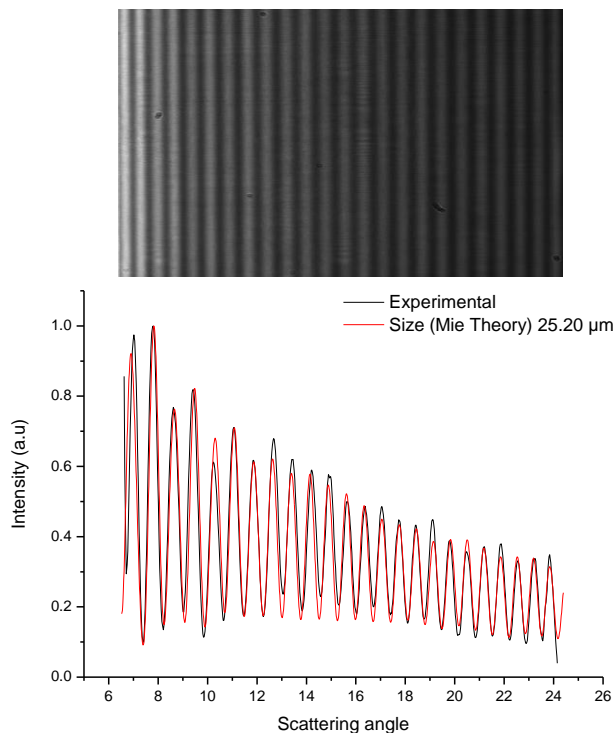


Fig S5 : Images of fringes resulted from the Mie scattering of the laser beam by micro-droplets of water. Projection of the intensity of the scattered light regarding the scattering angle (black curve) and comparison with the simulation (red curve) using Mie theory. Droplets are produced by a droplet generator.

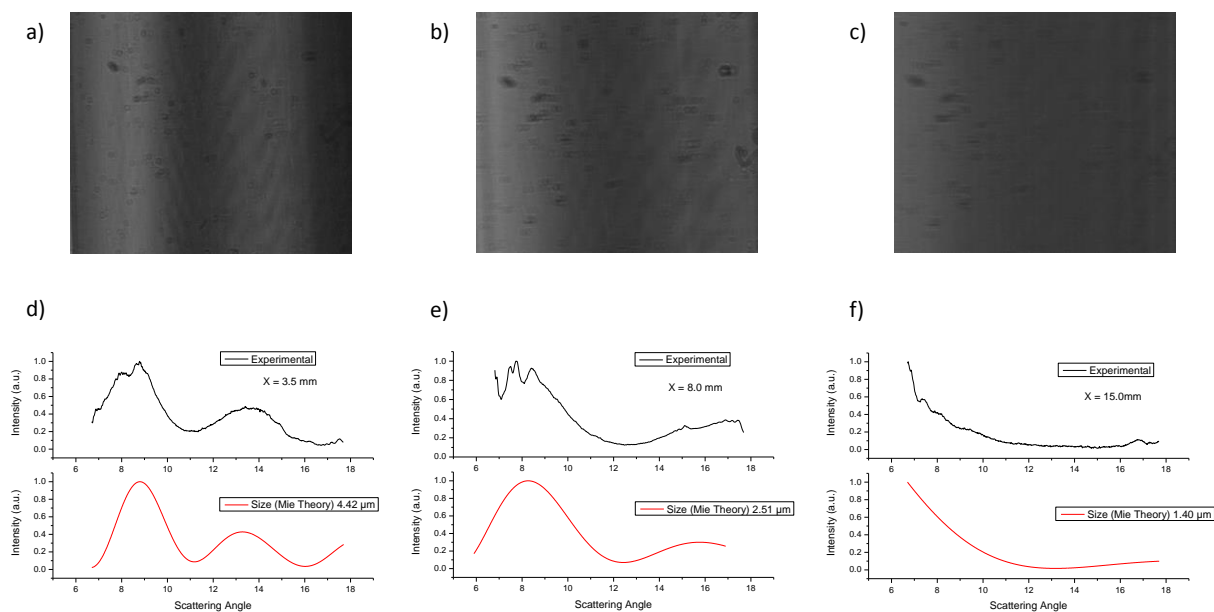


Fig S6 : (a), (b), (c), Images of fringes resulted from the Mie scattering of the laser beam by the micro-droplets at several locations (X,Y) at the edge of the ESI plume. (d), (e), (f), Respective projection of the intensity of the scattered light as a function of the scattering angle (black curve) and comparison with the simulation (red curve) using Mie theory. Droplets are produced by spraying a mixture of Rhodamine 110 at $0.2 \mu\text{M}$ and Rhodamine B at $2 \mu\text{M}$ in methanol (SGT = 423 K, SGF = 3L/min).

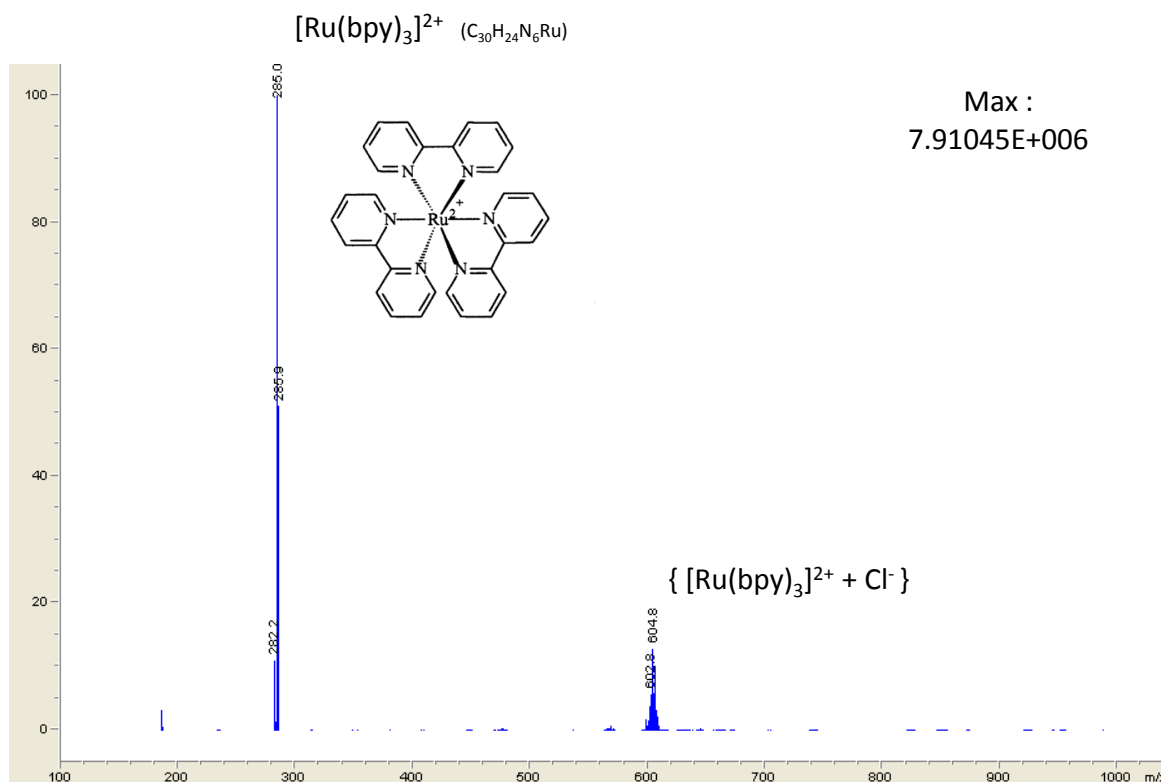


Fig S7 : Positive ion mode ESI-MS spectrum of 1×10^{-4} M $[\text{Ru}(\text{bpy})_3]^{2+}$ in MeOH. An ion count of 7.91×10^6 is measured.

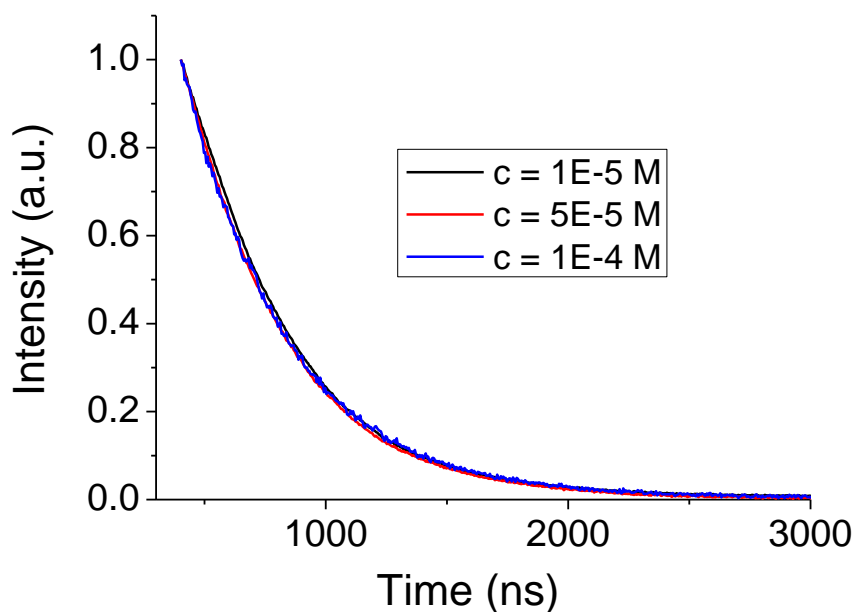


Fig. S8 : Typical Fluorescence decay of a solution of [Ru(bpy)₃]²⁺ in methanol for three different concentrations of dye.

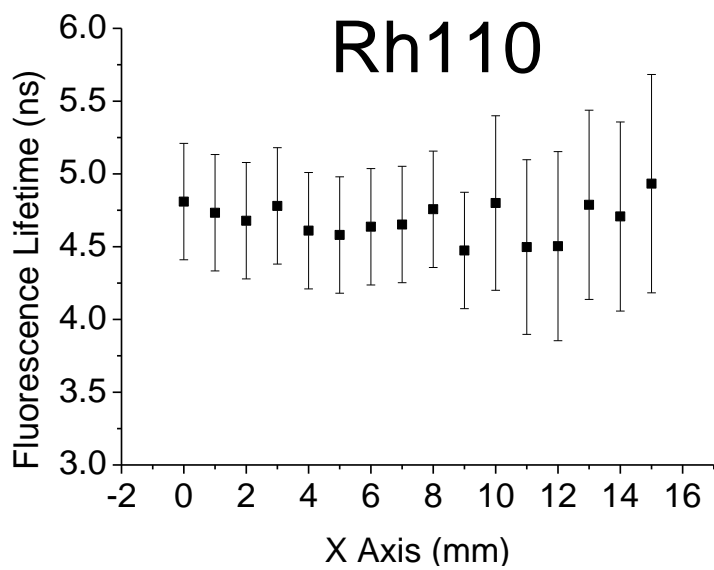


Fig. S9 : Fluorescence lifetime of rhodamine 110 in methanol recorded along the center of the spray

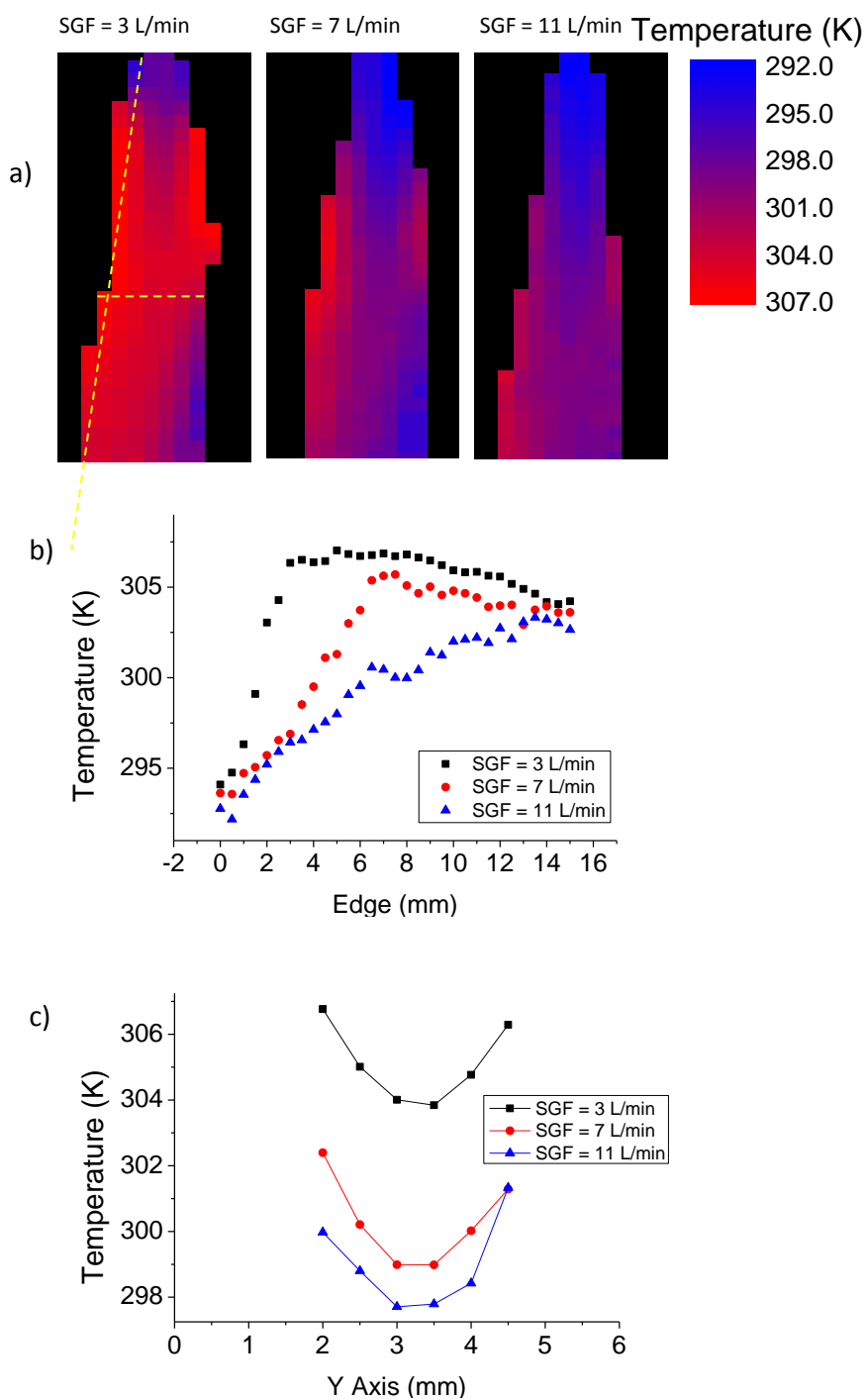


Fig. S10 : a) XY profiles from Time-Resolved Fluorescence of a solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ at 0.1 mM in methanol (SGF = 7 L/min, SGF = 7 L/min) for three different sheath gas flow rates. (b) Axial temperature profiles at the edge of the spray and (c) lateral temperature profile at X = 7.5 mm.

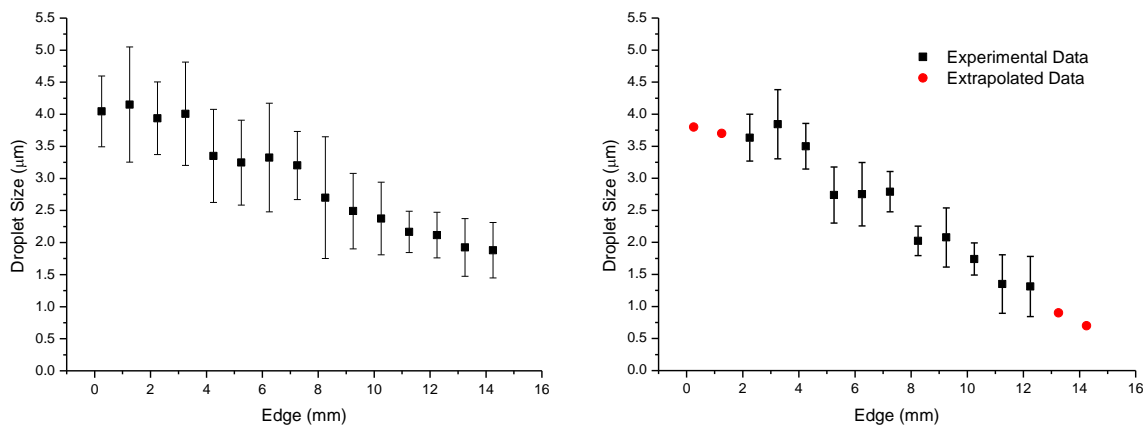


Fig. S11 : Droplet size along an edge of the ESI plume recorded from (left) a methanol (SGT = 423 K, SGF = 7 L/min) and from (right) a methanol solution (SGT = 523 K, SGF = 7 L/min)

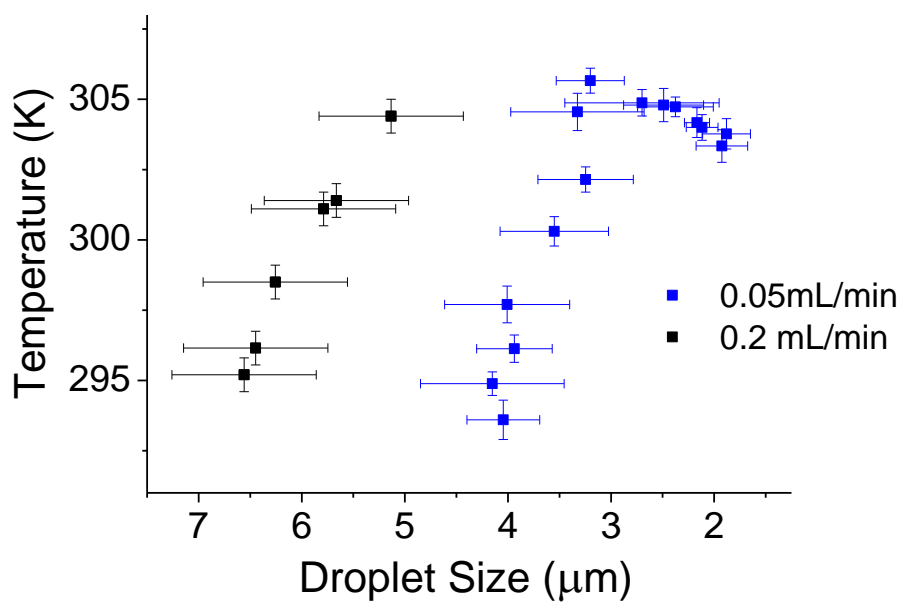


Fig. S12 : Correlation between the temperature and the droplet size along an edge of the ESI plume for methanol (SGT = 423 K, SGF = 7L/min) for two different sampling flow rates.

Modeling: Diffusion Controlled Evaporation Model

Davies, C. N. *Evaporation of Airborne Droplets*. In *Fundamentals of Aerosol Science*; Shaw, D. T., Ed.; Wiley-Interscience: New York, 1978; pp 135–164.

Stephen C. Gibson, Charles S. Feigerle, and Kelsey D. Cook, *Fluorometric Measurement and Modeling of Droplet Temperature Changes in an Electrospray Plume*, dx.doi.org/10.1021/ac402364g, *Anal. Chem.* 2014, 86, 464–472

Condition for the Diffusion Controlled Evaporation Model (DCEM) or Surface Controlled Evaporation Model (SCEM):

Surface controlled Evaporation Model for

$$a < a_c = \frac{4\lambda}{3\alpha} \sim 0.1\mu\text{m}^*$$

α evaporation coefficient
(*For methanol in Cook's conditions ~ 0.9)

λ mean free path of vapor molecules
(*In Cook's conditions $\sim 0.06\ \mu\text{m}$)

The evolution of the temperature at the surface of an evaporating droplet can be expressed for the DCEM as:

$$dT_a = \frac{3}{a^2 \rho' c_m'} \frac{\delta X}{v} \left\{ k(T_\infty - T_a) - l'D \frac{M}{R_m} \left(\frac{P_a}{T_a} - \frac{P_\infty}{T_\infty} \right) \right\}$$

Indeed, for the evaporation process of a droplet in a heated surrounding medium, r two major phenomena have to be considered : the **conduction**, i.e. the heat transfer from the surrounding medium to the liquid (when the temperature of the surrounding medium is greater than the temperature of the droplet) and the **evaporation** of the droplet (endothermic transition). If we assume the quasi-steady state conditions, over a short time period, the evolution of the temperature is given by

$$dT_a = \frac{|Heat\ transfer\ from\ conduction| - |Heat\ transfer\ from\ evaporation|}{mc_m'}$$

CONDUCTION:

The heat flux density (J_{cond}) is given by the first Fick's law:

$$\overrightarrow{J_{cond}} = -k \overrightarrow{grad}(T)$$

The heat flux density can be seen as the time derivative of the conductive heat over the surface of the droplet, and considering the geometry of the system,

$$\left| \frac{\dot{Q}_{cond}}{S} \right| = k \left(\frac{\partial T}{\partial r} \right)_a$$

In order to evaluate the derivative in the right hand-side, we can give the second Fick's law:

$$\frac{\partial T}{\partial t} = \frac{k}{c_m \rho} \left(\frac{2}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right)$$

Near the surface of the droplet (steady state condition): $\frac{\partial T}{\partial t} = 0$ then,

$$\frac{\partial T}{\partial t} = k \left(\frac{2}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) = 0 \Rightarrow \frac{2}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} = 0 \Rightarrow \frac{\partial T}{\partial r} = \frac{A}{r^2}$$

$$\int_{T_a}^{T_\infty} dT = \int_a^\infty \frac{A}{r^2} dr$$

$$(T_\infty - T_a) = \left[-\frac{A}{r} \right]_a^\infty = \frac{A}{a}$$

$$\frac{\partial T}{\partial r} = \frac{a(T_\infty - T_a)}{r^2}$$

$$\left(\frac{\partial T}{\partial r} \right)_a = \frac{1}{a} (T_\infty - T_a)$$

So that:

$$\delta Q_{cond} = Sk \frac{1}{a} (T_\infty - T_a) \delta t = 4\pi ak (T_\infty - T_a) \frac{\delta X}{v}$$

EVAPORATION:

Mass flux density (j_{mass}) is given by the first Fick's law:

$$\overrightarrow{j_{mass}} = -D \overrightarrow{grad}(c)$$

Similarly,

$$\left| \frac{\dot{Q}_{evap}}{S} \right| = \left| \frac{l\dot{m}}{S} \right| = -lD \left(\frac{\partial c}{\partial r} \right)_a$$

The second Fick's second law gives

$$\frac{\partial c}{\partial t} = D \left(\frac{2}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right)$$

Near the surface of the droplet (steady state condition): $\frac{\partial c}{\partial t} = 0$ and perfect gas hypothesis

$$\left(\frac{dc}{dr}\right)_a = \frac{1}{a}(c_\infty - c_a) = \frac{M}{aR_m} \left(\frac{P_\infty}{T_\infty} - \frac{P_a}{T_a}\right)$$

So that:

$$\delta Q_{evap} = -SlD \frac{M}{aR_m} \left(\frac{P_\infty}{T_\infty} - \frac{P_a}{T_a}\right) \delta t = -4\pi a l D \frac{M}{R_m} \left(\frac{P_\infty}{T_\infty} - \frac{P_a}{T_a}\right) \frac{\delta X}{v}$$

Finally:

$$dT_a = \frac{|\delta Q_{cond}| - |\delta Q_{evap}|}{\frac{4}{3}\pi a^3 \rho' c_m'}$$

$$dT_a = \frac{3}{a^2 \rho' c_m'} \frac{\delta X}{v} \left\{ k(T_\infty - T_a) - l'D \frac{M}{R_m} \left(\frac{P_a}{T_a} - \frac{P_\infty}{T_\infty}\right) \right\}$$

Table SI parameters used for computation:

| | Description | Notes | Value | Expression | Unit |
|---------------|---|--|----------------------------|---|--------------------|
| a | Radius of the droplet | Experimental, polynomial fit | | | |
| c | Vapor concentration by mass at $r = a$ | | | | |
| c_m' | Specific heat of the liquid phase | Fixed | 2531 | | J/kg/K |
| D | Diffusion coefficient of the surrounding gas | Geometrical mean, T-dependent | $\sqrt{D(T_a)D(T_\infty)}$ | $D(T) = D(T_r) \left(\frac{T}{T_r}\right)^{1.81}$ | cm ² /s |
| k | Thermal conductivity of surrounding gas | Extrapolation, geometrical mean, T-dependent | $\sqrt{k(T_a)k(T_\infty)}$ | | W/m/K |
| l' | Latent heat of vaporization of liquid | T-dependent | | $l'(T) = l'_0 e^{-\alpha \frac{T}{T_c}} \left(1 - \frac{T}{T_c}\right)^\beta$ | |
| m | Mass of the droplet | | | | |
| M | Molecular weight | | 32.04 | | g/mol |
| P_a | Partial vapor pressure of methanol at $r = a$ | T-dependent, Antoine equation | | $10^{\left(A - \frac{B}{C + (T - 273.15)}\right)}$ | Torr |
| P_∞ | Partial vapor pressure of methanol | Fitting parameter | 423 K : 130 523 K : 110 | | Torr |
| R_m | Perfect gas constant | | 8.3144621 | | J/mol/K |
| S | Surface of the droplet | | | | |
| T_∞ | Temperature of the surrounding gas | Sheath gas temperature | | | |
| $T_{ambient}$ | Room temperature | | | | |
| T_a | Temperature of the droplet at $r = a$ | | | | |
| v | Velocity of the droplet | Fixed | 2 | | m/s |
| X | Position of the droplet along the vertical axis | | | | |
| δX | Increment distance | | 0.25 | | μm |
| ρ' | Density of the liquid phase | Fixed | 791.4 | | kg/m ³ |

For Methanol with Nitrogen as surrounding gas:

$$k(T) = 0.00478 + 6.92696 \cdot 10^{-5} \times T - 6.47038 \cdot 10^{-9} \times T^2$$

$$D(T_r = 298.15 \text{ K}) = 0.155$$

$$I'_0 = 45.3 \quad \alpha = -0.3100 \quad \beta = 0.4241 \quad T_c = 512.6 \text{ K}$$

$$A = 8.0809, B = 1582.27, C = 239.7$$