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DE LA RECHERCHE À L'INDUSTRIE



Near-field laser ablation for surface nano-analysis: modeling and experiments

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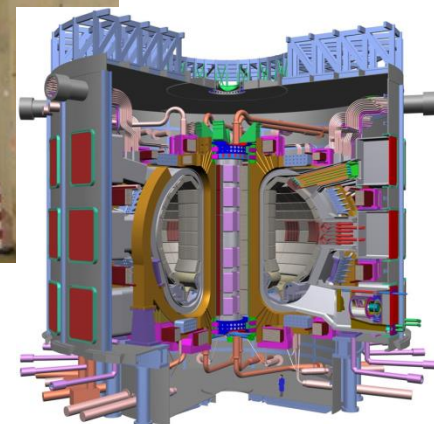
³ *Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Moscow region, Russia*

⁴ *SPEC, CNRS, CEA, Université Paris-Saclay, F-91191, Gif sur Yvette, France*

FLAMN-2019, Saint Petersburg, Russia 01 - 04 July, 2019

- **Surface Cleaning and Decontamination:**

- paint on concrete;
- metals;
- laser detritiation for ITER (heating and ablation);



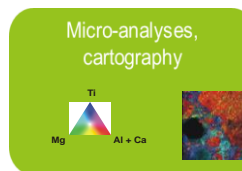
- **Surface Improvement and Micro-Processing:**

- material durability by rapid laser heating (corrosion resistance);
- laser projection of powder (3D-printing);
- micro-gravure (micro-systems);



- **Analytical Methods:**

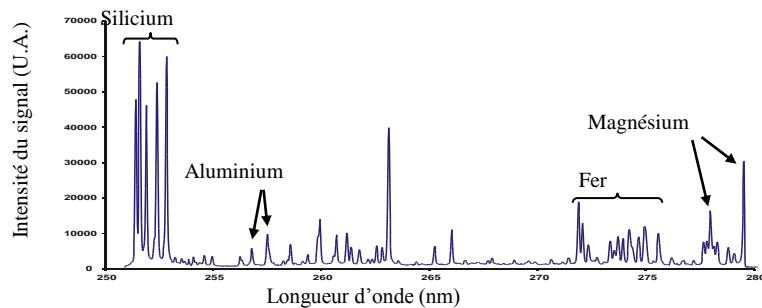
- LIBS (elemental bulk- and μ -analysis):
 - ✓ in nuclear environment (portable LIBS);
 - ✓ in situ purity control of liquid sodium;
 - ✓ on-line analysis of liquid glasses (wastes);
 - ✓ elemental μ -cartography;
- ChemCam for the Mars exploration;
- Active laser pyrometry (layer thickness, resistance, conductivity, etc);
- Lock-in Thermography for characterization of nuclear materials;
- **Near-Field Laser Ablation – ICP MS**



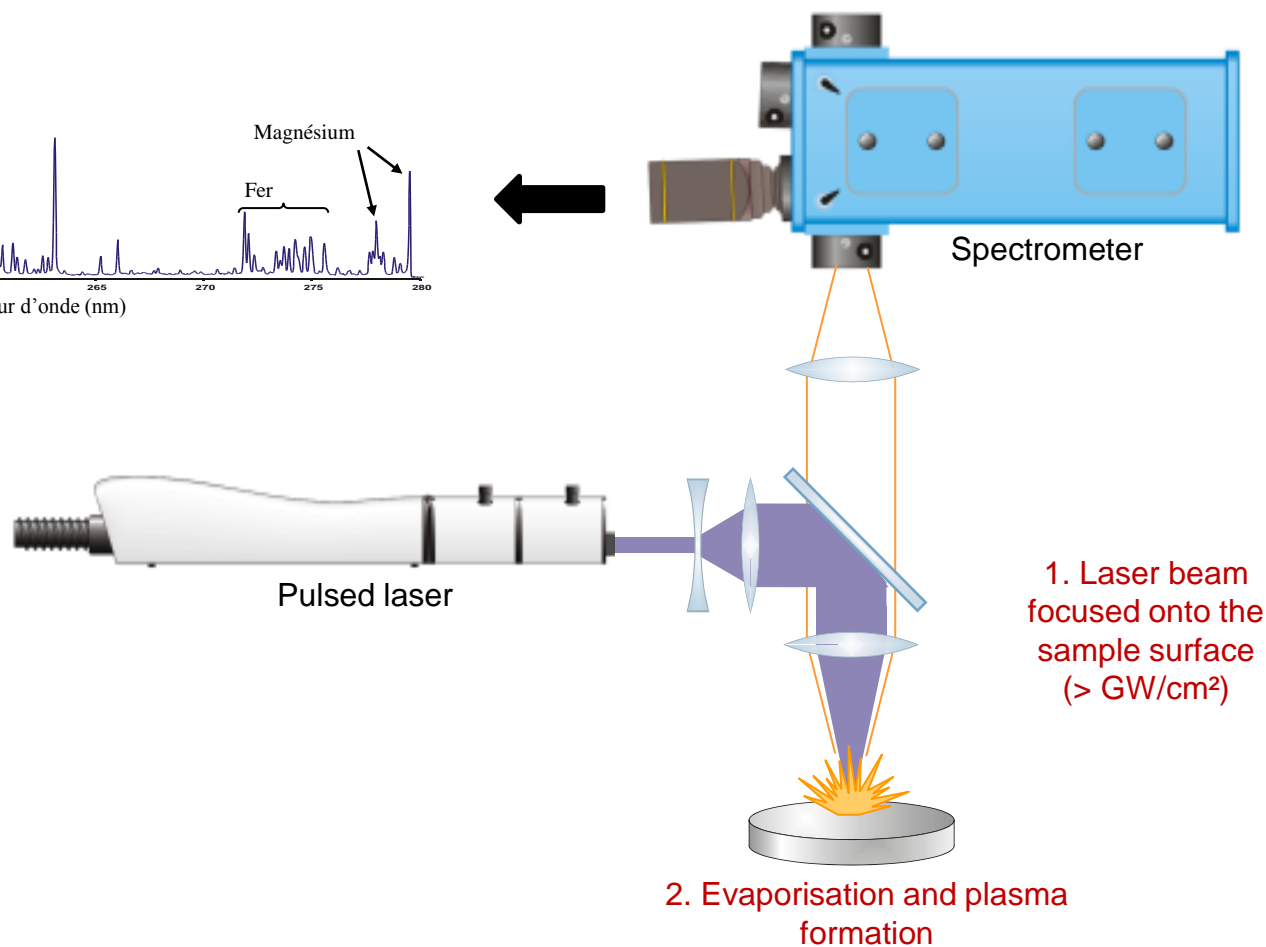
Surface cartography with micrometric and nanometric resolution

(elemental and isotopic analysis)

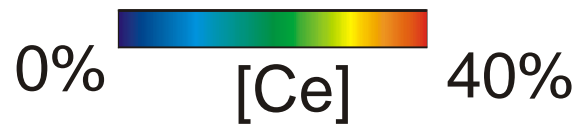
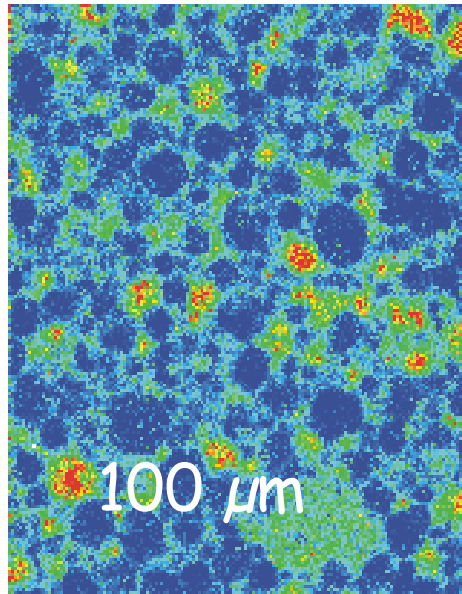
4. Identification and quantification of elements



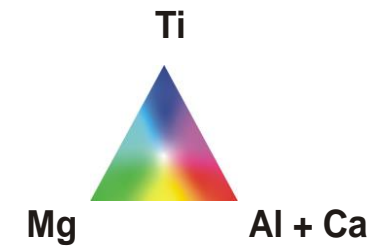
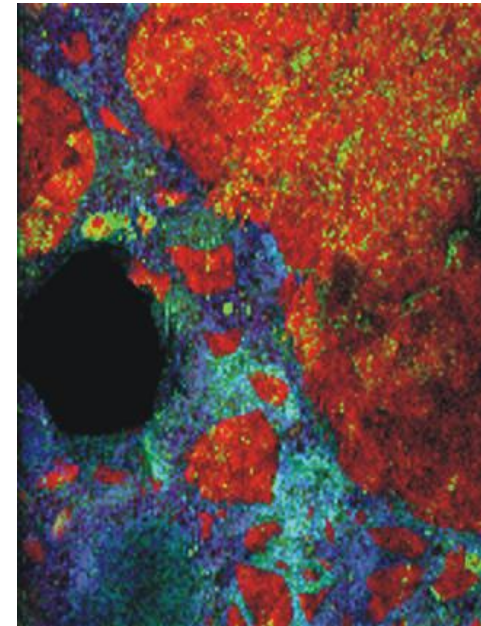
3. Plasma emission spectrum recording



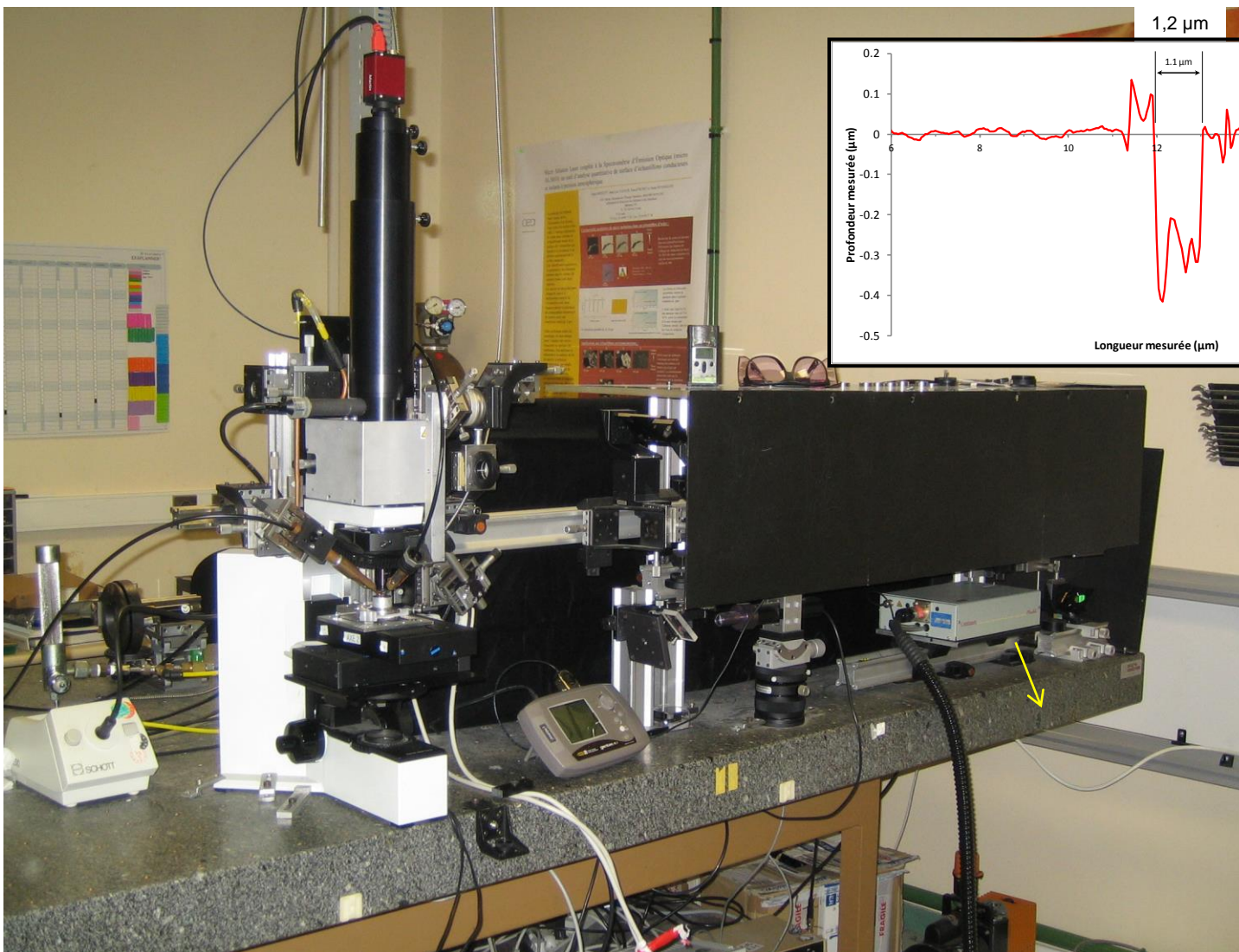
MOX pellet



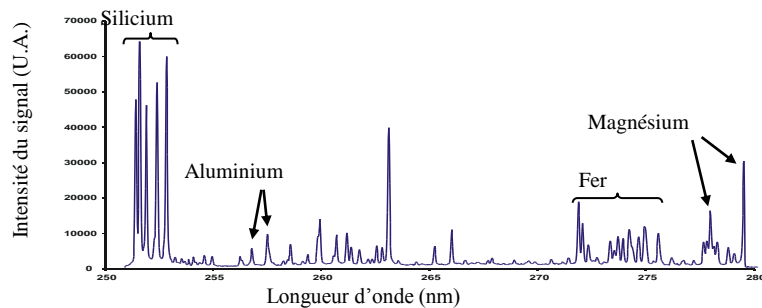
Concrete



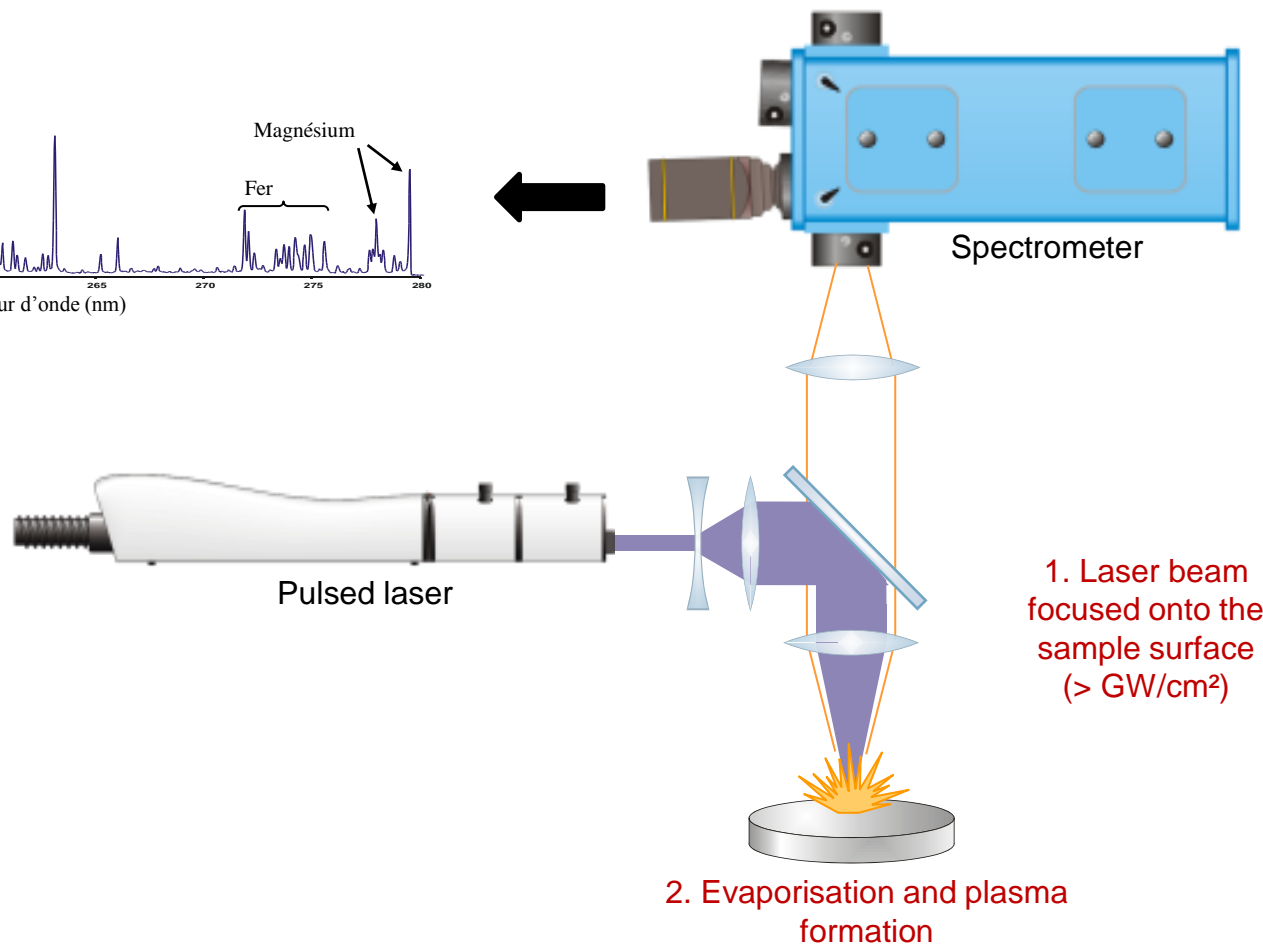
CEA Saclay micro-LIBS



4. Identification and quantification of elements

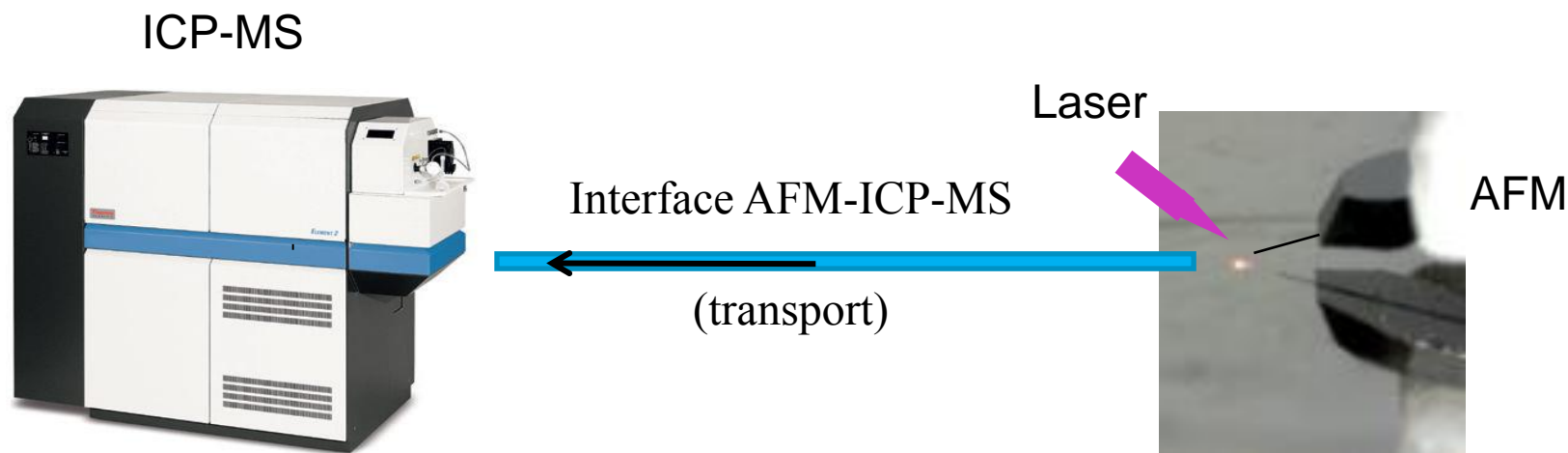


3. Plasma emission spectrum recording



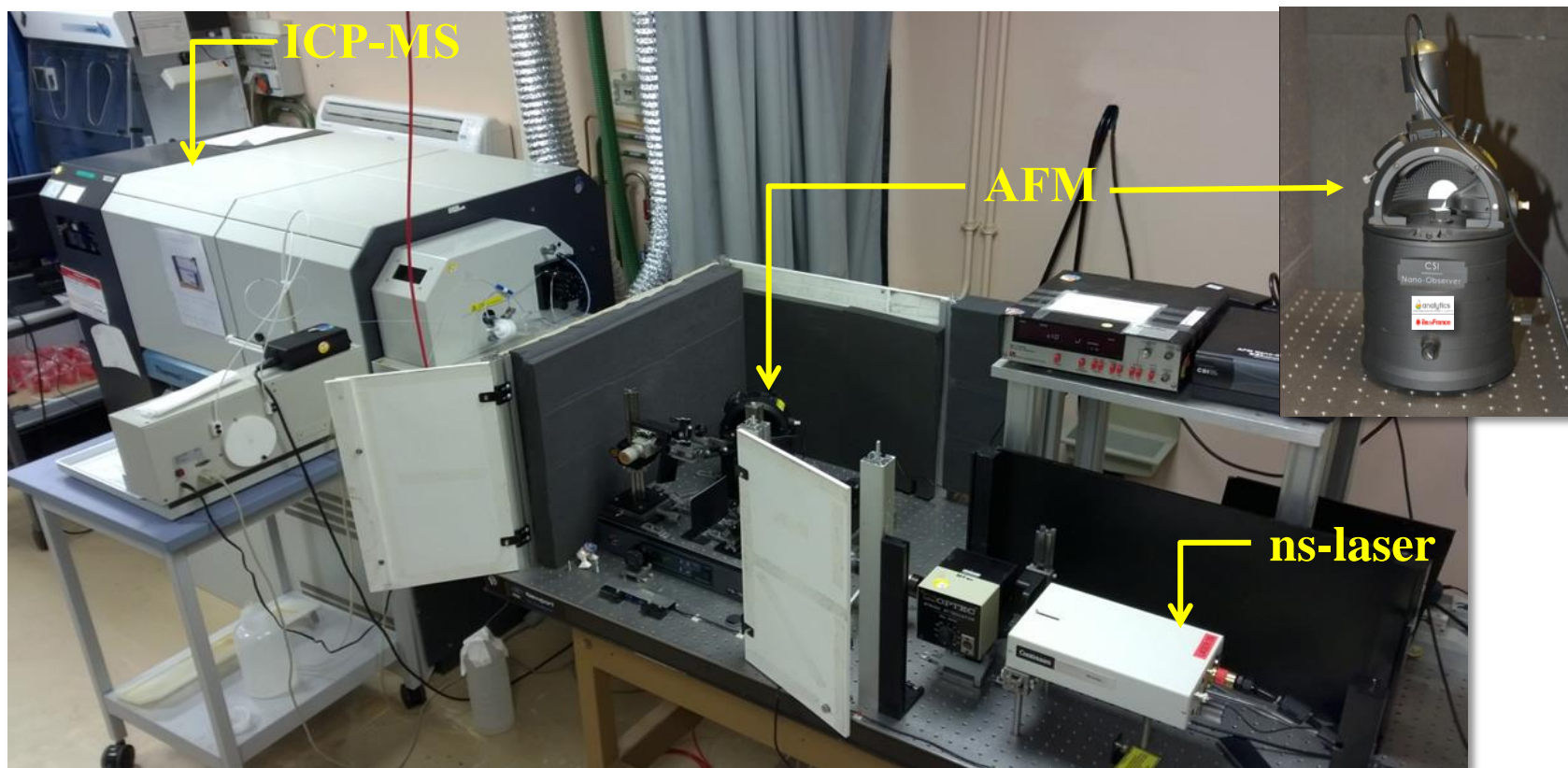
Surface cartography (10-100 nm resolution)

AFM-ICP-MS development



- 1. Near-field enhancement**
- 2. Near-field laser ablation**
3. Ablated matter transport to ICP-MS
4. MS-detection

Experimental installation

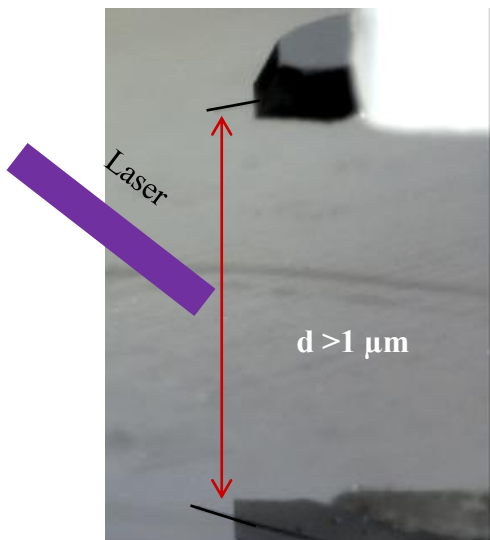


Laser Nd:YAG (266 nm) , 4 ns pulse duration.

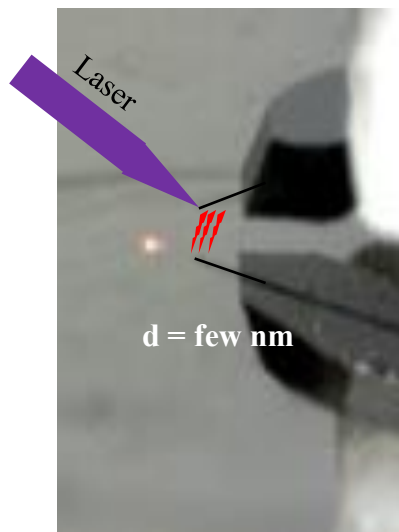
AFM: Atomic Force Microscope.

ICP-MS: Inductively Coupled Plasma - Mass Spectrometry : double-focusing sector field

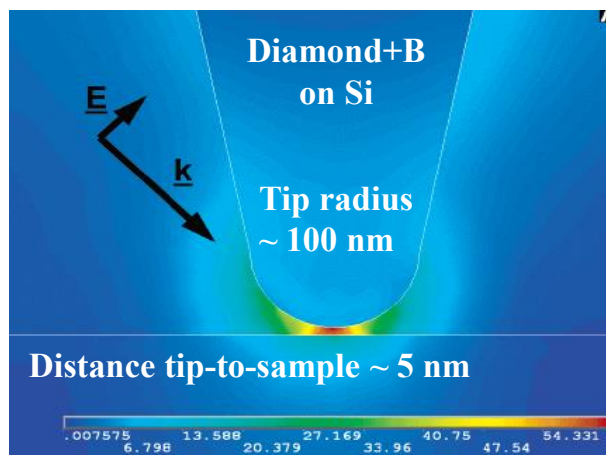
Near-field Laser Ablation



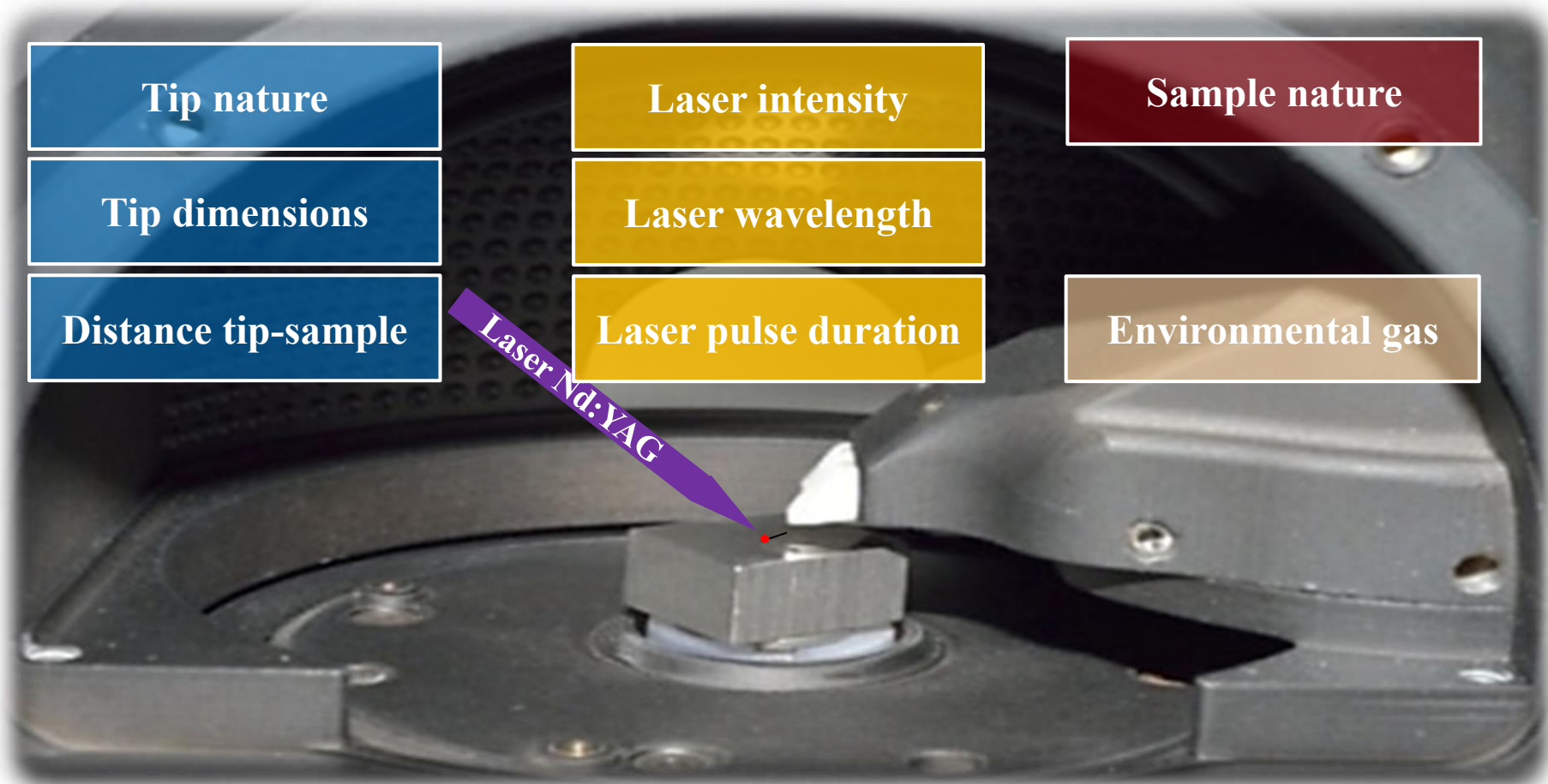
No tip enhancement effect
(no ablation)



Laser energy enhancement
(near-field ablation)



Multi-parametric study



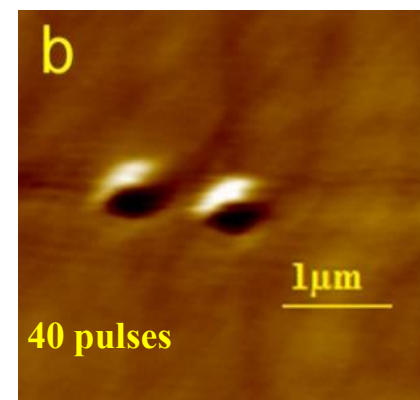
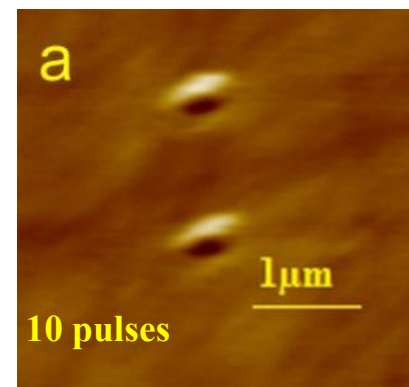
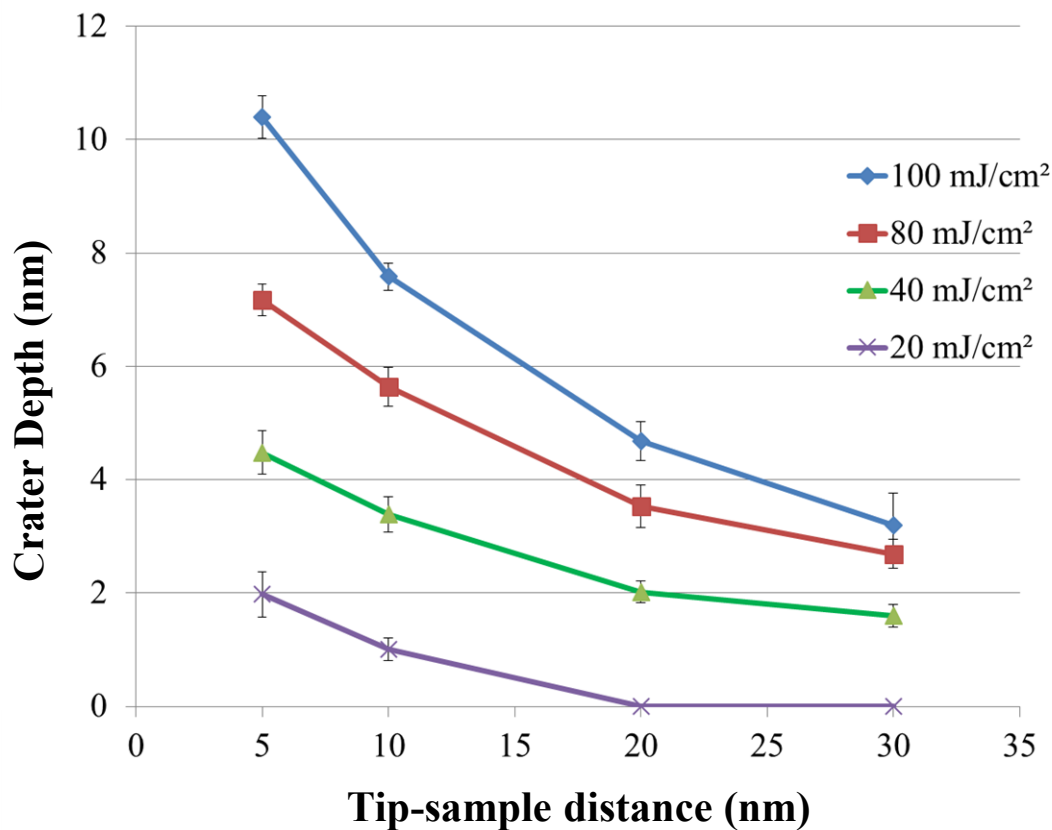
Parameters affecting the near-field ablation efficiency
and craters dimensions (ablated mass amount)

Experimental results (with Au)

Tip-sample distance and laser irradiance effects on the craters dimensions

$\lambda_{laser} = 266 \text{ nm}$, $\tau = 4 \text{ ns}$, 80 mJ/cm^2 ,
Tip-sample distance: 5 nm

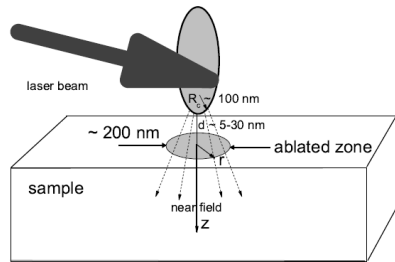
(single laser pulse)



Sampling mass ~ 1 fg / pulse

Modeling of near-field distribution and ablation

$$I_{NF}(x, y, z, t) \Rightarrow T_{\text{Sample}}(x, y, z, t) \Rightarrow \text{ablation rate}$$



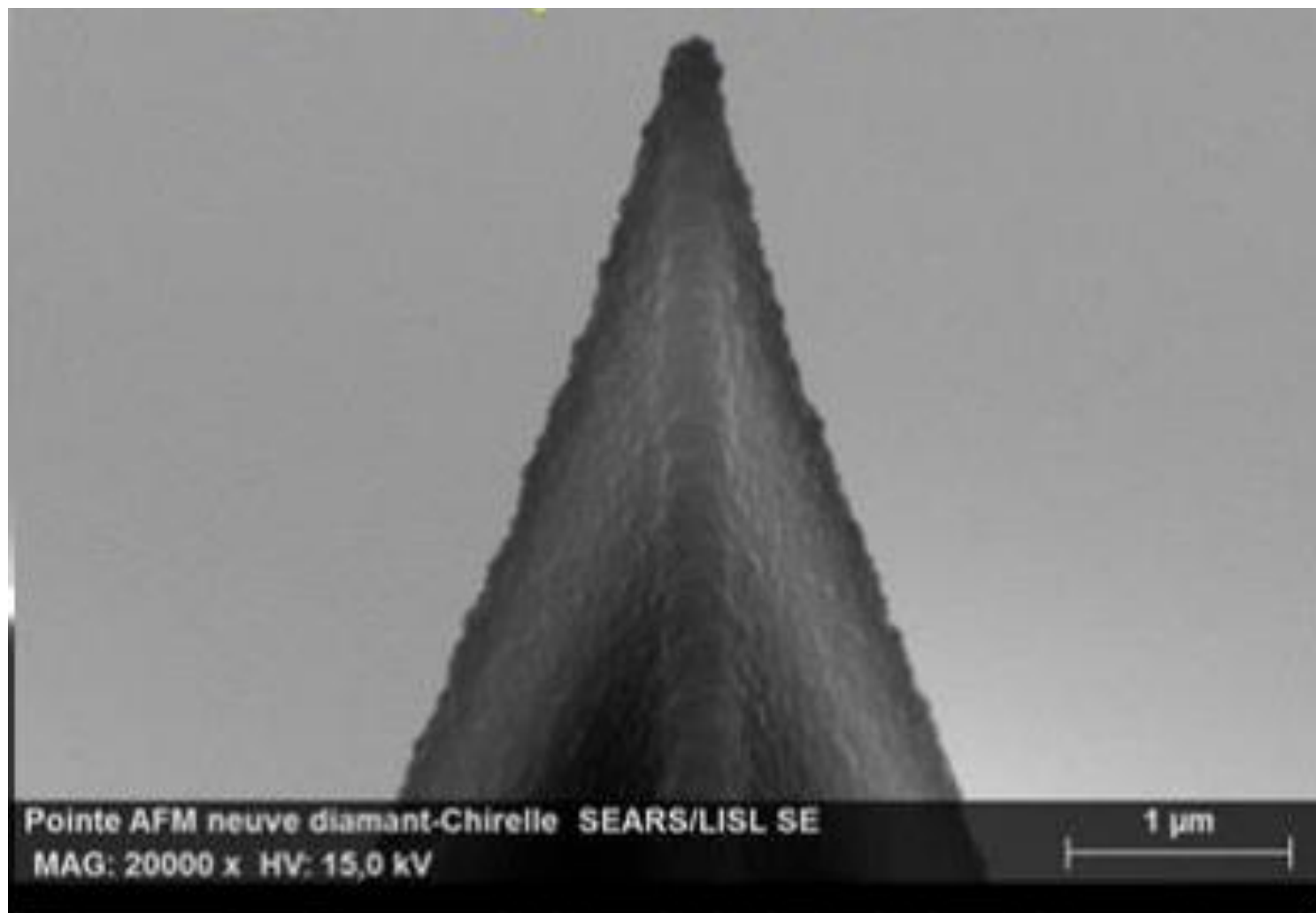
Two-temperature model

$$\begin{aligned} c_e \frac{\partial T_e}{\partial t} &= \text{div}(k_e \nabla T_e) - \beta(T_e - T_i) + Q \\ c_i \frac{\partial T_i}{\partial t} &= \text{div}(k_i \nabla T_i) + \beta(T_e - T_i) \end{aligned}$$

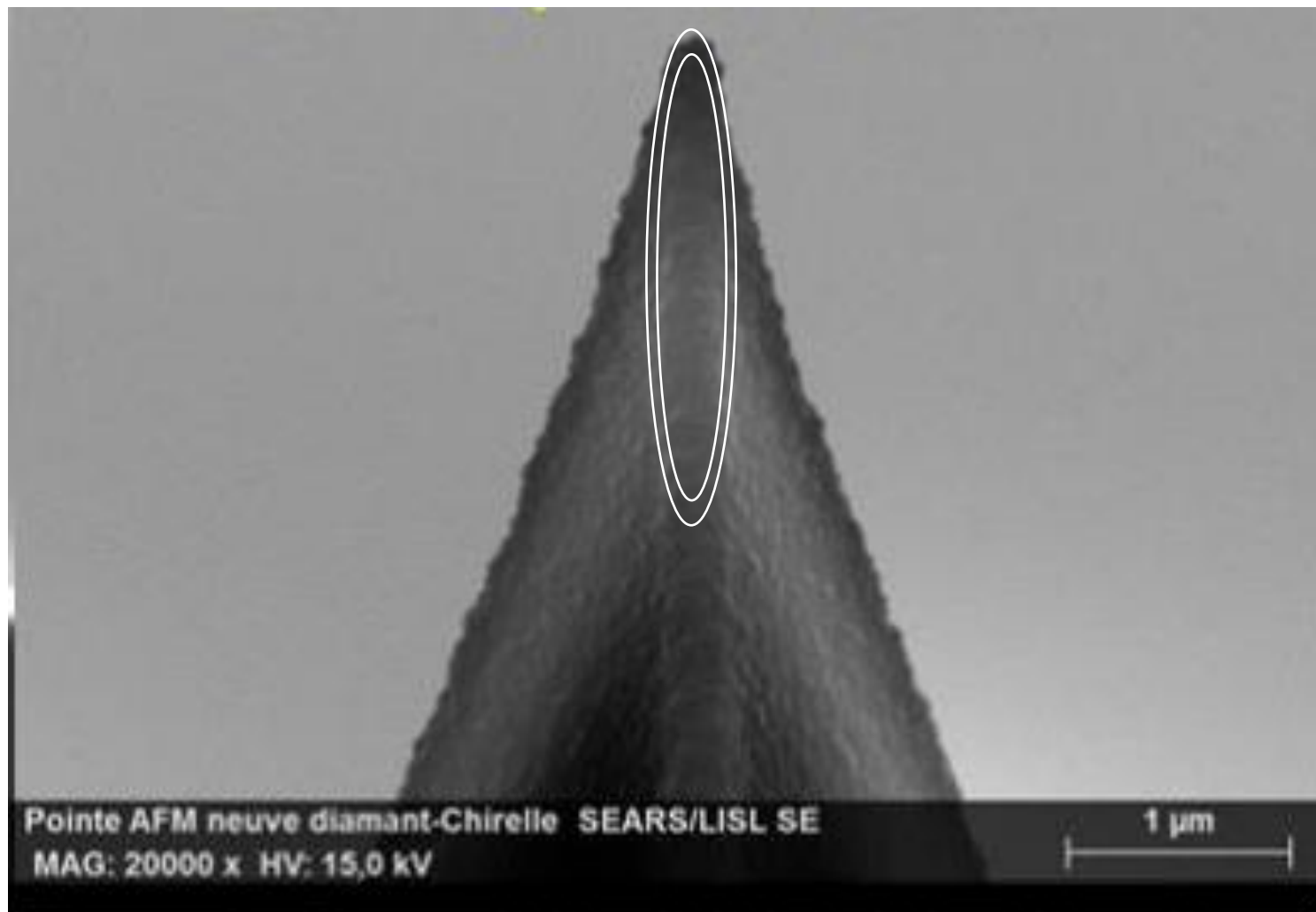
Q – from near-field calculation

$$\begin{aligned} k_i(T_b) \frac{\partial T_i(t, r, z)}{\partial z} \Big|_{z=z_{abl}(t, r)} &= \rho \Delta H V_{abl}(t, r), \\ \frac{\partial T_e(t, r, z)}{\partial z} \Big|_{z=z_{abl}(t, r)} &= 0. \end{aligned}$$

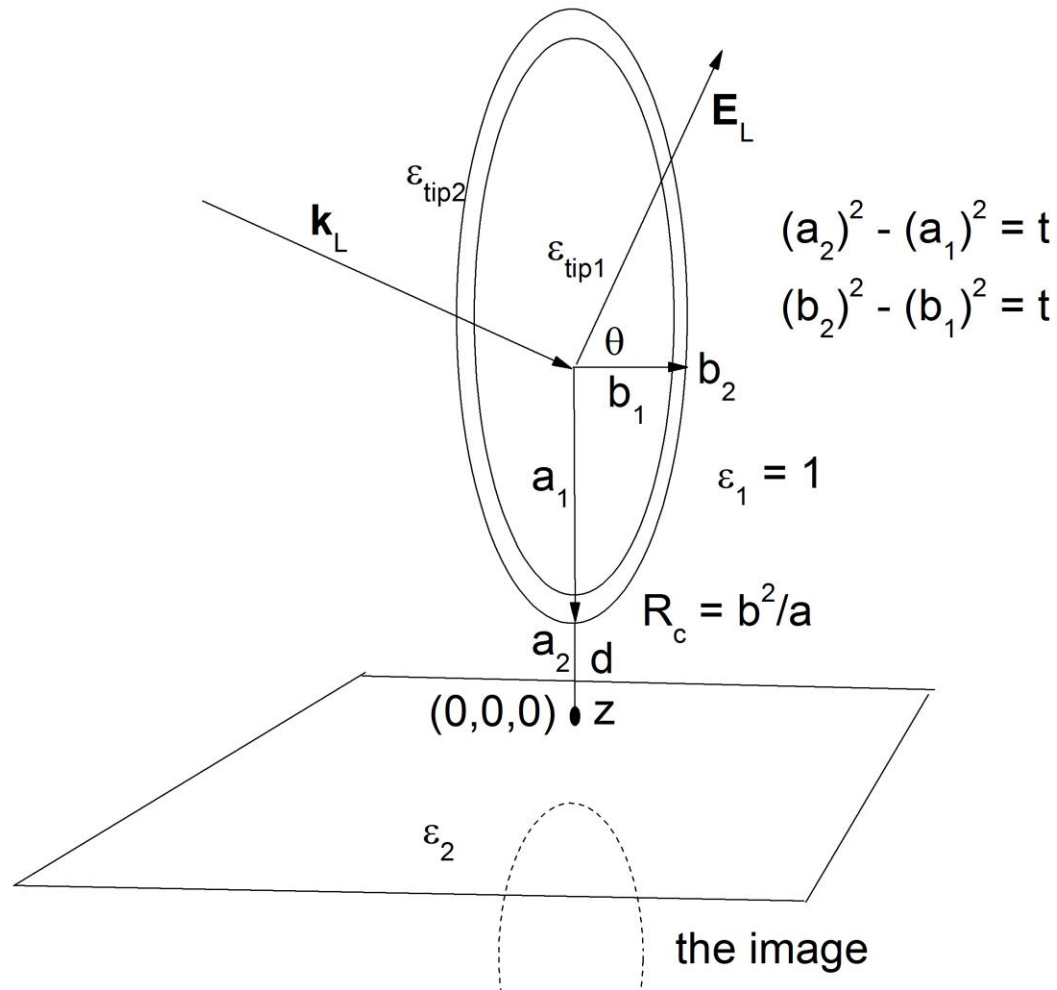
Si-tip of AFM with diamond cladding



Si-tip of AFM with diamond cladding



Near-field model for ellipsoidal tip with coating



Near-field model for ellipsoidal tip with coating (electrostatic approximation)

In the electrostatic approximation, the equations that describe the near electric field inside the medium under study (the medium 2) from the ellipsoid with a coating have the form:

$$E_x = -\frac{\partial\varphi}{\partial x}, \quad E_y = -\frac{\partial\varphi}{\partial y}, \quad E_z = -\frac{\partial\varphi}{\partial z},$$

$$\varphi(x, y, z) = -\frac{2E_L \sin\theta \Phi_a(x, y, z)}{1 + \varepsilon_2 + (1 - \varepsilon_2)\Phi'_{az}(0, 0, a_2 + d)},$$

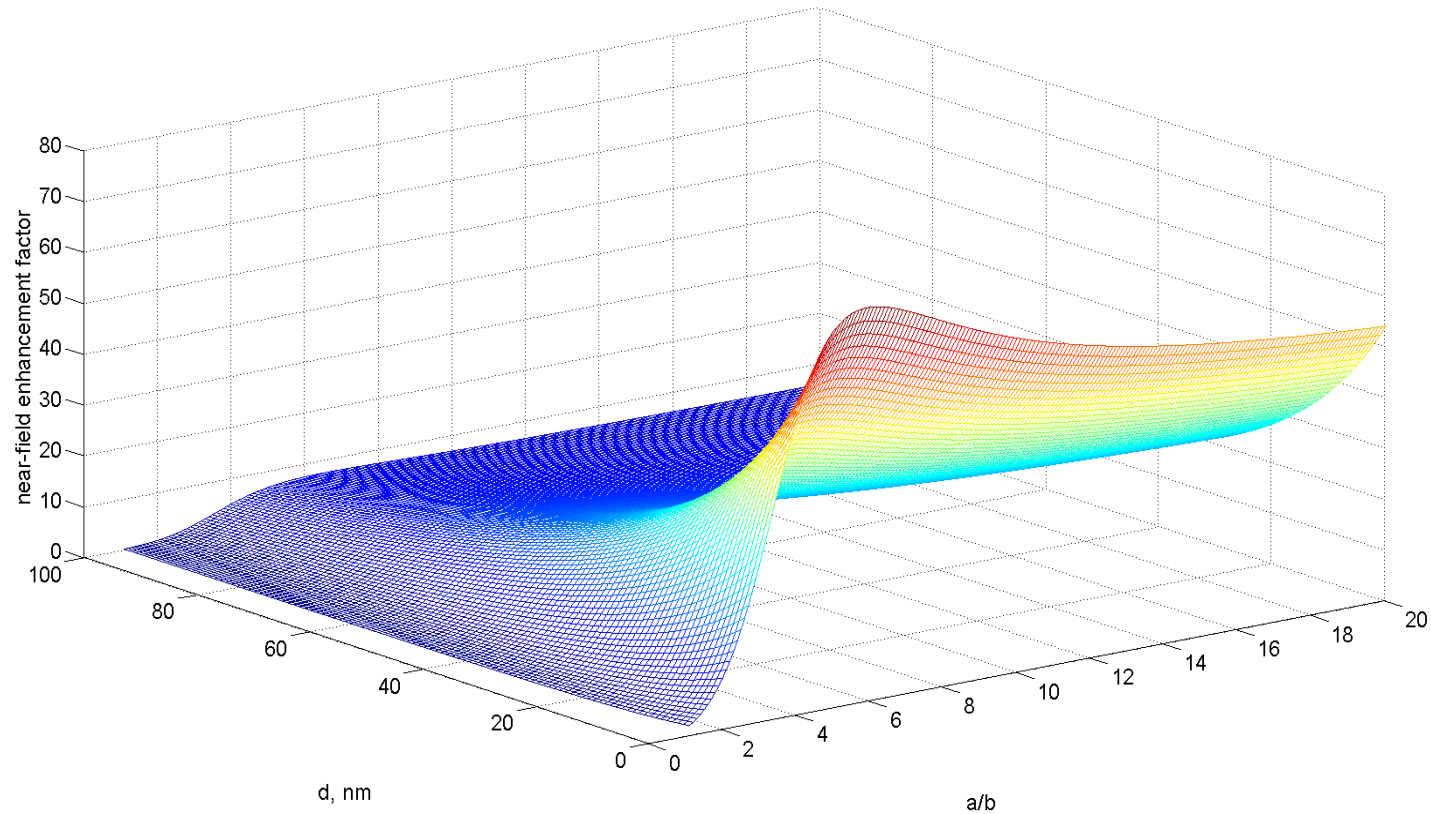
$$\Phi_a(x, y, z) = (z + a_2 + d) \frac{\frac{a_2 b_2^2}{2} (1 - Q) \int_{\xi}^{\infty} \frac{dq}{(b_1^2 + q)(a_1^2 + q)^{3/2}}}{1 - \frac{a_2 b_2^2}{2} (1 - Q) \int_t^{\infty} \frac{dq}{(b_1^2 + q)(a_1^2 + q)^{3/2}}},$$

$$Q = \frac{\varepsilon_{tip2} \left(\varepsilon_{tip2} + (\varepsilon_{tip1} - \varepsilon_{tip2}) \frac{a_1 b_1^2}{2} \int_0^t \frac{dq}{(b_1^2 + q)(a_1^2 + q)^{3/2}} + (\varepsilon_{tip1} - \varepsilon_{tip2}) \frac{a_1 b_1^2}{a_2 b_2^2} \right)}{\varepsilon_{tip2} + (\varepsilon_{tip1} - \varepsilon_{tip2}) \frac{a_1 b_1^2}{2} \int_0^t \frac{dq}{(b_1^2 + q)(a_1^2 + q)^{3/2}}},$$

$$\xi = \left(\frac{r_1 + r_2}{2} \right)^2 - a_1^2, \quad r_{1,2} = \sqrt{x^2 + y^2 + (z + a_2 + d \mp \sqrt{a_1^2 - b_1^2})^2}.$$

Near-field enhancement factor

$R_c = 100$ nm, $\lambda = 266$ nm, tip = Si+Diamond(0.3), medium = Au



Enhancement factors for the near-field for some cases as functions of a distance (d) of the tip from the surface and the tip aspect ratio (a/b).

➤ BEM-method:

- is applied to solve the Maxwell equations for dielectric environment where bodies with homogeneous and isotropic dielectric functions are separated by abrupt interfaces;
- is suited, in principle, for arbitrary body sizes and photon energies;
- is best suited for metallic nanoparticles with the sizes from a few to a few hundreds of nanometers, and for frequencies in the optical and near-infrared regime;
- advantages: total surface utilisation = 2D-mesh of surfaces = rapid method / method for 3D-mesh

U. Hohenester and A. Trügler, *Comp. Phys. Commun.* **183**, 370 (2012)

U. Hohenester, *Comp. Phys. Commun.* **185**, 1177 (2014)

J. Waxenegger, A. Trügler, and U. Hohenester, *Comp. Phys. Commun.* **193**, 138 (2015)

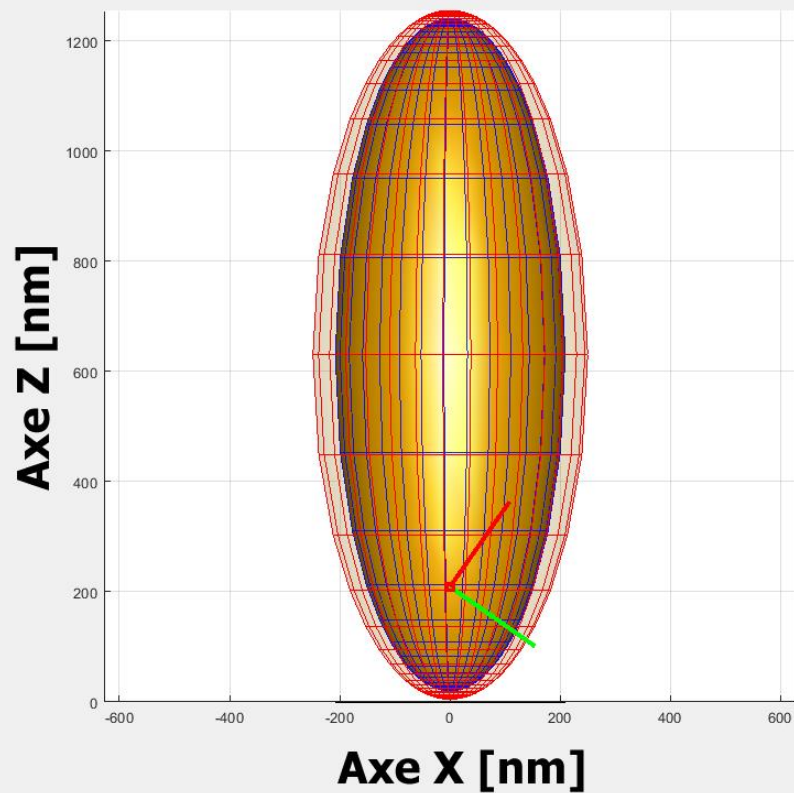
➤ **MNPBEM** - a toolbox to provide a flexible simulation toolkit for calculation of electromagnetic properties of metallic nanoparticles (MNP) by BEM-method

Current version **MNPBEM17**: developed by U. Hohenester and A. Trügler, University of Graz, Austria

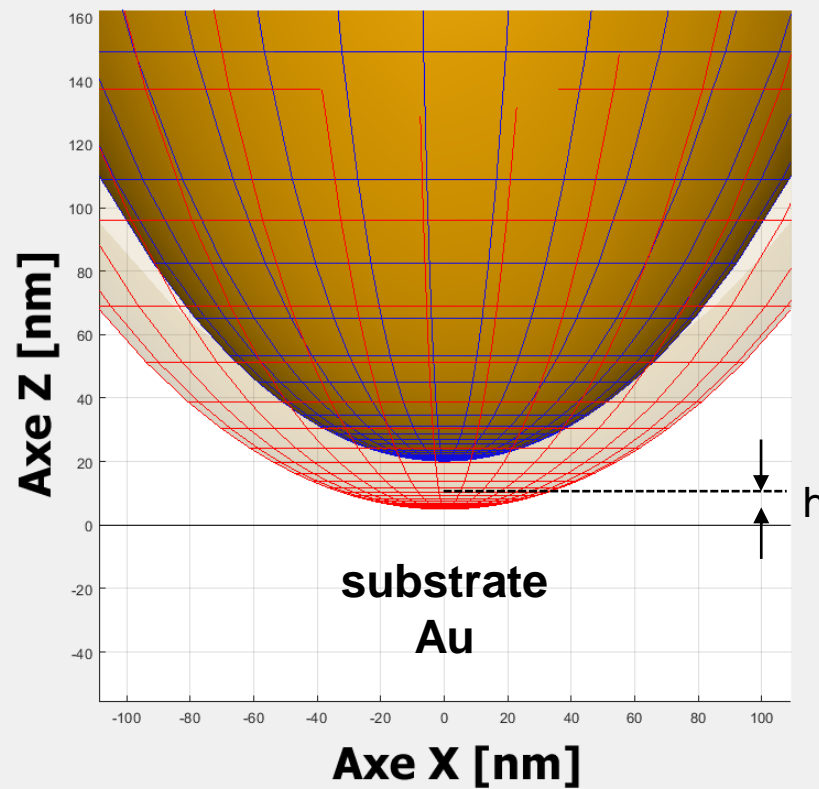
Software implementation: MATLAB, version \geq R2015b

Download: <https://physik.uni-graz.at/mnpbem/>

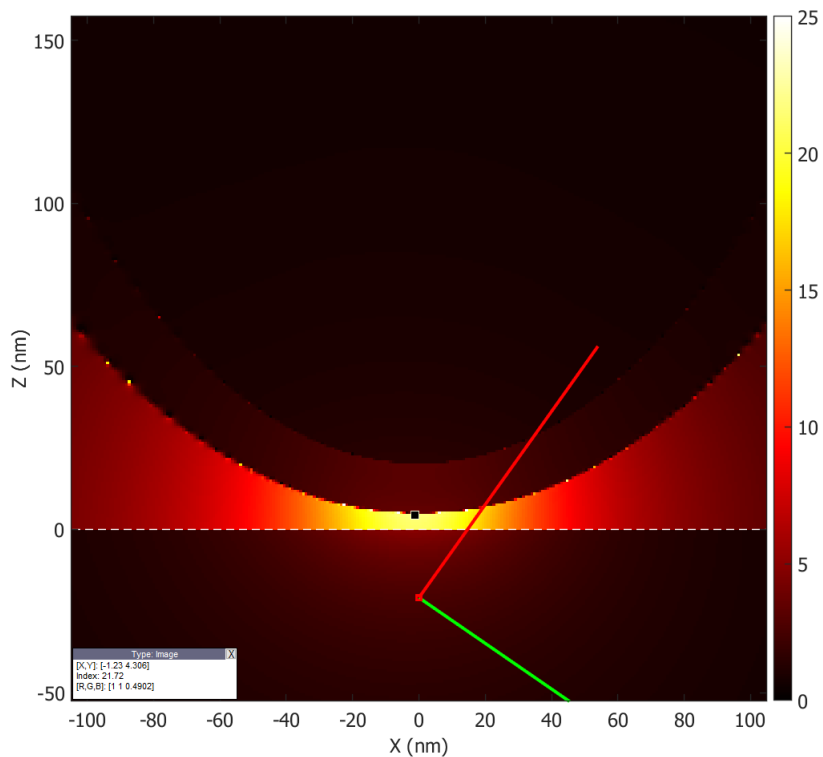
Géométrie Ellipsoïdes Concentriques



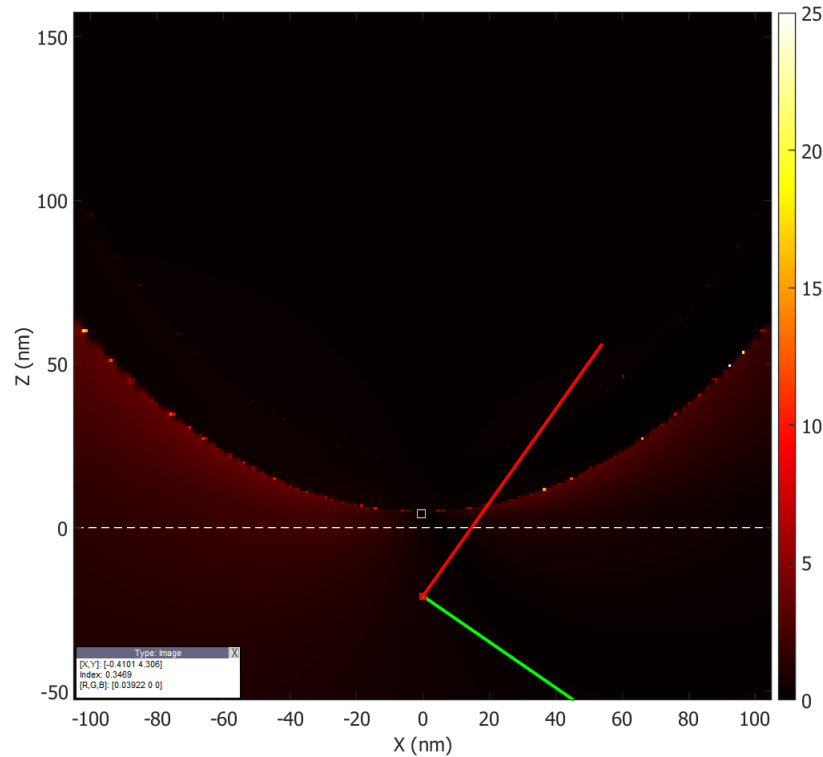
Geometrie Pointe



Ellipsoïde - Module du champ électrique, composante Ez - STAT

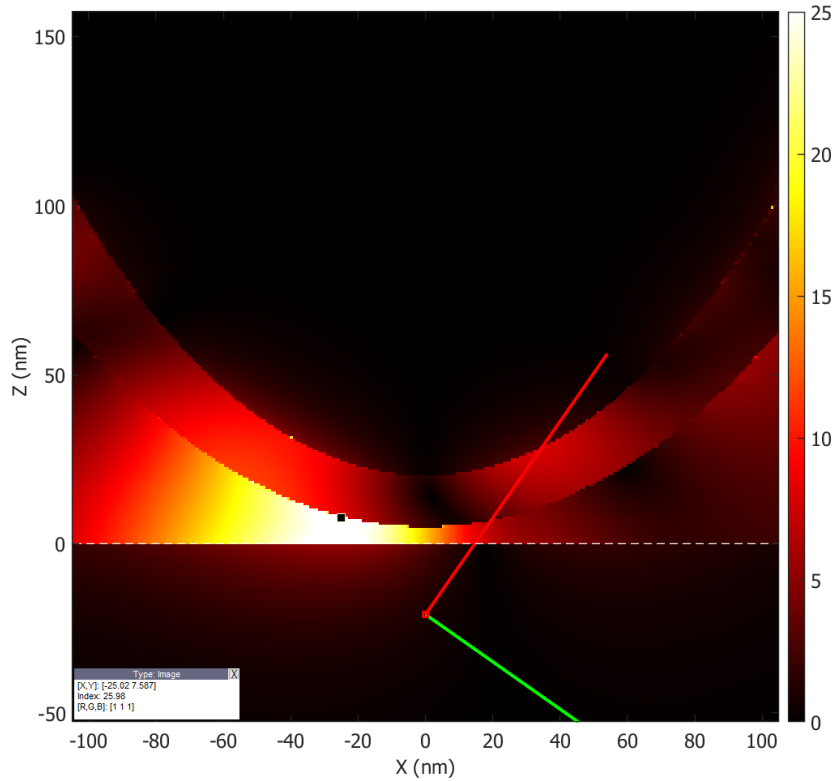


Ellipsoïde - Module du champ électrique, composante Ex - STAT

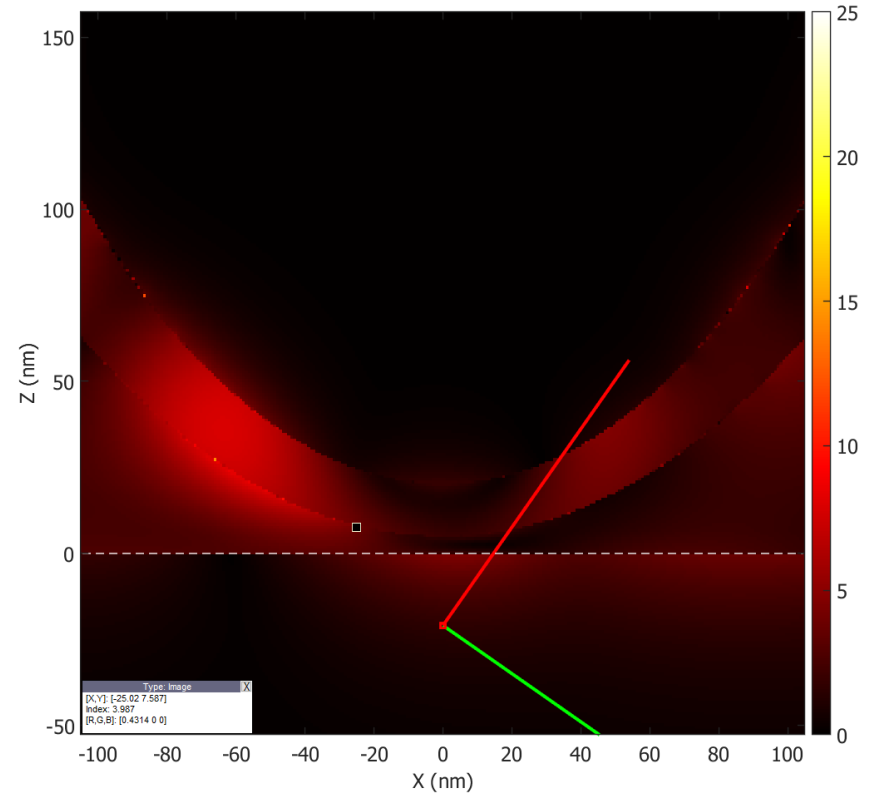


➤ NF amplification factor for component $E_z \approx 22$

Ellipsoïde - Module du champ électrique, composante Ez - RET



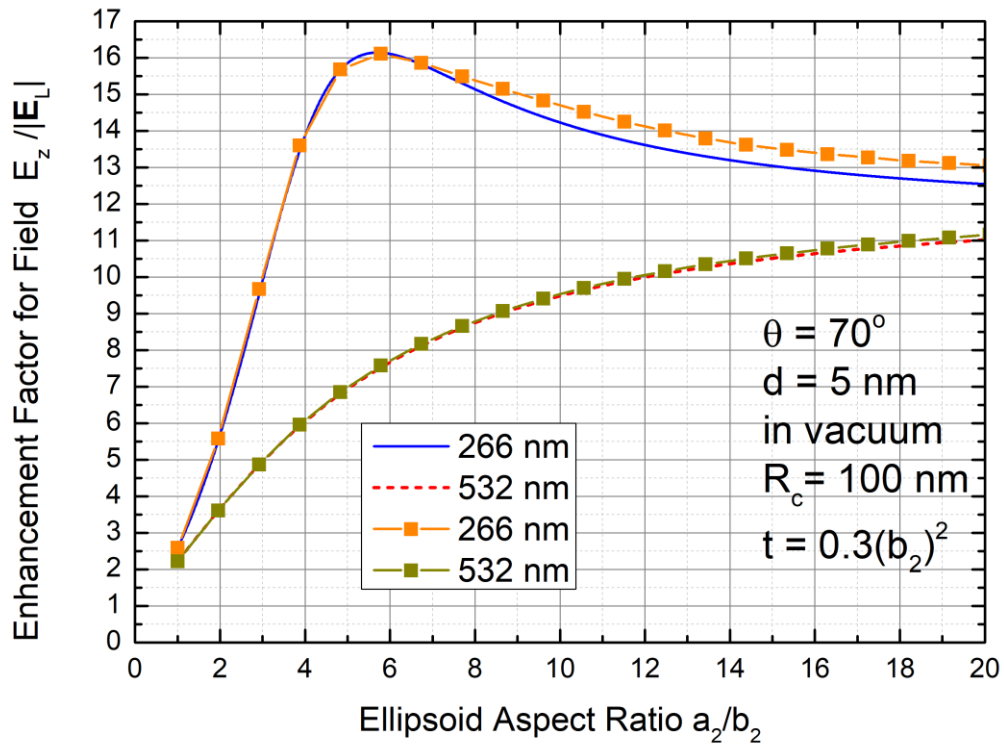
Ellipsoïde - Module du champ électrique, composante Ex - RET



➤ NF amplification factor for component $E_z \approx 26$

E_z component evolution with a_2/b_2 aspect ratio

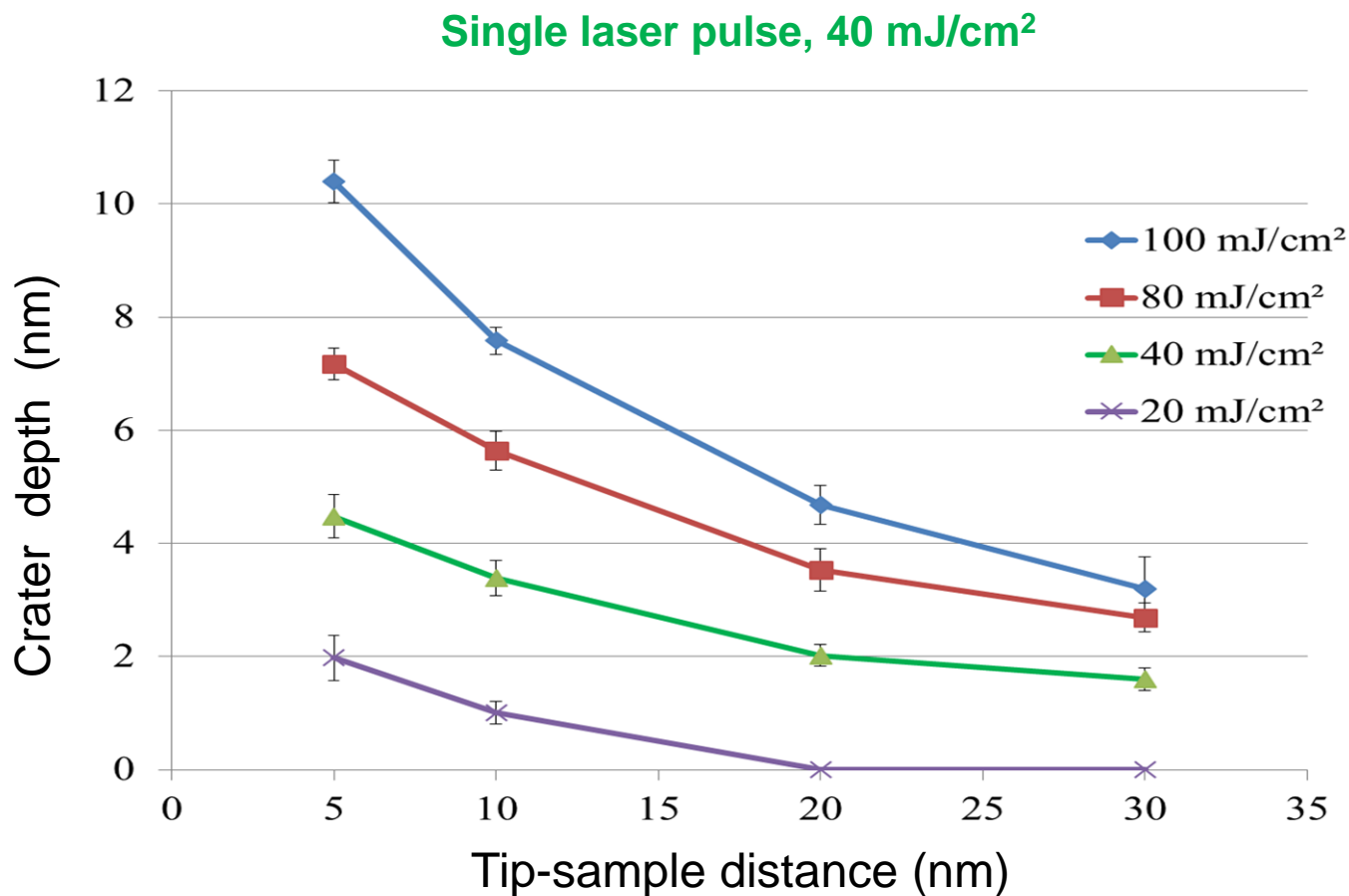
(without Au substrate, 266 nm and 532 nm wavelengths)



➤ Analytical model and BEM simulations are in **good agreement**.

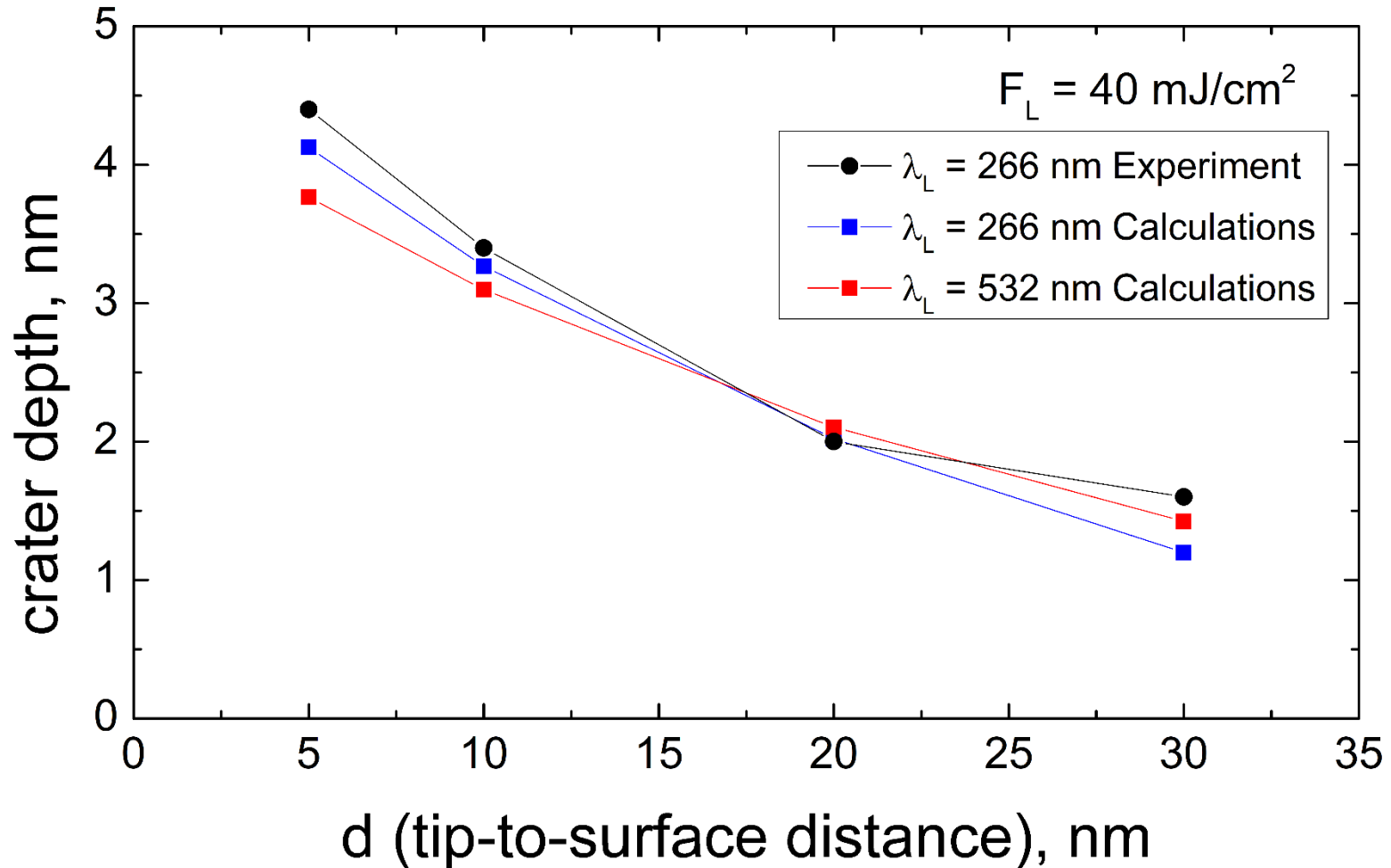
Experimental results (with Au)

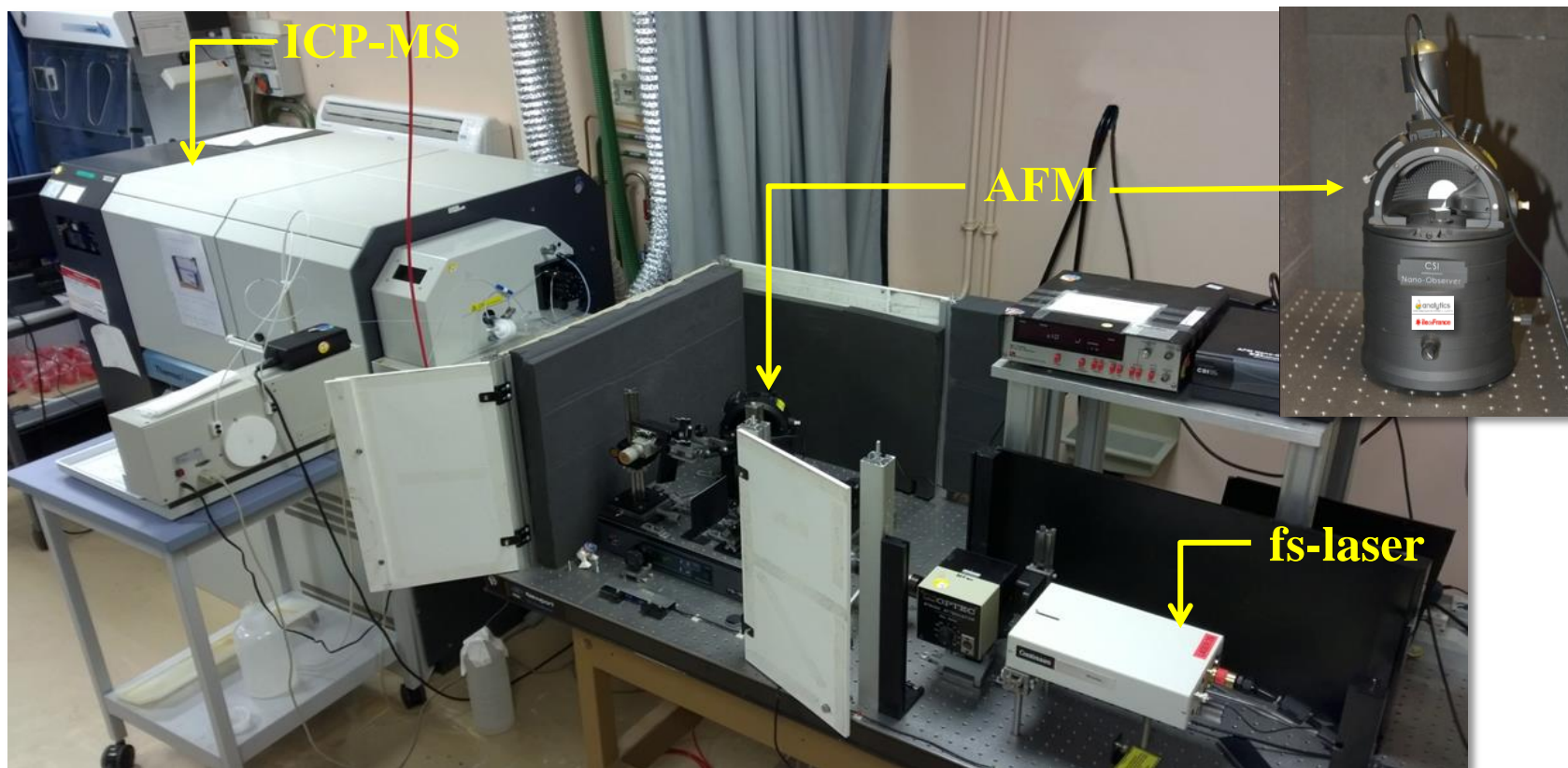
Tip-sample distance and laser irradiance effects on the craters dimensions



Simulation results (with Au)

Tip-sample distance effects on crater depth





- ❑ Laser Ti-Sa (800, 400 or 266 nm), 100 fs pulse duration.
- ❑ Development of NF-AFM interface with ICP-MS (on-going).
- ❑ Particle characterization: particle size, mass, shape ... (on-going).
- ❑ Element and isotope analysis by NF-AFM-ICP-MS.

Спасибо
за
внимание!

Thank you
for your
attention!

Commissariat à l'énergie atomique et aux énergies alternatives
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685 019

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➤ Champ électrique sur une surface métallique - Equation de Fresnel généralisée - Indice de réfraction complexe

$$(\vec{E}_x^{Exc.}, \vec{E}_y^{Exc.}, \vec{E}_z^{Exc.}) = E_0((r_{//} - 1) \cos \alpha \cdot \cos \theta, (1 + r_{\perp}) \sin \theta, (1 + r_{//}) \sin \alpha \cdot \cos \theta)$$

α Angle d'incidence / normale

θ Angle de polarisation

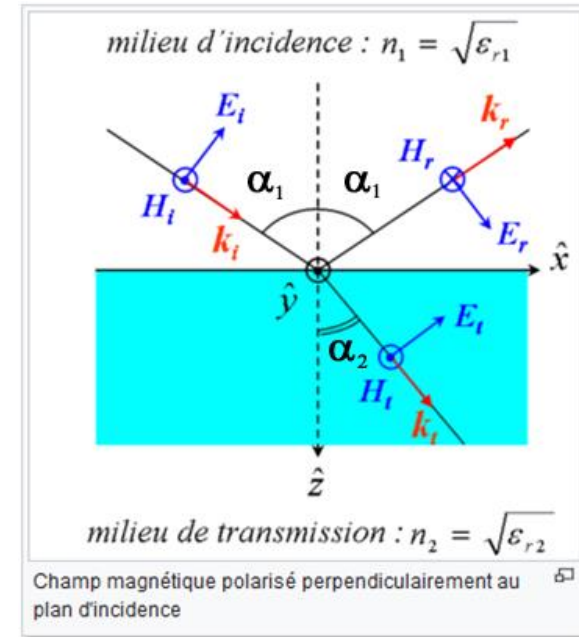
$r_{//} = r_{TM}$ Coefficient de Fresnel en polarisation TM

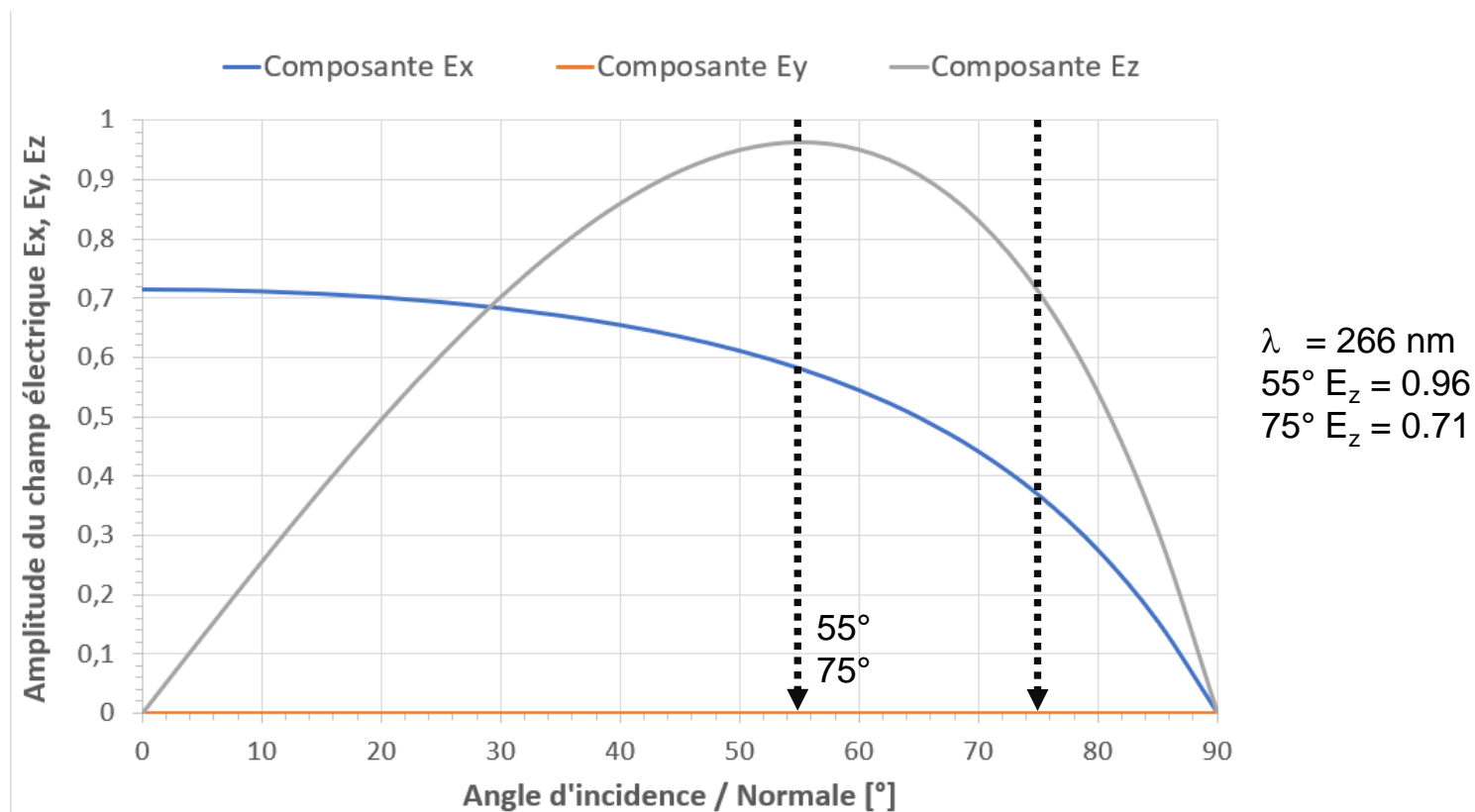
$r_{\perp} = r_{TE}$ Coefficient de Fresnel en polarisation TE

$$r_{//} = \frac{n_2^2 \cos(\theta) - n_1 \sqrt{n_2^2 - n_1^2 \sin^2(\theta)}}{n_2^2 \cos(\theta) + n_1 \sqrt{n_2^2 - n_1^2 \sin^2(\theta)}}$$

$$r_{\perp} = \frac{n_1 \cos(\theta) - \sqrt{n_2^2 - n_1^2 \sin^2(\theta)}}{n_1 \cos(\theta) + \sqrt{n_2^2 - n_1^2 \sin^2(\theta)}}$$

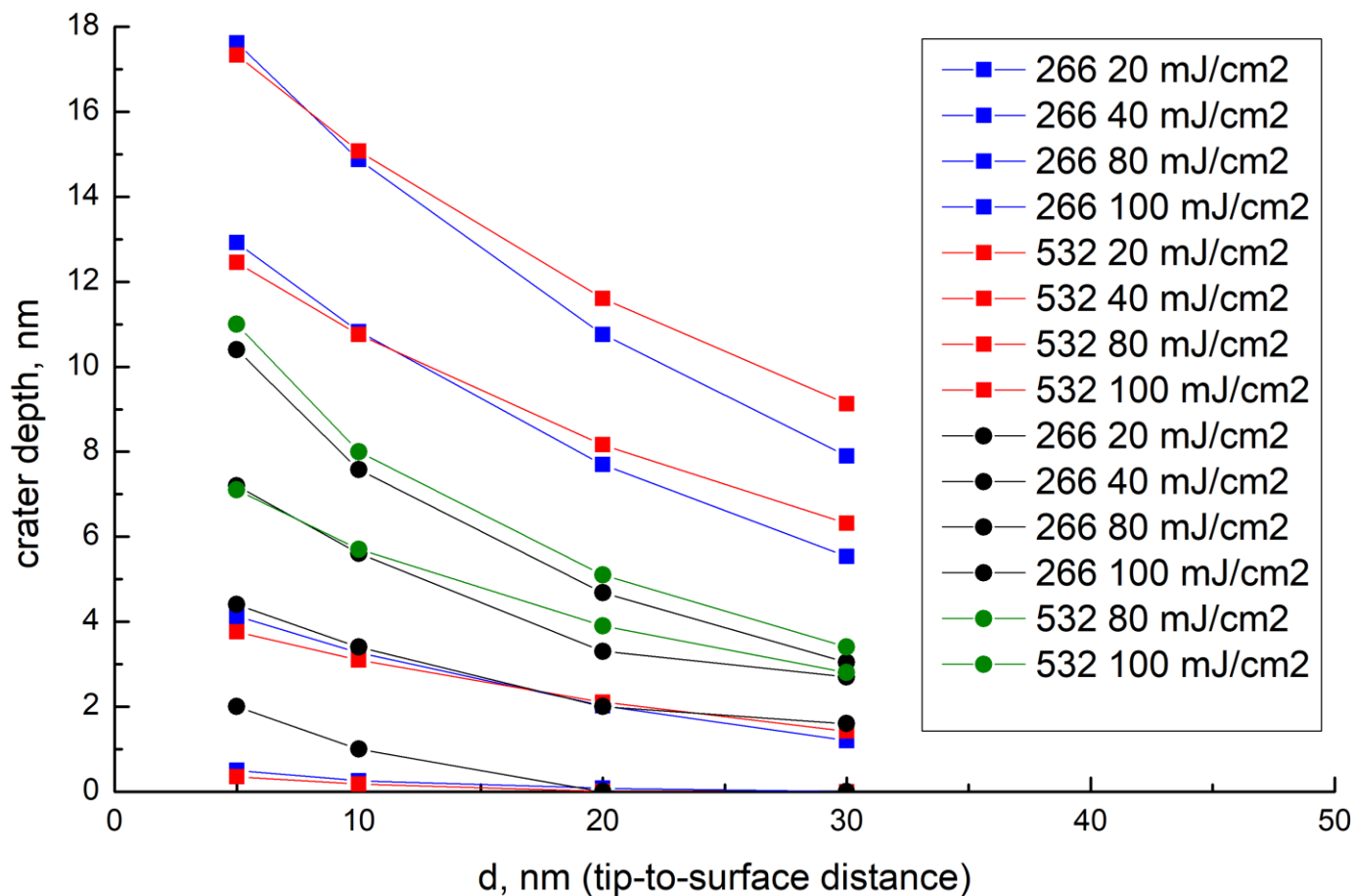
avec $n = n_1 + i.n_2$ Indice de réfraction complexe du substrat métallique



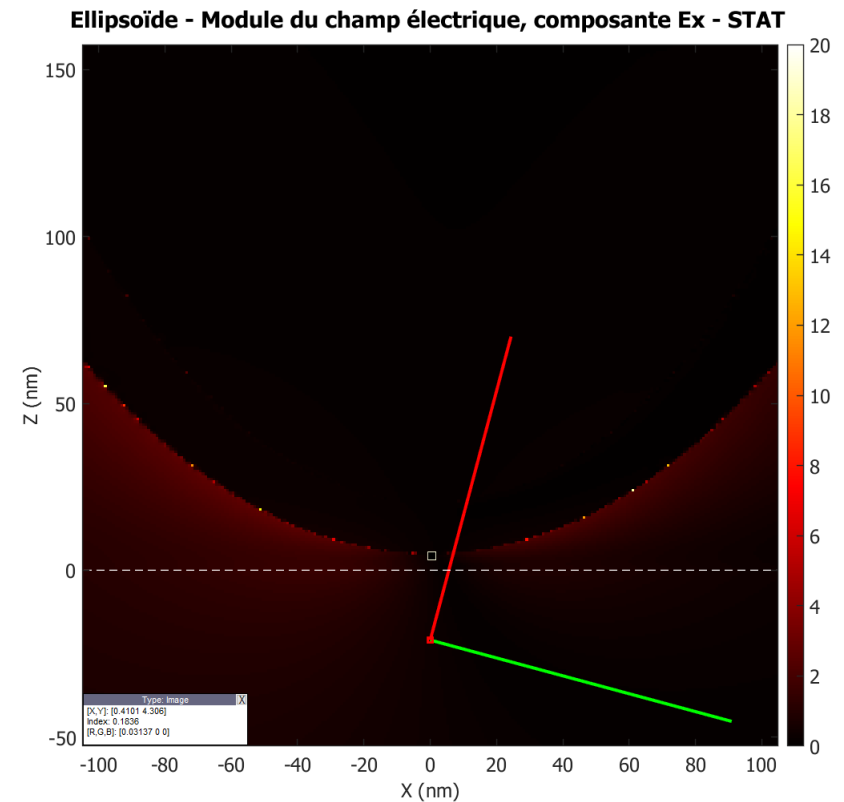
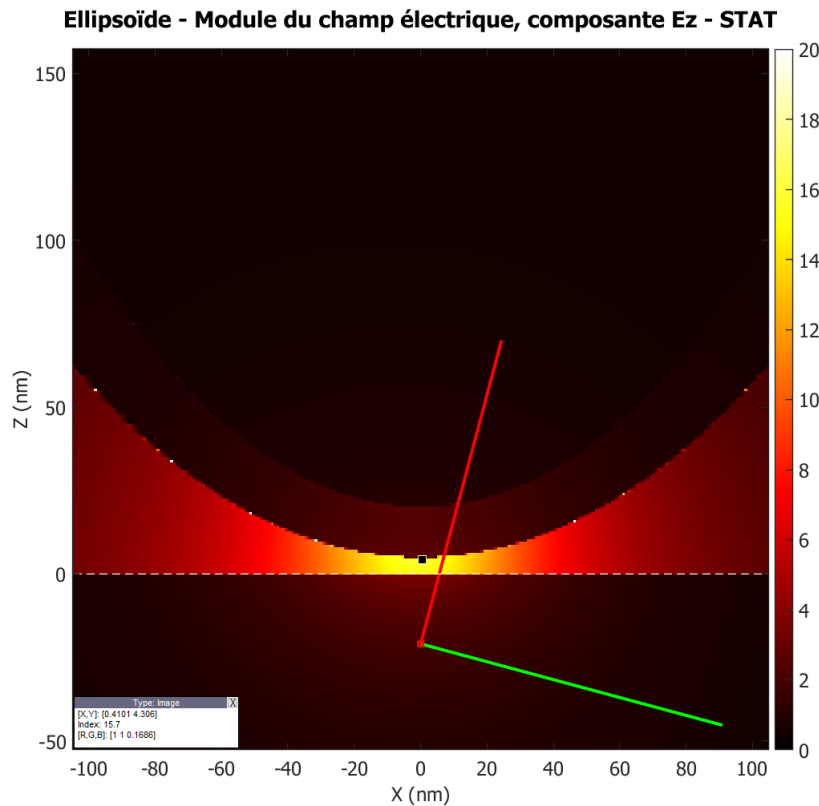


- Maximisation de la composante E_z pour un angle d'illumination de 55° / normale

Tip-sample distance and laser irradiance effects on craters dimensions



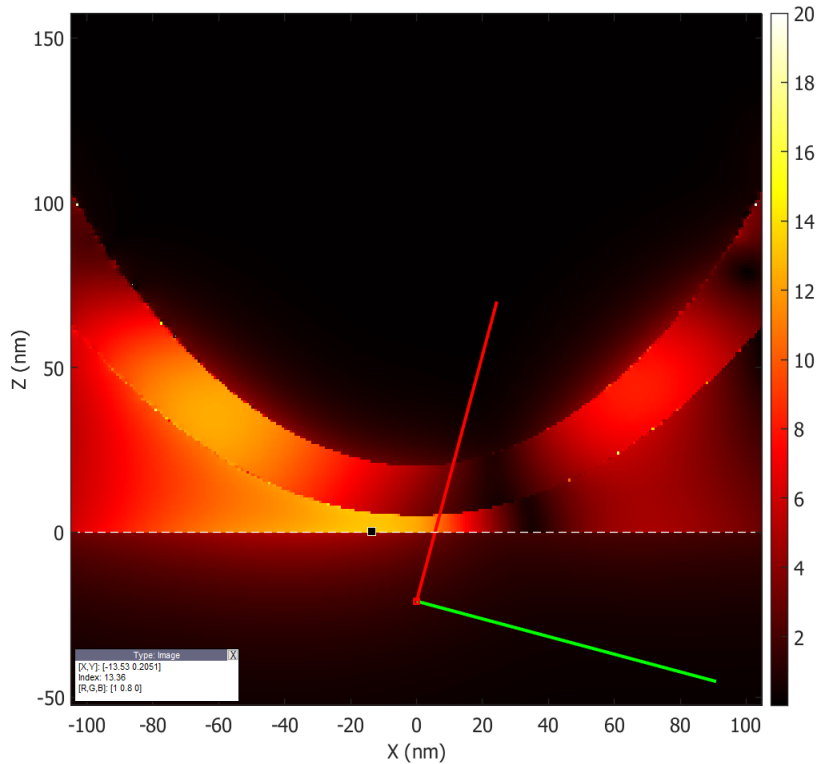
Incidence 75°



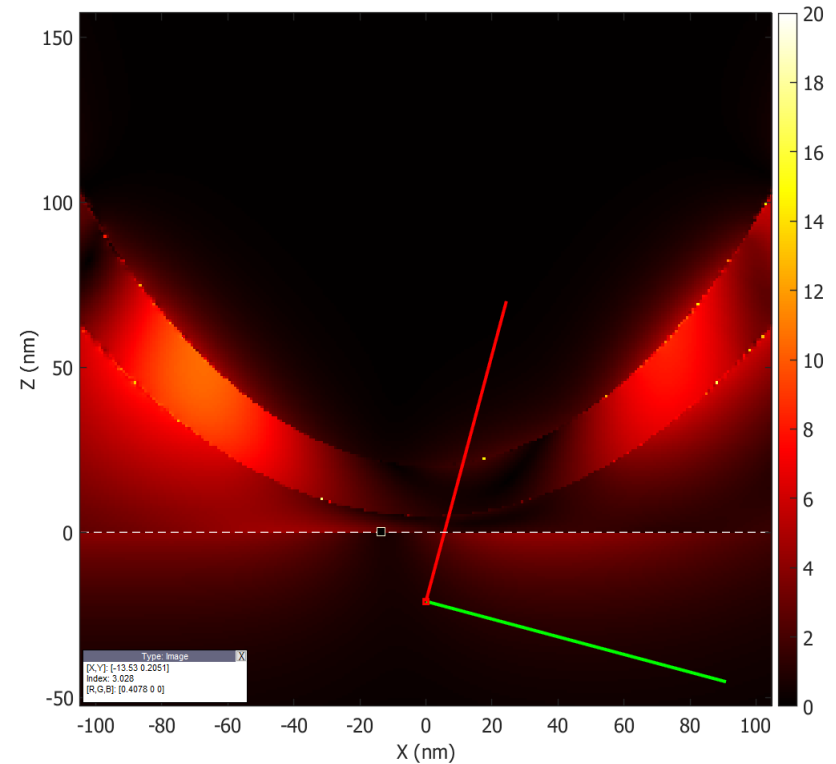
➤ Facteur d'exaltation de la composante $E_z \approx 16$

Incidence 75°

Ellipsoïde - Module du champ électrique, composante E_z - RET

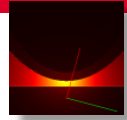


Ellipsoïde - Module du champ électrique, composante E_x - RET

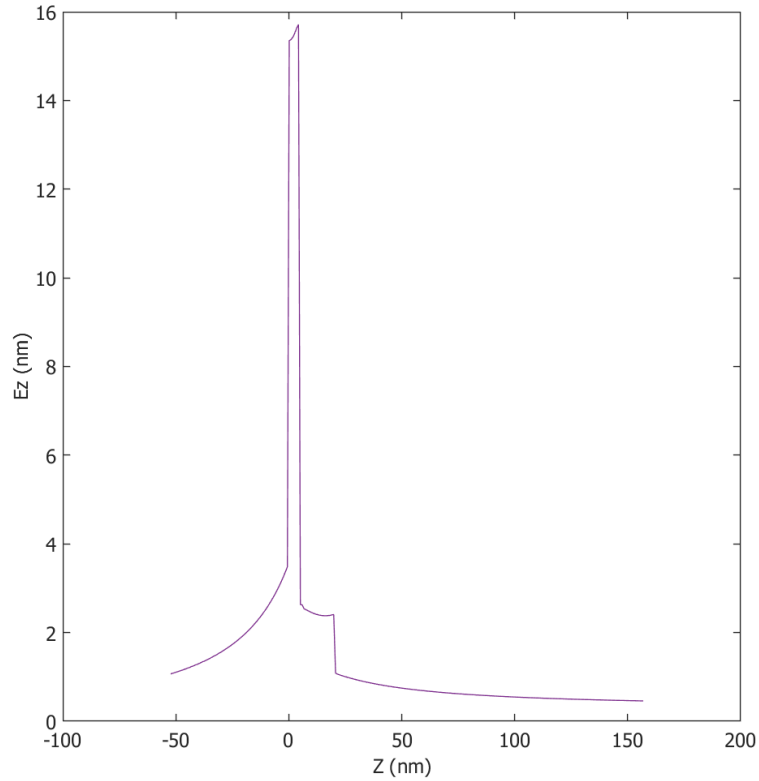


➤ Facteur d'exaltation de la composante $E_z \approx 13$

BEM results simulation – electric field profile (suivant l'axe de la pointe – 75°)



Profil de la composante Ez suivant l'axe de la pointe - STAT



Profil de la composante Ez suivant l'axe de la pointe - RET

