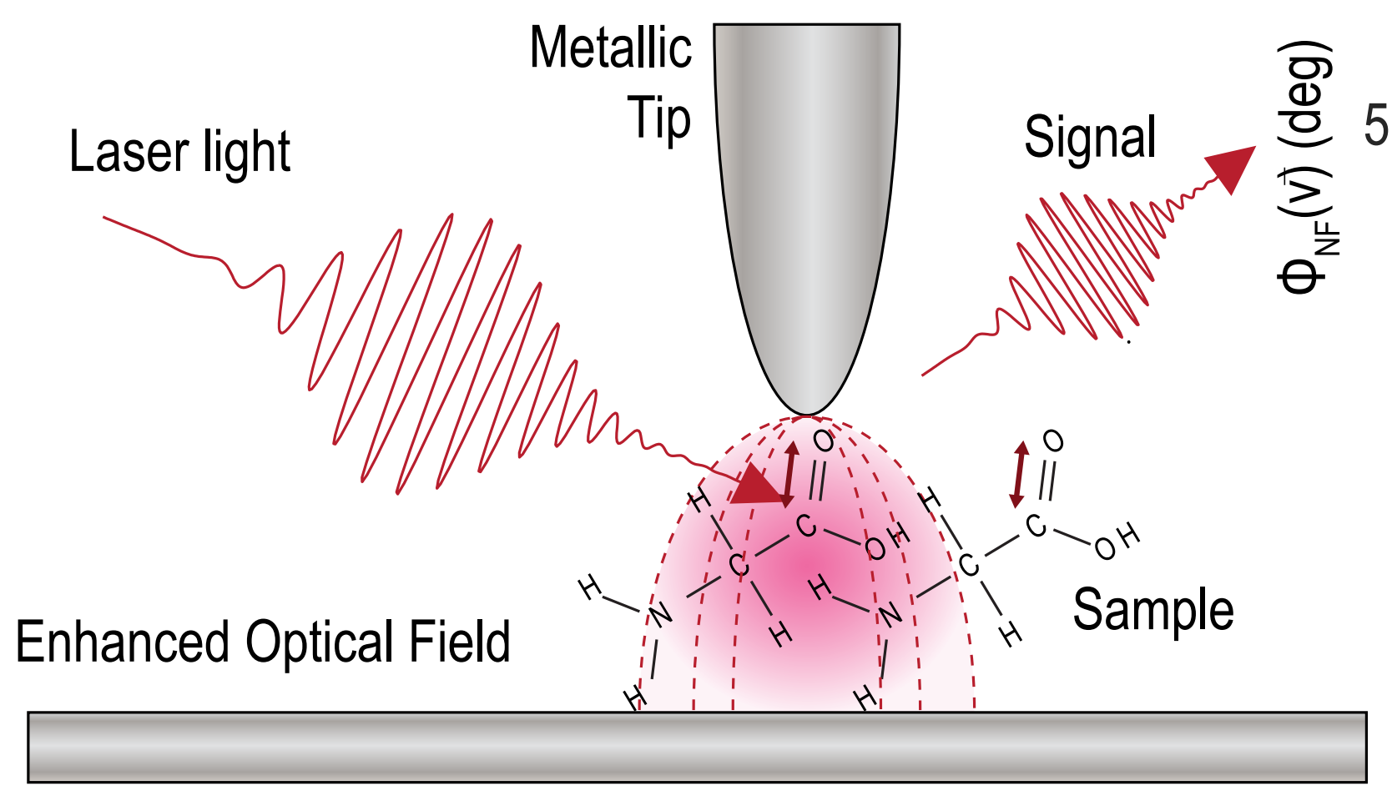
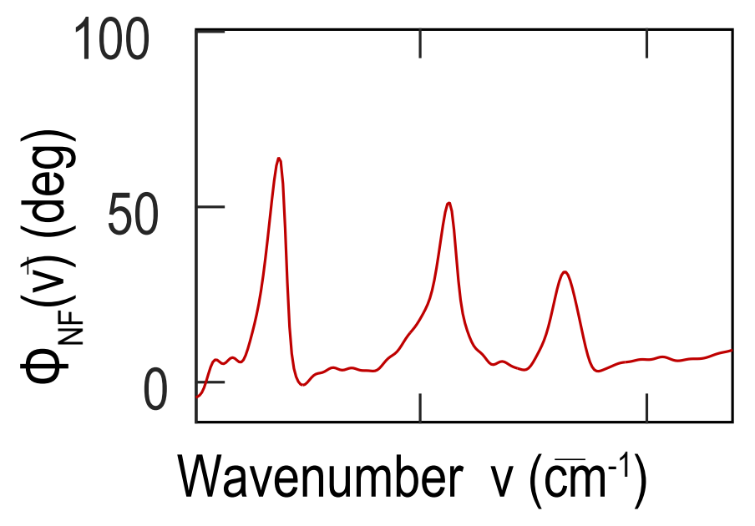
Simulated Infrared Tip-Enhanced Spectroscopy in a Liquid Environment

Tarik Cigeroglu, John R. Underhill, Zachary M. Williams,
Brian T. O'Callahan, A. Scott Lea, Eric A. Muller

Nanoscale Vibrational Spectroscopy

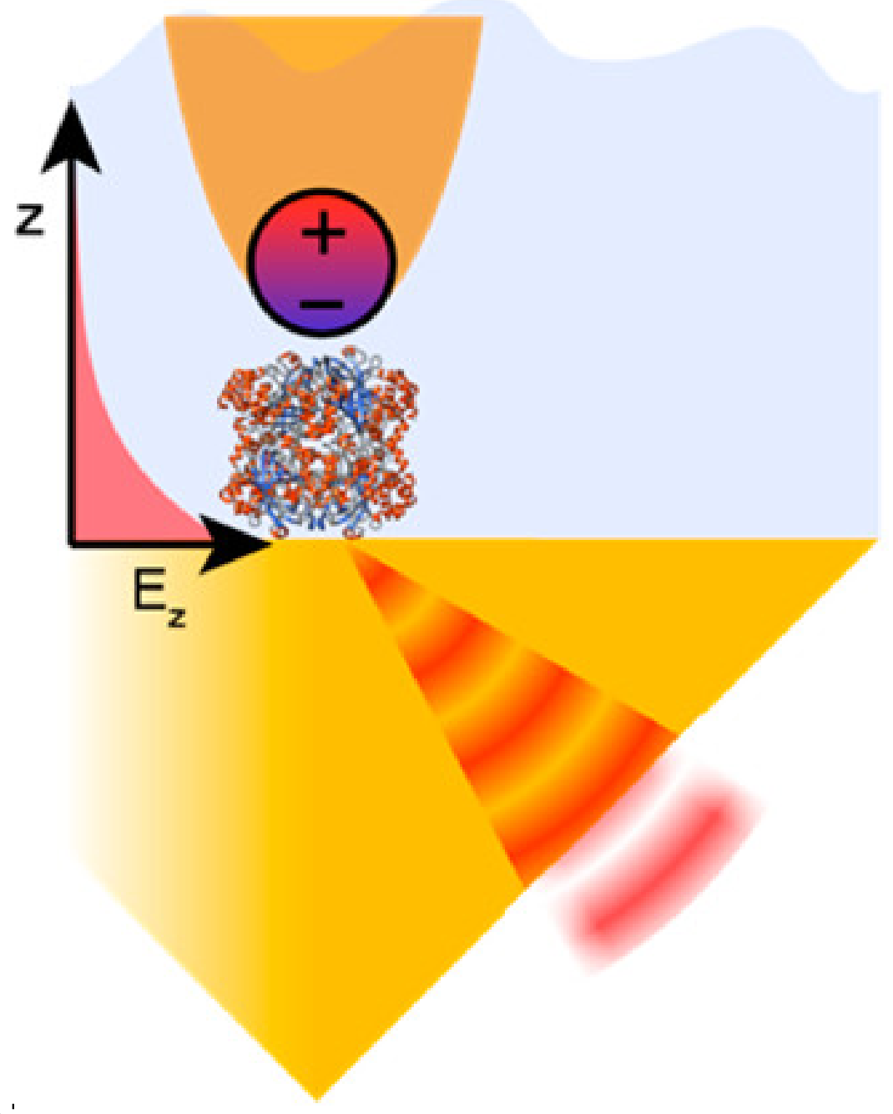
Vibrational spectroscopy provides information on chemical identity as well as insight into molecular scale and nanoscale structure. However, the wave nature of light limits both imaging spatial resolution spectroscopic sensitivity. Our lab is developing a new approach based upon infrared scattering-scanning near-field optical microscopy (IR s-SNOM) to overcome spatial resolution and sensitivity limits. In this approach, a sharp metallic tip localizes and enhances optical fields, enabling spatial resolution <20 nm and sensitivity to as little as a few hundred individual bonds.





E.A. Muller, B. Pollard, M.B. Raschke "Infrared chemical nano-imaging: Accessing structure, coupling, and dynamics on molecular length scales"
J. Phys. Chem. Lett. 6, 1275-1284 (2015).

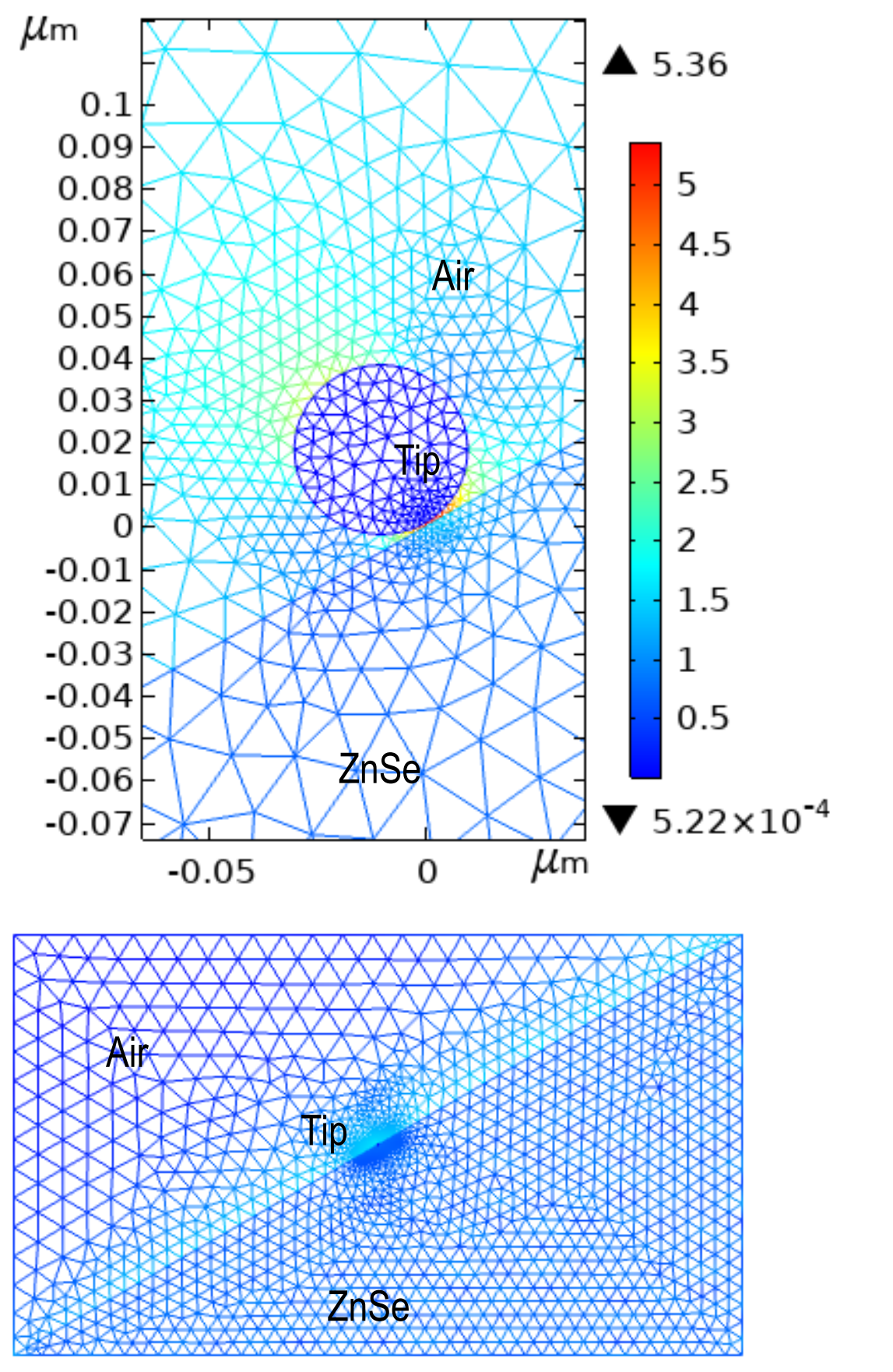
In order to study proteins and molecules in the chemically relevant environment, we extend our approach with the development of in liquid IR s-SNOM. The liquid environment creates new spectroscopic challenges. We develop a new optical geometry for our experimental apparatus based upon total internal reflection that enables imaging and spectroscopy in liquid, but also fundamentally changes the optical field enhancement at the tip apex.



Brian T. O'Callahan, Kyoung-Duck Park, Irina V. Novikova, Tengyue Jian, Chun-Long Chen,
Eric A. Muller, Patrick Z. El-Khoury, Markus B. Raschke, and A. Scott Lea "In Liquid Infrared Scattering Scanni
Near-Field Optical Microscopy for Chemical and Biological Nanoimaging" Nano Lett. 20, 6, 4497–4504 (2020)

Calculating Electromagnetic Field Enhancement

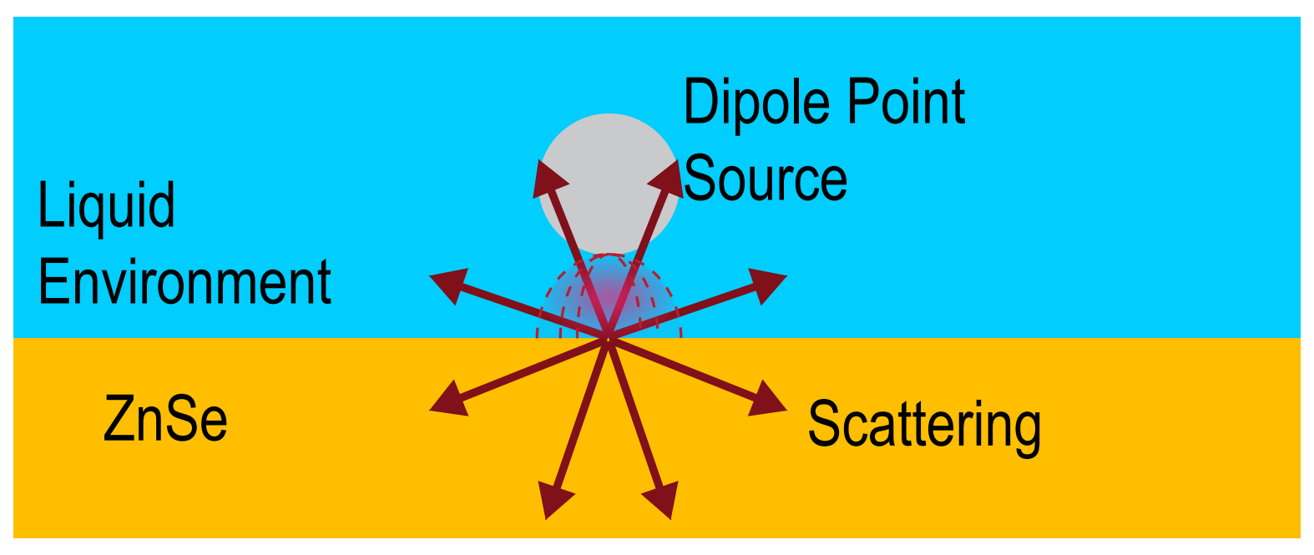
We calculate the optical enhancement and localization at the tip apex as solutions to Maxwell's equations using the finite element method solver Comsol Multiphysics. The finite element method is an approach to solving partial differential equations that obtains solutions for the field at a set of discretely spaced points. First, the relevant differential equations for the selected physics are identified. Next, we create a simplified representation of the geometry of our apparatus in one- two- or three-dimensions. We choose a set of discrete points, known as a mesh, to represent the material properties and boundaries. A numerical solver then finds solutions to the partial differential equations for those mesh points expressed as a matrix equation. This approach has the advantage that the calculated solution will converge to the exact solution for an infinite number of mesh points.

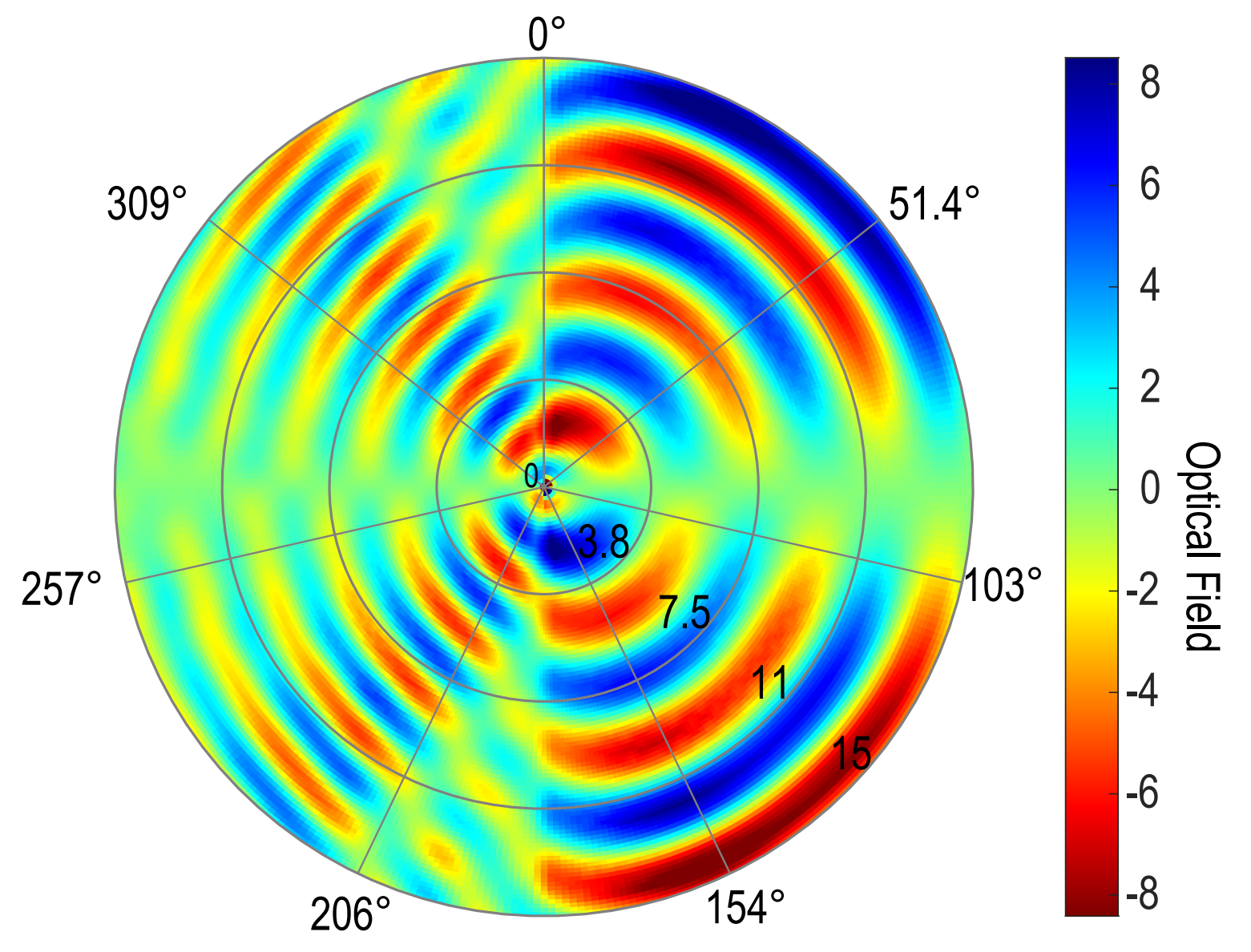


Comsol Multiphysics mesh for finite element solver created for a circular tip (radius=20 nm) in air above a ZnSe surface.

Simulated Point Dipole Above a ZnSe/Air interface

The simplest approximation is to treat the tip as a point source above a sample on a ZnSe substrate. We use this simplified structure to model the distance dependence of the tip and the angular distribution of intensity. We calculate optical field intensity and directionality of emitted light through the ZnSe prism or into the air or liquid above the tip and sample.

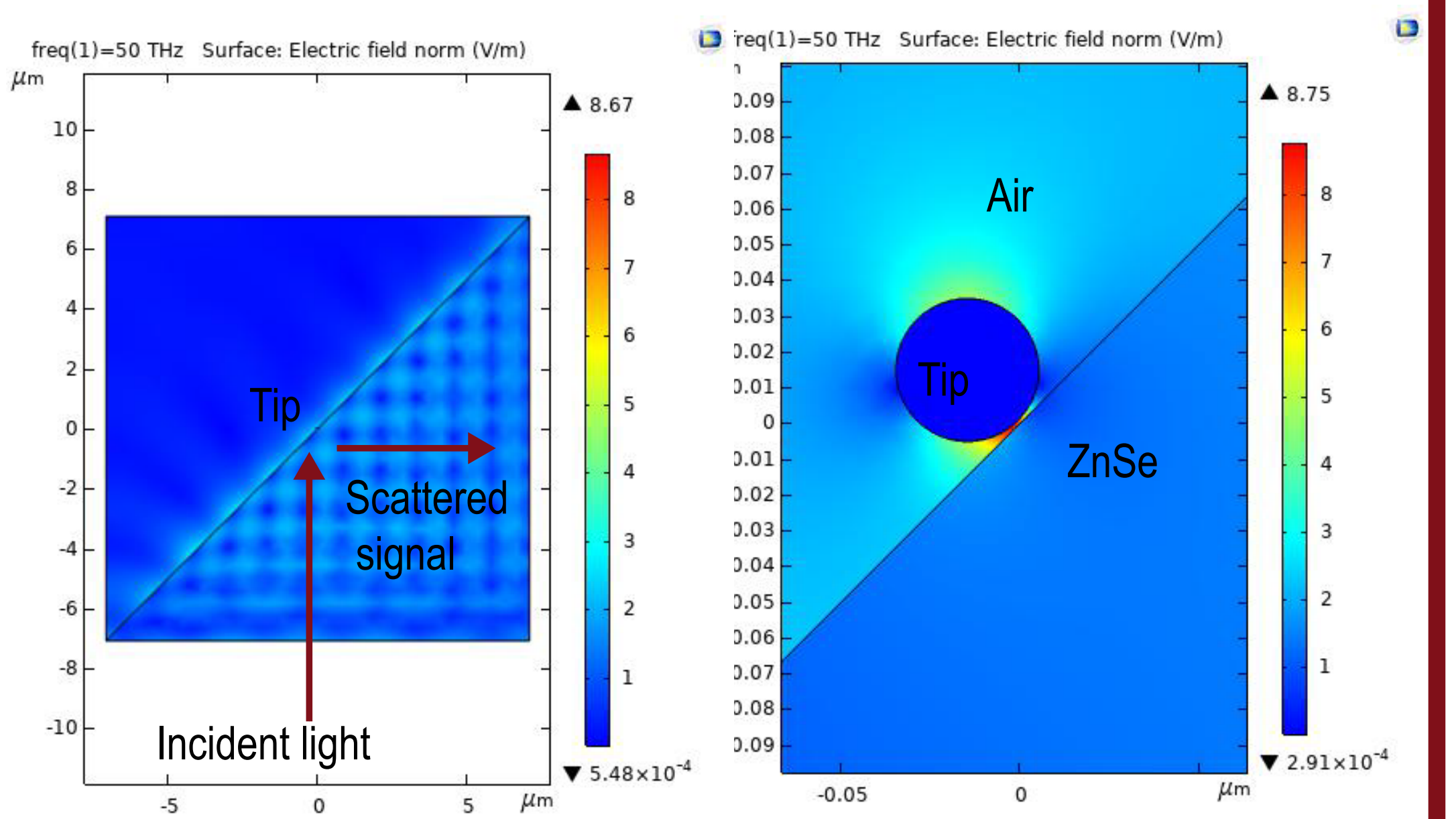




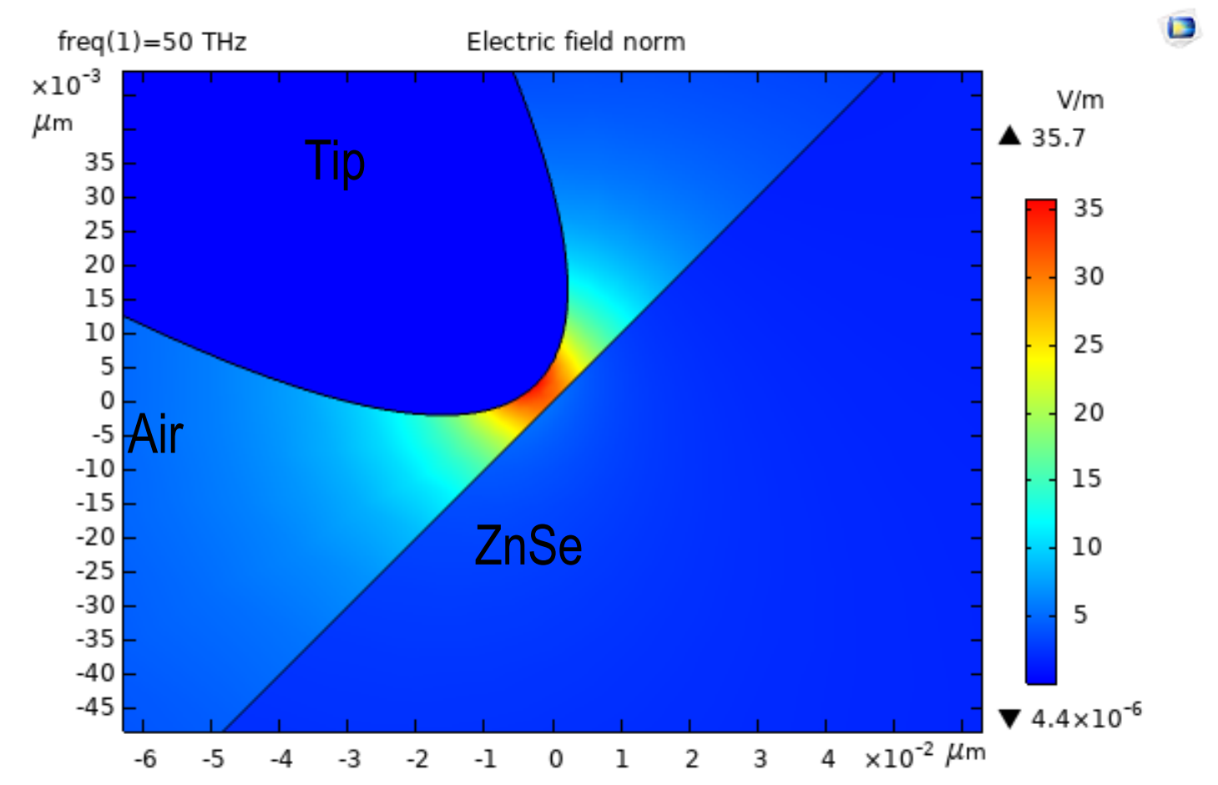
Optical fields coming from a point dipole (center) propagating into ZnSe(left) and air (right)

2D Simulations of Optical Field Enhancement

We simulate a gold nanosphere with radius 20 nm above a ZnSe substrate. A background electric field is defined with a plane wave with frequency 50 THz. We calculate local enhancement of the optical field as a function of tip-sample distance, angle of incident light, optical frequency, and with different substrate materials



Gold sphere (r=20 nm) above a ZnSe crystal. Plane wave incident at 45°.

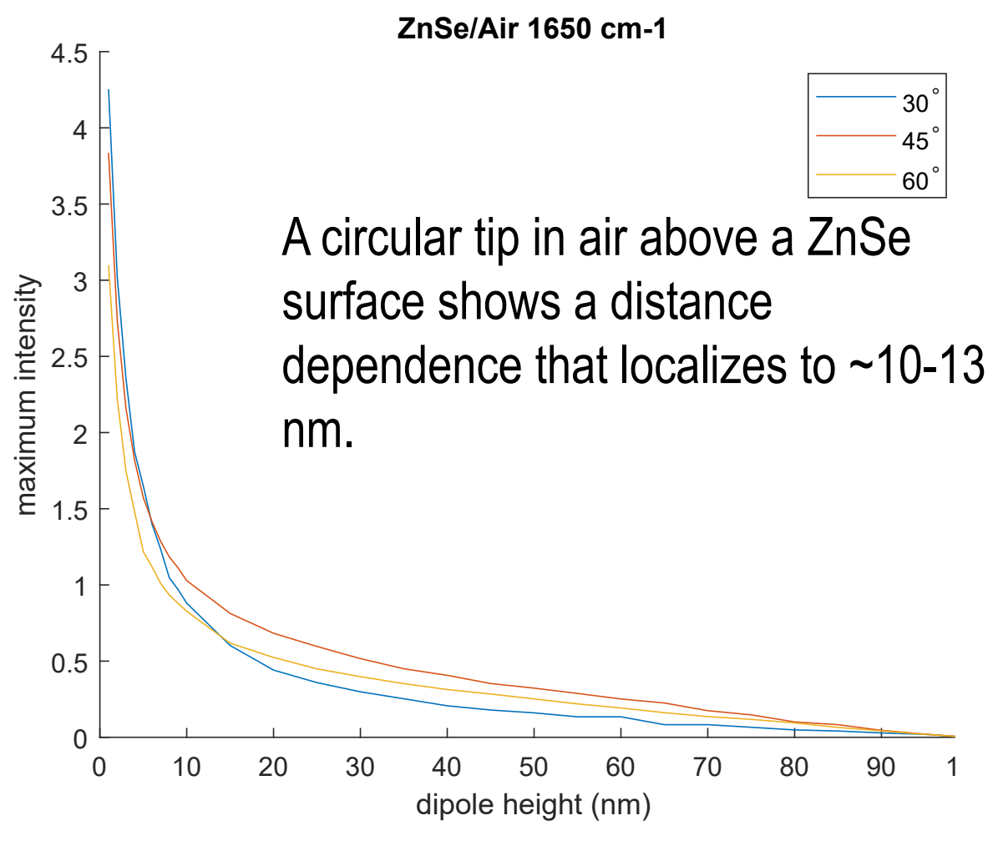


Gold ellipsoid (r = 20 nm) above a ZnSe crystal. Plane wave incident at 45° and 1650 cm-1.

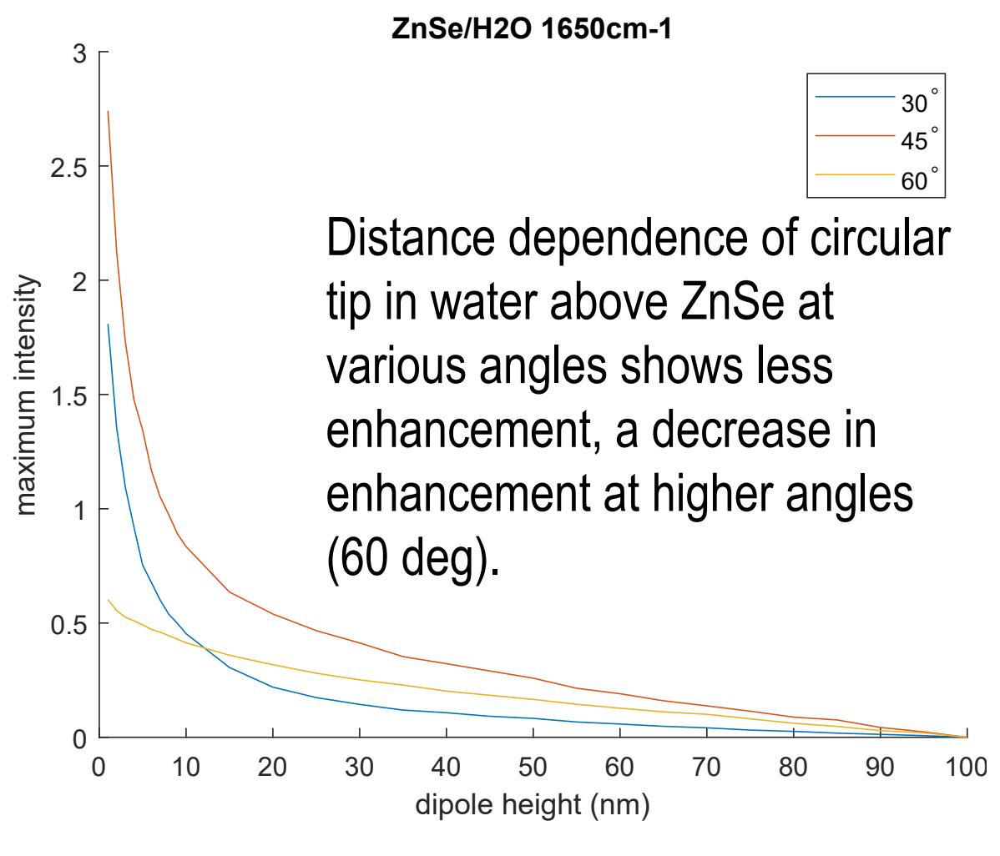
We repeat these calculations with a gold ellipsoidal tip above a ZnSe crystal. The enhancement of the ellipsoidal tip is greater than the enhancement we calculated for a spherical tip, and the optical field is significantly more confined.

Approach Curves and Near-field localization

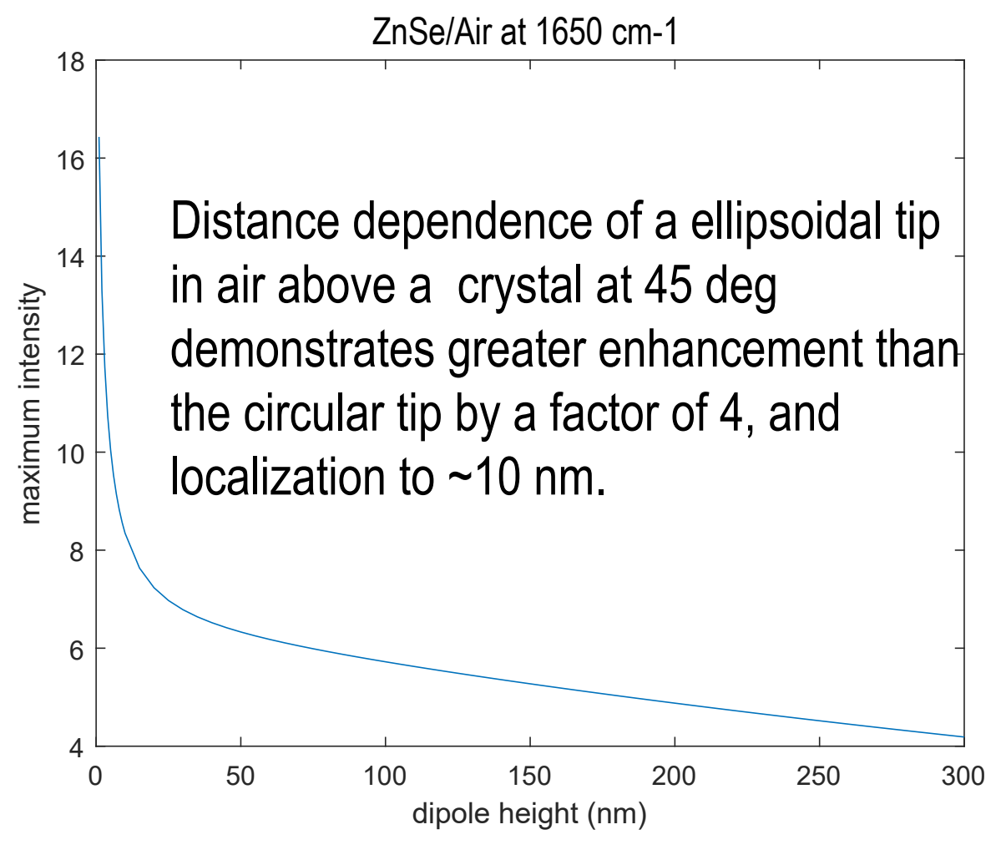
Electromagnetic field calculations show spatial confinement of the field enhancement and signal. We calculate the s-SNOM signal as a function of tip-sample distance with a sinusoidal tip tapping motion. Simulations show that the near-field signal comes predominantly from the first 5-20 nm above the surface.



A circular tip in air above a ZnSe surface shows a distance dependence that localizes to ~10-13 nm.

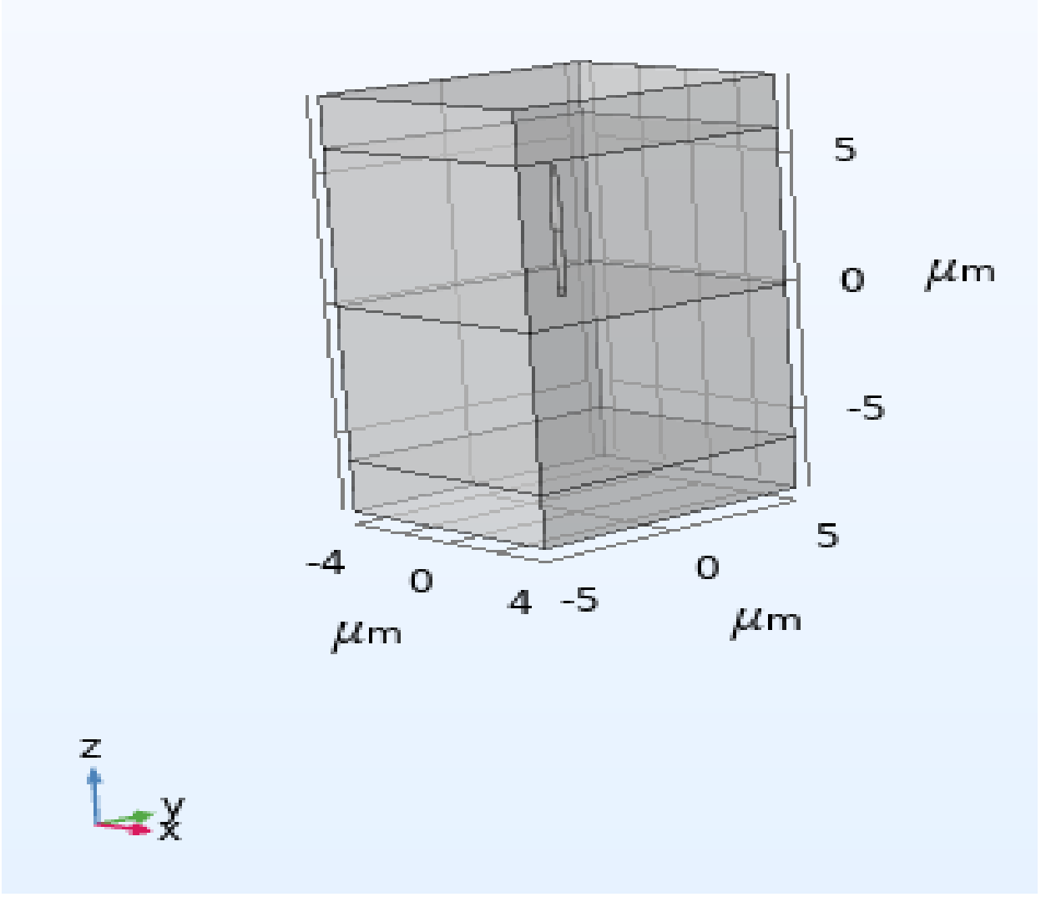


Distance dependence of circular tip in water above ZnSe at various angles shows less enhancement, a decrease in enhancement at higher angles (60 deg).

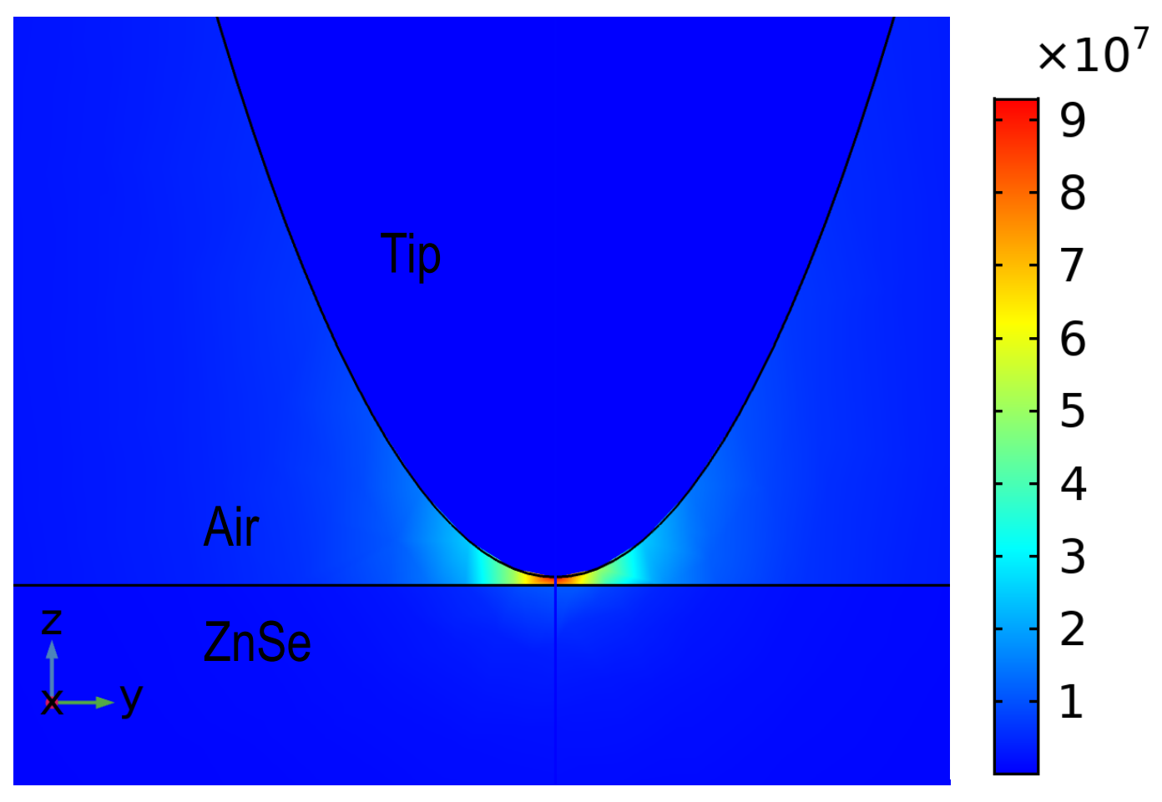


Distance dependence of a ellipsoidal tip in air above a crystal at 45 deg demonstrates greater enhancement than the circular tip by a factor of 4, and localization to ~10 nm.

3D Simulations of Optical Field Enhancement



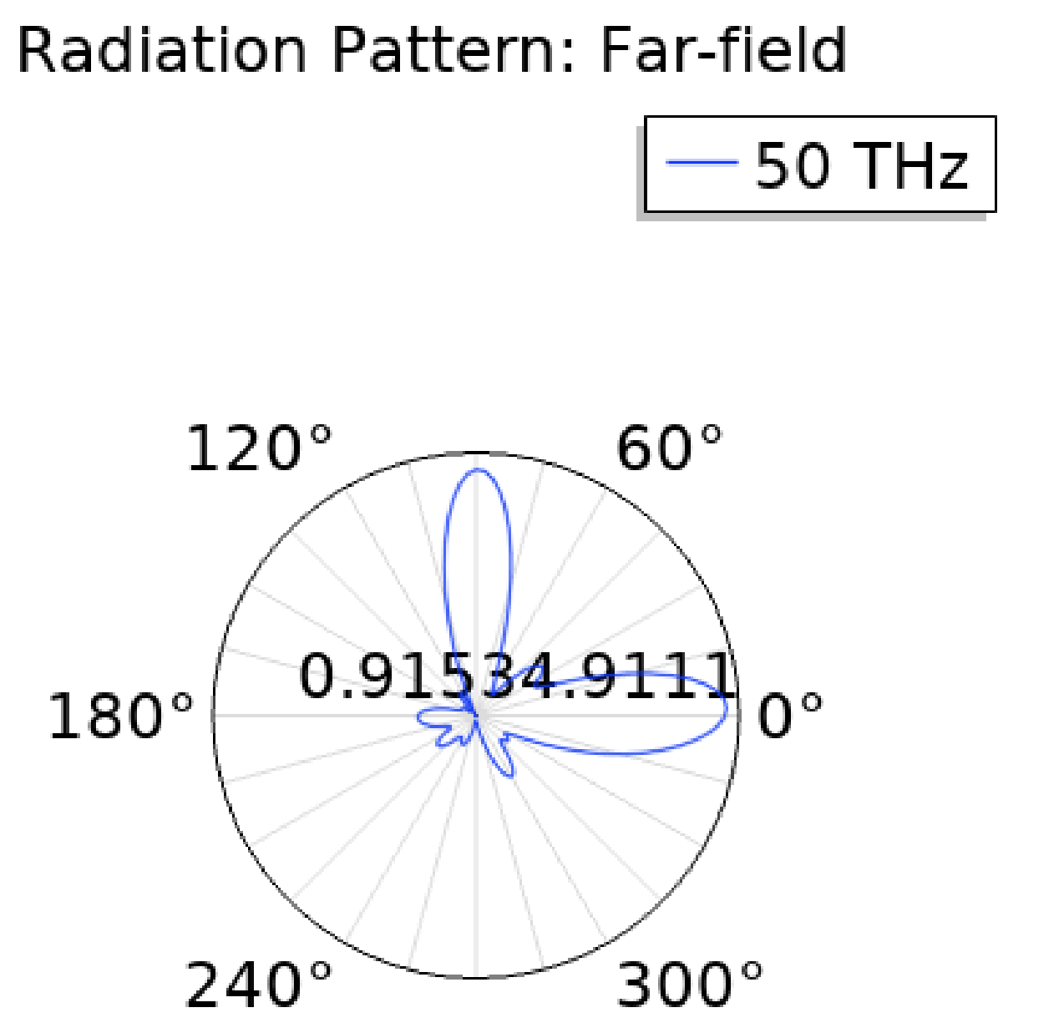
We have begun transitioning our 2D Comsol model into a 3D geometry. The 3D geometry required new methods to correctly treat the boundary conditions at the edge of our simulation region, the use of a perfectly matched layers, port conditions for the incident field, and periodic boundary conditions. The 3D model shows similar field enhancement and localization as compared to the 2D model, and it will allow us to more accurately describe the geometry and physics of a real device.



Future Directions

As the complexity of the geometry increases, we need to fully model the background field, which is no longer a simple plane wave. We explicitly calculate this background field as the reflection and scattering off of the ZnSe prism and then include those results in our calculation of the scattered field from the tip.

Ultimately, we would like to simulate the actual detected signal for novel s-SNOM apprarata. We calculate the signal that reaches the detector as the light scattered into the far-field. Commercial finite element solvers such as Comsol are limited in this type of calculation, because they can only calculate far-field signal for a scatterer completely surrounded by air.
We use two approaches to overcome this limitation:
1) Create a geometry that fully encloses the simulated prism in air.
2) Use Matlab to implement a recently demonstrated approach to calculate far-field signal using a more complete description of the scattering physics.
Ultimately, this will provide us with a robust and general tool set to model s-SNOM in a liquid environment and other tip-enhanced spectroscopies.



Polar plot showing intensity and directionality of the far-field component for scattering from a tip and prism surrounded by an air layer.