

# First-Principles Simulation of Tip-enhanced Raman Spectroscopy

*Yair Litman*

Aug 04, 2023

# Acknowledgement



M. Rossi



F. Bonafé

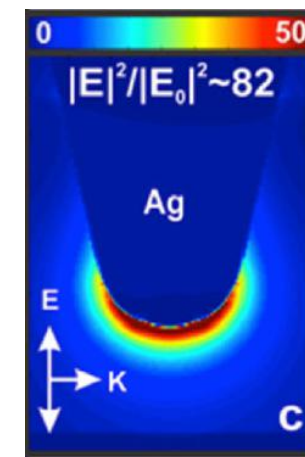
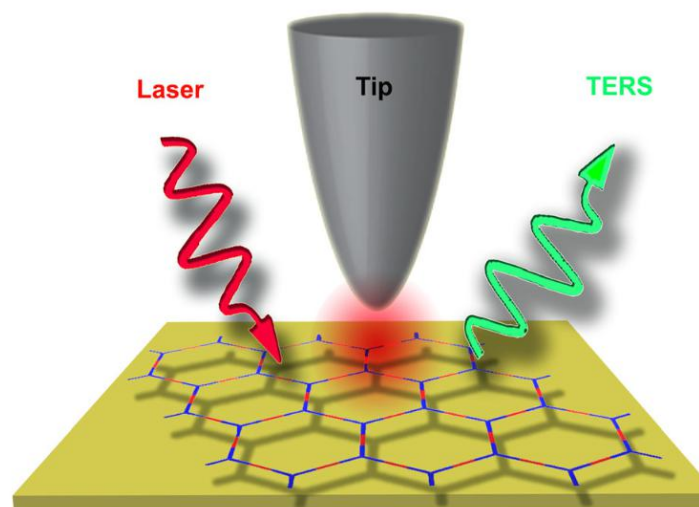
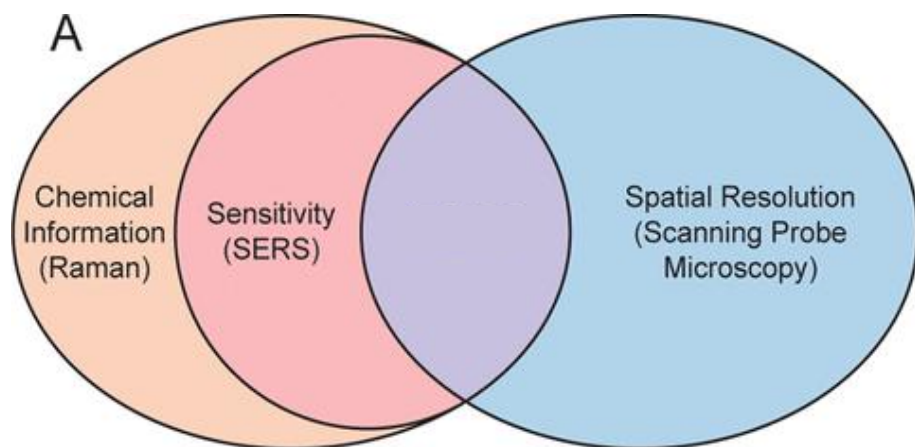
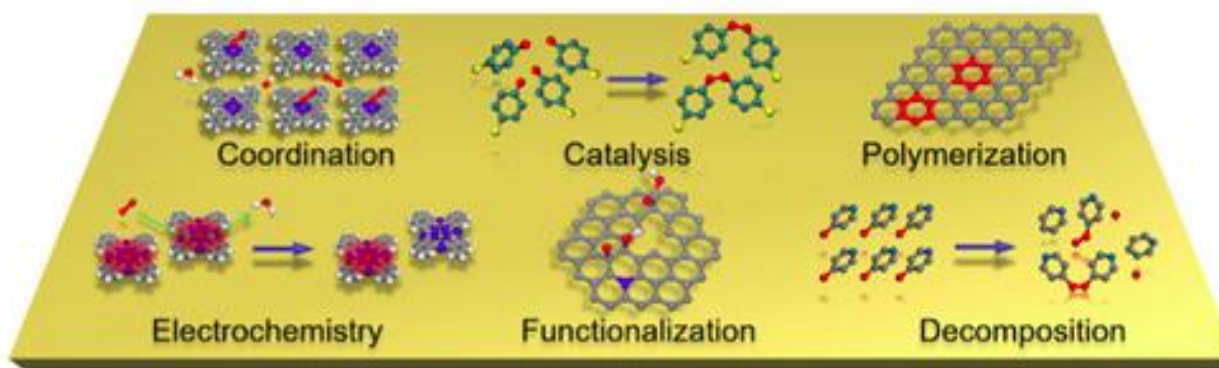


A. Akkoush



H. Appel

# Tip-Enhanced Raman Spectroscopy



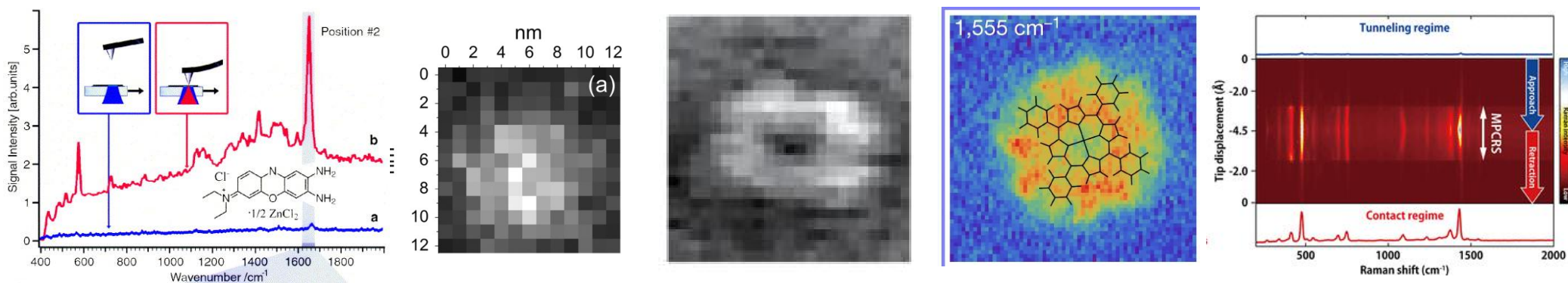
## TERS: Tip-Enhanced Raman Spectroscopy

Pozzi, *et al.* Chem. Rev. **117**, 4961 (2017)

Zhao, *et al.*, Anal. Bioanal. Chem. **411**, 37 (2019)

Cai, *et al.*, CCS Chem. **5**, 55 (2023)

# Two Decades of TERS



2000

## First demonstrations

Appl. Phys. Lett. **76**, 3130 (2000)  
 Opt. Commun. **183**, 333 (2000)  
 Chem. Phys. Lett. **318**, 131, (2000)

2008

## Single molecule

Phys. Rev. Lett. **100**, 236101 (2008)

## Sub-molecular resolution

Nature **498**, 82 (2013)

2013

## Angstrom resolution TERS

Nature **568**, 78 (2019)

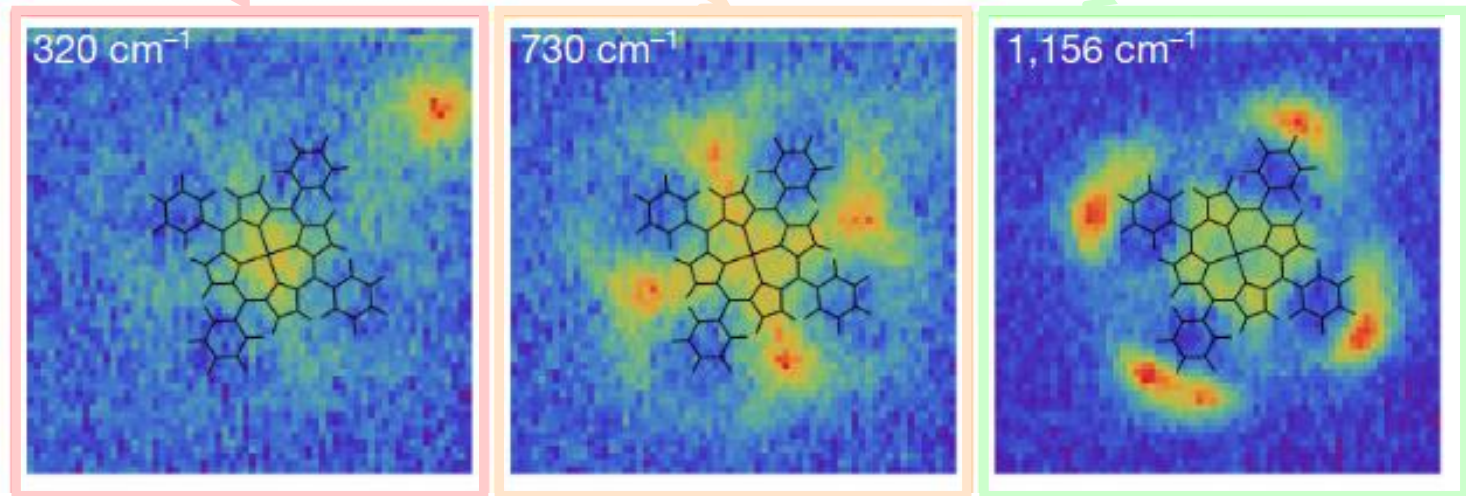
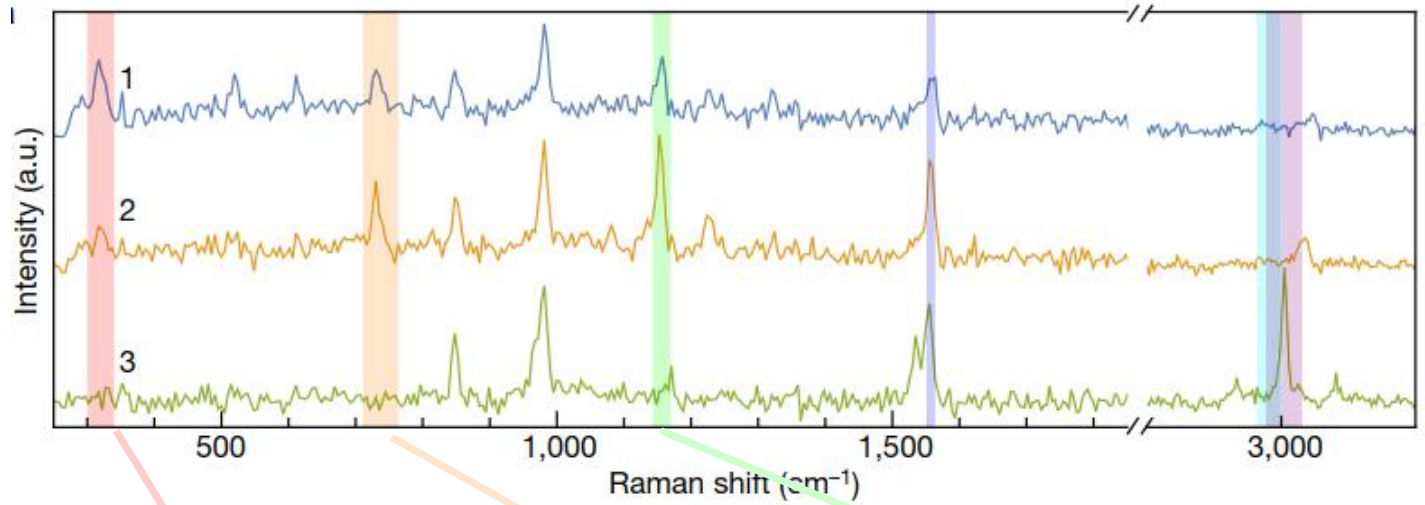
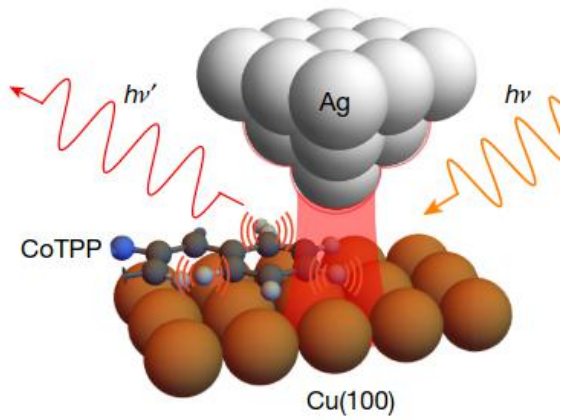
2019

## Molecular point Contact

Nano. Lett. **6**, 2170 (2022)

2022

# TERS Images



$29 \times 29 \text{ \AA}^2$

# Tip-Enhanced Raman Simulations



## Raman Simulation

$$I^{\text{Raman}}(\omega_i) \propto \left| \frac{\partial \alpha_{zz}}{\partial Q_i} \right|^2$$

$\omega_i$  ← i-th normal mode frequency
 → Polarizability
  
→ i-th normal mode vector

# Raman Enhancement Mechanisms

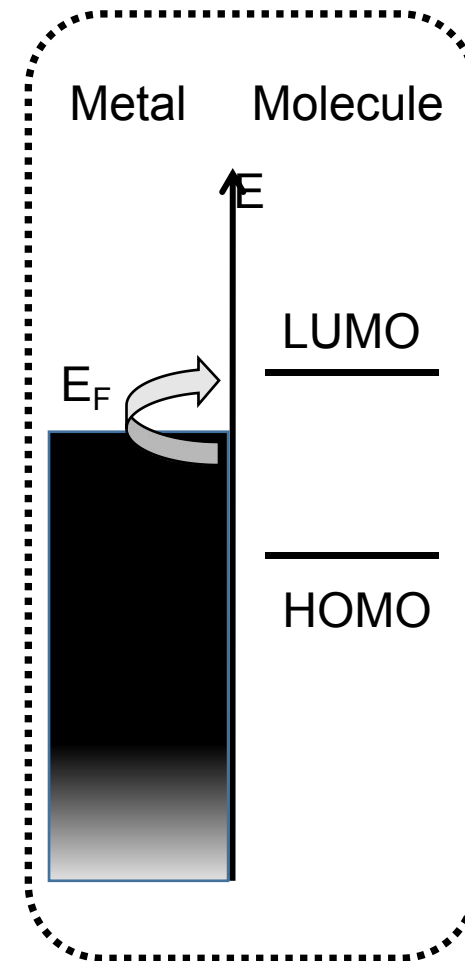
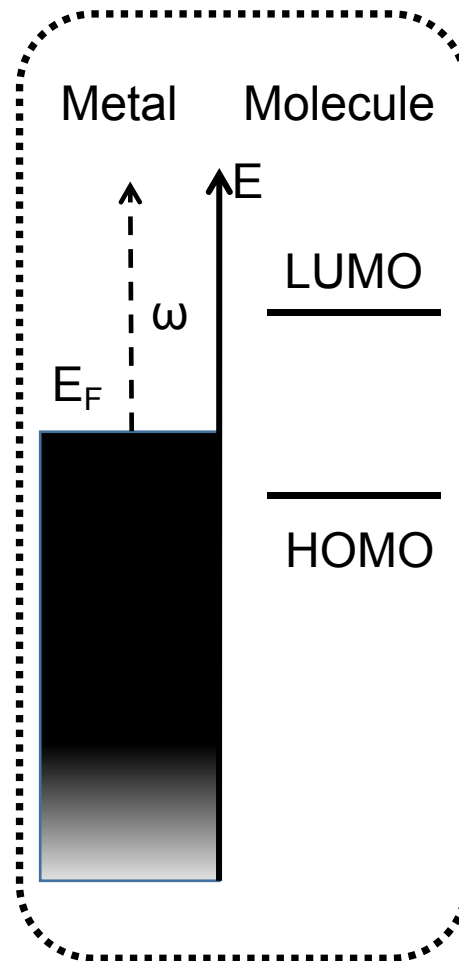
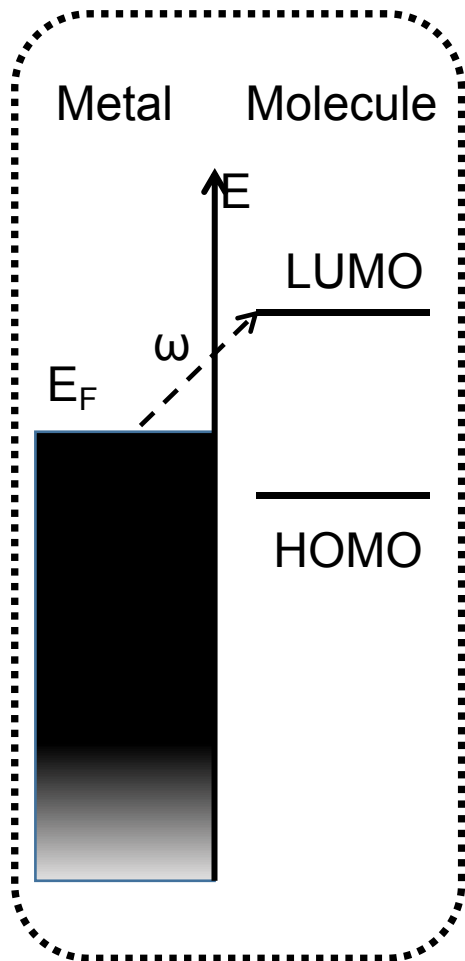
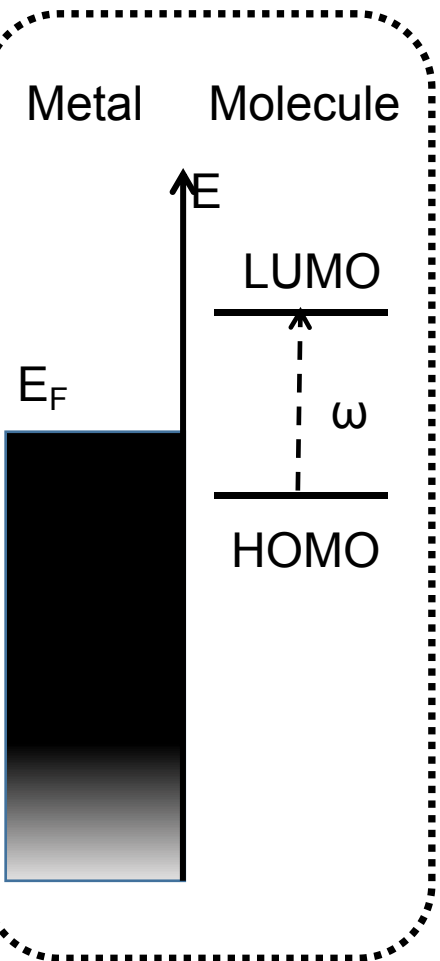
There are several mechanisms that can enhance Raman signals

Molecular Resonance

Resonance Charge Transfer

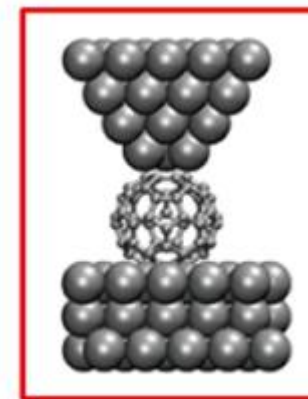
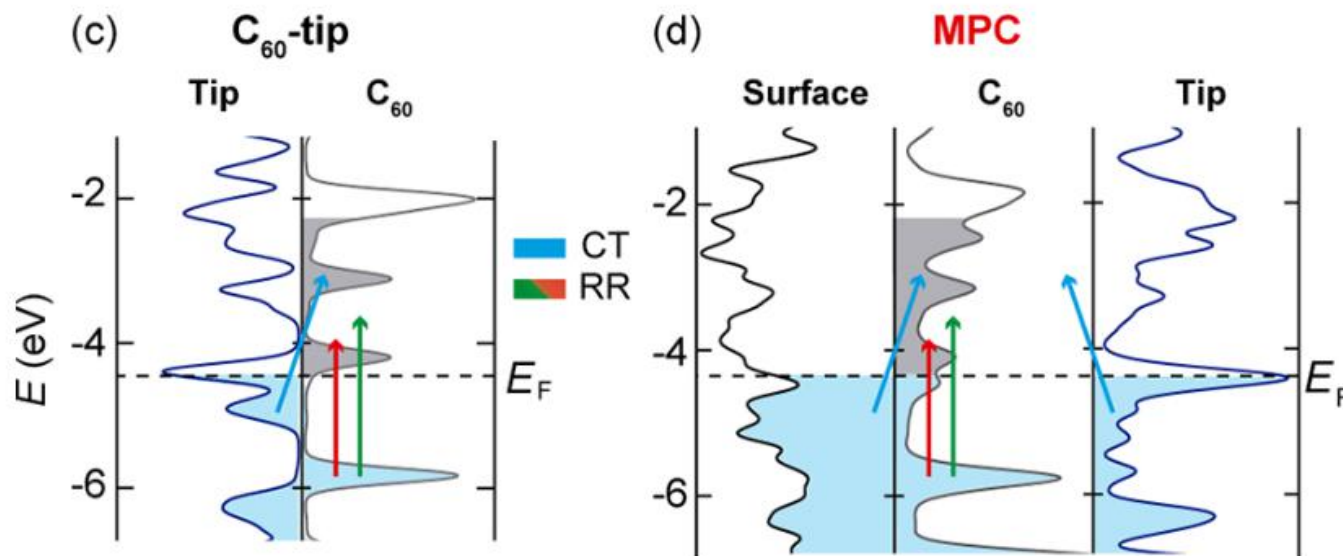
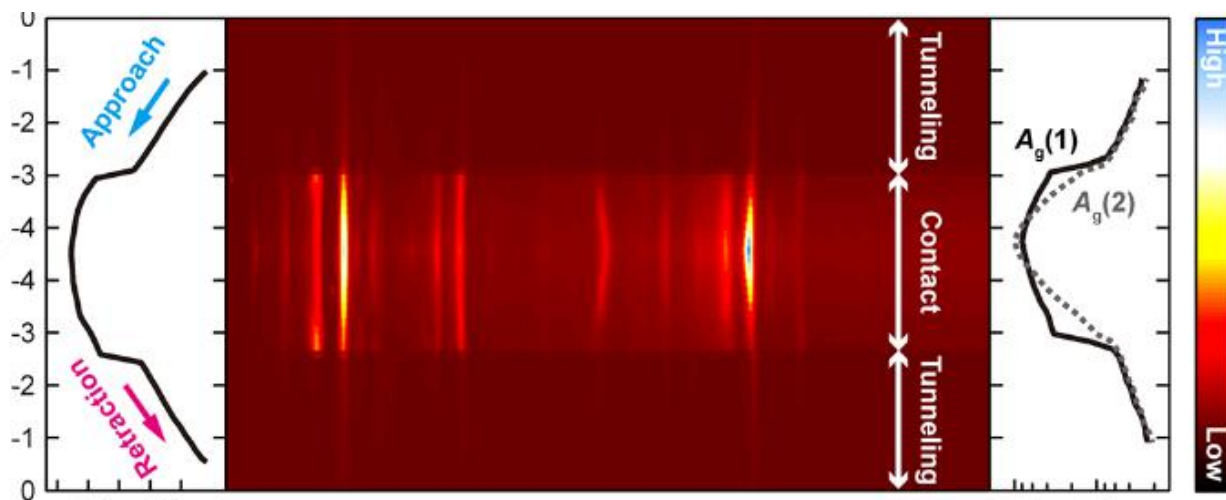
Plasmon Resonance

Chemical Enhancement



Jensen, Aikens, Schatz, Chem. Soc. Rev. 37, 1061, (2008)

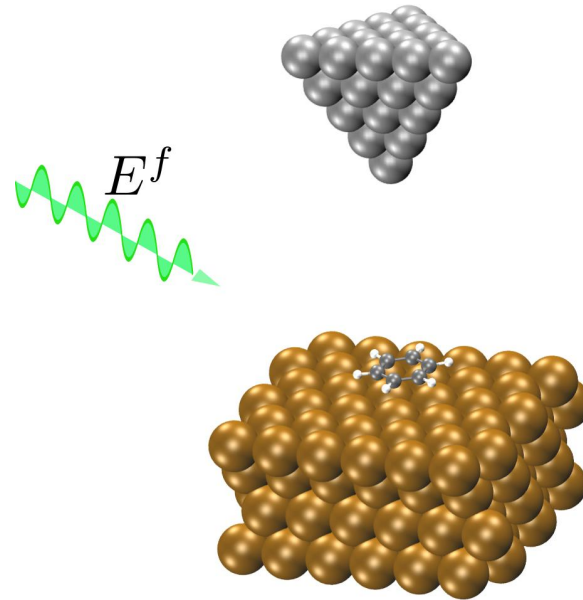
# Molecular Point Contact TERS



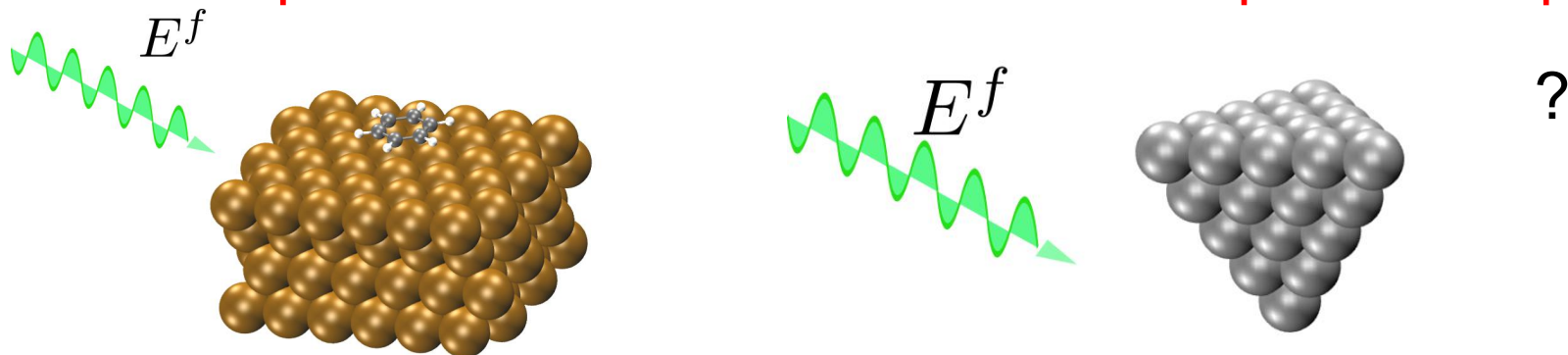


# Long-Distance Approximation

Recently, we have developed a new and efficient method to compute TERS images



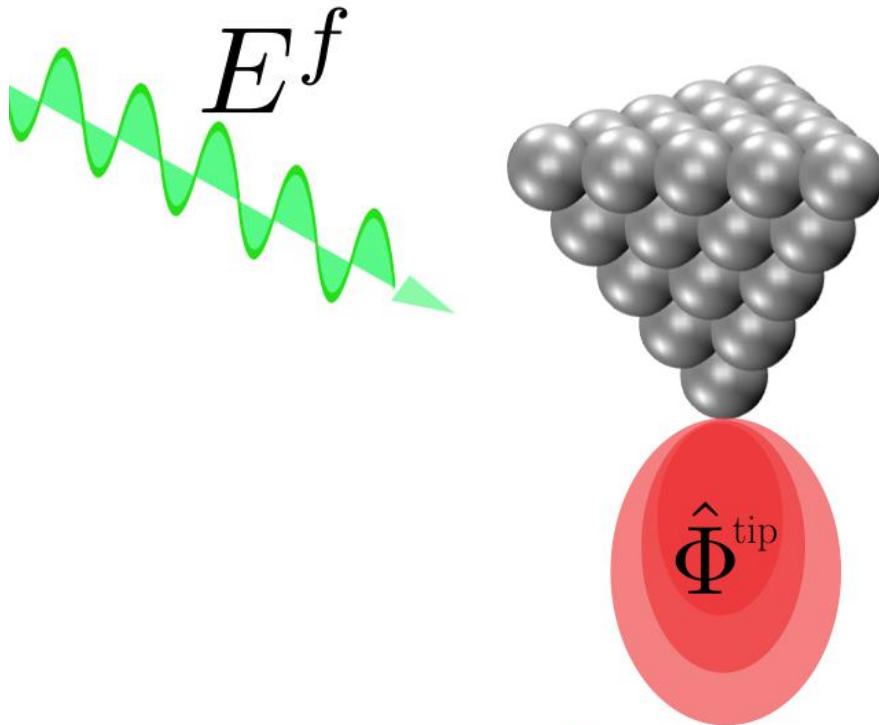
$$\hat{H}(t) = \underbrace{\hat{H}_0^{\text{sm}} - \hat{\mu}^{\text{sm}} \cdot \bar{E}^f(t)} + \underbrace{\hat{H}_0^{\text{tip}} - \hat{\mu}^{\text{tip}} \cdot \bar{E}^f(t)} + \underbrace{\hat{V}^{\text{int}}(t)}$$



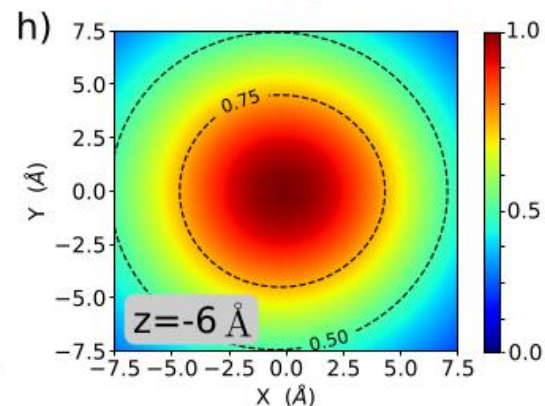
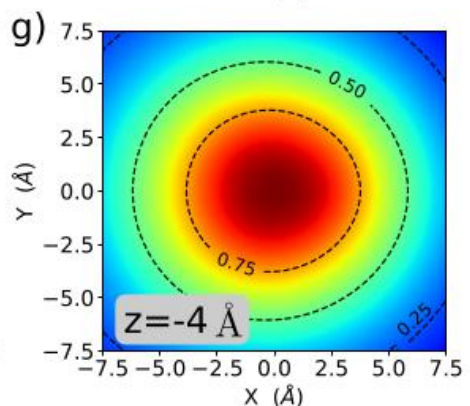
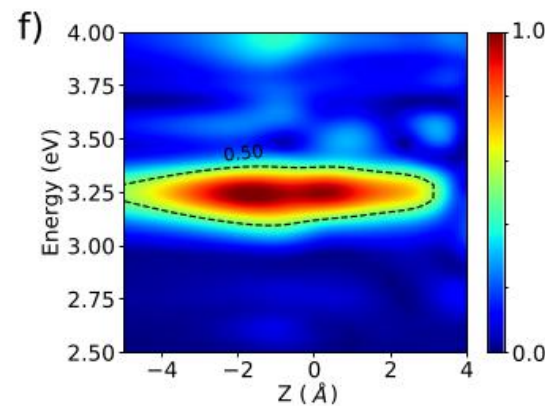
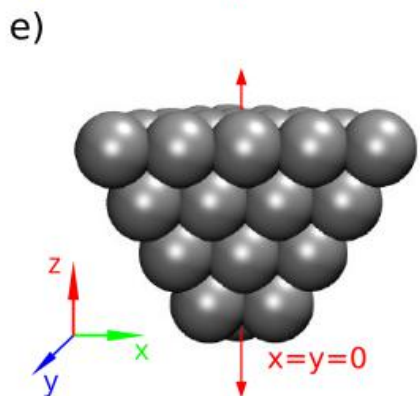
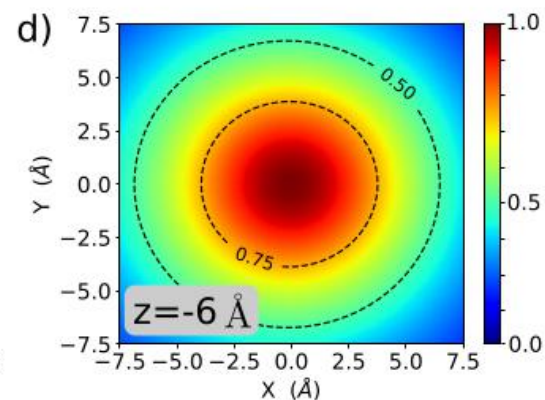
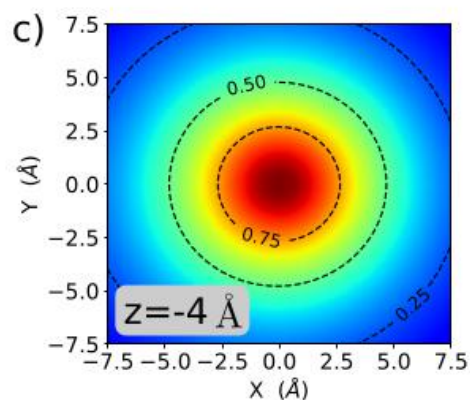
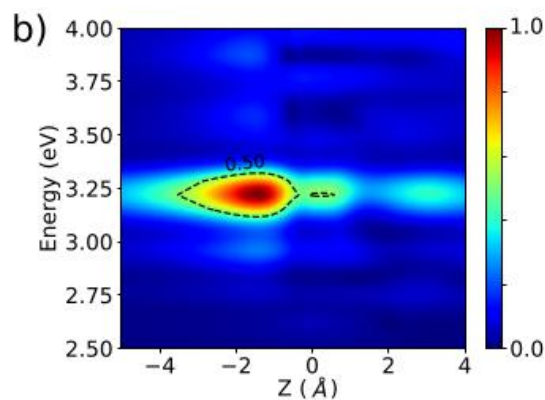
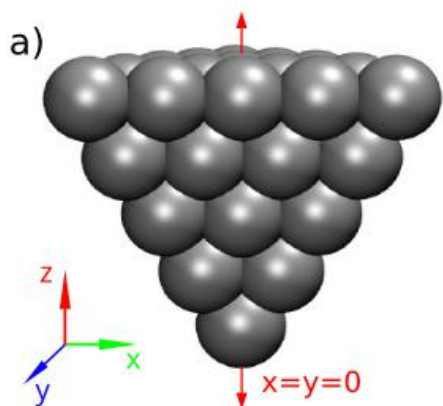
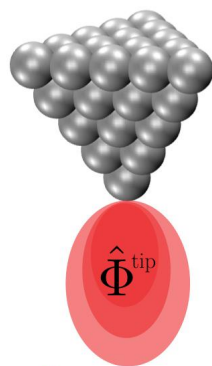
# Long-Distance Approximation

If the tip and substrate are a few angstroms apart, we can solve the electron dynamics for the tip independently

$$\hat{V}_{\text{int}}(\mathbf{r}_{\text{sm}}, t; \mathbf{R}_{\text{tip}}) =$$



# Near Field



# Calculation of Polarizability with DFPT

Within Kohn-Sham density functional perturbation theory, we have

$$\hat{h}_{\text{KS}} = \hat{h}_{\text{KS}}^{(0)} + \hat{h}_{\text{KS}}^{(1)} \lambda_{\alpha} + \dots$$

$$\hat{h}_{\text{KS}}^{(1)} = +\hat{v}_{\text{ext}}^{(1)} + \hat{v}_{\text{H}}^{(1)} + \hat{v}_{\text{xc}}^{(1)} + \hat{v}_{\text{E}},$$

where

$$\hat{h}_{\text{KS}} \psi_p = \epsilon_p \psi_p \quad \hat{h}_{\text{KS}} = \hat{t}_{\text{s}} + \hat{v}_{\text{ext}} + \hat{v}_{\text{H}} + \hat{v}_{\text{xc}}$$

The solution of the Sternheimer equation gives

$$\rho_{\alpha}^{(1)}(\mathbf{r}) = \frac{\partial \rho(\mathbf{r})}{\partial \lambda_{\alpha}} = \sum_p f(\epsilon_p) [\psi_p^{(1)}(\mathbf{r}) \psi_p^{(0)}(\mathbf{r}) + \psi_p^{(0)}(\mathbf{r}) \psi_p^{(1)}(\mathbf{r})],$$

and finally we get

$$\alpha_{\alpha\beta} = \frac{\partial \mu_{\alpha}^{\text{ind}}}{\partial \lambda_{\beta}} = \int d\mathbf{r} \rho_{\beta}^{(1)}(\mathbf{r}) r_{\alpha}$$

# Calculation of Polarizability with DFPT

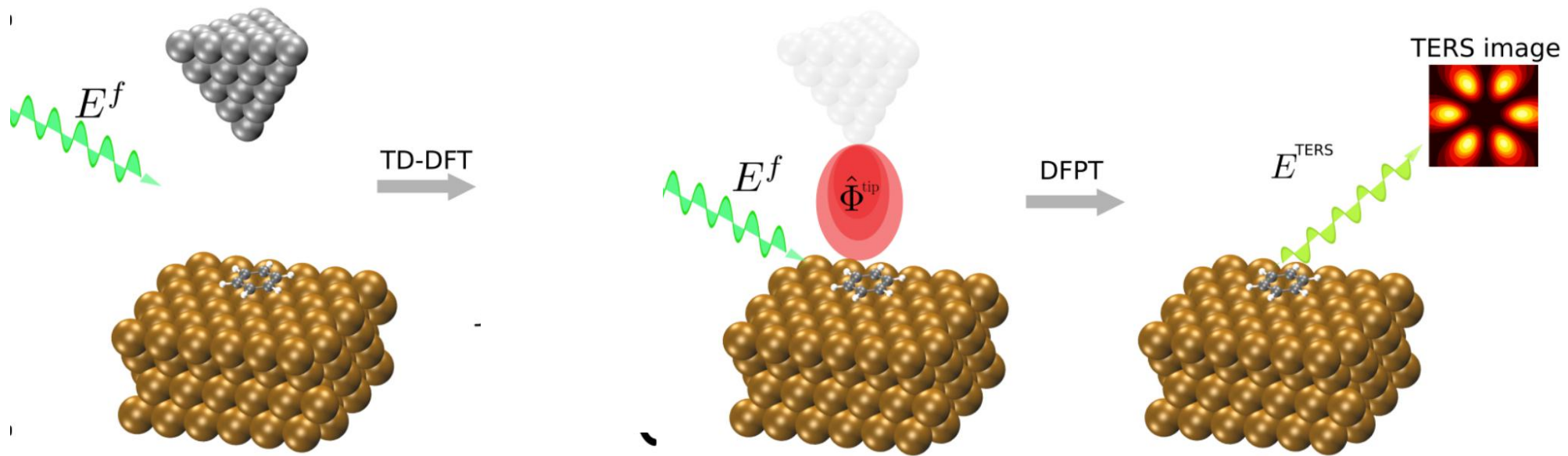
In standard Raman calculations we have,

$$\hat{\nu}_{\mathbf{E}} = -r_{\alpha}$$

For the substrate-molecule we then have,

$$\hat{\nu}_{\mathbf{E}} = -r_{\alpha} + \Re \left[ \frac{\partial \tilde{\Phi}_{\alpha}^{\text{tip}}(\mathbf{r}, \omega_0; \mathbf{R}^{\text{tip}})}{\partial \lambda_{\alpha}} \Big|_{\lambda_{\alpha}=0} \right]$$

# Tip-Enhanced Raman Simulations



Raman Simulation

$$I^{\text{Raman}}(\omega_i) \propto \left| \frac{\partial \alpha_{zz}}{\partial Q_i} \right|^2$$

# Tutorial

The screenshot shows the GitHub interface for the repository 'TERS\_Tutorial'. At the top, the repository name is displayed with a 'Public' badge. To the right, there are buttons for 'Edit Pins' and 'Watch' (with a count of 1). Below this, navigation options include 'master' (selected), '2 branches', and '0 tags'. Action buttons include 'Go to file', 'Add file', and 'Code' (highlighted in green). A commit history table follows, listing recent updates by user 'litman90'. The table includes columns for file names, commit messages, and commit times. Below the table, the 'README.md' file is previewed, showing the title 'TERS Tutorial' and a brief description of the tutorial's purpose.

TERS\_Tutorial Public

Edit Pins Watch 1

master 2 branches 0 tags

Go to file Add file Code

File	Commit Message	Commit Time
litman90 Update README.md	567701e	1 minute ago 38 commits
example	better improvement of local.py	9 months ago
.gitignore	cleanup	9 months ago
README.md	Update README.md	1 minute ago
Tutorial.ipynb	better improvement of local.py	9 months ago
get_vibrations.py	cleanup	9 months ago
local.py	remove uncommented sentences	9 months ago

README.md

## TERS Tutorial

A small tutorial to run DFPT local field calculation and plot TERS images with the FHI-aims code. Corresponding publication can be found [here](#)

[https://github.com/sabia-group/TERS\\_Tutorial/tree/master](https://github.com/sabia-group/TERS_Tutorial/tree/master)

# Control.in

Standard Raman

```
DFPT polarizability
```

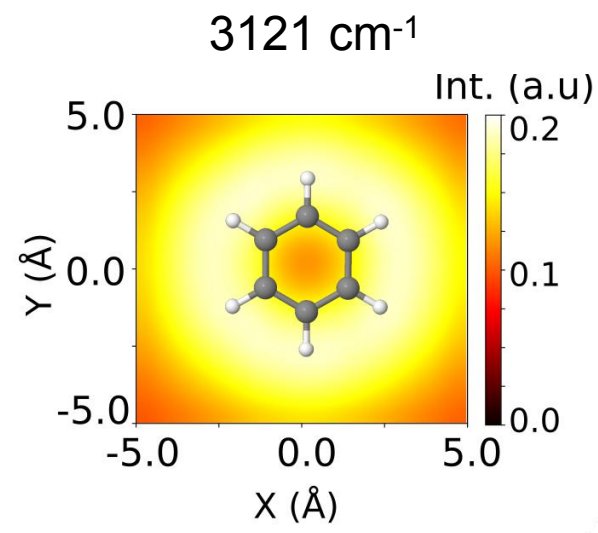
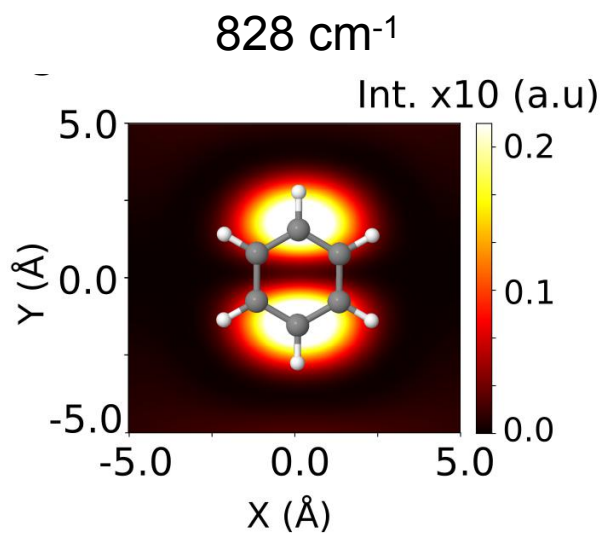
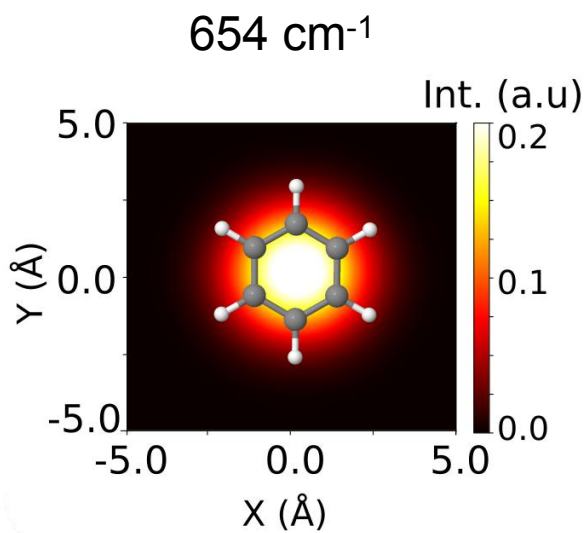
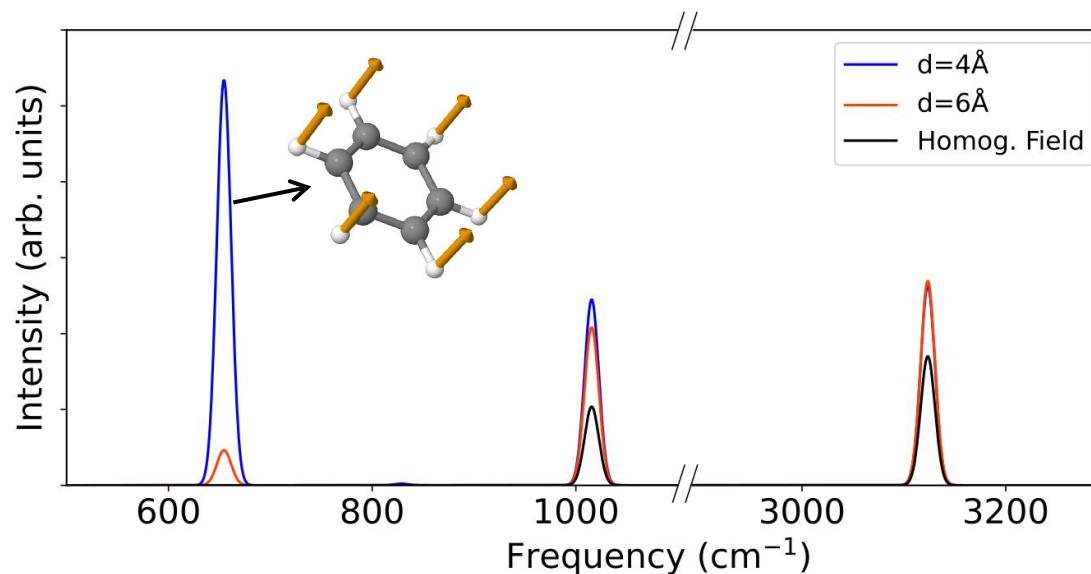
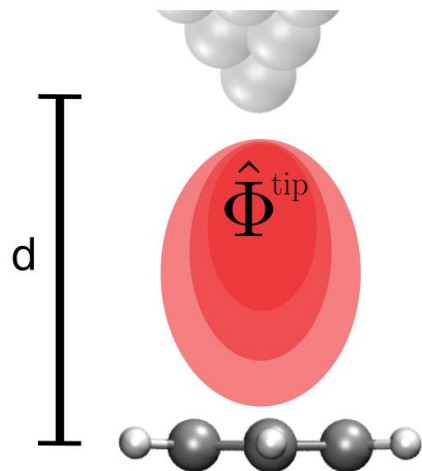
TERS input

```
DFPT local_polarizability nearfield
```

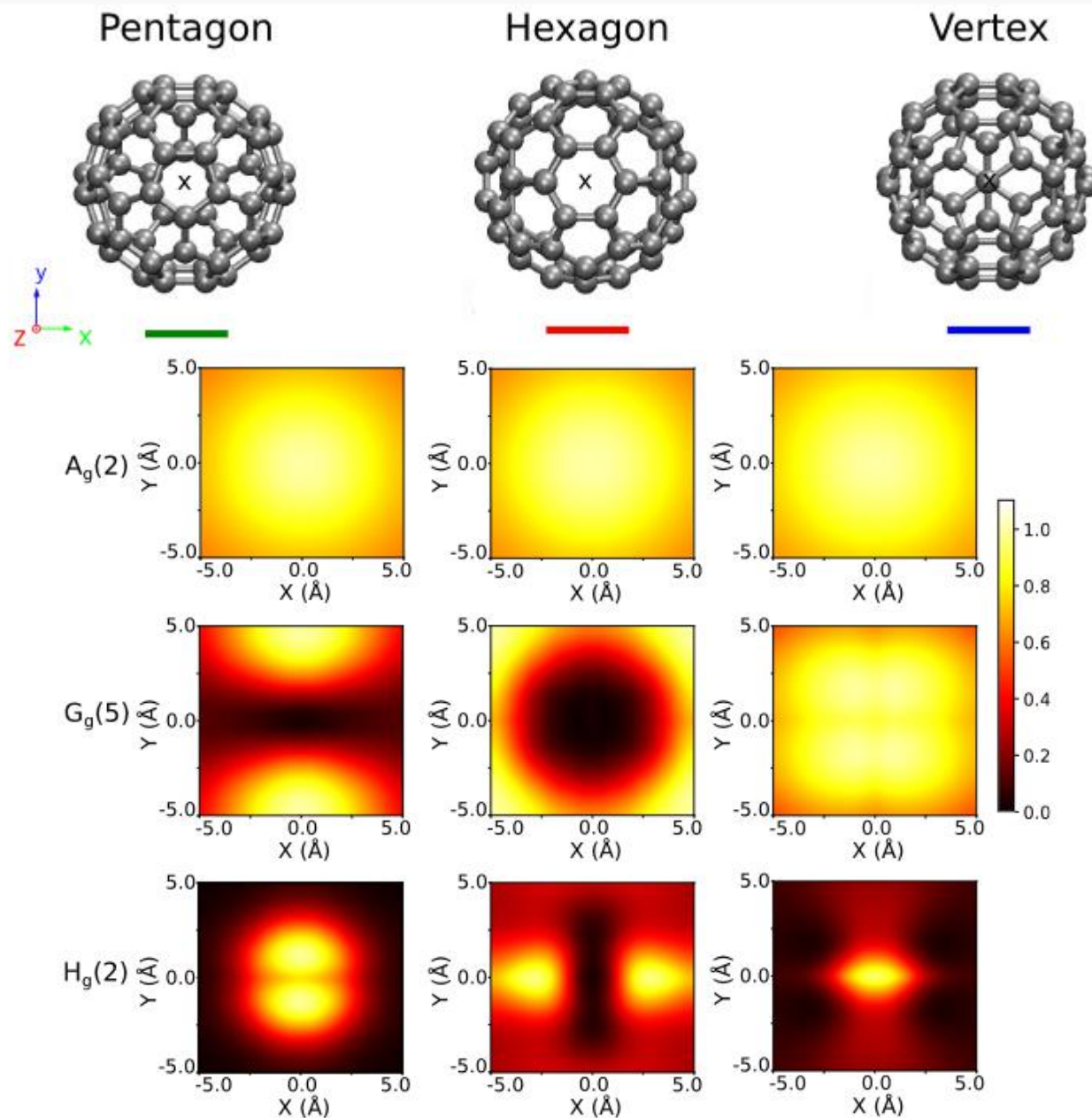
```
DFPT local_parameters numerical zeros.cube zeros.cube tipA_05_vh_ft_0049_3221meV_x1000.cube
```



# The case of Benzene Molecule

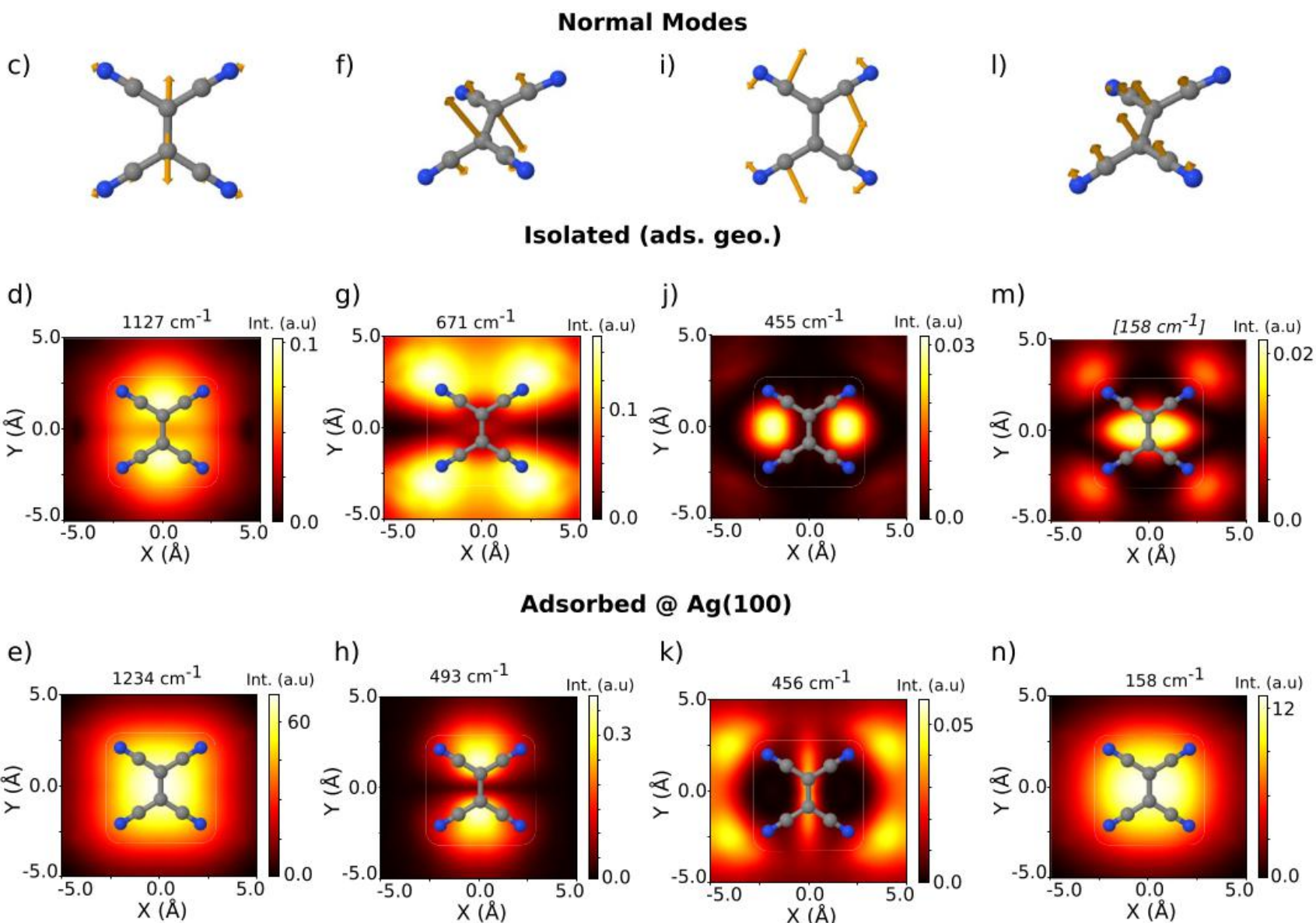
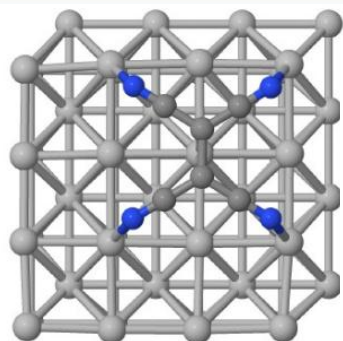


# Determining Molecular Orientations with TERS



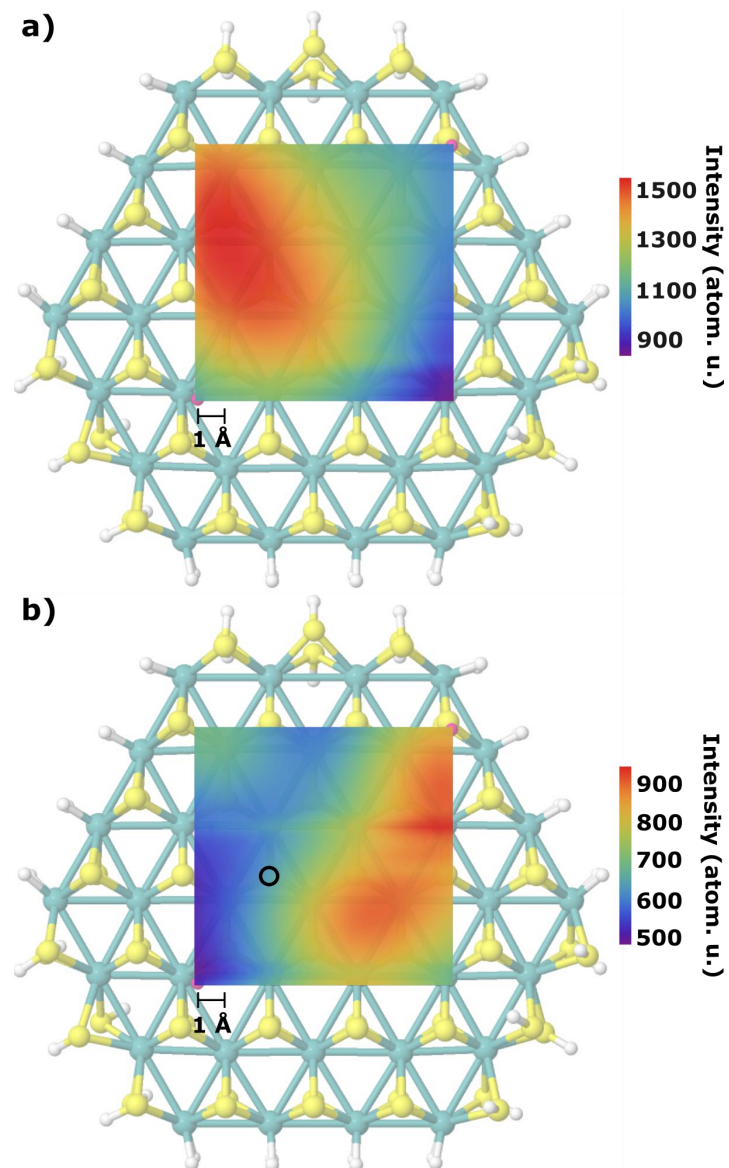
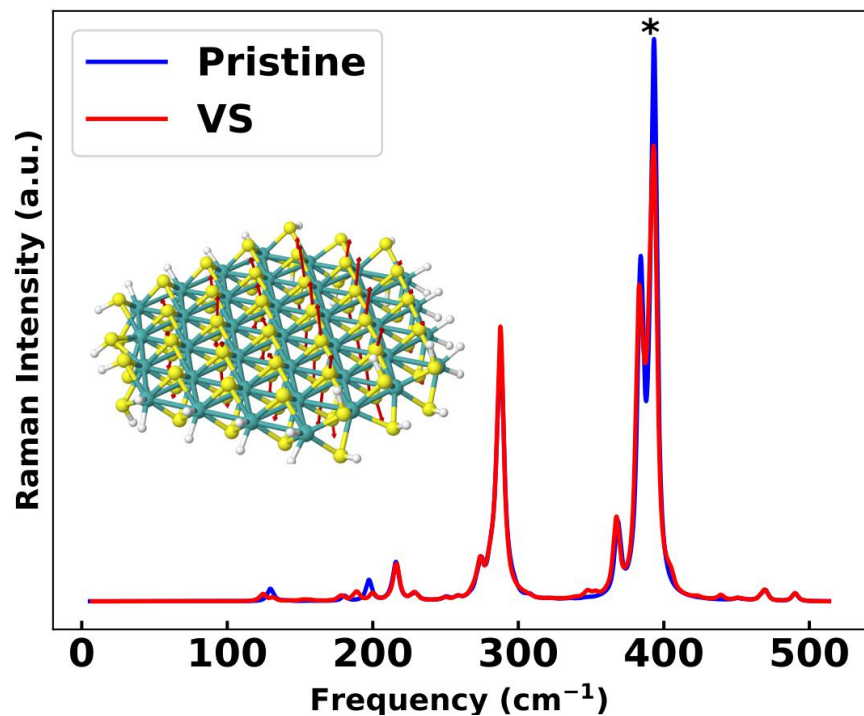
Litman, *et al.* J. Phys. Chem. Lett. 14,6850 (2023)

# Raman Enhancement and Simulations



Litman, *et al.* J. Phys. Chem. Lett. 14,6850 (2023)

# Characterization of Defects in 2D Materials



# Closing Remarks and Outlook

- New first-principles simulation method of tip enhanced Raman scattering (available in FHI-Aims)
- Substrates can play an important role on TERS experiments
- TERS can be used to determine molecular orientations
- Implementation with periodic boundary conditions,
- Investigate finite temperature effects at the single molecule level

