# First-Principles Simulation of Tip-enhanced Raman Spectroscopy

*Yair Litman*

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# Acknowledgement


mpsd
Max-Planck-Institut für
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DFG
Deutsche
Forschungsgemeinschaft

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CAMBRIDGE

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Centro Svizzero di Calcolo Scientifico
Swiss National Supercomputing Centre

MPCDF
Max Planck
Computing &
Data Facility

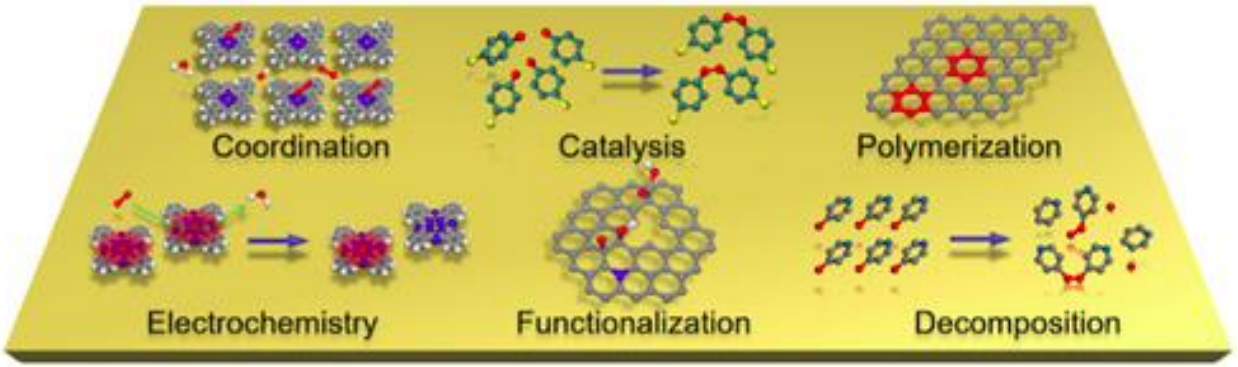

M. Rossi

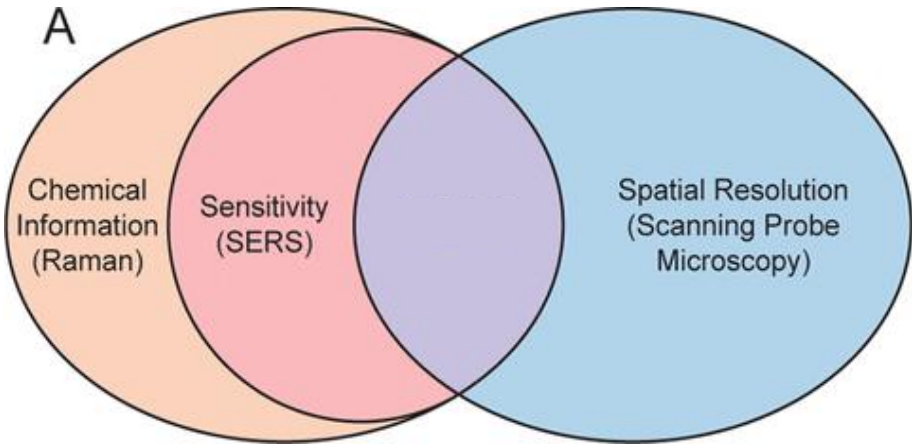
F. Bonafé

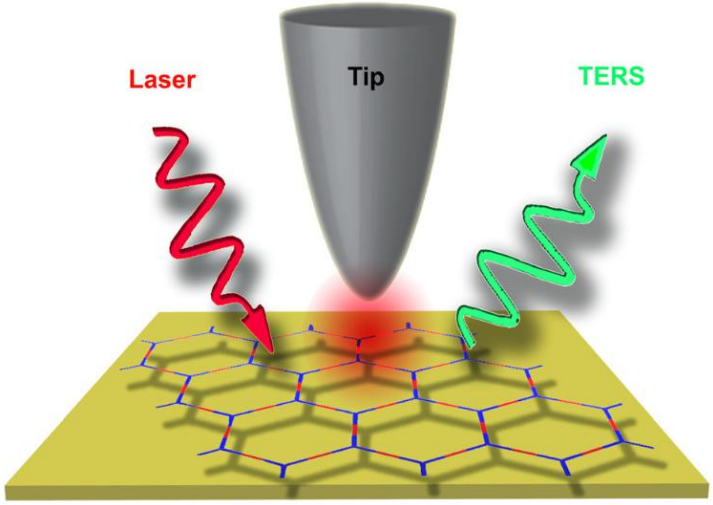
A. Akkoush

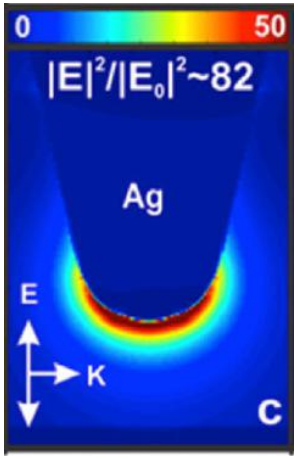
H. Appel

# Tip-Enhanced Raman Spectroscopy



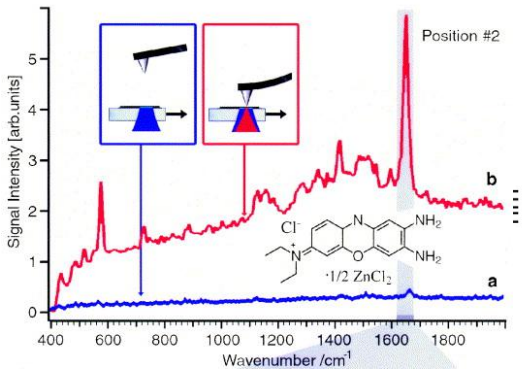



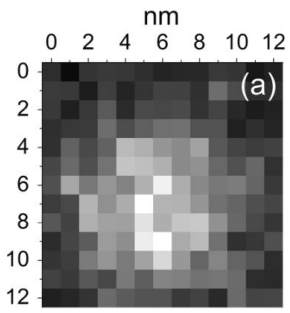



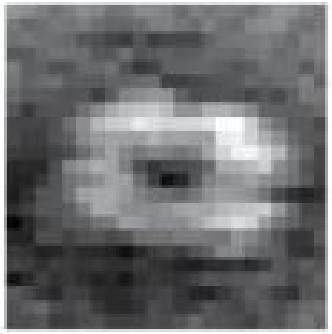

TERS: Tip-Enhanced Raman Spectroscopy

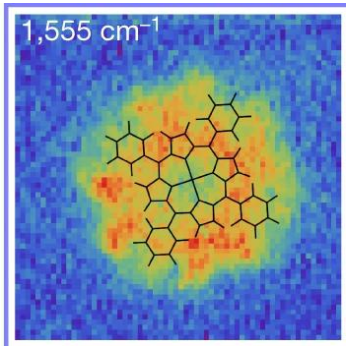
Pozzi, *et al.* Chem. Rev. **117**, 4961 (2017) Zhao, *et al.*, Anal. Bioanal. Chem. **411**, 37 (2019) Cai, *et al.*, CCS Chem. **5**, 55 (2023)

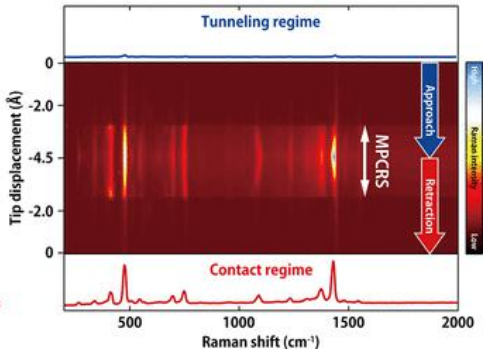
# Two Decades of TERS






2000 — 2008 — 2013 — 2019 — 2022

**First demonstrations**

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

**Single molecule**

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

**Sub-molecular resolution**

Nature **498,** 82 (2013)

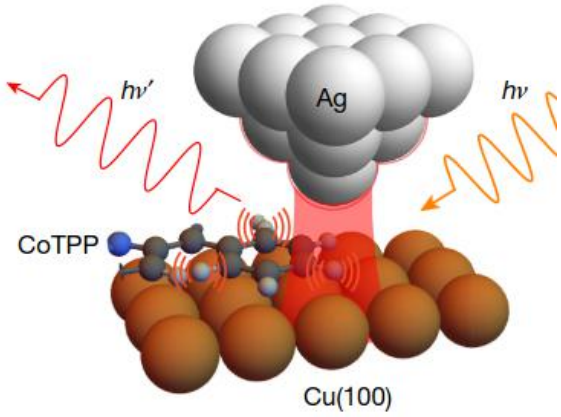
**Angstrom resolution TERS**

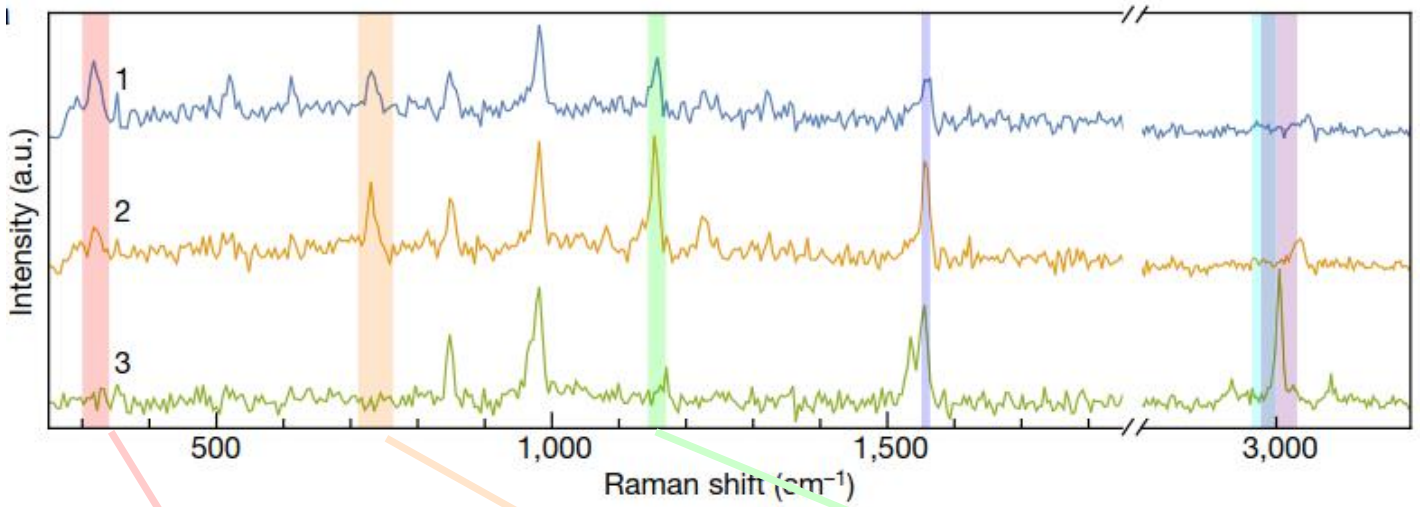
Nature **568,** 78 (2019)

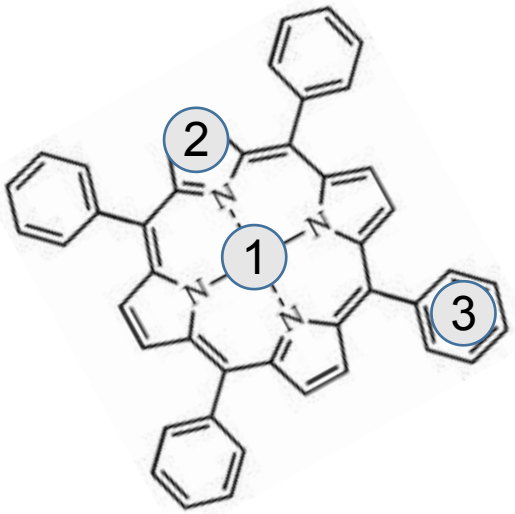
**Molecular point Contact**

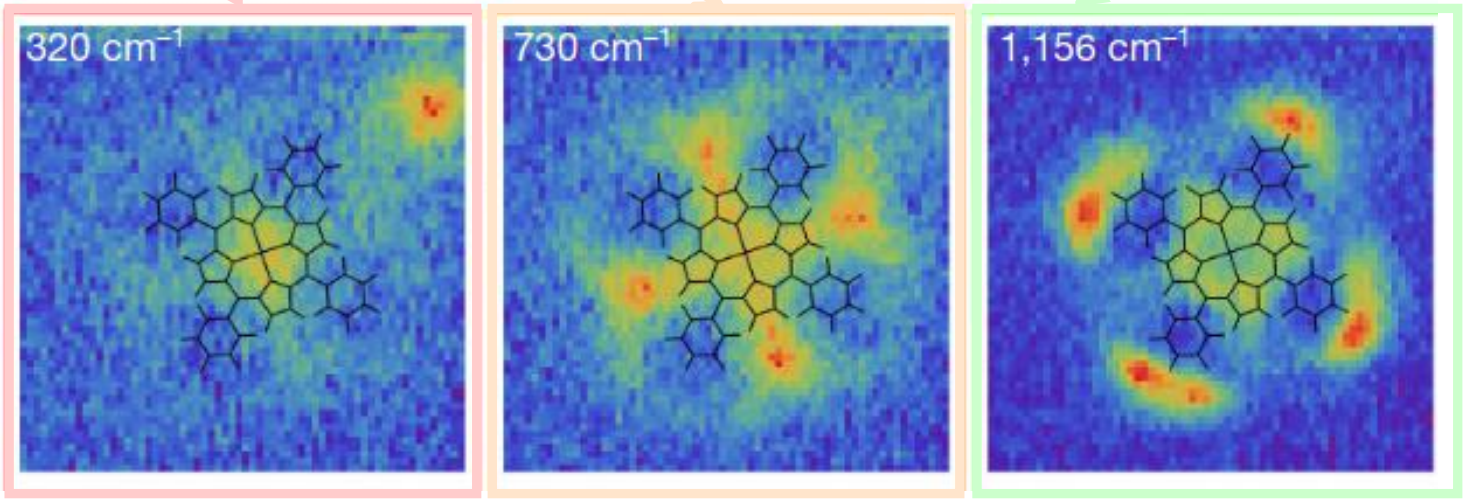
Nano. Lett. **6,** 2170 (2022)

# TERS Images




29 × 29 Å$^2$

# Tip-Enhanced Raman Simulations


Raman Simulation

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

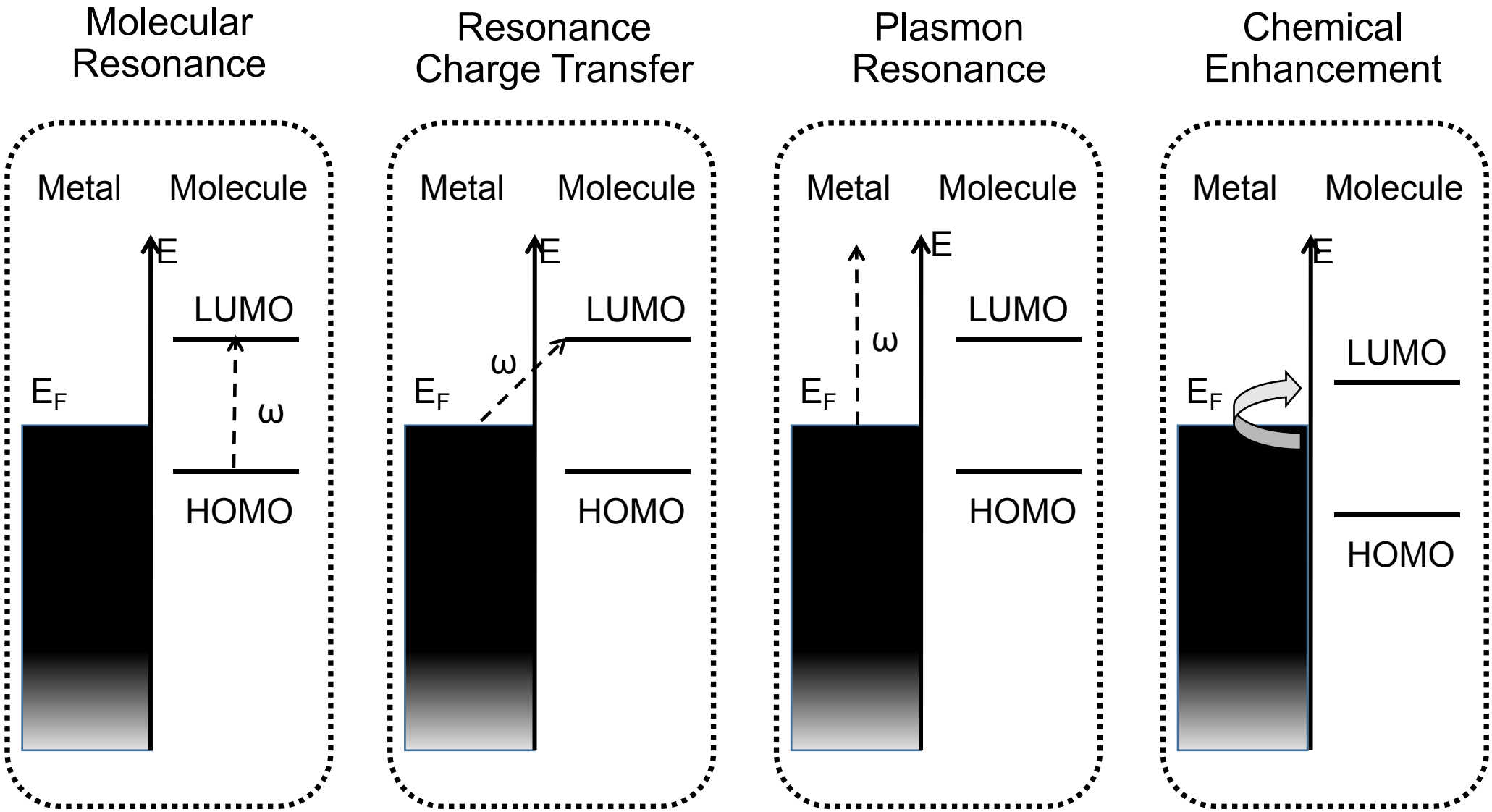
Polarizability

i-th normal mode frequency

i-th normal mode vector

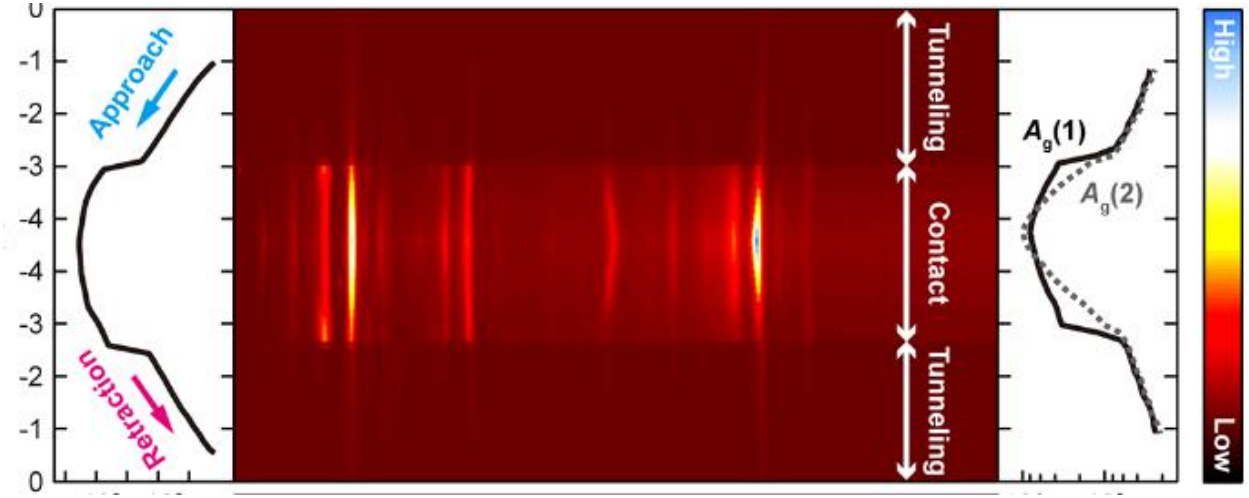
# Raman Enhancement Mechanisms

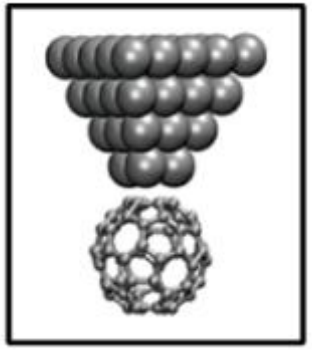
There are several mechanisms that can enhance Raman signals

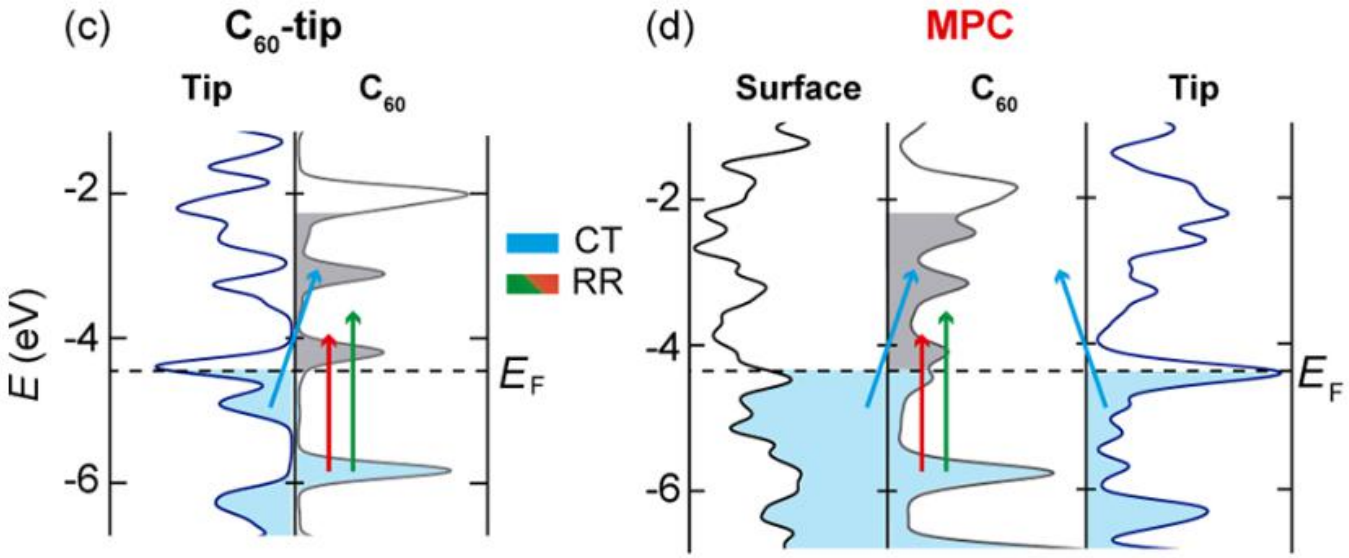


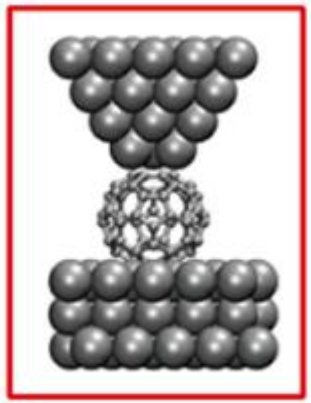

Jensen, Aikens, Schatz, Chem. Soc. Rev. 37, 1061, (2008)

# Molecular Point Contact TERS



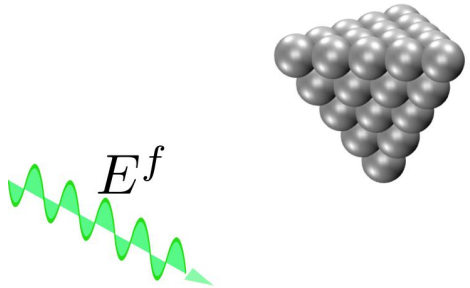


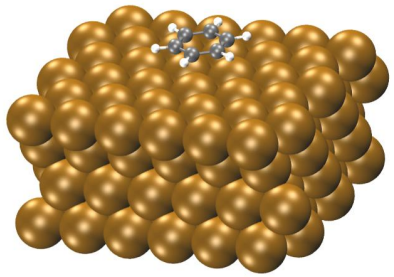



Cirera, Litman, *et al.* Nano Lett. 22, 2170 (2022)

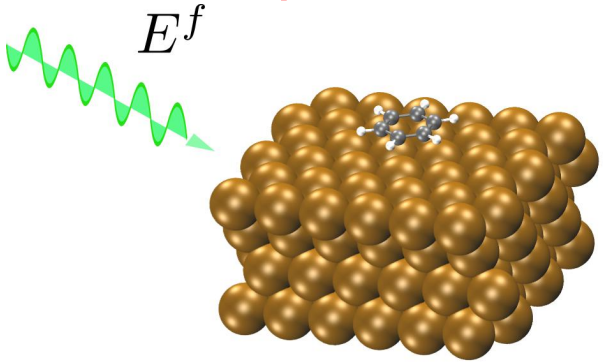
# Long-Distance Approximation

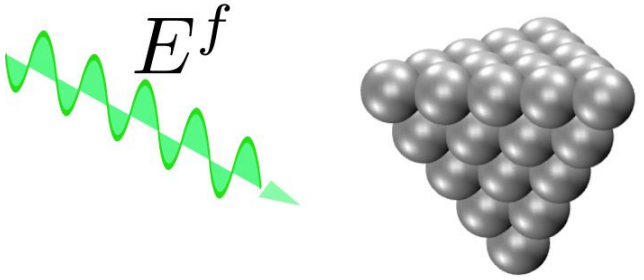
Recently, we have developed a new and efficient method to compute TERS images



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



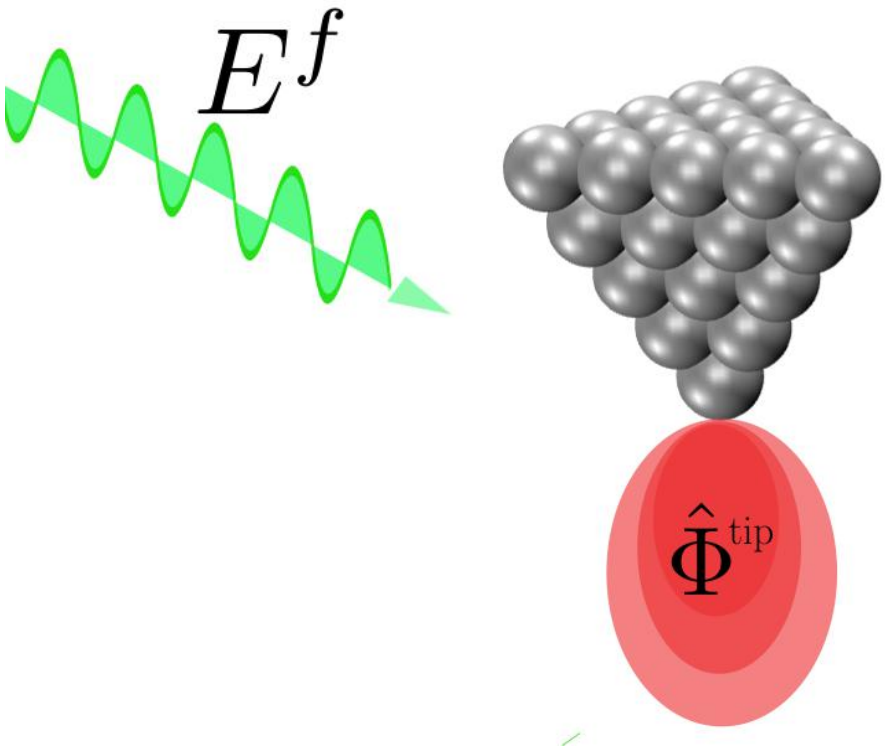




?

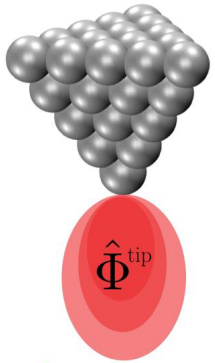
# Long-Distance Approximation

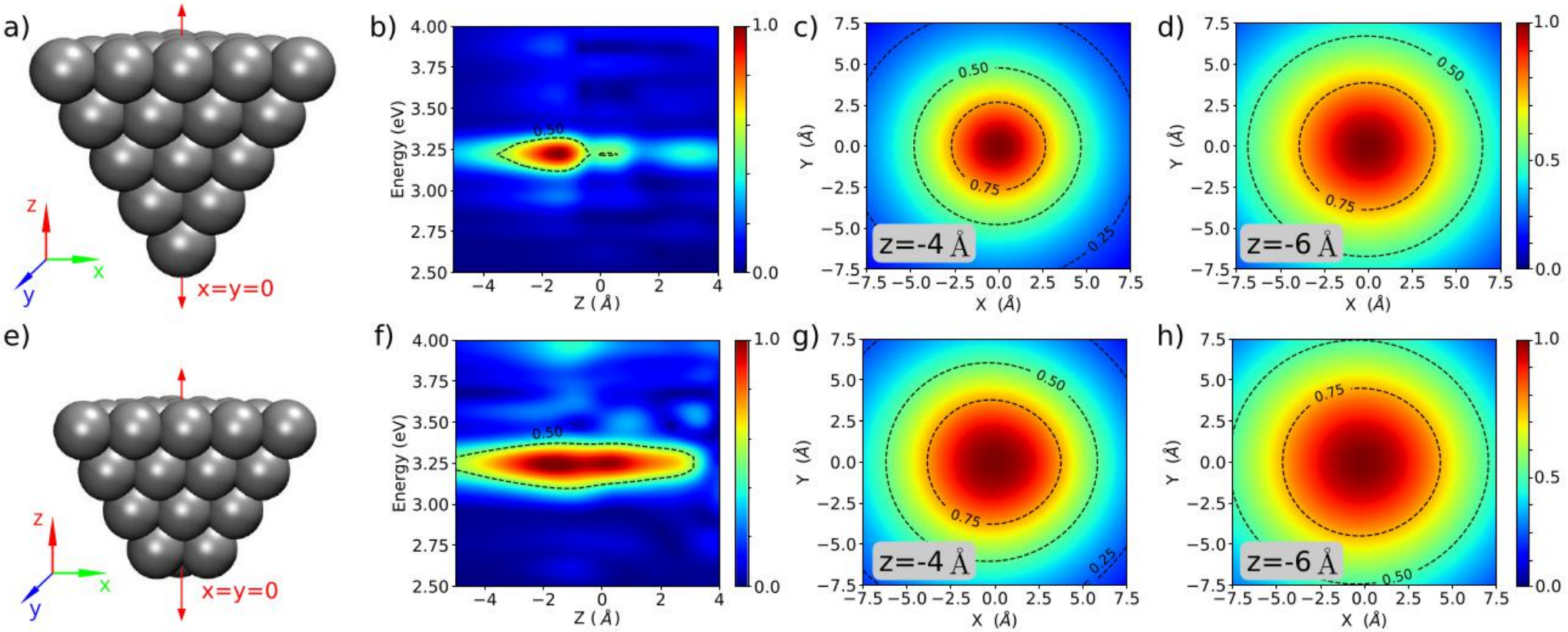
If the tip and substrate are a few angstroms apart, we can solve the electron dynamics for the tip independently

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



# Near Field




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

# Calculation of Polarizability with DFPT

Within Kohn-Sham density functional perturbation theory, we have

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

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

where

$$\hat{h}_{\mathrm{KS}}\psi_p = \epsilon_p\psi_p \qquad \hat{h}_{\mathrm{KS}} = \hat{t}_{\mathrm{s}} + \hat{\nu}_{\mathrm{ext}} + \hat{\nu}_{\mathrm{H}} + \hat{\nu}_{\mathrm{xc}}$$

The solution of the Sternheimer equation gives

$$\rho^{(1)}_\alpha(\boldsymbol{r}) = \frac{\partial\rho(\boldsymbol{r})}{\partial\lambda_\alpha} = \sum_p f(\epsilon_p)[\psi^{(1)}_p(\boldsymbol{r})\psi^{(0)}_p(\boldsymbol{r}) + \psi^{(0)}_p(\boldsymbol{r})\psi^{(1)}_p(\boldsymbol{r})],$$

and finally we get

$$\alpha_{\alpha\beta} = \frac{\partial\mu^{\mathrm{ind}}_\alpha}{\partial\lambda_\beta} = \int d\boldsymbol{r}\,\rho^{(1)}_\beta(\boldsymbol{r})r_\alpha$$

# Calculation of Polarizability with DFPT

In standard Raman calculations we have,

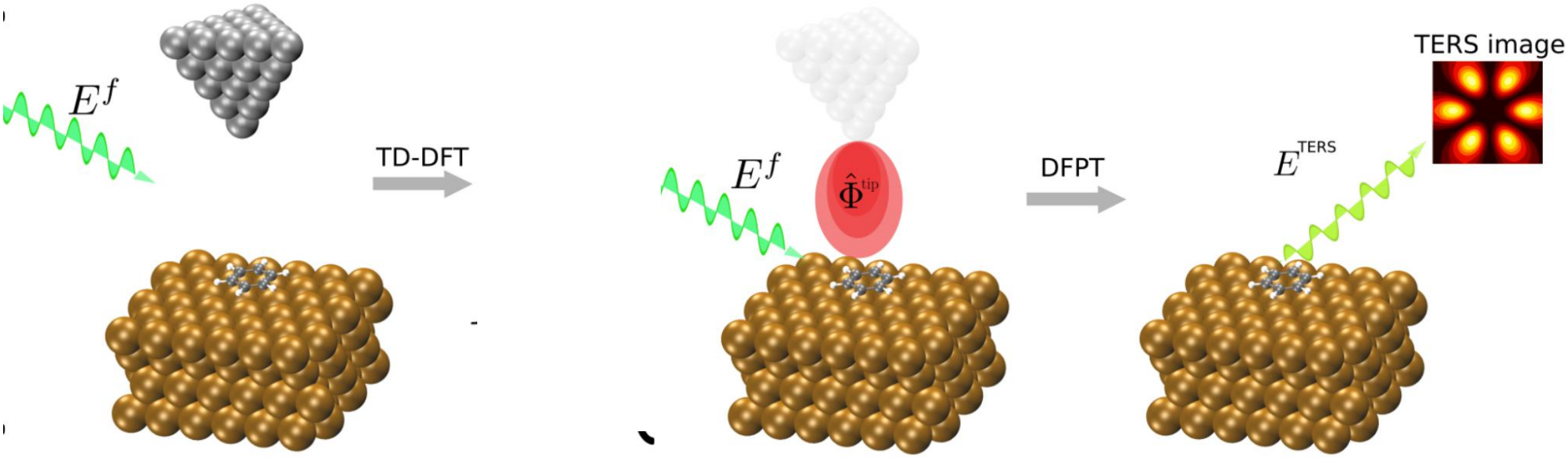
$$\hat{\nu}_{\mathrm{E}} = -r_{\alpha}$$

For the substrate-molecule we then have,

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

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

# Tip-Enhanced Raman Simulations

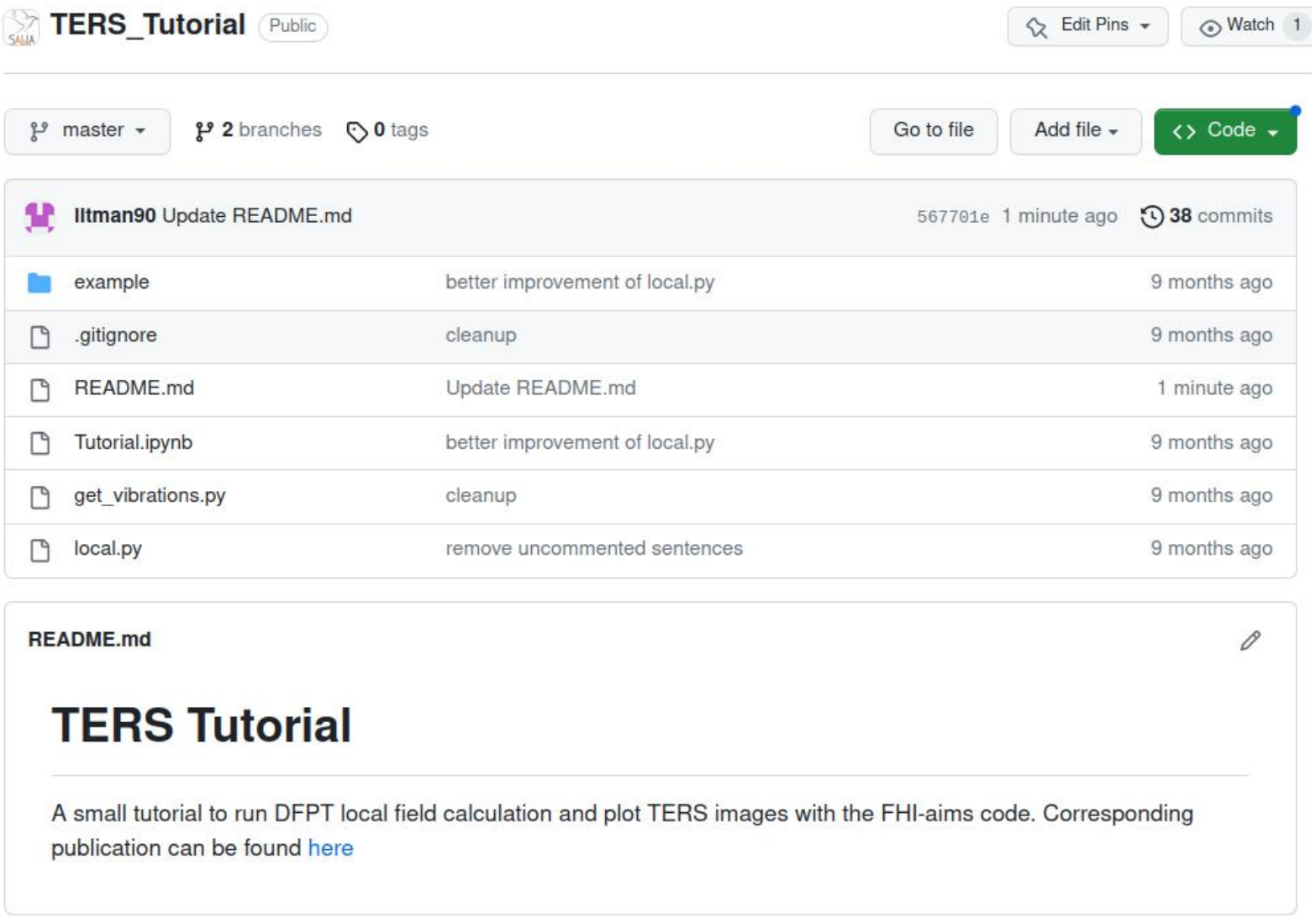



Raman Simulation

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

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

# Tutorial




https://github.com/sabia-group/TERS_Tutorial/tree/master

# Control.in

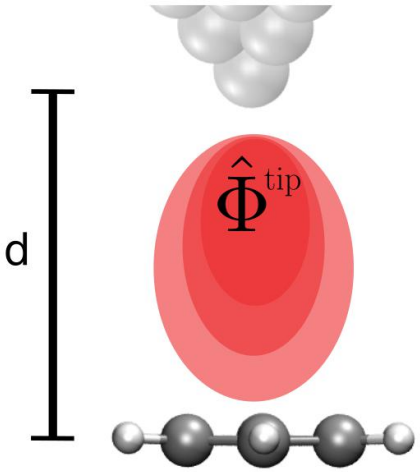
Standard Raman

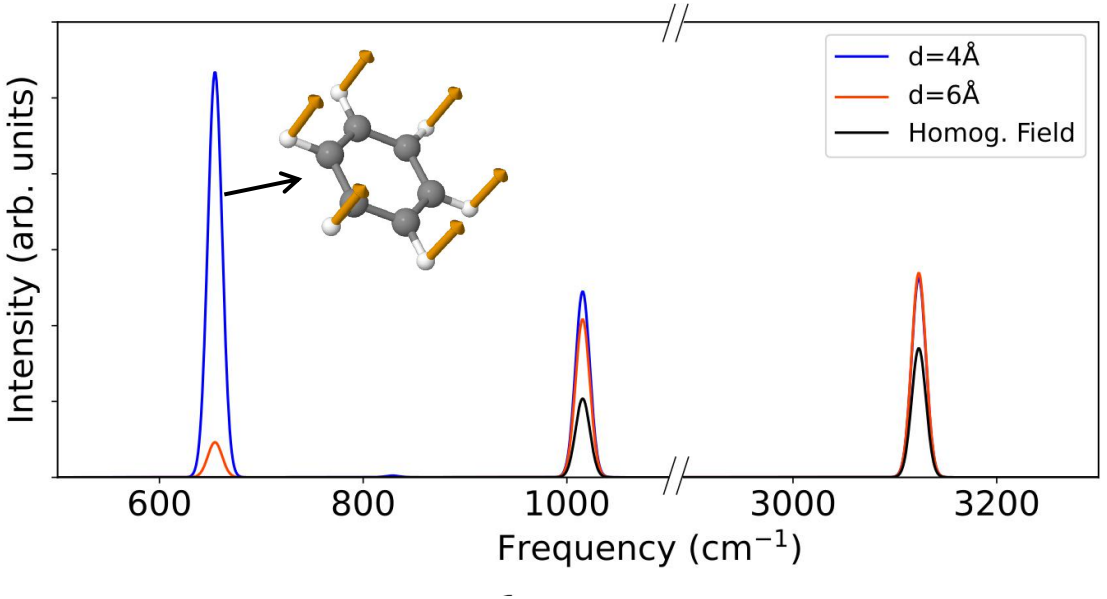
```
DFPT polarizability
```

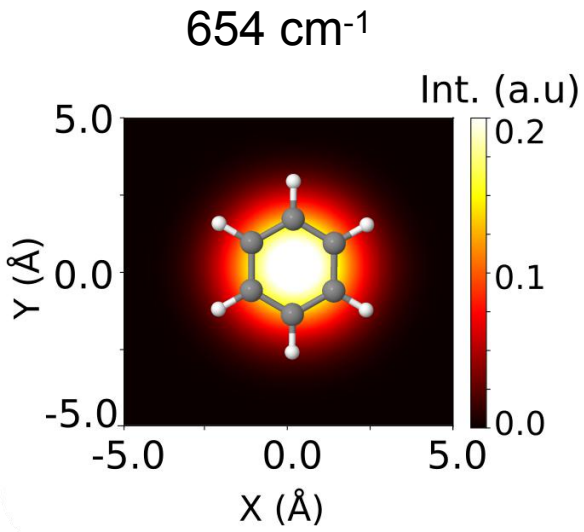
TERS input

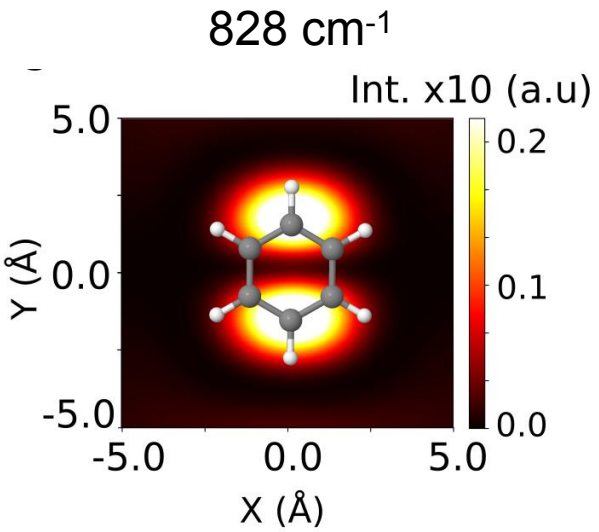
```
DFPT local_polarizability nearfield

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

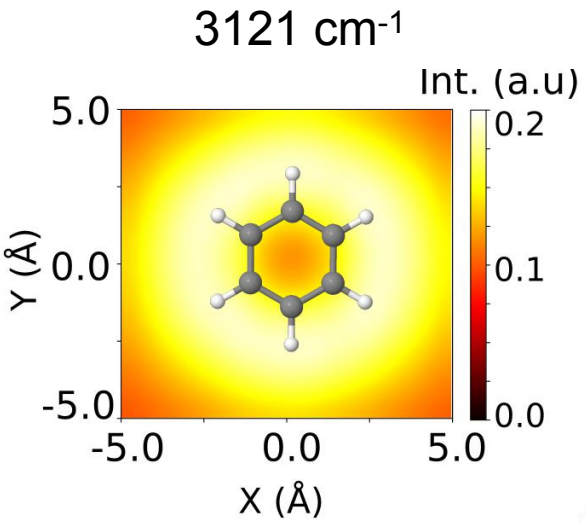
# The case of Benzene Molecule



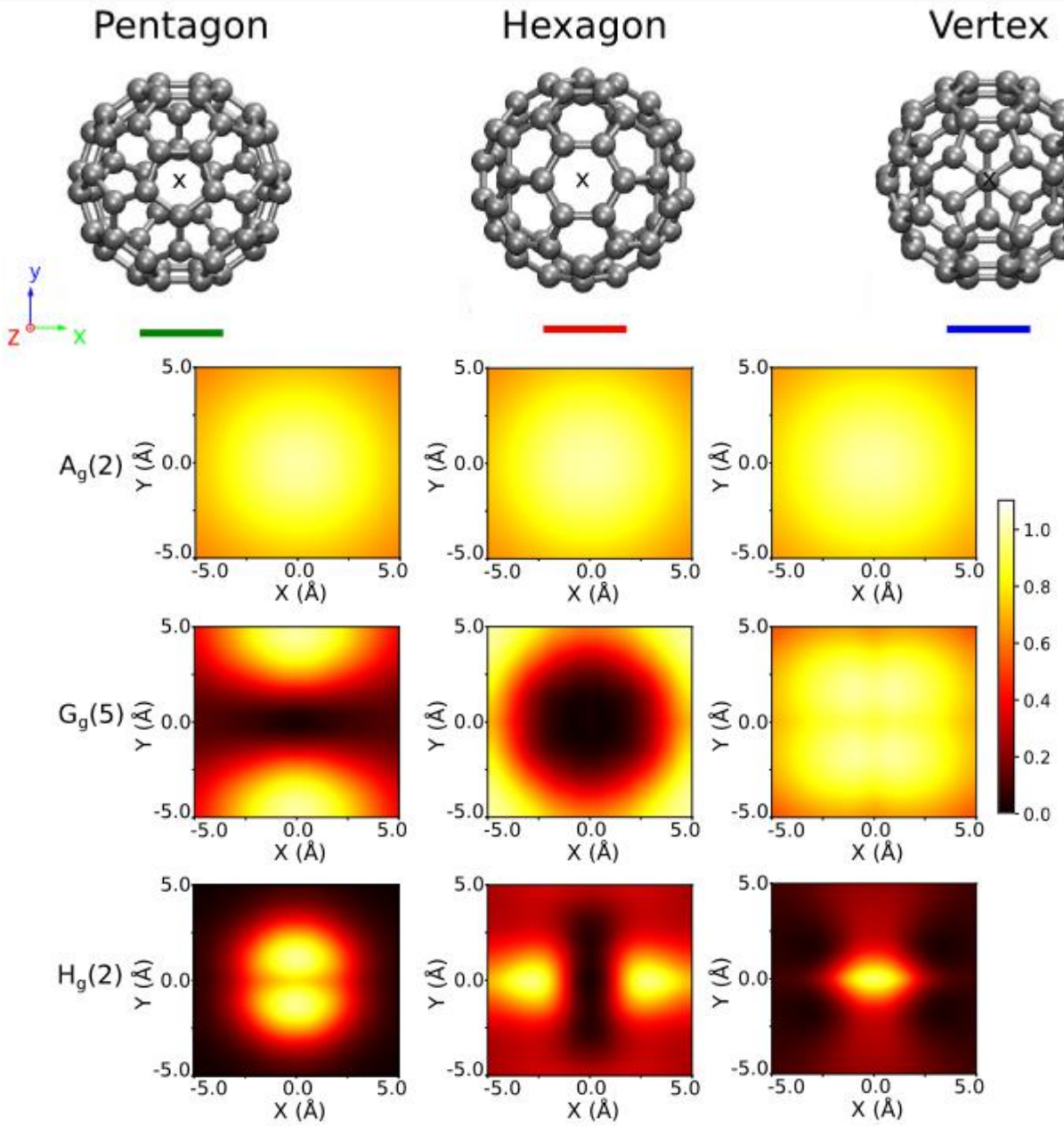



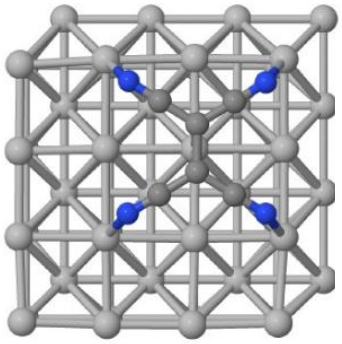

Litman, *et al.* J. Phys. Chem. Lett. 14,6850 (2023)

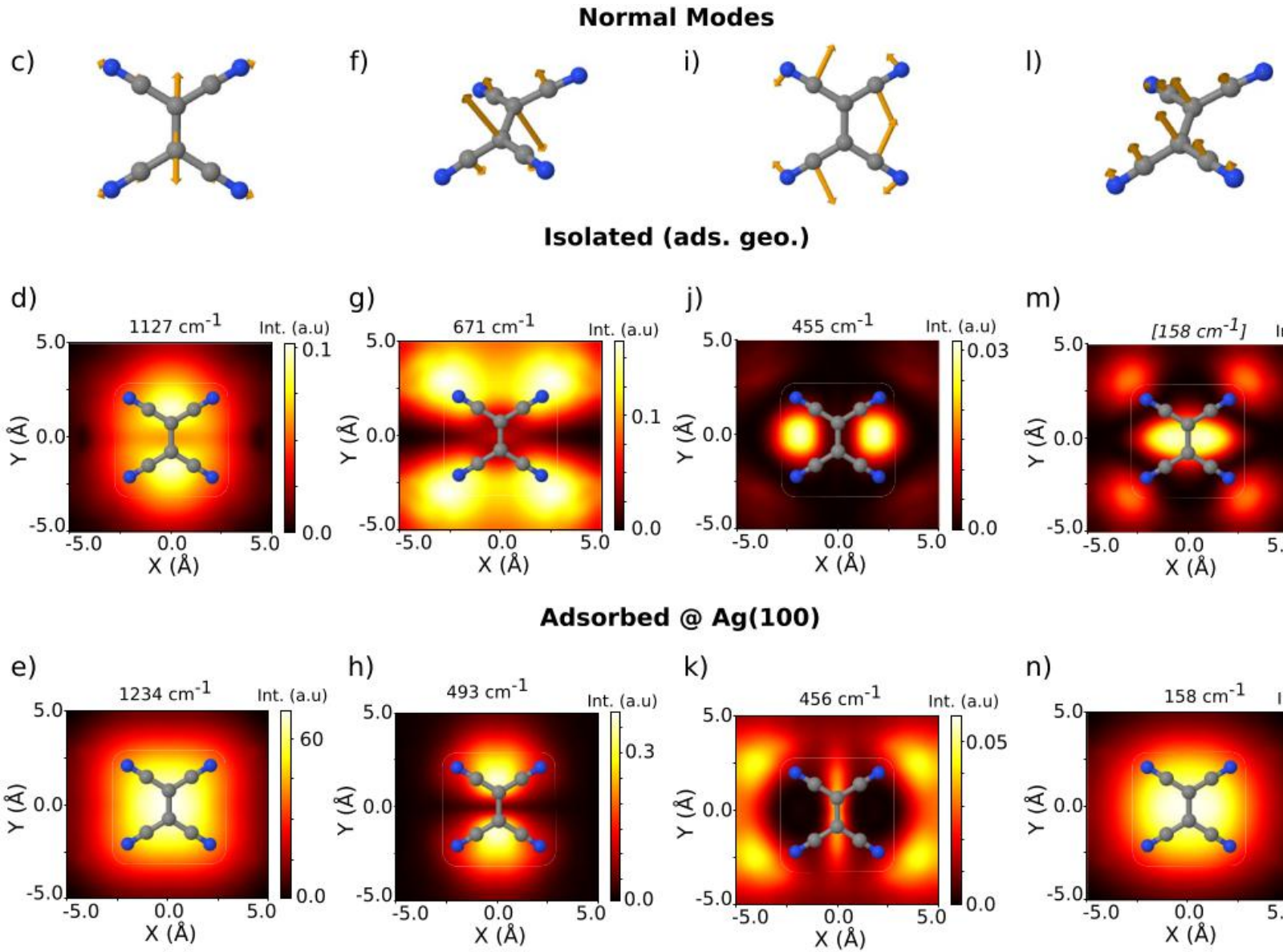
# Determining Molecular Orientations with TERS




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

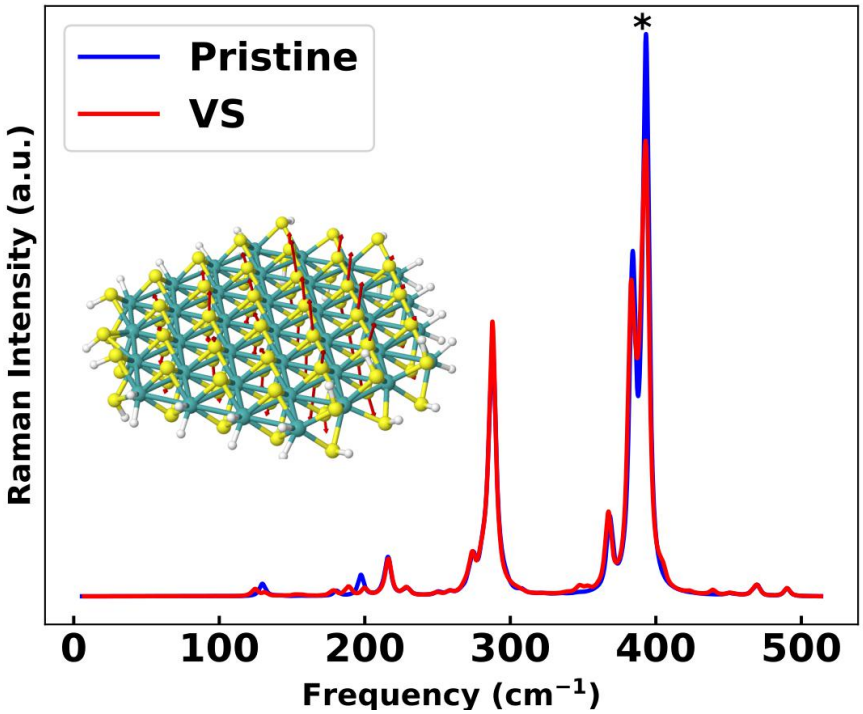
# Raman Enhancement and Simulations

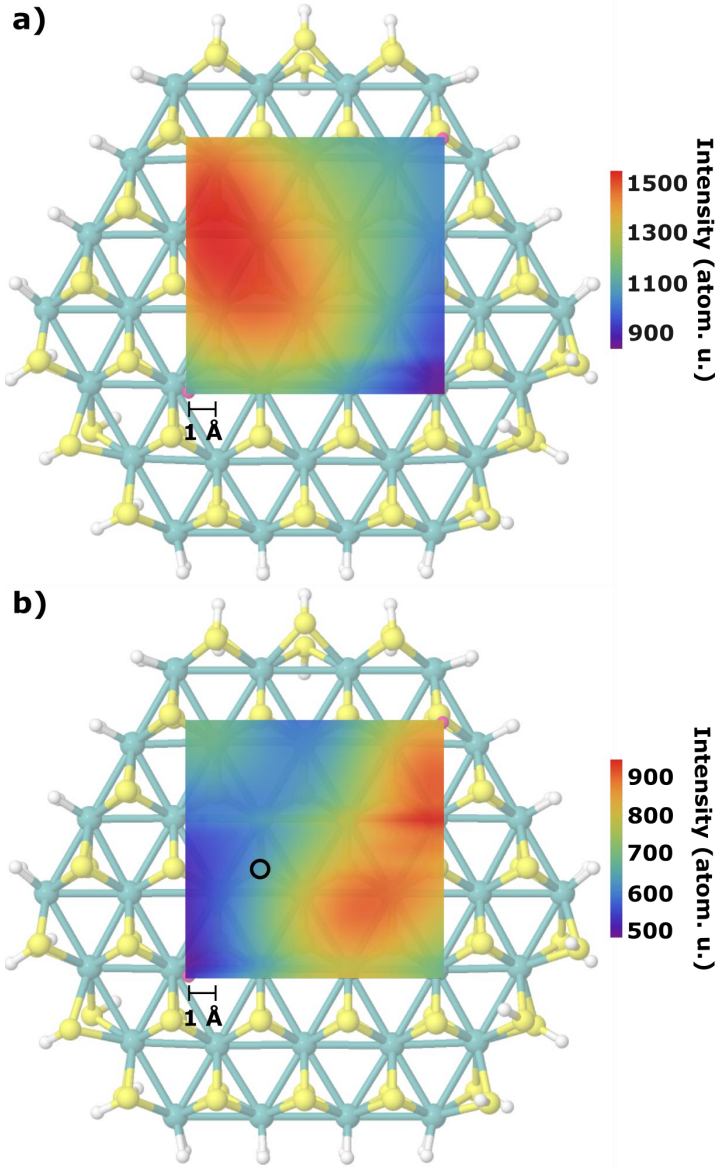





Litman, *et al.* J. Phys. Chem. Lett. 14,6850 (2023)

# Characterization of Defects in 2D Materials




Akkoush, Litman, Rossi, Phys. Status Solidi A, 2300180 (2023)

# 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


THANK YOU