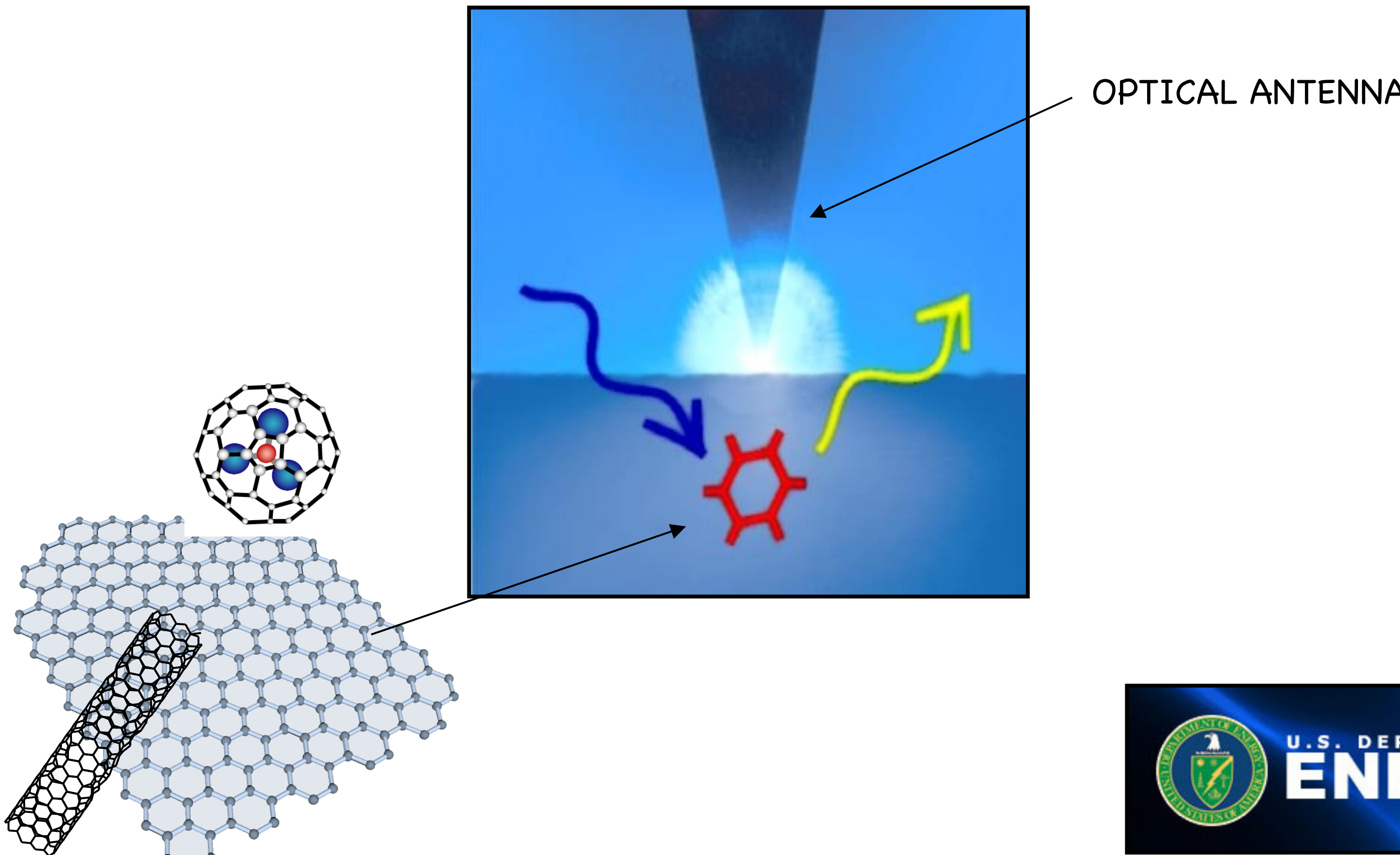
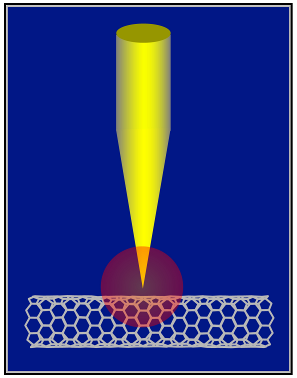
# OPTICAL SPECTROSCOPY OF DEFECTS AND DOPANTS IN NANOCARBON MATERIALS

*Lukas Novotny, Ryan Beams, Hayk Harutyunyan, Gustavo Cancado, Neil Anderson, Achim Hartschuh*

*Institute of Optics, University of Rochester, Rochester, NY, 14627.*




U.S. DEPARTMENT OF ENERGY



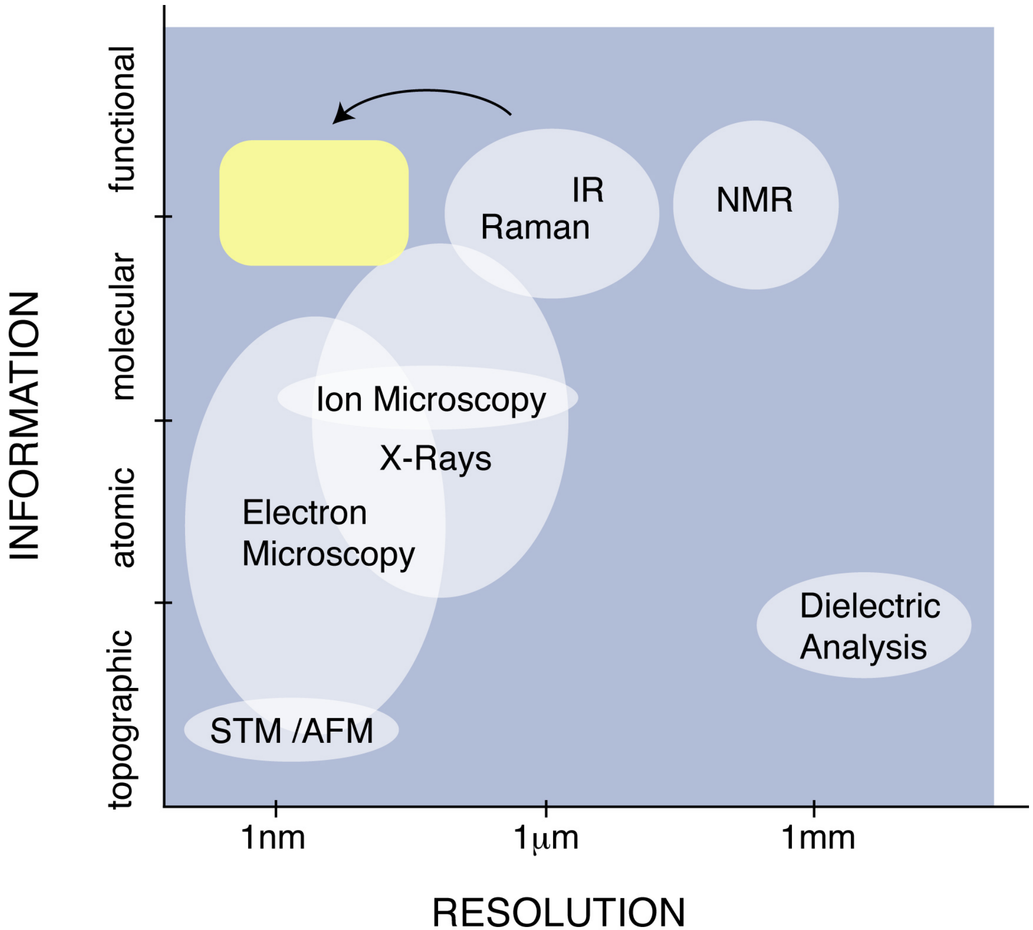
## MOTIVATION

Defects and dopants provide an opportunity to engineer the electronic and optical properties in carbon nanomaterials, similar to semiconductor devices.

## OBJECTIVE

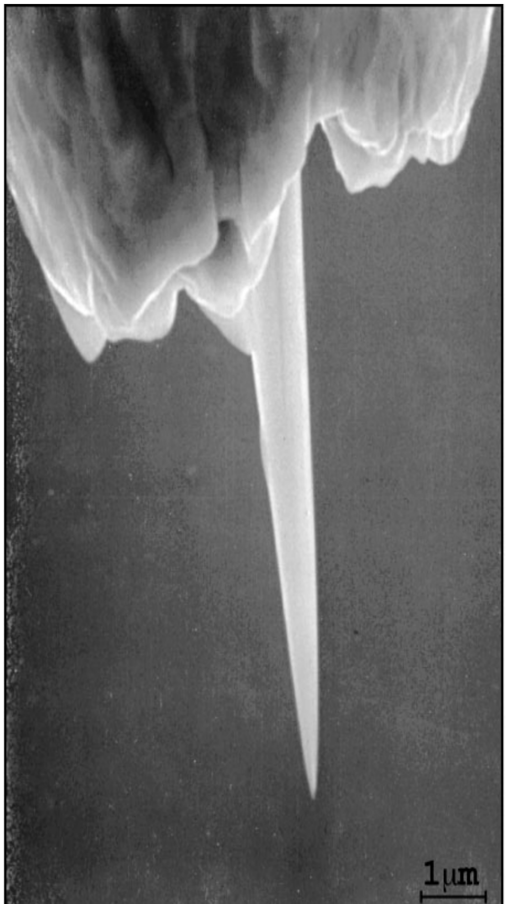
Control and understand the influence of defects and dopants on the physical properties of carbon nanotubes and graphene.

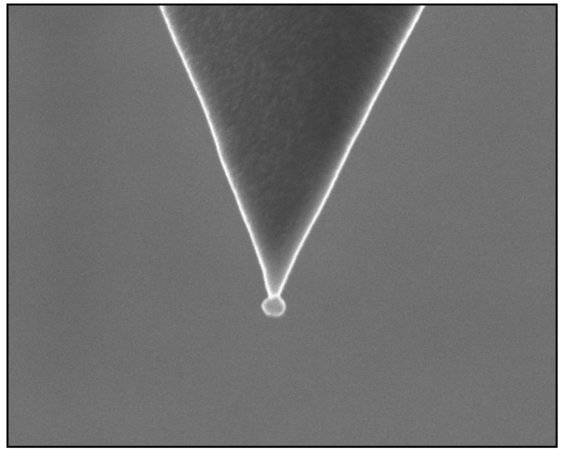
# SPECTROSCOPIC IMAGING

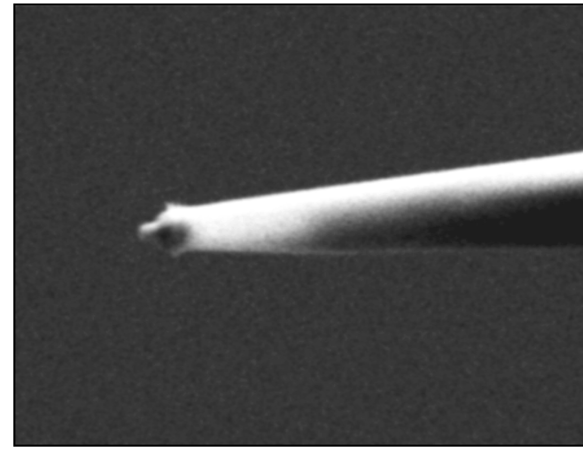


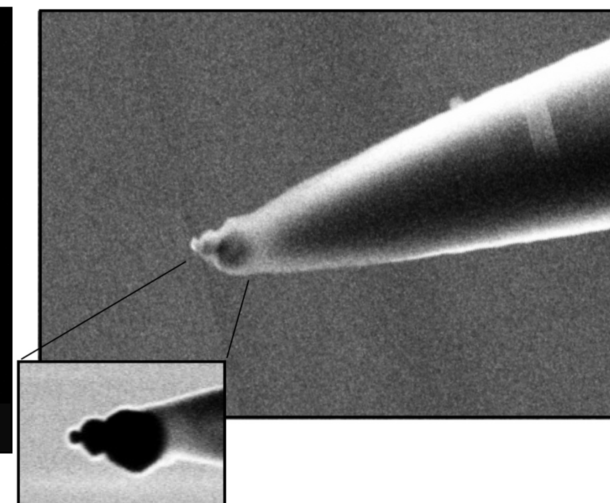

S. Stranick (NIST)

# OPTICAL ANTENNAS

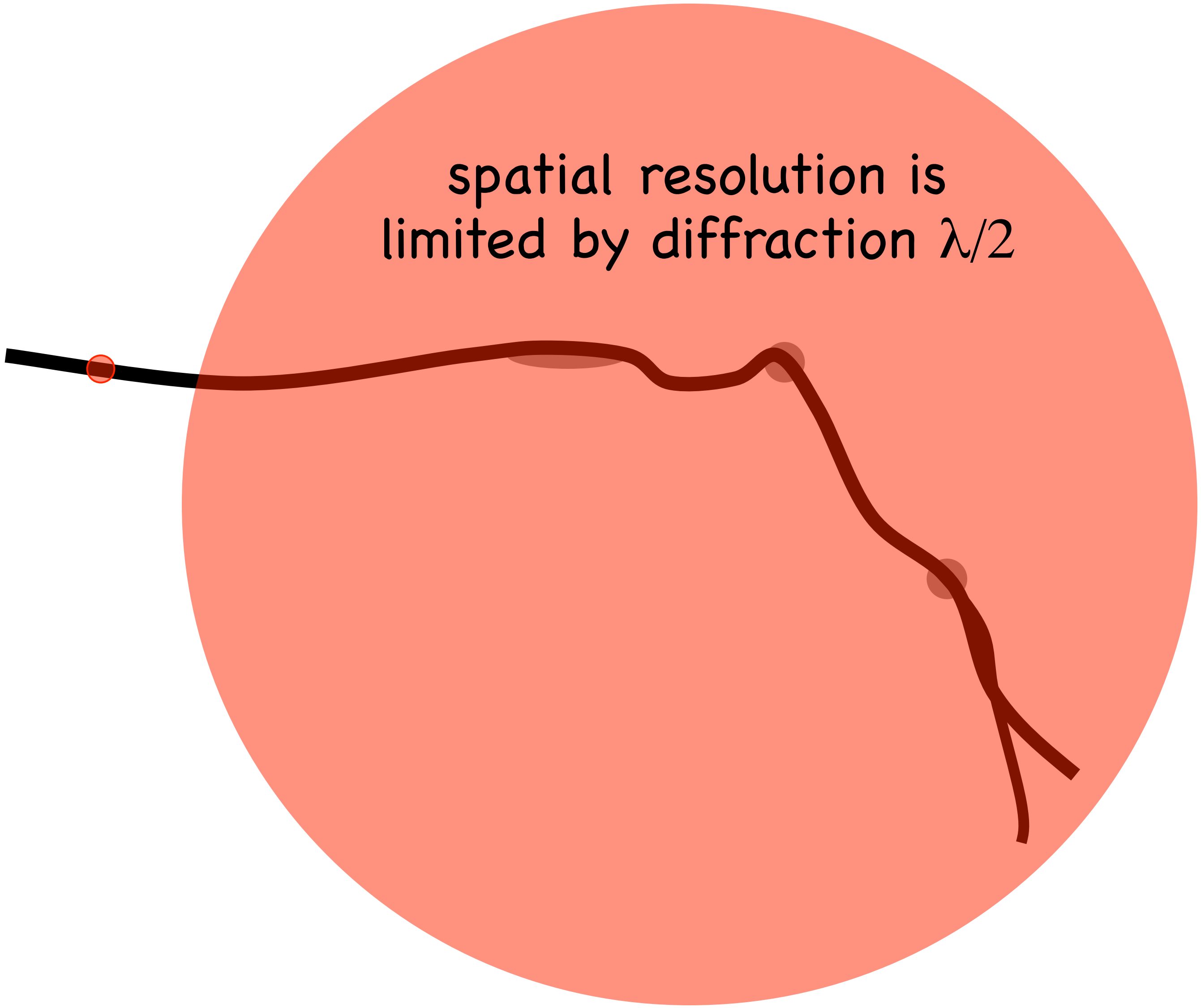


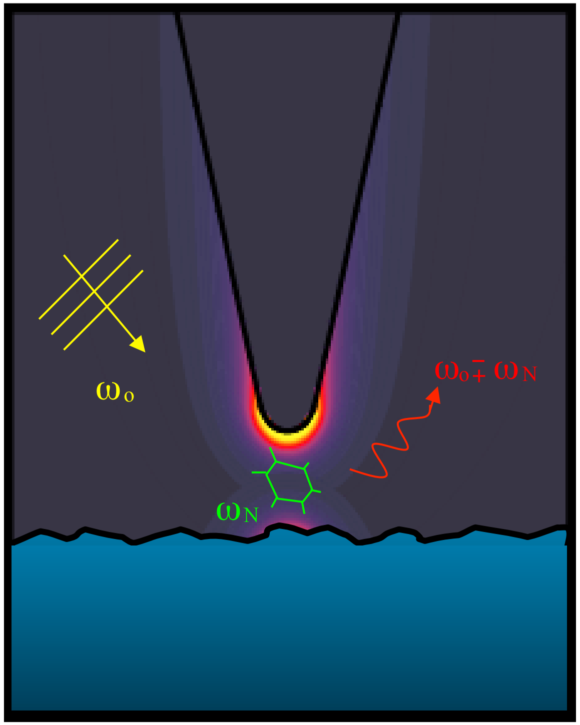


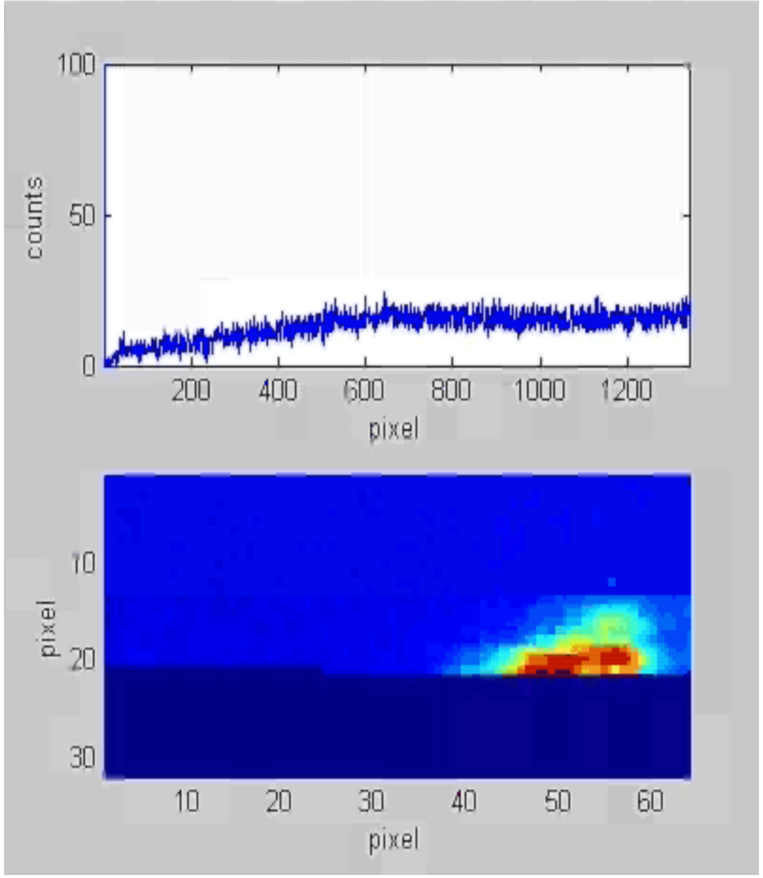



# WHY NEAR-FIELD SPECTROSCOPY ?

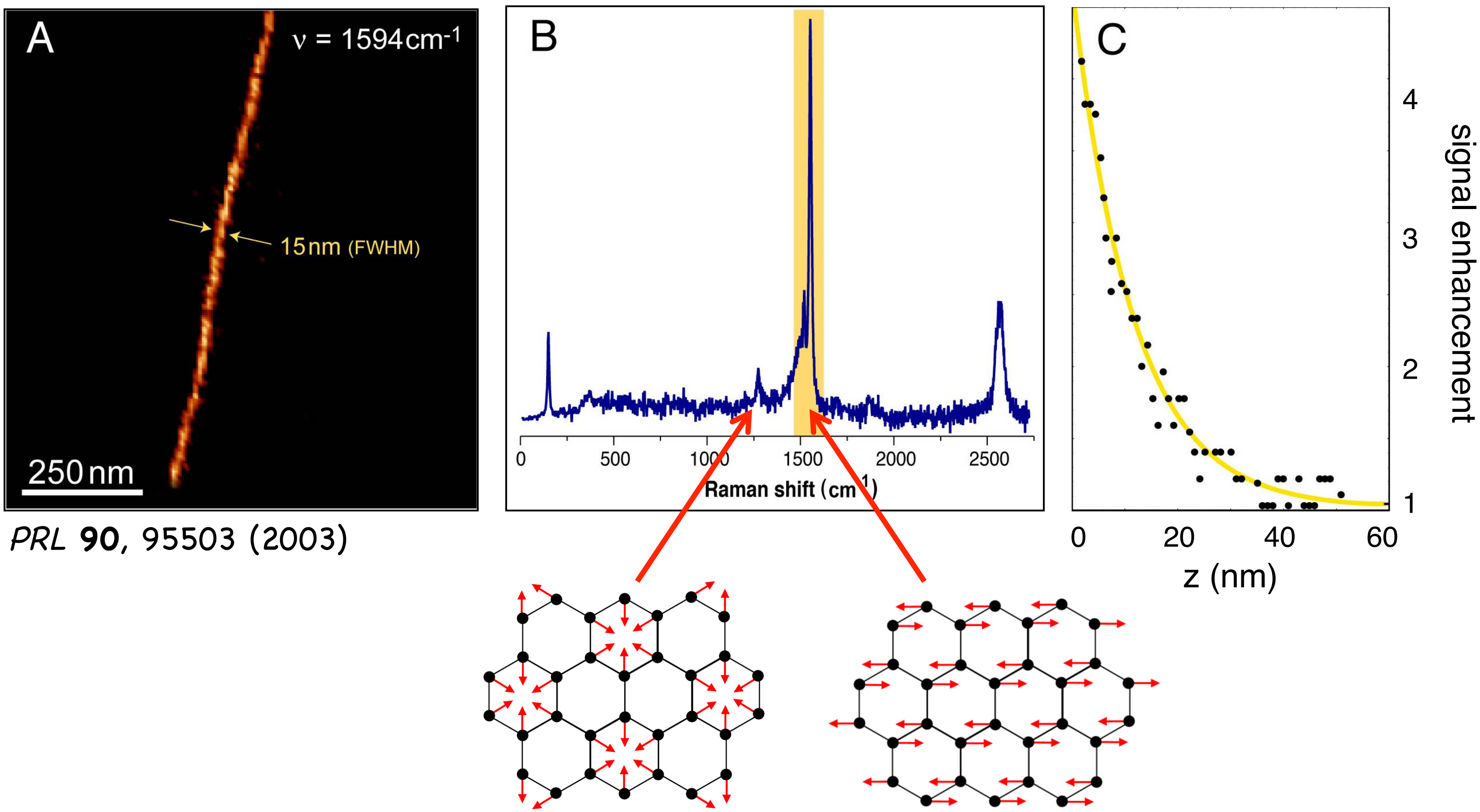


# NEAR-FIELD RAMAN SCATTERING



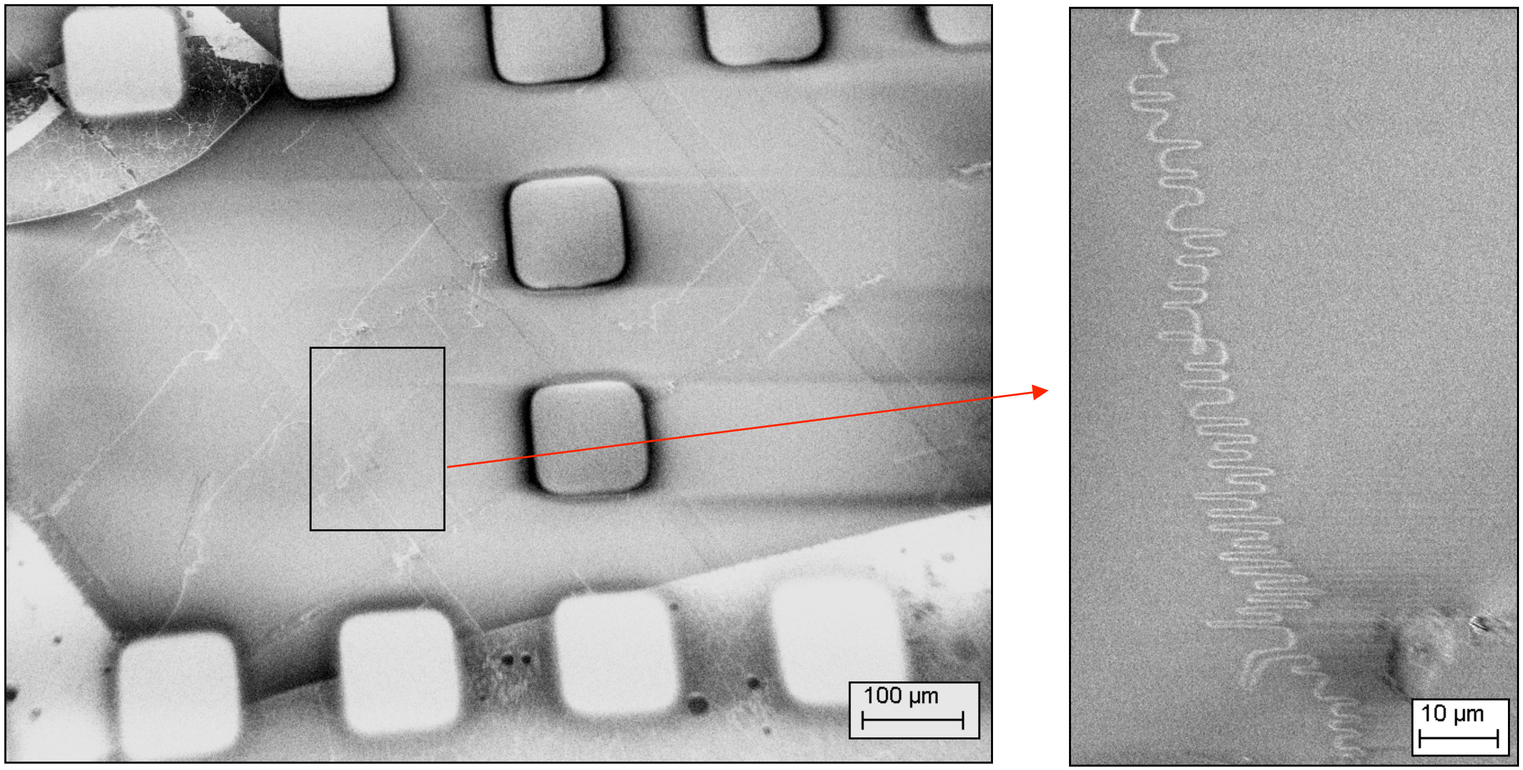
# 3D CONFINEMENT OF SIGNAL




*PRL* **90**, 95503 (2003)

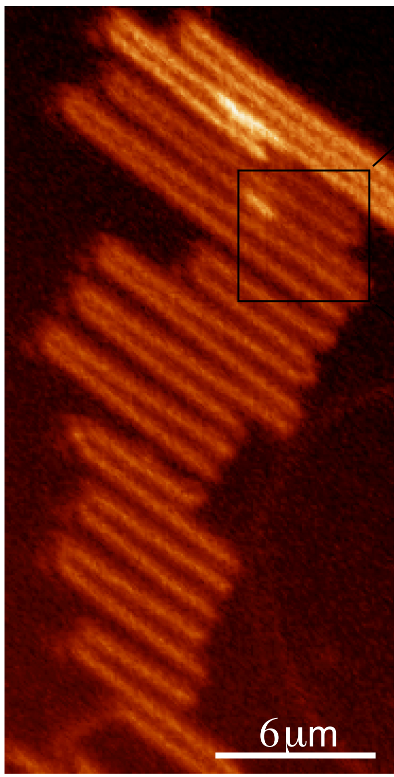
www.nano-optics.org

# SERPENTINE NANOTUBES
## (CVD grown)

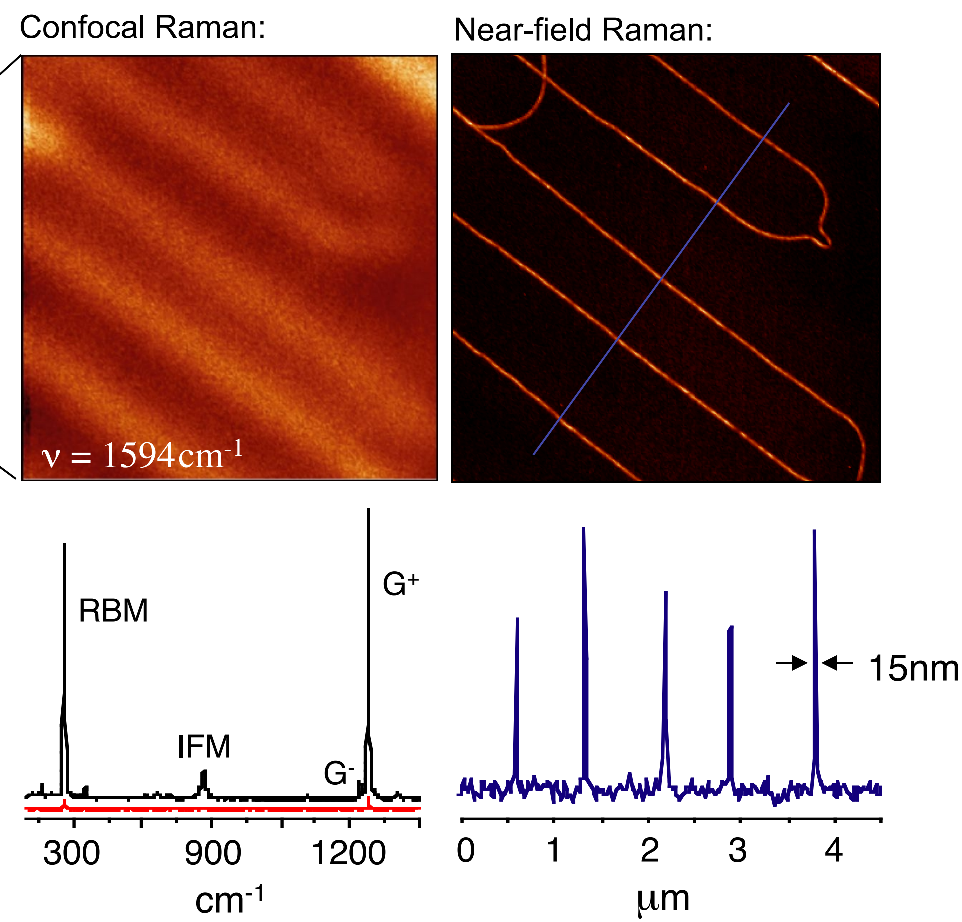



*E. Joselevich (Weizmann Inst.)*

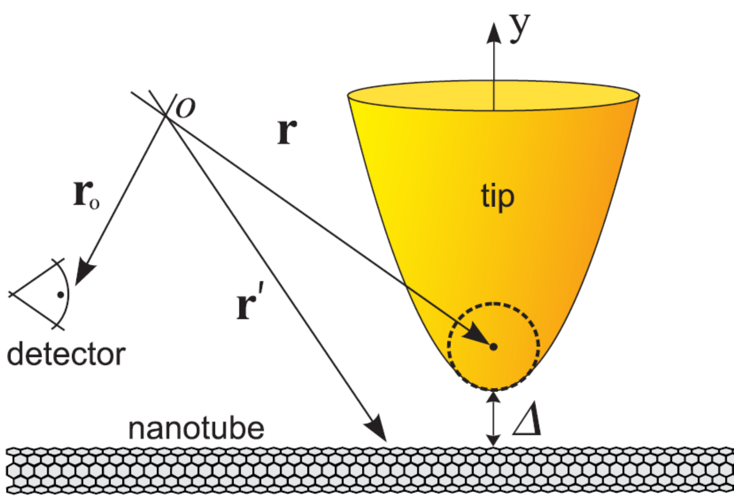
# NEAR-FIELD RAMAN IMAGING OF SERPENTINE NANOTUBES

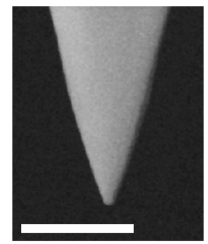



*PRL* **103**, 186101 (2009)



# THEORY OF NEAR-FIELD RAMAN SCATTERING IN 1D SYSTEMS



$$\overleftrightarrow{\alpha}_i^R = \begin{bmatrix} \alpha_{\perp,i}^R & 0 & 0 \\ 0 & \alpha_{\perp,i}^R & 0 \\ 0 & 0 & \alpha_{\parallel,i}^R \end{bmatrix} .$$

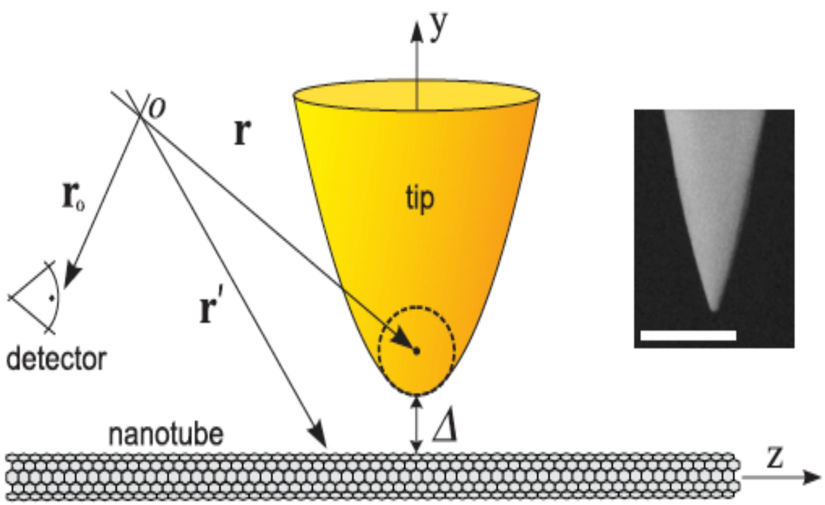
$$i \in \{RBM,\, G^+,\, G^-\}$$

$$\mathbf{p}(\mathbf{r}',\omega_s) \propto \overleftrightarrow{\alpha}^R(\mathbf{r}',\omega_s;\omega)\,\mathbf{E}(\mathbf{r}',\omega) \propto \overleftrightarrow{\mathrm{G}}^{\mathrm{o}}(\mathbf{r}',\mathbf{r};\omega)\,\overleftrightarrow{\alpha}_{\mathrm{tip}}(\omega)\,\mathbf{E}_{\mathrm{o}}(\mathbf{r},\omega)$$

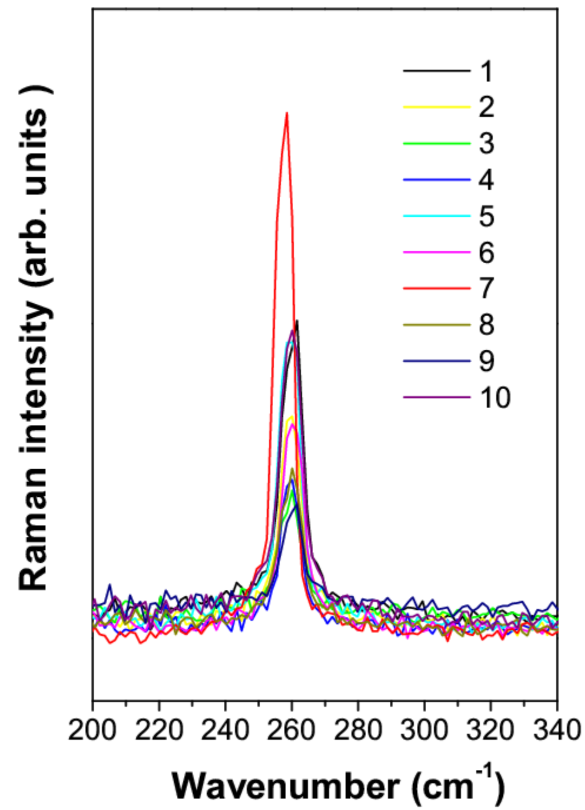
$$\mathbf{E}(\mathbf{r}_{\mathrm{o}},\omega_s) \propto \int_{-\infty}^{+\infty} dz'\,\overleftrightarrow{\alpha}_{\mathrm{tip}}(\omega_s)\,\overleftrightarrow{\mathrm{G}}^{\mathrm{o}}(\mathbf{r},z';\omega_s)\;\mathbf{p}(z',\omega_s)$$

*L. G. Cançado et al., PRL **103**, 186101 (2009).*

# ENHANCEMENT OF RAMAN MODES IN 1D SYSTEMS

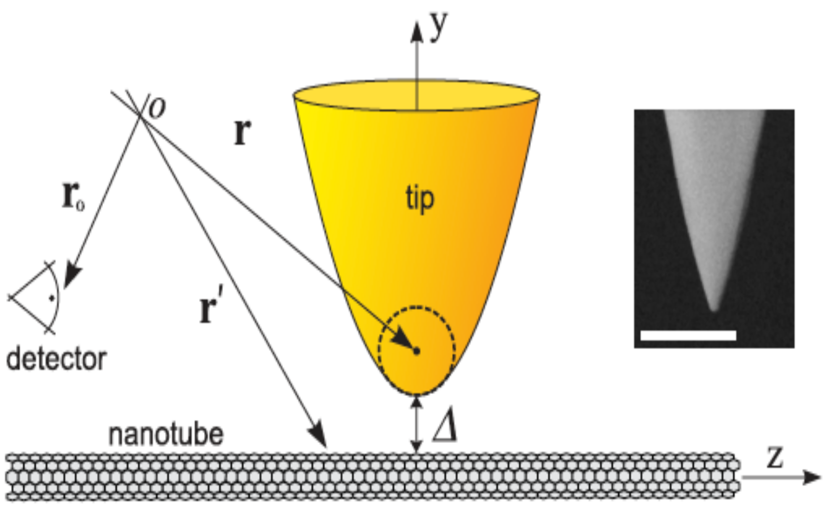


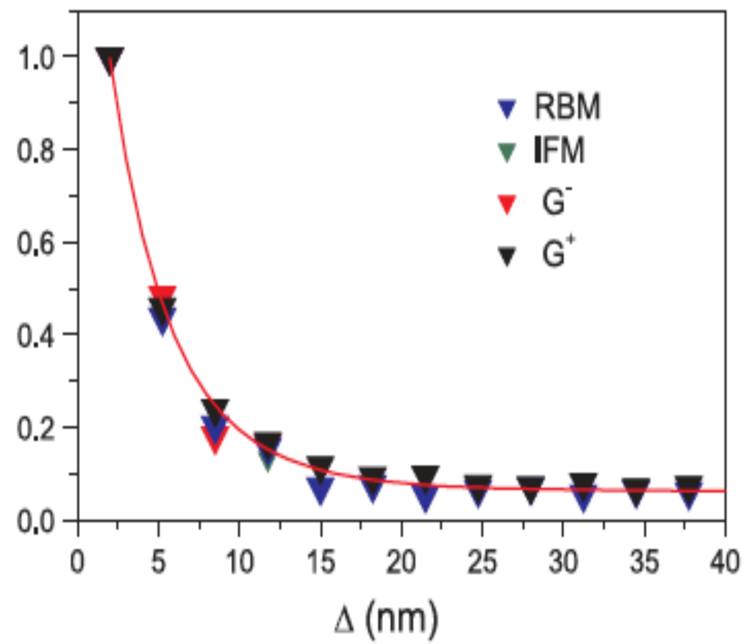

$$\frac{I}{I_{\max}} = \frac{1}{M} + \frac{C}{(\Delta + \rho_{\mathrm{tip}})^{10}}$$




*PRL* **103**, 186101 (2009)

# ENHANCEMENT OF RAMAN MODES IN 1D SYSTEMS

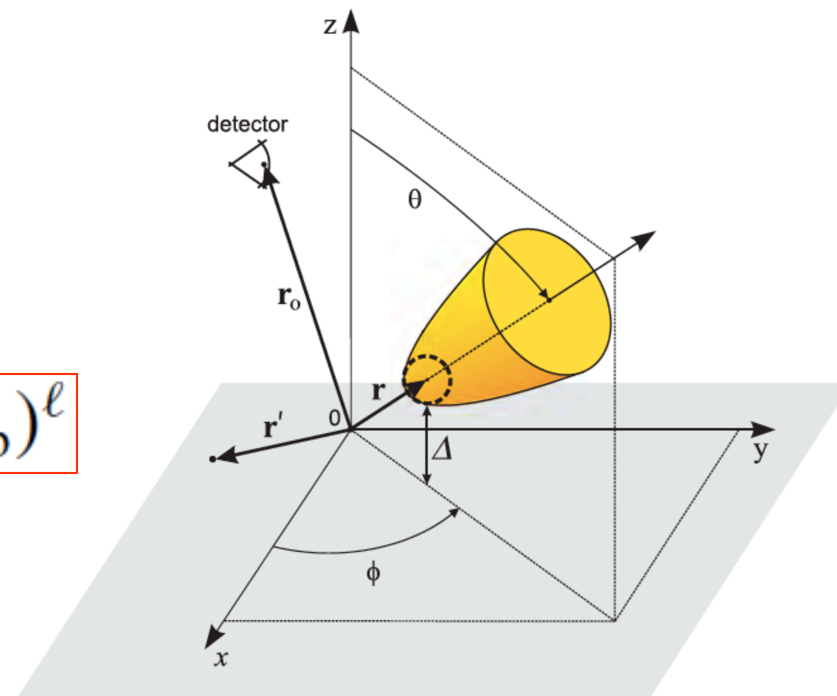



$$\frac{I}{I_{\max}} = \frac{1}{M} + \frac{C}{(\Delta + \rho_{\mathrm{tip}})^{10}}$$

*PRL* **103**, 186101 (2009)

# ENHANCEMENT OF RAMAN MODES IN 2D SYSTEMS ?

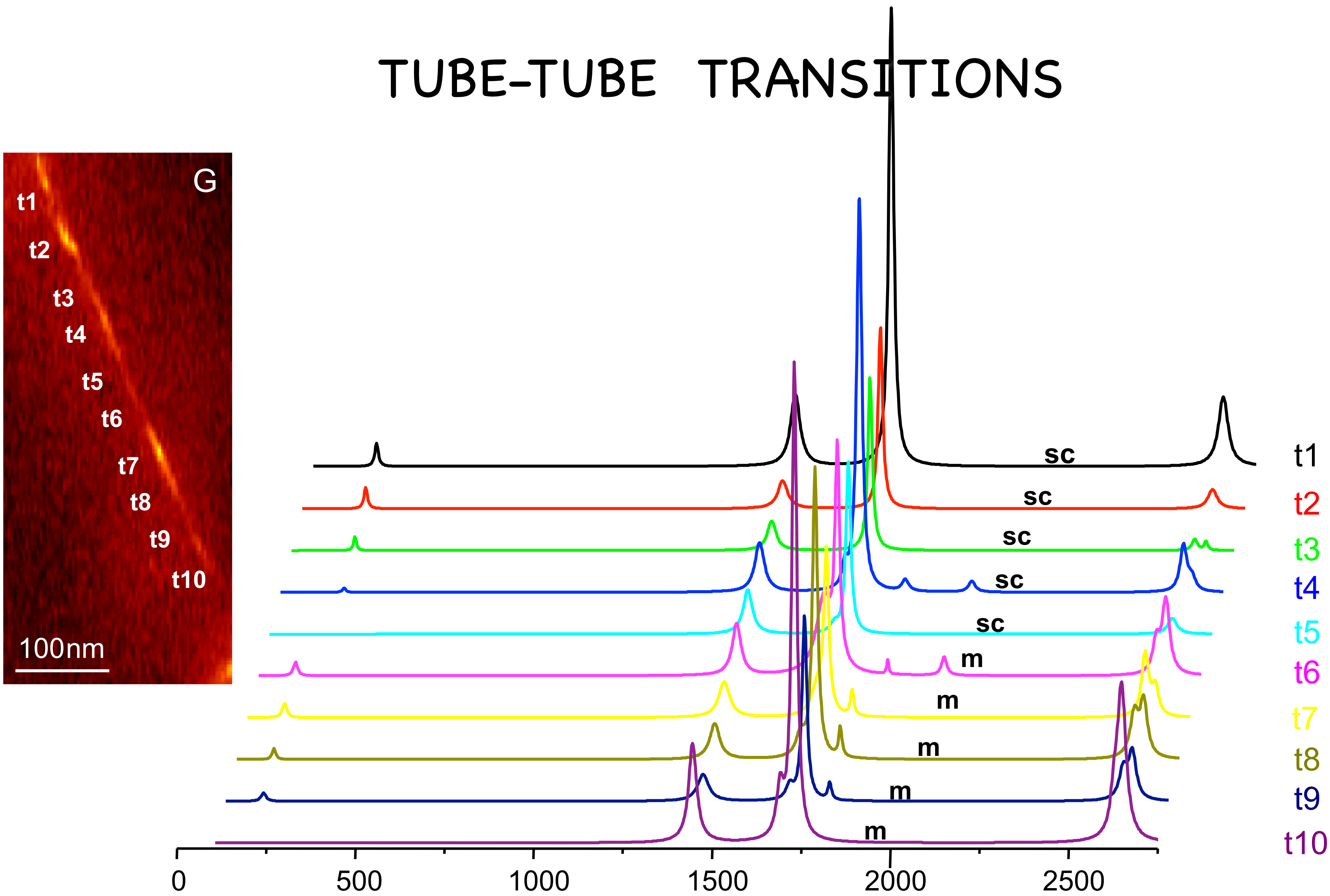



$$I_{NF} \propto (\Delta + \rho_{tip})^{\ell}$$

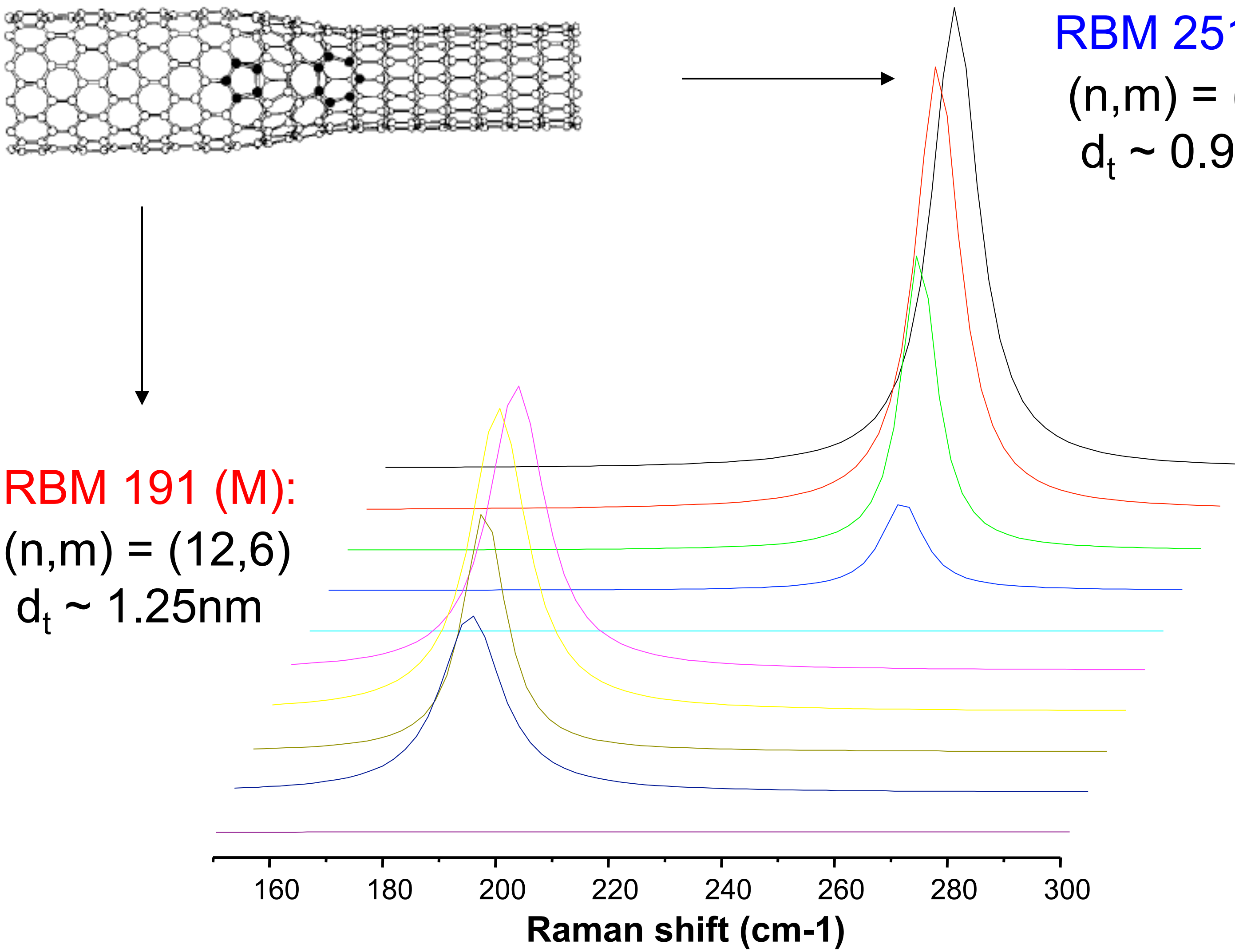
| | 0D | 1D | 2D |
|---|---|---|---|
| Coherent | −12 | −10 | −8 |
| Incoherent | −12 | −11 | −10 |

Maximiano et al., *PRB* **85**, 235434 (2012)

# TUBE-TUBE TRANSITIONS




*Nano Lett.* **7**, 577 (2007)

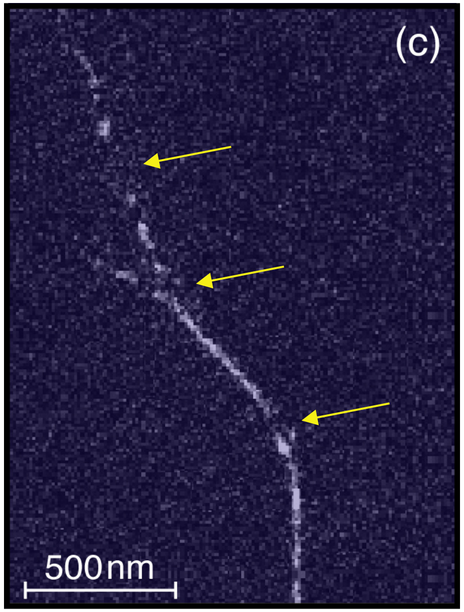


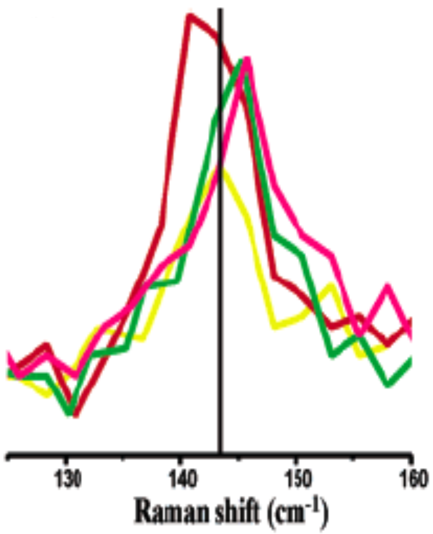

*Nano Lett.* **7**, 577 (2007)

# STRUCTURAL DEFECTS
## (arc-discharge and HiPco tubes)

Confocal Raman:


Near-field Raman:



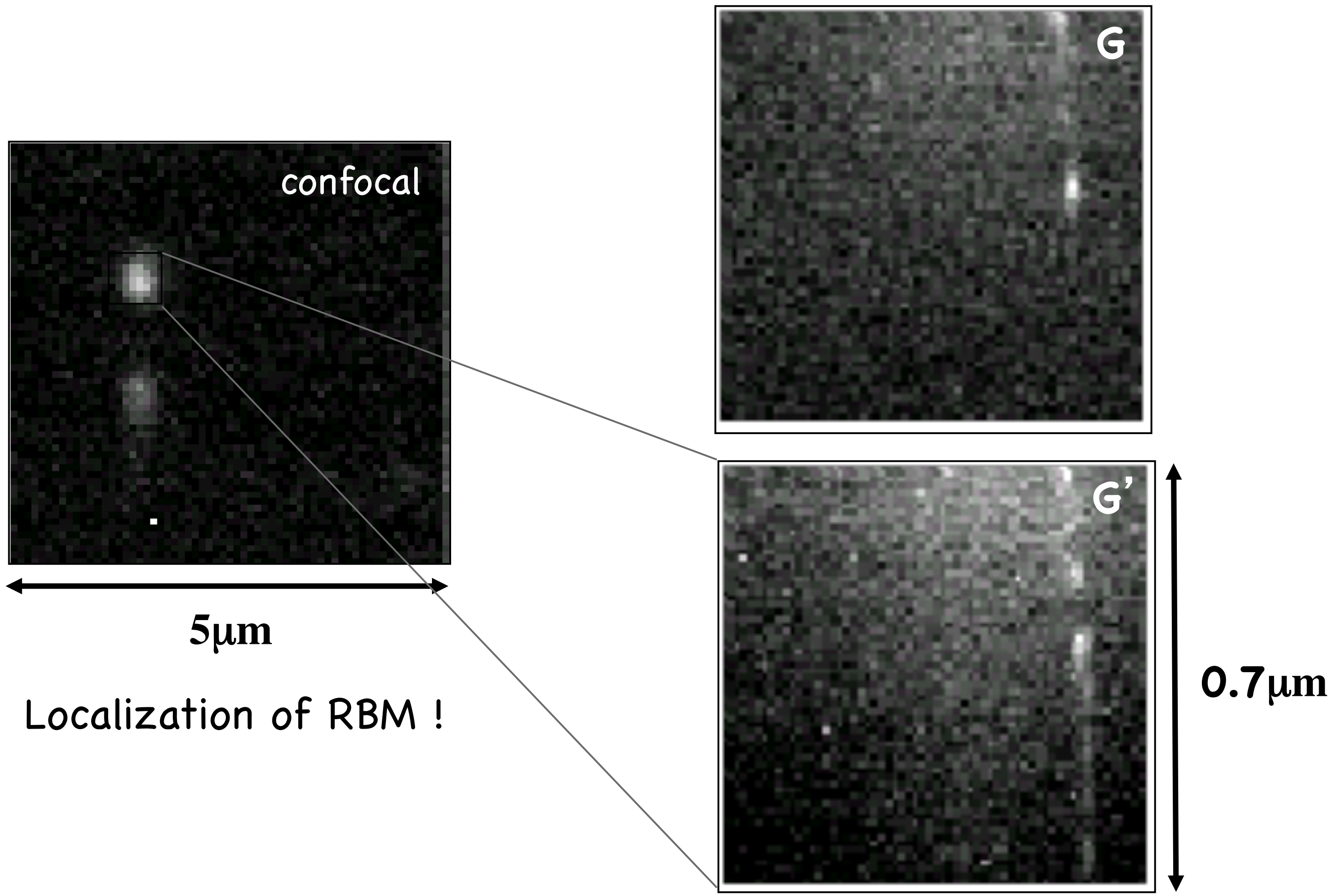




*Nano Lett.* **6**, 744 (2006)

*JACS* **127**, 2533 (2005)

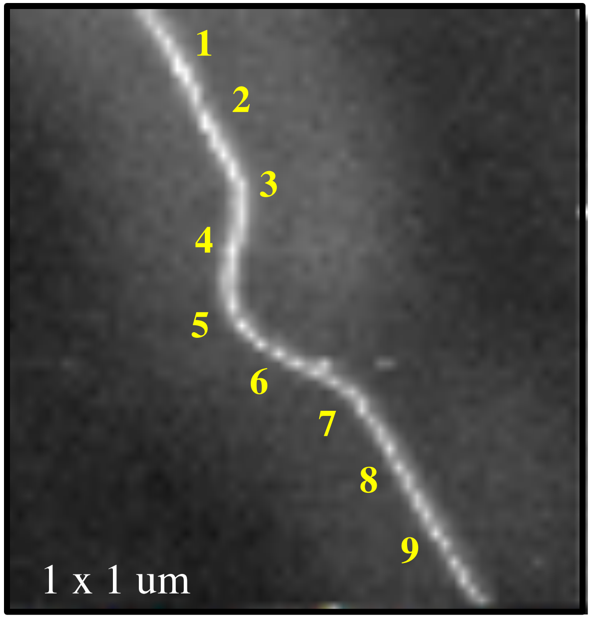
# BORON-DOPED NANOTUBES

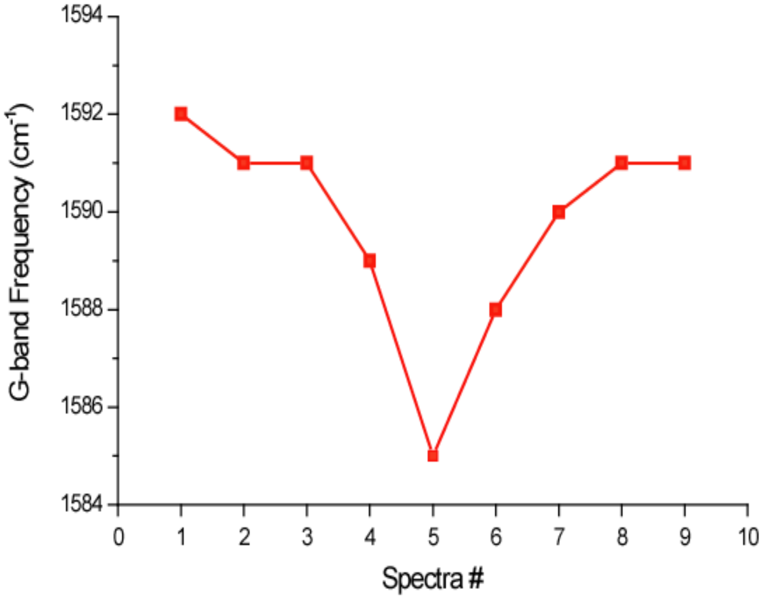
with A. M. Rao, Clemson University




Localization of RBM !

# LOCAL STRAIN

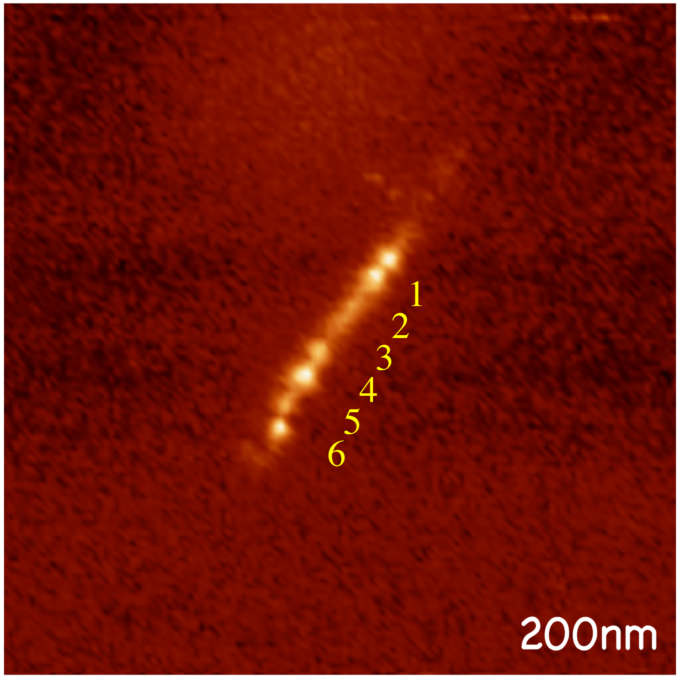


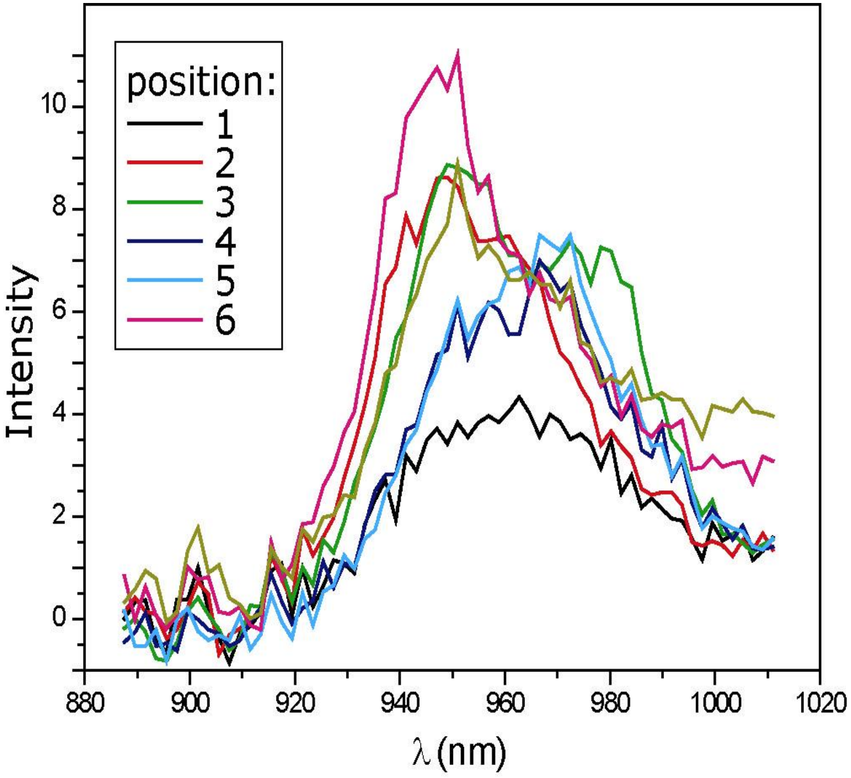

Young's modulus ~1TPa
Displacement due to kink ~40nm
} Strain ~1.6%

$$\sigma_{xx}\ (\text{MPa}) = [200\ ..\ 800]\ \Delta\nu_G\ (\text{cm}^{-1})$$

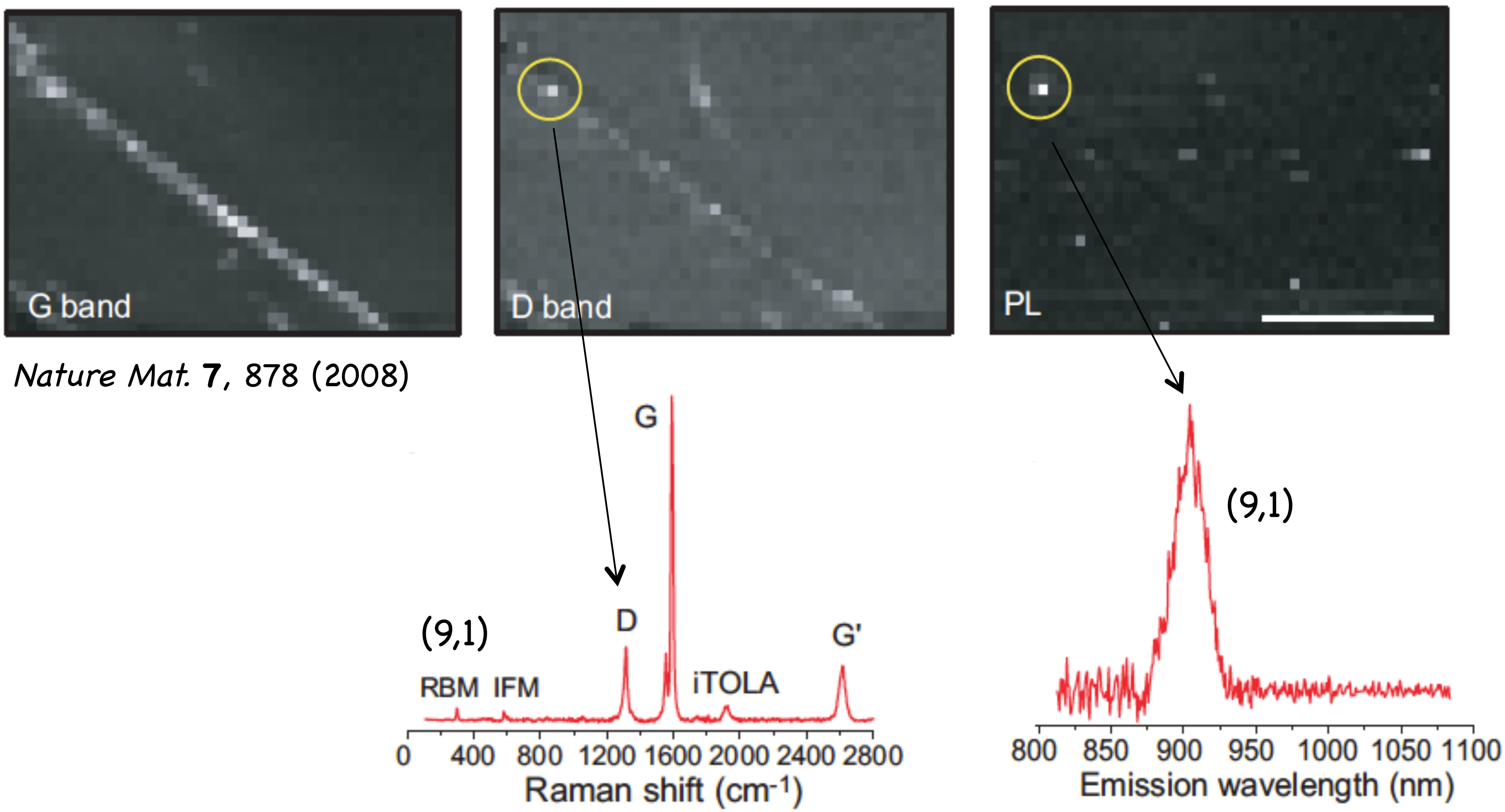
# VARIATIONS IN PL SPECTRA




*Nano Lett.* **5**, 2310 (2005)

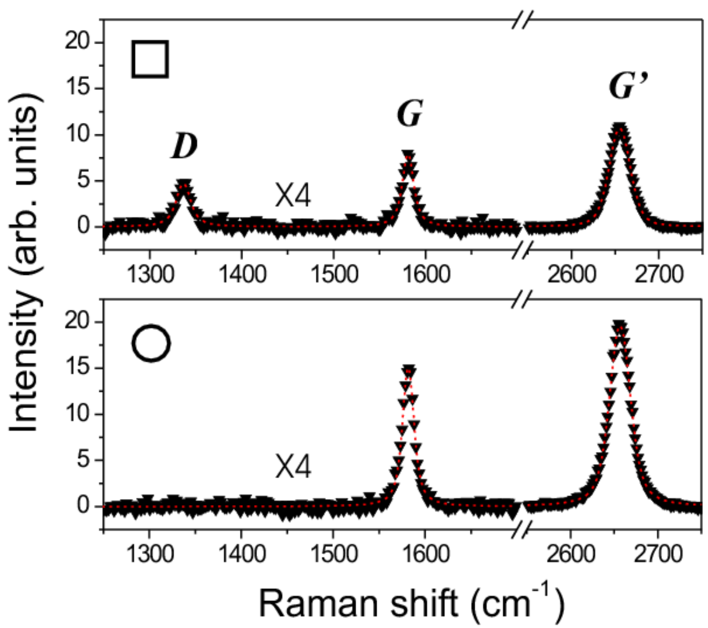


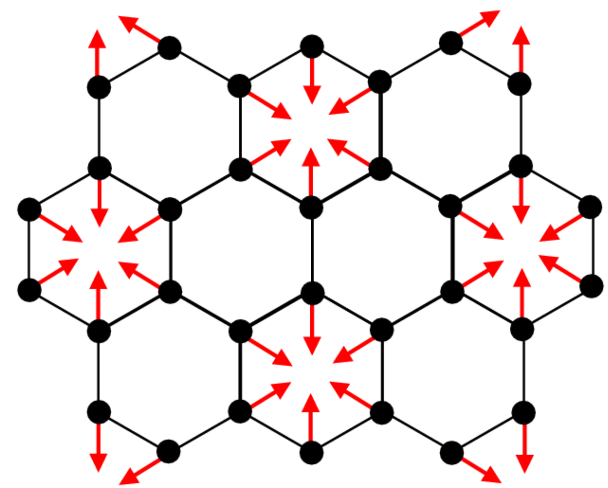
# LOCALIZATION OF DEFECTS




*Nature Mat.* **7**, 878 (2008)

# RAMAN D-BAND

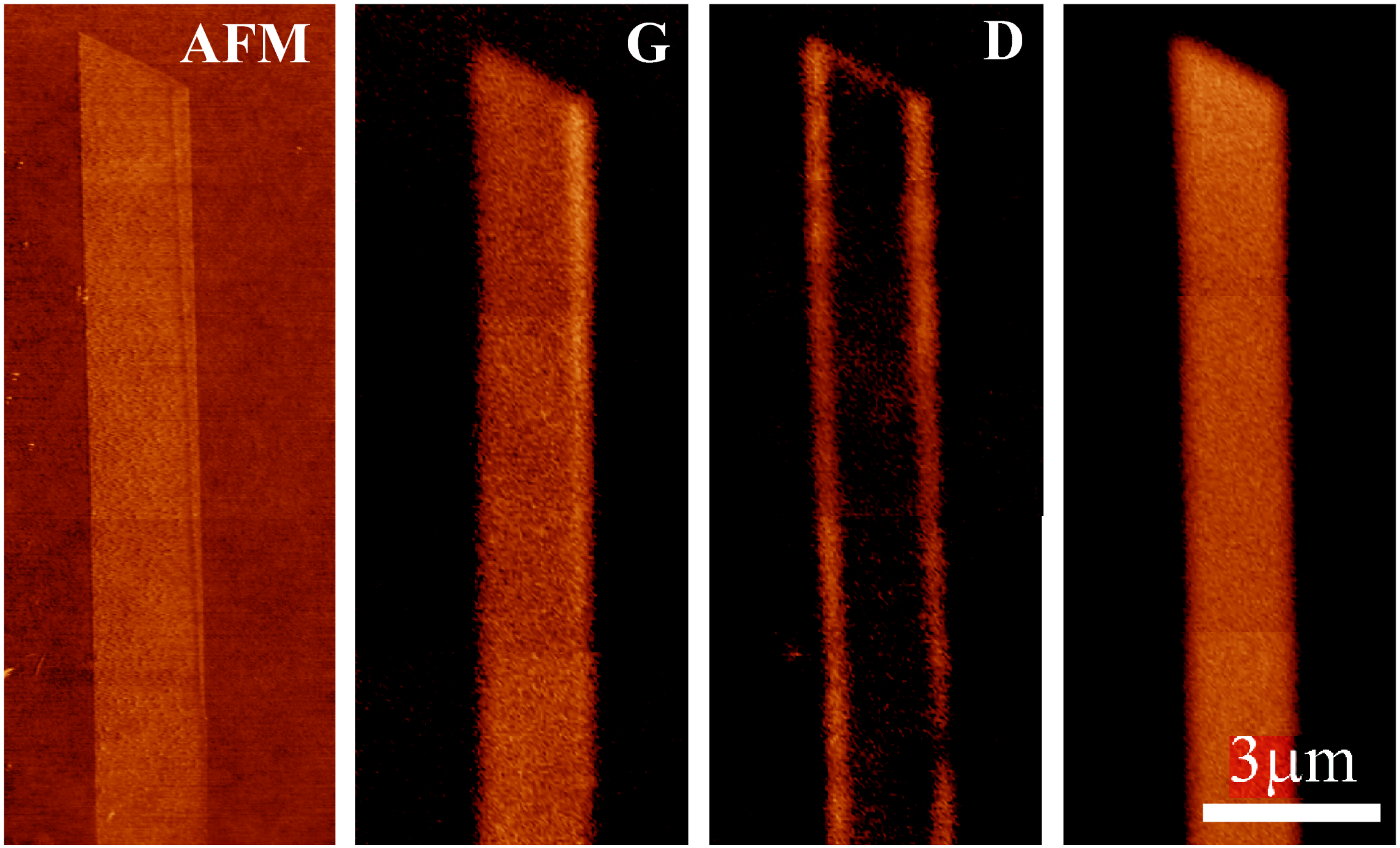


( iTO mode at the K point )

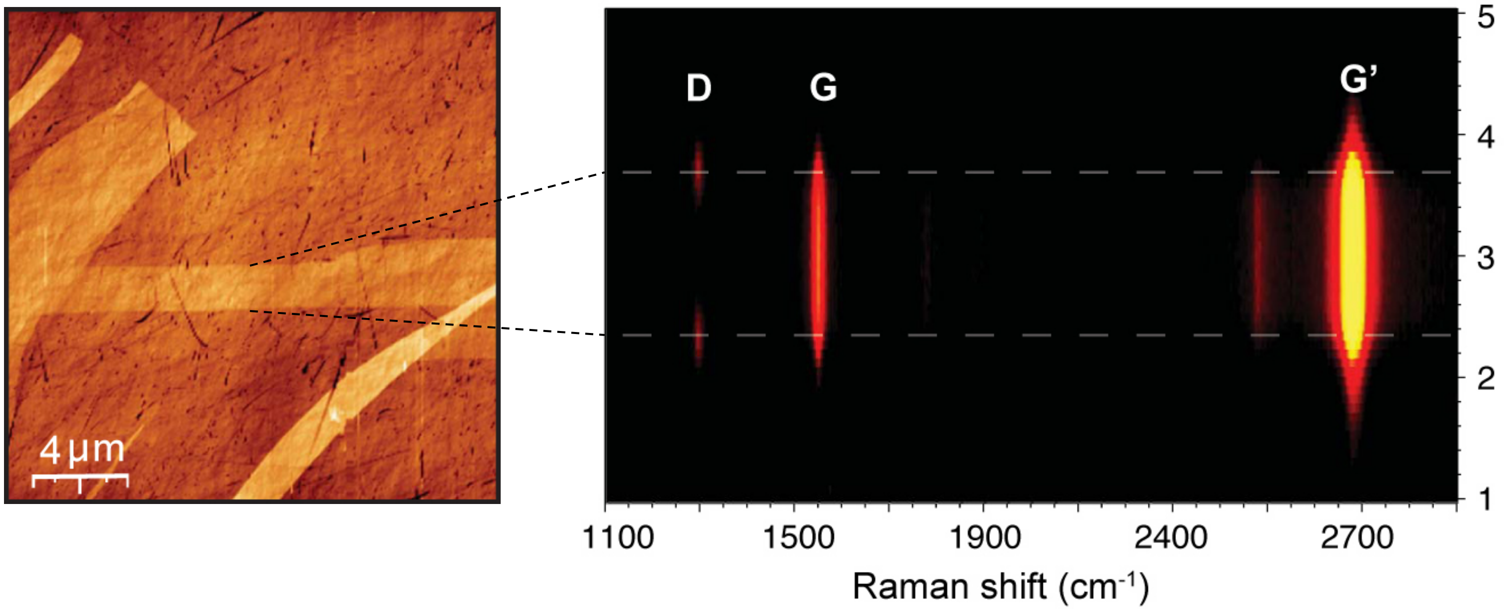
Due to momentum conservation, the TO phonons giving rise to the D-band only become Raman active if the electrons or holes involved in the scattering process undergo elastic scattering by a lattice defect.

# D-BAND LOCALIZATION IN GRAPHENE



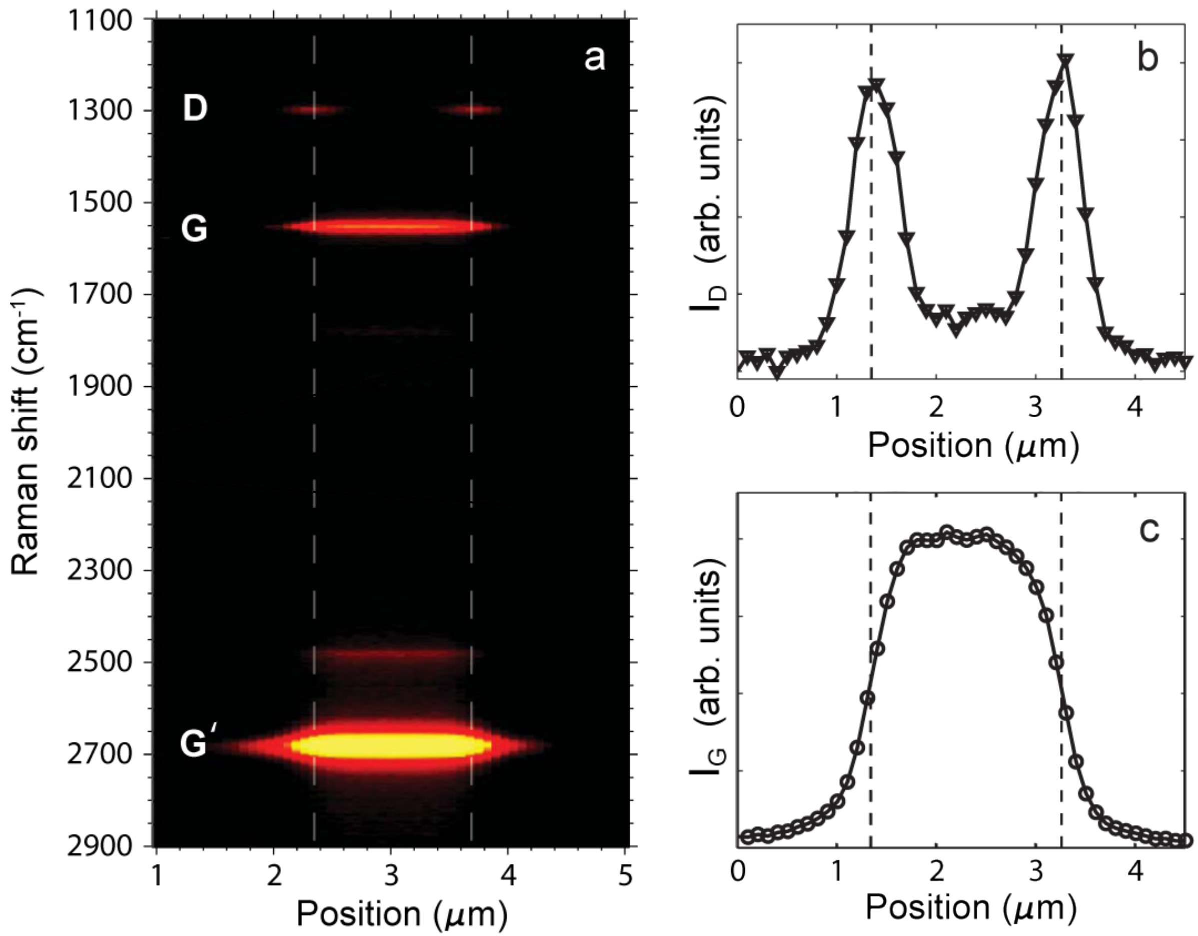

arXiv:0802.3709 (2008)

# D-BAND LOCALIZATION IN GRAPHENE



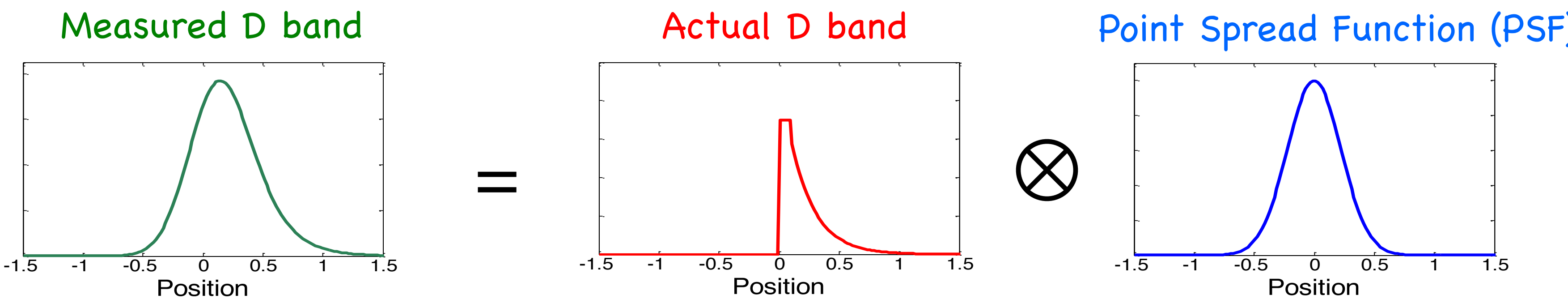

*Nano Lett.* **11**, 1177 (2011)

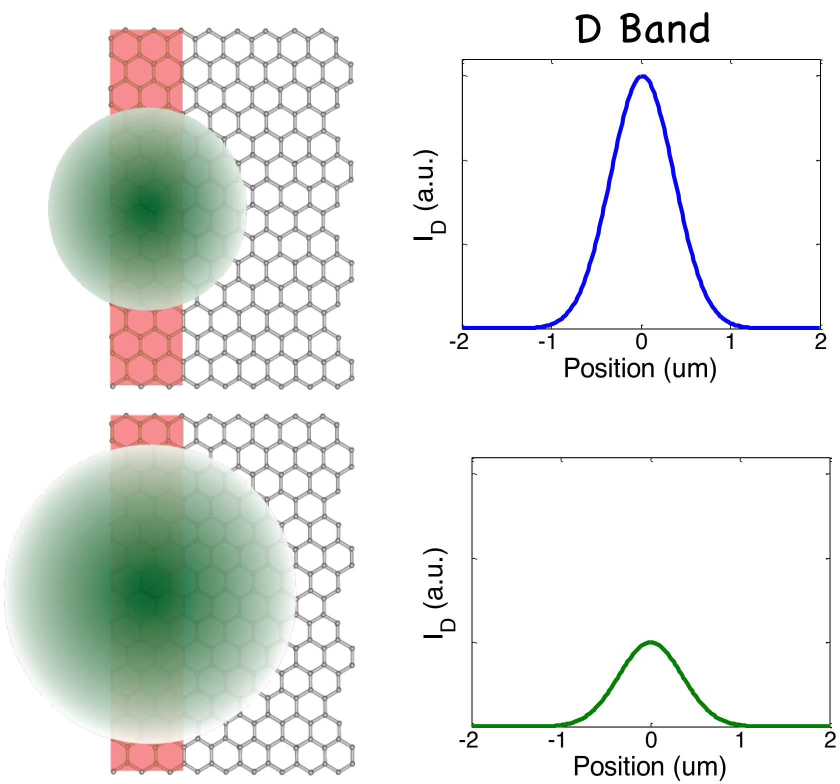
# D-BAND LOCALIZATION IN GRAPHENE

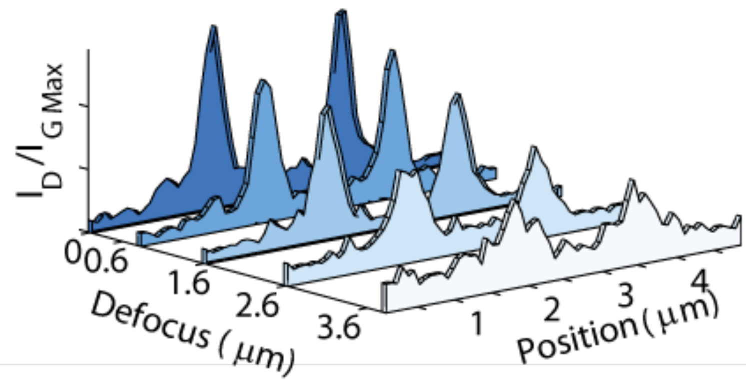



*Nano Lett.* **11**, 1177 (2011)

# DEFOCUSING TECHNIQUE



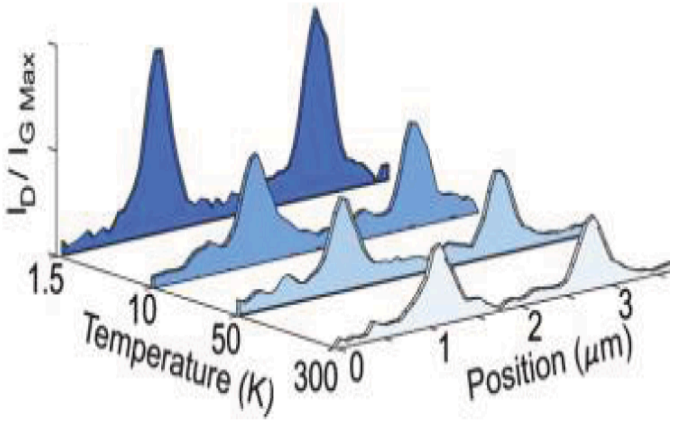



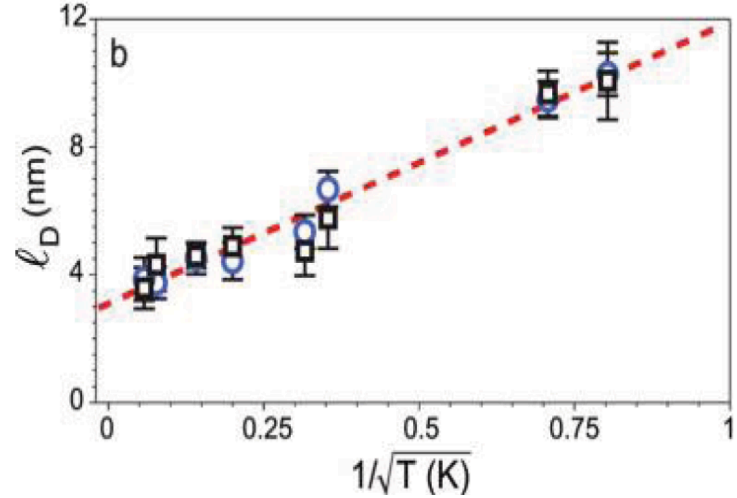




$$\ell_D \approx 3\,nm$$

*Nano Lett.* **11**, 1177 (2011)

# D-BAND LOCALIZATION IN GRAPHENE



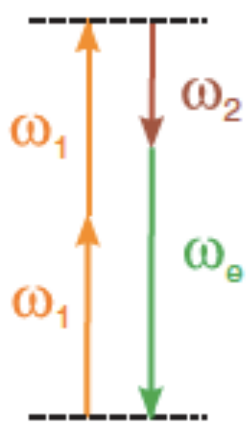

$$l_D\ (\mathrm{nm}) = 3 + 9/T^{1/2}$$

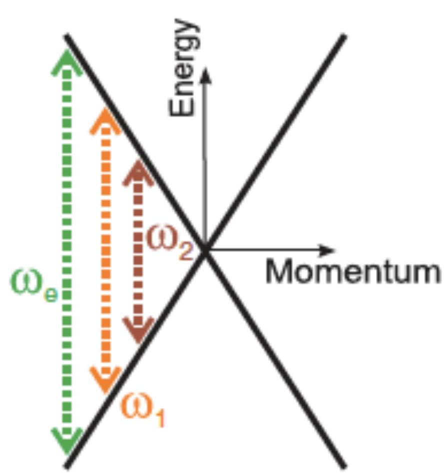
*Nano Lett.* **11**, 1177 (2011)

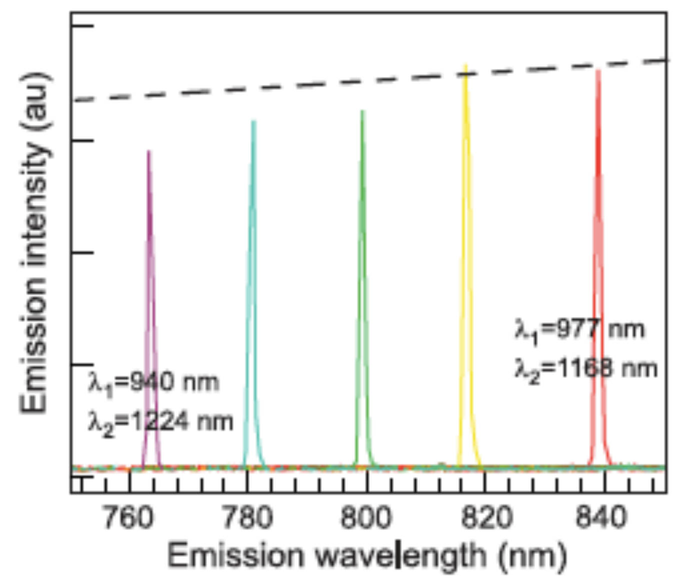
# Coherent Nonlinear Optical Response of Graphene

E. Hendry,* P. J. Hale, J. Moger, and A. K. Savchenko
*School of Physics, University of Exeter, EX4 4QL, United Kingdom*

S. A. Mikhailov
*Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany*
(Received 19 May 2010; published 26 August 2010)



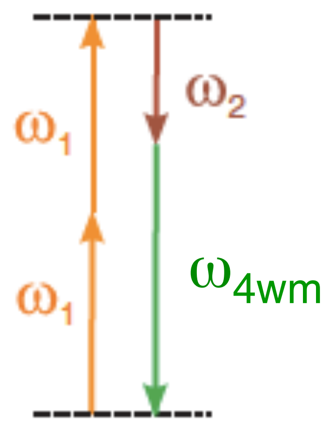



# NONLINEAR FOUR-WAVE MIXING

$$\mathbf{P} = \varepsilon_o \chi^{(3)}(-\omega_{4\mathrm{WM}}; \omega_1, \omega_1, -\omega_2)\mathbf{E}_1\mathbf{E}_1\mathbf{E}_2^*$$

$$\downarrow$$

$$2\omega_1 - \omega_2$$



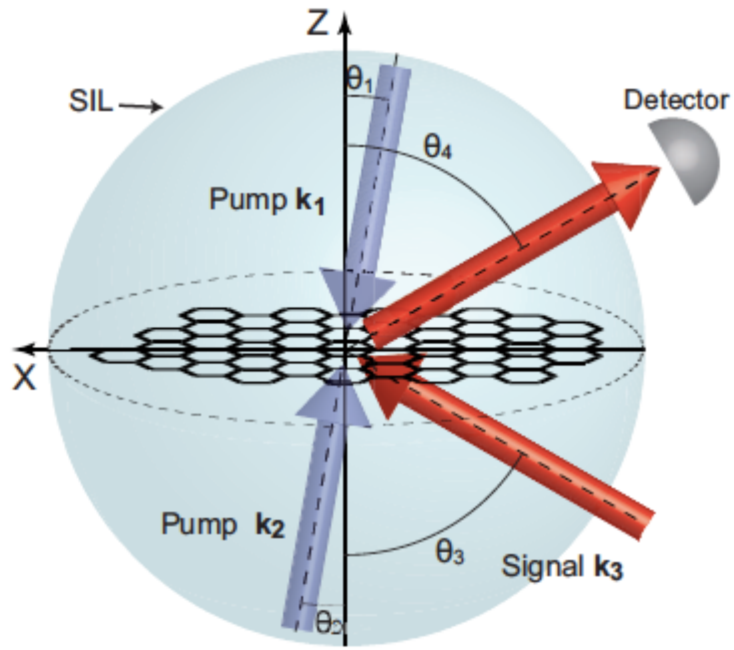

Degenerate 4WM :

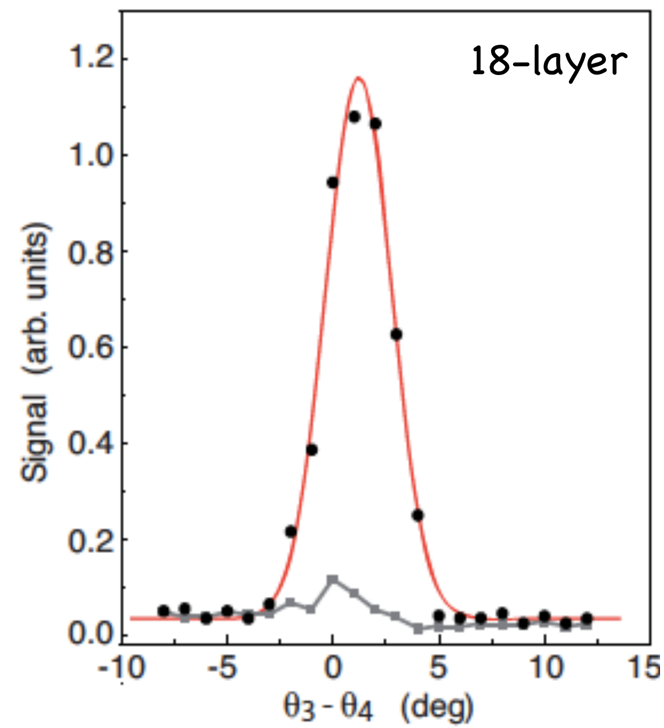
$$\mathbf{P}^{(3)}(\omega) = \varepsilon_0\, \chi^{(3)}(\omega; \omega, \omega, -\omega)\, \mathbf{E}_1 \exp(i\mathbf{k}_1\mathbf{r})\, \mathbf{E}_2 \exp(i\mathbf{k}_2\mathbf{r})\, \mathbf{E}_3^* \exp(-i\mathbf{k}_3\mathbf{r})$$

Choose $\mathbf{k}_1 + \mathbf{k}_2 = 0$ :

$$\mathbf{E}_4 = \begin{cases} \mathbf{E}_0^{(1)} \exp\left(-ik_1 \sin\theta_3\, x + ik_1 \cos\theta_3\, z\right) & z > 0 \quad \text{Negative refraction} \\ \mathbf{E}_0^{(2)} \exp\left(-ik_1 \sin\theta_3\, x - ik_1 \cos\theta_3\, z\right) & z < 0 \quad \text{Phase conjugation} \end{cases}$$

# NEGATIVE REFRACTION WITH GRAPHENE



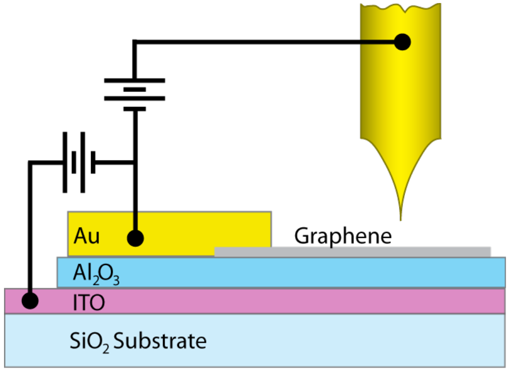



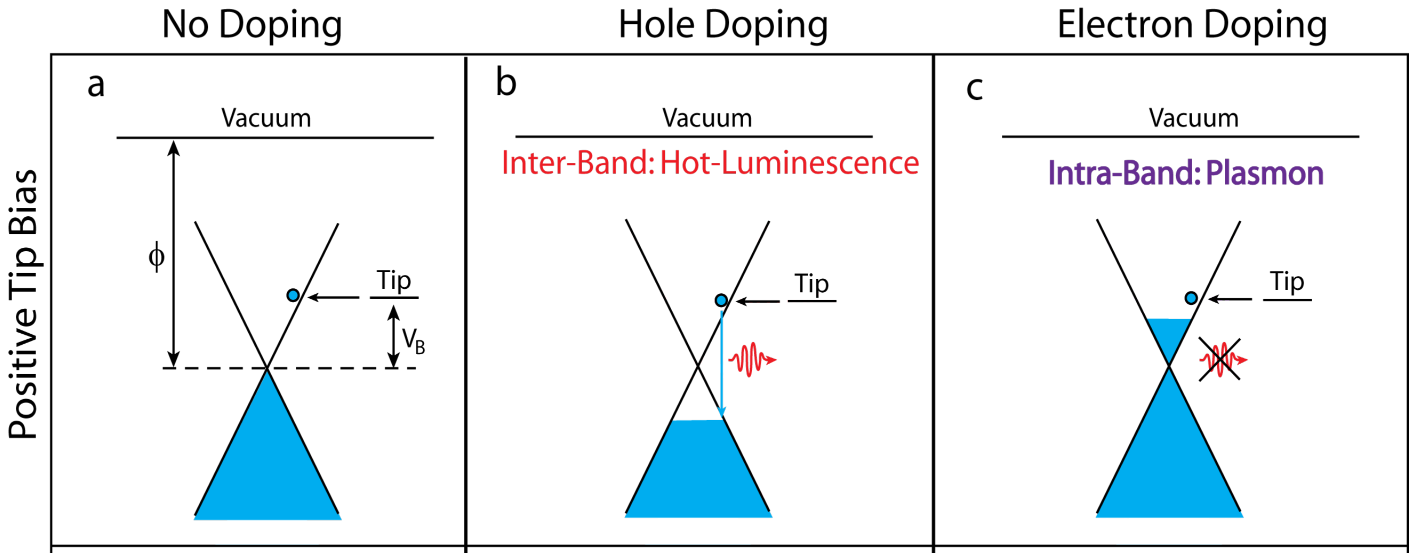

arXiv: 1210.4563 (2012)

# PHOTOEMISSION FROM GRAPHENE

Ryan Beams

(Poster #13)



# CONCLUSIONS

**NEAR-FIELD SPECTROSCOPY:**

1) REVEALS PHONON (EXCITON) LOCALIZATION

2) OPTICAL MEASUREMENT OF ELECTRON COHERENCE LENGTH

3) NEGATIVE REFRACTION

COLLABORATORS:

A. Jorio, E. Joselevich, M. Her, T. Krauss, B. Deutsch, B. McIntyre, M. Dresselhaus, A. Noy

**www.nano-optics.org**

U.S. DEPARTMENT OF ENERGY