

Reinaldo Arturo Zapata Peña presents

# Novel Optical Effects in Functionalized Graphene: Formalism and Simulations

to earn the degree of Doctor of Science (Optics)

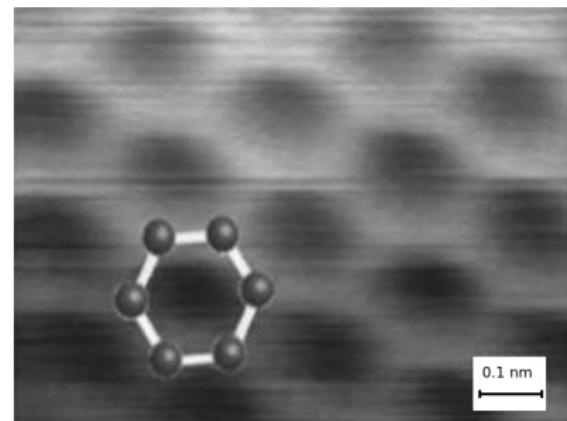


CENTRO DE INVESTIGACIONES  
EN ÓPTICA, A.C.

December 11, 2017

# General properties of graphene

- Good heat conductor <sup>1</sup>
- Extremely strong <sup>2</sup>
- Flexible <sup>3</sup>



Transmission electron microscopy of  
graphene. <sup>4</sup>

<sup>1</sup>A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.

<sup>2</sup>C. Lee, et al. Science, 321(5887):385-388, 2008.

<sup>3</sup>Briggs, B. D. et. al. App. Phys. Lett. 97: 223102. 2010.

<sup>4</sup>E. Stolyarova, et al. PNAS, 104(22):9209, 2007.

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# Synthesis of graphene

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- Exfoliation<sup>1</sup>
- Micromechanical cleavage <sup>2</sup>
- Reduction of graphite oxide in dimethylformamide <sup>3</sup>
- Chemical Vapor Deposition <sup>4</sup>



Graphite, a tape dispenser, and graphene transistor,  
donated to the Nobel Museum.<sup>5</sup>

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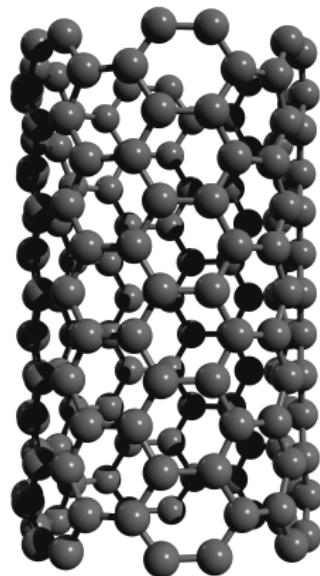
<sup>1</sup> A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.

<sup>2</sup> R.R. Nair, et al. Science, 320(5881):1308-1308, 2008.

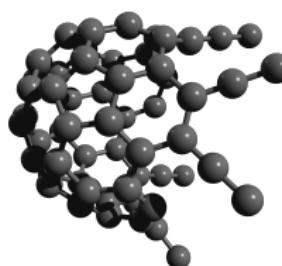
<sup>3</sup> S. Park, J. et al. Nano letters, 9(4):1593-1597, 2009.

<sup>4</sup> E. Rollings, et al. JPCS, 67(9-10):2172-2177, 2006.

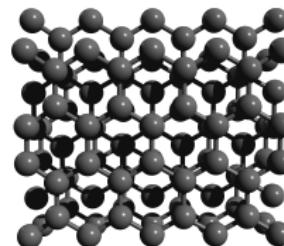
<sup>5</sup> By Gabriel Hildebrand - Nobelmuseet, Public Domain.



Carbon nanotube



Fullerene

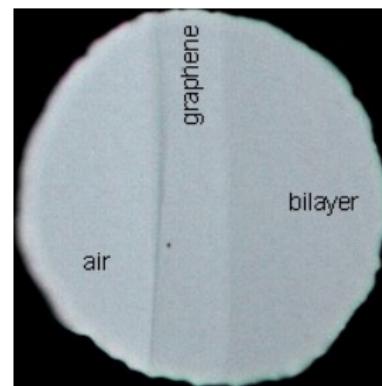


Graphite

Structures obtained from graphene

# Electronic properties of graphene

- Quantum Hall effect at room temperature<sup>1</sup>
- Excellent electrical current conduction <sup>1</sup>
- Transparent to visible light <sup>2</sup>
- Tunable bandgap <sup>3</sup>



Photograph of graphene in transmitted light.<sup>4</sup>

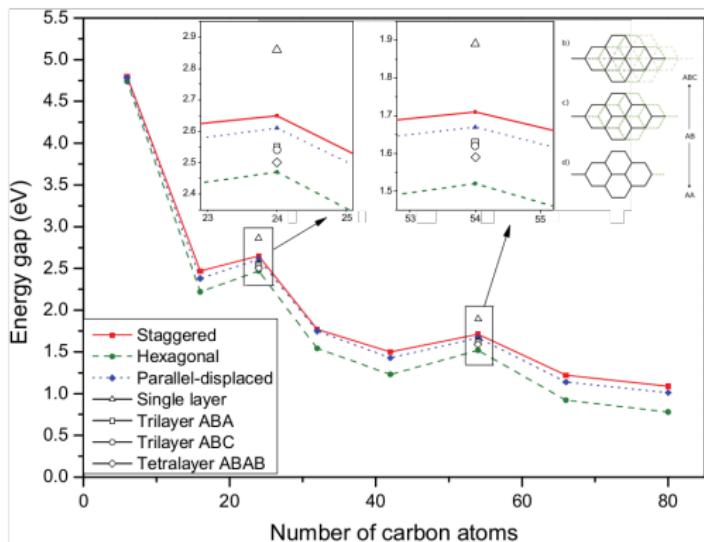
<sup>1</sup>A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.

<sup>2</sup>R.R. Nair, et al. Science, 320(5881):1308-1308, 2008.

<sup>3</sup>M.Y. Han, et. al. Physical Review Letters, 98(20):206805, 2007

<sup>4</sup>By Rahul Nair - Manchester group.

- Tunable bandgap by:
  - Changing sheet size <sup>1</sup>
  - Changing the number of sheets<sup>1</sup>
  - Stacking<sup>1</sup>
  - Applying an electric field <sup>2</sup>
  - Doping <sup>3</sup>
  - Hydrogenation <sup>4</sup>



Variation of the energy gap with the size of graphene sheet model.<sup>1</sup>

<sup>1</sup>C. Feng et al. 2009. Jour. of Chem. Phys. 131:194702, 2009.

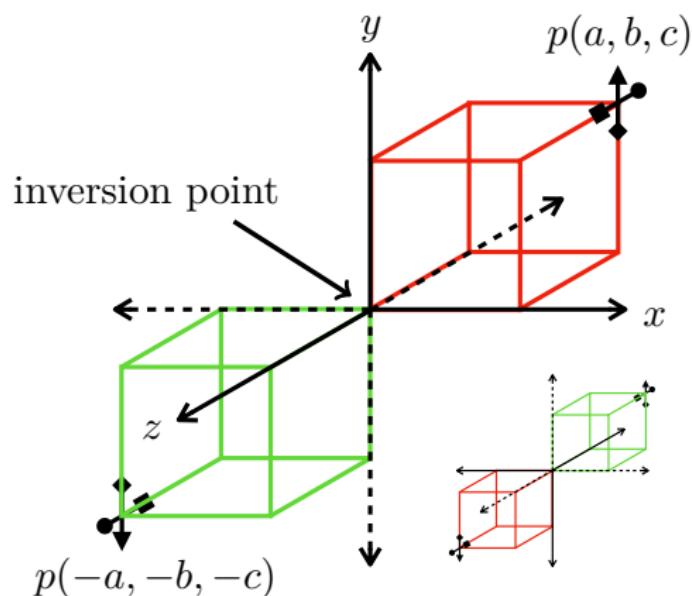
<sup>2</sup>Y. Zhang et al. Nature, 459(7248):820-823, 2009.

<sup>3</sup>T. Ohta et al. Science, 313(5789):951-954, 2006.

<sup>4</sup>D.C. Elias et al. Science, 323(5914):610-613, 2009.

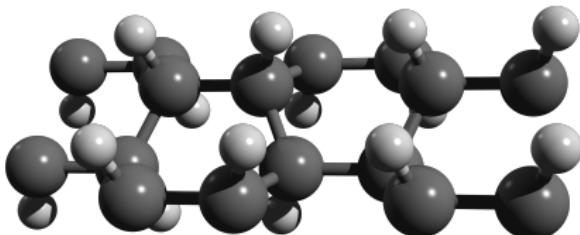
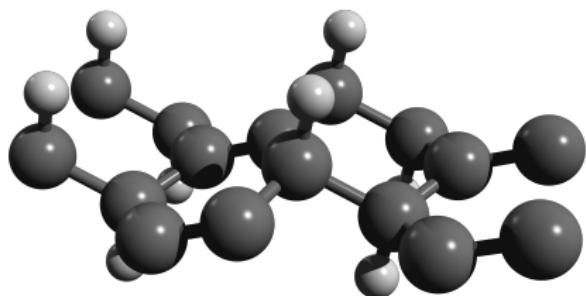
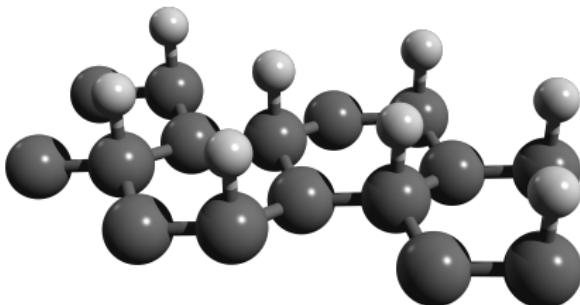
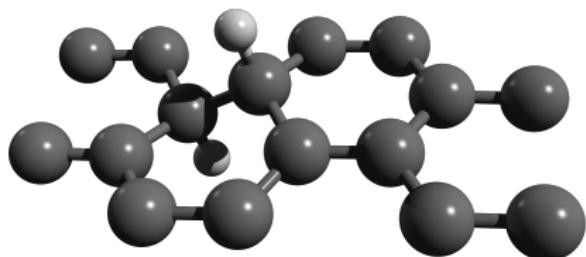
## Centrosymmetric Materials

- A centrosymmetric system presents inversion of symmetry, such that for every point in the unit cell  $p(a, b, c)$  there is an indistinguishable point  $p'(-a, -b, -c)$ .

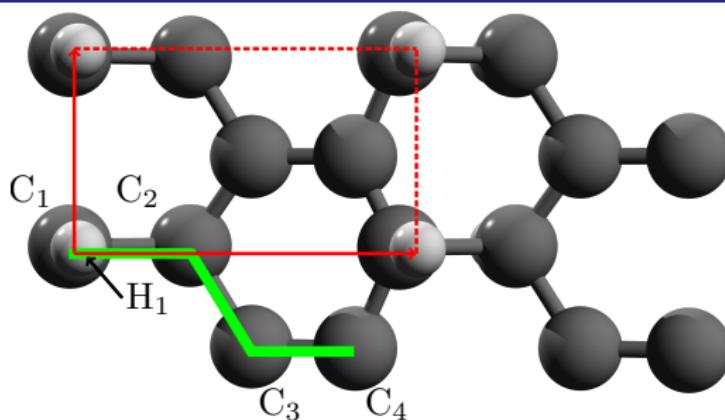


- Second-order nonlinear optical interactions can occur only in noncentrosymmetric crystals.<sup>1</sup>

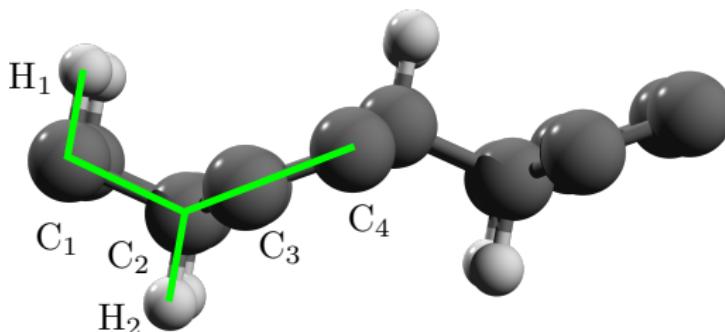
<sup>1</sup>Boyd, Robert W. Nonlinear optics. Academic press, 2003.



Functionalization by hydrogenation

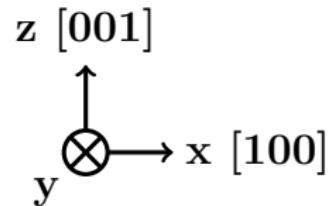
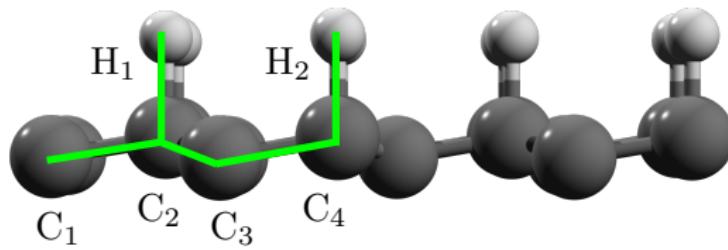
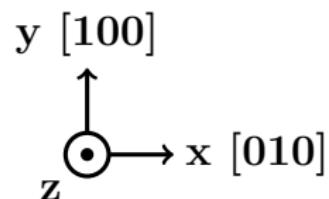
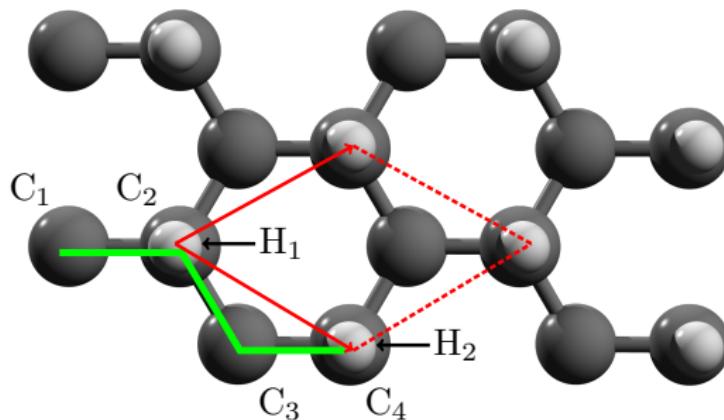


y [100]  
z  
x [010]



z [001]  
y  
x [100]

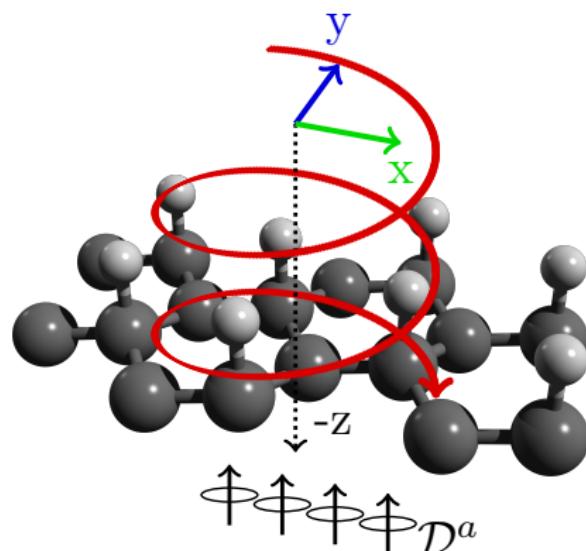
Alt structure: 50% hydrogenation; hydrogen at bot sides.



**Up structure:** 50% hydrogenation; hydrogen on the upper side.

## Optical spin injection and degree of spin polarization (DSP)

- Spintronics is based in the injection, detection and transport of spin polarized electrons in nonmagnetic materials.<sup>1</sup>
- Spin polarized electrons in a given  $a$  direction can be injected through circularly polarized light.<sup>2</sup>



<sup>1</sup>A. Fert et. al. Rev. Mod. Phys., 80(4):1517, 2008.

<sup>2</sup>N. Arzate et al. Phys. Rev. B, 90(20):205310, 2014.

- The Spin generation rate and the carrier generation rate can be written as

$$\dot{S}^a(\omega) = \zeta^{abc}(\omega)E^b(-\omega)E^c(\omega),$$
$$\dot{n}(\omega) = \xi^{ab}(\omega)E^a(-\omega)E^b(\omega),$$

where  $\zeta^{abc}(\omega)$  is the spin injection rate tensor and  $\xi^{ab}(\omega)$  is the carrier generation rate tensor.

- The degree of spin polarization (DSP) quantifies the fraction of injected electrons in the conduction bands that are spin polarized along direction  $a$  and is given by

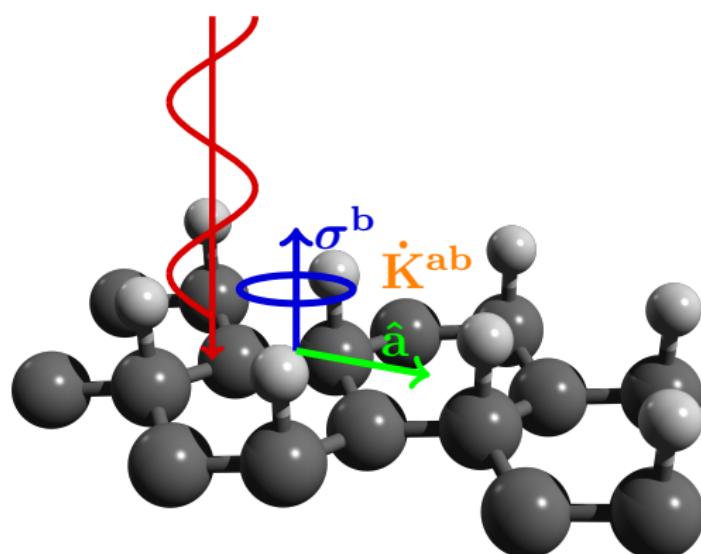
$$\mathcal{D}^a(\omega) = \frac{\dot{S}^a(\omega)}{(\hbar/2)\dot{n}(\omega)} \quad (1)$$

- DSP is a second order optical effect; it is possible to generate spin polarized electrons along three Cartesian directions with an incident circularly polarized beam.

## Pure spin current and spin velocity injection (SVI)

### Pure spin current injection

- There is no net motion of charge but a spin current is produced.<sup>1</sup>
- The spin current  $\dot{K}^{ab}(\omega)$  moves along direction  $\hat{\mathbf{a}}$  with the spin polarized along direction  $\hat{\mathbf{b}}$ .<sup>1</sup>



<sup>1</sup>A. Najmaie et. al. Phys. Rev. B, 68(16):165348, 2003.

- Is a second-order optical nonlinear effect.
- A pure spin current can be produced by a single linearly polarized beam in noncentrosymmetric materials<sup>1</sup> and is given by<sup>2</sup>

$$\dot{K}^{ab}(\omega) = \mu^{abcd}(\omega) E^c(\omega) E^{d*}(\omega), \quad (2)$$

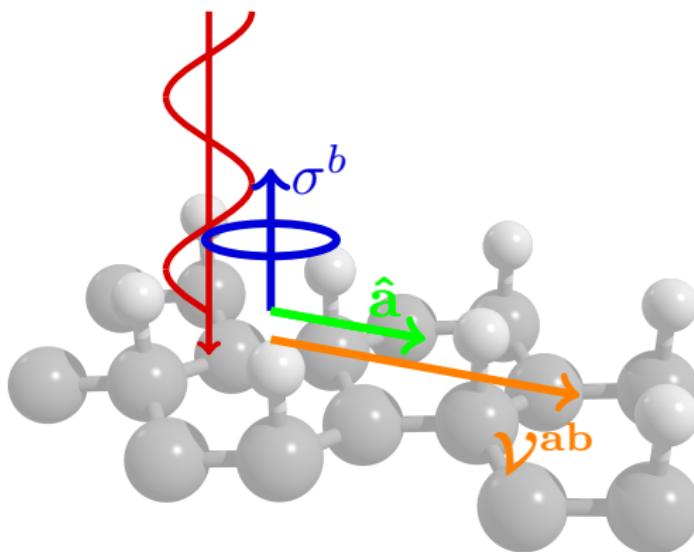
where  $\mu^{abcd}(\omega)$  is the pseudotensor that describes the rate of change of the PSC.

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<sup>1</sup>A. Najmaie et. al. Phys. Rev. B, 68(16):165348, 2003.

<sup>2</sup>Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

## Spin velocity injection



- The spin velocity injection is defined as<sup>1</sup>

$$\mathcal{V}^{ab}(\omega) \equiv \frac{\dot{K}^{ab}(\omega)}{(\hbar/2)\dot{n}(\omega)}, \quad (3)$$

which gives the velocity, along direction  $\hat{\mathbf{a}}$ , at which the spin moves in a polarized state along direction  $\hat{\mathbf{b}}$ .

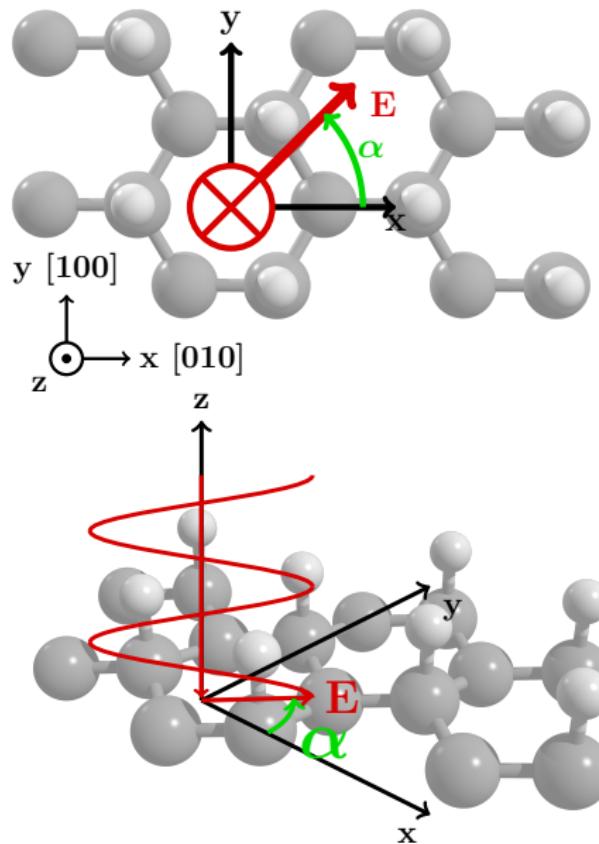
<sup>1</sup>Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

## └ Theory

## └ Pure spin current injection

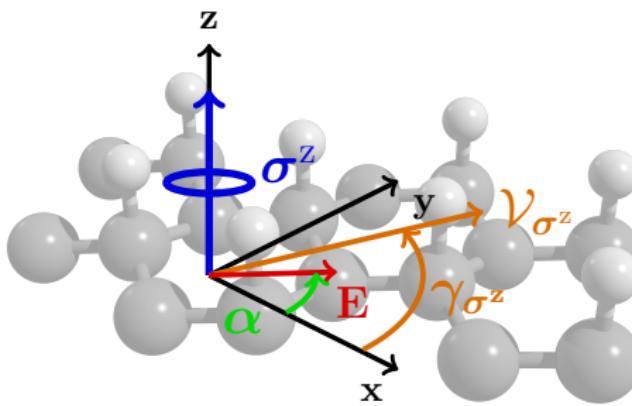
- With 2D structures we can use the direction of the polarized electric field,  $\alpha$ , to control  $\mathcal{V}^{ab}(\omega)$ .
- Writing  $\mathbf{E}(\omega) = E_0(\omega)(\cos \alpha \hat{\mathbf{x}} + \sin \alpha \hat{\mathbf{y}})$ , where  $\alpha$  is the polarization angle, we obtain that

$$\mathcal{V}^{ab}(\omega, \alpha) = \frac{2}{\hbar \xi(\omega)} (\mu^{abxx}(\omega) \cos^2 \alpha + \mu^{abyy}(\omega) \sin^2 \alpha + \mu^{abxy}(\omega) \sin 2\alpha). \quad (4)$$



# Fixing the spin polarization<sup>1</sup>

Spin fixed along  $z$  direction



- Magnitude of the velocity when the spin is fixed in the  $b$  direction

$$\mathcal{V}_{\sigma^b}(\omega, \alpha) \equiv \sqrt{(\mathcal{V}_{xb}(\omega, \alpha))^2 + (\mathcal{V}_{yb}(\omega, \alpha))^2} \quad (5)$$

- Angle of the velocity when the spin is fixed in the  $b$

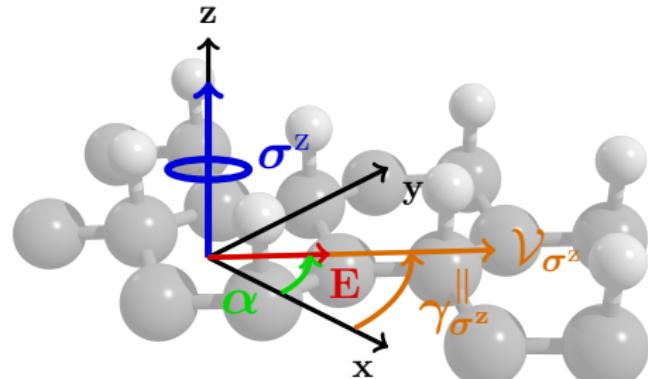
$$\gamma_{\sigma^b}(\omega, \alpha) = \tan^{-1} \left( \frac{\mathcal{V}_{yb}(\omega, \alpha)}{\mathcal{V}_{xb}(\omega, \alpha)} \right) \quad (6)$$

<sup>1</sup>Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

We have two special cases

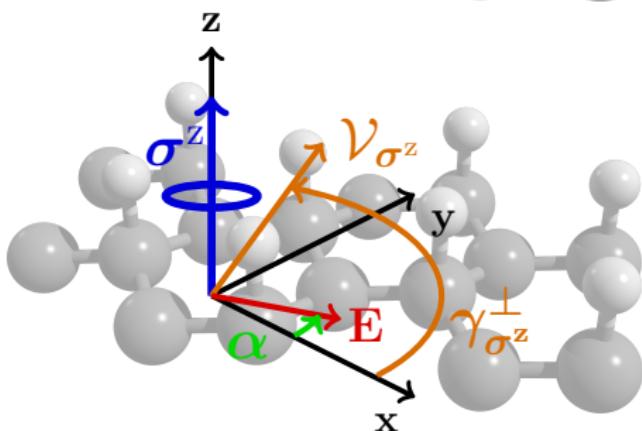
- When the velocity vector is parallel to the electric incident field

$$\gamma_{\sigma^b}^{\parallel}(\omega, \alpha) = \alpha, \quad (7)$$



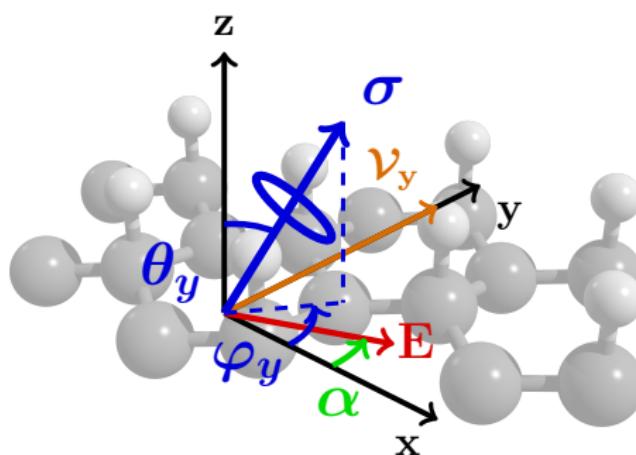
- When the velocity vector is perpendicular to the electric incident field

$$\gamma_{\sigma^b}^{\perp}(\omega, \alpha) = \alpha \pm 90^\circ, \quad (8)$$



# Fixing the spin velocity<sup>1</sup>

Velocity fixed along  $y$  direction



- Magnitude of the velocity when it is fixed along  $\hat{a}$  direction

$$\mathcal{V}_a(\omega, \alpha) \equiv \left[ (\mathcal{V}^{ax}(\omega, \alpha))^2 + (\mathcal{V}^{ay}(\omega, \alpha))^2 + (\mathcal{V}^{az}(\omega, \alpha))^2 \right]. \quad (9)$$

- Angles of the spin

Polar angle

$$\theta_a(\omega, \alpha) = \cos^{-1} \left( \frac{\mathcal{V}^{az}(\omega, \alpha)}{\mathcal{V}_a(\omega, \alpha)} \right). \quad (10)$$

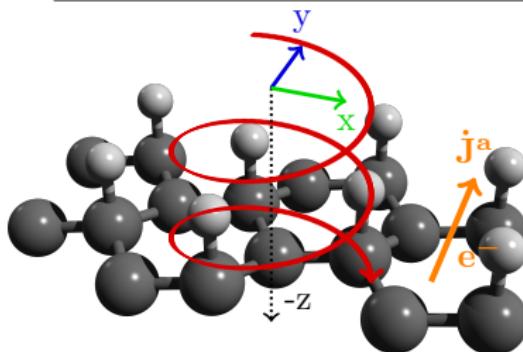
Azimuthal angle

$$\varphi_a(\omega, \alpha) = \tan^{-1} \left( \frac{\mathcal{V}^{ay}(\omega, \alpha)}{\mathcal{V}^{ax}(\omega, \alpha)} \right). \quad (11)$$

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<sup>1</sup>Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

## Optical current injection



- Is a second-order optical nonlinear effect that can be produced with a circularly-polarized beam.<sup>2</sup>
- It is possible to control a photocurrent  $\mathbf{j}^a$  in a non-centrosymmetric bulk material,<sup>1</sup> at the surface af a centrosymmetric media,<sup>2</sup> and on the surface of 2D systems<sup>3</sup>

The optical current injection is given by

$$\mathbf{j}_{\text{inj}}^a(\omega) = \eta^{abc}(\omega) E_b(\omega) E_c(\omega),$$

where  $\eta^{abc}(\omega)$  is the current injection tensor which quantifies the current injection along the direction a.

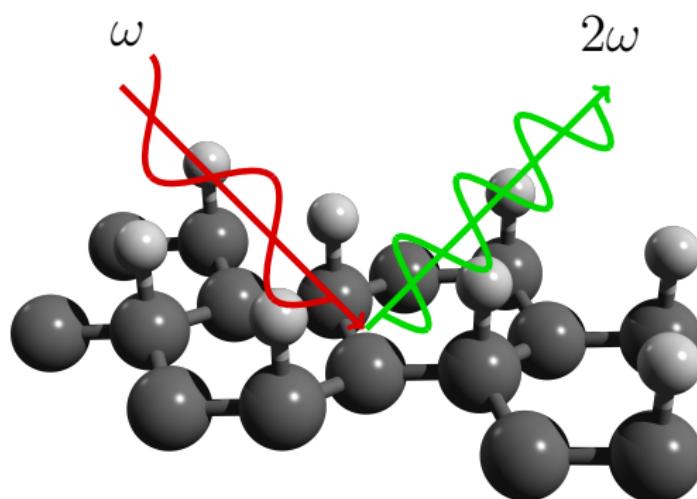
<sup>1</sup> A. Haché et. al. Phys. Rev. Lett., 78:306-309, Jan1997.

<sup>2</sup> N. Arzate et al. Phys. Rev. B, 90(20):205310, 2014.

<sup>3</sup> R. Zapata-Peña, et. al. Phys. Stat. Sol. (b), 253(2):226-233, 2016.

## Second harmonic generation (SHG)

- Is a second-order optical nonlinear effect and a particular case of sum frequency generation.
- The nonlinear polarization in the media acts as a source for the electromagnetic waves of frequency  $2\omega$ .
- SHG spectroscopy offer a non-invasive technique to study material properties.



- The second-order nonlinear polarization is given by <sup>1</sup>

$$\mathcal{P}(2\omega) = \chi^{abc}(-2\omega; \omega, \omega) E^b(\omega) E^c(\omega),$$

where  $\chi^{abc}(-2\omega; \omega, \omega)$  is the nonlinear susceptibility tensor responsible for the SHG.

- The formalism includes <sup>1</sup>
  - the scissors correction,
  - the contribution of the nonlocal part of the pseudopotentials
  - the cut function used to select the individual contribution for a given layer.

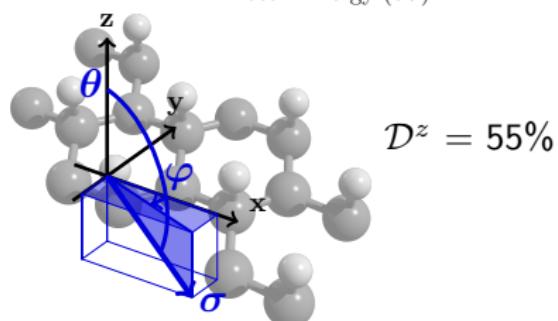
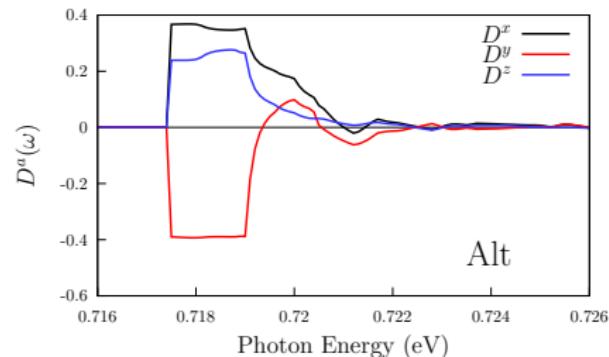
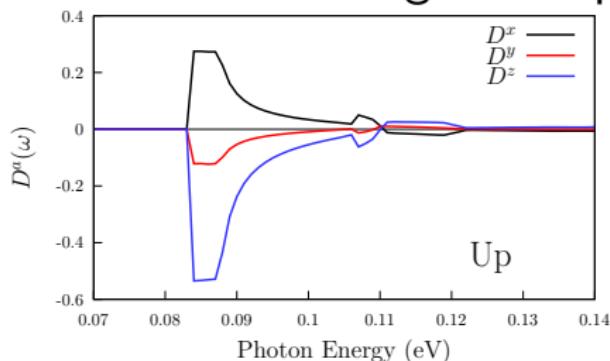
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<sup>1</sup>S. M. Anderson et al. Phys. Rev. B, 91(7):075302, 2015.

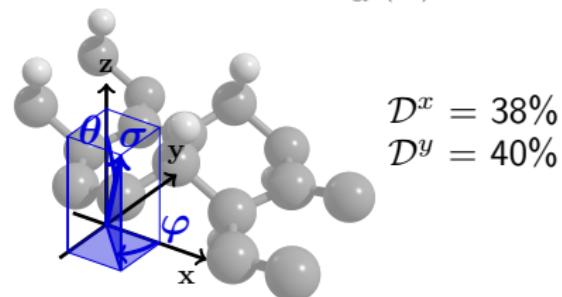
## └ Results

## └ Degree of spin polarization

# Degree of spin polarization

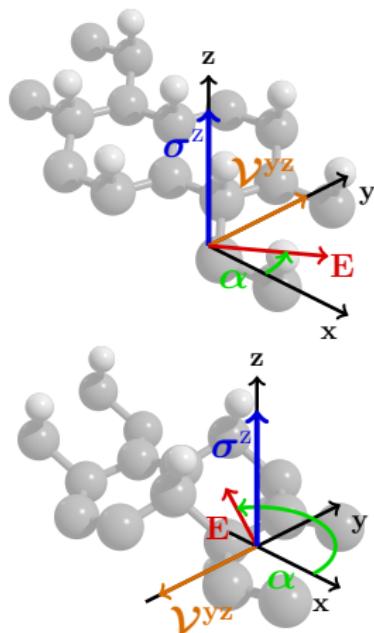


Response in the Mid Infrared  
 $0.084 \text{ eV} = 14.7 \mu\text{m} = 20.3 \text{ THz}$

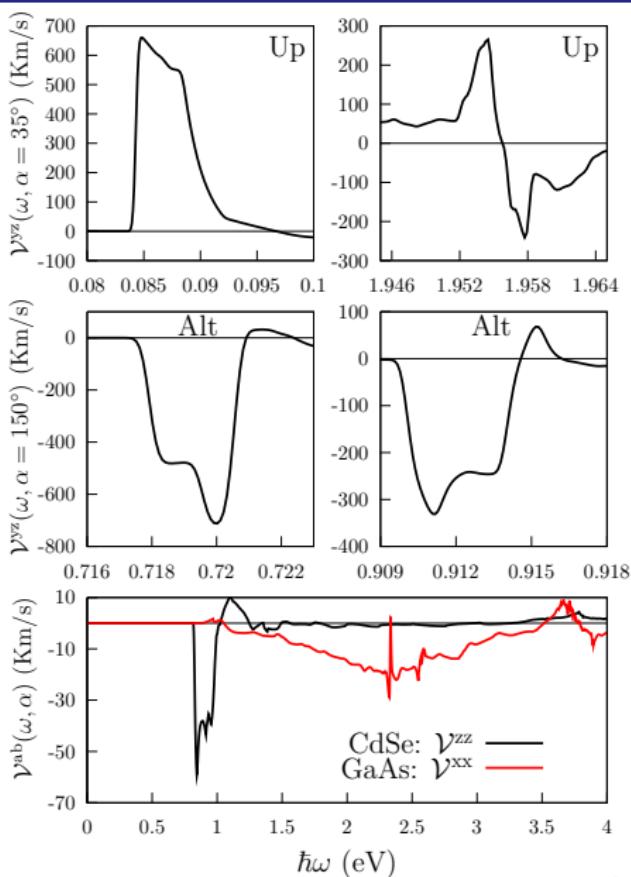


Response in the Near Infrared  
 $0.717 \text{ eV} = 1.72 \mu\text{m} = 173 \text{ THz}$

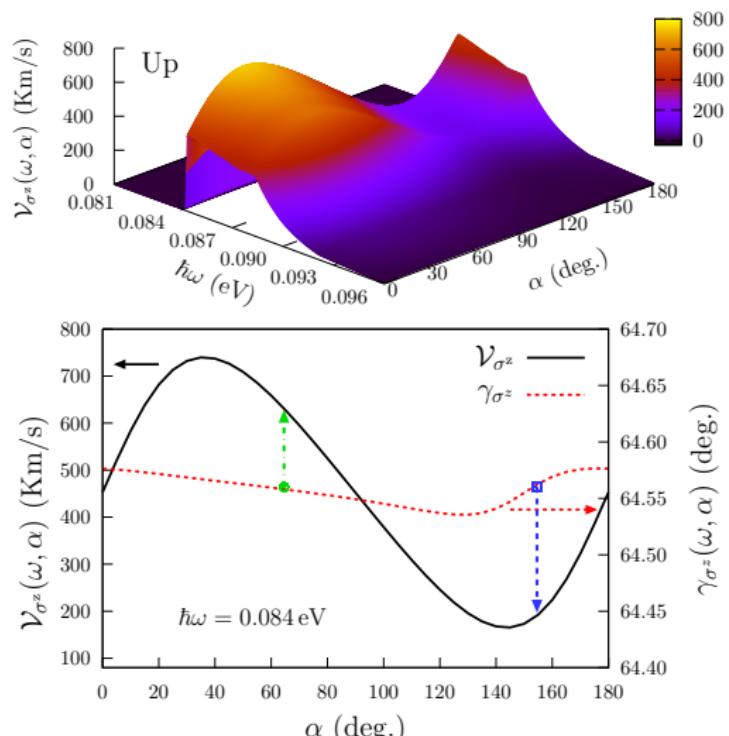
# Spin velocity injection



Components with maximum values of  $\mathcal{V}^{ab}$  for the alt, up, CdSe and GaAs structures.

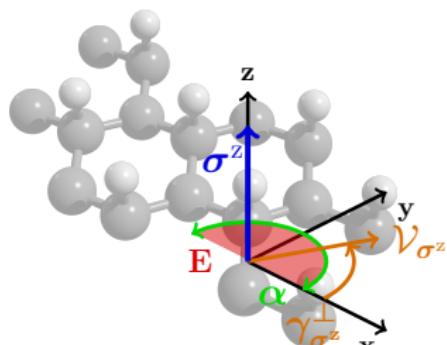


Fixing the spin along  $z$  for up



When the spin is polarized along  $z$  the spin velocity  $V_{\sigma^z}(\omega, \alpha)$  (Eq. 5):

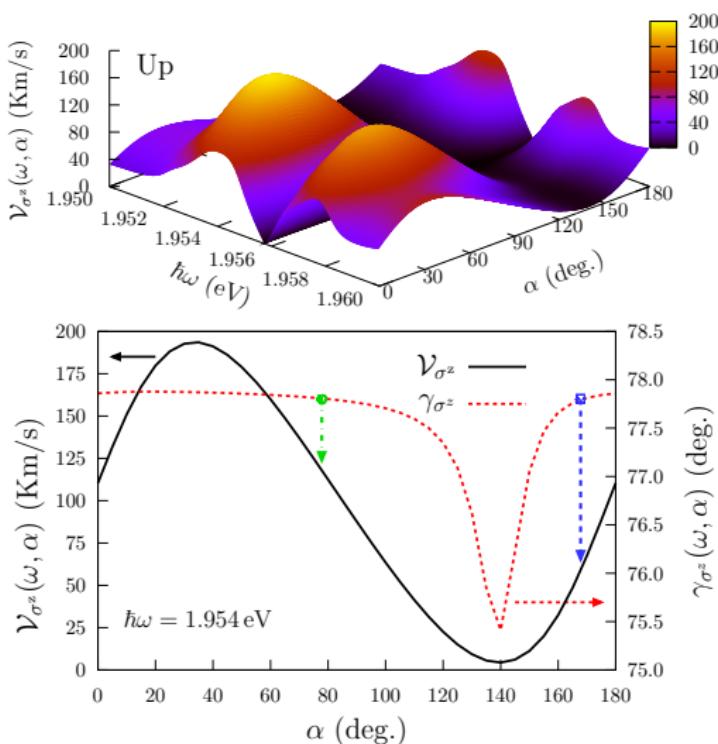
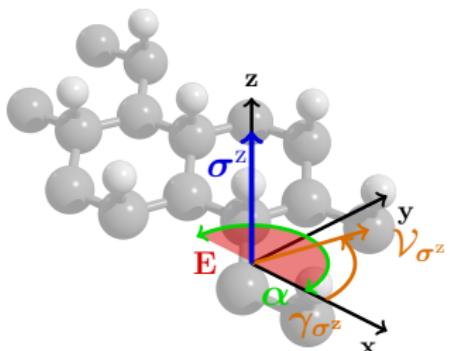
- Is maximized for  $\hbar\omega = 0.084$  eV
- The absolute maxima is 739.7 Km/s for  $\alpha = 35^\circ$
- The velocity is directed almost at a constant angle  $\gamma_{\sigma^z} = 64.5^\circ$



## └ Results

## └ Spin velocity injection

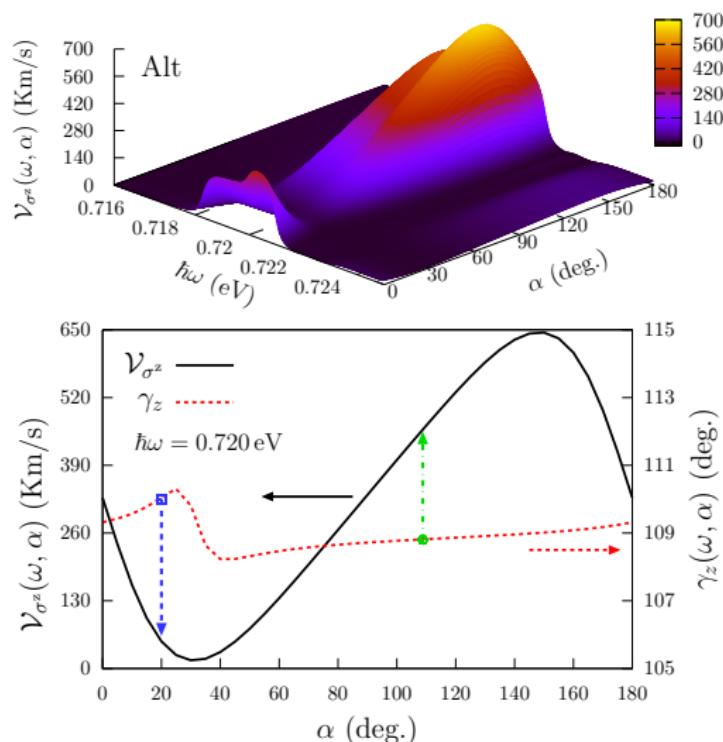
- A local maxima is found for  $\hbar\omega = 1.954 \text{ eV}$  (634 nm, visible red)
- The maxima is 193.5 Km/s for  $\alpha = 35^\circ$
- The velocity angle  $\gamma_{\sigma^z}$  has values between  $75.5^\circ$  and  $77.8^\circ$



## └ Results

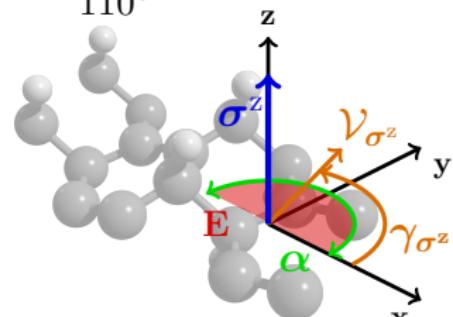
## └ Spin velocity injection

Fixing the spin along  $z$  for *alt*



Again with the spin polarized along  $z$  the spin velocity  $V_{\sigma^z}(\omega, \alpha)$  (Eq. 5):

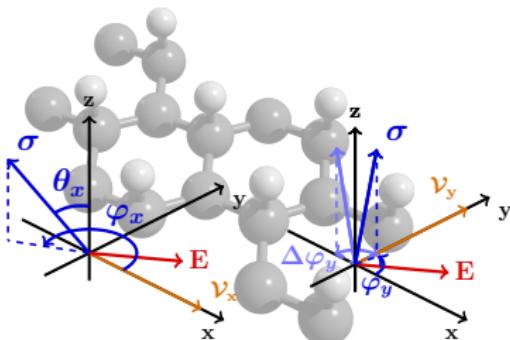
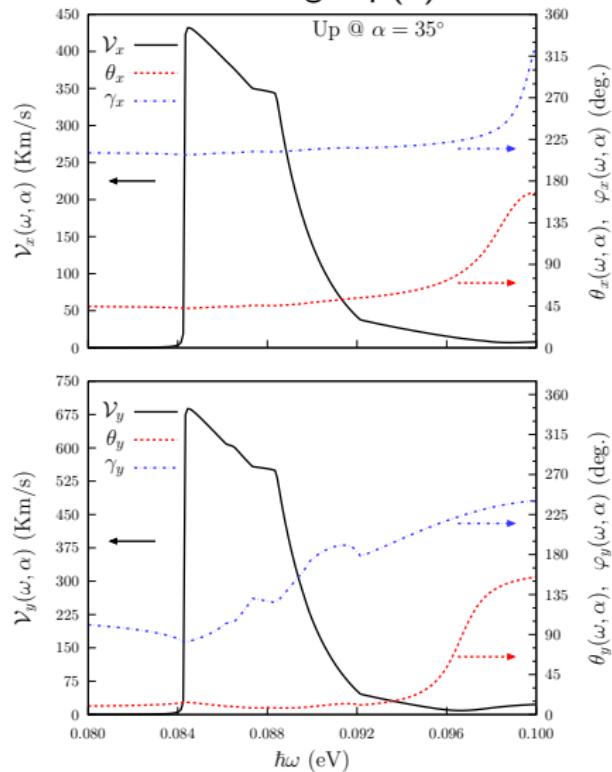
- Is maximized for  $\hbar\omega = 0.720$  eV (near infrared,  $1.72 \mu\text{m}$ )
- The absolute maxima is 645 Km/s for  $\alpha = 150^\circ$
- The velocity angle  $\gamma_{\sigma^z}$  has values from  $108^\circ$  to  $110^\circ$



## └ Results

## └ Spin velocity injection

Fixing the velocity on  $x$  and  $y$  directions for *up*  
and using Eq (9)

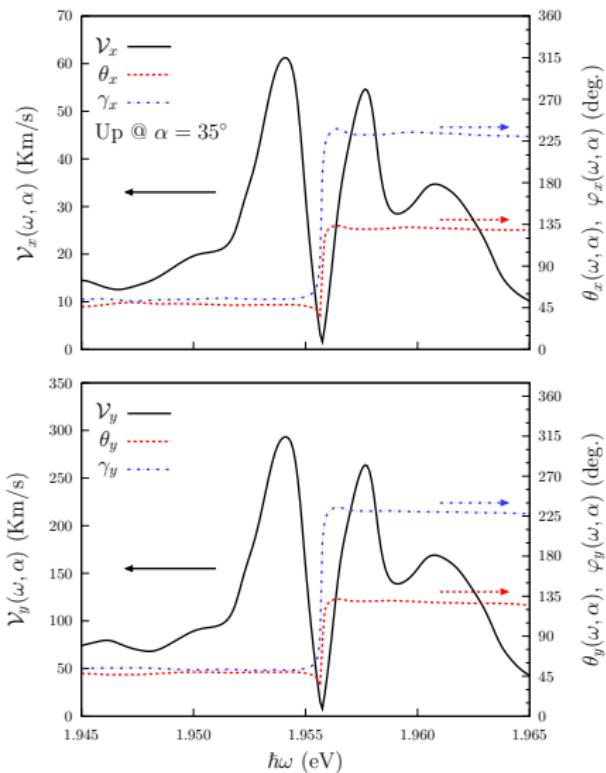
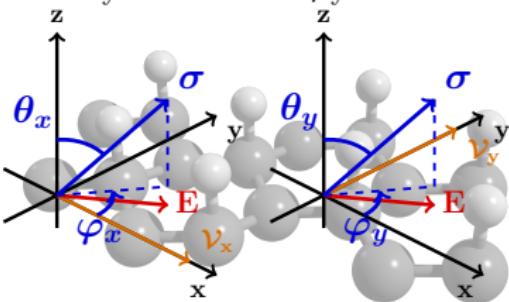


- The responses are maximized for  $\alpha = 35^\circ$  and  $\hbar\omega = 0.084$  eV
- The absolute  $x$  maxima is  $V_x = 432$  Km/s at  $\theta_x = 43^\circ$  and  $\varphi_x = 208^\circ$
- The absolute  $y$  maxima is  $V_y = 688$  Km/s at  $\theta_y = 14^\circ$  and  $\varphi_y = 82^\circ$

## └ Results

## └ Spin velocity injection

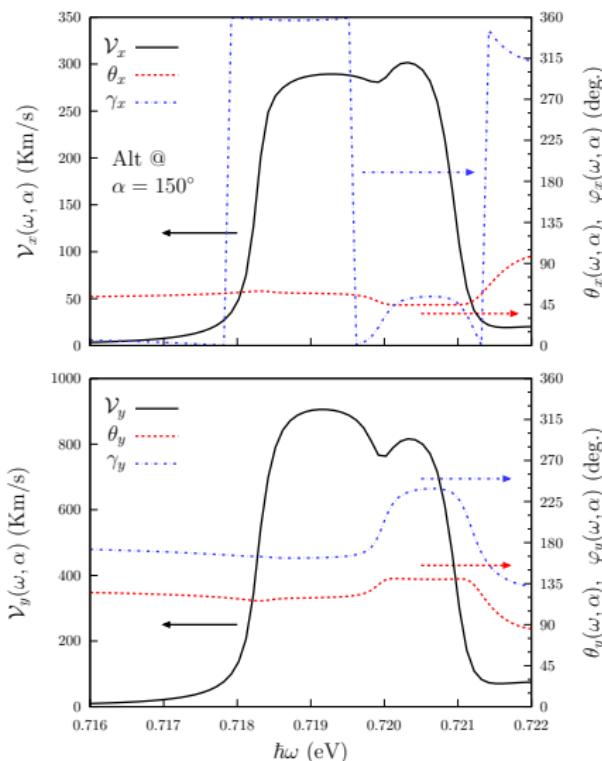
- The responses has a local maxima for  $\alpha = 35^\circ$  and  $\hbar\omega = 1.954 \text{ eV}$
- The local  $x$  maxima is  $\mathcal{V}_x = 61 \text{ Km/s}$  at  $\theta_x = 48^\circ$  and  $\varphi_x = 54^\circ$
- The local  $y$  maxima is  $\mathcal{V}_y = 293 \text{ Km/s}$  at  $\theta_y = 50^\circ$  and  $\varphi_y = 52^\circ$



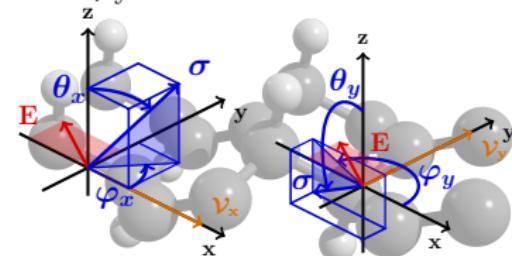
## └ Results

## └ Spin velocity injection

Fixing the velocity on  $x$  and  $y$  directions for  $\alpha \neq 0^\circ$



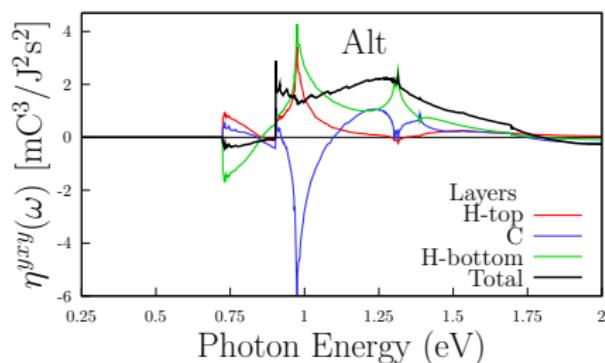
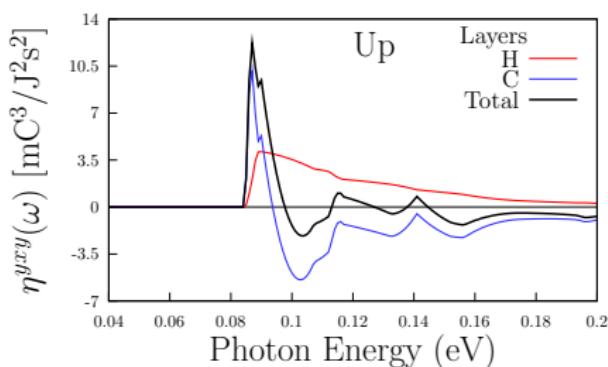
- The responses has local maxima for  $\alpha = 150^\circ$
- The local  $x$  maxima is at  $\hbar\omega = 0.720$  eV:  
 $v_x = 302$  Km/s at  
 $\theta_x = 45^\circ$  and  $\varphi_x = 51^\circ$
- The absolute  $y$  maxima is at  $\hbar\omega = 0.719$  eV:  
 $v_y = 906$  Km/s at  
 $\theta_y = 120^\circ$  and  
 $\varphi_y = 163^\circ$



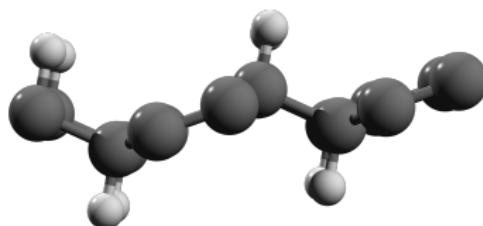
## └ Results

## └ optical current injection

# Optical current injection

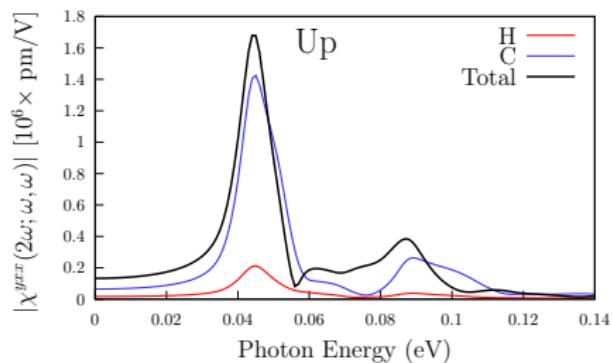


Response in the Mid Infrared  
 $0.084 \text{ eV} = 14.7 \mu\text{m} = 20.3 \text{ THz}$

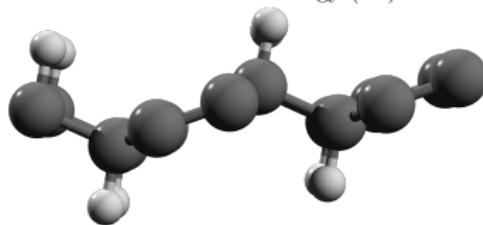
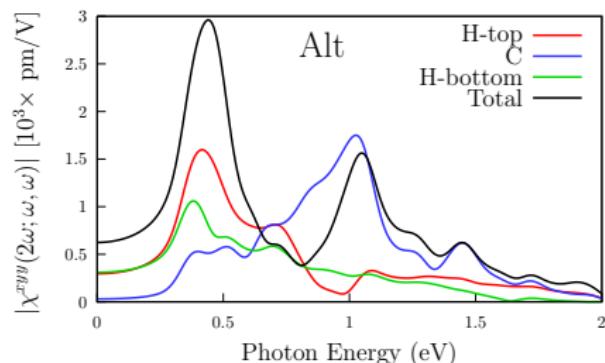


Intense response in the Near Infrared  
 $0.90 \text{ eV} = 230 \mu\text{m}$

# Second harmonic generation



Intense response and second feature  
in the Mid Infrared  
 $0.04 \text{ eV} = 11 \text{ THz}$   
 $0.09 \text{ eV} = 22 \text{ THz}$



Intense response and second feature  
in the Near Infrared  
 $0.4 \text{ eV} = 3.1 \mu\text{m}$   
 $1.1 \text{ eV} = 1.2 \mu\text{m}$

# Conclusions

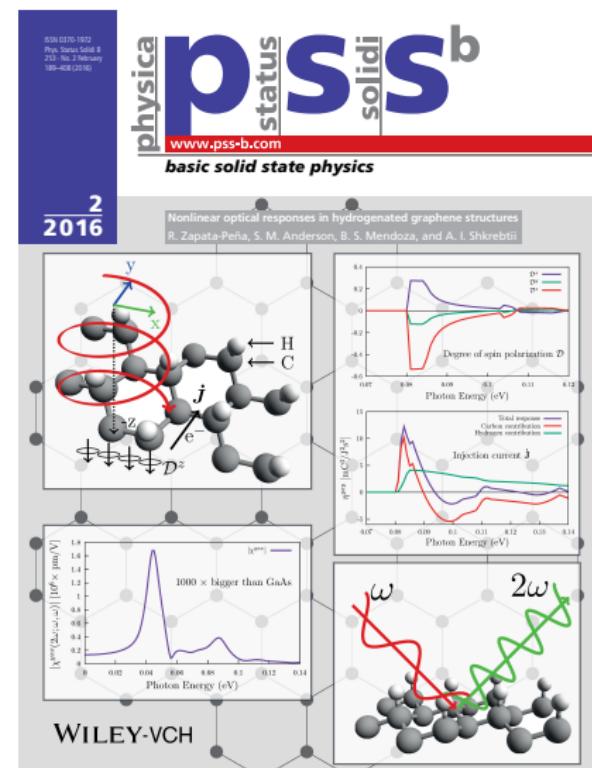
- Due to the fact that both structures are high non-centrosymmetric materials, then it is possible to induced high intensity nonlinear responses in them.
- Both structures are excellent candidates for spintronics applications:
  - \* We found that the *up* is more spin-polarizable than the *alt* but both reaches more than 50% of DSP.
  - \* It is possible to generate pure-spin currents in our structures; also it is possible to control the spin orientation or the current direction making variations in the angle of the polarization of the incoming beam.
  - \* The spin velocities reached in the structures are usable for spintronics devices.
- The *up* structure can achieve a large injection current being the response bigger than most of other structures.<sup>1</sup>
- Both structures are excellent candidates to generate second harmonic, particularly the *up* one.

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<sup>1</sup>R. Zapata-Peña, et. al. Phys. Rev. B 96, 195415, 2017.

# Articles

- R. Zapata-Peña, et. al. Pure spin current injection in hydrogenated graphene structures. Phys. Rev. B 96, 195415, 2017.
- Anatoli I. Shkrebtii, R. Zapata-Peña, et. al. Graphene-Boron Nitride 2D Heterosystems Functionalized with Hydrogen. Advances in Science and Technology 98:117-124, 2017.
- R. Zapata-Peña, et. al. Nonlinear optical responses in hydrogenated graphene structures. Phys. Stat. Sol. (b), 253(2):226-233, 2016.



## Conferences

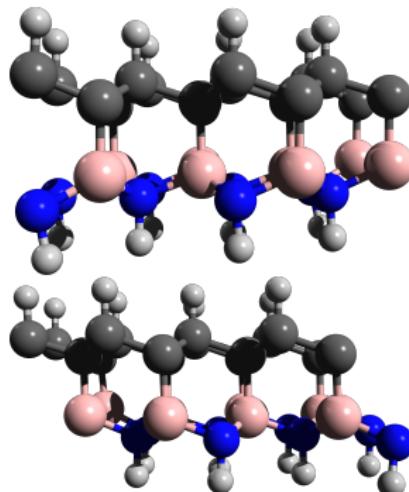
- IX Riao-Optilas 2016 (Poster)  
IX Reunión Iberoamericana de Óptica y XII Reunión Iberoamericana de  
Óptica, Láseres y Aplicaciones. Pucón, Chile.
- OSI-11 2015 (Poster)  
The International Conference on Optics of Surfaces and Interfaces.  
Austin, Texas, USA.

## Specialized courses

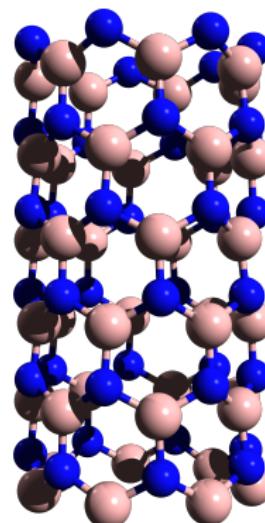
- Control de versiones usando Git y GitHub (2013)
- Cómputo en paralelo mediante FORTRAN/C++ con MPI y  
OpenMP (2013)
- Cálculo de propiedades ópticas de la materia con el uso de  
teoría de muchos cuerpos (2013)

## Perspectives

Continue the study of this phenomenon in other structures and make new publication:



Functionalized  
boron-nitride-graphene with  
hydrogen



Boron-nitride nanotubes

## Acknowledgments

- Dr. Bernardo Mendoza, *el jefe*
- Dr. Ramón Carriles Jaimes
- Dr. Gabriel Merino Hernández
- My really good friend Dr. Sean M. Anderson
- My lovely wife, Patricia, and my kids
- My mother, Eloisa
- My sisters
- All my friends who shared time with me
- The CIO
- The CONACYT

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- The spin injection rate tensor is given by

$$\zeta^{abc} = \frac{\pi e^2}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum'_{vc c'} \left( \text{Im} [\mathcal{S}_{c'c}^a r_{cv}^b r_{vc'}^c] + \text{Im} [\mathcal{S}_{cc'}^a r_{c'v}^b r_{vc}^c] \right) \delta(\omega - \omega_{cv}), \quad (12)$$

where the ' in the sum, reminds us that  $c$  and  $c'$  are quasi degenerate, and thus the sum only covers these states.

- The carrier generation rate tensor is given by

$$\xi^{ab}(\omega) = \frac{2\pi e^2}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum_{vc} r_{vc}^a(\mathbf{k}) r_{cv}^b(\mathbf{k}) \delta(\omega_{cv}(\mathbf{k}) - \omega). \quad (13)$$

- The pure spin current pseudotensor is given by

$$\mu^{abcd} = \frac{\pi e^2}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum'_{vc c'} \text{Re} \left[ K_{c'c}^{ab} \left( r_{vc'}^c r_{cv}^d + (c \leftrightarrow d) \right) \right] \delta(\omega - \omega_{cv}), \quad (14)$$

where  $K_{nm}^{ab} = \sum_l v_{nl}^a S_{lm}^b$ .

- The optical current injection tensor is given by

$$\eta^{abc} = \frac{\pi e^3}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum'_{vc c'} \left[ v_{cc'}^a r_{vc}^b r_{c'v}^c + v_{c'c}^a r_{vc'}^b r_{cv}^c \right] \delta(\omega - \omega_{cv}). \quad (15)$$