Reinaldo Arturo Zapata Peña presents

Novel Optical Effects in Functionalized Graphene: Formalism and Simulations

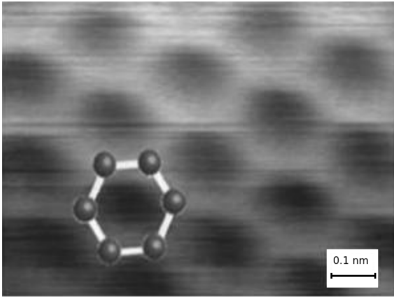
to earn the degree of Doctor of Science (Optics)

CENTRO DE INVESTIGACIONES
EN OPTICA, A.C.

December 11, 2017

General properties of graphene

- Good heat conductor [1]
- Extremely strong [2]
- Flexible [3]



Transmission electron microscopy of graphene. [4]

[1] A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.

[2] C. Lee, et al. Science, 321(5887):385-388, 2008.

[3] Briggs, B. D. et. al. App. Phys. Lett. 97: 223102. 2010.

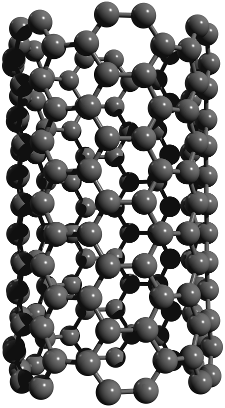
[4] E. Stolyarova, et al. PNAS, 104(22):9209, 2007.

Synthesis of graphene

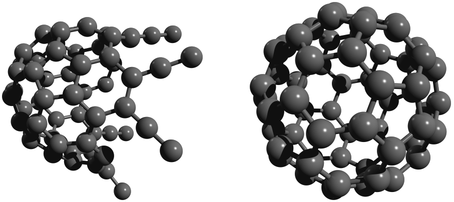
- Exfoliation[1]
- Micromechanical cleavage [2]
- Reduction of graphite oxide in dimethylformamide [3]
- Chemical Vapor Deposition [4]

Graphite, a tape dispenser, and graphene transistor, donated to the Nobel Museum.[5]

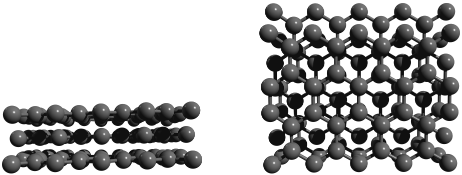
[1] A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.
[2] R.R. Nair, et al. Science, 320(5881):1308-1308, 2008.
[3] S. Park, J. et al. Nano letters, 9(4):1593-1597, 2009.
[4] E. Rollings, et al. JPCS, 67(9-10):2172-2177, 2006.
[5] By Gabriel Hildebrand - Nobelmuseet, Public Domain.



Carbon nanotube



Fullerene



Graphite

Structures obtained from graphene

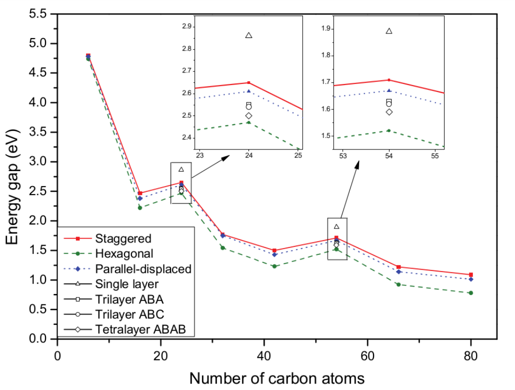
Electronic properties of graphene

- Quantum Hall effect at room temperature[1]
- Excellent electrical current conduction [1]
- Transparent to visible light [2]
- Tunable bandgap [3]

Photograph of graphene in transmitted light. [4]

[1] A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.
[2] R.R. Nair, et al. Science, 320(5881):1308-1308, 2008.
[3] M.Y. Han, et. al. Physical Review Letters, 98(20):206805, 2007
[4] By Rahul Nair - Manchester group.

- Tunable bandgap by:
  - Changing sheet size [1]
  - Changing the number of sheets[1]
  - Stacking[1]
  - Applying an electric field [2]
  - Doping [3]
  - Hydrogenation [4]

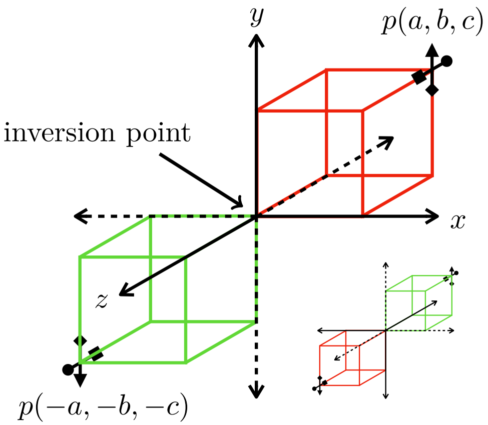


Variation of the energy gap with the size of graphene sheet model. [1]

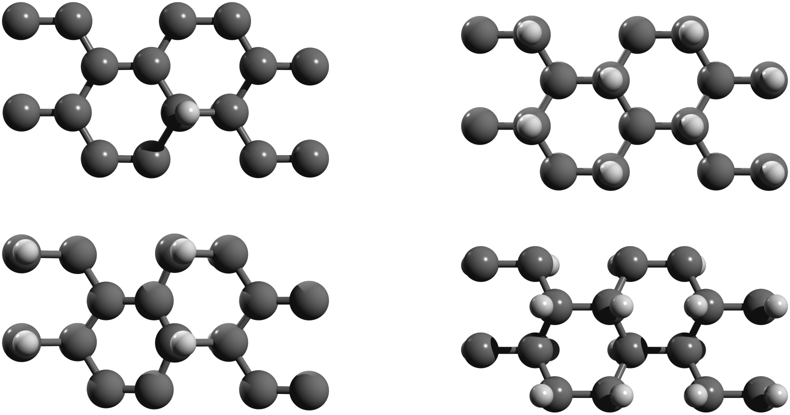
[1] C. Feng et al. 2009. Jour. of Chem. Phis. 131:194702, 2009.
[2] Y. Zhang et al. Nature, 459(7248):820-823, 2009.
[3] T. Ohta et al. Science, 313(5789):951-954, 2006.
[4] D.C. Elias et al. Science, 323(5914):610-613, 2009.

Centrosymmetric Materials

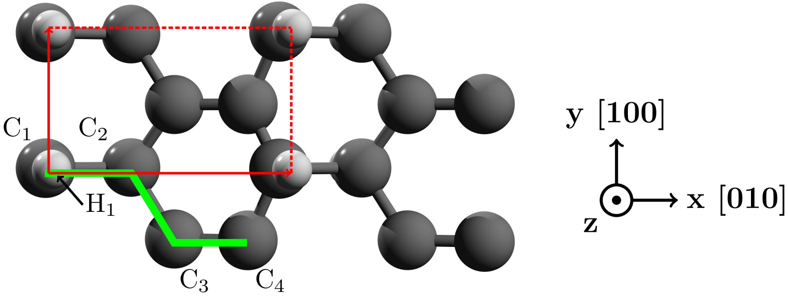
- A centrosymmetric system presents inversion of symmetry, such that for every point in the unit cell $p(a,b,c)$ there is an indistinguishable point $p'(-a,-b,-c)$.
- Second-order nonlinear optical interactions can occur only in noncentrosymmetric crystals.[1]

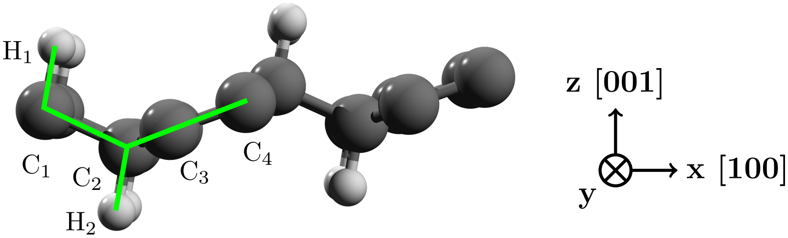


[1] Boyd, Robert W. Nonlinear optics. Academic press, 2003.

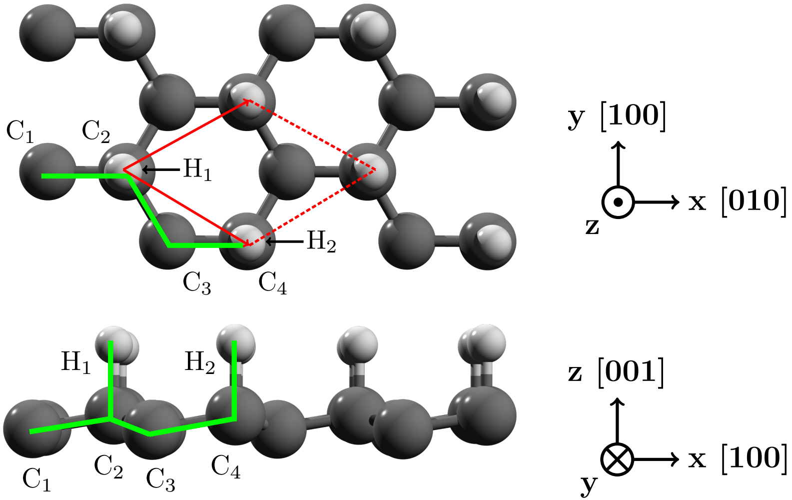


Functionalization by hydrogenation





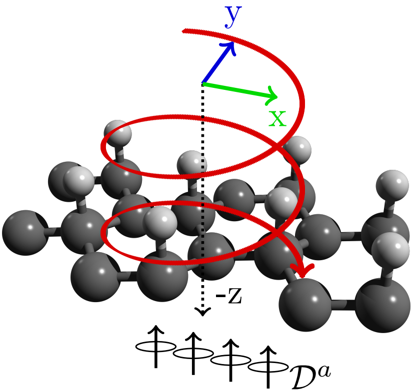
Alt structure: 50% hydrogenation; hydrogen at bot sides.



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.[1]
- Spin polarized electrons in a given a direction can be injected through circularly polarized light.[2]



[1] A. Fert et. al. Rev. Mod. Phys., 80(4):1517, 2008.
[2] 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 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

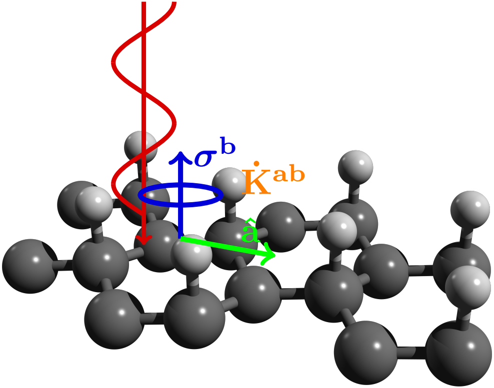
$$\mathcal{D}^a(\omega) = \frac{\dot{S}^a(\omega)}{(\hbar/2)\dot{n}(\omega)} \tag{1}$$

- 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. [1]
- The spin current $\dot{K}^{\mathrm{ab}}(\omega)$ moves along direction $\hat{\mathbf{a}}$ with the spin polarized along direction $\hat{\mathbf{b}}$. [1]



[1] A. Najmaie et. al. Phys. Rev. B,68(16):165348, 2003.

- Is a second-order optical nonlinear effect.

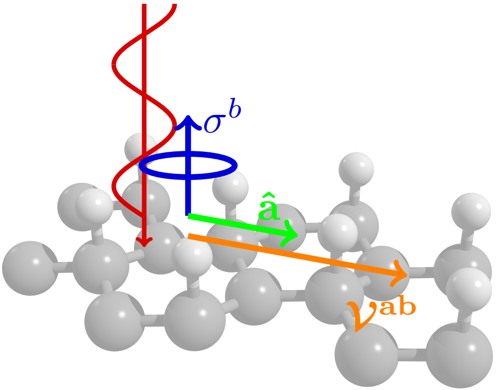
- A pure spin current can be produced by a single linearly polarized beam in noncentrosymmetric materials[1] and is given by[2]

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

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

[1] A. Najmaie et. al. Phys. Rev. B, 68(16):165348, 2003.
[2] Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

Spin velocity injection



- The spin velocity injection is defined as[1]

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

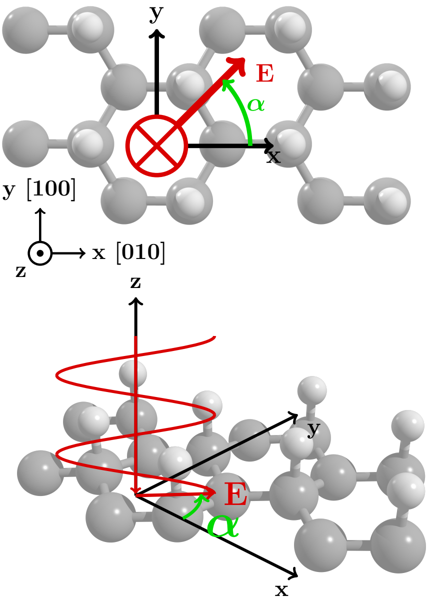
which gives the velocity, along direction $\hat{\mathbf{a}}$, at which the spin moves in a polarized state along direction $\hat{\mathbf{b}}$.

[1] Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

- With 2D structures we can use the direction of the polarized electric field, α, to control $\mathcal{V}^{\rm ab}(\omega)$.

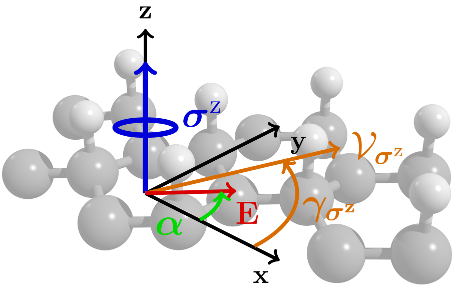
- Writing $\mathbf{E}(\omega) = E_0(\omega)(\cos\alpha\,\hat{\mathbf{x}} + \sin\alpha\,\hat{\mathbf{y}})$, where α is the polarization angle, we obtain that

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



Fixing the spin polarization[1]

Spin fixed along z direction



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

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

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

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

[1] Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

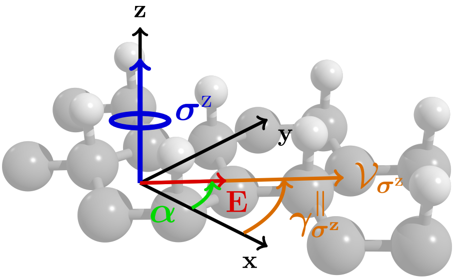
We have two special cases

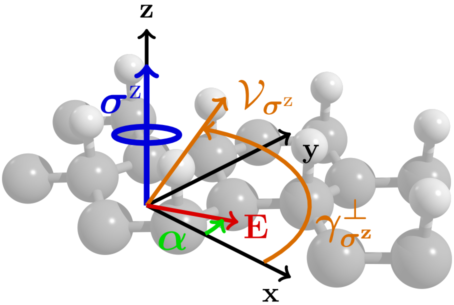
- When the velocity vector is parallel to the electric incident field

$$\gamma^{\|}_{\sigma^{\mathrm{b}}}(\omega,\alpha)=\alpha, \tag{7}$$

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

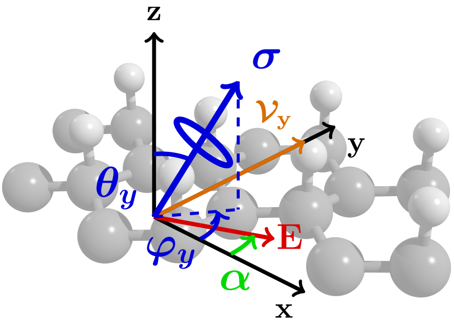
$$\gamma^{\perp}_{\sigma^{\mathrm{b}}}(\omega,\alpha)=\alpha\pm 90^{\circ}, \tag{8}$$





Fixing the spin velocity[1]

Velocity fixed along y direction



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

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

- Angles of the spin

Polar angle

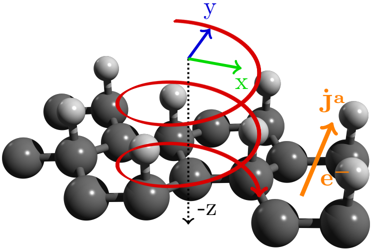
$$\theta_a(\omega,\alpha) = \cos^{-1}\left(\frac{\mathcal{V}^{az}(\omega,\alpha)}{\mathcal{V}_a(\omega,\alpha)}\right). \tag{10}$$

Azimuthal angle

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

[1] 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. [2]
- It is possible to control a photocurrent $\mathbf{j}^{\mathrm{a}}$ in a non-centrosymmetric bulk material,[1] at the surface af a centrosymmetric media,[2] and on the surface of 2D systems[3]

The optical current injection is given by

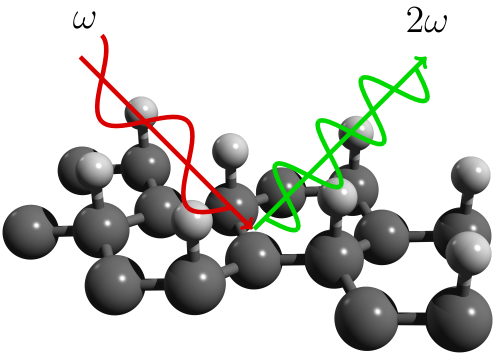
$$\mathbf{j}^{\mathrm{a}}_{\mathrm{inj}}(\omega) = \eta^{abc}(\omega)E_b(\omega)E_c(\omega),$$

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

[1] A. Haché et. al. Phys. Rev. Lett., 78:306-309, Jan1997.
[2] N. Arzate et al. Phys. Rev. B, 90(20):205310, 2014.
[3] 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 2ω.
- SHG spectroscopy offer a non-invasive technique to study material properties.



- The second-order nonlinear polarization is given by [1]

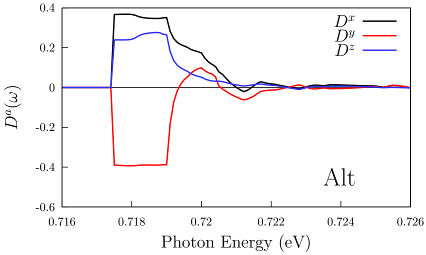
$$\mathcal{P}(2\omega) = \chi^{abc}(-2\omega;\omega,\omega)E^{b}(\omega)E^{c}(\omega),$$

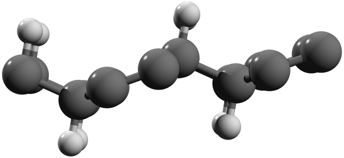
  where $\chi^{abc}(-2\omega;\omega,\omega)$ is the nonlinear susceptibility tensor responsible for the SHG.

- The formalism includes [1]
  - 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.

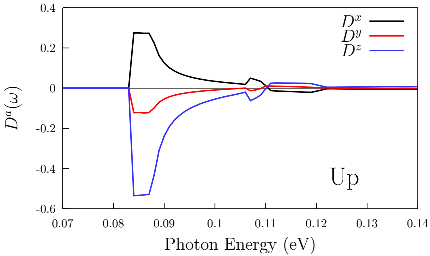
[1] S. M. Anderson et al. Phys. Rev. B, 91(7):075302, 2015.

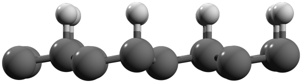
Degree of spin polarization





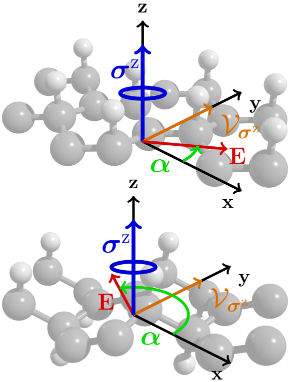
Response in the Near Infrared
0.717 eV $=$ 1.72 μm $=$ 173 THz

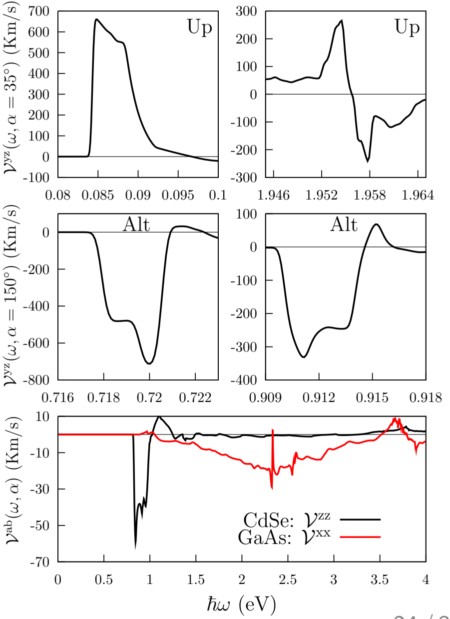




Response in the Mid Infrared
0.084 eV $=$ 14.7 μm $=$ 20.3 THz

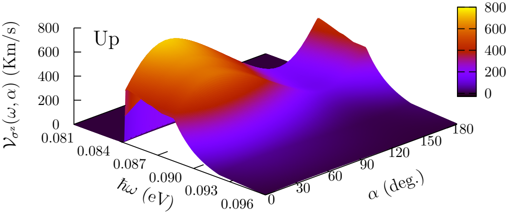
Spin velocity injection

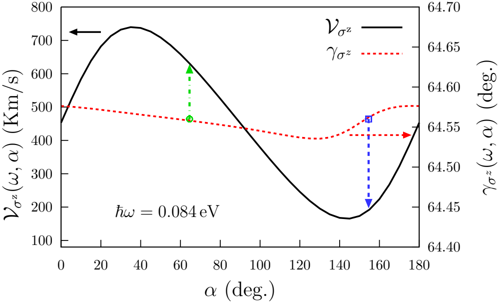




Components with maximum values of the $\mathcal{V}^{\mathrm{ab}}$ for the *alt*, *up*, CdSe and GaAs structures.

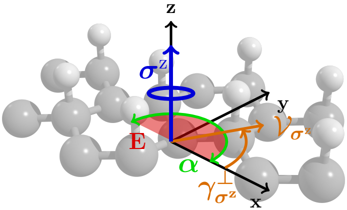
Fixing the spin along z for *up*



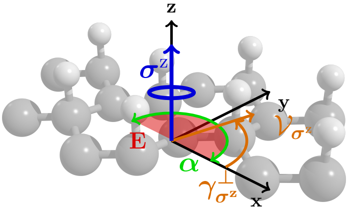


When the spin is polarized along z the spin velocity $\mathcal{V}_{\sigma^z}$:

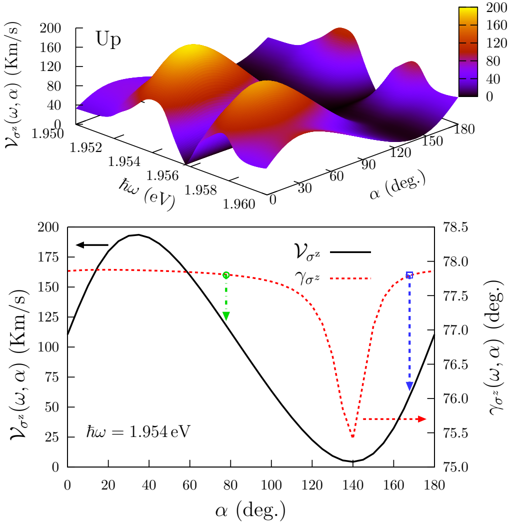
- Is maximized for $\hbar\omega = 0.084\,eV$
- The absolute maxima is 739.7 Km/s for $\alpha = 35°$
- The velocity is directed almost at a constant angle $\gamma_{\sigma^z} = 64.5°$



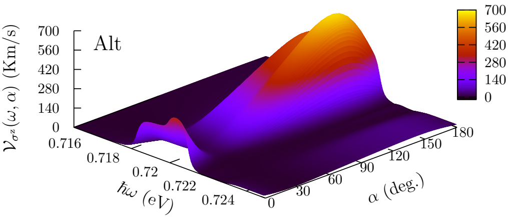
- A local maxima is found for $\hbar\omega = 1.954\,\text{eV}$ (634 nm, visible red)
- The maxima is 193.5 Km/s for $\alpha = 35°$
- The velocity angle γ_{σ^z} has values between $75.5°$ and $77.8°$

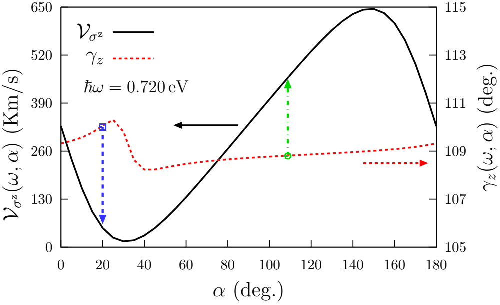


Fixing the spin along z for *up*



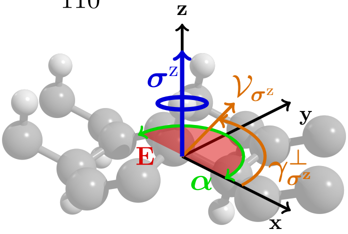
Fixing the spin along z for *alt*



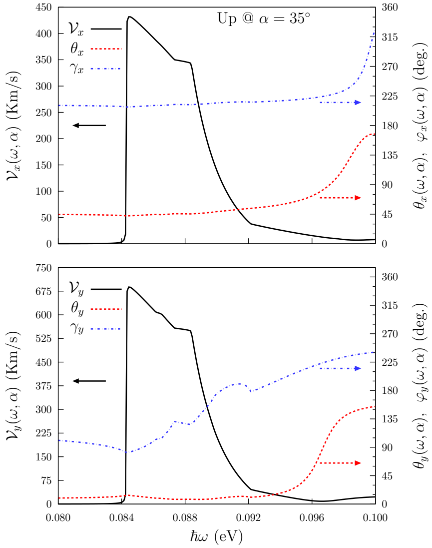


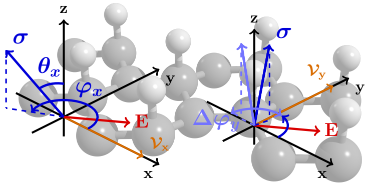
When the spin is polarized along z the spin velocity $\mathcal{V}_{\sigma^z}$:

- Is maximized for $\hbar\omega = 0.720\,\mathrm{eV}$ (near infrared, $1.72\,\mu$m)
- The absolute maxima is $644.9\,\mathrm{Km/s}$ for $\alpha = 150°$
- The velocity angle γ_{σ^z} has values from $108°$ to $110°$



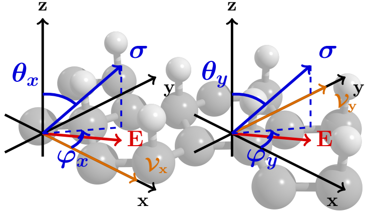
Fixing the velocity on x and y directions for *up*

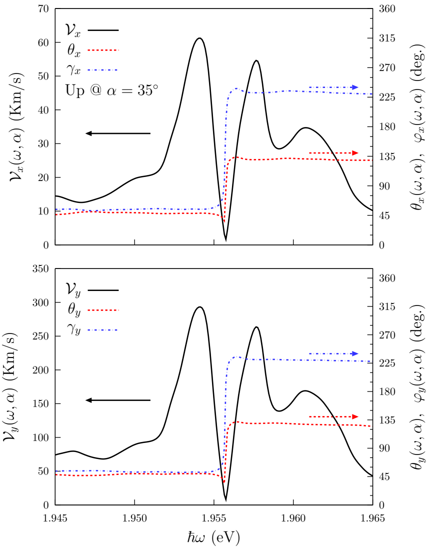




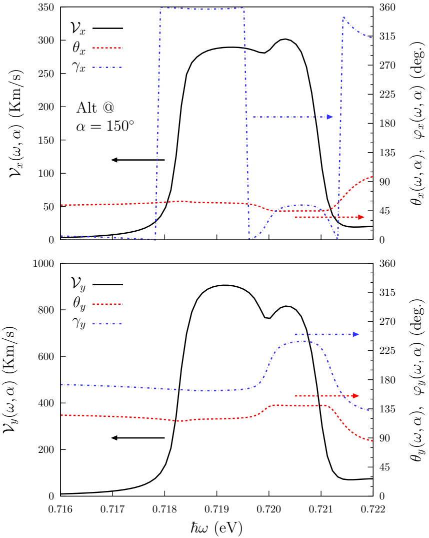
- The responses are maximized for $\alpha = 35°$ and $\hbar\omega = 0.084\,$eV
- The absolute x maxima is $\mathcal{V}_\mathrm{x} = 431.7\,$Km/s at $\theta_\mathrm{x} = 42.5°$ and $\varphi_\mathrm{x} = 208.3°$
- The absolute y maxima is $\mathcal{V}_\mathrm{y} = 687.9\,$Km/s at $\theta_\mathrm{y} = 13.9°$ and $\varphi_\mathrm{y} = 82.1°$

- The responses has a local maxima for $\alpha = 35^\circ$ and $\hbar\omega = 0.084\,\text{eV}$
- The local x maxima is $\mathcal{V}_{\text{x}} = 61.2\,\text{Km/s}$ at $\theta_{\text{x}} = 48.3^\circ$ and $\varphi_{\text{x}} = 54.3^\circ$
- The local y maxima is $\mathcal{V}_{\text{y}} = 293.2\,\text{Km/s}$ at $\theta_{\text{y}} = 49.8^\circ$ and $\varphi_{\text{y}} = 51.9^\circ$

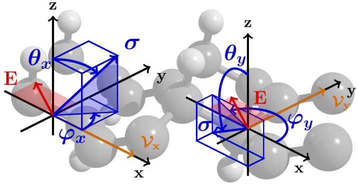




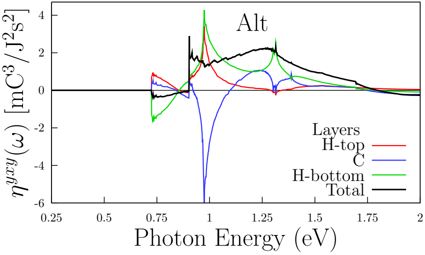
Fixing the velocity on x and y directions for *alt*

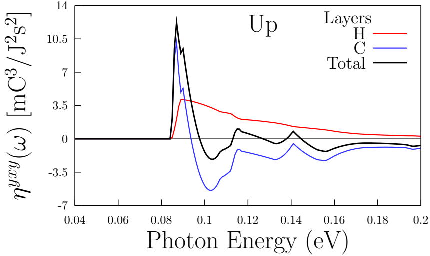


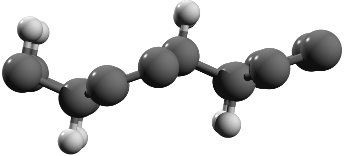
- The responses has a local maxima for $\alpha = 150°$ and $\hbar\omega = 0.720$ eV
- The local x maxima is $\mathcal{V}_{\mathrm{x}} = 301.7$ Km/s at $\theta_{\mathrm{x}} = 44.5°$ and $\varphi_{\mathrm{x}} = 51.2°$
- The absolute y maxima is $\mathcal{V}_{\mathrm{y}} = 905.6$ Km/s at $\theta_{\mathrm{y}} = 119.7°$ and $\varphi_{\mathrm{y}} = 163.4°$

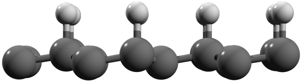


Optical current injection





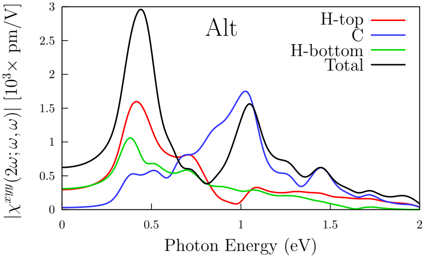


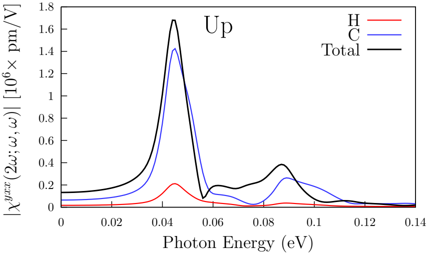


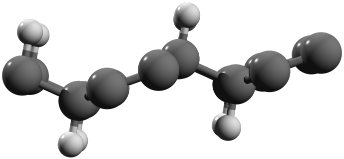
Intense response in the Near Infrared
$0.95\,\text{eV} = 230\,\mu\text{m}$

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

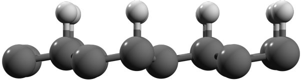
Second harmonic generation







Intense response in the Near Infrared
0.95 eV = 230 μm



Response in the Mid Infrared
0.084 eV = 14.7 μm = 20.3 THz

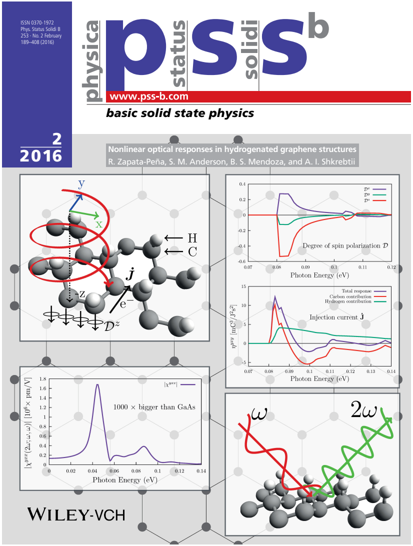
Conclusions

- 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. [1]
- Both structures are excellent candidates to generate second harmonic, particularly the *up* one.

[1] 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

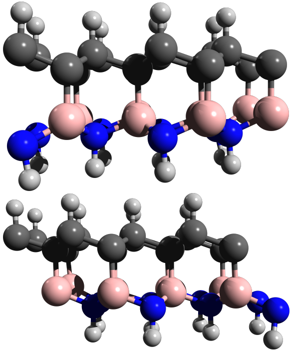
- IX Riao-Optilas 2016 (Poster)
  IX Reunión Iberoamericana de Óptica y XII Reunión Iberoamericana de Óptica, Láseres y Aplicaciones. Pucón, Chile.
- OSI-11 2015 (Poster)
  The International Conference on Optics of Surfaces and Interfaces. Austin, Texas, USA.

Specialized courses

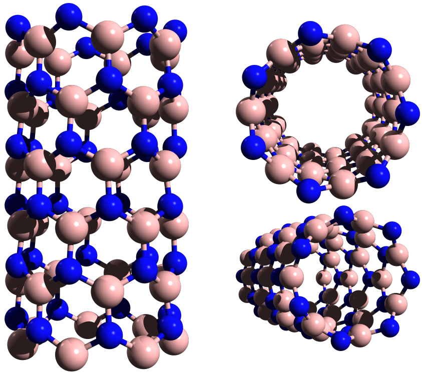
- Control de versiones usando Git y GitHub (2013)
- Cómputo en paralelo mediante FORTRAN/C++ con MPI y OpenMP (2013)
- Cálculo de propiedades oópticas de la materia con el uso de teoría de muchos cuerpos (2013)

Perspectives

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



Functionalized boron-nitride-graphene with hydrogen



Boron-nitride nanotubes

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- My sisters
- All my friends who shared time with me
- The CIO
- The CONACYT


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