

Reinaldo Arturo Zapata Peña presents

Novel Optical Effects in Functionalized Graphene: Formalism and Simulations

to earn the degree of Doctor of Science (Optics)

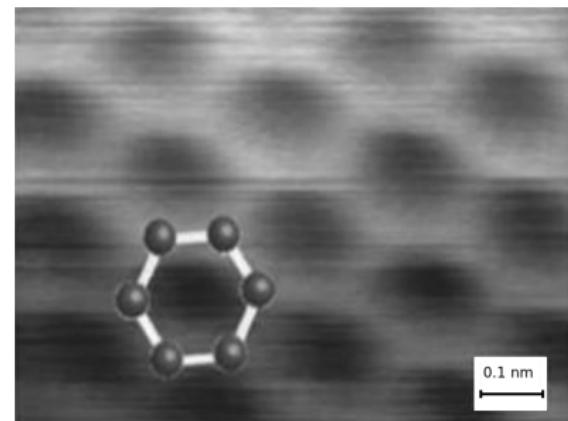


CENTRO DE INVESTIGACIONES
EN ÓPTICA, A.C.

December 11, 2017

General properties of graphene

- Good heat conductor 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

- Exfoliation¹
- 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

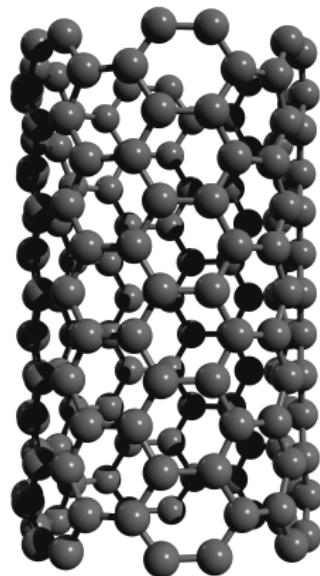
¹ A.K. Geim and K.S. Novoselov. Nature Materials, 6(3):183-191, 2007.

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

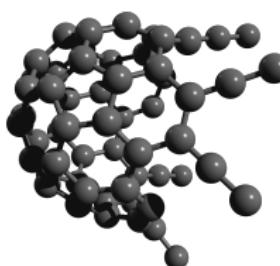
³ S. Park, J. et al. Nano letters, 9(4):1593-1597, 2009.

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

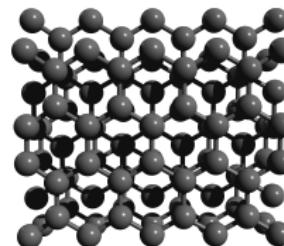
⁵ By Gabriel Hildebrand - Nobelmuseet, Public Domain.



Carbon nanotube



Fullerene



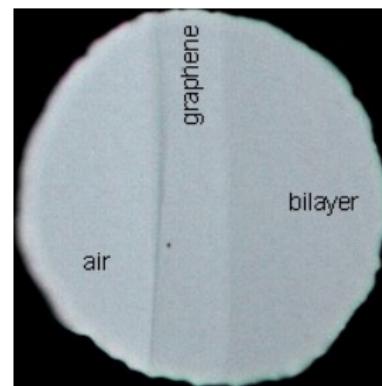
Graphite



Structures obtained from graphene

Electronic properties of graphene

- Quantum Hall effect at room temperature¹
- Excellent electrical current conduction ¹
- Transparent to visible light ²
- Tunable bandgap ³



Photograph of graphene in transmitted light.⁴

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

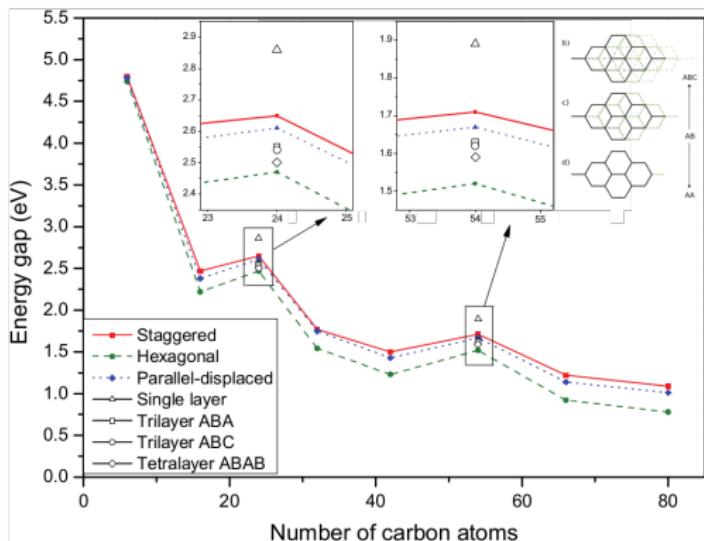
²R.R. Nair, et al. Science, 320(5881):1308-1308, 2008.

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

⁴By Rahul Nair - Manchester group.

■ Tunable bandgap by:

- Changing sheet size¹
- Changing the number of sheets¹
- Stacking¹
- Applying an electric field²
- Doping³
- Hydrogenation⁴



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

¹C. Feng et al. 2009. Jour. of Chem. Phys. 131:194702, 2009.

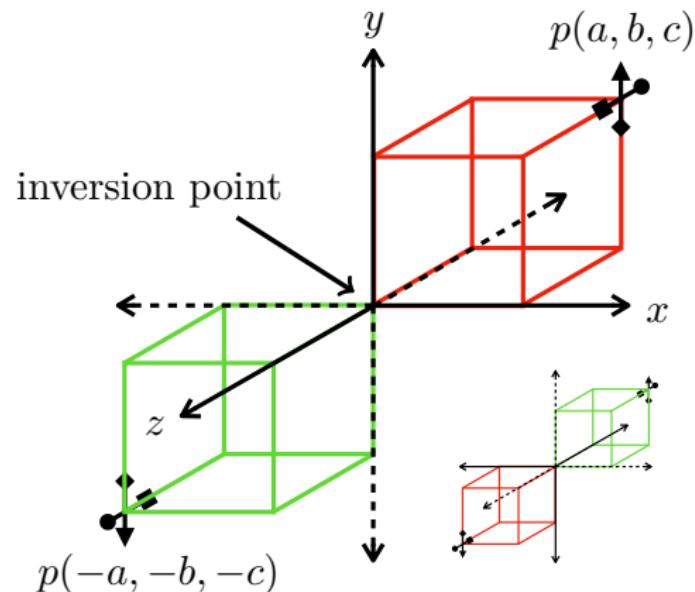
²Y. Zhang et al. Nature, 459(7248):820-823, 2009.

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

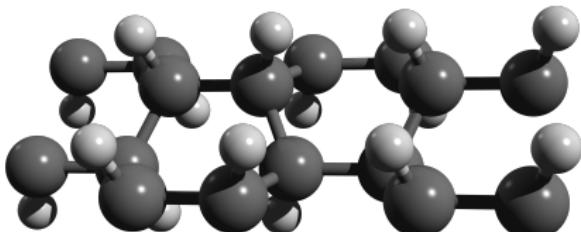
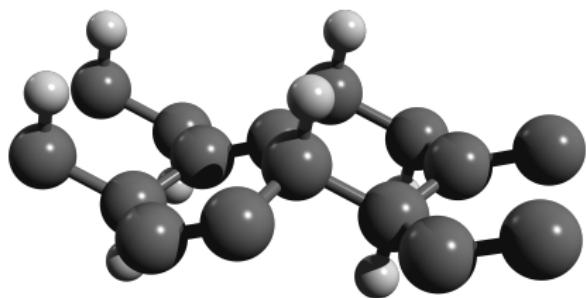
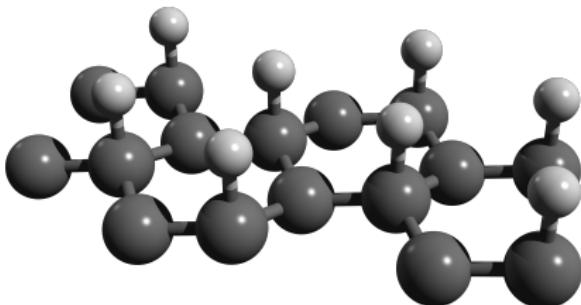
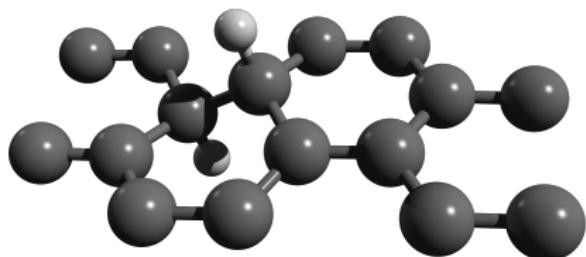
⁴D.C. Elias et al. Science, 323(5914):610-613, 2009.

Centrosymmetric Materials

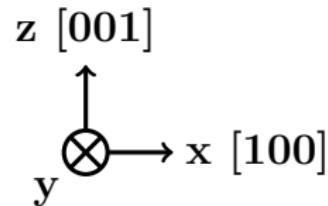
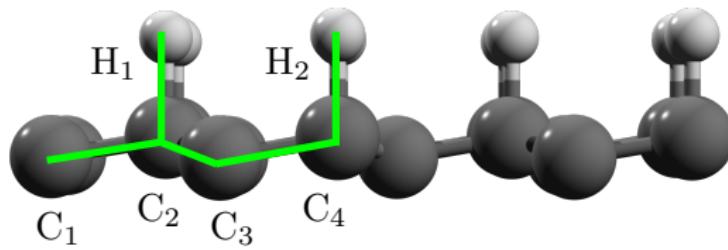
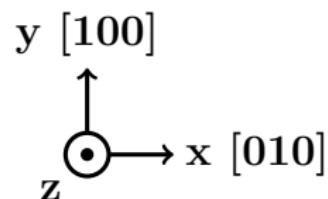
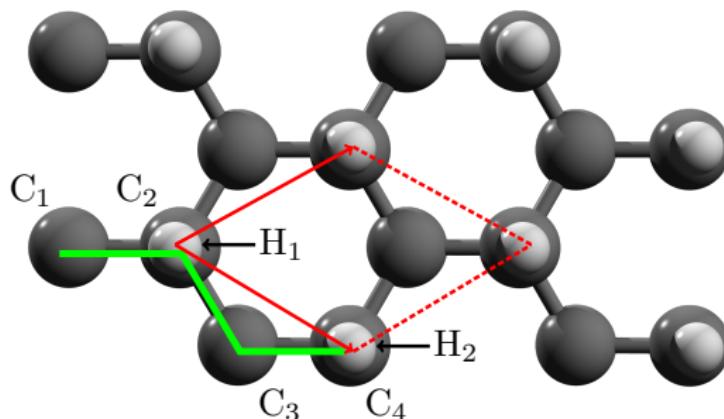
- A centrosymmetric system presents inversion of symmetry, such that for every point in the unit cell $p(a, b, c)$ there is an indistinguishable point $p'(-a, -b, -c)$.
- Second-order nonlinear optical interactions can occur only in noncentrosymmetric crystals.¹



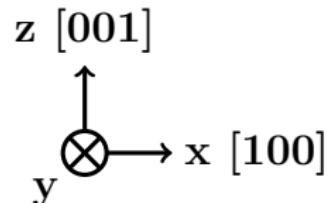
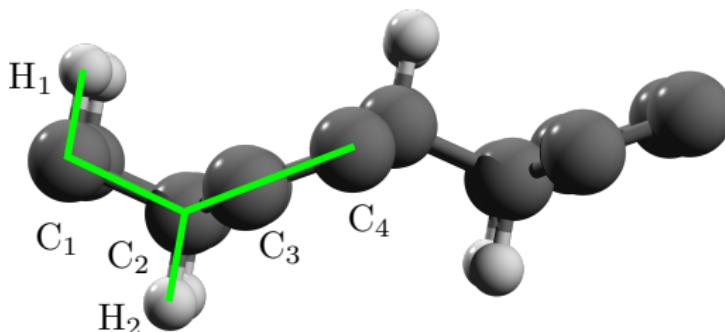
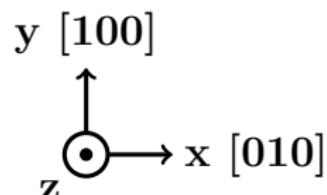
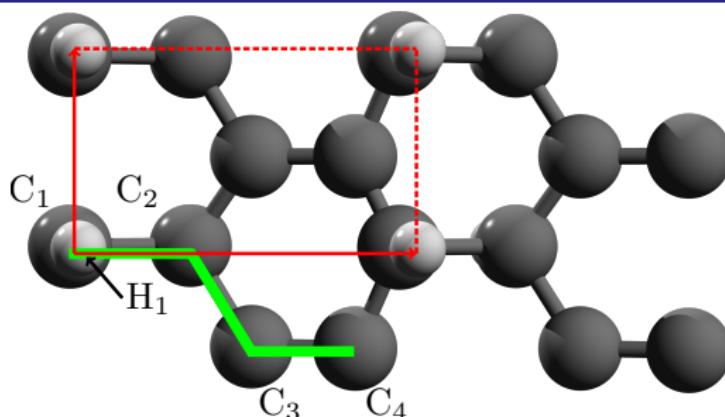
¹Boyd, Robert W. Nonlinear optics. Academic press, 2003.



Functionalization by hydrogenation



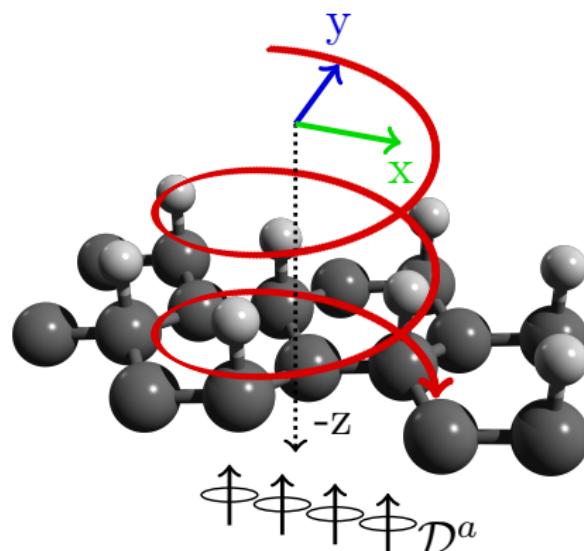
Up structure: 50% hydrogenation; hydrogen on the upper side.



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

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



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

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

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

$$\dot{S}^a(\omega) = \zeta^{abc}(\omega)E^b(-\omega)E^c(\omega), \quad (1)$$

$$\dot{n}(\omega) = \xi^{ab}(\omega)E^a(-\omega)E^b(\omega), \quad (2)$$

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 from previous equations is given by

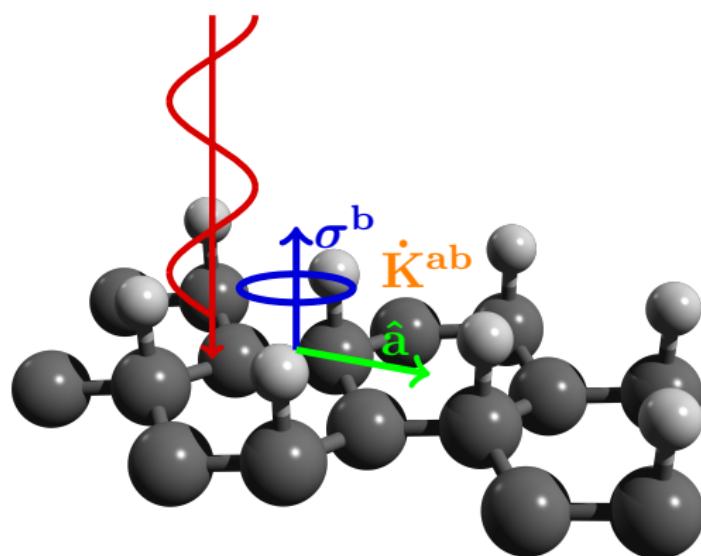
$$\mathcal{D}^a(\omega) = \frac{\dot{S}^a(\omega)}{(\hbar/2)\dot{n}(\omega)} \quad (3)$$

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



¹A. 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 materials¹ and is given by²

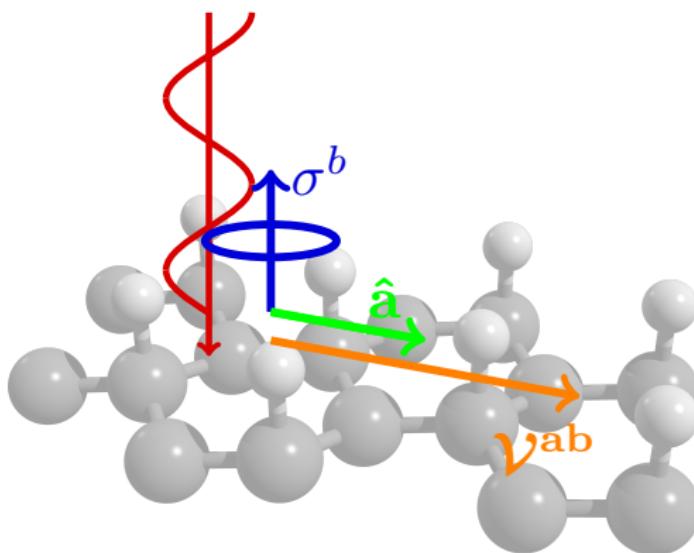
$$\dot{K}^{ab}(\omega) = \mu^{abcd}(\omega) E^c(\omega) E^{d*}(\omega), \quad (4)$$

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

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

²Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

Spin velocity injection



- The spin velocity injection is defined as¹

$$\mathcal{V}^{ab}(\omega) \equiv \frac{\dot{K}^{ab}(\omega)}{(\hbar/2)\dot{n}(\omega)}, \quad (5)$$

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

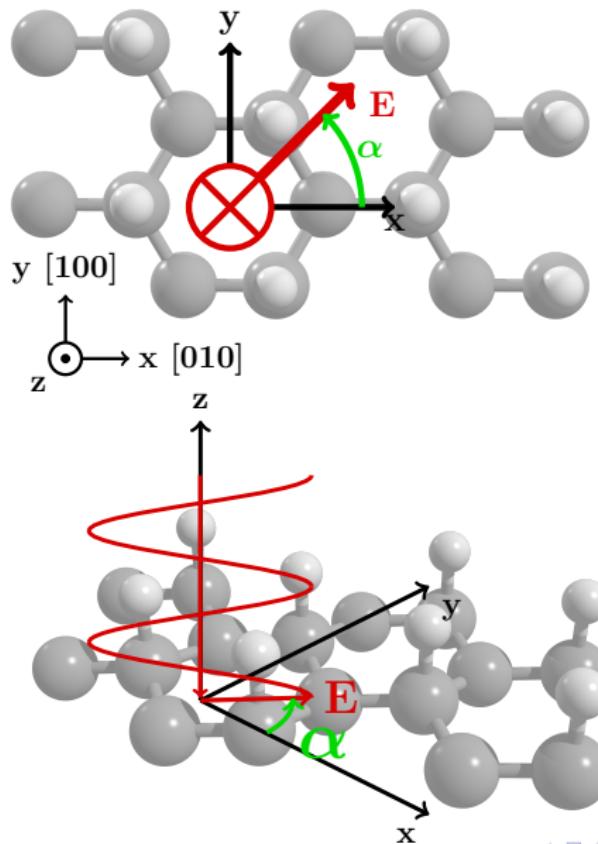
¹Reinaldo Zapata-Peña et. al. Phys. Rev. B 96, 195415. 2017

└ Theory

└ Pure spin current injection

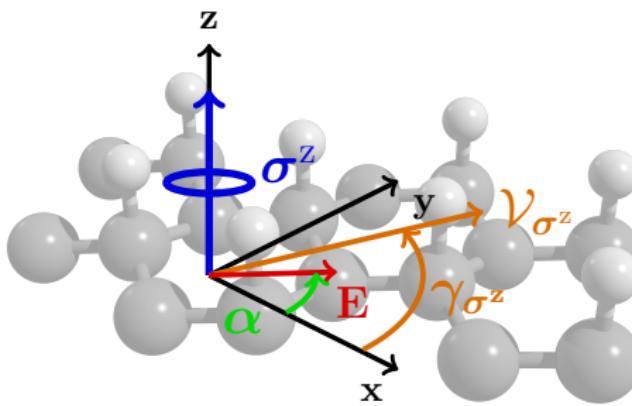
- With 2D structures we can use the direction of the polarized electric field, α , to control $\mathcal{V}^{ab}(\omega)$.
- Writing $\mathbf{E}(\omega) = E_0(\omega)(\cos \alpha \hat{\mathbf{x}} + \sin \alpha \hat{\mathbf{y}})$, where α is the polarization angle, we obtain that

$$\mathcal{V}^{ab}(\omega, \alpha) = \frac{2}{\hbar \xi(\omega)} (\mu^{abxx}(\omega) \cos^2 \alpha + \mu^{abyy}(\omega) \sin^2 \alpha + \mu^{abxy}(\omega) \sin 2\alpha). \quad (6)$$



Fixing the spin polarization¹

Spin fixed along z direction



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

$$\begin{aligned} \mathcal{V}_{\sigma^b}(\omega, \alpha) \equiv \\ \sqrt{(\mathcal{V}_{xb}(\omega, \alpha))^2 + (\mathcal{V}_{yb}(\omega, \alpha))^2} \end{aligned} \quad (7)$$

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

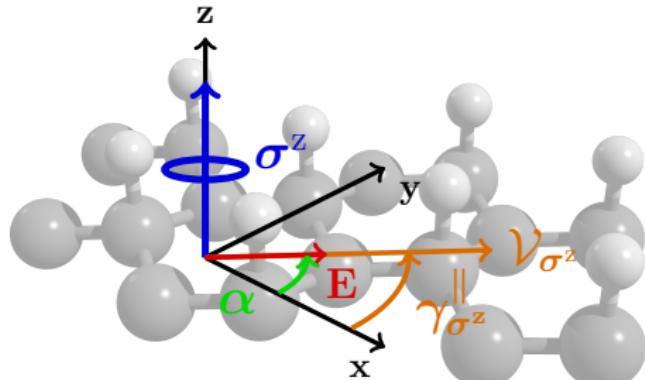
$$\gamma_{\sigma^b}(\omega, \alpha) = \tan^{-1} \left(\frac{\mathcal{V}_{yb}(\omega, \alpha)}{\mathcal{V}_{xb}(\omega, \alpha)} \right) \quad (8)$$

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

We have two special cases

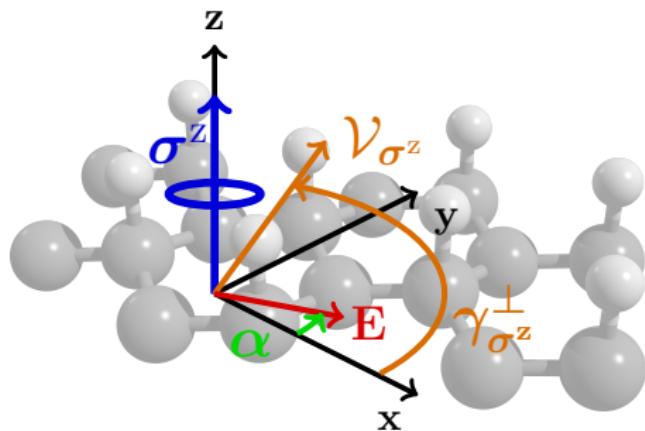
- When the velocity vector is parallel to the electric incident field

$$\gamma_{\sigma^b}^{\parallel}(\omega, \alpha) = \alpha, \quad (9)$$



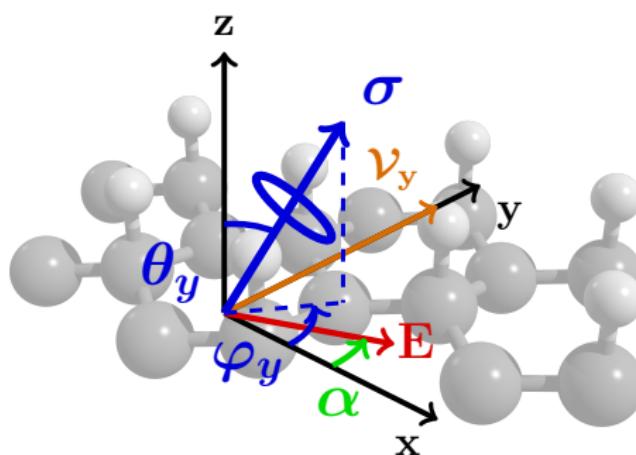
- When the velocity vector is perpendicular to the electric incident field

$$\gamma_{\sigma^b}^{\perp}(\omega, \alpha) = \alpha \pm 90^\circ, \quad (10)$$



Fixing the spin velocity¹

Velocity fixed along y direction



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

$$\mathcal{V}_a(\omega, \alpha) \equiv \left[(\mathcal{V}^{ax}(\omega, \alpha))^2 + (\mathcal{V}^{ay}(\omega, \alpha))^2 + (\mathcal{V}^{az}(\omega, \alpha))^2 \right]. \quad (11)$$

- Angles of the spin

Polar angle

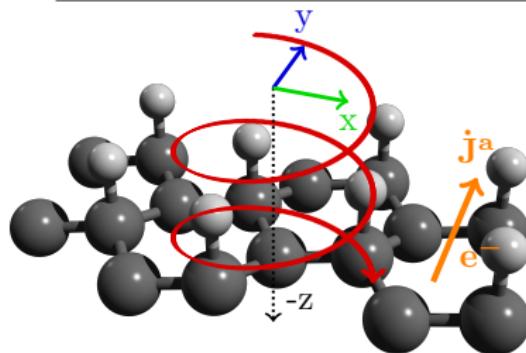
$$\theta_a(\omega, \alpha) = \cos^{-1} \left(\frac{\mathcal{V}^{az}(\omega, \alpha)}{\mathcal{V}_a(\omega, \alpha)} \right). \quad (12)$$

Azimuthal angle

$$\varphi_a(\omega, \alpha) = \tan^{-1} \left(\frac{\mathcal{V}^{ay}(\omega, \alpha)}{\mathcal{V}^{ax}(\omega, \alpha)} \right). \quad (13)$$

¹Reinaldo 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}^a in a non-centrosymmetric bulk material,¹ at the surface af a centrosymmetric media,² and on the surface of 2D systems³

The optical current injection is given by

$$\mathbf{j}_{\text{inj}}^a(\omega) = \eta^{abc}(\omega) E_b(\omega) E_c(\omega), \quad (14)$$

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

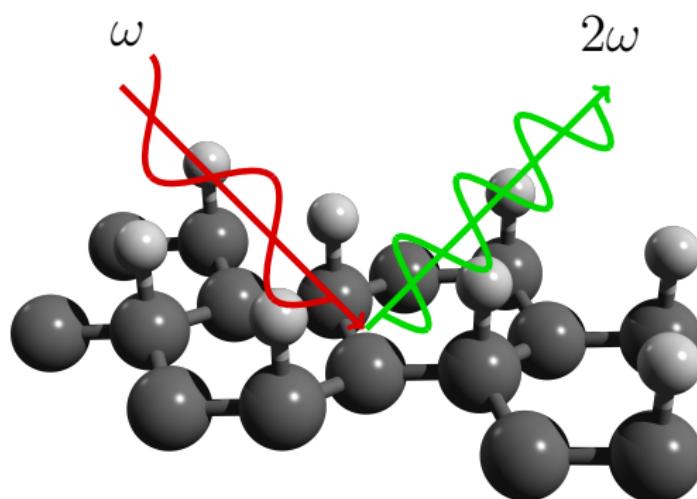
¹ A. Haché et. al. Phys. Rev. Lett., 78:306-309, Jan1997.

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

$$\mathcal{P}(2\omega) = \chi^{abc}(-2\omega; \omega, \omega) E^b(\omega) E^c(\omega), \quad (15)$$

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

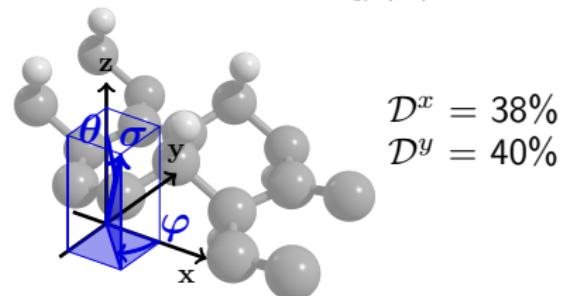
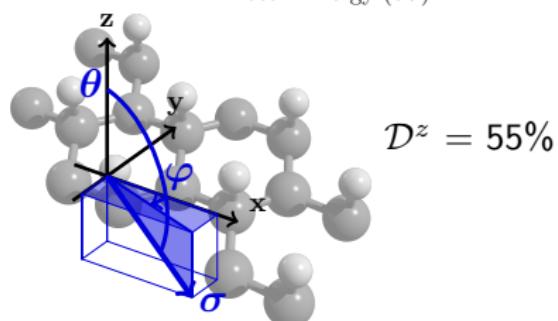
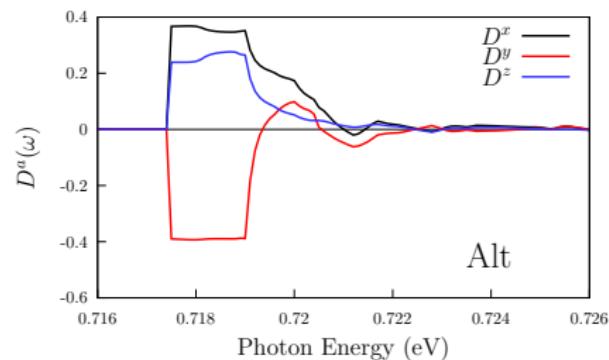
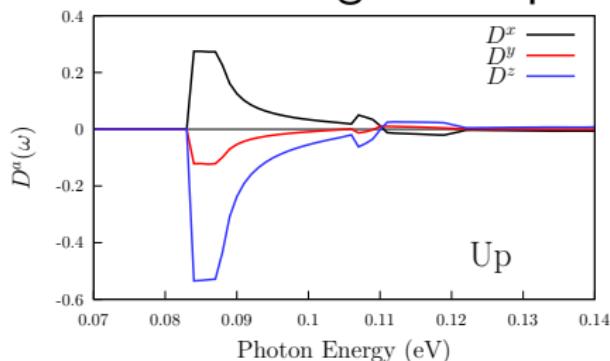
- The formalism includes ¹
 - The scissors correction,
 - The contribution of the nonlocal part of the pseudopotentials
 - The cut function used to select the individual contribution for a given layer.

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

└ Results

└ Degree of spin polarization

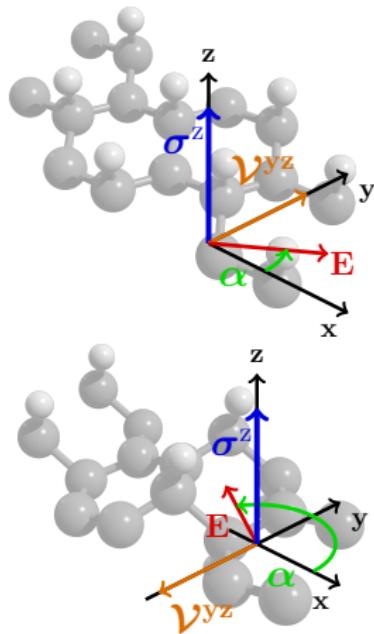
Degree of spin polarization (Eq. 3)



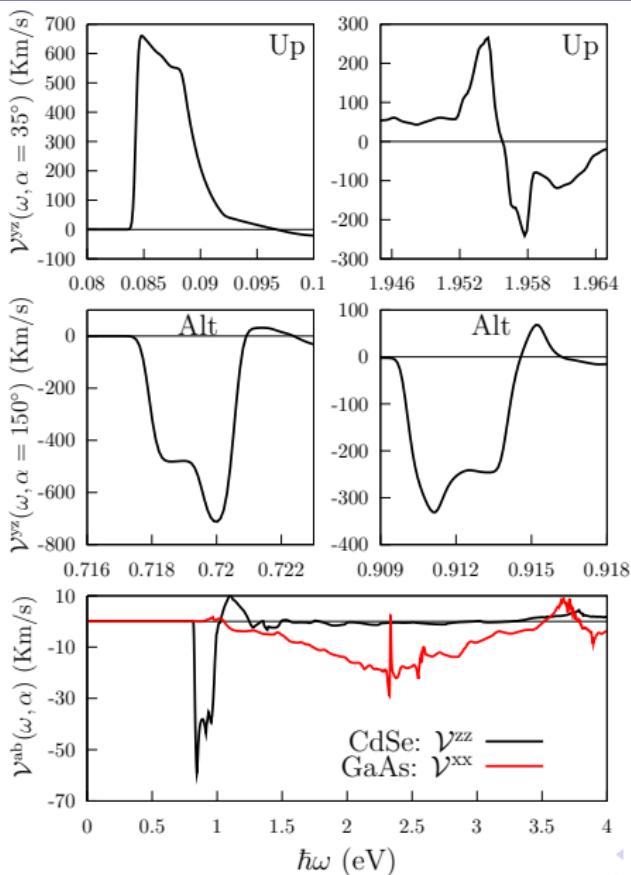
Response in the Mid Infrared
 $0.084 \text{ eV} = 14.7 \mu\text{m} = 20.3 \text{ THz}$

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

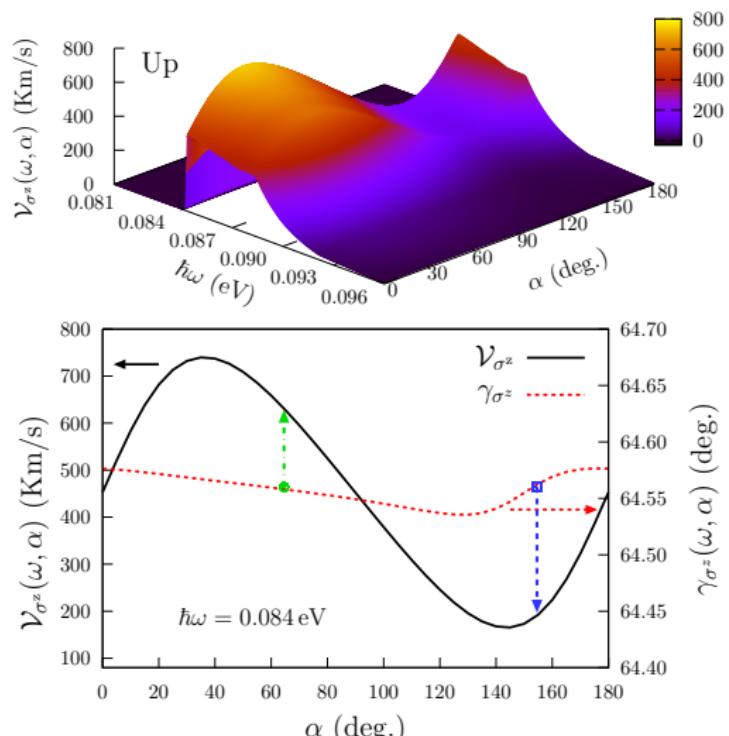
Spin velocity injection



Components with maximum values of \mathcal{V}^{ab} for the alt, up, CdSe and GaAs structures (Eq. 4).

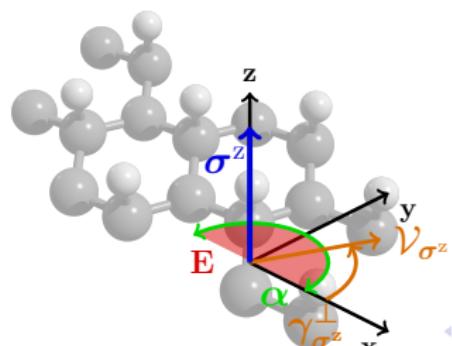


Fixing the spin along z for up



When the spin is polarized along z the spin velocity $V_{\sigma^z}(\omega, \alpha)$ (Eq. 7):

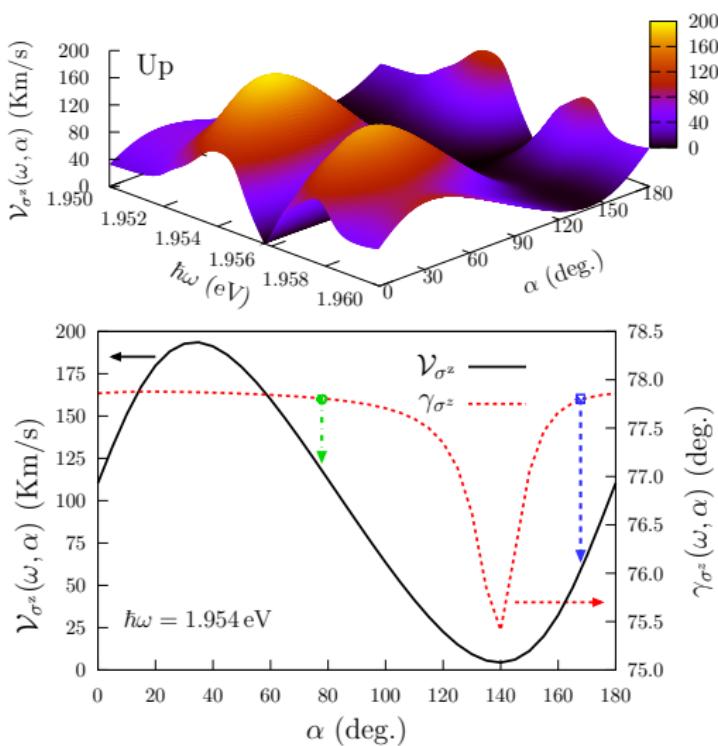
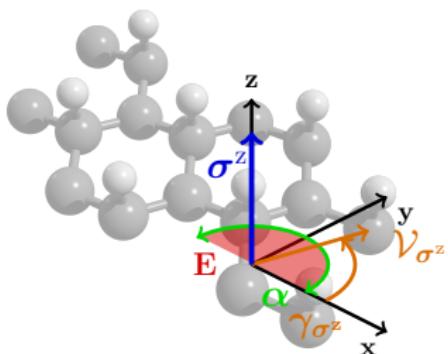
- Is maximized for $\hbar\omega = 0.084$ eV
- The absolute maxima is 740 Km/s for $\alpha = 35^\circ$
- The velocity is directed almost at a constant angle $\gamma_{\sigma^z} = 65^\circ$



└ Results

└ Spin velocity injection

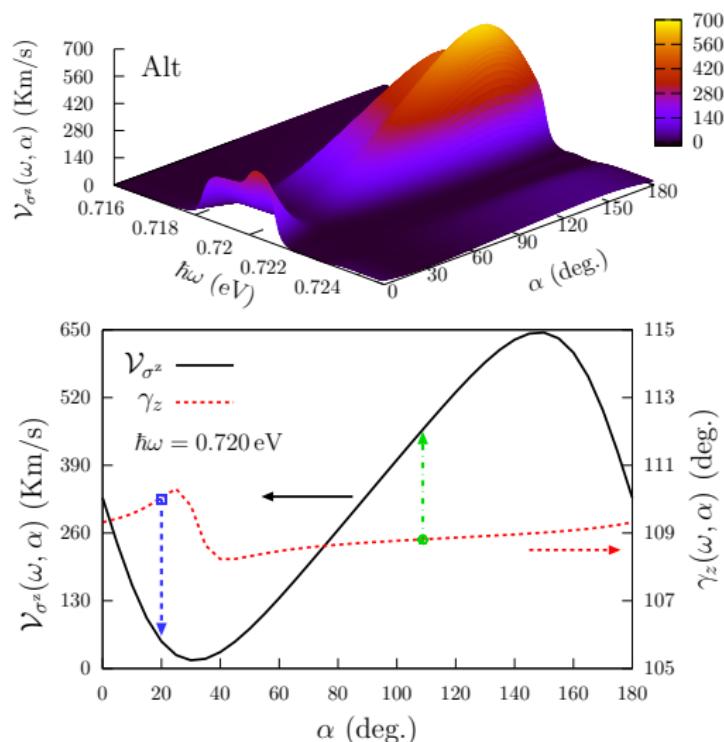
- A local maxima is found for $\hbar\omega = 1.954 \text{ eV}$ (634 nm, visible red)
- The maxima is 193 Km/s for $\alpha = 35^\circ$
- The velocity angle γ_{σ^z} has values between 75° and 78°



└ Results

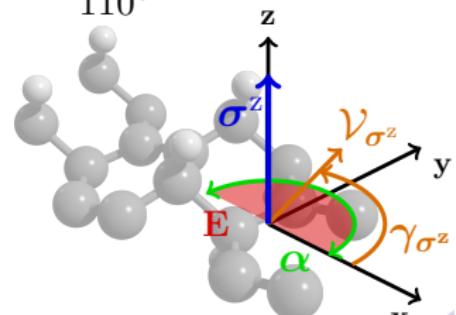
└ Spin velocity injection

Fixing the spin along z for *alt*



Again with the spin polarized along z the spin velocity $V_{\sigma^z}(\omega, \alpha)$ (Eq. 7):

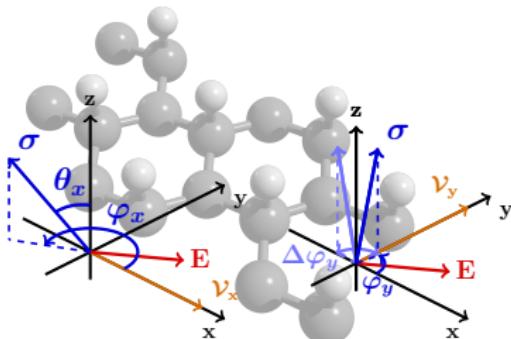
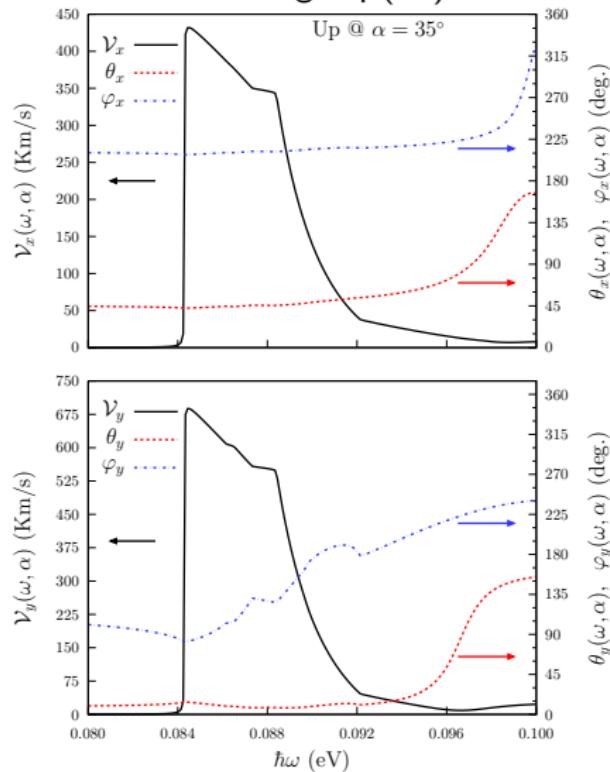
- Is maximized for $\hbar\omega = 0.720$ eV (near infrared, $1.72 \mu\text{m}$)
- The absolute maxima is 645 Km/s for $\alpha = 150^\circ$
- The velocity angle γ_{σ^z} has values from 108° to 110°



└ Results

└ Spin velocity injection

Fixing the velocity on x and y directions for *up*
and using Eq (11)

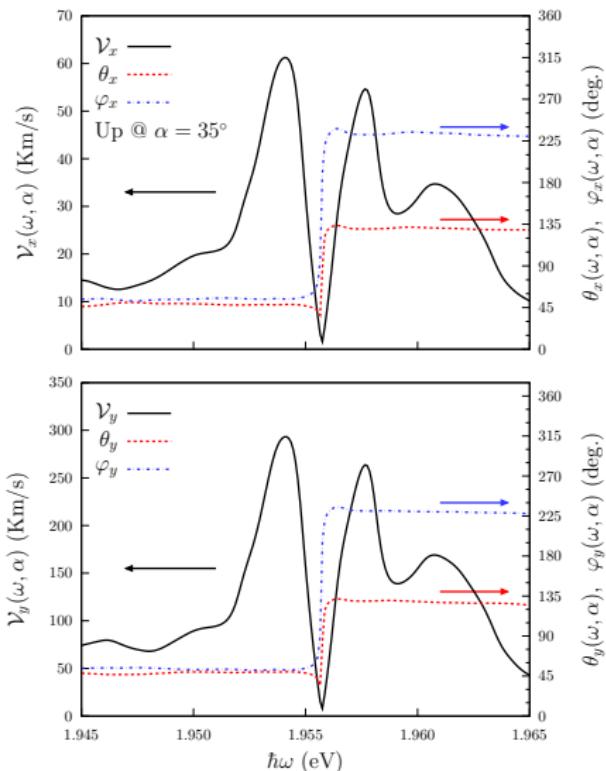
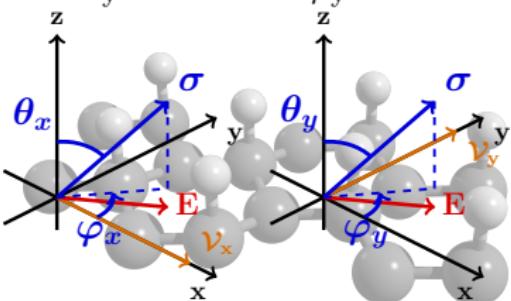


- The responses are maximized for $\alpha = 35^\circ$ and $\hbar\omega = 0.084$ eV
- The absolute x maxima is $V_x = 432$ Km/s at $\theta_x = 43^\circ$ and $\varphi_x = 208^\circ$
- The absolute y maxima is $V_y = 688$ Km/s at $\theta_y = 14^\circ$ and $\varphi_y = 82^\circ$

└ Results

└ Spin velocity injection

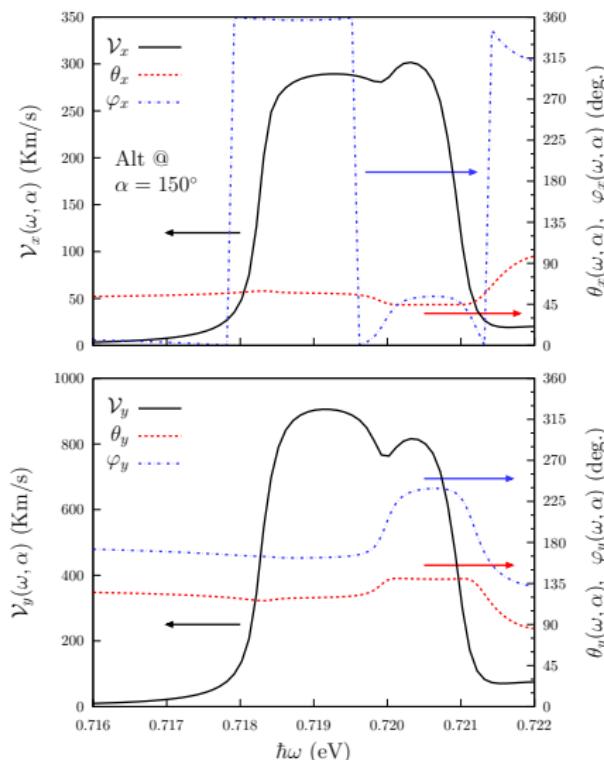
- The responses has a local maxima for $\alpha = 35^\circ$ and $\hbar\omega = 1.954 \text{ eV}$
- The local x maxima is $\mathcal{V}_x = 61 \text{ Km/s}$ at $\theta_x = 48^\circ$ and $\varphi_x = 54^\circ$
- The local y maxima is $\mathcal{V}_y = 293 \text{ Km/s}$ at $\theta_y = 50^\circ$ and $\varphi_y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



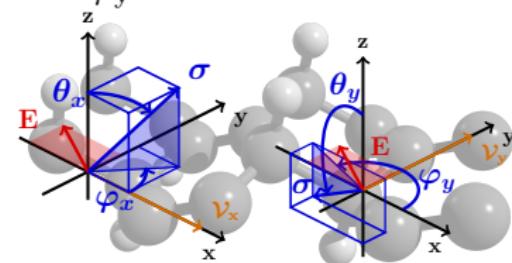
└ Results

└ Spin velocity injection

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



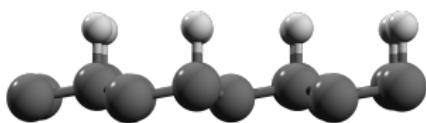
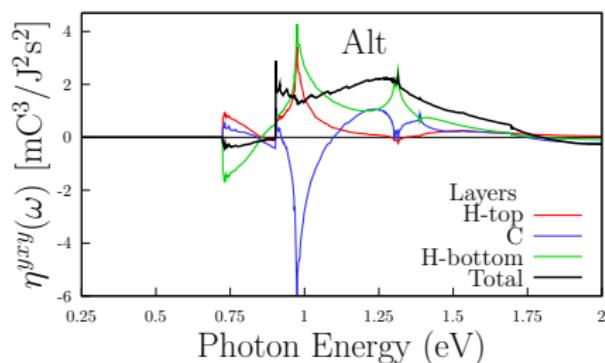
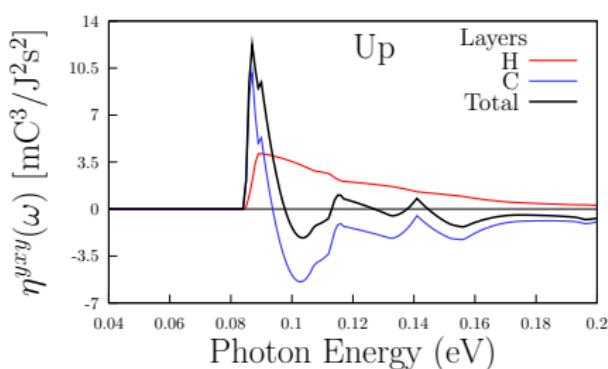
- The responses has local maxima for $\alpha = 150^\circ$
- The local x maxima is at $\hbar\omega = 0.720$ eV:
 $v_x = 302$ Km/s at
 $\theta_x = 45^\circ$ and $\varphi_x = 51^\circ$
- The absolute y maxima is at $\hbar\omega = 0.719$ eV:
 $v_y = 906$ Km/s at
 $\theta_y = 120^\circ$ and
 $\varphi_y =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



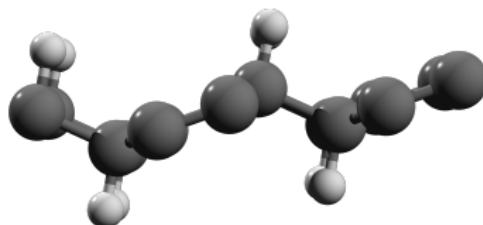
└ Results

└ optical current injection

Optical current injection

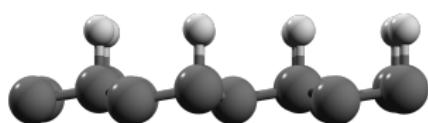
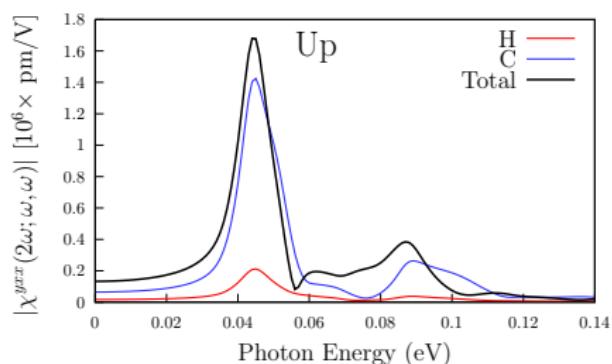


Response in the Mid Infrared
 $0.084 \text{ eV} = 14.7 \mu\text{m} = 20.3 \text{ THz}$

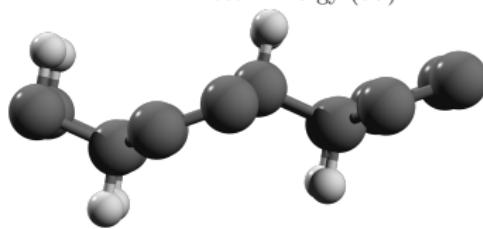
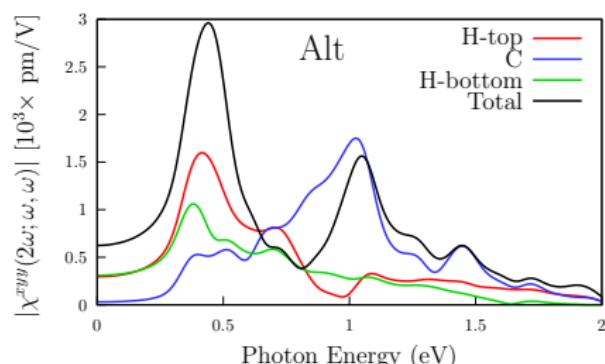


Intense response in the Near Infrared
 $0.90 \text{ eV} = 230 \mu\text{m}$

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
 $0.4 \text{ eV} = 3.1 \mu\text{m}$
 $1.1 \text{ eV} = 1.2 \mu\text{m}$

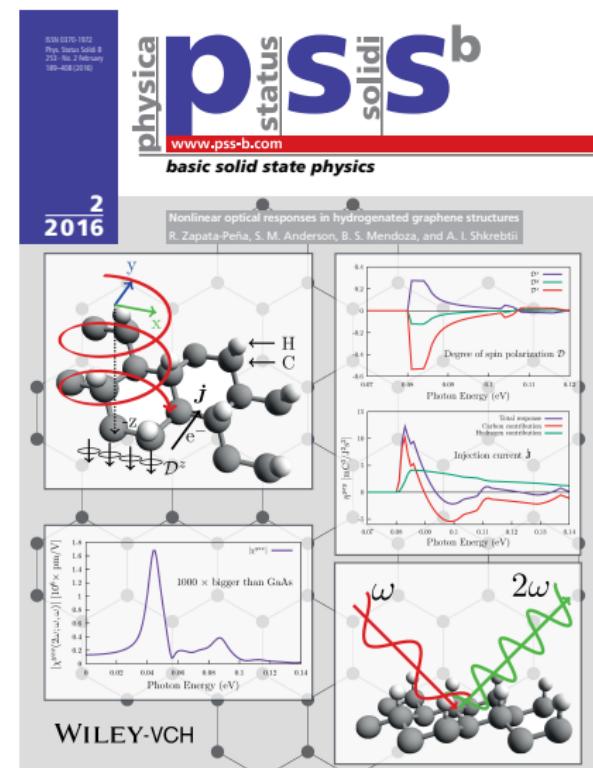
Conclusions

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

¹R. 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

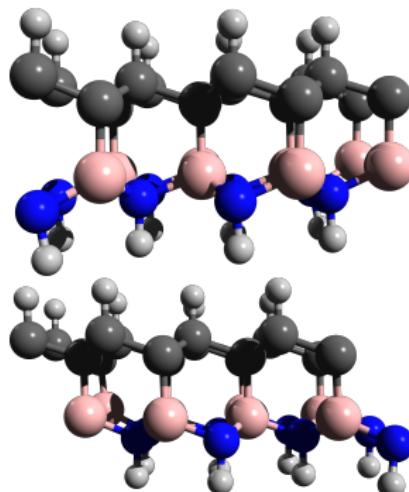
- Control de versiones usando Git y GitHub (2013)

- Cómputo en paralelo mediante FORTRAN/C++ con MPI y OpenMP (2013)

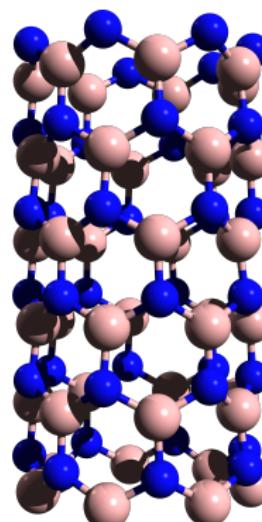
- Cálculo de propiedades ópticas de la materia con el uso de teoría de muchos cuerpos (2013)

Perspectives

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



Functionalized
boron-nitride-graphene with
hydrogen



Boron-nitride nanotubes



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- Dr. Bernardo Mendoza, *el jefe*
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- 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

$$\zeta^{abc} = \frac{\pi e^2}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum'_{vc c'} \left(\text{Im}[\mathcal{S}_{c'c}^a r_{cv}^b r_{vc'}^c] + \text{Im}[\mathcal{S}_{cc'}^a r_{c'v}^b r_{vc}^c] \right) \delta(\omega - \omega_{cv}), \quad (16)$$

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

$$\xi^{ab}(\omega) = \frac{2\pi e^2}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum_{vc} r_{vc}^a(\mathbf{k}) r_{cv}^b(\mathbf{k}) \delta(\omega_{cv}(\mathbf{k}) - \omega). \quad (17)$$

- The pure spin current pseudotensor is given by

$$\mu^{abcd} = \frac{\pi e^2}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum'_{vc c'} \text{Re} \left[K_{c'c}^{ab} \left(r_{vc'}^c r_{cv}^d + (c \leftrightarrow d) \right) \right] \delta(\omega - \omega_{cv}), \quad (18)$$

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

- The optical current injection tensor is given by

$$\eta^{abc} = \frac{\pi e^3}{\hbar^2} \int \frac{d^3 k}{8\pi^3} \sum'_{vc c'} \left[v_{cc'}^a r_{vc}^b r_{c'v}^c + v_{c'c}^a r_{vc'}^b r_{cv}^c \right] \delta(\omega - \omega_{cv}). \quad (19)$$