Novel Optical Effects in Functionalized Graphene: Formalism and Simulations

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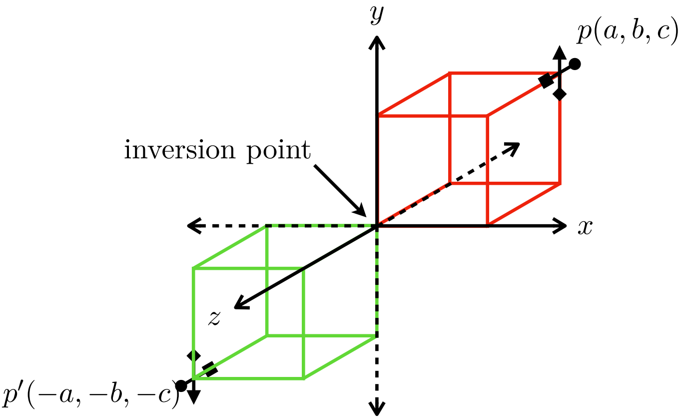
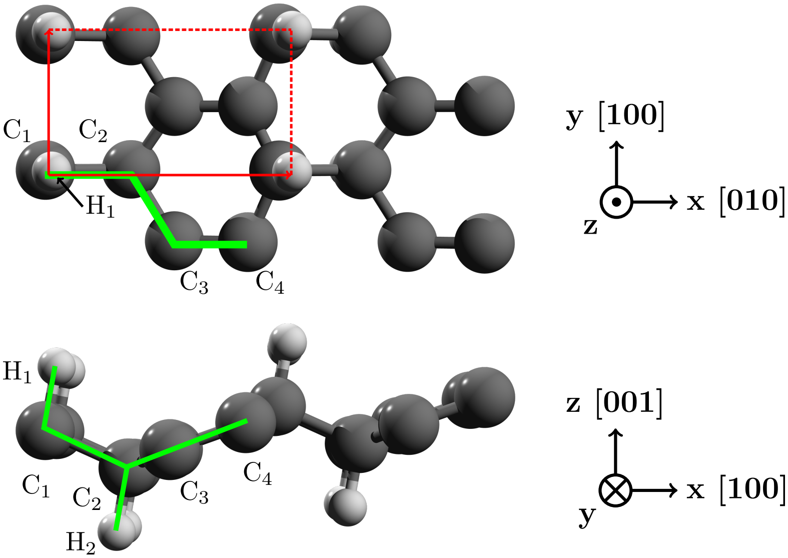
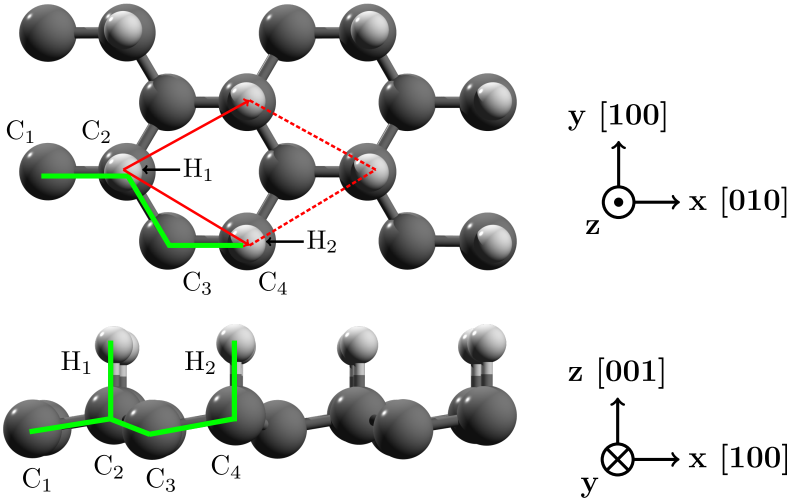
Centrosymmetric Materials

A centrosymmetric system presents inversion of symmetry, such that a point $p(a, b, c)$ corresponds a point $p'(-a, -b, -c)$.





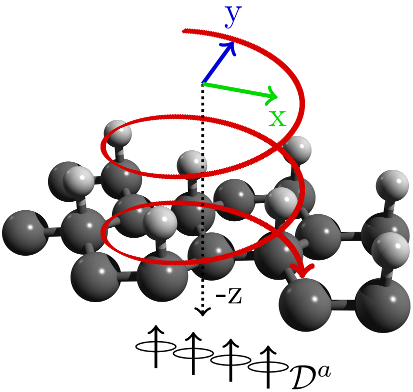
Alt structure: 50% hydrogenation; hydrogen at bot sides.



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 quantifies the fraction of injected electrons in the conduction bands that are spin polarized along direction a and is given by

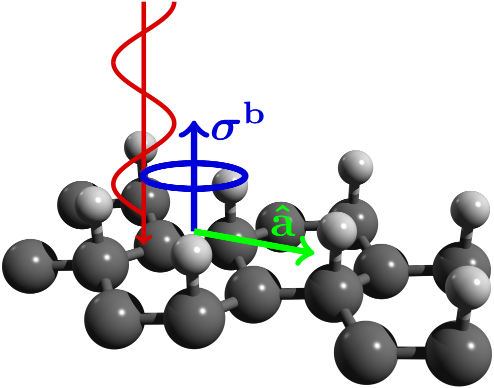
$$\mathcal{D}^a(\omega) = \frac{\dot{S}^a(\omega)}{(\hbar/2)\dot{n}(\omega)} \tag{1}$$

- Is a second order optical effect and it is possible to generate spin polarized electron along three Cartesian directions with an incident circularly polarized beam.

Pure spin current and spin velocity injection (SVI)

Pure spin current injection

- The spin current moves along direction $\hat{\mathbf{a}}$ with the spin polarized along direction $\hat{\mathbf{b}}$.[1]
- There is no net motion of charge but a spin current is produced. [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]

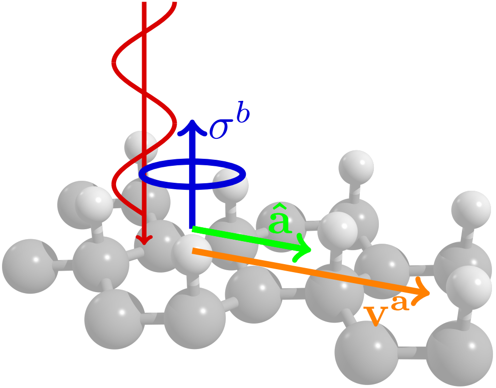
$$\dot{K}^{\mathrm{ab}}(\omega) = \mu^{\mathrm{abcd}}(\omega) E^{\mathrm{c}}(\omega) E^{\mathrm{d}*}(\omega), \tag{2}$$

  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]

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

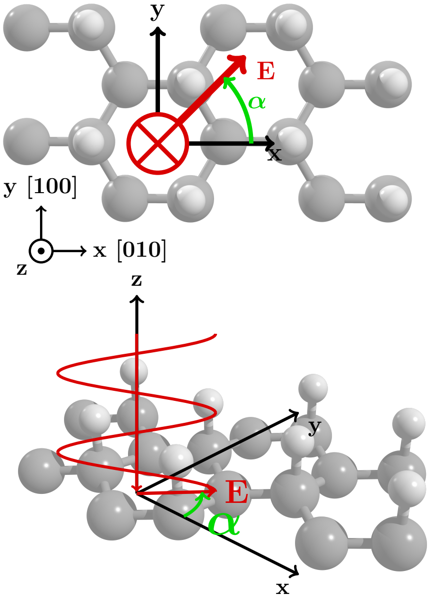
which gives the velocity, along direction $\hat{\mathbf{a}}$, at which the spin moves in a polarized state along direction $\hat{\mathbf{b}}$.

[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 to control $\mathcal{V}^{\mathrm{ab}}(\omega)$.

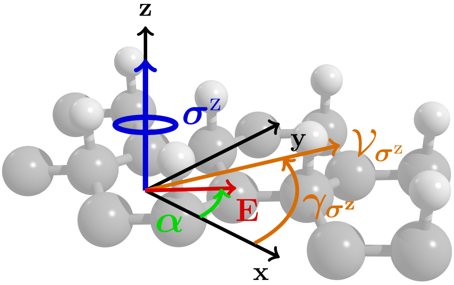
- Writing $\mathbf{E}(\omega) = E_0(\omega)(\cos\alpha\,\hat{\mathbf{x}} + \sin\alpha\,\hat{\mathbf{y}})$, where α is the polarization angle, we obtain that

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



Fixing the spin polarization[1]

Spin fixed along z direction



- Magnitude of the velocity when the spin is fixed in the $\mathbf{b}$ direction

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

- Angle of the velocity when the spin is fixed in the $\mathbf{b}$

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

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

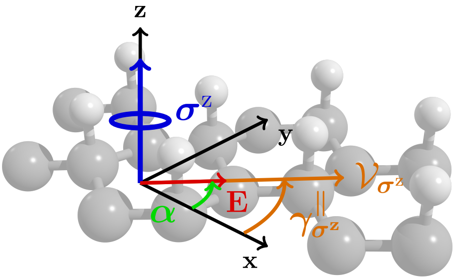
We have two special cases

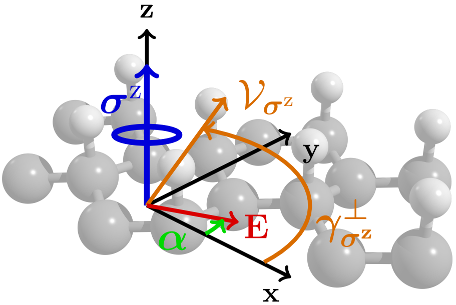
- When the velocity vector is parallel to the electric incident field

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

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

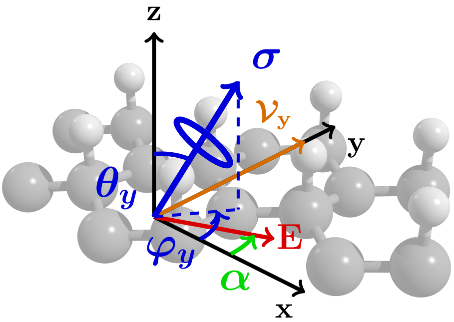
$$\gamma^{\perp}_{\sigma^{\mathrm{b}}}(\omega,\alpha)=\alpha\pm 90^{\circ}, \qquad (8)$$





Fixing the spin velocity[1]

Velocity fixed along y direction



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

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

- Angles of the spin

Polar angle

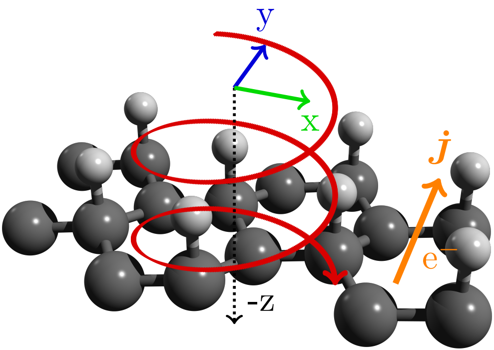
$$\theta_{\mathrm{a}}(\omega,\alpha) = \cos^{-1}\left(\frac{\mathcal{V}^{\mathrm{az}}(\omega,\alpha)}{\mathcal{V}_{\mathrm{a}}(\omega,\alpha)}\right). \tag{10}$$

Azimuthal angle

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

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

Optical current injection



- It is possible to control a photocurrent in a bulk structure [1] or in the surface of a 2D system. [2, 3]
- Is a second-order optical nonlinear effect that can be produced with a single optical circularly-polarized beam. [2]

[1] A. Hacheét. al. Phys. Rev. Lett., 78:306-309, Jan 1997.
[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.

- A photocurrent can be injected into noncentrosymmetric materials or at the surface of bulk centrosymmetric materials and is given by [1]

$$\dot{\mathbf{J}}^a_{\mathrm{inj}}(\omega) = \eta^{abc}(\omega)E_b(\omega)E_c(\omega),$$

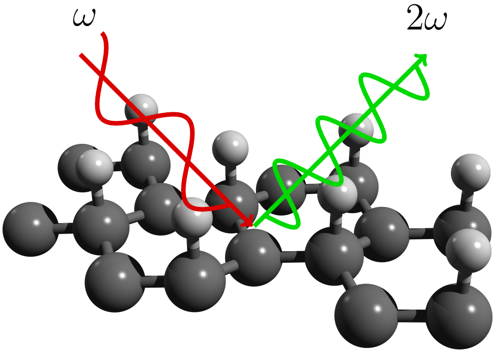
  where $\eta^{abc}(\omega)$ is the current injection tensor which quantifies the current injection along the a direction a.

- The response was calculated layer by layer.

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

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.

Structure	Energy [eV]	χ^{abc} abc	χ^{abc} value	Ref.
$C_{16}H_8$-up	0.04	yxx	1.7×10^6 pm/V	*
$C_{16}H_8$-alt	0.44	xyy	3×10^3 pm/V	*
Si(100)2×1	1.82	xxx	660 pm/V	??
BNNT(6,0) pristine	5.00	zzz	35 pm/V	1
BNNT(6,0)+4(H_2)	5.00	zzz	33 pm/V	1
BNNT(6,0)+12(H_2)	4.80	zzz	15 pm/V	1
GaAs(001)	3.00	xyz	750 pm/V	2

Table: Comparison of the highest reported absolute values of SHG for different structures and components. (*This work.)

[1] R. V. Salazar-Aparicio et. al Phys. Rev. B, 90 (15):155403, 2014.
[2] S. Bergfeld et. al. Phys. Rev. Lett., 90(3):036801, 2003.

Pure Spin Current Injection in Hydrogenated Graphene Structures

- The spin velocity injection (SVI) resulting from the pure spin current (PSC).
- To calculate the velocity of the spin injection $\mathcal{V}^{\mathrm{ab}}(\omega)$ along direction $\hat{\mathbf{a}}$ at which the spin moves in a polarized state along direction $\hat{\mathbf{b}}$, we start with the operator that describes the electronic SVI, written as

$$\dot{K}^{\mathrm{ab}}(\omega) = \mu^{\mathrm{abcd}}(\omega) E^{\mathrm{c}}(\omega) E^{\mathrm{d}*}(\omega), \tag{12}$$

- The pseudotensor of the response is given by

$$\mu^{\mathrm{abcd}}(\omega) = \frac{\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vcc'}{}' \delta(\omega - \omega_{cv}(\mathbf{k}) \\ \mathrm{Re}\left[K^{\mathrm{ab}}_{cc'}(\mathbf{k}) \left(r^{\mathrm{c}}_{vc'}(\mathbf{k}) r^{\mathrm{d}}_{cv}(\mathbf{k}) + (c \leftrightarrow d)\right)\right] \tag{13}$$

  and since $\mu^{\mathrm{abcd}}(\omega)$ is real, we have that $\mu^{\mathrm{abcd}}(\omega) = \mu^{\mathrm{abdc}}(\omega)$.

- Using the closure relation,

$$K^{\mathrm{ab}}_{cc'}(\mathbf{k}) = \frac{1}{2} \sum_{l=v,c} \left(v^{\mathrm{a}}_{cl}(\mathbf{k}) S^{\mathrm{b}}_{lc'}(\mathbf{k}) + S^{\mathrm{b}}_{cl}(\mathbf{k}) v^{\mathrm{a}}_{lc'}(\mathbf{k})\right). \tag{14}$$

- We define the spin velocity injection (SVI) as

$$\mathcal{V}^{\mathrm{ab}}(\omega) \equiv \frac{\dot{K}^{\mathrm{ab}}(\omega)}{(\hbar/2)\dot{n}(\omega)}, \tag{15}$$

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

- The carrier injection rate $\dot{n}(\omega)$ is written as

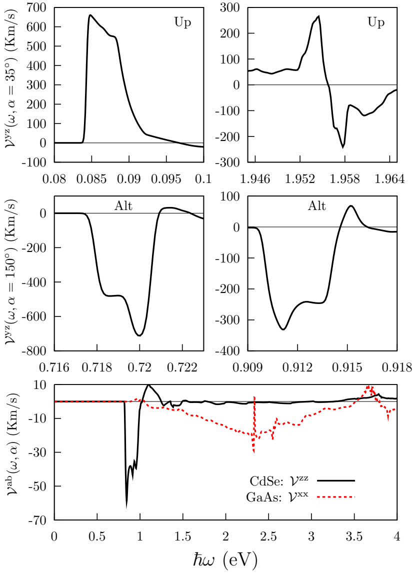
$$\dot{n}(\omega) = \xi^{\mathrm{ab}}(\omega) E^{c}(\omega) E^{d*}(\omega), \tag{16}$$

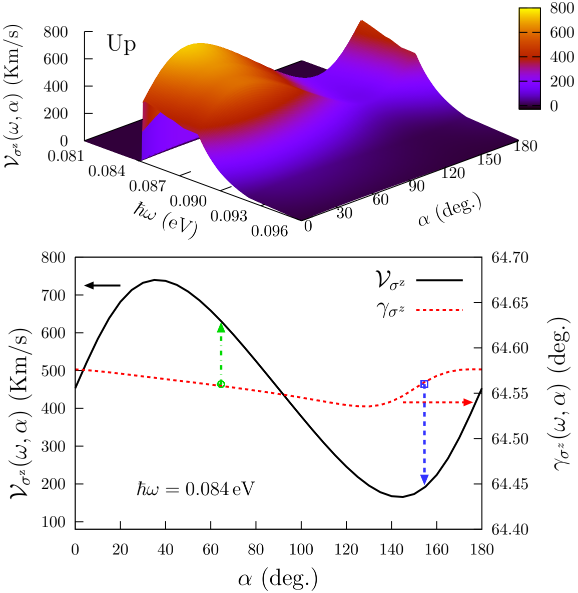
where the tensor

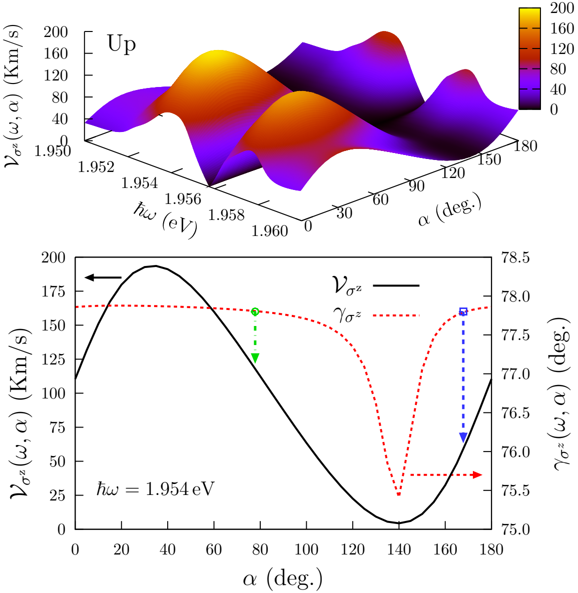
$$\xi^{\mathrm{ab}}(\omega) = \frac{2\pi e^2}{\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} r^{\mathrm{a}}_{vc}(\mathbf{k}) r^{\mathrm{b}}_{cv}(\mathbf{k}) \delta(\omega - \omega_{cv}(\mathbf{k})) \tag{17}$$

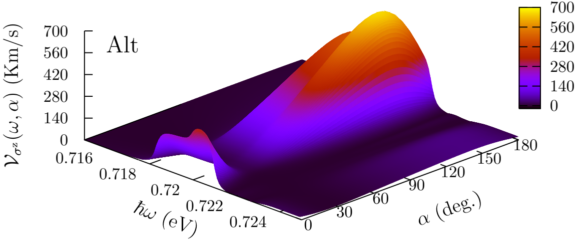
is related to the imaginary part of the linear optical response tensor by $\mathrm{Im}[\epsilon^{\mathrm{ab}}(\omega)] = 2\pi\epsilon_0\hbar\xi^{\mathrm{ab}}(\omega)$.

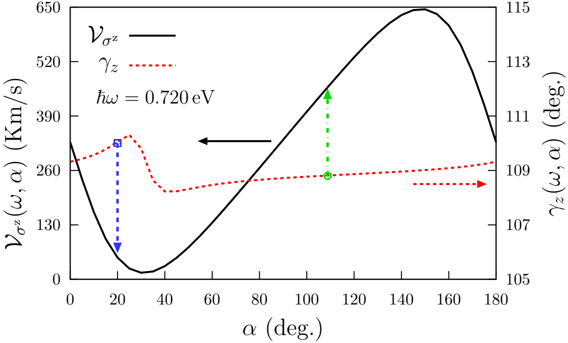
- The function $\mathcal{V}^{\mathrm{ab}}(\omega)$ allows us to quantify two aspects of PSC.
  - Fix the spin along $\hat{\mathbf{b}}$ and calculate the resulting electron velocity.
  - Fix the velocity of the electron along $\hat{\mathbf{a}}$ and study the direction along which the spin is polarized.



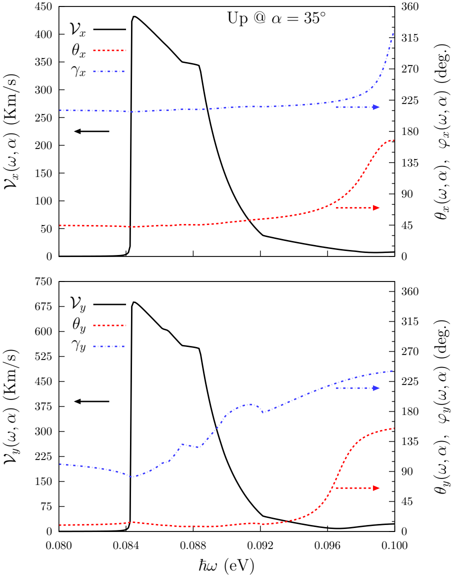

Up
$\mathcal{V}_{\sigma^z}(\omega,\alpha)$ (Km/s)
$\hbar\omega$ (eV)
α (deg.)
$\mathcal{V}_{\sigma^z}$
γ_{σ^z}
$\hbar\omega = 0.084\,\mathrm{eV}$
$\gamma_{\sigma^z}(\omega,\alpha)$ (deg.)

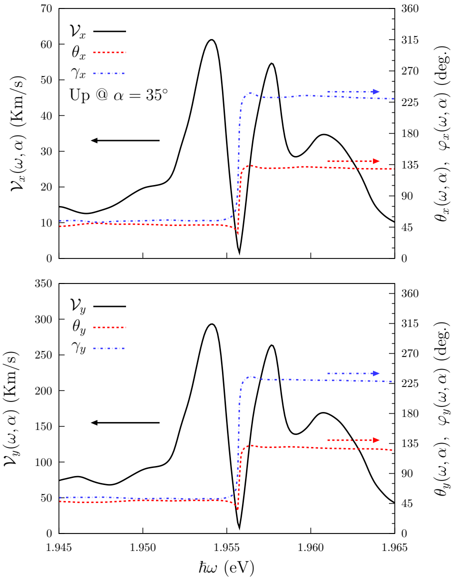

Up
$\mathcal{V}_{\sigma^z}(\omega,\alpha)$ (Km/s)
$\hbar\omega$ (eV)
α (deg.)
200
160
120
80
40
0
1.950
1.952
1.954
1.956
1.958
1.960
0
30
60
90
120
150
180
$\mathcal{V}_{\sigma^z}$
γ_{σ^z}
$\hbar\omega = 1.954\,\mathrm{eV}$
$\gamma_{\sigma^z}(\omega,\alpha)$ (deg.)
175
125
100
75
50
25
20
40
60
80
100
140
160
78.5
78.0
77.5
77.0
76.5
76.0
75.5
75.0

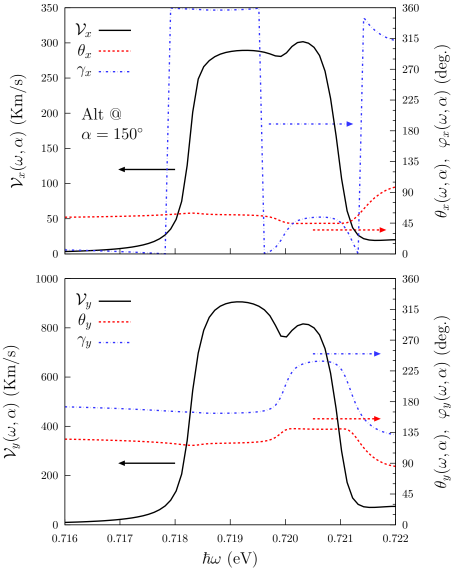

Alt
$\mathcal{V}_{\sigma^z}(\omega,\alpha)$ (Km/s)
700
560
420
280
140
0
0.716
0.718
0.72
0.722
0.724
$\hbar\omega$ (eV)
0
30
60
90
120
150
180
α (deg.)


$\mathcal{V}_{\sigma^z}$
γ_z
$\hbar\omega = 0.720\,\mathrm{eV}$
$\mathcal{V}_{\sigma^z}(\omega,\alpha)$ (Km/s)
$\gamma_z(\omega,\alpha)$ (deg.)
650
520
390
260
130
0
115
113
111
109
107
105
0
20
40
60
80
100
120
140
160
180
α (deg.)

Fixing the electron velocity


Up @ $\alpha = 35°$
$\mathcal{V}_x$
θ_x
γ_x
$\mathcal{V}_x(\omega,\alpha)$ (Km/s)
$\theta_x(\omega,\alpha)$, $\varphi_x(\omega,\alpha)$ (deg.)
$\mathcal{V}_y$
θ_y
γ_y
$\mathcal{V}_y(\omega,\alpha)$ (Km/s)
$\theta_y(\omega,\alpha)$, $\varphi_y(\omega,\alpha)$ (deg.)
$\hbar\omega$ (eV)
0.080
0.084
0.088
0.092
0.096
0.100


$\mathcal{V}_x$
θ_x
γ_x
Up @ $\alpha = 35°$
$\mathcal{V}_x(\omega,\alpha)$ (Km/s)
$\theta_x(\omega,\alpha)$, $\varphi_x(\omega,\alpha)$ (deg.)
0
10
20
30
40
50
60
70
0
45
90
135
180
225
270
315
360
$\mathcal{V}_y$
θ_y
γ_y
$\mathcal{V}_y(\omega,\alpha)$ (Km/s)
$\theta_y(\omega,\alpha)$, $\varphi_y(\omega,\alpha)$ (deg.)
0
50
100
150
200
250
300
350
1.945
1.950
1.955
1.960
1.965
$\hbar\omega$ (eV)


$\mathcal{V}_x$
θ_x
γ_x
Alt @
$\alpha = 150°$
$\mathcal{V}_x(\omega,\alpha)$ (Km/s)
$\theta_x(\omega,\alpha)$, $\varphi_x(\omega,\alpha)$ (deg.)
$\mathcal{V}_y$
θ_y
γ_y
$\mathcal{V}_y(\omega,\alpha)$ (Km/s)
$\theta_y(\omega,\alpha)$, $\varphi_y(\omega,\alpha)$ (deg.)
$\hbar\omega$ (eV)

Conclusions and perspectives

Conclusions

- We found that the *up* is more spin–polarizable than the *alt*.
- The *up* structure is can achieve a larger injection current being the response bigger than other structures but being overcome by the CdSe.
- Both structures are excellent candidates to generate second harmonic, particularly the *up* one.
- 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.

Perspectives

- Continue the study of this phenomenon in other structures and make new publication:
  - Functionalized hydrogen-boron-nitride-graphene
  - Boron-nitride nanotubes
-