Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Bulk Photovoltaic Effect in GaNGeC Quaternary Compound Semiconductors

Ping Lou*,†,‡ and Jin Yong Lee*,†

Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea, and Department of Physics, Anhui University, Hefei 230039, Anhui, China

E-mail: loup@ahu.edu.cn; jinylee@skku.edu

*To whom correspondence should be addressed
†Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea
‡Department of Physics, Anhui University, Hefei 230039, Anhui, China

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Table S1: Fractional Coordinates of the Atoms in the Primitive Cell, and Wyckoff Positions of Group.

	S-1	*P*3*m*1 (No.156)
Ge	0.6666666666666714, 0.3333333333333286, 0.3624599819999971	1c
C	0.3333333333333286, 0.6666666666666714, 0.4790199799999968	1b
Ga	0.3333333333333286, 0.6666666666666714, 0.8624199910000031	1b
N	0.6666666666666714, 0.3333333333333286, 0.9960899690000034	1c
	S-2	*Pmm*2 (No. 25)
Ge	0.5000000000000000, 0.0000000000000000, 0.3069426505183119	1c
C	0.0000000000000000, 0.0000000000000000, 0.5409335387865466	1a
Ga	0.0000000000000000, 0.5000000000000000, 0.7934918935126746	1b
N	0.5000000000000000, 0.5000000000000000, 0.0586318951824683	1d
	S-3	*Pmm*2 (No. 25)
Ge	0.0000000000000000, 0.0000000000000000, 0.5877554933025234	1a
C	0.5000000000000000, 0.0000000000000000, 0.8216899701073591	1c
Ga	0.5000000000000000, 0.5000000000000000, 0.0742271464295536	1d
N	0.0000000000000000, 0.5000000000000000, 0.3394273351605525	1a
	S-4	*Pmm*2 (No. 25)
Ge	0.5000000000000000, 0.5000000000000000, 0.8158552834755285	1d
C	0.0000000000000000, 0.5000000000000000, 0.5818794706489309	1b
Ga	0.0000000000000000, 0.0000000000000000, 0.3293138608568018	1a
N	0.5000000000000000, 0.0000000000000000, 0.0641713230187433	1c
	S-5	*R*3*m* (No. 160)
Ge	0.6709841743474934, 0.6709841743474934, 0.6709841743474934	1a
C	0.2911739297909084, 0.2911739297909084, 0.2911739297909084	1a
Ga	0.8190742803260118, 0.8190742803260118, 0.8190742803260118	1a
N	0.1995873262022444, 0.1995873262022444, 0.1995873262022444	1a
	S-6	*P*3*m*1 (No.156)
Ge	0.6666667436180234, 0.3333333243819752, 0.3305940463622838	1c
C	0.3333333069338735, 0.6666667660661290, 0.1905461627035190	1b
Ga	0.6666668219594882, 0.3333332460405103, 0.7739294995641177	1c
N	0.3333332694886195, 0.6666668035113830, 0.9157003673700826	1b

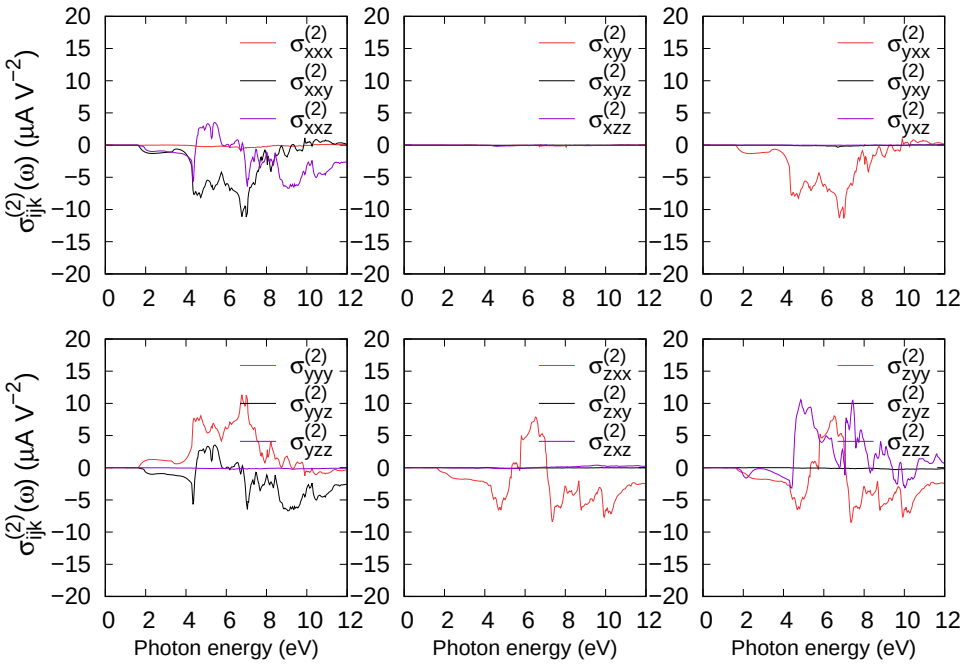
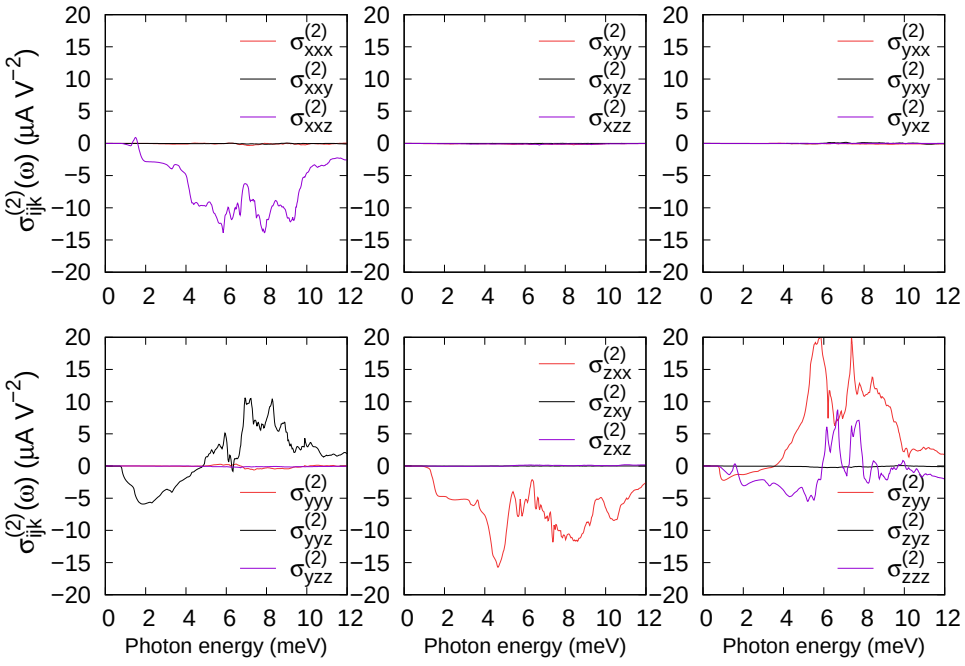


Figure S1: (Color online) Shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-1 crystal, where ω is the photon energy, and $i, j, k = x, y, z$.



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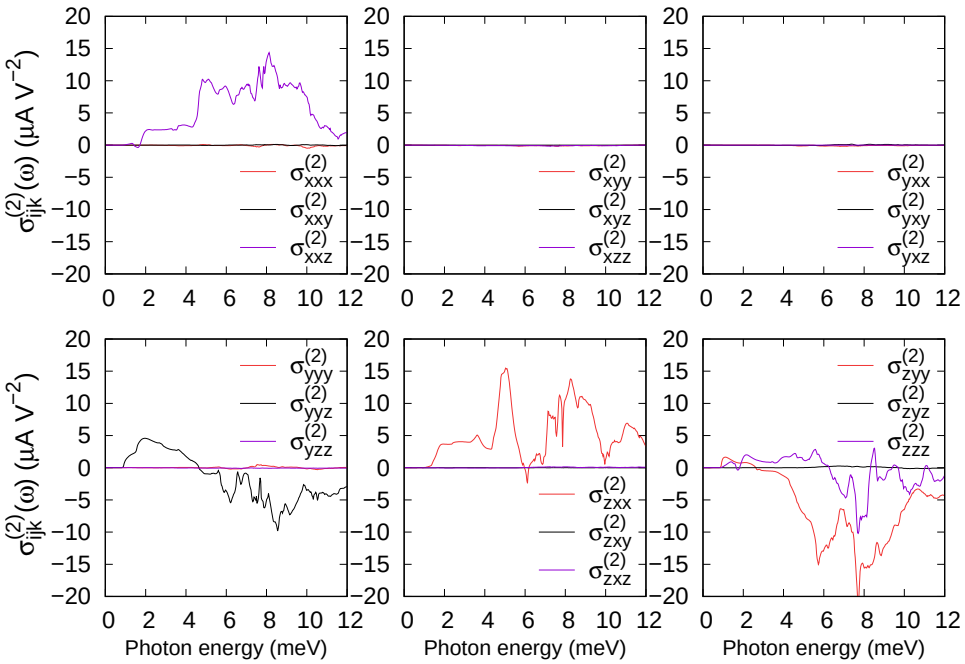


Figure S3: (Color online) Shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-3 crystal, where ω is the photon energy, and $i, j, k = x, y, z$.

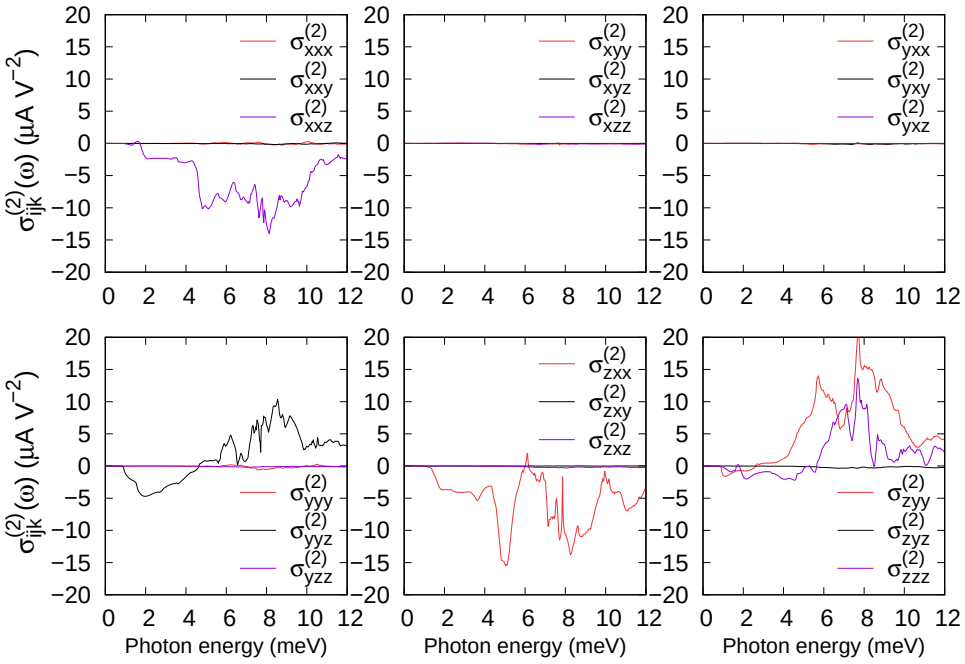


Figure S4: (Color online) Shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-4 crystal, where ω is the photon energy, and $i, j, k = x, y, z$.

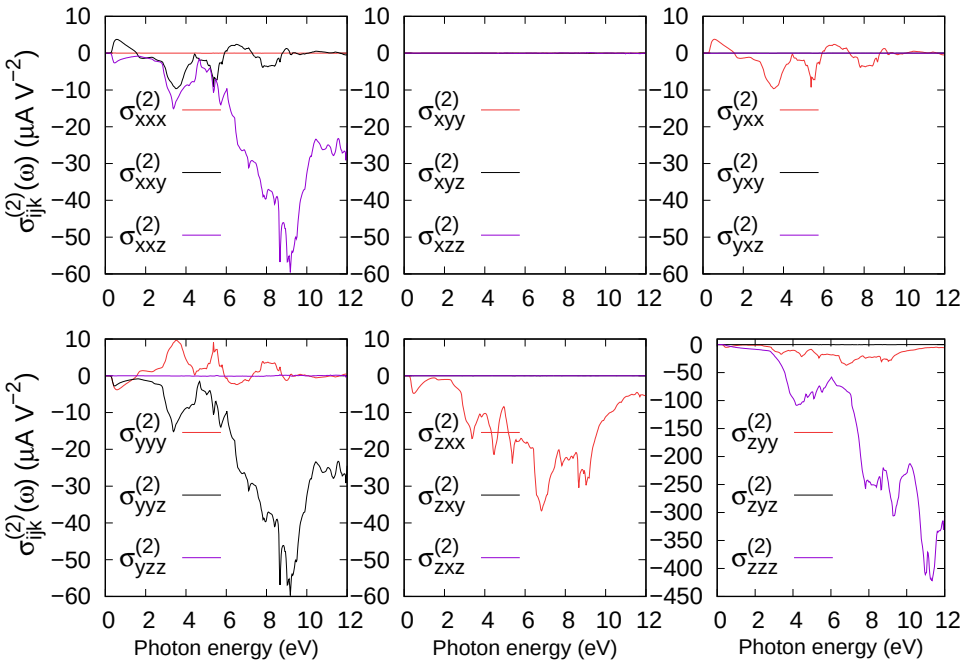
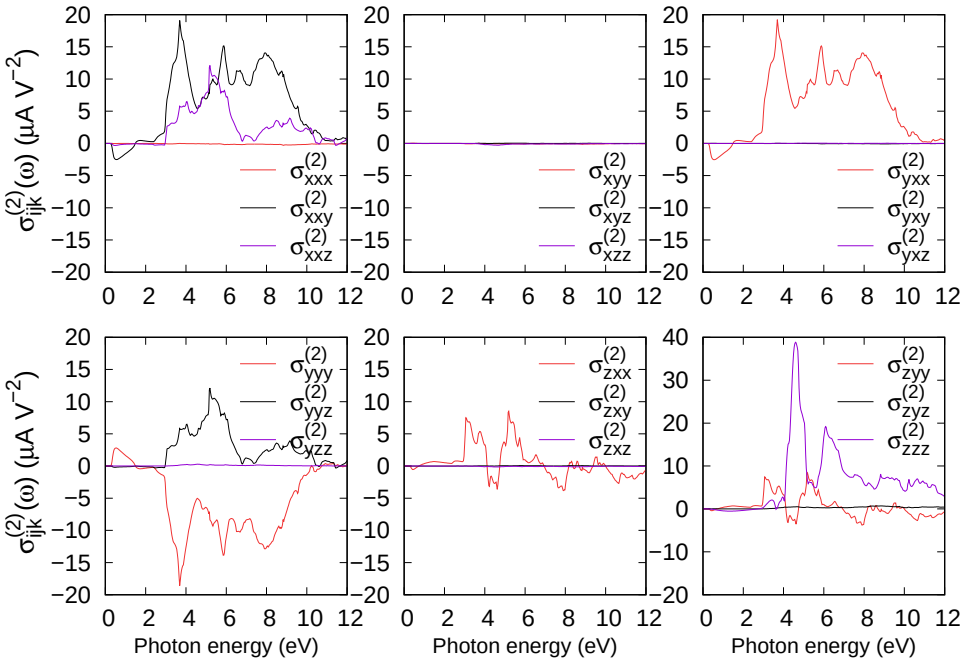


Figure S5: (Color online) Shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-5 crystal, where ω is the photon energy, and $i, j, k = x, y, z$.



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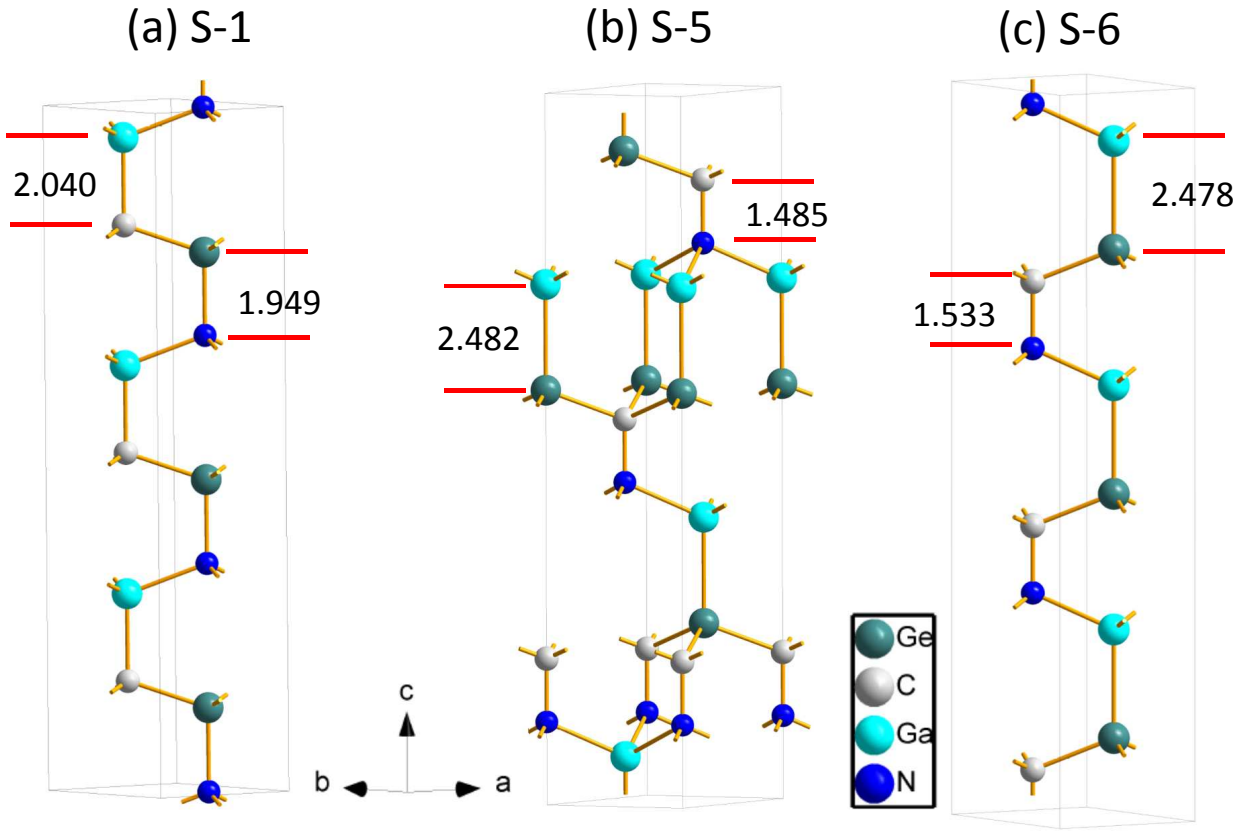
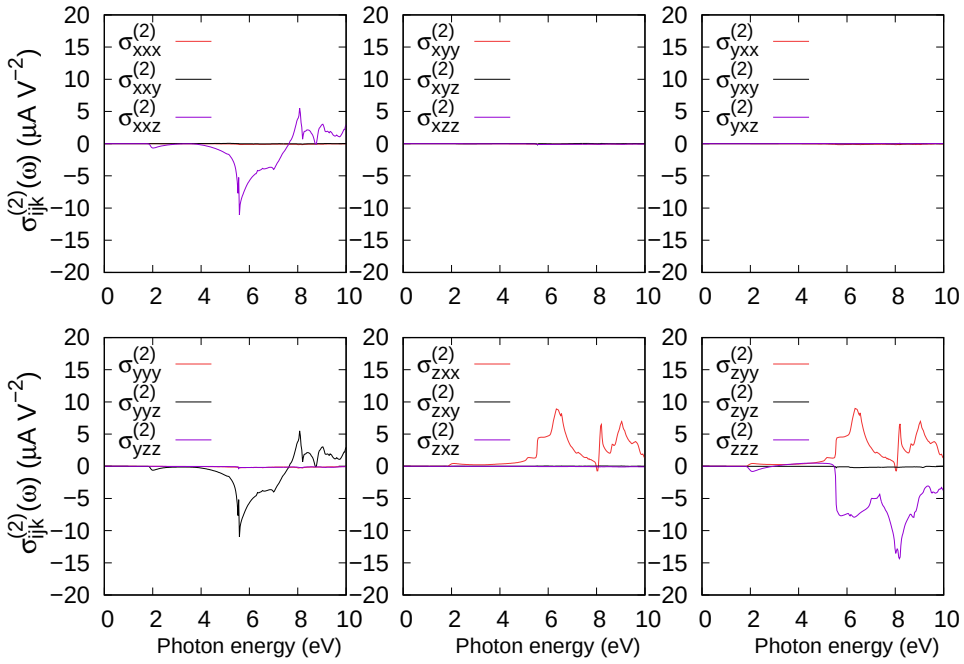


Figure S7: (Color online) (a) S-1 $1 \times 1 \times 3$ supercell, (b) S-5 hexagonal unit cell, and (c) S-6 $1 \times 1 \times 3$ super unit cells. The numbers 2.040 and 1.949 in (a) indicate the bonding length of C-Ga and the bonding length of N-Ge, and the unit is Å. The numbers 2.482 and 1.485 in (b) indicate the bonding length of Ge-Ga and the bonding length of N-C, and the unit is Å. The numbers 2.478 and 1.533 in (c) indicate the bonding length of Ge-Ga and the bonding length of C-N, and the unit is Å.



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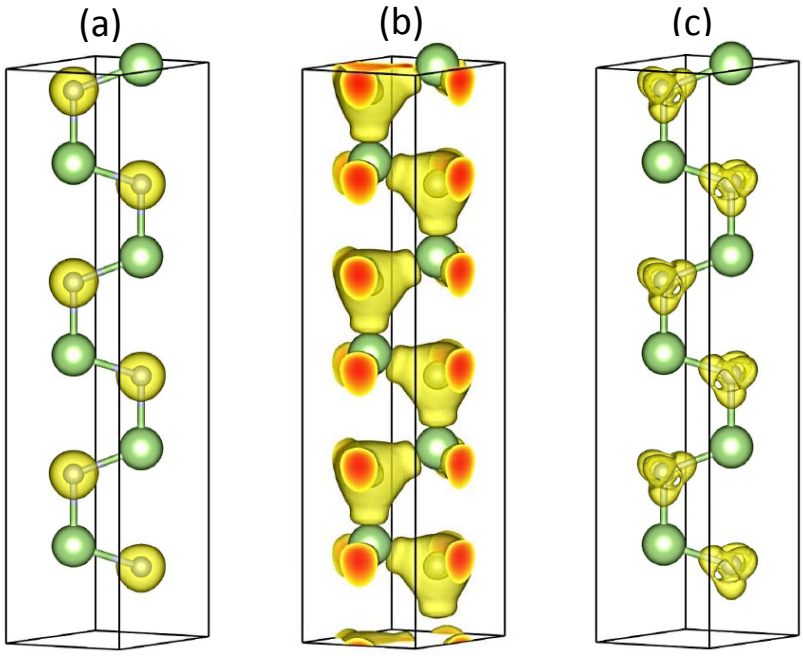

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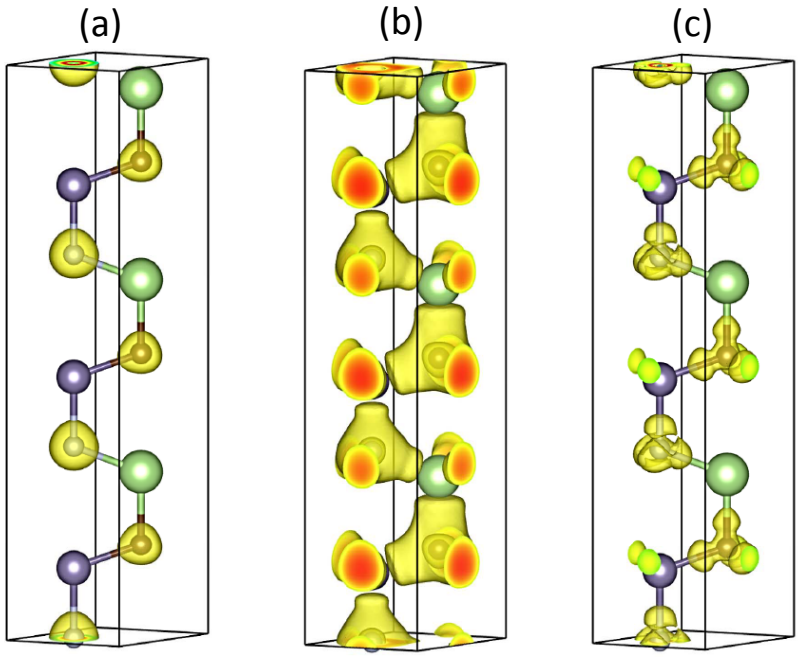

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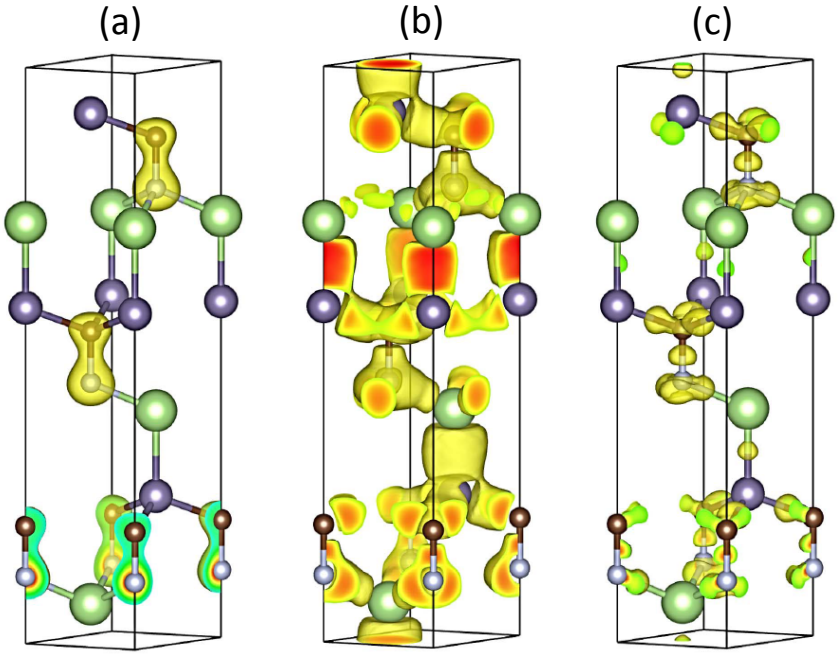

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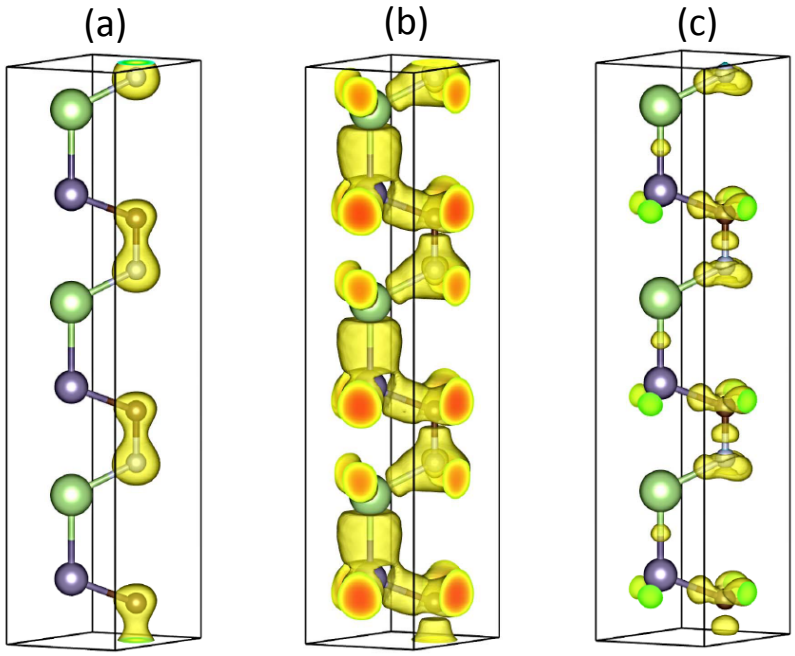

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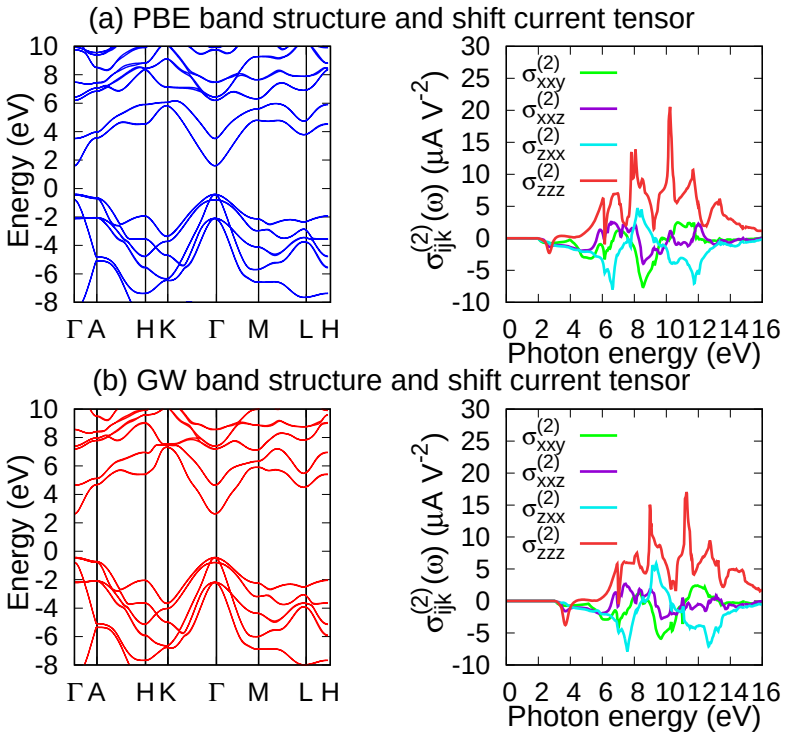
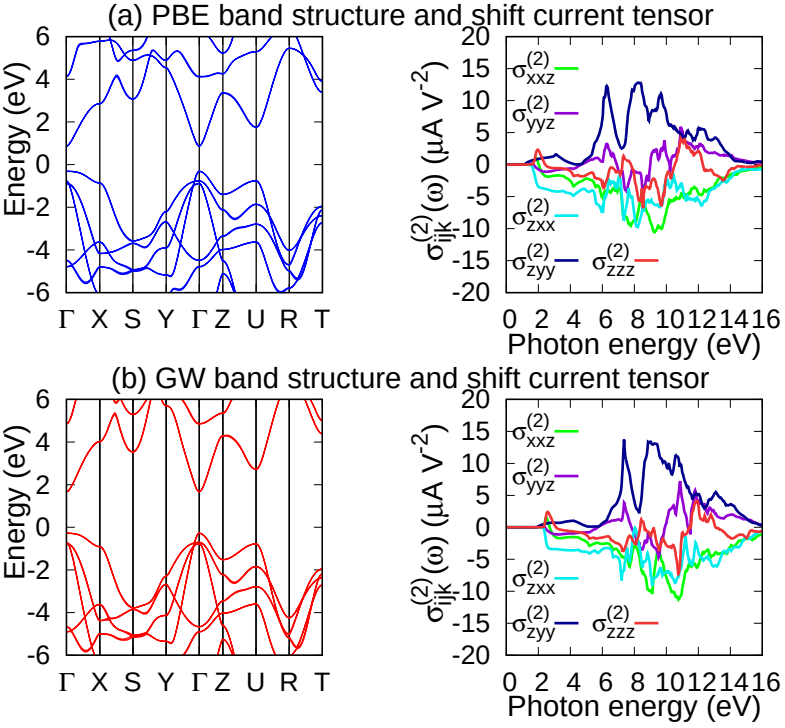


Figure S13: (Color online) Band structure and shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-1 crystal: (a) PBE functional and (b) GW approximation performed using the Vienna Ab initio Simulation Package (VASP).



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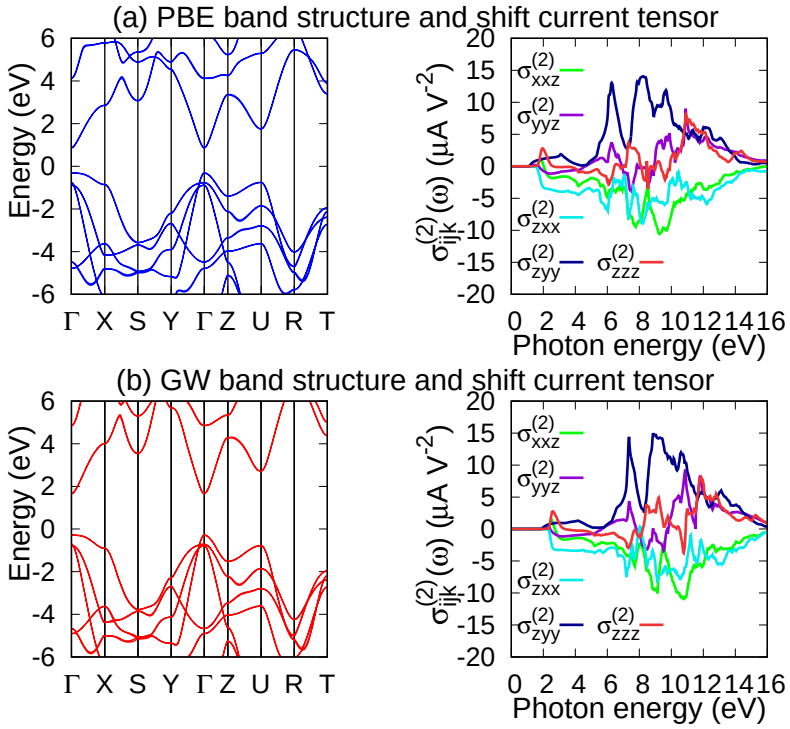

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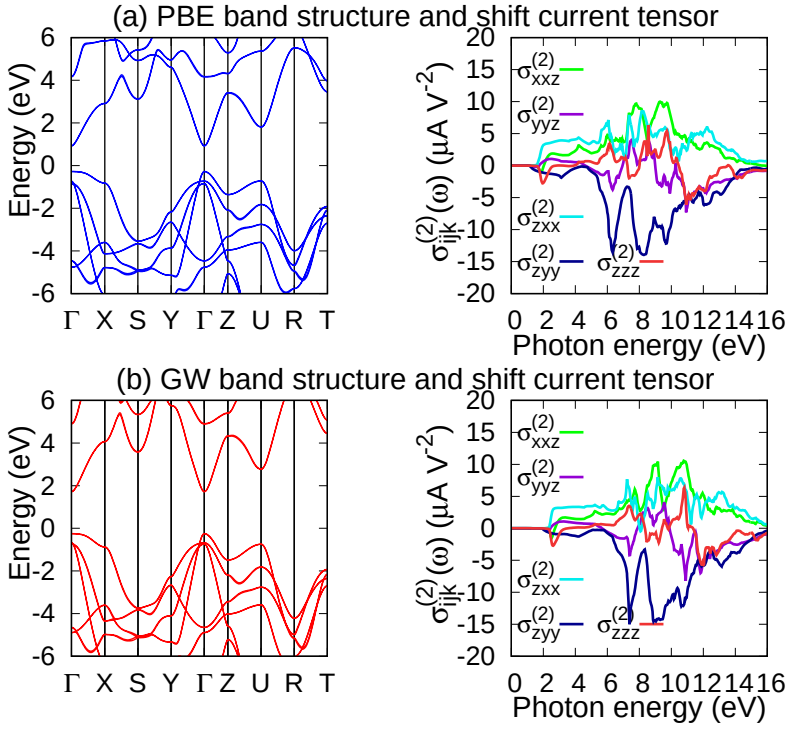

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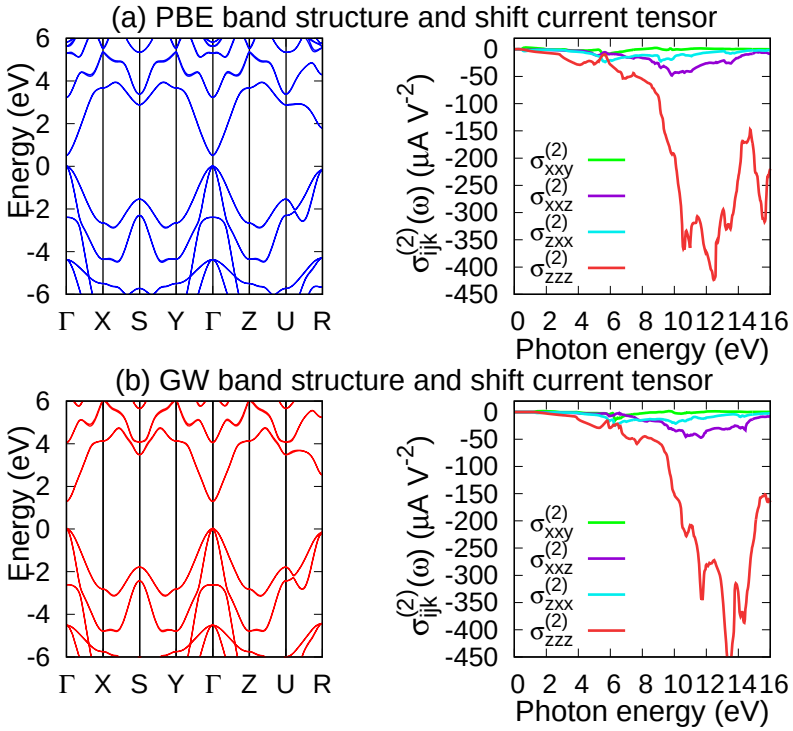


Figure S17: (Color online) Band structure and shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-5 crystal: (a) PBE functional and (b) GW approximation performed using the Vienna Ab initio Simulation Package (VASP).

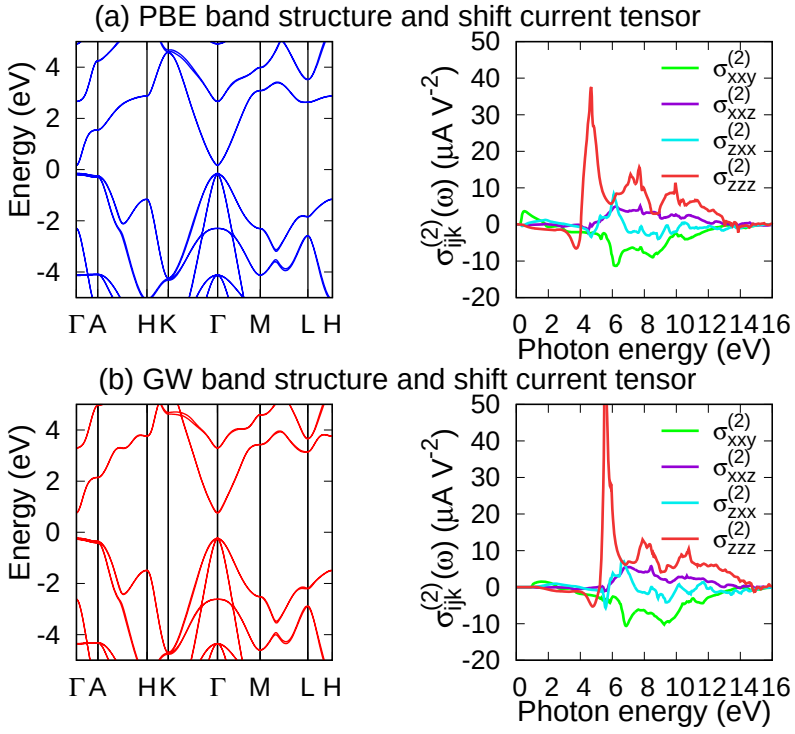
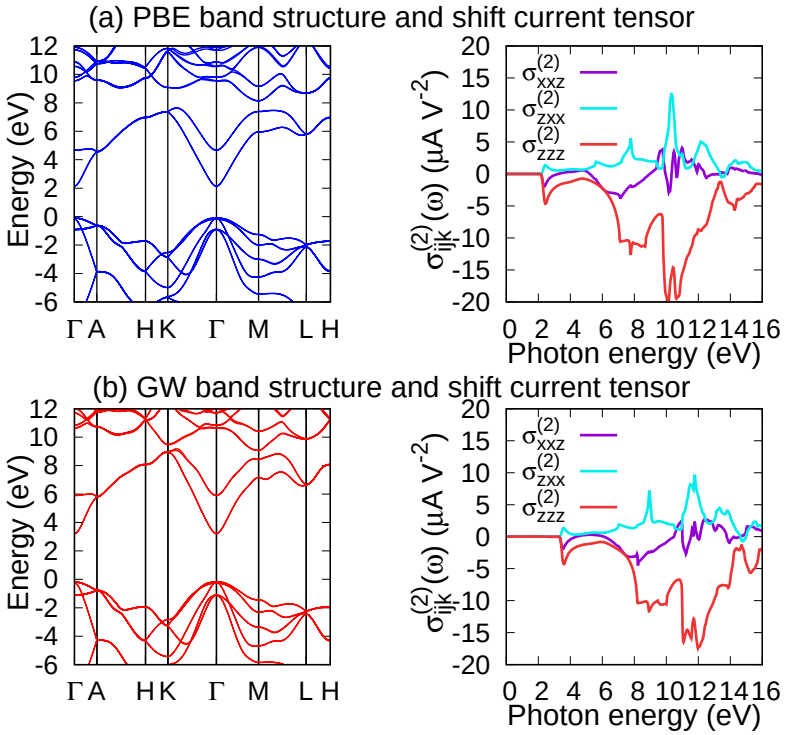


Figure S18: (Color online) Band structure and shift current conductivity tensor $\sigma^{(2)}_{ijk}(\omega)$ spectra of S-6 crystal: (a) PBE functional and (b) GW approximation performed using the Vienna Ab initio Simulation Package (VASP).



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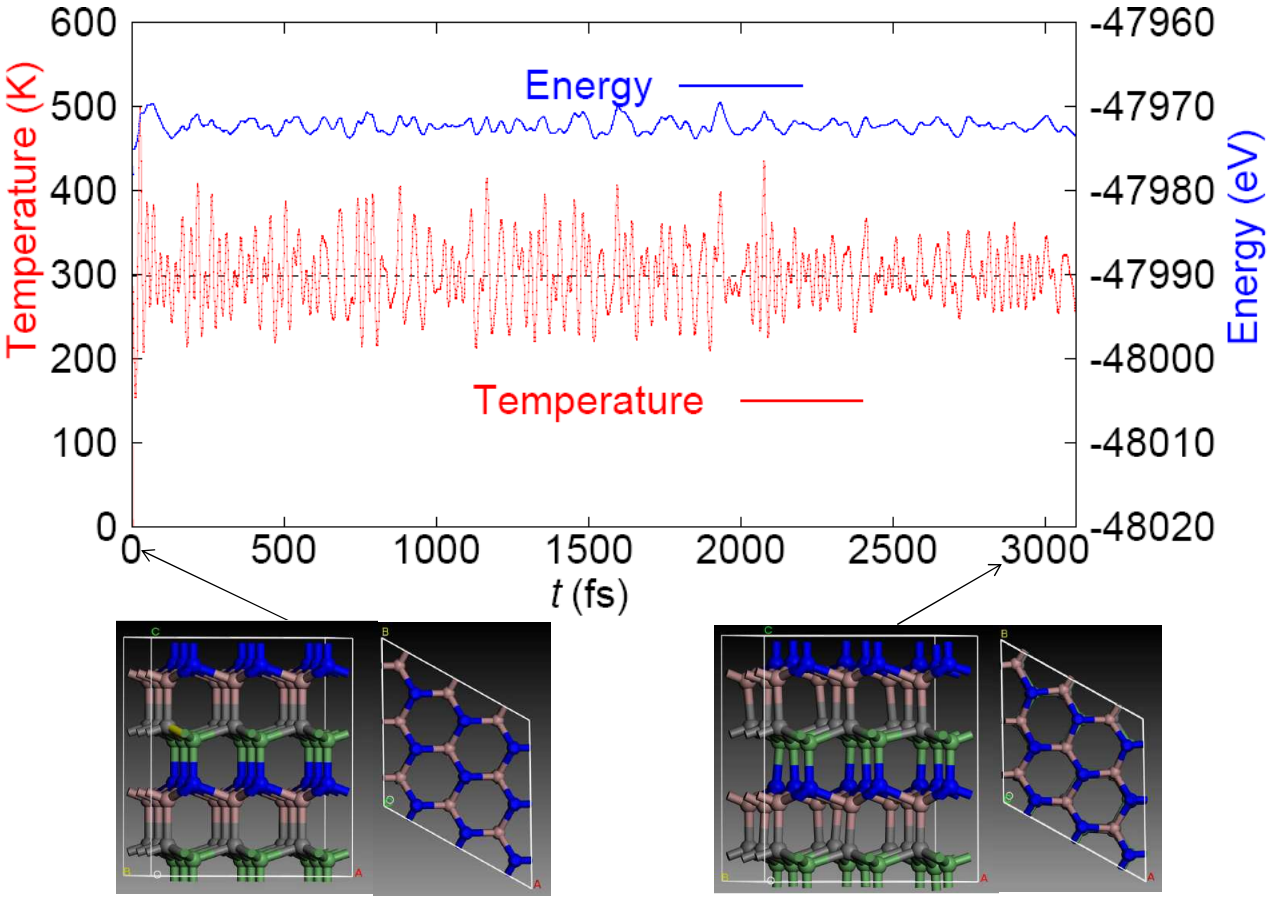
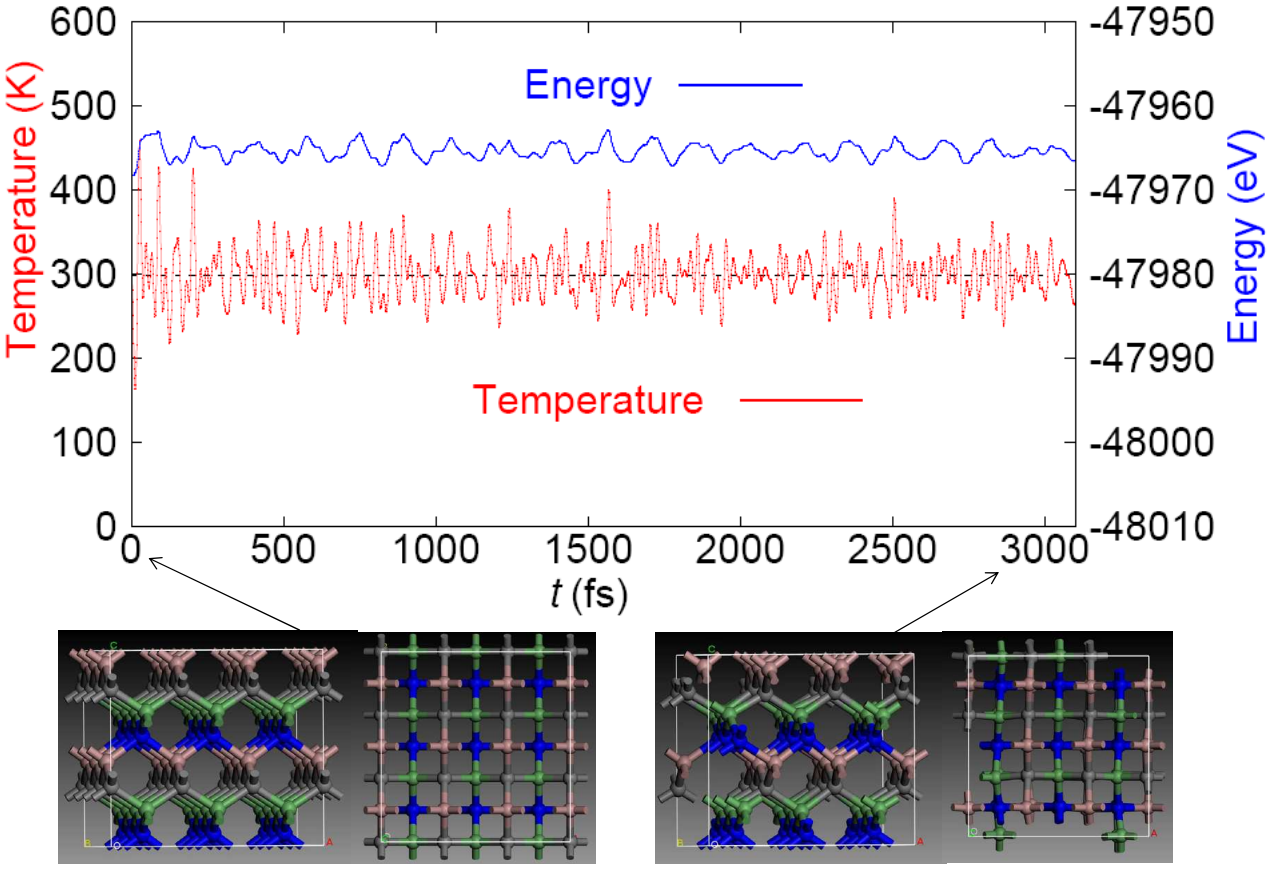


Figure S20: (Color online) S-1 crystal stacking of side and top views of geometric structures at t =0 and 3000 fs. Energy (blue) and temperature (red) as a function of quantum molecular dynamics (QMD) simulations time (t) at 300 K in a $3 \times 3 \times 2$ hexagonal supercell.



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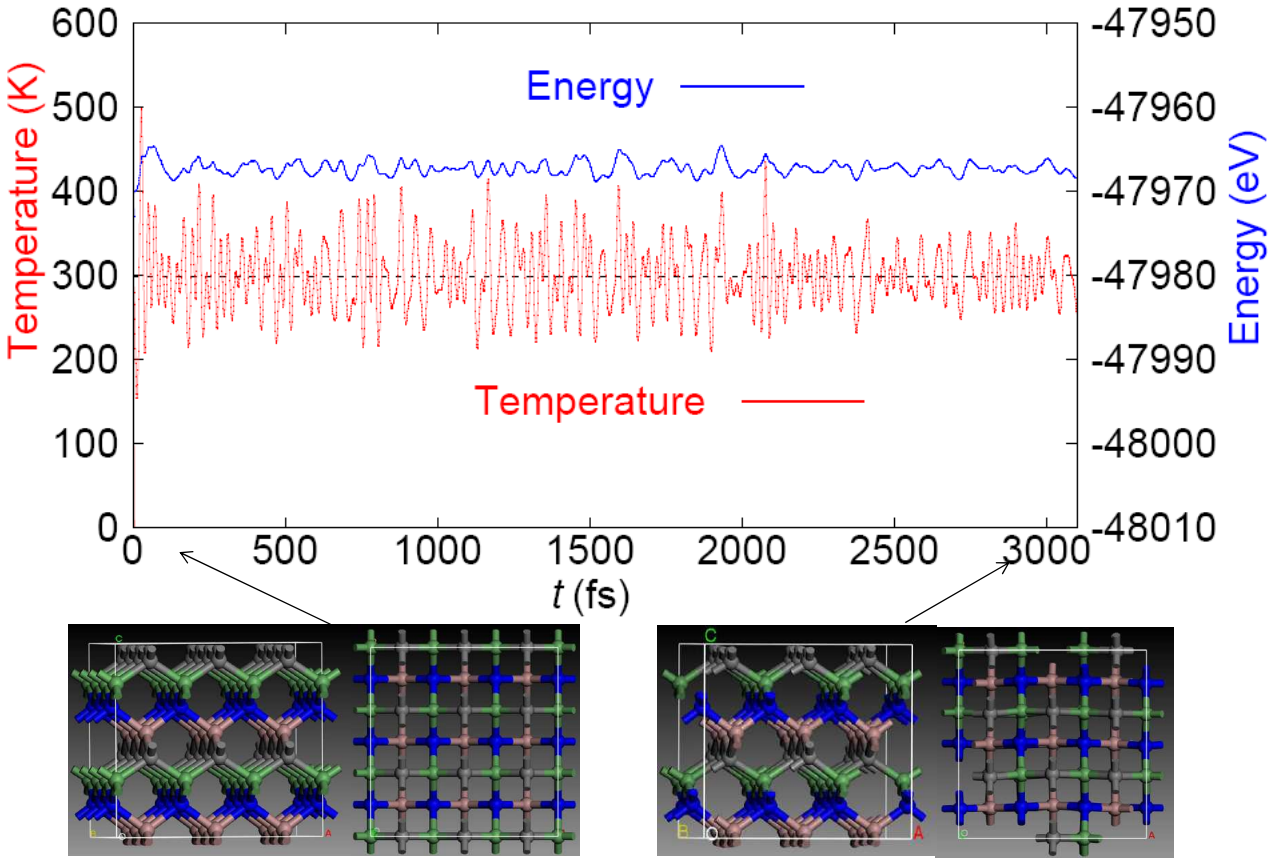

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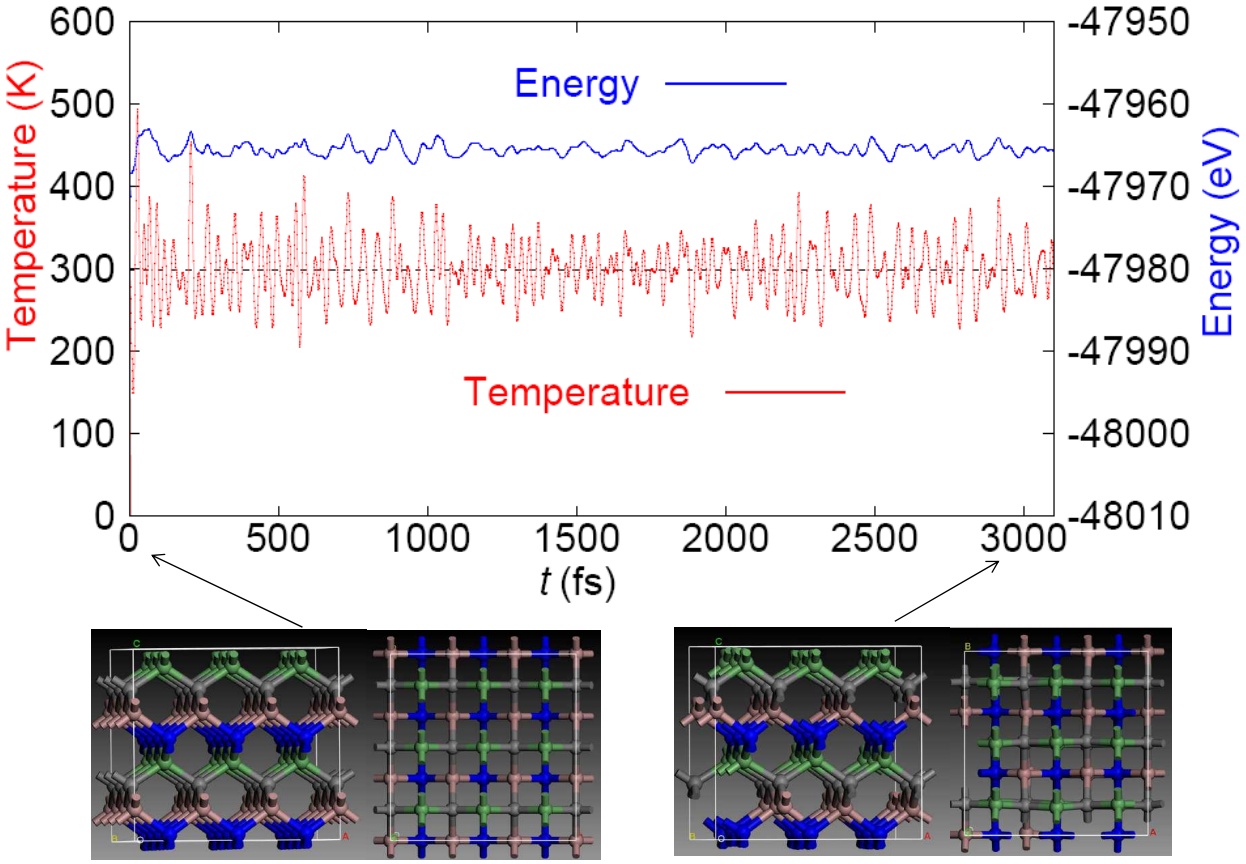

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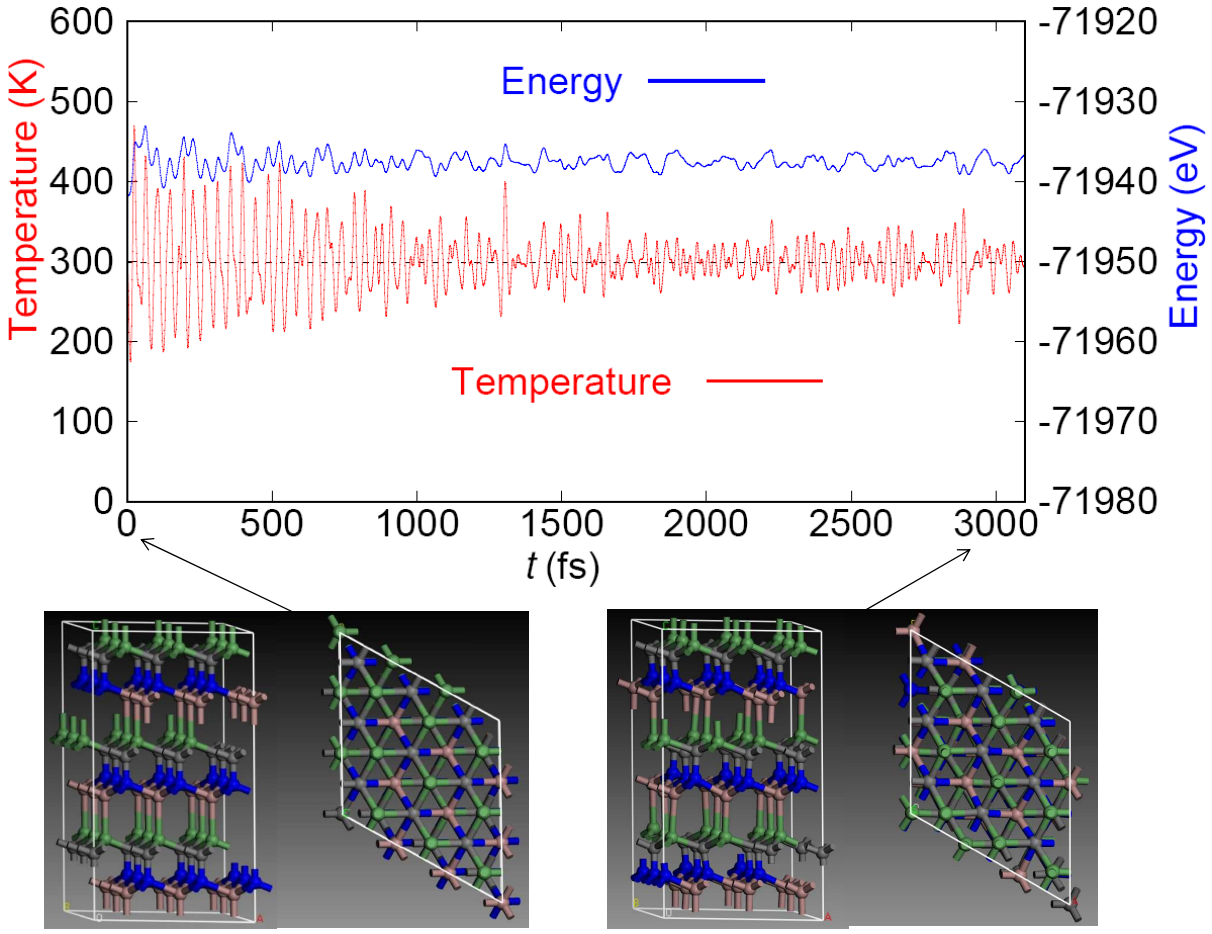

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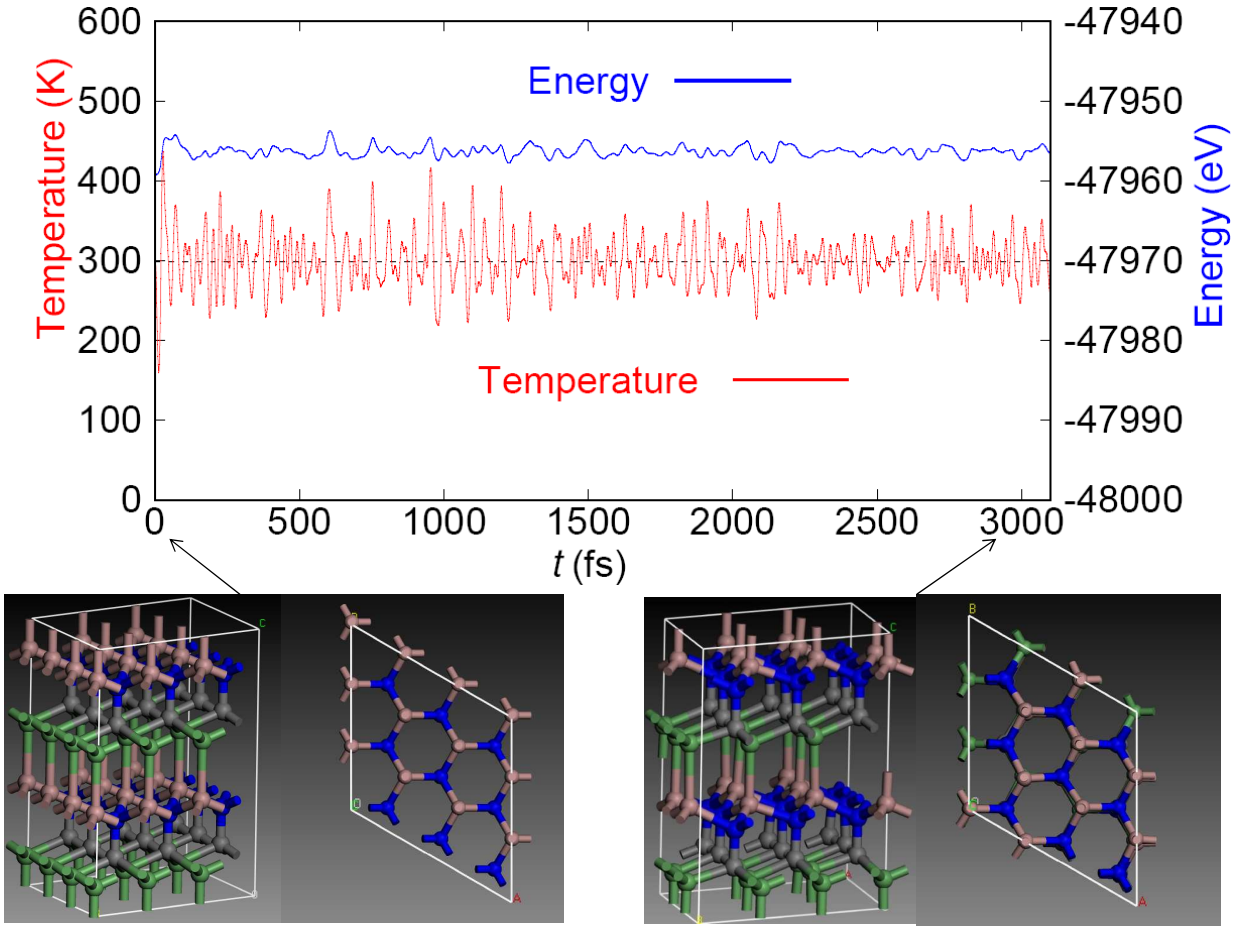

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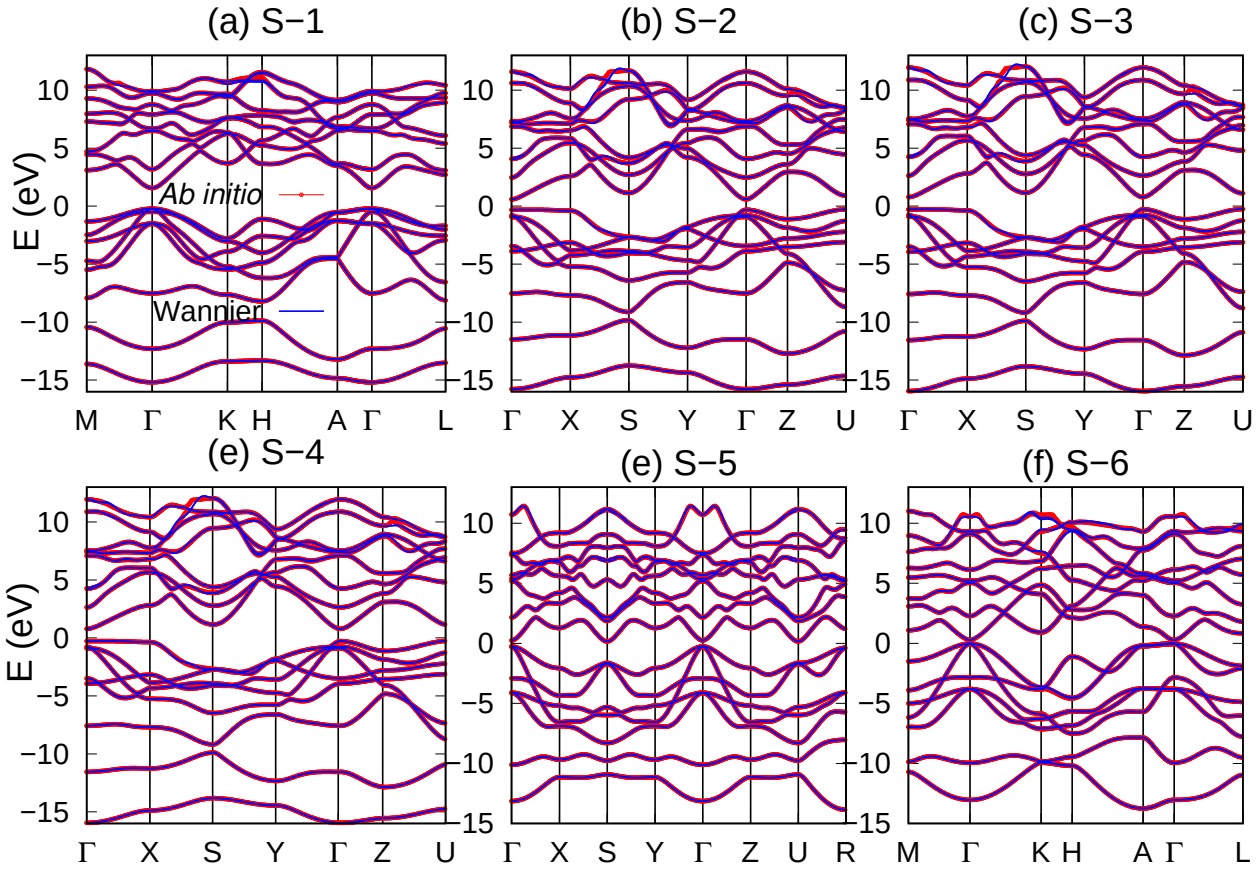

Figure S26: (Color online) The *ab initio* and Wannier-interpolated band structures of (a) S-1, (b) S-2, (c) S-3, (d) S-4, (e) S-5, and (f) S-6 crystals for the energy window.

1. Influence of Spatial Symmetry on Linear Optical Conductivity

The S-2, S-3 and S-4 belong to the C_{2v} (mm2) point group. For C_{2v} (mm2) point group, the $\hat{C}_2(z)$ and $\hat{\sigma}_v(zy)$ symmetries play the crucial role of deciding the shape of the linear optical conductivity tensor. The $\hat{C}_2(z)$ and $\hat{\sigma}_v(zy)$ are given as:

$$\hat{C}_2(z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \hat{\sigma}_v(zy) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{S1}$$

where $\hat{C}_2(z)$ displays rotational symmetry (the crystal were rotated by 90 degrees about the z axis) and $\hat{\sigma}_v(zy)$ displays mirror refection symmetry (a mirror plane perpendicular to x, i.e., in the $z-y$ plane). First, the $\hat{\sigma}_v(zy)$ leads that the linear optical conductivity tensor is

$$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & \sigma_{yz} \\ 0 & \sigma_{zy} & \sigma_{zz} \end{pmatrix}.$$

Then, the $\hat{C}_2(z)$ further leads that the linear optical conductivity tensor should be

$$\sigma = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}. \tag{S2}$$

The S-1, S-5 and S-6 belong to the C_{3v} (3m) point group. For C_{3v} (3m) point group, the $\hat{C}_3(z)$ and $\hat{\sigma}_v(zy)$ symmetries play the crucial role of deciding the shape of the linear optical conductivity tensor. The $\hat{C}_3(z)$ and $\hat{\sigma}_v(zy)$ are given as:

$$\hat{C}_3(z) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \hat{\sigma}_v(zy) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{S3}$$

where $\hat{C}_3(z)$ displays rotational symmetry (the crystal were rotated by 120 degrees about the z axis)

and $\hat{\sigma}_v(zy)$ displays mirror refection symmetry (a mirror plane perpendicular to x, i.e., in the $z-y$ plane). First, The $\hat{\sigma}_v(zy)$ leads that the linear optical conductivity tensor is

$$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & \sigma_{yz} \\ 0 & \sigma_{zy} & \sigma_{zz} \end{pmatrix}.$$

Then, the $\hat{C}_3(z)$ further leads that the linear optical conductivity tensor should be

$$\sigma = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \tag{S4}$$

2. Influence of Spatial Symmetry on Shift Current Conductivity

The S-2, S-3 and S-4 belong to the C_{2v} (3m) point group. For C_{2v} (mm2) point group, the $\hat{C}_2(z)$ and $\hat{\sigma}_v(zy)$ symmetries play the crucial role of deciding the shape of the shift current conductivity tensor. First, the $\hat{\sigma}_v(zy)$ leads that the shift current conductivity tensor should be

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \sigma^{(2)}_{xxz} & \sigma^{(2)}_{xxy} \\ \sigma^{(2)}_{yxx} & \sigma^{(2)}_{yyy} & \sigma^{(2)}_{yzz} & \sigma^{(2)}_{yyz} & 0 & 0 \\ \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zyy} & \sigma^{(2)}_{zzz} & \sigma^{(2)}_{zyz} & 0 & 0 \end{pmatrix}.$$

Then, the $\hat{C}_2(z)$ further leads that the shift current conductivity tensor should be

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \sigma^{(2)}_{xxz} & 0 \\ 0 & 0 & 0 & \sigma^{(2)}_{yyz} & 0 & 0 \\ \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zyy} & \sigma^{(2)}_{zzz} & 0 & 0 & 0 \end{pmatrix} \tag{S5}$$

The S-1, S-5 and S-6 belong to the C_{3v} (3m) point group. For C_{3v} (mm2) point group, the $\hat{C}_3(z)$ and $\hat{\sigma}_v(zy)$ symmetries play the crucial role of deciding the shape of the shift current conductivity

tensor. First, the $\hat{\sigma}_v(zy)$ leads that the shift current conductivity tensor should be

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \sigma^{(2)}_{xxz} & \sigma^{(2)}_{xxy} \\ \sigma^{(2)}_{yxx} & \sigma^{(2)}_{yyy} & \sigma^{(2)}_{yzz} & \sigma^{(2)}_{yyz} & 0 & 0 \\ \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zyy} & \sigma^{(2)}_{zzz} & \sigma^{(2)}_{zyz} & 0 & 0 \end{pmatrix}.$$

Then, the $\hat{C}_3(z)$ further leads that the shift current conductivity tensor should be

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \sigma^{(2)}_{xxz} & \sigma^{(2)}_{xxy} \\ \sigma^{(2)}_{xxy} & -\sigma^{(2)}_{xxy} & 0 & \sigma^{(2)}_{xxz} & 0 & 0 \\ \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zzz} & 0 & 0 & 0 \end{pmatrix}. \tag{S6}$$

The GaN belongs to the point group C_{6v} ($6mm$). The $\hat{C}_6(z)$ (the crystal were rotated by 60 degrees about the z axis)) and $\hat{\sigma}_v(zy)$ symmetries play the crucial role of deciding the shape of the shift current conductivity tensor, where

$$\hat{C}_6(z) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{S7}$$

First, the $\hat{\sigma}_v(zy)$ leads that the shift current conductivity tensor should be leads to the shift current conductivity tensor of the form:

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \sigma^{(2)}_{xxz} & \sigma^{(2)}_{xxy} \\ \sigma^{(2)}_{yxx} & \sigma^{(2)}_{yyy} & \sigma^{(2)}_{yzz} & \sigma^{(2)}_{yyz} & 0 & 0 \\ \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zyy} & \sigma^{(2)}_{zzz} & \sigma^{(2)}_{zyz} & 0 & 0 \end{pmatrix}.$$

Then, the $\hat{C}_6(z)$ further leads that the shift current conductivity tensor should be

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \sigma^{(2)}_{xxz} & 0 \\ 0 & 0 & 0 & \sigma^{(2)}_{xxz} & 0 & 0 \\ \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zxx} & \sigma^{(2)}_{zzz} & 0 & 0 & 0 \end{pmatrix}. \tag{S8}$$