Supporting Information

Raman tensor of layered black phosphorous

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Derivation of Raman phase difference considering birefringence theory

Assuming incident light propagates along $b(y)$-axis of BP, the polarization direction of incident light is located in the basal plane. The refractivity $n_x = n_{xr} + in_{xi}$ and $n_z = n_{zr} + in_{zi}$ when the polarization direction is in x and z direction, respectively. When incident light propagates to the crystal surface (y = 0), the electric field intensity can be written as

$$\vec{E}_0 = (E_0 cos\theta \vec{\imath} + E_0 sin\theta \vec{\jmath})\, exp(-i\omega_L t), \tag{S1}$$

where $\vec{\imath}$ and $\vec{\jmath}$ denote unit vectors along $c(z)$-axis and $a(x)$-axis respectively, ω_L represents the frequency of incident light, and θ denotes the angle between polarization direction of incident light and c-axis. Thus the electric field intensity along c-axis at incident depth y is given by

$$\begin{aligned} E_z &= E_0 cos\theta \exp(-i\omega_L t + iky) \\ &= E_0 cos\theta\, exp(-i\omega_L t + in_{zr}k_0 y)\, exp(-n_{zi}k_0 y). \end{aligned} \tag{S2}$$

where k and k_0 represents wave vectors in media and vacuum respectively. Thus the polarization intensity along *x*-axis can be written as

$$P_z = \chi_{zz}\varepsilon_0 E_0 cos\theta\, exp(-i\omega_L t + in_{xr}k_0 z)\, exp(-n_{xi}k_0 z), \qquad \text{(S3)}$$

where χ is electric susceptibility tensor, Which is diagonal in principal axes coordinate system. Thus, the polarization of crystal is only along *z*-axis when electric field is along *z*-axis. Only considering the stokes process, polarization intensity along *z*-axis is given by

$$P_z = \left.\frac{\partial \chi_{zz}}{\partial Q}\right|_{Q_0} \Delta Q_0 \varepsilon_0 E_0 cos\theta\, exp\left(i\omega_p t\right) \exp(-i\omega_L t + in_{zr}k_0 y)\, exp(-n_{zi}k_0 y)$$

$$= \left.\frac{\partial \chi_{zz}}{\partial Q}\right|_{Q_0} \Delta Q_0 \varepsilon_0 E_0 cos\theta\, exp\left[-i\left(\omega_L - \omega_p\right)t + in_{zr}k_0 y\right] exp(-n_{zi}k_0 y), \qquad \text{(S4)}$$

where $\Delta Q_0 \exp\left(i\omega_p t\right)$ represents the atomic vibration, and ΔQ_0 and ω_p are amplitude and vibration frequency respectively. Similarly, when electric field is along *x*-axis, polarization intensity along *z*-axis can be written as

$$P_x = \left.\frac{\partial \chi_{xx}}{\partial Q}\right|_{Q_0} \Delta Q_0 \varepsilon_0 E_0 sin\theta\, exp\left[-i\left(\omega_L - \omega_p\right)t + in_{xr}k_0 y\right] exp(-n_{xi}k_0 y), \qquad \text{(S5)}$$

Based on light scattering theory, when incident light irradiates on the sample, electric dipole will be induced and then radiate electromagnetic waves outward. the radiated electromagnetic waves propagate back to the crystal surface ($y = 0$). Thus, for $\boldsymbol{e_i}//\boldsymbol{e_s}$, electric field intensity along $\boldsymbol{e_s}$ contributed by Pz and Px can be written as

$$E'_z \propto \omega^2 \left.\frac{\partial \chi_{zz}}{\partial Q}\right|_{Q_0} \Delta Q_0 \varepsilon_0 E_0 cos^2\theta\, exp\left[-i\left(\omega_L - \omega_p\right)t + 2in_{zr}k_0 y\right] exp(-2n_{zi}k_0 y)$$

$$= \omega^2 R_z \varepsilon_0 E_0 cos^2\theta\, exp\left[-i\left(\omega_L - \omega_p\right)t + 2in_{zr}k_0 y\right] exp(-2n_{zi}k_0 y) \qquad \text{(S6)}$$

$$E'_x \propto \omega^2 \left.\frac{\partial \chi_{xx}}{\partial Q}\right|_{Q_0} \Delta Q_0 \varepsilon_0 E_0 sin^2\theta\, exp\left[-i\left(\omega_L - \omega_p\right)t + 2in_{xr}k_0 y\right] exp(-2n_{xi}k_0 y)$$

$$= \omega^2 R_x \varepsilon_0 E_0 sin^2\theta\, exp\left[-i\left(\omega_L - \omega_p\right)t + 2in_{xr}k_0 y\right] exp(-2n_{xi}k_0 y) \qquad \text{(S7)}$$

where R_x and R_z denote Raman tensor element, and can be written as

$$R_x = R_{x0}\, exp(-i\varphi_{Rx}),$$

$$R_z = R_{z0}\, exp(-i\varphi_{Rz}), \tag{S8}$$

R_{x0} and R_{z0} are Raman tensor element amplitude, φ_{Rx} and φ_{Rz} represent argument of Raman tensor element.

Considering the superposition of scattering intensity at different depth, electric field intensity along *x*-axis and *z*-axis can be written as

$$E_x'' \propto \int_0^\infty E_x' dy = E_{x0} \int_0^\infty exp[2in_{xr}k_0 y - 2n_{xi}k_0 y]\, dy = \frac{E_{x0}}{2n_{xi}k_0 - 2in_{xr}k_0},$$

$$E_z'' \propto \int_0^\infty E_z' dy = E_{z0} \int_0^\infty exp[2in_{zr}k_0 y - 2n_{zi}k_0 y]\, dy = \frac{E_{z0}}{2n_{zi}k_0 - 2in_{zr}k_0}, \tag{S9}$$

where E_{x0} and E_{z0} is given by

$$E_{x0} \propto \omega^2 R_{x0}\varepsilon_0 E_0 sin^2\theta\, \exp\left(-i\left(\omega_L - \omega_p\right)t - i\varphi_{Rx}\right),$$

$$E_{z0} \propto \omega^2 R_{z0}\varepsilon_0 E_0 cos^2\theta\, \exp\left(-i\left(\omega_L - \omega_p\right)t - i\varphi_{Rz}\right), \tag{S10}$$

Thus, the total electric field intensity along $\boldsymbol{e_s}$ can be written as

$$E = E_x'' + E_z'' \propto \frac{E_{x0}}{2n_{xi}k_0 - 2in_{xr}k_0} + \frac{E_{z0}}{2n_{zi}k_0 - 2in_{zr}k_0}, \tag{S11}$$

Raman scattering intensity is defined as the square of the total electric field intensity, thus Raman scattering intensity is given by

$$I_{//} \propto (R_{z0}cos^2\theta)^2 + (R_{x0}sin^2\theta)^2 + 2R_{z0}R_{x0}cos^2\theta sin^2\theta \left\{\left[\frac{n_{xi}n_{zi} + n_{xr}n_{zr}}{(n_{xi}^2 + n_{xr}^2)(n_{zi}^2 + n_{zr}^2)}\right] cos(\varphi_{Rx} - \varphi_{Rz}) + \left[\frac{n_{xr}n_{zi} - n_{xi}n_{zr}}{(n_{xi}^2 + n_{xr}^2)(n_{zi}^2 + n_{zr}^2)}\right] sin(\varphi_{Rx} - \varphi_{Rz})\right\}$$

$$= (R_{z0}cos^2\theta)^2 + (R_{x0}sin^2\theta)^2 + 2R_{z0}R_{x0}cos^2\theta sin^2\theta \cdot \boldsymbol{w} \cdot cos(\varphi_{Rx} - \varphi_{Rz} - \boldsymbol{\phi}) \tag{S12}$$

where $\boldsymbol{w}$ and $\boldsymbol{\phi}$ are given by

$$\boldsymbol{\phi} = arctg\left(\frac{n_{xr}n_{zi} - n_{xi}n_{zr}}{n_{xi}n_{zr} + n_{xr}n_{zi}}\right),$$

$$\boldsymbol{w} == \frac{1}{\sqrt{(n_{xi}^2 + n_{xr}^2)(n_{yi}^2 + n_{yr}^2)}}, \qquad \text{(S13)}$$