In-Plane Optical Anisotropy and Linear Dichroism in

Low-Symmetry Layered TISe

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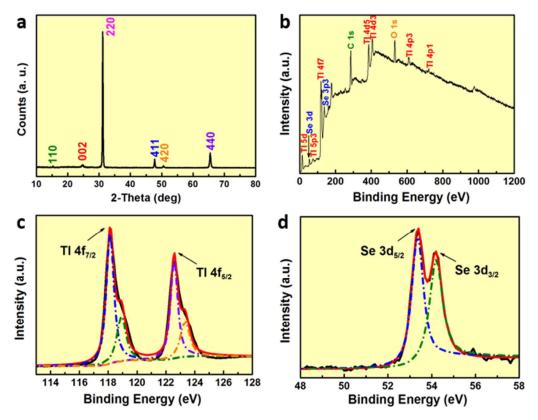


Figure S1. (a) XRD pattern of TlSe single crystals. (b) XPS full spectrum of bulk TlSe. The high-solution XPS signals of Tl 4f (c) and Se 3d (d).

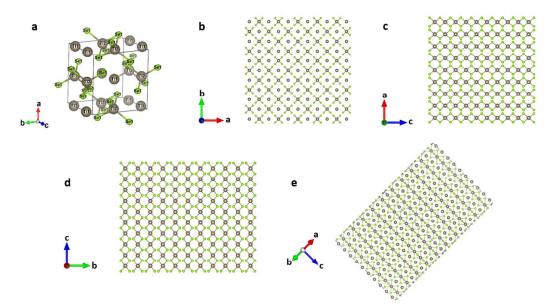


Figure S2. (a) The conventional cell of bulk TlSe. Top view (b) and side views (c-e) of TlSe crystal structure.

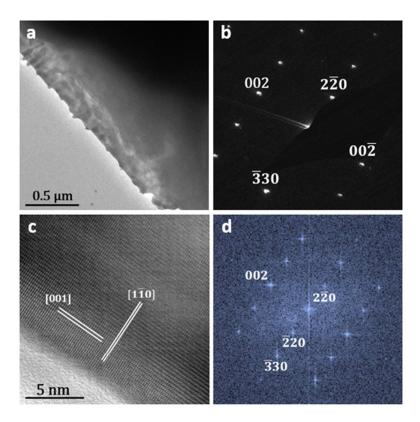


Figure S3. (a) TEM image of a thin area of the mechanically exfoliated TISe flake. (b) SADP, (c) HRTEM image and (d) FFT image of this flake.

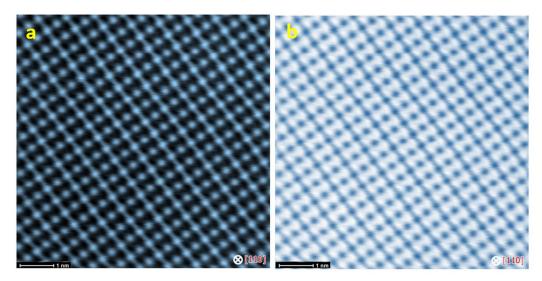


Figure S4. Atomic-resolution HAADF (a) and BF STEM (b) images viewed from [110] direction.

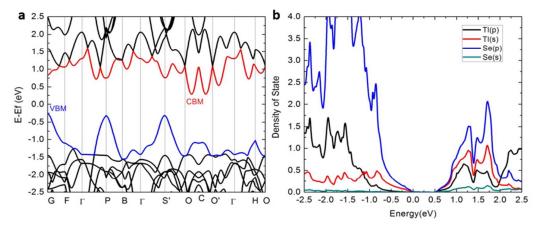


Figure S5. (a) Band structure and (b) partial density of state (PDOS) of bulk TISe.

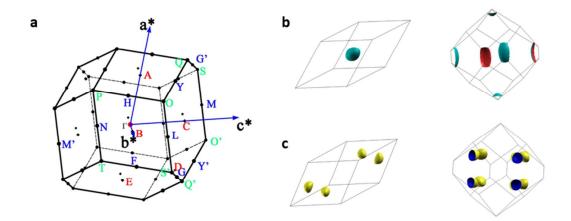


Figure S6. (a) The first Brillouin zone (BZ) of bulk TISe with high-symmetry points. Fermi surface around VBM (b) and CBM (c) is about 0.2 eV. The left of the figure shows the Fermi surface in the reciprocal unite cell and the right of the figure is the first BZ.

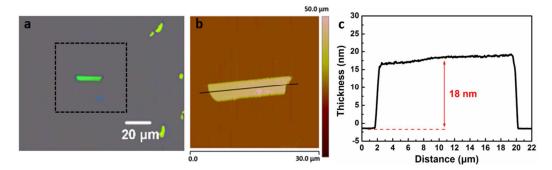


Figure S7. (a) The optical image of few-layer TISe flakes on a Si wafer with a 300 nm SiO_2 layer. (b) AFM image of a typical TISe flake. (c) The corresponding cross-section scan along the black line in b.

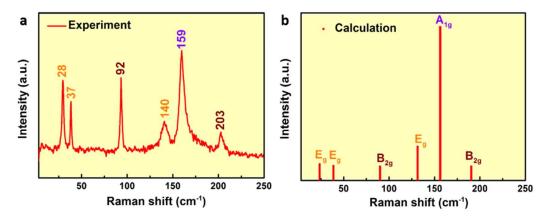


Figure S8. (a) Unpolarized Raman spectrum of an 18-nm TlSe flake at excitation wavelength of 633 nm. (b) The Raman intensity of bulk TlSe calculated by the DFT methods.

D4h Point Group

not Abelian, 10(12) irreducible representations point group: C₉, C₁, C₂, C₄, D₂, D₄, C₂₇, C₄₇, C₂₀, C₄₀, D₂₆, D₂₆, S₄

Character table for D4h point group

	E	2C4 (z)	C2	2C'2	2C"2	i	284	σh	20,	2 _{0d}	linears, rotations	quadratio
Alg	1	1	1	1	1	1	1	1	1	1		x2+y2, z2
A2g	1	1	1	-1	-1	1	1	1	-1	-1	Rz	
Blg	1	-1	1	1	-1	1	-1	1	1	-1		x2-y2
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
Eg	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
Alu	1	1	1	1	1	-1	-1	-1	-1	-1		
A24	1	1	1	-1	-1	-1	-1	-1	1	1	z	
Blu	1	-1	1	1	-1	-1	1	-1	-1	1		
B24	1	-1	1	-1	1	-1	1	-1	1	-1		
Eu	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

					Product table for D	4h P	omt ;	troat	2	
	Alg	A2g	B1g	B2g	Eg	Alu	A _{2u}	B _{1u}	B _{2u}	Eu
Alg	Alg	A _{2g}	Big	B2g	Eg	Als	A20	B _{1s}	B _{2s}	Eu
A24	A28	A _{1g}	B _{2g}	B_{1g}	Eg	A _{2u}	A _{1u}	B _{2u}	B _{1u}	Eu
B1:	Big	B2g	Alg	A2g	Eg	Biu	B20	Aiu	A20	Eu
B2g	B2g	Big	A _{2g}	Alg	Eg	B20	Blu	A20	A10	Eu
Eg	Eg	Eg	Eg	Eg	A1g+A2g+B1g+B2g	E_{0}	E_{μ}	Eu	Eu	A1u+A2u+B1u+B2
Alu	Alu	A20	B _{1u}	B_{2u}	Eu	A _{1g}	A28	Big	B2g	Eg
A24	A20	Alu	B20	Blu	Eu	A _{2g}	Alg	B2g	Big	Eg
B _{1u}	Blu	B20	Alu	A20	Eu	Big	B2g	Alg	A2g	Eg
B2.	B20	B ₁₀	A20	Alu	Eu	B2g	Big	A28	A18	Eg
Eu	Eu	E ₀	Ea	E ₀	A10+A20+B10+B20	Eg	Eg	Eg	Eg	A1g+A2g+B1g+B2

D_{2h} point group n, 8 irreducible representat bgroups: C., C., C., C., C., C.,

	E	C ₂ (z)	C ₂ (y)	C2 (X)	1	σ (xy)	σ (xz)	σ (yz)	linear, rotations	quadratio
Ag	1	1	1	1	1	1	1	1		x2, y2, z2
B19	1	1	-1	-1	1	1	-1	-1	Rz	xy
B29	1	-1	1	-1	1	-1	1	-1	Ry	xz
B39	1	-1	-1	1	1	-1	-1	1	R _x	yz
Au	1	1	1	1	-1	-1	-1	-1		
B _{1u}	1	1	-1	-1	-1	-1	1	1	z	
B _{2u}	1	-1	1	-1	-1	1	-1	1	У	
B _{3u}	1	-1	-1	1	-1	1	1	-1	×	

Ag

C4h Point Group

Abelian, 6(3) irreducible representations roups of C_{4h} point group: C₅, C₆, C₂, C₄, C_{2h}, S₄

	E	C4(z)	C2	(C4)3	1	(S4)3	σh	S 4	linear, rotations	quadratio
Ag	1	1	1	1	1	1	1	1	Rz	x2+y2, z2
Bg	1	-1	1	-1	1	-1	1	-1		x2-y2, xy
E	1	i -i	-1 -1	-i i	11	i -i	-1 -1	4	R _x +iR _y R _x -iR _y	(xz, yz)
Au	1	1	1	1	-1	-1	-1	-1	z	
B _u	1	-1	1	-1	-1	1	-1	1		
Eu	1	i -i	-1 -1	4	-1 -1	-i i	1	14	x+iy x-iy	
			Pro	duct t	abl	e for (Cab.	poi	at group	
			Ag	Bg	1	E.	Au	B	Eu	7
		Ag	A _g	Bg	1	i,	A _s	B,	Eu	
		Bg	Bg	Ag	1	5,	Ba	A,	Eu	
		1.00	-					1		

	Ag	Bg	Eg	Ag	Bu	Eu
٩,	A _g	Bg	Eg	A _s	Bu	Eu
Bg	Bg	Ag	Eg	Ba	Au	Eu
E,	Eg	Eg	Ag+Bg+Eg	E ₂	Eu	A _a +B _a +E _a
۹.,	Ag	Bs	Es	Ag	Bg	Eg
B.,	B ₀	A _s	Eu	Bg	Ag	Eg
E.,	E,	E,	Au+Bu+Eu	Eg	Eg	Ag+Bg+Eg

D4 Point Group

elian, 5(6) irreducible of D4 point gr C2. C4. D

cter table for D₄ point g 2C4 (z) C2 (z) 2C'2 2C'' 1 1 1

	AI	A ₂	B1	B2	E
A1	A1	A ₂	B1	B ₂	Е
A2	A2	A ₁	B2	B ₁	Е
\mathbf{B}_1	B ₁	B ₂	A ₁	A ₂	E
B ₂	B ₂	B ₁	A ₂	A	E
E	Ε	Е	Е	E	A1+A2+B1+B2

	E	2C4 ()) C;	24	o. 1	204	linear, rotations	quadratic
A	1	1	1		1	1	z	x2+y2, z2
A2	1	1	1		1	-1	Rz	
B 1	1	-1	1	1	1	-1		x2-y2
B ₂	1	-1	1	-	1	1		xy
-	-		Τ.	Ξ.			() (D D)	
E	2	0 Pre	-2		ble	-	(x, y) (R _x , R _y)	
E	2		duct	tal	ble	for	C _{4v} point grou	
E	2	Pre	duct A1	tal	ble B ₁	for B ₂	C _{tv} point grou E	
E	2	Pro A1	A1 A1	tal A2 A2	B1 B1	for B2 B2	C _{4v} point grou E E	
E	2	Pro A1	duct A1	tal A2 A2	B1 B1	for B2 B2	C _{4v} point grou E E	
E	2	Pro A1 A2	A1 A1	tal A2 A2 A1	B1 B1 B2	for B2 B2 B1	C _{4v} point grou E E	
E	2	Pre A ₁ A ₂ B ₁	duct A1 A1 A2	tal A2 A2 A1 B2	ble B1 B1 B2 A1	for B2 B2 B1 A2	C _{4v} point gros E E E E	

C4v Point Group

t Abelian, 5(6) irreducible representations sgroups of C_{4v} point group: C_1, C_2, C_4, C_{2v}

A2	B ₁	B2	E
A2	B ₁	B ₂	Е
AI	B ₂	B ₁	E
B2	A	A ₂	E
B1	A2	A ₁	E
E	Ε	Е	A1+A2+B1+B2

	E	254	C	: (z)	20	2	2 o d	linear, rotations	quadratie
A1	1	1	Г	1	1	C.	1		x2+y2, z2
A:	1	1	Г	1	-	1	-1	Ra	
B1	1	-1	Г	1	1		-1		x2-y2
B ₂	1	-1	Г	1	-	1	1	z	xy
E	2	0	Г	-2	(0	(x, y) (R _x , R _y)	(xz, yz)
		ſ	10				for B2	D _{2d} point grou E	P
		[Al	A ₂	B			9
			A1	A1 A1	A2 A2	B ₁ B ₁	B ₂	E	P
			A1 A2	A1 A1 A2	A2 A2 A1	B ₁ B ₂ B ₂	B2 B2	E	P
			A1 A2 B1	A1 A1 A2 B1	A2 A2 A1 B2	B1 B1 B2 A1	B2 B2 B1	E E E	P

D_{2d} Point Group

not Abelian, 5(6) irreducible representations bgroups of D_{2d} point group: C₁₀, C₂, D₂, C₂₀₀, S₄

C2h Point Group Abelian, 4 irreducible re

 Ag
 1
 1
 1
 Rg
 x².

 Bg
 1
 -1
 1
 -1
 Rg, Ry

 Ag
 1
 1
 -1
 -1
 Rg, Ry

 Bg
 1
 1
 -1
 -1
 z

 Bg
 1
 1
 -1
 -1
 z

 Bg
 1
 1
 -1
 -1
 x, y

Ag Bg Au Bu

E C₂(z) i

C_s Point Group bgroups of C2h point group: C1, Ci, C

ian, 2 is (r) i $\sigma_h \frac{\text{linear}_i}{\text{rotations}}$ quadratic 1 1 $R_z = x^2, y^2, z^2, xy$ 1 1 -1 $R_{y_h} R_y = xz, yz$ r table for C, poi
 E
 σ_h linear, trations
 quadratic

 A*
 1
 1
 x, y, R_g
 x², y², z², xy

 A*
 1
 1
 x, y, R_g
 x², y², z², xy

 A*
 1
 1
 x, y, R_g
 x², y², z², xy



S ₄ Point Group	D ₂ Point Group	C ₄ Point Group	C2 Point Group
Abelian, 3(4) irreducible representations Subgroups of S4 point group: C2	Abelian, 4 irreducible representations Subgroups of D ₂ point group: C ₂	Abelian, 3(4) irreducible representations C ₁ Point Group Subgroups of C ₄ point group: C ₂	Abelian, 2 irreducible representations
Character table for S4 point group	Character table for D ₂ point group	Character table for C4 point group Abelian, 2 irreducible representations	Character table for C2 point group
E S4 C2 (S4) ³ linear, quadratic	E C2 (z) C2 (y) C2 (x) Intear, quadratic	E C4 C2 (C4) linear, quadratic Character table for C1 point group	E C2 linear, quadratic
A 1 1 1 1 Rz x ² +y ² , z ²	A 1 1 1 1 x ² , y ² , z ²	A I I I I I Z.Rz x ² +y ² , z ² E i linear, quadratic	A 1 1 z, Rz x ² , y ² , z ² , xy
B 1 -1 1 -1 z x ² -y ² , xy	B ₁ 1 1 -1 -1 z, R _z xy	B 1 -1 1 -1 x ² -y ² , xy Ag 1 1 R ₁₀ , R ₁ , R ₂ x ² , y ² , z ² , xy, xz, yz	B 1 -1 x, y, R _x , R _y yz, xz
E 1 i -1 -i x+iy; Rx+iRy (xz, yz)	B ₂ 1 -1 1 -1 y, R _y xz	E 1 i -1 -i x+iy; Rx+iRy (yz, xz)	Product table for C2 point group
$\label{eq:response} \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\label{eq:response} \begin{array}{ c c c c c } \hline 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1$	A B A A B B B A

Figure S9. Character table of D_{4h} and its subgroups.

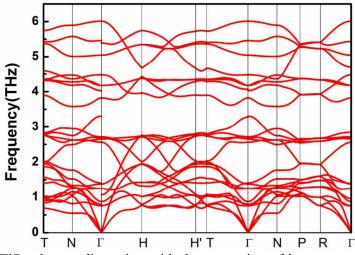


Figure S10. TISe phonon dispersion with the correction of long range interaction of macroscopic electric field induced by polarization of collective ionic motion near Gamma point.

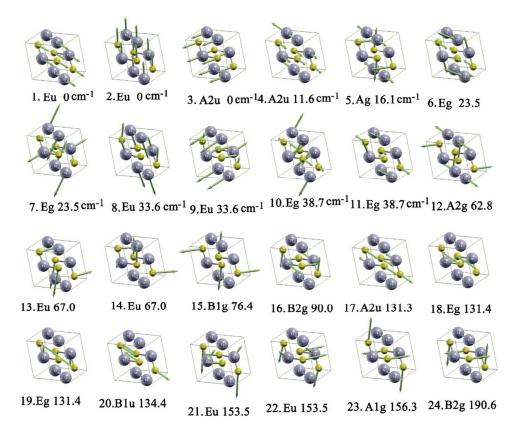


Figure S11. Atom moving directions of phonon modes at Gamma point for bulk TISe.

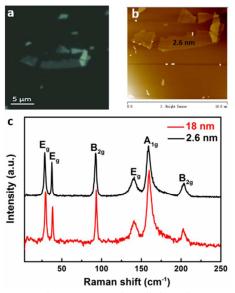


Figure 12. (a) Optical image of a 2.6-nm TlSe flake. (b) AFM image of this flake. (c) The comparison of Raman spectra for two flakes with different thicknesses (18 nm and 2.6 nm).

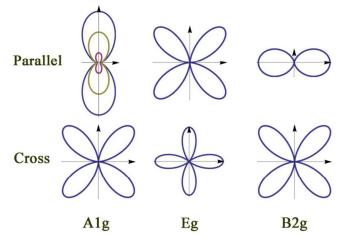


Figure S13. Possible patterns of polar plots for anisotropic Raman intensities simulated according to the Raman tensor.

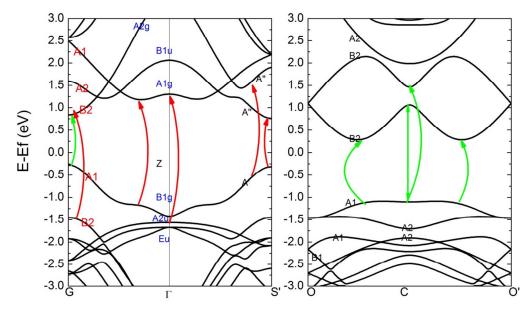


Figure S14. HSE06 obtained band structure of TlSe, the red lines denote the possible [001] polarized light jump, while green lines denote the jump of $[1\overline{1}0]$ polarized light.

A _{2u} , <i>I</i>	Н	E _g pho	onon	B _{2g} pl	nonon	A _{1g} p	honon
A2u, 1	Toe	$H_{ep}(E_g)$	$H_{\rm oe}(A_{2\rm u})$	$H_{ep}(B_{2g})$	$H_{oe}(A_{2u})$	$H_{ep}(A_{1g})$	$H_{oe}(A_{2u})$
$ i\rangle$	$ m'\rangle$	m angle	$ f\rangle$	$ m\rangle$	$ f\rangle$	m angle	$ f\rangle$
$A_{1g}(\Gamma 1)$	A_{2u}	Eu	Eg	B _{1u}	B _{2g}	A_{2u}	A_{1g}
$A_{2g}(\Gamma 2)$	A _{1u}	Eu	Eg	B ₂ u	B _{1g}	A _{1u}	A_{2g}
$B_{1g}(\Gamma 3)$	B_{2u}	Eu	Eg	A _{1u}	A_{2g}	B_{2u}	B_{1g}
$B_{2g}(\Gamma 4)$	B _{1u}	Eu	Eg	A _{2u}	A _{1g}	B_{1u}	B_{2g}
$E_g(\Gamma 5)$	Eu	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	$A_{1g}+A_{2g}+B_{1g}+B_{2g}$	Eu	Eg	Eu	Eg
$A_{1u}(\Gamma 6)$	A_{2g}	Eg	E_u	B_{1g}	B_{2u}	A_{2g}	A _{1u}
$A_{2u}(\Gamma 7)$	A_{1g}	Eg	Eu	B _{2g}	B _{1u}	A_{1g}	A_{2u}
$B_{1u}(\Gamma 8)$	B _{2g}	Eg	Eu	A _{1g}	A _{2u}	B_{2g}	B_{1u}
$B_{2u}(\Gamma 9)$	B _{1g}	Eg	Eu	A _{2g}	A _{1u}	B_{1g}	B_{2u}
$E_u(\Gamma 10)$	Eg	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	Eu	Eg	Eu

Table S1 Selection rule for A_{2u} Polarization light, [001]-direction.

	E _u , H _{oe}	E _g phonon	1	B ₂	g phonon	A _{1g}	phonon
-	2u, 110e	$H_{ep}(E_g)$	$H_{oe}(E_u)$	$H_{\rm ep}({\rm B}_{\rm 2g})$	$H_{oe}(E_u)$	$H_{\rm ep}(A_{1g})$	$H_{oe}(E_u)$
$ i\rangle$	m' angle	$ m\rangle$	$ f\rangle$	$ m\rangle$	$ f\rangle$	$ m\rangle$	$ f\rangle$
A _{1g}	Eu	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$
A _{2g}	Eu	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$
B_{1g}	Eu	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$
B_{2g}	Eu	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	Eu	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	E_u	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$
Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eu	$\begin{array}{c} A_{1g} + A_{2g} + \\ B_{1g} + B_{2g} \end{array}$	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	E_{g}
A_{1u}	Eg	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	E_u	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$
A _{2u}	Eg	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	Eu	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$
B _{1u}	Eg	$A_{1g} + A_{2g} + B_{1g} + B_{2g}$	E_u	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$
B _{2u}	Eg	$A_{1g}+A_{2g}+B_{1g}+B_{2g}$	Eu	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$
E _u	$\begin{array}{c} A_{1g} + A_{2g} + \\ B_{1g} + B_{2g} \end{array}$	Eg	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	$\begin{array}{c} A_{1g}\!+\!A_{2g}\!+\!B_{1g}\!+\!\\ B_{2g} \end{array}$	E _u	$\begin{array}{c}A_{1g}\!+\!A_{2g}\!+\!B_{1g}\!+\\B_{2g}\end{array}$	Eu

Table S2 Selection rule for E_u Polarization light, [1 -1 0] direction.

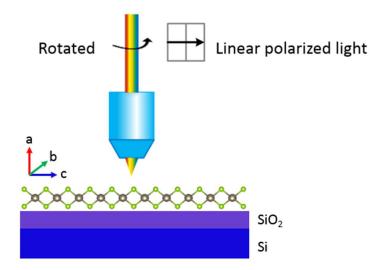


Figure S15. Schematic diagram of the ADRDM measurement.

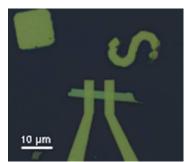


Figure S16. The optical image of a typical TISe two-terminal device.

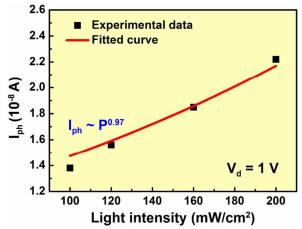


Figure S17. Experimental data fitting of photocurrent curves as changing of light intensities shown in Figure 5b.

Analysis of Raman anisotropy

The one-step Raman spectroscopy contains three micro-steps: (1) An electron absorbs a photon and jumps into a high energy level state. The scattering matrix of this process can be described as $\langle m | H_{eo} | i \rangle$, where H_{eo} is the Hamiltonian of electron-photon interaction. At first-order approximation, H_{eo} can be described as

$$H_{eo} = -\frac{e}{mc} \mathbf{A}(\mathbf{r}) \mathbf{P}$$
(1)

where *c* is the speed of light, $\mathbf{A}(\mathbf{r})$ is the vector potential of optical electromagnetic field and **P** is the momentum of electron. As the vector potential is an external field, the Schrödinger group is determined by **P**; (2) An excitation electron interacts with a phonon. In one-step Raman spectroscopy, only the phonon nearby the center zone can be involved into the electron-photon interaction. The scattering matrix of this process can be described as $\langle m' | H_{ep} | m \rangle$, where H_{ep} is the Hamiltonian of electron-phonon interaction, which can be expressed as

$$H_{ep} = \Delta V(\mathbf{r}) \tag{2}$$

where ΔV is the change of potential caused by the phonon vibration. It is obvious that the Schrödinger group of this Hamiltonian follows the symmetry of corresponding phonon mode; (3) The last step is also an electron-photon interaction process, in which the excitation electron emits a photo when jumping into a low energy level state. The expression of Hamiltonian is same as the first step. In summary, the whole process of one-step Raman spectroscopy based on the Fermi-Gold rule can be described as,

$$I_{\nu}\left(E_{L}\right) = \left|\sum_{i,m,m'} \frac{\left\langle f \left| H_{op} \left| m' \right\rangle \left\langle m' \right| H_{ep}^{\nu} \left| m \right\rangle \left\langle m \left| H_{op} \left| i \right\rangle \right|^{2} \right. \right.}{\left(E_{L} - \Delta E_{mi}\right) \left(E_{L} - \hbar \omega_{\nu} - \Delta E_{m'i}\right)}\right|^{2}$$
(3)

where *I* is the scattering strength, $\Delta E_{mi} = E_m - E_i - i\Gamma$, m(m') represents the intermediate state and Γ is a broadening factor, corresponding to the lifetime of photo-excited electrons.

For the active Raman modes in TlSe, their Raman tensor *R* can be expressed as follows

$$R(A_{1g}) = \begin{pmatrix} a \cdot e^{i\phi_a} & 0 & 0 \\ 0 & b \cdot e^{i\phi_b} & 0 \\ 0 & 0 & b \cdot e^{i\phi_b} \end{pmatrix};$$
(4)

$$R(\mathbf{B}_{2g}) = \begin{pmatrix} 0 & 0 & d \cdot e^{i\phi_d} \\ 0 & d \cdot e^{i\phi_d} & 0 \\ 0 & 0 & 0 \end{pmatrix};$$
 (5)

$$R_{1}(\mathbf{E}_{g}) = \begin{pmatrix} 0 & f \cdot e^{i\phi_{e}} & 0 \\ f \cdot e^{i\phi_{e}} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$
 (6)

where ϕ_a , ϕ_b , ϕ_d , ϕ_e are phases of Raman tensor elements. The Raman intensity I(j) of the mode *j* can be expressed as

$$I(j) \propto \left| \widehat{\mathbf{g}}_{s} \cdot \overline{\widetilde{R}}(j) \cdot \widehat{\mathbf{g}}_{i}^{T} \right|, \tag{7}$$

where \hat{g}_i and \hat{g}_s are the polarized direction of the incident and scattered lights, respectively.

In the parallel configuration, since the angle between \hat{g}_i and \hat{g}_s is 0°, the Raman intensity for A_g mode is described as

$$I^{\text{Para}}\left(A_{1g}\right) \propto \left(\cos^{2}\left(\theta\right) + \frac{|a|}{|b|} \cdot \sin^{2}\left(\theta\right) \cdot \cos\phi_{ab}\right)^{2} + \frac{|a|}{|b|} \sin^{4}\left(\theta\right) \sin^{2}\left(\phi_{ab}\right);$$
(8)

for B_{2g} mode, it is described as

$$I^{\text{Para}}(\mathbf{B}_{2g}) \propto |d|^2 \cos^4(\theta); \qquad (9)$$

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and for E_g mode, it is described as

$$I^{\text{Para}}\left(\mathbf{E}_{g}\right) \propto 4|f|^{2}\sin^{2}\left(2\theta\right).$$
(10)

In the cross configuration, the angle between \hat{g}_i and \hat{g}_s is 90°, and the Raman intensity for A_g mode is described as

$$I^{\text{Cross}}\left(A_{1g}\right) \propto \left(|a| - |b|\right)^{2} \sin^{2}\left(\theta\right) \cos^{2}\left(\theta\right); \qquad (11)$$

for B_{2g} mode, it is described as

$$I^{Cross}\left(\mathbf{B}_{2g}\right) \propto |d|^{2} \sin^{2}\left(2\theta\right); \tag{12}$$

and for Eg mode, it is described as

$$I^{Cross}\left(\mathrm{E}_{g}\right) \propto |f|^{2} \cos^{2}\left(2\theta\right).$$
(13)

In all these equations, θ is the angle between the probe direction and x-axis direction of polar plots, and $\phi_{ab} = \phi_a - \phi_b$ defines phase difference. From Eqs. (8) to (13), one can notice that the polar plots depend not only on the configuration but also on the phase difference of Raman tensor. We simulated the polarized Raman intensity based on the Raman tensor, and the possible patterns of polar plots are shown in Figure S12. The calculated curves match well with the experimental ones (Figure 2c). The polar plots of E_g modes are 4-leaf patterns, and the pattern for the cross configuration seems to be rotated by 45° in comparison to that in the parallel configuration. In the parallel configuration, the polar plots of A_{1g} and B_{2g} modes are 2-leaf patterns, while they are changed to 4-leaf patterns under cross configuration. According to Eq. (8), the $\frac{|a|}{|b|}$ value determines the direction of the main axis: if $\frac{|a|}{|b|}$

>1, the main axis is along the y-direction.