Supporting Information

Single Layer Lead Iodide: Computational Exploration of Structural, Electronic and Optical Properties, Strain induced Band Modulation and the Role of Spin-orbital-Coupling

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1. Phonon dispersion of bulk and monolayer PbI₂

To take into account the polarity, Longitudinal Optical–Transverse Optical (LO-TO) splitting is rather large in the 2H bulk PbI₂ crystal. According to our calculations, the infrared active modes E_u and A_{2u} split into $E_u(LO)$ 59.71 cm^{-1} , $E_u(TO)$ 110.41 $cm^{-1}A_{2u}(LO)$ 107.07 cm^{-1} and $A_{2u}(TO)_{117.4} cm^{-1}$, which are in well consistent with the experimental values (Phys. Status Solidi B 73 (1976) 587). The Raman active modes of bulk PbI₂, E_g 82.39 cm^{-1} and A_{1g} 95.40 cm^{-1} , are also in good agreement with experimental (Phys. Status Solidi B 73 (1976) 587) and other theoretical values (Phys. Rev. B 55, 8219 (1997)).

bulk	Eu(TO)	Eu(LO)	Eg	Alg	A2u(TO)	A2u(LO)
experiment	51.70	106.07	78.05	98.07	95.07	113.08
Our work	59.71	110.41	82.39	95.40	107.07	117.41
monolayer	Eu(TO)	Eu(LO)	Eg	A1g	A2u	
Our work	59.71	101.07	77.39	88.73	116.08	

Table S1. Zone center phonon frequencies (in cm⁻¹) for bulk and monolayer PbI_2 obtained from calculation using Phonopy code and from various experimental measurements (Phys. Status Solidi B 73 (1976) 587).

In the single layer PbI₂, a large LO-TO splitting can be seen in E_u modes, that is $E_u(LO)$ 59.71 cm^{-1} and $E_u(TO)$ 101.71 cm^{-1} . At the same time, the frequencies of Raman active modes decrease with respect to LO-TO splitting. It's interesting that there's no LO-TO splitting in A_{2u} mode possibly due to the confinement effects. From bulk form to quasi two dimensional PbI₂, the most significant change goes to iodine atoms due to their special positions in the layers, where the strong effect from neighboring layers is gone. Compared to phonon spectrum of bulk PbI₂ in Fig. S1, we find that the information about phonon dispersion along $\Gamma - A$ (which is along the z direction in real space) is lost. As we can see in our manuscript, the dimensional confinement effects also make PbI₂ change from a direct band gap in bulk form to an indirect band gap semiconductor in 2D monolayer form.



Fig. S1. The phonon spectrum for bulk PbI_2 without (a) and with (b) LO-TO splitting. Similar to (a) and (b), (c) and (d) plotted phonon spectrum for monolayer PbI_2 without and with LO-TO splitting.

2. The electronic and optical structure of bulk PbI₂

The 2H phase bulk PbI₂ that takes the layered CdI₂ structural type has a hexagonal lattice as depicted in Fig. S2. Our optimized lattice parameters are a = 4.60 Å and c = 7.04 Å, which are well consistent with the experimental lattice constants a = 4.56 Å and c = 6.99 Å (J. Phys.: Condens. Matter, 2, 5285 (1990)). The associated Brillouin zone and the electronic band structures of bulk PbI₂ are shown in Fig. S2. As shown in Fig. S2(c), the smallest band gap of bulk PbI₂ calculated with PBE functional appears at A point, which is in good agreement with other calculations (Phys. Rev. B 9, 1652 (1974)). The band gap value of bulk PbI₂ estimated

using this method is about 2.34 eV. The lowest conduction band mainly comes from p_z orbital of Pb atoms in bulk PbI₂, while the highest valence band comes from p_z orbitals of I atoms. In bulk PbI₂, the spin orbit coupling is very important because it not only reduces the band gap by about 0.85 eV but also splits degenerated bands. Combined HSE06 functional and spin orbit interaction, we can get a gap value of 2.47 eV, which is in good agreement with experimental results (Phys. Rev. 171, 1047, (1968); Phys. Rev. B 7, 1539 (1973); J. Appl. Phys. 92, 7219 (2002)).



Fig. S2. (a) The crystal structure of bulk PbI_2 and (b) associated first Brillouin zone path. The electronic band structure of bulk PbI_2 calculated with (c) PBE, (d) PBE+SOC and (e) HSE+SOC method.

Some research groups have conducted experiments about dielectric function of bulk PbI_2 (J. Phys. C: Solid State Phys. 10 761(1977), J. Appl. Phys., 92, 1215 (2002)). According to experiment data, the absorption edge of imaginary part of dielectric function should be around 2.5 eV. Basically, there're three peaks above the fundamental gap, which can be found around 2.9 eV, 3.2 eV and between 3.8 and 4.5 eV. Correspondingly, real part of dielectric function exhibits peak around 2.5 eV, a peak at 2.8 eV, a peak around 3.2 eV and also a minimum at about 4.5 eV.



Fig. S3. The imaginary (a) and real (b) part of dielectric function of bulk PbI2 calculated with HSE+SOC method. The incident light direction is set to be z direction.

As shown in Fig. S3 (a), the absorption edge is located at about 2.5 eV. The imaginary part of dielectric function ε_2 of bulk PbI₂ shows peaks around 3.4 eV, 3.9 eV and 4.7 eV. One can notice that the anisotropy of $\varepsilon_2^{\frac{1}{2}}$ and $\varepsilon_2^{\frac{1}{2}}$ is very small, which is in agreement with Ahuja et al.'s work (J. Appl. Phys., 92, 1215 (2002). We also present the real part of dielectric function of bulk PbI₂ in Fig S3 (b). This exhibits a peak around 3.3 eV, a peak around 3.9 eV and 4.6 eV, and also a minimum around 3.5 eV. Compared to experimental data, our calculations have captured the main features of dielectric function of bulk PbI₂, which is in consistent with other theoretical calculations (J. Appl. Phys., 92, 1215 (2002)). Although the calculation using HSE06 with spin orbit coupling cannot predict exactly the same photon energy positions as experimental results, it gives relative accurate absorption band edge.

3. The ideal strength of monolayer PbI₂

To study the mechanical stability of PbI₂ under biaxial strain, we present stress-strain relation in Fig. S4. To calculate the ideal strength, which can be defined as the highest attainable stress under a uniform strain field in a defect-free crystal at zero temperature, the method described in Phys. Rev. B 76, 064120 (2007) was used. In order to compare with experiments and other calculations, we rescale the stress by Z/d_0 to obtain the equivalent stress, where Z is the vacuum space along z direction for monolayer PbI₂ and d_0 is the effective thickness of bulk PbI₂. Here the vacuum space is Z = 20 Å and we choose d_0 as one half of the lattice constant along z direction of bulk PbI₂, i.e. $d_0 = 3.52$ Å. Fig. S4 represented stress-strain relation in a larger range from -25% to 25%.



Fig. S4. The stress-strain relation of monolayer PbI_2 under biaxial strain (left axis) and the bond between Pb and I atoms (right axis).

The stress in monolayer increases slowly with increasing tensile strain and there is no fracture under 25%, which suggests PbI_2 can sustain a tensile strain higher than 25%. While for

compressive strain, stress loses its linear character when the strain is 22 %. An ideal strength is 24 GPa for monolayer PbI_2 with a critical strain of 22%. The predicted critical strain for single layer PbI_2 is close to that of other 2D materials such as graphene (Phys. Rev. B 76, 064120 (2007), Phys. Rev. B 89, 184111 (2014)), MoS₂ (Phys. Rev. B 85, 235407 (2012)), black phosphorus (Appl. Phys. Lett. 104, 251915 (2014), Nanotechnology 25 (2014) 455703), which indicates great mechanical flexibility in 2D PbI₂ monolayer. The above calculations indicate that the 2D PbI₂ layers could support 10-20% strain.

The pseudopotential we used here is PAW-PBE type, in which the outmost cutoff radius of I atoms is RCUT(I) = 2.3 a.u. and that of Pb is RCUT(Pb) = 3.1 a.u.. Thus the results obtained from this pseudopotential for PbI2 can be seen as reliable on the condition that the bond between I and Pb is larger than the minimum distance from I to Pb, which is RCUT(I) + RCUT(Pb) = 5.4 a.u. (i.e. 2.86 Å). The bond between I and Pb as a function of strain we considered in our manuscript is given in Fig. S4. It is can be easily seen that the bond decreases almost linearly with compressive strain applied, and under all various strains, the bond between I and Pb is larger than 3 Å. In this case, we believe our results are reliable.

4. The mobility of monolayer PbI2 estimated using phonon limited scattering model

The electronic transport properties of a material are largely determined by its carrier mobility, which is heavily influenced (but not completely) by its effective mass reversely. Thus, here following the Referee's suggestions, we have performed effective mass and mobility calculations of carriers in monolayer PbI2 along both x and y directions using phonon-limited scattering model (Physical Review **1950**, 80, (1), 72-80, Applied Physics Letters **2011**, 99, (22), 222108, IEEE Transactions on **1994**, 41, (12), 2357-2362).

The formula of phonon-limited scattering model to estimate carrier mobility in 2D material is

$$\mu_{i,j} = \frac{e\hbar^{3}C_{i_{2}D}}{k_{B}Tm_{i,j}^{*}m_{j_{d}}(E_{i,j})^{2}}$$
(1)

Where i indicates the transport direction (x or y) and j denotes the type of carrier (electron or hole), respectively. In this case, $m_{i,j}^*$ represents the effective mass of electron (or hole) along x (or y) direction and m_{j_d} is the effective mass of density of states estimated by the formula $m_{j_d} = \sqrt{m_{x,j} m_{y,j}}$. The effective mass of electrons and holes can be obtained according to the formula $m^* = \hbar^2/(\partial^2 E/\partial^2 k)$ from the band structure. The deformation potential constant $E_{i,j}$ is defined as $E_{i,j} = \Delta E_i/(\Delta l/l_{i0})$, where ΔE_i is energy change of the conduction band maximum of electron or that of the valence band minimum for hole induced by the lattice compression or dilatation along i (x or y) direction with a step of $\Delta l/l_{i0} = 0.5\%$. Here l_{i0} is the

lattice constant in the transport direction and $\triangle l$ is the deformation of l_{i0} . The elastic moduli of the longitudinal acoustic C_{i_2D} in the propagation direction is defined as $C_{i_2D} = 2(E - E_0)/[S_0(\triangle l/l_{i0})^2]$, where *E* and E_0 are the total energy with lattice changes in the transport direction and at equilibrium state, respectively, and S_0 is the area of the 2D material at equilibrium state. The temperature used for the mobility calculations was 300 K.

In order to calculate the carrier mobility of monolayer PbI₂, we construct a $\sqrt{3} \times 1$ supercell with a = 8.07 Å, b = 4.66 Å as shown in Fig. S5(a) (red dash rectangle). The corresponding electronic band structure is shown in Fig. S5(b). According to our calculation, monolayer PbI₂ is a wide indirect band gap semiconductor with a gap value of about 2.63 eV. It can be seen that the value of valence band (VB) at $k_1(0.33, 0, 0)$ has little difference with that at $k_2(0, 0.22, 0)$, which indicates both may contribute to hole mobility of monolayer PbI₂. The effective mass and carrier mobility of single layer PbI₂ is presented in Table S2.



Fig. S5 (a) The original (black solid parallelogram) and $\sqrt{3} \times 1$ supercell (red dash rectangle) crystal structure of monolayer PbI₂. (b) The electronic band structure of monolayer PbI₂ in $\sqrt{3} \times 1$ supercell calculated by HSE06 functional with spin orbit coupling. The Fermi level is shifted to the top of valence band.

The predicted carrier mobility of monolayer PbI_2 is generally not very large, but asymmetric between electrons and holes, where electrons are more movable than holes in both x and y directions. Regarding the directional anisotropy, the electrons mobility along x direction is larger than that along y direction, that is, $122.22 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ versus $94.99 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, but the difference is not very distinct. This little difference is mainly a consequence of the small difference in effective mass along x and y directions. The value of deformation potential for electron in monolayer PbI₂ is about 3.60 eV at both directions, which is comparable with typical values of graphene (5.14 eV Nanoscale 4, 4348-4369 (2012)), MoS₂ (3.9 eV Phys. Rev. B 85, 115317 (2012)) and h-BN (3.66 eV Appl. Phys. Lett. 99, 2108(2011)). Our predicted elastic modulus of

monolayer PbI_2 in x direction is about 24 times smaller than graphene (Nanoscale 4, 4348-4369 (2012)), which indicates PbI_2 is very soft. Smaller elastic modulus and larger effective mass leads to a relative small electron mobility along x direction for monolayer PbI_2 .

As for the holes mobility of monolayer PbI₂ at k_1 and k_2 , the directional anisotropic is very large. In detail, the holes mobility at k_1 point along x direction is about ten times larger than that along y direction, while that for k_2 behaves contrarily. As shown in Fig. S5(b), the conduction band disperses more strongly than valence band along both $\Gamma - X$ and $\Gamma - Y$ directions, indicating a larger effective mass for holes. Compare to electrons in monolayer PbI₂, although deformation potential along y direction decreases, about 8 times increase of the effective mass of holes at k_1 point (4.20 m_e , very heavy) still directly leads to a sharp reduce holes mobility along y direction. Similarly, the increase in effective mass of holes at k_2 point along x direction reduces holes mobility along x direction. Thus, for monolayer PbI₂, effective mass is the key issue that affects carrier mobility.

Carrier type	C _{2D_x} (Jm ⁻²)	С _{2D_у} (Jm -2)	Effective mass(ΓX)	Effective mass(ΓY)	E _{1_x} (eV)	E _{1_y} (eV)	$\mu_{\chi}\left(\frac{cm^2}{sV}\right)$	$\mu_y\!\left(\!\frac{cm^2}{sV}\!\right)$
electron	14.60	14.24	0.42	0.53	3.59	3.60	122.22	94.99
Hole (k ₁)	14.60	14.24	0.65	4.20	2.23	3.04	58.30	4.99
Hole (k ₂)	14.60	14.24	2.57	1.10	3.67	1.57	5.35	66.58

Table S2. The predicted carrier mobility of monolayer PbI₂. C_{2D_x} (C_{2D_y}) and $E_{1_x}(E_{1_y})$ are the dimensional elastic modulus and deformation potential along x(y) direction, respectively. Motilities μ_x and μ_y are calculated using equation (1) with the temperature T set to 300 K.

In summary, we have shown that electron is the dominated type of carriers and electron is more mobile along x direction in monolayer PbI₂. The electron mobility along x direction is estimated to be 122.22 cm²V⁻¹S⁻¹, which is much smaller than that of graphene (~ 10⁴ cm²V⁻¹S⁻¹, Nature Nanotech. 5, 487–496 (2010)) but comparable to MoS₂ (~ 200 cm²V⁻¹S⁻¹ in single layer form, Nature Nanotech. 6, 147–150 (2011); > 100 cm²V⁻¹S⁻¹ in thin film form, Nat. Commun. 3, 1011(2012)) and Si thin film (~ 121 cm²V⁻¹S⁻¹, Electron Device Letters, IEEE, 1996, 17(4), 160-162). However, pristine graphene does not have a reasonable bandgap, a property that is essential for many applications, including transistors. In contrast, single layer MoS2 has a large intrinsic bandgap of 1.8 eV (Phys. Rev. Lett. 105, 136805 (2010)). Similarly, monolayer PbI₂ not only demonstrates same order of magnitude mobility as that of monolayer MoS₂ but with a sizable gap. Therefore, we might expect monolayer PbI₂ could complement graphene in potential applications such as transistors just like single layer MoS₂ (Nature Nanotech. 6, 147–150 (2011)).