



Mechanical stability and electronic and optical properties of AA and AA'' Janus 1T PdXY (X, Y = S, Se, Te) bilayers

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Abstract Using first-principles calculations, we report the electronic, mechanical and optical features of 1T PdSSe, PdSTe and PdSeTe bilayers, belonging to the AA and AA'' stacking orders. Both AA and AA'' are exactly aligned and possess three types of interlayer chalcogenide planes; they, however, differ in the way the chalcogenides are superimposed in the two layers. With the spin-orbit coupling involved, the majority of the materials exhibit a semimetallic or a metallic nature, except for the two AA PdSSe bilayers with S-S and Se-Se interlayer planes, and the AA'' system with an S-Se interlayer plane; these are semiconductors of indirect bandgaps, not exceeding 0.51 eV. All of the eighteen structures are mechanically stable, showing positive elastic constants. Along the parallel and perpendicular directions, and for the various regions of the electromagnetic spectrum, the absorption coefficient demonstrates high values. The maximum reflectivity of the materials is attained for the PdSSe AA bilayers with S-S interlayers, within the ultraviolet (UV) range; this makes it a suitable candidate for the fabrication of UV shields. Compared to their monolayer analogs, the bilayers show better absorption and reflectivity, throughout most of the electromagnetic spectrum. The disparate elastic and optical characteristics of the bilayer systems can provide hints that are essential for building robust optoelectronic devices and that can be tuned for various technological applications.

1 Introduction

After the successful isolation of graphene in 2004 [1,2], two-dimensional (2D) materials have attracted more attention due to the novel electronic, mechanical and optical properties they possess; such features can be exploited in a wide range of applications including field effect transistors, energy storage, photocatalyst technology and biomedical applications [3–7]. Among the innumerable 2D materials, layered transition metal dichalcogenides (TMDs) have emerged; they are usually represented by the chemical formula MX_2 , where M is a transition metal and X is a chalcogen $X=[S, Se, Te]$. The MX_2 structures are characterized by remarkable physical properties and sizable band gaps that can be tuned by different methods [8–11].

2D MoX_2 and WX_2 were the first TMDs to be studied, showing a transition from direct to indirect bandgap, as one goes from monolayer to bulk [12]. The electronic properties and stability of many TMDs including $M=Ti, Zr, Pt, Hf, V, Nb$ and Cr have followed, showing fascinating characteristics that make them useful in different applications [8,13]. These properties can be further enhanced by applying strain and/or an electric field, or even by doping [14–16].

Despite being known since the 1960s [17], layered structures of Pd TMDs remained unexplored due to the economic cost of Pd. However, these structures started to gain momentum, as soon as monolayer and few layered materials were deemed important for nanoelectronic applications. Theoretically, the electronic, mechanical, optical and thermoelectric properties of monolayer PdS_2 and $PdSe_2$ have been extensively studied by many authors [15,16,18]. The Dirac semimetal $PdTe_2$ has also been heavily researched [19–23]. On an experimental level, the use of X-ray diffraction was used to investigate the PdS_2 and pyrite-like types of $PdSe_2$ under large pressures reaching 30 GPa [24]. Pentagonal $PdSe_2$ monolayers have been recently exfoliated by Oyedele et al. [25]. Type II Dirac fermions in $PdTe_2$ were also experimentally realized, using angle-resolved photoemission spectroscopy [26].

In addition to the interesting features of $PdSe_2$ monolayers, building up an additional layer, to form bilayers, can exhibit significant properties that can be implemented in $PdSe_2$ -based devices [27]. For instance, bilayer pentagonal $PdSe_2$ was grown on monolayer and bilayer graphene [28], where it has been reported that a shift in the bandgap occurs, when the bilayers are built on different substrates; this makes it possible to tune the electronic or optoelectronic properties for potential technological applications. Electronic and optical properties of PdS_2 and $PdSe_2$ bilayers, with various stacking possibilities, were further theoretically inspected, confirming that the bandgap is affected by the way the layers are piled up [16,27,29–32].

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Due to their distinctive properties that differ from those of their PdX_2 analogs, new 2D TMDs—named Janus structures—became a hot spot of research; they generally have the formula MXY , with $X \neq Y$. The structures are basically formed by attaching the metal atom to two different chalcogens on both sides, resulting in a breaking of the out-of-plane symmetry. The research on these materials is still in its infancy; despite the challenges that hinder the synthesis of these materials, some experimental achievements made it through, such as Janus MoSSe [33, 34] and WSSe [35]. Very recently, the Raman spectra of one layered MoSSe and WSSe have also been computed [36].

Many theoretical studies have been conducted to investigate the electronic structure, stability and thermoelectric properties of the Janus materials [37–39]; yet, Janus PdXY systems—in particular—have not been lately the center of attention. Thermometric properties of 1T PdSSe , PdSTe and PdSeTe have been first considered in our previous work, showing better performance over 1T PdS_2 and PdSe_2 [40]. These systems, as well as the Pt dichalcogenides, were later investigated by [41]. Not long ago, we have examined the effect of compressive and tensile biaxial strains on the Pd Janus monolayers [42].

Owing to the asymmetry of the MXY configuration, a wide range of stacking orders for bilayer structures are possible, making them a rich area for investigation. Depending on how the upper monolayer is stacked, [43, 44] argue that the nature of the band gap can be either direct or indirect in bilayer Janus MXY ($M=\text{Mo}, \text{W}$). A. Kandemir *et al.* [45] investigated the stability of different types of WSSe bilayers, showing that only three of them depict unique Raman characteristics. Up to our knowledge, no work has yet tackled bilayer Pd Janus structures.

In this research paper, we specifically explore the properties of, what we will call, the AA and AA'' stacking orders in bilayer 1T PdSSe , PdSTe and PdSeTe . Considering the three possible interlayer planes X-X, Y-Y and X-Y, this gives rise to six configurations per PdXY structure. The rest of the paper is organized as follows: the computational methodology, used in the subsequent calculations, is given in Sect. 2. Sections 3.1, 3.2 and 3.3 are devoted to the electronic, elastic and optical properties of the systems in question. Finally, a summary of the results is presented in Sect. 4.

2 Computational details

All electronic properties are calculated using first-principles methods, based on density functional theory (DFT), as implemented in the Quantum Espresso (QE) code [46]. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) [47] scheme is used to describe the electron exchange and correlation functional, with a norm-conserving (NC) Troullier-Martins (TM) pseudopotential [48]. The van der Waals (vdW) correction to the GGA functional was taken into account, using Grimme's DFT-D semi-empirical method [49, 50]. We adopt a $16 \times 16 \times 1$ K-points Monkhorst-Pack and a plane wave energy cutoff of 90 Ry to achieve well-converged results. To avoid unwanted interactions between the periodic images of the bilayers, a vacuum spacing of at least 15 Å was used along the nonperiodic z-direction. During the structural relaxation process, the positions of the atoms are completely relaxed until the forces on each one are less than 10^{-4} Ry/au. All the calculations are performed with the spin-orbit coupling (SOC) effect included.

The THERMO_PW code [51] is then used to obtain the elastic constants from energy-strain relationships; these are crucial to verify the mechanical stability of the materials. The linear optical properties of the bilayers are calculated using the epsilon.x toolset of QE [52]. This provides the real and imaginary parts of the dielectric tensor from which physical quantities, such as the absorption coefficients and reflectivity can be determined.

3 Results and discussion

3.1 Electronic band structure and density of states (DOS)

The side and top views of the AA and AA'' bilayers, with X-Y interlayers, are displayed in Fig. 1. These are formed by putting together two PdXY monolayers, each of which belong to the C_{3v} point group. In both types, the two monolayers are exactly aligned. The difference lies in how the chalcogenide planes are stacked. In the AA type, the X (Y) atoms in the upper monolayer lie above the X (Y) atoms in the monolayer beneath. In contrast, if the X atoms in the upper monolayer are exactly above the Y atoms in the bottom monolayer (and vice-versa), the structure will be referred to as AA''. AA structures with an X-Y, X-X and Y-Y interlayer planes will be labeled as AA₁, AA₂ and AA₃, respectively. Likewise, it is understood that AA₁'', AA₂'', and AA₃'' correspond to AA'' structures with X-Y, X-X and Y-Y interlayer planes. It is essential to state that the AA' label was not used to refer to the second stacking order, because this term is reserved (in the literature) to aligned bilayer structures with the Pd atoms, of one monolayer, above/below the chalcogens of the other.

The AA₁ and AA₁'' structures belong to the C_{3v} point group. While the AA₂ and AA₃ bilayers pertain to the D_{3h} point group, the AA₂'' and AA₃'' are represented by the D_{3d} point group. To migrate from one type to another within the same stacking order, the chalcogen layers have to be swapped accordingly. The description of each system can be found in Table 1.

Fig. 1 Top and side views of a 3×3 supercell of an AA bilayer and an AA'' bilayer—with X-Y interlayer planes—showing the interlayer distances d_1 and d_2 . Blue spheres are Pd atoms; yellow and green spheres refer to the X and Y chalcogens. Structures with X-X or Y-Y interlayer planes can be easily obtained by swapping the chalcogen planes in the upper or lower monolayers. The planar a and b directions are also shown

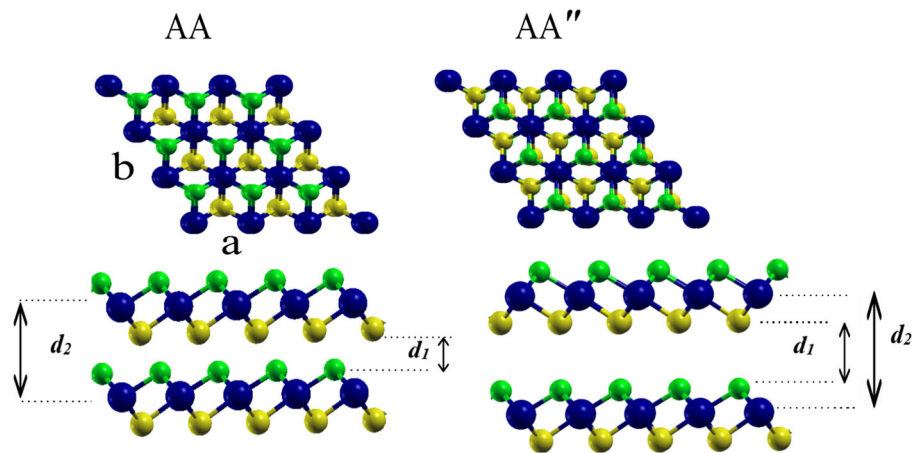


Table 1 The equilibrium lattice parameters (a_0), the interlayer distances d_1 and d_2 , the formation energies (ϵ_f), the bandgaps E_g and the phase of the various AA and AA'' bilayer materials. “—” means not applicable

Material	Type	Interlayer	$a_0(\text{\AA})$	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$\epsilon_f(\text{eV})$	$E_g(\text{eV})$	Phase
PdSSe	AA ₁	S-Se	3.656	2.063	4.785	−0.371	—	Metallic
	AA ₂	S-S	3.626	3.528	6.058	−0.126	0.448	Semiconductor
	AA ₃	Se-Se	3.624	3.743	6.563	−0.146	0.503	Semiconductor
	AA'' ₁	S-Se	3.631	3.577	6.241	−0.144	0.264	Semiconductor
	AA'' ₂	S-S	3.635	1.950	4.449	−0.385	—	Semimetallic
	AA'' ₃	Se-Se	3.675	2.259	4.987	−0.282	—	Semimetallic
PdSTe	AA ₁	S-Te	3.801	2.053	4.472	−0.751	—	Metallic
	AA ₂	S-S	3.778	2.064	4.738	−0.696	—	Metallic
	AA ₃	Te-Te	3.775	3.936	6.941	−0.180	—	Semimetallic
	AA'' ₁	S-Te	3.814	2.751	5.426	−0.333	—	Metallic
	AA'' ₂	S-S	3.722	1.890	4.375	−0.602	—	Metallic
	AA'' ₃	Te-Te	3.869	2.484	5.313	−0.404	—	Metallic
PdSeTe	AA ₁	Se-Te	3.866	2.185	4.966	−0.684	—	Metallic
	AA ₂	Se-Se	3.846	2.669	5.335	−0.407	—	Metallic
	AA ₃	Te-Te	3.816	3.878	6.796	−0.221	—	Metallic
	AA'' ₁	Se-Te	3.862	2.959	5.745	−0.305	—	Metallic
	AA'' ₂	Se-Se	3.822	2.055	4.756	−0.653	—	Metallic
	AA'' ₃	Te-Te	3.908	2.436	5.259	−0.527	—	Metallic

The interlayer distance separating the chalcogen planes (d_1), and that between the planes of the Pd atoms (d_2), can be measured (Fig. 1). These values, as well as the equilibrium lattice constants, are summarized in Table 1. For the AA bilayers, d_1 and d_2 are smaller if the superimposed planes are made of different chalcogen atoms; contrarily, if the bilayers belong to the AA'' stacking order, d_1 and d_2 are larger when the interlayer planes consist of different atomic species.

The formation energies (ϵ_f) can be defined as the energies needed to build the bilayer materials, by bringing together the corresponding monolayers. Mathematically, this can be expressed as:

$$\epsilon_f = E_{PdXY}^{bi} - 2E_{PdXY}^{mono},$$

where E_{PdXY}^{bi} and E_{PdXY}^{mono} are the bilayer and monolayer energies, respectively, as obtained from ground state DFT+SOC calculations. The values of ϵ_f , found in the 7th column of Table 1, are all negative indicating that all structures are energetically favorable.

Before discussing the bilayer structures, it is instructive to review the properties of the 1T monolayers, from which they are derived (Fig. 2). With the SOC turned on, a 1T PdSSe monolayer is a semiconductor with an indirect bandgap of 0.633 eV. On the other hand, monolayered PdSTe and PdSeTe are both semimetallic. With the exclusion of the SOC, and for a scalar relativistic PBE+TM pseudopotential calculation, the Janus Pd monolayers were all predicted to be semiconductors with indirect bandgaps

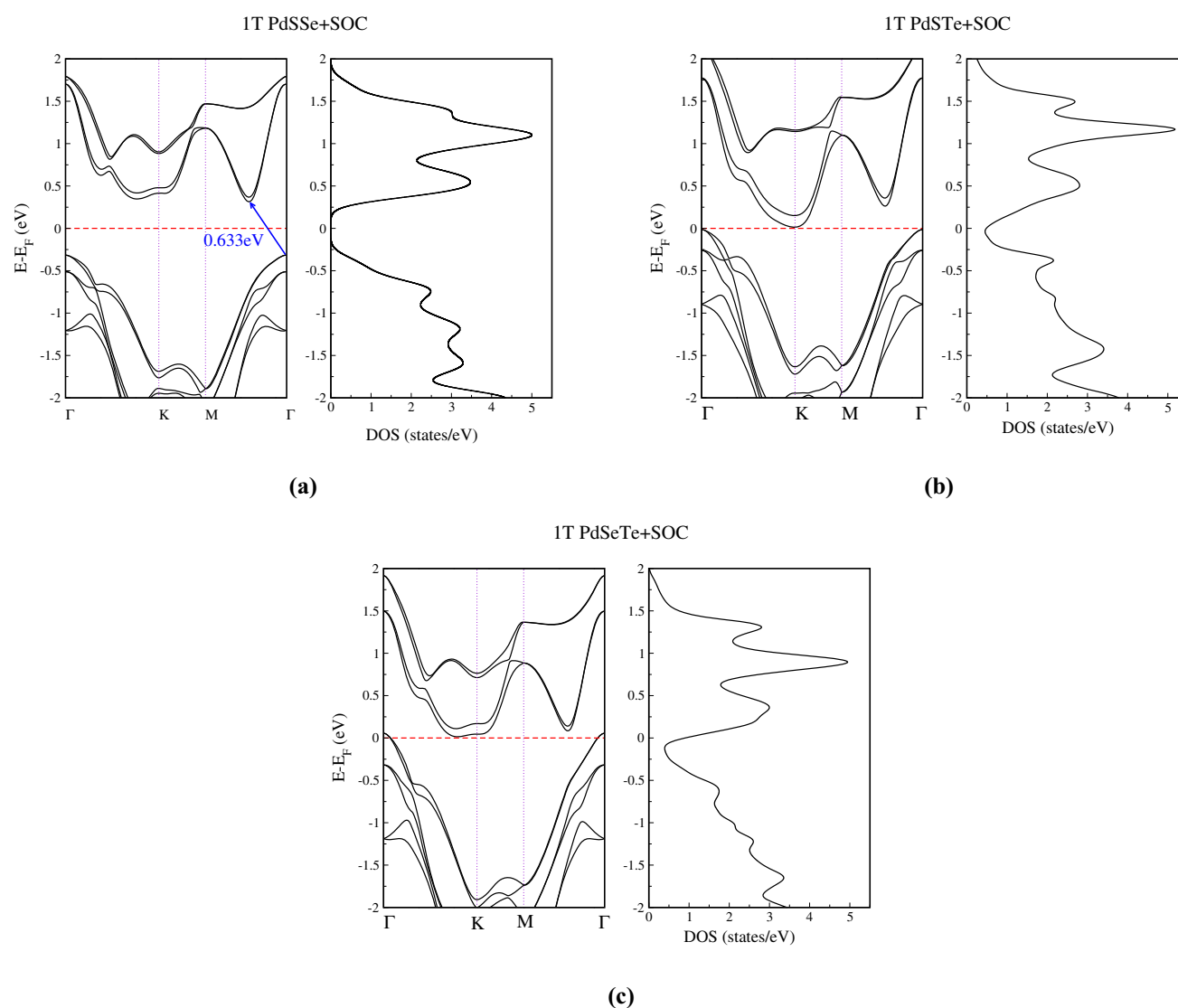


Fig. 2 Electronic bands and density of states (DOS) of 1T PdSSe, PdSTe and PdSeTe monolayers with SOC included. PdSSe is a semiconductor with an indirect bandgap of 0.633 eV, whereas PdSTe and PdSeTe are semimetallic

0.94 eV, 0.33 eV and 0.34 eV for PdSSe, PdSTe and PdSeTe, respectively [40]. This reveals the importance of the SOC in these materials.

For a specific PdXY system, the various bilayers have diverse properties, even within the same stacking order. While the S-S and Se-Se AA bilayers (AA₂ and AA₃), in PdSSe, are semiconductors of 0.448 eV and 0.503 eV indirect bandgaps, respectively, the S-Se (AA₁) bilayer exhibits a semimetallic nature (Fig. 3). This situation is reversed for the AA'' stacking order, where the S-S and Se-Se interlayer systems (AA₂' and AA₃'') are semimetallic; the S-Se bilayer (AA₁'') is a 0.264 eV indirect bandgap semiconductor. PdSTe bilayers are all metallic except for the semimetallic AA₃ system, which shows a small overlap between the valence and conduction bands (Fig. 4). Likewise, as shown in Fig. 5, all PdSeTe systems are metallic, displaying appreciable overlaps between the two types of bands.

The atomic contributions to the DOS, within the [-2 eV, 2 eV] range, are also exhibited. The highest contributions to the valence and conduction bands, for all AA and AA'' PdSSe structures, principally come from the S and Se atoms.

Similarly in PdSTe and PdSeTe, the highest contributions to the valence and conduction bands are dominated by the chalcogen atoms.

We have also looked into which orbitals of the atoms carry the highest contributions to the DOS. When the SOC is taken into account, the states are expressed in terms of the total angular momentum $\hat{J}$ and its quantum numbers j and m_j . The mixed states, corresponding to $m_j = \pm 1/2$, normally have an out-of-plane character. Mixed states corresponding to higher values, such as $m_j = \{\pm 3/2, \pm 5/2\}$, have an in-plane character; this means they contain terms whose combined spherical harmonics lie in a plane

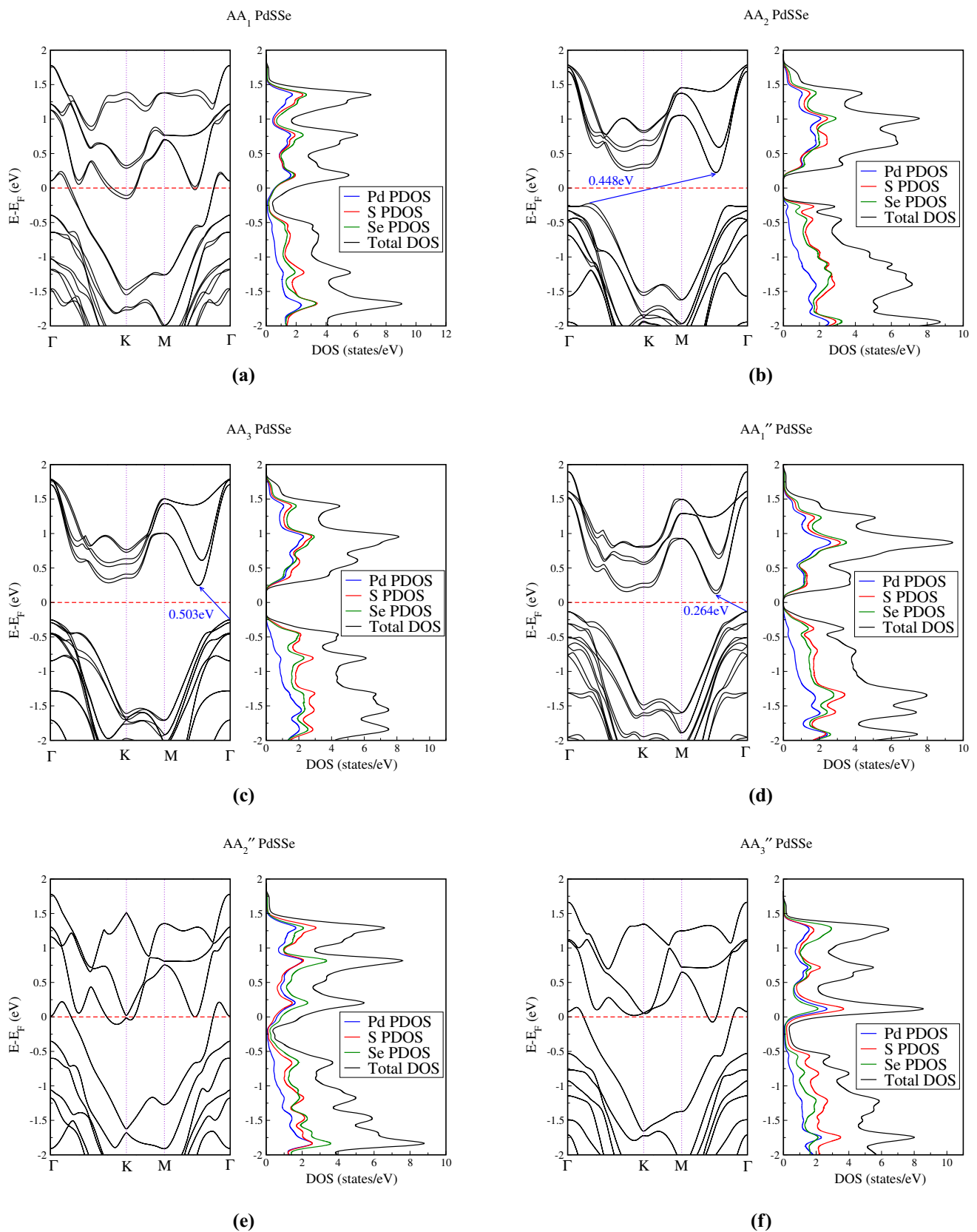


Fig. 3 Electronic bands and density of states (DOS) of the AA and AA' PdSSe bilayers. $E=E_F$ corresponds to the 0eV energy. The S-S and Se-Se AA bilayers are semiconductors, while the S-Se bilayer is semimetallic. The opposite is true for the AA' bilayers

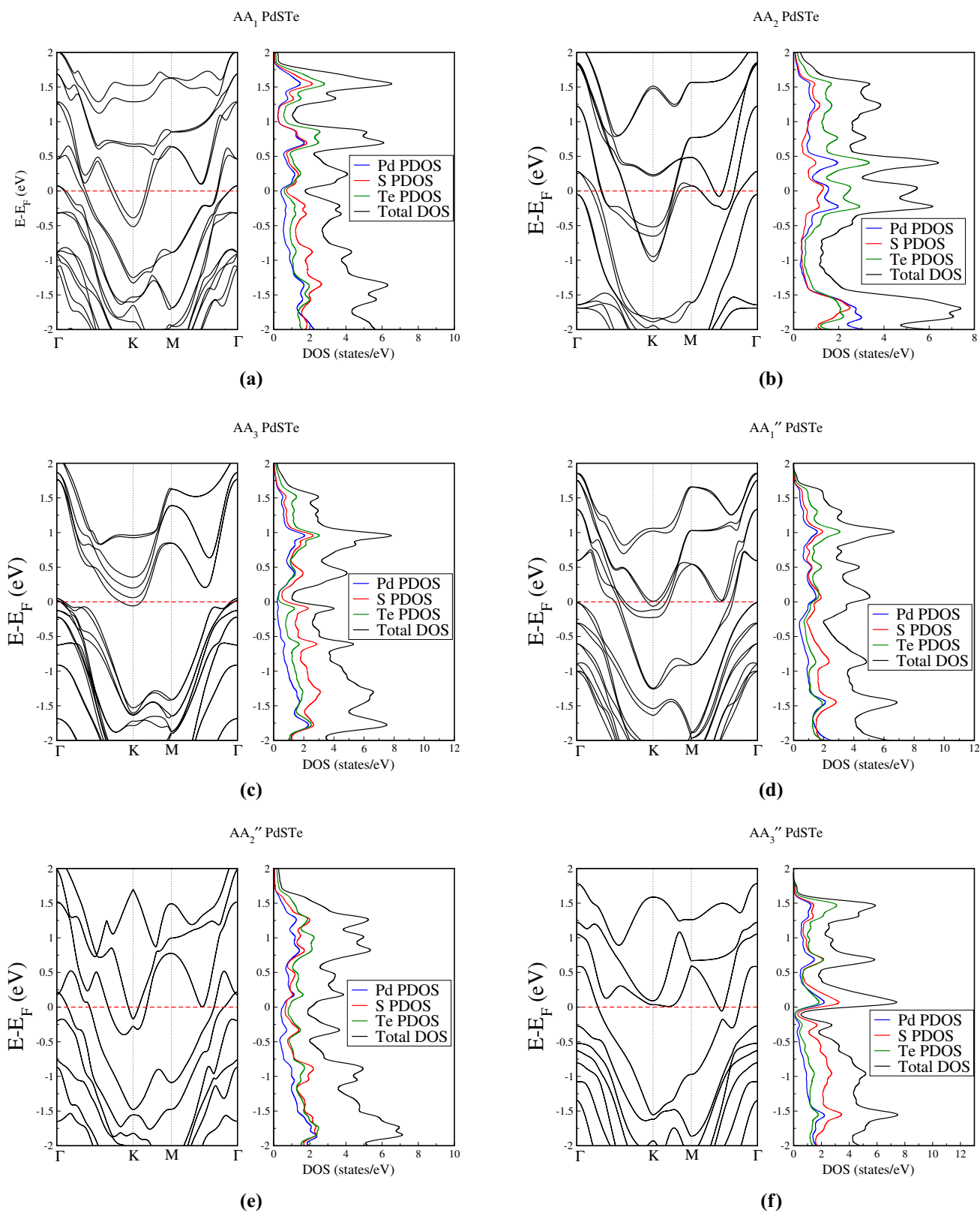


Fig. 4 Electronic bands and DOS of the AA and AA'' PdTe bilayers. Most bilayers are metallic with the exception of the semimetallic AA₃

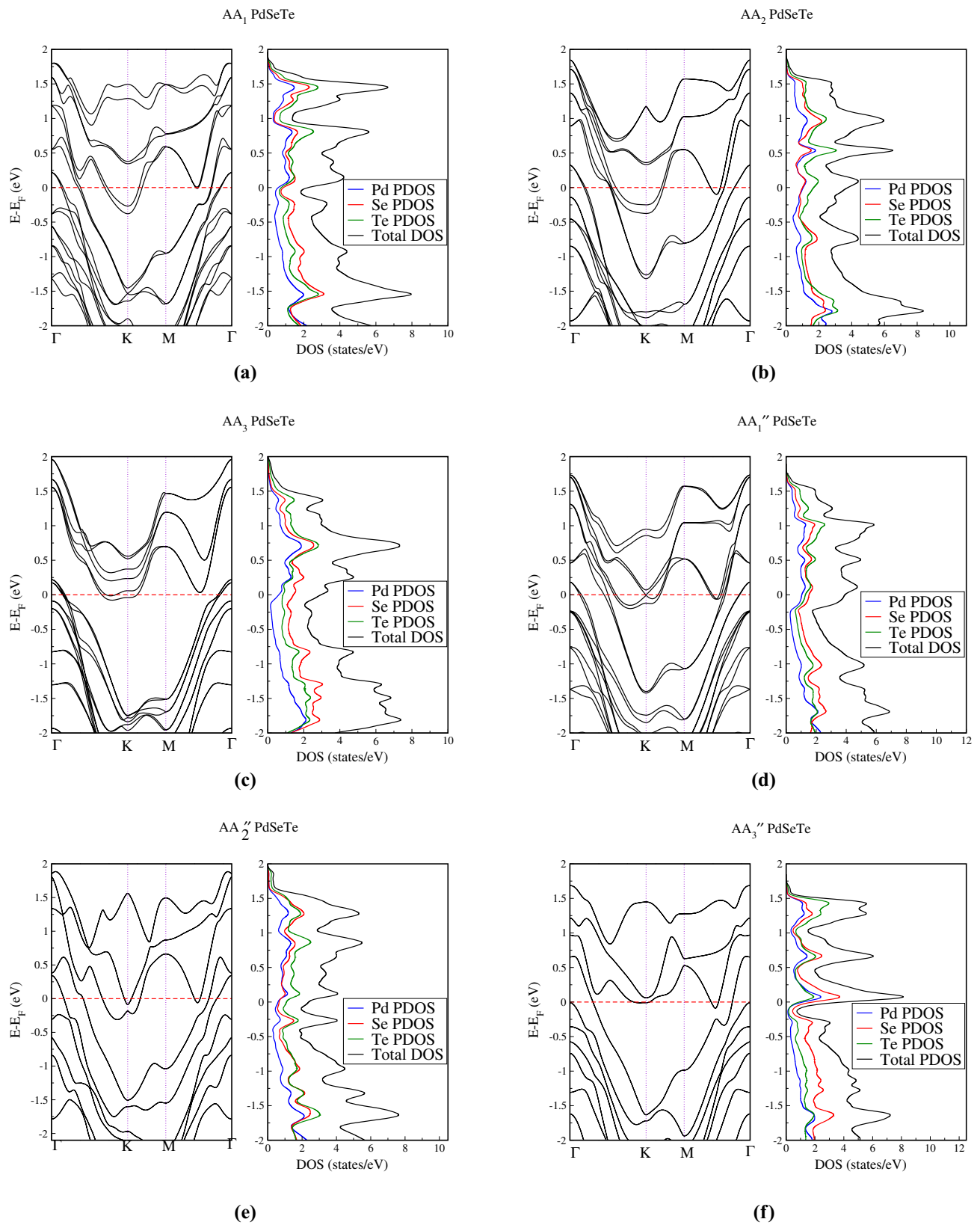


Fig. 5 Same as in Figs 4 and 5 but for AA and AA'' PdSeTe bilayers. All the structures demonstrate a metallic nature

Fig. 6 partial DOS showing that the p_z orbitals of S and Se register the highest contributions to the valence, as well as to the conduction bands. The Pd $m_j=\pm 3/2$ contribute the most to the conduction bands

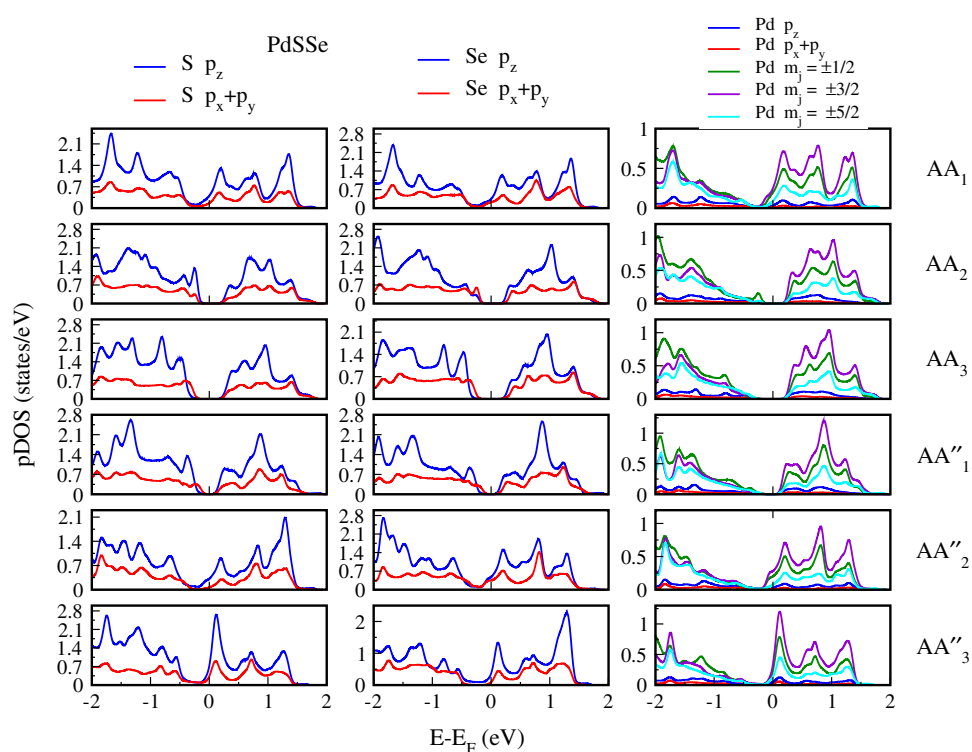


Fig. 7 Same as Fig. 6 but for the PdSTe bilayers. The largest contributions emanate from the p_z orbitals of the S and Te atoms, and the $m_j=\pm 3/2$ states of the Pd atom contribute the most to the conduction bands

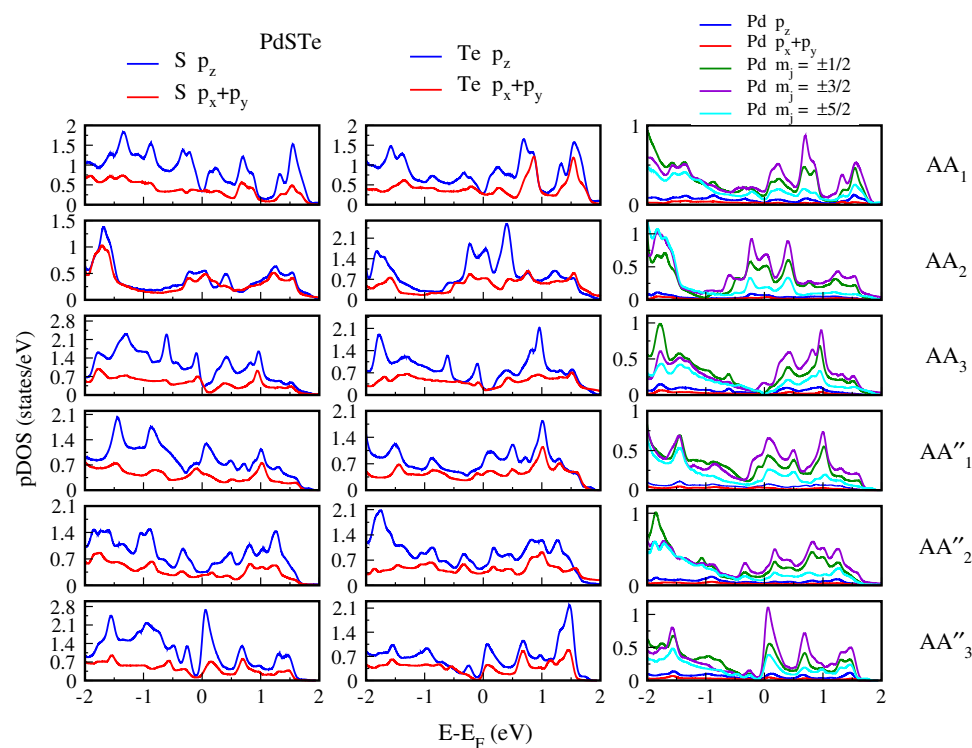
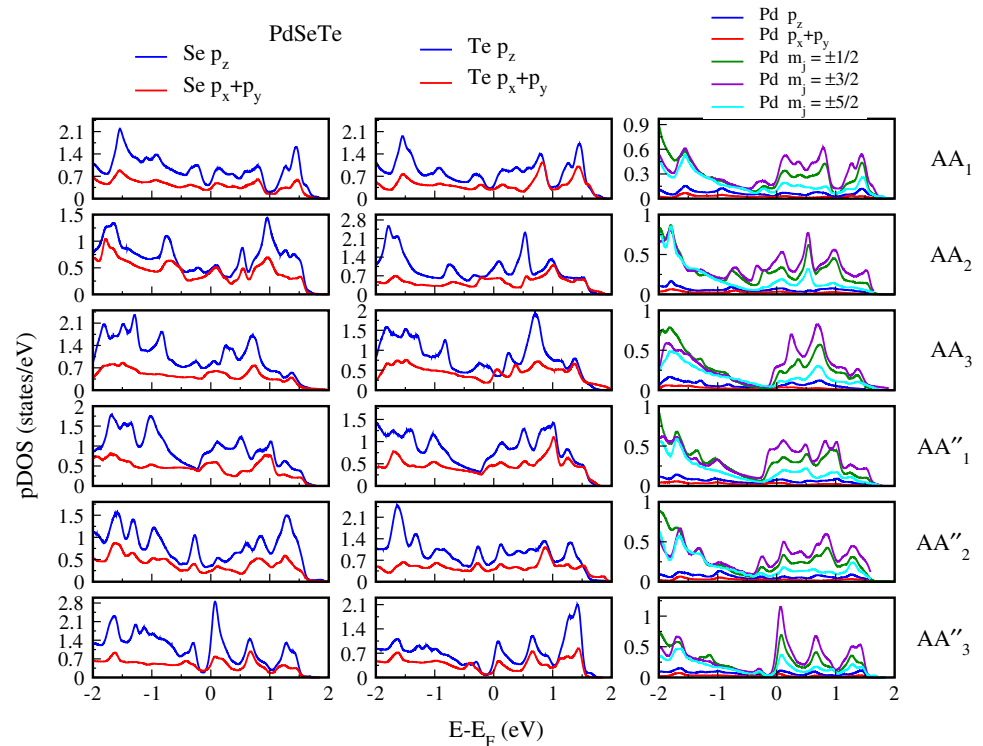


Fig. 8 Same as Figs. 6 and 7 but for the PdSeTe bilayers. The DOS is dominated by the contributions of the p_z orbitals of the Se and Te atoms. The $m_j = \pm 3/2$ mixed orbitals of the Pd atoms have the highest contribution within the conduction bands



[53]. For the p orbitals, it is easy to attribute the out-of-plane contributions to p_z and the in-plane contributions to a mixture of p_x and p_y (referred to as $p_x + p_y$). For the d orbitals, it is more complicated and the contributions will have to be specified by the different m_j values. From Figs. 6, 7 and 8, we realize that the highest contribution of the chalcogens' p orbitals, for both valence and conduction bands, comes from the out-of-plane p_z part. For the Pd d orbitals, the $m_j = \pm 3/2$ terms prevail within the conduction bands; these can be viewed as a mixture of all d -orbitals, with the exclusion of the d_{z^2} part.

4 Elastic properties and mechanical stability

The relaxation procedure and the formation energy criteria are not enough to guarantee the stability of the structures in question, especially against external deformations. In order to establish the mechanical stability, it is vital to compute the elastic constants. Since the bilayers are 2D, we will only concentrate on the in-plane components.

For a hexagonal symmetry, there are three independent in-plane elastic constants to be computed, namely C_{11} , C_{22} ($=C_{11}$) and C_{66} . The first two represent the response of the a and b planar directions to linear compression, whereas the last one is the resistance to a possible shear along the $\langle 110 \rangle$ direction. A fourth useful (dependent) elastic constant is $C_{12} = C_{11} - 2C_{66}$.

The layer modulus (C_{2D}) can be defined, in terms of the above elastic constants, as [54]:

$$C_{2D} = \frac{C_{11}C_{22} - C_{12}^2}{C_{11} + C_{22} - 2C_{12}}.$$

It should be noted that the values outputted by the THERMO_PW code take into account the vacuum distance d along the perpendicular z direction, and are in unit of N/m^2 . To obtain the relevant 2D versions, we have multiplied these values by d ; the results, in N/m , are listed in Table 2.

All eighteen structures are mechanically stable, as they satisfy the Born stability criteria [55], that is $C_{11} > 0$, $C_{22} > 0$, and $C_{66} > 0$. The rigidity of the materials appears to be random: for the PdSSe bilayers, the AA_2 type is the most rigid, whereas the AA_3 PdSTe and the AA_1 PdSeTe bilayers are the stiffest. Among all structures, the AA_2 PdSSe system is the firmest, and AA_2'' PdSTe is the most malleable.

Table 2 Elastic constants and the 2D layer modulus (C_{2D}), in N/m, for the AA and AA'' bilayer PdSSe, PdSTe and PdSeTe systems

Material	Type	$C_{11} = C_{22}$	C_{66}	C_{12}	C_{2D}
PdSSe	AA ₁	125.70	38.17	43.77	81.94
	AA ₂	134.20	36.98	48.61	85.89
	AA ₃	132.35	35.35	48.49	83.85
	AA'' ₁	126.29	29.68	48.31	77.98
	AA'' ₂	120.81	31.82	44.49	76.32
	AA'' ₃	116.57	28.48	44.04	72.52
PdSTe	AA ₁	80.33	23.96	28.19	52.15
	AA ₂	46.08	40.35	2.86	43.21
	AA ₃	75.96	19.79	28.08	47.88
	AA'' ₁	71.53	31.26	20.13	51.39
	AA'' ₂	39.14	32.83	3.65	35.99
	AA'' ₃	79.26	31.17	24.04	55.21
PdSeTe	AA ₁	87.85	24.75	31.55	56.30
	AA ₂	67.00	30.69	18.15	48.85
	AA ₃	68.64	20.89	23.88	44.76
	AA'' ₁	73.59	27.16	23.21	50.38
	AA'' ₂	71.72	27.46	22.13	49.59
	AA'' ₃	73.59	27.16	23.21	50.38

4.1 Optical properties

The dielectric properties of the materials are crucial for the inspection of possible optoelectronic applications; they can be obtained via the real and imaginary parts of the complex dielectric function:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega),$$

where ε_1 is related to the polarization of the material, and ε_2 is important to investigate photon absorption; ω is the frequency of the incident polarized light.

The expression of the complex dielectric function, whose tensor components are given by:

$$\varepsilon_{\alpha,\beta}(\omega) = 1 - \frac{4\pi q^2}{VN_k m^2} \sum_{n,k} \frac{df(E_{k,n})}{dE_{k,n}} \frac{\hat{M}_{\alpha,\beta}}{\omega^2 + i\eta\omega} + \dots + \frac{8\pi q^2}{VN_k m^2} \\ \times \sum_{n \neq n'} \sum_k \frac{\hat{M}_{\alpha,\beta}}{E_{k,n'} - E_{k,n}} \dots \frac{f(E_{k,n})}{(\omega_{k,n'} - \omega_{k,n})^2 + \omega^2 + i\Gamma\omega},$$

incorporates both the ε_1 and ε_2 contributions. In the above equation, V is the volume of the unit cell, N_k is the number of points sampling the reciprocal BZ, q is the electron's charge, and m is its mass. $E_{n,k}$ and $E_{n',k}$ are the energies of the k^{th} point in the valence band n and conduction band n' , respectively. The matrix elements $\hat{M}_{\alpha,\beta}$ are momentum operator calculations, sandwiched between Bloch states. Γ and η are broadening parameters that describe the interband and intraband contributions, respectively.

Once $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are known, optical properties such as the electron energy loss spectrum ($E_L(\omega)$), the coefficient of absorption $\alpha(\omega)$ and the reflectivity $R(\omega)$ can be determined via:

$$E_L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \\ \alpha(\omega) = \frac{\sqrt{2}\omega}{c} \sqrt{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)} \\ R(\omega) = \left| \frac{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} + 1} \right|^2,$$

Fig. 9 The optical absorption/emission, absorption coefficient and reflectivity for the AA and AA'' PdSse bilayers along the x (or y) directions

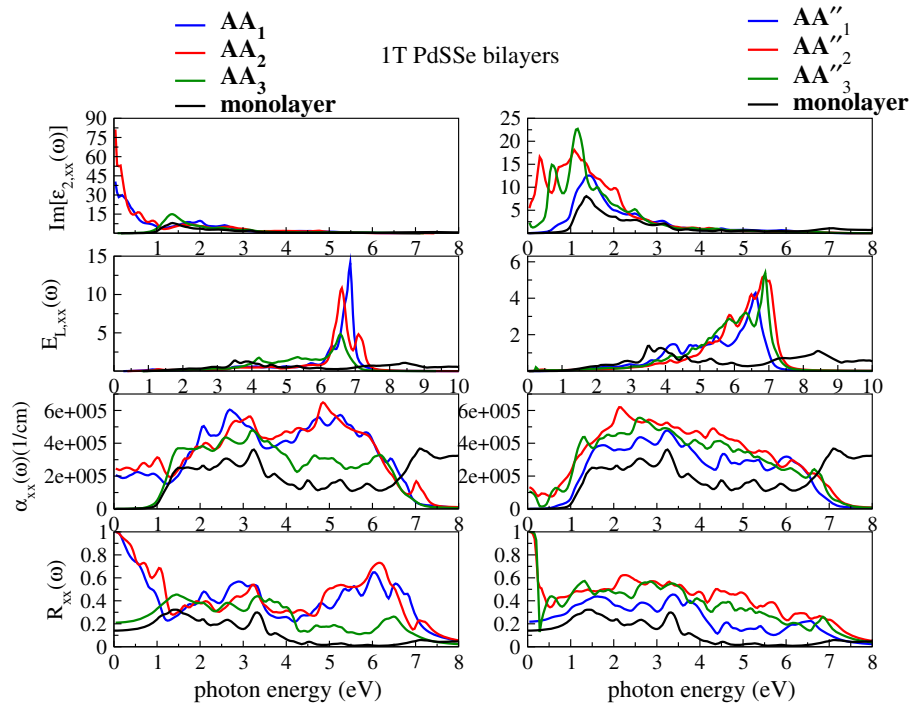
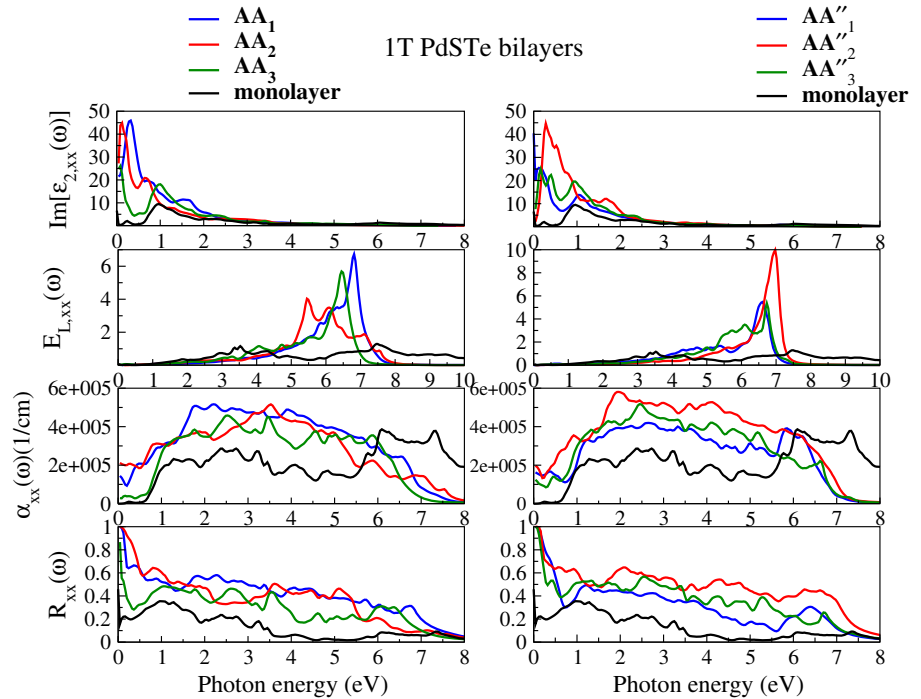


Fig. 10 The optical absorption/emission, absorption coefficient and reflectivity for the AA and AA'' PdSte bilayers along the x (or y) directions



c being the velocity of light. The above quantities can be computed when the electric field $\mathbf{E}$ of the incident light is parallel to the x and y directions, or along the direction perpendicular to the structure ($\mathbf{E}/z$). The bilayers are isotropic for incident light parallel to the structures' planes, implying that the optical properties are the same along the x and y directions. In this case, the labels will be described by an "xx" subscript, while for properties along the z direction, they will carry a "zz" subscript. All results are displayed in Figs. 9, 10, 11, 12, 13 and 14.

The in-plane optical spectra show that all 18 bilayers have maximum sharp peaks limited to the infrared (IR) level. Absorption along the perpendicular direction indicates more sharp peaks for all structures, with the maximum value of $\varepsilon_{2,zz}$, occurring within the [0–2.6eV] range. Additionally, along the z direction, maximum absorption and emission at the level of the visible spectrum are also feasible. For instance, two sharp peaks occur at ~ 1.64 eV and 2.52eV in AA''₃ PdSse, at ~ 1.52 eV and 2.24eV in AA''₃ PdSte,

Fig. 11 Same as Figs 9 and 10, but for the AA and AA'' PdSeTe bilayers

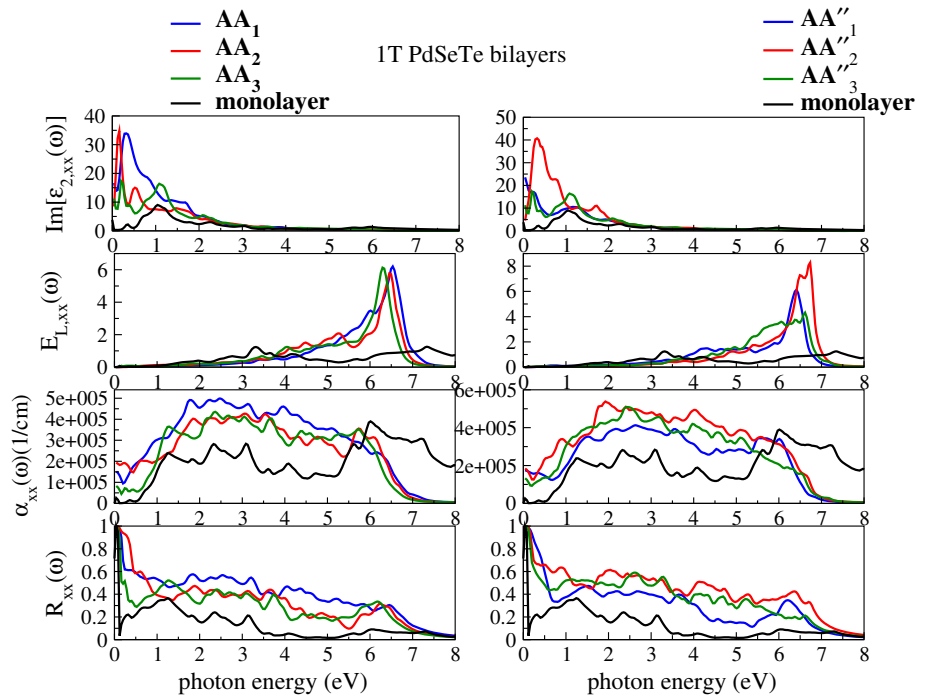
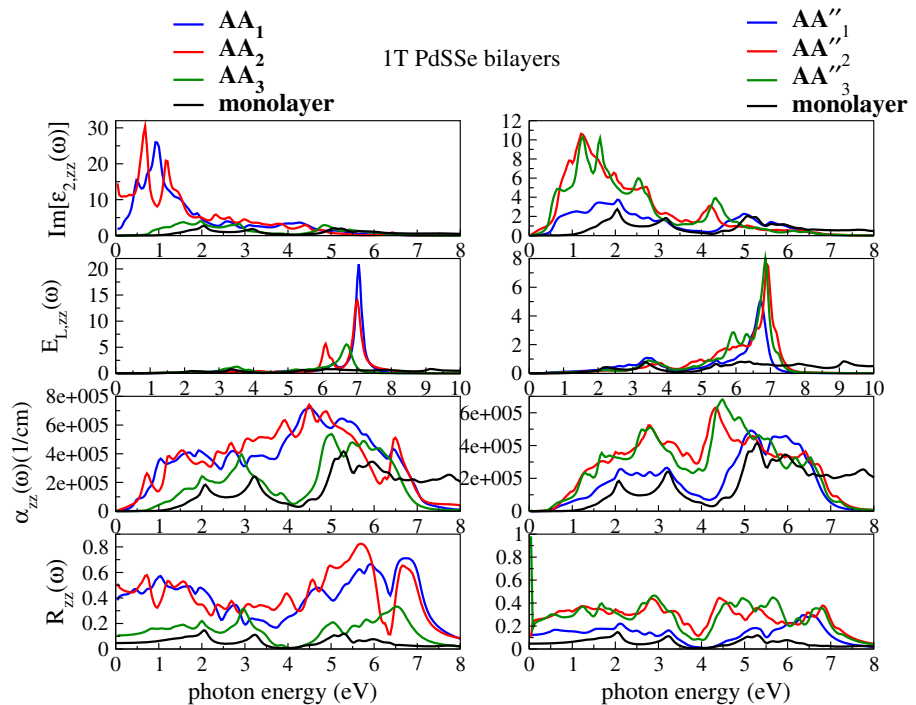


Fig. 12 The optical absorption/emission, absorption coefficient and reflectivity for the AA and AA'' PdSeTe bilayers along the perpendicular z direction



and at $\sim 2.24\text{eV}$ in AA_3 PdSeTe. Other modest peaks appear for energies $\geq 3\text{eV}$, making an absorption/emission within the UV range also achievable.

The EELS dictates how the incident photons interact with the electronic systems. There is one noticeable peak per structure. Whether $\mathbf{E} \parallel (x, y)$ or to z , the peaks arise within the $[6\text{eV}-7\text{eV}]$ energy interval for all bilayered systems.

In the semiconductor bilayers, the absorption coefficients α_{xx} and α_{zz} are negligible for energies smaller than 1eV . Several peaks appear throughout the energy range considered, implying that all bilayers have different absorption regions for $\mathbf{E} \parallel (x, y)$. These energies fall within the visible and the UV spectrum. Likewise, for polarized light parallel to the z -direction, absorption is possible for all regions of the electromagnetic spectrum; nevertheless, almost all of the maxima occur for energies $> 3\text{eV}$, which correspond

Fig. 13 The optical absorption/emission, absorption coefficient and reflectivity for the AA and AA'' PdTe bilayers along the z direction

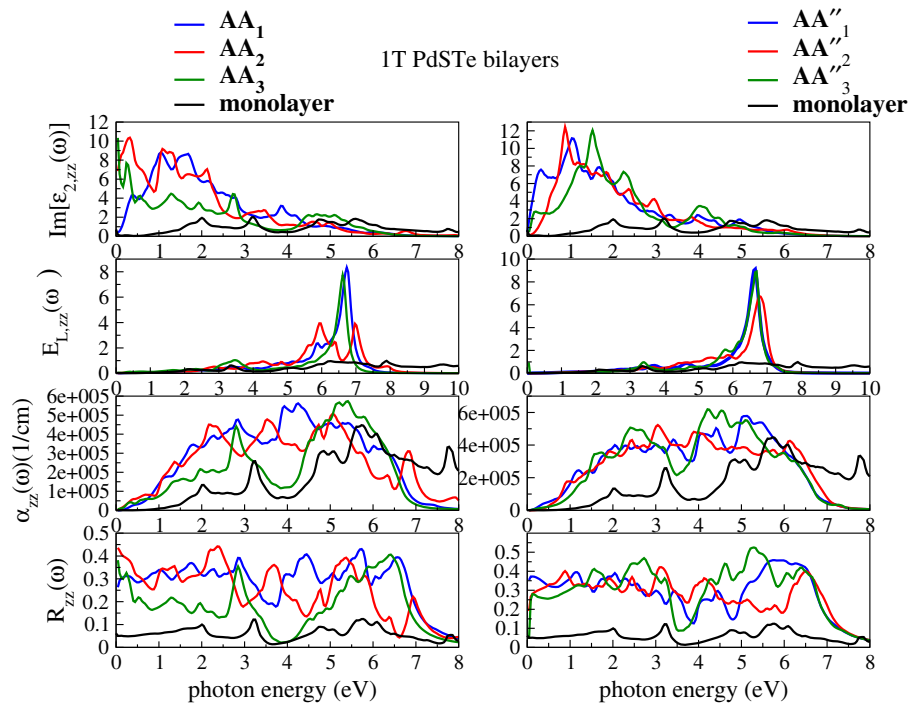
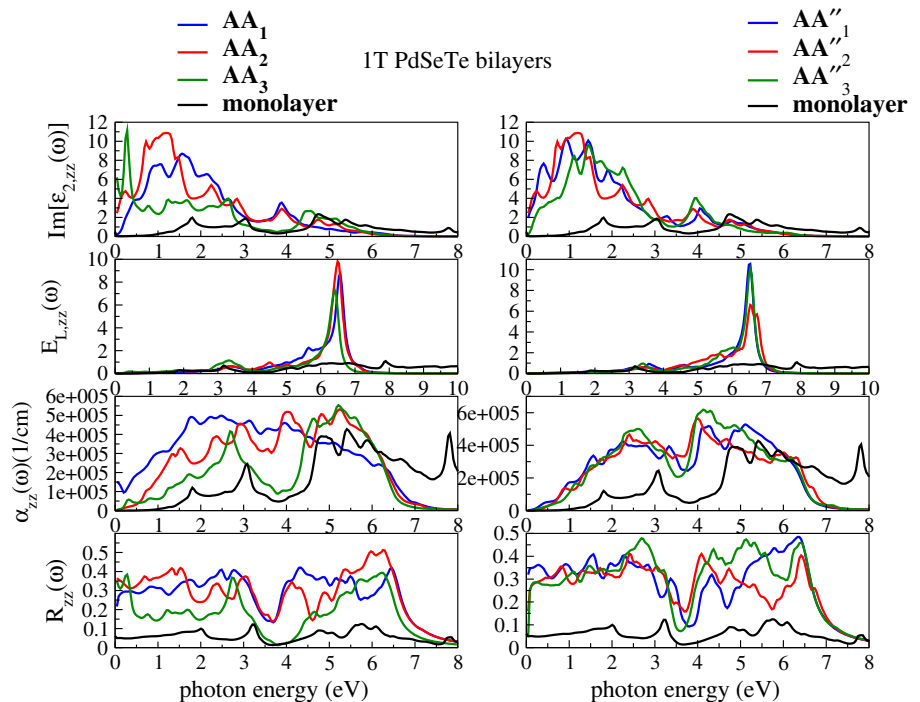


Fig. 14 Same as Figs 12 and 13, but for the AA and AA'' PdSeTe bilayers



to the UV range, as is displayed in Figs. 12, 13 and 14. The maximum absorption coefficients, and the energies at which they occur, are detailed in Table 3.

The reflectivity of all structures fluctuates, declining rapidly and approaching zero for energies larger than ~ 6 eV. Regions of high R signal opaque structures, whereas those with low values of R are more transparent, and thus less reflective. The maximum reflectivities and their energies are found in Table 4.

For all semimetallic and metallic systems, we perceive that the reflectivity is very close to 1 at an energy of 0.04 eV. Disregarding this value, we note that the maximum reflectivities, achieved along the perpendicular direction, are mostly smaller than those along the x (or y directions). These maxima do not correspond to photon energies within a single regime of the electromagnetic spectrum; depending on the type of the bilayer, maximum reflectivity can be attained within the IR, visible or UV regions. The bilayers whose

Table 3 The maximum absorption along the x (α_{xx}) and z (α_{zz}) directions, and the photon energies ($E_{ph,x}^{max}$ and $E_{ph,z}^{max}$) at which they occur for the bilayer systems. Results for the monolayers are included for comparison

Material	Type	$E_{ph,x}^{max}$ (eV)	$\alpha_{xx}^{max} \times 10^5 (cm^{-1})$	$E_{ph,z}^{max}$ (eV)	$\alpha_{zz}^{max} \times 10^5 (cm^{-1})$
PdSSe	Monolayer	7.09	3.68	5.29	4.17
	AA ₁	2.68	6.05	4.49	7.20
	AA ₂	4.85	6.49	4.49	7.41
	AA ₃	3.21	4.80	5.01	5.37
	AA ₁ ''	3.25	4.77	5.17	4.91
	AA ₂ ''	2.13	6.19	4.33	6.32
	AA ₃ ''	2.61	5.56	4.49	6.81
PdSTe	Monolayer	6.09	3.87	5.73	4.48
	AA ₁	2.20	5.17	4.25	5.62
	AA ₂	3.53	5.16	5.05	5.06
	AA ₃	2.53	4.58	5.41	5.73
	AA ₁ ''	2.65	4.19	5.13	5.78
	AA ₂ ''	1.96	5.81	3.04	5.23
	AA ₃ ''	2.45	5.17	4.20	6.19
PdSeTe	Monolayer	6.01	3.90	5.41	4.28
	AA ₁	2.49	4.99	3.97	5.76
	AA ₂	3.05	4.27	5.25	5.33
	AA ₃	2.37	4.35	5.21	5.53
	AA ₁ ''	2.65	4.13	5.09	5.26
	AA ₂ ''	1.92	5.38	4.00	5.64
	AA ₃ ''	2.41	5.09	4.13	6.19

reflectivities are high in the UV range, could be used as shields from UV radiation. All in all, these values could be fundamental to providing the key ingredients to technological applications in the areas of photovoltaics and optoelectronics.

For comparison purposes, we have included the EELS, absorption coefficients and reflectivities of the monolayers in Figs. 9, 10, 11, 12, 13 and 14. For all polarization directions, we notice that the monolayers have lower absorption coefficients up to energies of around 6 eV. Besides, their reflectivities are smaller than those of all bilayers, across the electromagnetic spectrum considered. This establishes the advantages of the bilayers over the monolayered structures.

5 Conclusion

This paper's goal is to investigate the AA and AA'' bilayers of the 1T Pd Janus PdSSe, PdSTe and PdSeTe structures. For the two stacking orders, both monolayers are superimposed, one on top of the other; yet in the AA type, the chalcogen atoms (X or Y) in the upper monolayer lie above the chalcogen atoms of the same type (X or Y) of the bottom monolayer. Conversely, the AA'' structures have a layer of one type of chalcogens lying above a layer of a different type. Since each of X and Y can be either S, Se or Te, this gives rise to three structures per stacking order, that is a total of 18 systems. The SOC is included in all of the reported calculations.

The different structures can be indirect gap semiconductors, semimetals or metals. PdSTe and PdSeTe can only be semimetals or metals. Instead, some of the PdSSe bilayers exhibit a semiconducting nature; compared to the monolayers, the bandgaps of such semiconductors are reduced. As far as mechanical stability is concerned, all 18 structures are stable with positive in-plane elastic constants.

Partial density of states calculations show that the valence and conduction bands are mostly contributed by the p_z -orbitals of both chalcogens. The d orbital contributions to the conduction bands, coming from the Pd atom, are mostly due to the $m_j = \pm 3/2$ states; these carry the signature of all d -orbitals, apart from d_{z^2} .

The bilayer structures have the advantage to possess higher absorption coefficients, and reflectivities, along in-plane and out-of-plane directions, than the corresponding monolayers. All structures show nonzero large absorption coefficients at the infrared, visible and ultraviolet levels. Intriguingly, for most of the structures, the reflectivity within the plane of the structures is larger than that along the perpendicular direction. It is observed that AA₂ PdSSe has the largest reflectivity along all directions, namely 74% in the x(y) direction and 82% along the z direction. Since this is fulfilled within the UV range, such a structure represents an impeccable

Table 4 The maximum reflectivities along the x (R_{xx}) and z (R_{zz}) directions, and the photon energies ($E_{ph,x}^{max}$ and $E_{ph,z}^{max}$) at which they occur for the bilayer systems. The values pertaining to the monolayers are also shown

Material	Type	$E_{ph,x}^{max}$ (eV)	R_{xx}^{max}	$E_{ph,z}^{max}$ (eV)	R_{zz}^{max}
PdSSe	Monolayer	1.36	0.32	2.04	0.15
	AA ₁	6.05	0.66	6.69	0.71
	AA ₂	6.17	0.74	5.69	0.82
	AA ₃	1.44	0.45	6.53	0.33
	AA ₁ ''	3.36	0.45	6.37	0.29
	AA ₂ ''	2.25	0.63	4.41	0.44
	AA ₃ ''	1.34	0.58	2.89	0.47
	Monolayer	0.97	0.36	5.77	0.12
PdSTe	AA ₁	0.37	0.67	5.73	0.43
	AA ₂	0.81	0.65	2.37	0.44
	AA ₃	1.07	0.49	6.41	0.41
	AA ₁ ''	1.20	0.50	5.77	0.46
	AA ₂ ''	2.11	0.65	3.13	0.42
	AA ₃ ''	2.56	0.57	5.29	0.52
	Monolayer	1.24	0.37	4.77	0.13
	AA ₁	1.83	0.58	4.33	0.42
PdSeTe	AA ₂	0.59	0.60	6.25	0.51
	AA ₃	1.26	0.53	6.21	0.39
	AA ₁ ''	1.49	0.48	6.33	0.48
	AA ₂ ''	0.88	0.64	2.40	0.41
	AA ₃ ''	2.62	0.59	2.69	0.48

candidate for shields against UV radiation. In general, the diversified optical properties of the AA and AA'' bilayers at individual photon energies should, in principle, pave the way to design sensitive optical devices and to exploit the bilayer structures in varied technological applications.

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Data Availability Statement This manuscript has associated data in a data repository. [Authors' comment: The data are not publicly available and can be discussed (or shared), on request from the corresponding author Elie A. Moujaes.]

References

1. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I. Grigorieva, S. Dubonos, A.A. Firsov, *Nature* **438**, 197 (2005)
2. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* **306**, 666 (2004)
3. S. Benka, *Phys. Today* **58**, 9 (2005)
4. P. Miró, M. Audiffred, T. Heine, *Chem. Soc. Rev.* **43**, 6537 (2014)
5. J.N. Coleman, M. Lotya, A. O'Neill, S.D. Bergin, P.J. King, U. Khan, K. Young, A. Gaucher, S. De, R.J. Smith et al., *Science* **331**, 568 (2011)
6. J. Tan, S. Li, B. Liu, H.-M. Cheng, *Small Struct.* **2**, 2000093 (2021)
7. Z. Li, S.L. Wong, *Mater. Sci. Eng. C* **70**, 1095 (2017)
8. Y. Ding, Y. Wang, J. Ni, L. Shi, S. Shi, W. Tang, *Physica B: Condens. Matter* **406**, 2254 (2011)
9. K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010)
10. A.V. Kolobov, J. Tominaga, *Two-dimensional transition-metal dichalcogenides*, Vol. 239 (Springer, 2016)
11. S. Manzeli, D. Ovchinnikov, D. Pasquier, O.V. Yazyev, A. Kis, *Nat. Rev. Mater.* **2**, 1 (2017)
12. J. Gusakova, X. Wang, L.L. Shiao, A. Krivosheeva, V. Shaposhnikov, V. Borisenko, V. Gusakov, B.K. Tay, *Phys. Status Solidi (a)* **214**, 1700218 (2017)
13. Z. Huang, W. Zhang, W. Zhang, *Materials* **9**, 716 (2016)
14. Y. Chen, S. Huang, X. Ji, K. Adeplli, K. Yin, X. Ling, X. Wang, J. Xue, M. Dresselhaus, J. Kong et al., *ACS Nano* **12**, 2569 (2018)
15. S. Ahmad, *Mater. Chem. Phys.* **198**, 162 (2017)
16. S. Ahmad, G. Schreckenbach, *Mater. Today Commun.* **24**, 100976 (2020)
17. F. Gronvold, E. Rost, *Acta Chemica Scandinavica* **10**, 1620 (1956)
18. Y. Wang, Y. Li, Z. Chen, *J. Mater. Chem. C* **3**, 9603 (2015)
19. H. Leng, C. Paulsen, Y. Huang, A. De Visser, *Phys. Rev. B* **96**, 220506 (2017)

20. R. Xiao, P. Gong, Q. Wu, W. Lu, M. Wei, J. Li, H. Lv, X. Luo, P. Tong, X. Zhu et al., Phys. Rev. B **96**, 075101 (2017)
21. K. Kim, S. Kim, J. Kim, H. Kim, J.-H. Park, B. Min, Phys. Rev. B **97**, 165102 (2018)
22. O. Clark, M. Neat, K. Okawa, L. Bawden, I. Marković, F. Mazzola, J. Feng, V. Sunko, J. Riley, W. Meevasana et al., Phys. Rev. Lett. **120**, 156401 (2018)
23. C. Liu, C.-S. Lian, M.-H. Liao, Y. Wang, Y. Zhong, C. Ding, W. Li, C.-L. Song, K. He, X.-C. Ma et al., Phys. Rev. Mater. **2**, 094001 (2018)
24. C. Souillard, X. Rocquefelte, P.-E. Petit, M. Evain, S. Jobic, J.-P. Itié, P. Munsch, H.-J. Koo, M.-H. Whangbo, Inorganic Chem. **43**, 1943 (2004)
25. A.D. Oyedele, S. Yang, L. Liang, A.A. Puzdsky, K. Wang, J. Zhang, P. Yu, P.R. Pudasaini, A.W. Ghosh, Z. Liu et al., J. Am. Chem. Soc. **139**, 14090 (2017)
26. H.-J. Noh, J. Jeong, E.-J. Cho, K. Kim, B. Min, B.-G. Park, Phys. Rev. Lett. **119**, 016401 (2017)
27. A.V. Kuklin, H. Ågren, Phys. Rev. B **99**, 245114 (2019)
28. E. Li, D. Wang, P. Fan, R. Zhang, Y.-Y. Zhang, G. Li, J. Mao, Y. Wang, X. Lin, S. Du et al., Nano Res. **11**, 5858 (2018)
29. E.G. Marin, D. Marian, M. Perucchini, G. Fiori, G. Iannaccone, arXiv preprint [arXiv:2001.03139](https://arxiv.org/abs/2001.03139) (2020)
30. S.A. Tawfik, O. Isayev, C. Stampfl, J. Shapter, D.A. Winkler, M.J. Ford, Adv. Theory Simulations **2**, 1800128 (2019)
31. X. Zhao, Q. Zhao, B. Zhao, X. Dai, S. Wei, Y. Ma, Superlattices Microstruct. **142**, 106514 (2020)
32. P.K. Cheng, S. Liu, S. Ahmed, J. Qu, J. Qiao, Q. Wen, Y.H. Tsang, Nanomaterials **10**, 2441 (2020)
33. A.-Y. Lu, H. Zhu, J. Xiao, C.-P. Chuu, Y. Han, M.-H. Chiu, C.-C. Cheng, C.-W. Yang, K.-H. Wei, Y. Yang et al., Nat. Nanotechnol. **12**, 744 (2017)
34. J. Zhang, S. Jia, I. Kholmanov, L. Dong, D. Er, W. Chen, H. Guo, Z. Jin, V.B. Shenoy, L. Shi et al., ACS Nano **11**, 8192 (2017)
35. Y.-C. Lin, C. Liu, Y. Yu, E. Zarkadoulas, M. Yoon, A.A. Puzdsky, L. Liang, X. Kong, Y. Gu, A. Strasser et al., ACS Nano **14**, 3896 (2020)
36. M.M. Petrić, M. Kremser, M. Barbone, Y. Qin, Y. Sayyad, Y. Shen, S. Tongay, J.J. Finley, A.R. Botello-Méndez, K. Müller, Phys. Rev. B **103**, 035414 (2021)
37. D. Er, H. Ye, N.C. Frey, H. Kumar, J. Lou, V.B. Shenoy, Nano Lett. **18**, 3943 (2018)
38. W.-L. Tao, Y. Mu, C.-E. Hu, Y. Cheng, G.-F. Ji, Philos. Magazine **99**, 1025 (2019)
39. W. Shi, Z. Wang, J. Phys. Condensed Matter **30**, 215301 (2018)
40. E.A. Moujaes, W. Diery, J. Phys. Condensed Matter **31**, 455502 (2019)
41. W.-L. Tao, J.-Q. Lan, C.-E. Hu, Y. Cheng, J. Zhu, H.-Y. Geng, J. Appl. Phys. **127**, 035101 (2020)
42. W. Diery, E.A. Moujaes, Mater. Today Commun. **29**, 102735 (2021)
43. X. Zhang, R. Pang, X. Hou, S. Wang, New J. Phys. **23**, 013003 (2021)
44. Y. Yang, Y. Zhang, H. Ye, Z. Yu, Y. Liu, B. Su, W. Xu, Superlattices Microstruct. **131**, 8 (2019)
45. A. Kandemir, H. Sahin, Phys. Chem. Chem. Phys. **20**, 17380 (2018)
46. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo et al., J. Phys. Condensed Matter **21**, 395502 (2009)
47. J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **80**, 891 (1998)
48. N. Troullier, J.L. Martins, Phys. Rev. B **43**, 1993 (1991)
49. S. Grimme, J. Comput. Chem. **27**, 1787 (2006)
50. V. Barone, M. Casarin, D. Forrer, M. Pavone, M. Sami, A. Vittadini, J. Comput. Chem. **30**, 934 (2009)
51. A. Dal Corso, (2014) https://dalcorsi.github.io/thermo_pw/
52. A. Benassi, A. Ferreti, C. Cavazzoni, PWSCF's epsilon. x user's manual (2017) https://ir.library.utoronto.ca/bitstream/10155/159/3/McNelles_Phillip_appendixA.pdf
53. A. Dal Corso, A.M. Conte, Phys. Rev. B **71**, 115106 (2005)
54. D. Liu, C. Daniels, V. Meunier, A.G. Every, D. Tománek, Carbon **157**, 364 (2020)
55. R.C. Andrew, R.E. Mapasha, A.M. Ukpong, N. Chetty, Phys. Rev. B **85**, 125428 (2012)