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To cite this article: M Palumbo *et al* 2019 *J. Phys.: Condens. Matter* **31** 235701

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Tailoring the optical properties of MoS₂ and WS₂ single layers via organic functionalization

M Palumbo¹, A N D'Auria¹, J C Grossman² and G Cicero³

¹ Dipartimento di Fisica, Università di Roma Tor Vergata and INFN, Via della Ricerca Scientifica 1, 00133 Roma, Italy

² Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139-4307, United States of America

³ Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy

E-mail: giancarlo.cicero@polito.it and palumbo@roma2.infn.it

Received 8 November 2018, revised 24 February 2019

Accepted for publication 4 March 2019

Published 28 March 2019




CrossMark

Abstract

Tailoring the structural and electronic properties of 2D materials is fundamental to boost their use in a wide range of technological applications. In this paper, by means of first principles simulations, we show how methyl functionalization of MoS₂ and WS₂ monolayers can be employed to change their energy gap, tune their optoelectronic properties and modify the relative stability of their structural phases (or polytypes). In particular for both compound monolayers, we find that the most stable semiconducting H phase becomes metallic upon methyl functionalization, while in the metastable T' phase the band gap increases as a function of the -CH₃ coverage; correspondingly the phase stability is reversed and the on-set of the optical absorption is blue-shifted.

Keywords: MoS₂, WS₂, TDMs, functionalization, DFT, GW

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently 2D layered materials based on transition metal dichalcogenides (TMDs) have received a large amount of attention because of their peculiar and versatile physical properties [1]. Mono and few-layered TMDs may be metallic or semiconducting and, in the latter case, their band gap energy as well as carrier type (n- or p-) varies depending on the composition, structure and dimensionality of the system. For example, the optical gap of hexagonal MoS₂ (H-MoS₂) changes from 1.2 eV (indirect) to 1.9 eV (direct) when going from a bulk material to a single layer with hexagonal phase [2], while the monolayer becomes metallic when in the metastable tetragonal phase. Due to the highly efficient absorption in the visible energy range for the hexagonal structure, it has been proposed that single layer MoS₂ can be employed either

as active absorbing layer in photovoltaic applications [3] or as a photo-catalyst for hydrogen evolution reactions [4]. In addition to strong absorption in the visible, the efficiency of MoS₂ as well as other group-VI TMDs in these types of applications strongly depends on the spatial localization of the electron/hole pair upon excitation. Moreover, it will be important to be able to tune the conductivity of TMD monolayers (n- versus p-) by controllably modifying their electronic structure [5].

One strategy that has been proposed to tailor the physical properties of a monolayer TMD is organic functionalization of its surface, which has gained significant recent attention [6, 7]. Among possible functionalization chemistries, the use of methyl iodine precursors that directly attach to the chalcogen atoms of the monolayer through formation of a methyl-S covalent bond with spontaneous release of iodine molecules [8] is the most promising and leads to an organic coverage

of about 29% atomic. With this approach, which was demonstrated for both metallic MoS₂ and WS₂, the H-phase cannot be functionalized directly, while the metallic phase transforms to semiconducting upon functionalization, as demonstrated by the appearance of a photoluminescence emission peak. This protocol was applied to attach to the MoS₂ surface para-substituted iodobenzene, confirming the efficiency of the functionalization approach [9] to 2D TMDs. Backers *et al* [10] proposed an alternative organic modification of the metallic MoS₂ structure which employs reactive aryldiazonium salts, although the method appears to be less efficient than that employing alkyl-iodide. Other studies have reported organic functionalization both of the tetragonal [11] and of the H-MoS₂ phase [12, 13] through the ‘ligand conjugation’ functionalization procedure, where the reaction is believed to occur by interaction of thiol functional groups of the organic molecules and the sulphur vacancies present in the MoS₂ basal plane or at the sheet edges. Nevertheless, it has been recently pointed out that in this case there is no strong evidence of covalent interaction between the thiol and the TMD monolayer [7]: the thiol moieties would not fill sulphur vacancies, but they rather are converted to disulfide physisorbed on the MoS₂ surface [7].

In this paper, we present theoretical predictions on the effect of organic functionalization of single layer MS₂ (M = Mo and W) by the functionalization protocol proposed by Chowalla *et al* [8]. The equilibrium structures of the hybrid MS₂/organic systems and the reaction energies are obtained by means of *ab initio* density functional theory simulations (DFT) at increasing molecular coverage. DFT calculations have proven to accurately predict the mechanical and electronic properties of chemically functionalized semiconductor [14, 15] and metallic [16] surfaces. According to previous DFT studies [17] both MoS₂ and WS₂ exist in two different phases: the hexagonal H phase and the metastable tetragonal T' phase. The tetragonal T is unstable and spontaneously relaxes to the T' structure. At variance with previously published DFT results on TMDs functionalization [18–20], in this work we do not report results on the functionalized T phase since this structure evolve to T' structure upon energy minimization already when unmodified. Consistently with experiments [8], in our calculations the proposed molecules are found to chemically bind to the metallic MoS₂ monolayer while the attachment to the semiconducting phase is highly unfavorable. Correspondingly, the stability of the H and T' two phases is inverted if compared to that of the unmodified systems. Moreover, our results show that the proposed molecules are able to strongly change the electronic properties of the monolayers and effectively tune their optical properties.

2. Computational method

DFT calculations were carried out using the Quantum-espresso *ab initio* simulation package [21] by employing ultrasoft pseudopotentials, the generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE) formulation [22] was used for the exchange–correlation functional, the plane wave

energy cutoff was set to 40 Ry (400 Ry) for the plane wave (electron density) basis set and the k-point grid was set to (16 × 16 × 1) for monolayer unit cells and reduced accordingly as the supercell dimensions increased in order to ensure a consistent k-point density. A vacuum layer of about 10 Å was introduced in the supercell in the direction perpendicular to the 2D layer to avoid spurious interactions between periodic replicas. Methyl groups were symmetrically attached in pairs at the two sides of the MoS₂ layers to avoid spurious electric fields in the supercell. In particular, we considered hexagonal (2 × 2) and (4 × 4) supercells with 2 or 4 –CH₃ groups: these correspond to C/S coverages varying from 6.25% to 50%. Structural relaxation was considered converged when forces on atoms were below 10^{−3} a.u.

To make contact with experimental results on MS₂ functionalization, we calculated the reaction energies (ΔE_r) for the surface modification procedure realized experimentally in [8], which involves the reaction of a MS₂ monolayer with alkyl-iodide molecules to give alkyl-functionalized MS₂ and molecular iodine. The value of ΔE_r per molecule can be obtained as follows:

$$\Delta E_r = -\frac{1}{n} [E_{\text{MS}_2} + nE_{\text{CH}_3\text{I}} - (E_{\text{MS}_2-n\text{CH}_3} + nE_{\text{I}_2})] \quad (1)$$

where E_{MS_2} , $E_{\text{CH}_3\text{I}}$ and E_{I_2} are the total energies of the pure monolayer, of methyl-iodine and of the iodine molecule respectively, while $E_{\text{MS}_2-n\text{CH}_3}$ is the total energy of the functionalized monolayer. n is number of methyl groups attached to the monolayer. Further, to get an estimate of the relative stability of the functionalized H-MS₂ and T'-MS₂ at a given –CH₃ coverage, we calculated the total energy difference between the two functionalized phases as follows:

$$\Delta E = \frac{1}{m} [(E_{\text{H-MS}_2-n\text{CH}_3} - E_{\text{T'-MS}_2-n\text{CH}_3})] \quad (2)$$

where m is the number of MS₂ primitive cells in the simulation supercell and n in the number of –CH₃ attached to MS₂. For a given coverage, a negative ΔE indicates that the H phase is the more stable one, whereas a positive value highlights that the T' phase is lower in energy.

DFT-KS eigenvalues and eigenvectors of the relaxed structures were used to calculate the independent-particle (IP) ‘optical’ spectra. To check the role of many-body effects for selected structures, quasi-particle (QP) energies were obtained using the GW approximation (see [23] and references therein) and optical excitation energies by solving the Bethe–Salpeter equation (BSE) [23] using the YAMBO code [24]. For the GW simulations a plasmon-pole approximation for the inverse dielectric matrix was applied [25]. A cutoff of 10 Ry (60 Ry) was used for the correlation Σ_c (exchange Σ_x) part of the self-energy. The sum over unoccupied states for Σ_c and the dielectric matrix was performed up to about ~45 eV above the VBM. In order to speed up the convergence with respect to empty states we adopted the technique described in [26]. Finally, once QP energies and eigenfunctions were obtained, the optical properties were calculated by solving the BSE where the electron–hole interaction is also taken into account [23, 24, 27]. A k-point grid of (12 × 12 × 1) was

Table 1. Equilibrium lattice parameter, a (Å), metal-chalcogenide distance, d_{MS} (Å), total energy difference ΔE (eV), calculated with respect to the H polytype, and electronic energy band gap, E_g (eV), calculated for three MoS₂ and WS₂ monolayer phases (H, T and T'). The two values of energy gap reported for the H-WS₂ phase are calculated with (soc) and without (nosoc) spin-orbit interaction. For the T' phase two lattice parameters correspond to the two inequivalent primitive lattice directions.

| | MoS ₂ | | | | WS ₂ | | | |
|----|------------------|--------------|------------|-------|-----------------|--------------|------------|----------------------------|
| | a | d_{MS} | ΔE | E_g | a | d_{MS} | ΔE | E_g |
| H | 3.19 | 2.42 | 0.00 | 1.67 | 3.18 | 2.41 | 0.00 | 1.89 (nosoc) 1.57 (soc) |
| T | 3.20 | 2.44 | 0.83 | 0.00 | 3.21 | 2.44 | 0.88 | 0.0 |
| T' | 6.55 3.18 | 2.42 2.50 | 0.56 | 0.02 | 6.56 3.20 | 2.47 2.51 | 0.53 | 0.0 |

used to reach convergence of ~ 0.05 eV for both the GW and BSE calculations for (2×2) supercells, while a $(6 \times 6 \times 1)$ k-point grid was used for (4×4) supercells. A cutoff in the Coulomb potential in the direction perpendicular to the monolayer was used in the excited state calculations to eliminate the spurious interactions along the non-periodic direction and to simulate a real isolated nanosheet [28].

3. Results and discussion

As previously mentioned, MS₂ monolayers are known to exist in different polytype structures. The lowest energy phase corresponds to the hexagonal H phase in which each metal (M) atom is found in a trigonal prismatic coordination with equilibrium M–S bond distance reported in table 1. Two higher energy phases have also been reported: the tetragonal T phase in which M has an octahedral coordination and a distorted T' phase in which the sulfur atoms form two puckered layers characterized by outer and inner S atoms and dimerization of the M atoms (see figure S1 (in the supplementary information available online at stacks.iop.org/JPhysCM/31/235701/mmedia)). In the latter phase M–S distances are not all equivalent; the MS distances with the inner S atoms are longer than those with the outer S atoms; the corresponding two values are reported in column d_{MS} of table 1. In agreement with previous calculations [17] our DFT calculations predict that the lowest energy phase corresponds to the H phase for both MoS₂ and WS₂ while the T and T' phases are at higher energies (the relative energies are reported in table 1). In addition, the H-MoS₂ and H-WS₂ phase are semiconducting, while the T phase is metallic and the T' structure presents a small energy gap (for MoS₂). In the case of MoS₂ we performed a Nudged Elastic Band calculation along the path H \rightarrow T \rightarrow T' that revealed that while the first transition has a barrier of 1.53 eV/cell, the second step is barrierless (see figure S2). Thus, DFT calculations predict that the T phase is unstable and evolves spontaneously to the metastable T' phase when simulated in supercells, in agreement with [17]. For this reason, in the following we report the functionalization of the H and T' phase only. We highlight the fact that in the experimental literature no explicit distinction is made between the T and T' phase and results are generally discussed in terms of functionalization of a generic 'metallic' phase, while previous DFT calculations [18–20] report functionalized T structures which are

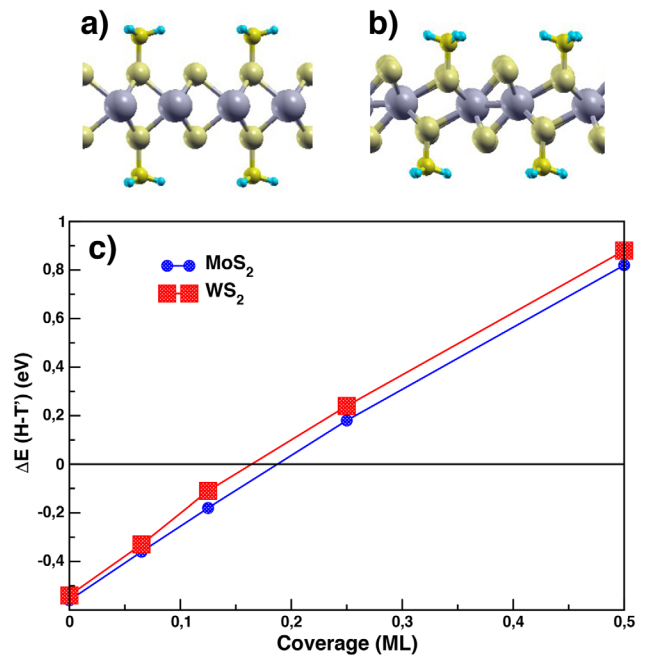


Figure 1. Panel (a) and (b) report a ball and stick representation of methyl functionalized H- and T'-MoS₂ at 25% coverage. Panel (c) represents the total energy difference, ΔE , between the H phase and the T' phase at varying $-CH_3$ coverage for both MoS₂ and WS₂ monolayers (negative values indicate that the H phase is lower in energy and viceversa).

unstable upon force minimization and completely neglect T' structures.

When $-CH_3$ groups are attached to the surface of MS₂ H-phase a covalent bond between the sulphur atom of the monolayer and the carbon atom of the methyl group forms at a distance of 1.86 Å in the case on MoS₂ and 1.90 Å in the case of WS₂, and correspondingly the underlying S–M bond distance becomes 2.40 Å (to be compared with 2.42 Å in the unmodified layer). The resulting structure is shown in panel (a) of figure 1. The reaction energy, ΔE_r , evaluated according to equation (1) is 1.3 eV/molecule and 0.1 eV/molecule for MoS₂ and WS₂, respectively. The reaction is endothermic and thus functionalization would not occur spontaneously at the H-phase surface, in agreement with the experimental findings [8]. When the coverage increases up to $\frac{1}{2}$ ML the methyl groups become too close and the reaction becomes more unfavorable. We highlight that in [18] the authors reported negative values of reaction energies of the methyl groups to the

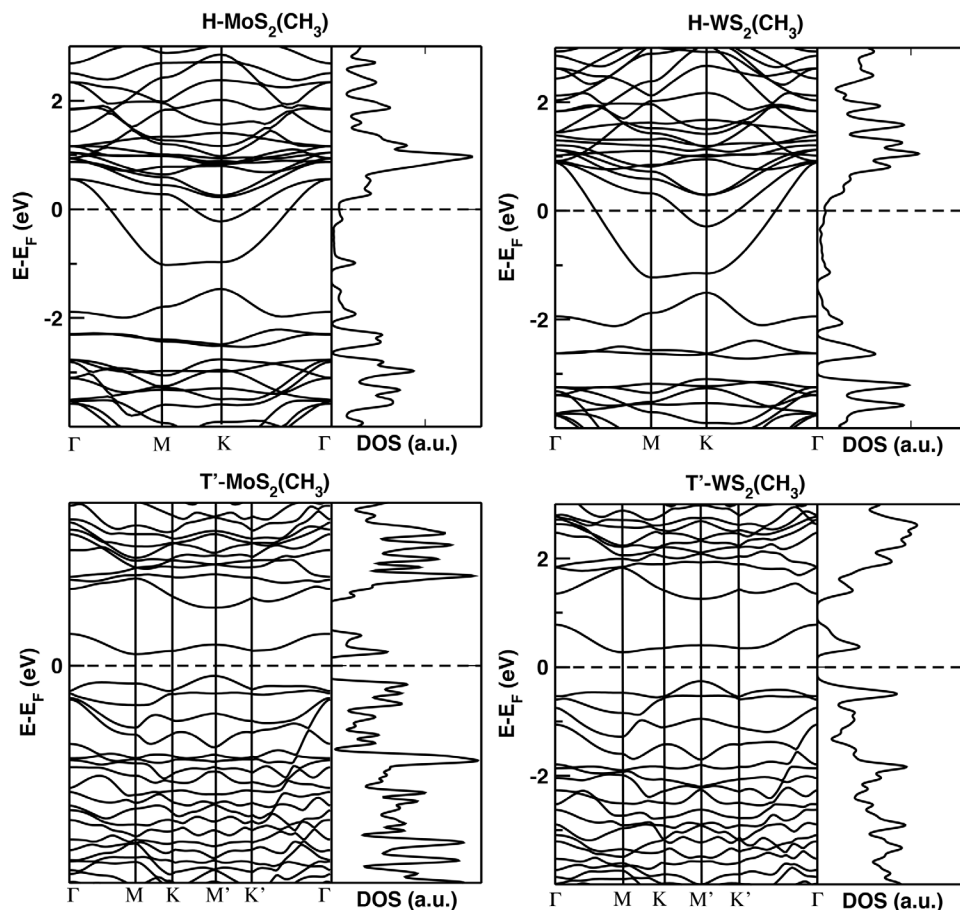


Figure 2. Band structure and corresponding DOS of MoS₂ (left panels) and WS₂ (right panels) monolayers in the H (top panels) and T' (bottom panels) phases functionalized with methyl groups at 25% coverage. The zero of energy corresponds to the Fermi level of the system.

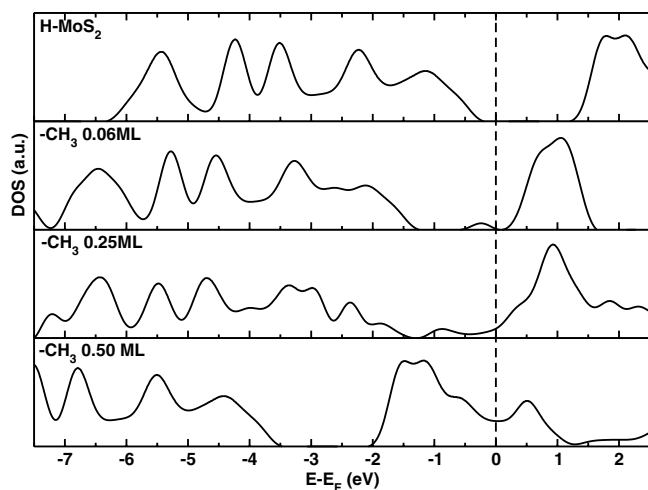


Figure 3. DOS of MoS₂ monolayers in the H phase functionalized with methyl groups at 0, 6, 25 and 50% coverage. The zero of energy corresponds to the Fermi level of the system.

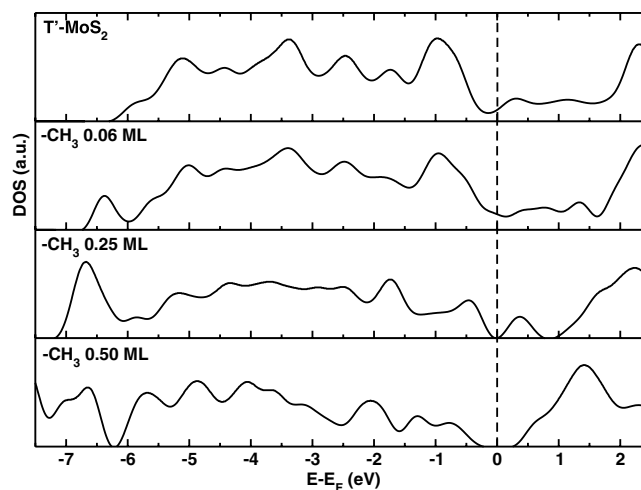


Figure 4. DOS of MoS₂ monolayers in the T' phase functionalized with methyl groups at 0, 6, 25 and 50% coverage. The zero of energy corresponds to the Fermi level of the system.

H-MoS₂ surface; although such values correspond to the interaction of highly reactive methyl radicals with the monolayer and thus cannot be compared directly with the functionalization procedure realized experimentally in a liquid environment [8]. Interestingly, at low coverage, the presence of -CH₃ groups at the H-MS₂ surface introduces donor states at the bottom of the conduction bands turning the monolayer into an

n-type semiconductor. As the coverage increases above 25% the system becomes metallic, as evidenced by an analysis of the band structure and density of states (DOS) reported in figures 2 and 3. The states around the Fermi energy mostly originate from the atomic orbital of the sulfur (s orbital) and carbon (p orbital) atoms involved in the C-S bond, but also from the underlying Mo (d orbitals) atoms as revealed by the

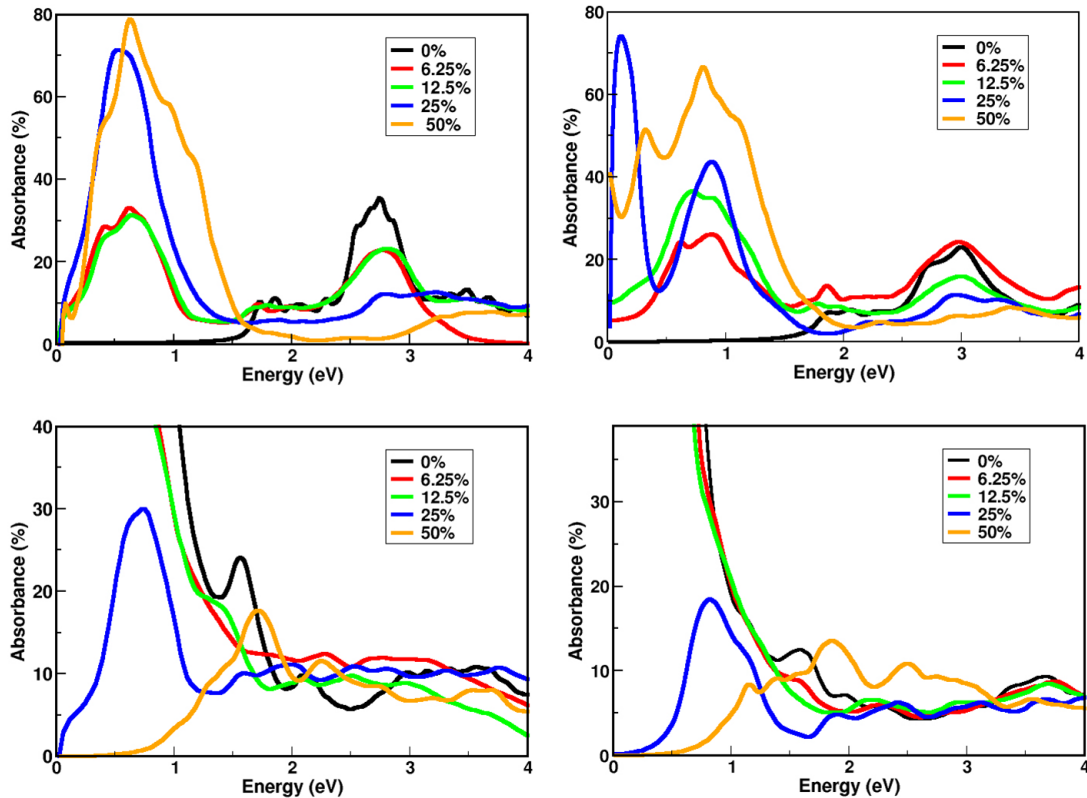


Figure 5. Absorbance spectra of the functionalized MoS₂ (left) and WS₂ (right) in the H (top panel) and T' (bottom panel) phases at varying $-\text{CH}_3$ coverages calculated at the independent-particle level (IP) of approximation.

isosurface density plot of electronic states around the Fermi level and represented in figure S3.

Upon molecular attachment, the T' phase behaves in a completely different manner compared to the H phase. Due to the puckered structure of the T' monolayer the sulphur atoms are not all equivalent and the methyl group attachment is favored when occurring at the lower sulphur atoms. The reaction energy calculated by employing equation (1) gives -0.23 eV/molecule for MoS₂ and -0.01 eV/molecule for WS₂ for up to 25% coverage, which is an indication that the reaction would be spontaneous for the T' phase. The equilibrium S–C bond length in this case is 1.82 Å and the underlying S–M bond increases by about 2%. An analysis of the electronic structure of the T' functionalized systems gives insight into the origin of the stability of these systems compared to the H phase. In particular, in this case the p orbitals of the carbon atoms contribute to states that are well below the Fermi energy, being hybridized with the MoS₂ valence band states. This is consistent with the fact that the S–C bond is stronger in the T' phase. Moreover, in contrast to the case of the H-MoS₂ functionalized structures the orbitals around the Fermi level are localized on the monolayer and not on the molecular fragments. Comparing the DOS of the functionalized T' phase with that of the pure phase, it is apparent that a gap opens, which increases with increasing coverage (see figure 4).

Interestingly, the relative stability of the H and T' phases depends on the $-\text{CH}_3$ coverage. This can be estimated by the total energy difference of the two phases as a function of the coverage and normalized to the number of TMD unit cells in the structure by employing equation (2). As shown in panel

(c) of figure 1, at coverages below about 20% the H polytype is lower in energy, while for higher coverages the T' becomes the lowest energy phase. In this respect, organic surface functionalization appears to be an effective way to engineer the phase of MoS₂ and WS₂ [29].

The changes in the electronic structure of functionalized MS₂ lead to strong modulations of their optical response with respect to the pristine monolayers. Even though our simulations predict that the functionalized H-phase is less stable than the T'-phase, the presence of both phases in the functionalized samples has been reported (see e.g. [8]). For this reason, in figure 5, we show the absorbance spectra of both the functionalized MoS₂ (left panels) and WS₂ (right panels) monolayers in the H (top panels) and T' (bottom panel) phases. For the T' structure an evident intensity reduction and a blue shift of the low energy optical peak is found with increasing the molecular coverage. In particular for coverage equal to or larger than 25% new broad optical peaks in the IR-VIS region appear. The observed trend is similar for both MoS₂ and WS₂. In the case of the hexagonal phase, the optical spectrum redshifts with increase coverage and grows in intensity in the IR-region. All the spectra reported in figure 5 are calculated at the independent-particle level (IP) and thus provide only a qualitative indication of what might be observed experimentally in functionalized (defect-free) monolayers. Since the role of the excitons in the optical properties of 2D-TMDs is well known, we performed GW and BSE calculations for a selected configuration (T' with 25% of molecular coverage). Figures S4 and S5 show clearly how, while the form of the optical peak changes upon inclusion of many-body effects, its

energetic position remains in the same region. Furthermore, in order to verify the importance of the spin–orbit coupling in the optical spectra of functionalized monolayers, for selected case, we performed calculations with fully-relativistic pseudo-potentials. Including spin–orbit coupling has negligible effects on the optical spectra of the functionalized T' phase (see figure S6), while for the H phase the main differences occur in the optical peaks of the pristine ML.

4. Conclusions

In conclusion, in this work we have predicted how the structural and electronic properties of MoS₂ and WS₂ monolayers are modified by attaching methyl groups to their surface. For both materials we found that only the T' phase can be directly functionalized via an exothermic reaction employing methyl-iodide. Moreover –CH₃ functionalization, at coverages higher than 20%, induces an inversion of stability between the H and T' phases. The results suggest that the ability to accurately select the concentration of organic molecules attached to the monolayer surfaces, may be an effective way to engineer the optoelectronic properties of MoS₂ and WS₂ monolayers for selected device applications. For example, functionalized T'-MS₂ is characterized by an optical gap which increases at increasing methyl concentration, making it of potential interest for harvesting light in a wide spectral energy range. On the other hand, functionalized H-MS₂ is predicted to be metallic and thus could be used to build innovative FET devices.

Acknowledgments

MP and GC acknowledge PRACE and ISCRA initiatives for awarding access to computing resources on Marconi at CINECA. GC thanks the 'Internationalization Project' of Politecnico di Torino for funding support and HPC@POLITO for high-performance computing resources. MP acknowledges Tor Vergata University for financial support through the Mission-Sustainability Project 2DUTOPI. JCG is grateful to NERSC for providing computational resources.

ORCID iDs

M Palummo  <https://orcid.org/0000-0002-3097-8523>

G Cicero  <https://orcid.org/0000-0002-2920-9882>

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