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Predicting stable phase monolayer Mo₂C (MXene), a superconductor with chemically-tunable critical temperature†

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Two-dimensional (2D) superconductors have attracted great attention in recent years due to the possibility of new phenomena in lower dimensions. With many bulk transition metal carbides being well-known conventional superconductors, here we perform first-principles calculations to evaluate the possible superconductivity in a 2D monolayer Mo₂C. Three candidate structures (monolayer alpha-Mo₂C, 1T MXene-Mo₂C, and 2H MXene-Mo₂C) are considered and the most stable form is found to be 2H MXene-Mo₂C. Electronic structure calculations indicate that both unpassivated and passivated 2H forms exhibit metallic properties. We obtain phonon frequencies and electron–phonon couplings using density-functional perturbation theory, and based on the BCS theory and the McMillan equation, estimate the critical temperatures to be in the ~0–13 K range, depending on the species of surface termination (O, H and OH). The optimal termination group is H, which can increase the electron–phonon coupling and bring the critical temperature to 13 K. This shows a rather high critical temperature, tunable by surface termination, making this 2D carbide an interesting test bed for low-dimensional superconductivity.

Introduction

Superconductivity in 2D materials has recently been the focus of intensive research. Previously, superconductivity was explored theoretically in doped graphane,¹ graphene,² B₂C single layers,³ doped phosphorene,⁴ and, most recently, in two-dimensional boron.^{5,6} However, graphane, graphene and phosphorene require substantial doping to achieve good metallicity, whereas other intrinsically metallic materials such as B₂C or 2D boron are either

hypothetical or may have their properties strongly affected by the growth substrate. In contrast, MXenes, or monolayer transition metal carbides and carbonitrides, have been synthesized as standalone 2D layers with good metallic conductivity.⁷ Additionally, bulk carbides, especially transition metal carbides, have been known for years as superconductors.⁸

Two-dimensional transition metal carbides have gained great attention in recent years as their 2D crystals have been grown by chemical vapor deposition (CVD), and have also been obtained through hydrofluoric acid etching of MAX phases. Recently, Xu *et al.*^{9,10} reported the CVD synthesis of large-scale, high-quality, ultrathin alpha-Mo₂C 2D crystals and demonstrated suppression of the superconducting temperature with decreasing thickness.⁹ Unfortunately, great challenges still exist in CVD growth of Mo₂C monolayer samples. At the same time, monolayer 2D transition metal carbides, known as MXenes, can be produced by selectively etching “A” layers out from the parent MAX bulk phase.⁷ Here, M designates an early transition metal, A represents group A elements, and X is C and/or N. Thus synthesized MXenes are always terminated with functional groups, like hydroxyl and oxygen.¹¹ Since 2011, a variety of MXenes have been successfully synthesized using this method.^{12–15} The exceptional combination of TMC core and surface terminating groups endows MXenes with good metallic conductivity and surface hydrophilicity, as well as outstanding properties¹⁶ for applications in electronic devices,¹⁷ gas sensors,¹⁸ water purification,¹⁹ energy storage,²⁰ *etc.*

Unlike few-layer alpha-Mo₂C crystals, superconductivity has not yet been demonstrated in monolayer MXenes, and it is still unclear whether the superconducting state could survive as the thickness is reduced to a monolayer. MXenes may thus be a good test bed for exploring superconductivity in monolayer transition metal carbides and some of the best candidates to display superconductivity among other 2D materials, provided that other important prerequisites for the BCS superconductivity are met. This prompts us to theoretically explore the conventional superconductivity of MXenes, as described by the BCS theory.²¹

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Quite recently, Mo₂C MXene was exfoliated from bulk Mo₂Ga₂C,^{22,23} a unique MAX phase with two “A” layers.²⁴ In this paper, we identified the most stable form of the monolayer Mo₂C and established the relationship between bulk alpha-Mo₂C and the monolayer. Here we focus on Mo₂C MXene as a feasible, nearly atomic-layer thin material. Other structures, such as thicker Mo₃C₂, have never been successfully synthesized in experiments, and have been considered as “highly unstable and are thus unlikely to be synthesized”.²⁵ In contrast, Mo₂C MXene has been synthesized as a monolayer in experiments,^{22,23} making it more practical to be considered for applications. In addition, Mo₂C MXene has the same stoichiometry as the alpha-Mo₂C bulk material, which was reported as a superconductor.⁹ Given that surface terminations can change the relative stability of different phases of a 2D material, the functionalized derivatives of the Mo₂C monolayer were studied as well. Basic band structure calculation indicates that all the considered monolayers are metals, meeting the prerequisite for superconductivity. The superconducting critical temperatures (T_c) of bulk alpha-Mo₂C and its monolayer counterpart have been estimated, and agree with the reported reduction of T_c with thickness in Mo₂C. The variations of T_c with surface termination functional groups in Mo₂C monolayers were further explored. The rather high and well-tunable T_c makes the Mo₂C monolayer an appealing superconductor.

Results and discussion

As a starting point, we focused on the atomic structure of monolayer Mo₂C. Halim *et al.*²³ carefully characterized this new member of the MXene family, but the exact atomic arrangement is still controversial: Khazaei²⁶ and Sun²⁷ have separately put forward two different atomic structures, which we designate as MXene 1T and 2H phases, in keeping with the notation of transition metal dichalcogenides (TMDs).²⁸ In addition, the CVD growth may potentially produce monolayer alpha-Mo₂C. Keeping these facts in mind, we built three different Mo₂C monolayer structures: monolayer alpha-Mo₂C, 1T MXene-Mo₂C,

and 2H MXene-Mo₂C. The monolayer alpha-Mo₂C was constructed by truncating the 3D bulk phase²⁹ perpendicular to the [001] direction, as shown in Fig. 1a. The structure obtained by truncating normal to other low-index directions is however higher in energy or cannot exist as a monolayer (see Fig. S1, ESI†) and will not be discussed further.

The relaxed alpha-Mo₂C monolayer has an orthorhombic unit cell, as shown in Fig. 1b. The equilibrium lattice parameters are found to be $a = 2.70$ Å and $b = 5.86$ Å. In contrast, the two types of MXene-Mo₂C monolayers are arranged in hexagonal lattices. Atoms stack in a triple layer in a sequence of Mo–C–Mo. For the 1T phase, two Mo atomic layers stack in the A–B packing mode, whereas in the 2H phase (see Fig. 1c), one Mo layer shifts, turning the packing into the A–A mode. More details on the lattice constants and total energies of these structures are given in Table 1.

The structural stability of the three possible structures (monolayer alpha-Mo₂C, 1T MXene-Mo₂C, and 2H MXene-Mo₂C) was estimated by comparing their relative total energies. Clearly, 2H MXene-Mo₂C is the most stable among the three. Therefore, in the monolayer form, the 2H structure is most likely to be observed. The monolayer alpha-Mo₂C is very likely to convert into MXene-Mo₂C due to the considerable differences in energy. Fig. 1b shows one possible pathway for the alpha-Mo₂C monolayer to transform into the lowest energy 2H MXene-Mo₂C (the initial unit cell in Fig. 1b transforms into the cell shown with the red dotted lines in Fig. 1c). However, further experimental and theoretical studies are needed to confirm this pathway. In view of the large energy excess of monolayer alpha-Mo₂C relative to MXene-Mo₂C structures and, consequently, high chances of spontaneous transformation from monolayer alpha-Mo₂C to MXene-Mo₂C, hereafter, we will mainly discuss the MXene-Mo₂C monolayers.

Note that the energy difference between the 1T and 2H phases of MXene-Mo₂C is 0.25 eV per Mo₂C unit, which is much less than that of MoS₂, where the difference is 0.84 eV per MoS₂ unit.²⁸ We therefore considered the influence of surface functionalization on the stability of the MXene-Mo₂C monolayer, since surface terminations can change the relative stability of

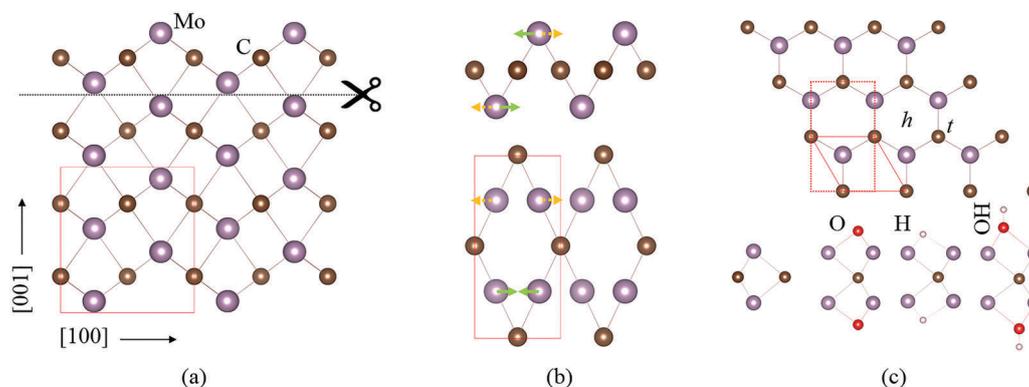


Fig. 1 Optimized geometries of (a) alpha-Mo₂C, (b) monolayer Mo₂C obtained by truncating from the alpha phase (side and top view), and (c) 2H MXene-Mo₂C (top and side view) and its derivatives (side view). h and t represent the possible adsorption sites for surface terminations. The red solid lines denote the unit cells.

Table 1 Lattice constants and relative total energies E (eV per Mo₂C unit) of Mo₂C monolayers. The lowest energy is used as the reference

Monolayer Mo ₂ C	a (Å)	b (Å)	E (eV)
Alpha phase	2.70	5.86	2.03
1T MXene	2.88	—	0.25
2H MXene	2.82	—	0

different phases of monolayer MoS₂.³⁰ The corresponding derivatives were constructed by saturating the surface Mo atoms, which are under-coordinated. Khazaei *et al.*²⁶ have investigated the possible functionalization of 1T MXene-Mo₂C with O and OH groups using DFT calculations. According to their study, the most stable configuration for 1T-Mo₂CO₂ is the one where all of the O atoms are located above the topmost sites of the C atoms. In contrast, all the OH terminations in 1T-Mo₂C(OH)₂ prefer the hollow sites between the three adjacent C atoms. Similar to the OH groups, Hui Pan found³¹ that the H atoms in 1T-Mo₂CH₂ tend to be positioned above the hollow sites. Hence, for the 1T MXene-Mo₂C monolayer, we only focus on these most stable configurations.

To the best of our knowledge, no previous work reported the functionalization of the 2H MXene phase, including Mo₂C. Here, for the first time, we systematically studied the functionalized derivatives of the 2H MXene-Mo₂C monolayer. In accordance with normal practice,³² we considered three different arrangements of functional groups on the surface of the 2H phase (see Fig. 1c): (I) all functional groups are placed above the hollow sites (site h); (II) all functional groups are situated on the topmost sites of the C atoms (site t), and (III) on one side, all the functional groups locate above the hollow sites, while on the other side, all the functional groups are at the topmost sites. It turns out that in the 2H MXene-Mo₂C monolayer, the H atoms still favor the hollow sites (model I), and O atoms are still most likely to stay at the topmost sites of the C atoms (model II). However, the OH groups now tend to adopt an asymmetric arrangement, *i.e.* above the hollow sites on one side while at the topmost sites on the other side (model III).

Table 2 summarizes the computed lattice constants and the relative total energies of the functionalized MXene-Mo₂C monolayer derivatives of the most stable 1T structures and the three possible 2H configurations. A general tendency of the lattice constant is that it decreases from the 1T phase to the 2H phase. The adsorption of functional groups on the surface generally results in lattice extension, except for 1T-Mo₂CO₂, which decreases by 1%. Comparing total energies, we found that all the 2H

Table 2 Lattice constants a (Å) and relative total energies E (eV per Mo₂C unit) of 1T and 2H MXene-Mo₂C functionalized derivatives. The lowest energies are used as the references

MXene derivative	1T Phase		2H Phase					
	a (Å)	E (eV)	Model I		Model II		Model III	
	a (Å)	E (eV)	a (Å)	E (eV)	a (Å)	E (eV)	a (Å)	E (eV)
Mo ₂ CO ₂	2.85	0.39	2.87	1.03	2.85	0	2.87	0.65
Mo ₂ CH ₂	2.90	0.26	2.88	0	2.87	0.55	2.88	0.23
Mo ₂ C(OH) ₂	3.24	0.38	2.89	0.05	2.91	0.10	2.89	0

configurations are lower in energy than the corresponding 1T structures, suggesting that the 2H phase MXene-Mo₂C is more stable than the 1T phase. This is in contrast to monolayer MoS₂, whose stability depends on the surface functionalization.³⁰ Note that we also tried to functionalize a single layer of the bulk alpha phase of Mo₂C, and found that the initial structures changed dramatically upon relaxation, with their final energies being still higher than those of the corresponding 2H structures. The 2H phase MXene-Mo₂C is thus the most energetically stable, regardless of the existence and type of the functional group. Note that Mo₂C is just one representative of the large MXene family. Herein we would like to call attention to the possibility of the 2H phase in other MXenes. Because of the difference in the atomic arrangements, substantially different properties may result, as seen below in the electronic properties of Mo₂C MXene.

As demonstrated in previous work,²⁶ the electronic properties of 1T MXene-Mo₂C are strongly correlated with surface terminations. For example, bare Mo₂C and Mo₂CO₂ are metals, while Mo₂C(OH)₂ are semiconductors with a band gap of 0.1 eV.²⁶ Unlike the 1T structures, 2H MXene-Mo₂C monolayers are quite different. Fig. 2 shows the band structures of the most stable 2H configurations. Unlike the 1T structures, all of them are metallic, which happens to meet the prerequisite for superconductivity. Note that the shown dependence of electronic properties on different phases could potentially be used to modulate MXene materials, which seems worth exploring further. In general, there are several bands crossing the Fermi level, indicating substantial density of states (DOS), beneficial for higher T_c . By further analyzing the projected electronic density of states (PDOS), we noted that DOS near the Fermi level is mainly contributed by the 4d orbitals of the molybdenum atoms.

Previously, a theoretical study by Zha *et al.*³³ reported no magnetization in 1T phase MXene-Mo₂C. In order to probe the possible magnetism in the 2H phase MXene-Mo₂C monolayers, we performed spin-polarized calculations in bare and functionalized structures. As can be seen from the electronic density of states (DOS) in Fig. 2, the majority and minority spin projections are symmetric, clearly indicating no magnetization. Thus, the nonmagnetic nature of the Mo₂C material is robust and cannot be altered readily by phase transformation or surface functionalization.

After fully exploring the electronic properties of MXene-Mo₂C and its functionalized derivatives, we now examine the possibility of conventional superconductivity. Due to the large computational cost, we studied only the energetically more favorable 2H MXene-Mo₂C and chose Mo₂CO₂, Mo₂CH₂ and Mo₂C(OH)₂ as the representatives for the functionalized derivatives, and considered only the most stable conformers. All calculations were performed with spin-unpolarized systems.

Fig. 3 shows the phonon spectra, electron-phonon interactions, Eliashberg spectral function, and the frequency-dependent electron-phonon coupling parameter $\lambda(\omega)$ of bare and functionalized 2H MXene-Mo₂C. The phonon spectra are characterized by distinct sets of well-separated frequency bands. The first band lies below 300 cm⁻¹ and consists of three acoustic modes and Mo optical modes. The acoustic modes near the Γ point display

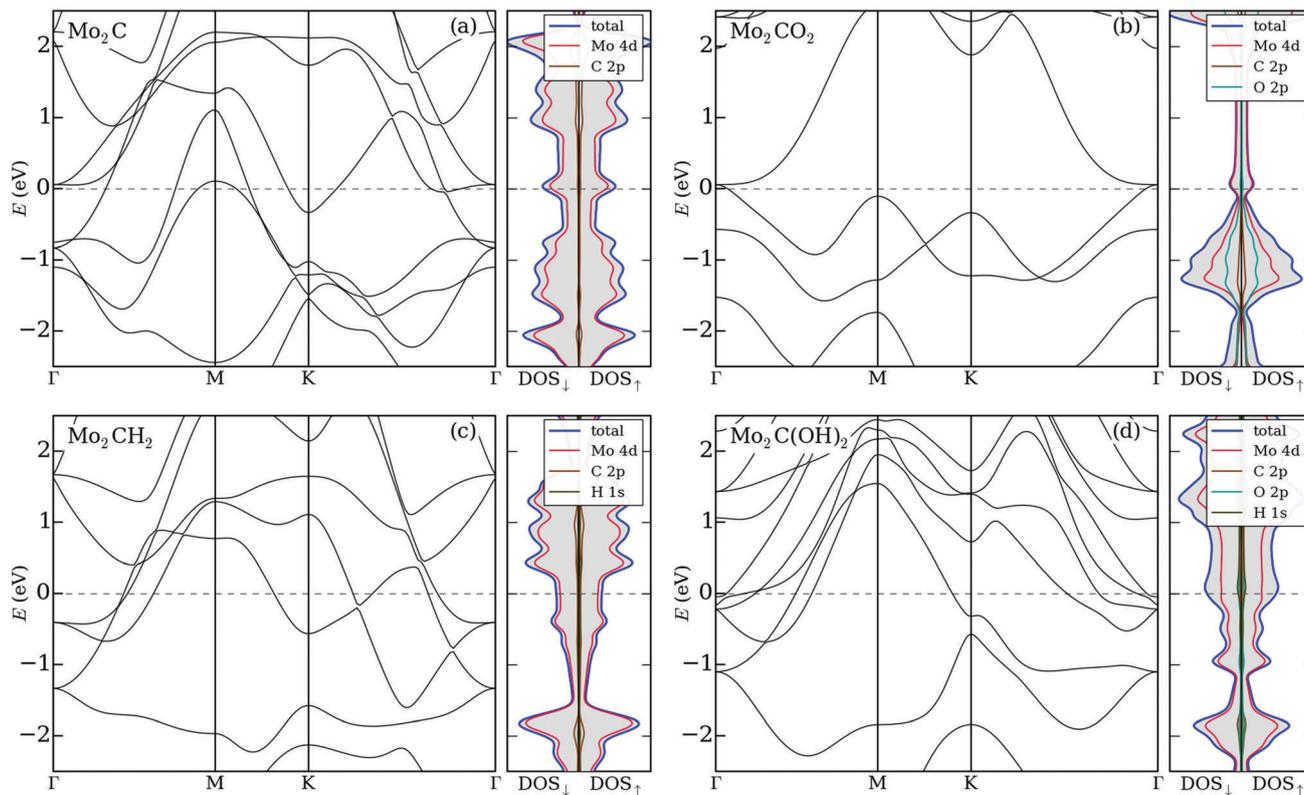


Fig. 2 Band structures and electronic density of states of (a) Mo_2C , (b) Mo_2CO_2 , (c) Mo_2CH_2 , and (d) $\text{Mo}_2\text{C}(\text{OH})_2$ 2H MXenes.

two linear in-plane and one parabolic out-of-plane dispersion curves, characteristic of a 2D system. Between the two in-plane linear acoustic modes, the lower energy one is longitudinal, and the higher energy one is transverse. Accordingly, along $\Gamma \rightarrow M$, the lower energy in-plane acoustic mode is polarized in the armchair direction, whereas the higher energy mode is polarized in the zigzag direction. The first two optical modes are doubly degenerate at the Γ point, and represent the in-plane twisting motion of the Mo atoms. The third optical mode is the transverse stretching vibration of the Mo_2 dimer. Remarkably, these low-frequency modes are present and have similar energies in all of the structures. The second band lies between 300 cm^{-1} and 800 cm^{-1} and mainly corresponds to the in-plane (lower branches) and out-of-plane (higher branches) optical vibrations of C and O atoms. For hydrogen-containing structures, there is also a band above 800 cm^{-1} (see Fig. S2 for $\text{Mo}_2\text{C}(\text{OH})_2$, ESI[†]) due to the vibrations of H atoms and/or the O–H bond.

The contributions of different phonon bands can be seen from the electron–phonon coupling parameter $\lambda(\omega)$. The first phonon band generally gives the greatest contribution to the total electron–phonon coupling. As can be seen from Fig. 3, the contribution of the band to the total coupling λ varies significantly among different monolayer structures: it is reduced from 0.50 in Mo_2C to 0.12 in Mo_2CO_2 , whereas it increases to 0.56 in Mo_2CH_2 , and to 1.53 in $\text{Mo}_2\text{C}(\text{OH})_2$. This indicates that functionalization can be used to effectively tune the coupling. The contribution of the second band increases from 0.05 in Mo_2C to 0.11 in Mo_2CO_2 and Mo_2CH_2 , to 0.18 in $\text{Mo}_2\text{C}(\text{OH})_2$, but remains

small overall. The third band gives small λ contributions of 0.07 and 0.01 in Mo_2CH_2 and $\text{Mo}_2\text{C}(\text{OH})_2$, respectively.

The flexural mode of the Mo_2CH_2 structure has very small imaginary frequencies near the Γ point (see Fig. S2, ESI[†]). The small imaginary frequency could be an artifact of the simulation, or reflect the actual lattice instability, in this case, the large-wave undulations of 2D materials. This type of instability has been previously seen in 2D boron structures, and can be remedied by applying a small strain or using a substrate.⁶ Accordingly, we applied a 1% strain to the Mo_2CH_2 structure and successfully eliminated the small imaginary frequencies. In contrast, the lowest phonon mode of the $\text{Mo}_2\text{C}(\text{OH})_2$ structure has large imaginary frequencies around the M point, as seen in Fig. 3d, indicating structural instability and a possible superstructure. Structural reconstruction has been confirmed from a calculation with a 2×2 supercell (see Fig. S3, ESI[†]). We also performed phonon calculations in a 2×2 supercell of $\text{Mo}_2\text{C}(\text{OH})_2$. Unfortunately, imaginary phonon frequencies still occur, possibly pointing to a continuous range of wavelengths at which $\text{Mo}_2\text{C}(\text{OH})_2$ is unstable, consistent with a large region of imaginary frequencies seen around the M point in Fig. 3d. We thus regard $\text{Mo}_2\text{C}(\text{OH})_2$ as being structurally unstable.

We have calculated the superconducting critical temperatures T_c , as given by the McMillan equation.³⁴ The obtained critical temperatures are 3.2 K for Mo_2C , ~ 0 K for Mo_2CO_2 , and 12.6 K for Mo_2CH_2 . Although unstable, we still formally evaluated T_c for the $\text{Mo}_2\text{C}(\text{OH})_2$ structure. The obtained $T_c = 25.5$ K for $\text{Mo}_2\text{C}(\text{OH})_2$ is surprisingly high, although it is unclear whether

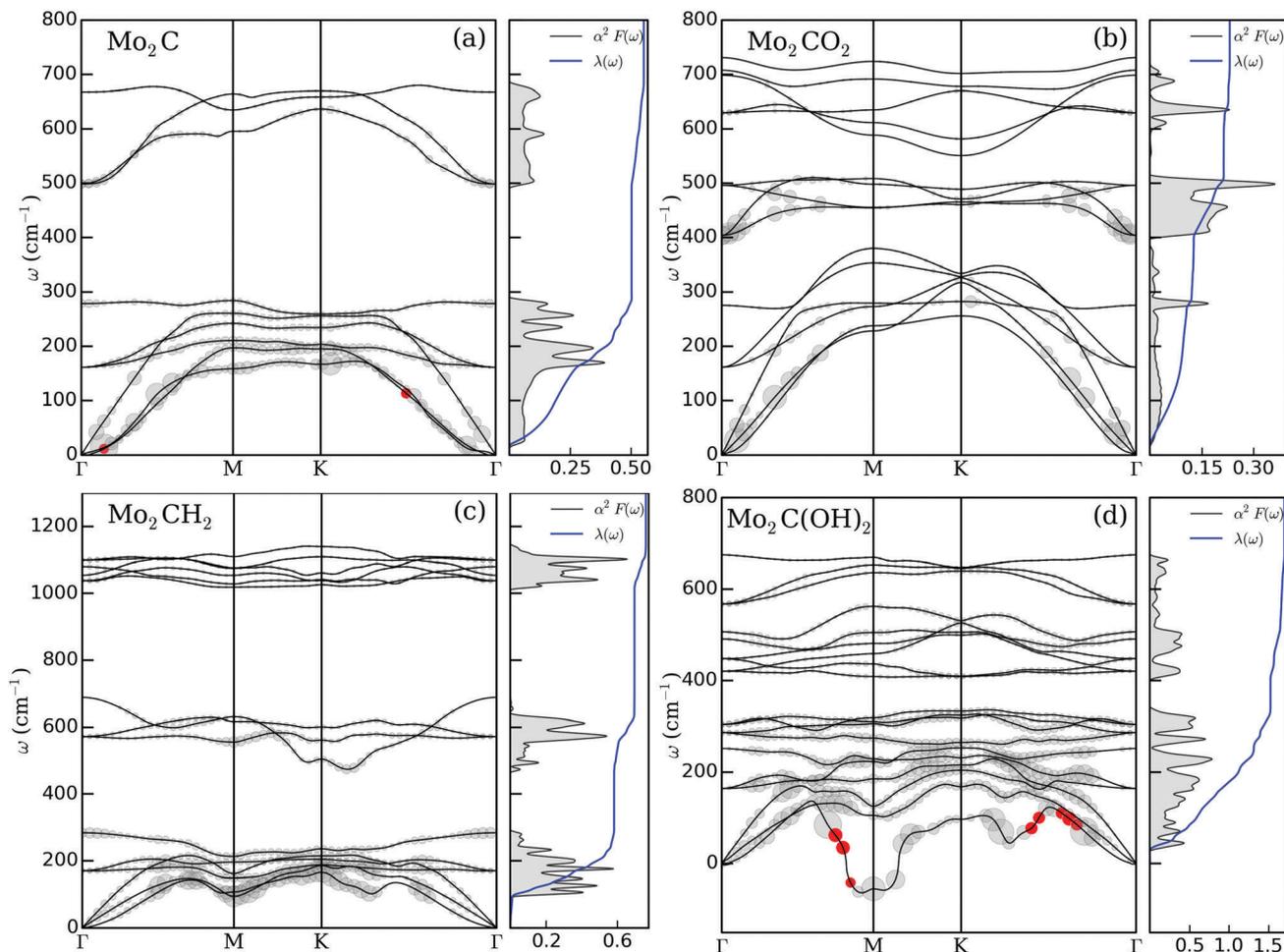


Fig. 3 Phonon dispersions, electron–phonon interactions, Eliashberg spectral function, and the frequency-dependent electron–phonon couplings of (a) Mo_2C , (b) Mo_2CO_2 , (c) Mo_2CH_2 , and (d) $\text{Mo}_2\text{C}(\text{OH})_2$ 2H MXenes. A small strain of 1% has been applied to the Mo_2CH_2 structure. The areas of the grey and red circles are proportional to the magnitude of the electron–phonon interaction. The areas of the red circles have been reduced 10-fold.

the lattice instability drives the T_c value up in this structure. The increase in T_c in hydrogen-containing structures as compared to bare Mo_2C is mostly due to the increased electron–phonon coupling, whereas the vanishing T_c for the Mo_2CO_2 structure is a result of the depletion of electronic density of states near the Fermi level, as can be seen in Fig. 2.

In order to gain some insight into the change in T_c from the monolayer to bulk, we have additionally performed a calculation of T_c for the bulk alpha phase Mo_2C , obtaining $T_c = 5$ K. This value agrees favorably with the experimentally measured T_c in this material, for which the reported values are in the range between 4 K and 12 K.⁸ The calculated T_c of 5 K in the bulk Mo_2C is slightly higher than the calculated value of 3 K in monolayer Mo_2C , in agreement with experimental trends for the dependence of T_c on thickness.⁹ In addition, our preliminary results for other MXenes, namely Ti_2C and Ti_2CH_2 (also see the ESI†), show much weaker electron–phonon coupling as compared with Mo_2C and Mo_2CH_2 , yielding much lower T_c (~ 1.3 K and 0 K for Ti_2C and Ti_2CH_2 , respectively). Further studies are needed to determine whether Mo_2C with its rather large T_c is an exception in the MXene family, or whether tuning by functionalization could lead to even higher

T_c in other MXenes. After the submission of our work, we became aware of a study³⁵ discussing superconductivity in the 1T phase MXene Mo_2C , which we expressly demonstrate to be less stable than the 2H phase. Moreover, we select more realistic termination groups occurring in experiments, all of them preserving Mo_2C metallicity, which is a prerequisite for superconductivity. The present analysis thus should provide valuable insight into the correct ground state structure of this 2D monolayer and the chemically tunable superconductivity.

Conclusions

In summary, first-principles calculations of monolayer Mo_2C were performed. Among the three considered structures (monolayer alpha- Mo_2C , 1T MXene- Mo_2C , and 2H MXene- Mo_2C), 2H MXene- Mo_2C was found to be the most stable. Despite possible passivation, 2H MXene- Mo_2C preserved its lowest energy status and the metallic state regardless of whether the functional groups exist or not. The possibility of conventional superconductivity and the effect of the functional groups on the critical temperature were

subsequently explored. The critical temperatures varied between ~ 0 and 13 K as the termination functional groups changed. The rather high and well-tunable critical temperatures make this new 2D material an appealing superconductor.

Computational method

All our results were obtained from first-principles density-functional theory (DFT) calculation within the local-density approximation (LDA)³⁶ using the projector-augmented wave method, as implemented in the Quantum ESPRESSO³⁷ package. The plane-wave cutoff energy was 60 Ry and converged results were obtained using a Monkhorst–Pack grid of $63 \times 63 \times 1$ for both k -mesh and q -mesh. A smearing of 0.01 Ry was used. In order to avoid the interactions generated by the periodic boundary condition, the interlayer distance was set to at least 10 Å. The geometries of all structures were relaxed to the minimum energy configurations by following the forces on atoms and the stress tensor on the unit cell.

The evaluation of the critical temperatures for the superconducting transition was based on the microscopic theory of Bardeen, Cooper, and Schrieffer (BCS),²¹ with the rigorous treatment of electron–phonon interactions introduced by Migdal³⁸ and Eliashberg.³⁹ Phonon frequencies and electron–phonon coupling coefficients were calculated using density-functional perturbation theory.⁴⁰ The actual T_c values reported here were obtained from the analytical approximation given by the McMillan equation,³⁴ further modified by Allen and Dynes:⁴¹

$$k_B T_c = \frac{\hbar \omega_{\text{ln}}}{1.20} \exp \left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right]$$

The prefactor ω_{ln} was the logarithmically averaged phonon frequency and the effective electron–electron repulsion μ^* was treated as an empirical parameter with the value $\mu^* = 0.1$.^{42,43}

Competing interest

The authors declare no competing financial interest.

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