Influence of surface functionalization on thermal transport and thermoelectric properties of MXene monolayers.

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1. Band Structures

1.1. Ti₂CO₂



Figure S1: Atomic orbital weights in the energy bands of Ti₂CO₂. p and d orbital weights for Model II are depicted in (a) and (b). p and d orbital weights for Model III are depicted in (c) and (d). The size of each

symbol is proportional to the weight of the atomic orbital. Spin orbit coupling (SOC) was neglected in these calculations.

1.2. Zr₂CO₂



Figure S2: Atomic orbital weights in the energy bands of Zr_2CO_2 . *p* and *d* orbital weights for Model II are depicted in (a) and (b). *p* and *d* orbital weights for Model III are depicted in (c) and (d). The size of each symbol is proportional to the weight of the atomic orbital. SOC was neglected in these calculations.

1.3. Hf₂CO₂



Figure S3: Atomic orbital weights in the energy bands of Hf_2CO_2 . *p* and *d* orbital weights for Model II are depicted in (a) and (b). *p* and *d* orbital weights for Model III are depicted in (c) and (d). The size of each symbol is proportional to the weight of the atomic orbital. SOC was neglected in these calculations.



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Figure S4: Atomic orbital weights in the energy bands of Sc_2CO_2 . *p* and *d* orbital weights for Model III are depicted in (a) and (b). The size of each symbol is proportional to the weight of the atomic orbital. SOC was neglected in these calculations.

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-4 ⊾ Γ $\begin{array}{c} O \\ O \\ \Box \\ d_{xy} + d_{xz} + d_{y} \\ d_{x^{2}} \\ \Delta \\ d_{z^{2}} \end{array}$

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2. Density of States



Figure S5: Total density of states and partial density of states of each atom composing (a) Ti_2CO_2 MD-II (b) Ti_2CO_2 MD-III c) Zr_2CO_2 MD-II (d) Zr_2CO_2 MD-III e) Hf_2CO_2 MD-II (f) Hf_2CO_2 MD-III g) Sc_2CO_2 MD-III.

3. Phonon Dispersions



Figure S6: Phonon dispersion curve of Ti_2CO_2 monolayer in (a) MD-II and (b) MD-III configuration. Color bar represent the calculated group velocity in km/h.



Figure S7: Phonon dispersion curves of Zr_2CO_2 monolayer in (a) MD-II and (b) MD-III configuration. Colour bar represent the calculated group velocity in km/h.



Figure S8: Phonon dispersion curves of Hf_2CO_2 monolayer in (a) MD-II and (b) MD-III configuration. Colour bar represent the calculated group velocity in km/h.



Figure S9: Phonon dispersion curve of Sc_2CO_2 monolayer in MD-III configuration. Colour bar represent the calculated group velocity in km/h.

4. Thermal Properties 4.1. Relaxation Time Approximation



Figure S10: The ratio of thermal conductivity values obtained by self-consistent and relaxation time approximation solutions for (a) MD-II and (b) MD-III structures.

In general, the difference between Relaxation Time Approximation (RTA) and Iterative Solution (IS) is on the order of 10% for 3D materials, but it becomes considerably large for 2D materials. Figure S10 (a) and (b) show the ratio of thermal conductivities calculated using RTA and IS. As shown in these figures, RTA and IS predict quite different TC values, especially, for low temperature values. This is because RTA always severely underestimates TC when the normal scattering (being dominant at low temperature) is strong, which can cause the repopulation of phonon states. At 300 K, the under-prediction is by a factor of around 1.08-1.18 for both MD-II and MD-III configurations. Lindsay *et al.*-\cite reported this under-prediction by a factor of 5 for single-layer graphene at 300 K. Nevertheless, it works reasonably well when Umklapp scattering (being dominant at high temperature) is strong. Therefore, we have a much better agreement at high temperatures, meaning that three phonons

scattering mechanisms are dominated by the Umklapp process. The calculated TC values based on IS are greater than RTA values and the ratio of TC has no significant dependency on temperature above room temperature (300 K). This is because of fact that the presence of low lying optical modes enhances Umklapp scattering involving an optical and an acoustic mode.



Figure S11: Contribution of phonon modes of functionalized MXene structures to the total lattice thermal conductivity.

The Figure S11 shows the ratio of thermal conductivity (TC) of three acoustic modes (denoted as ZA, TA, LA) and three lowest optical modes (denoted as O_I , O_{II} , O_{III}) to the total lattice TC. The sum of the remaining optical modes O_{sum} is also shown in the same figure. In the case of MD-II configurations, the contribution of ZA branch to the TC is generally larger than that of TA and LA branches. The LA mode gives prominently higher contributions to the total lattice TC in MD-III structures. Interestingly, the contribution of the ZA mode is significantly suppressed in MD-III configuration of M₂CO₂ (M=Ti, Zr, Hf) due to downward

shift of this branch (Figs. S6-S8). The lattice TC is mostly contributed by acoustic modes (more than 70% of the total lattice TC at room temperature) as compared to the optical modes. The optical modes provide more contribution to the total lattice TC in MD-II than in MD-III. Furthermore, the contribution of the acoustic and optical branches become less sensitive (nearly independent) to temperature above 300 K, meaning that all phonon modes are already excited when temperature exceeds 300 K.



Figure S12: The dependence of relaxation time to frequency.

Since the calculated group velocities only provide a limited insight, we also calculated the relaxation time to have a better understanding of thermal conductivities. The TC is also affected significantly by relaxation time. Different phonon relaxation times between different materials are one of the main reasons that lead to a difference in the lattice TC. The frequency dependence of relaxation time of acoustic (LA-TA and ZA) and three lowest optical modes are demonstrated in Figure S12 for all the MXene structures considered in this study. The

acoustic branches have much higher relaxation times than optical branches. The relaxation times of optical branches represent weak frequency dependence whereas the phonon relaxation times of acoustic modes decrease as the frequency increases and exhibit frequency dependence as ω^{-2} at low frequency region. This dependency of the phonon relaxation time on the frequency is consistent with Klemens' prediction. According to our phonon calculations, the ZA branch is softer in MD-III than in MD-II. Thus, the relaxation time of this mode in MD-III is quite short as compared to that in MD-II. This translates into a lower TC in the former.



Figure S13: Lattice TC as a function of Mean Free Path at T = 300 K, 500 K and 700 K.

The phonon Mean Free Path (MFP) provides information about the average distance travelled by a phonon between scattering events and also it helps to understand the thermal conduction process in the related system. Figure S13 illustrates the dependence of normalized lattice TC on the MFP at different temperatures, namely T = 300 K, 500 K and 700 K. The contribution to lattice TC increases with increasing MFP value and then saturates after a certain value of MFP for each MXene structures. On the other hand, the lattice TC has its maximum value at

lower MFP values as the temperature increases. For all temperature values, Ti₂CO₂ in MD-III configuration has the lowest MFP at which the TC reaches its maximum value (585 nm at T =300 K, 335 nm at T = 500 K and \sim 230 nm at T = 700 K). This means that; increasing temperature shortens the MFP and only phonons with MFP smaller than these values provides contribution to the lattice TC at related temperatures. Hence, the TC will have minimal contribution when the sample size is more than these MFP values. At T = 300 K, MD-II structures have maximum MFP values higher than 1.2 µm (~1.23 µm for Ti₂CO₂, ~1.48 µm for Zr₂CO₂ and Hf₂CO₂). This indicates that the heat is mostly transported by phonons with MFP in a wide range. Additionally, we listed the MFP values that corresponding to 50% contribution to normalized lattice TC for studied M₂CO₂ (M=Ti, Zr, Hf, Sc) materials at considered temperatures in Table I. This implies that; if the sample size becomes smaller than these MFP values, that effectively leads to a decrease in the lattice TC. Increasing temperature causes a reduction in the MFP. The lattice TC of the MD-III structure is saturated by phonons with much shorter MFPs as compared to the MD-II structure. For instance, in the MD-II configuration of Ti₂CO₂, the phonons with MFP shorter than 175 nm provide 50% of lattice TC, while the maximum MFP for MD-III configuration of Ti₂CO₂ to achieve a 50% contribution is only 120 nm. This means that TC is more ballistic (diffusive) in MD-II (MD-III) than MD-III (MD-II). Figure S13 also suggests that we may use much smaller sample sizes for the MD-III structure to achieve a maximum TC.

Table SI: The MFP value corresponding to 50% contribution to normalized lattice TC for MD-II and MD-III configurations of M_2CO_2 (M=Ti, Zr, Hf, Sc) at T = 300 K, 500 K and 700 K.

| | T=3 | T=300 K | | T=500 K | | T=700 K | |
|----------------------------------|---------|---------|---------|---------|---------|---------|--|
| MFP(nm |) MD-II | MD-III | MD-II | MD-III | MD-II | MD-III | |
| Ti_2CO_2 | 175 | 120 | 100 | 60 | 70 | 40 | |
| $\rm Zr_2CO_2$ | 145 | 115 | 85 | 70 | 55 | 45 | |
| $\mathrm{Hf}_{2}\mathrm{CO}_{2}$ | 160 | 135 | 90 | 70 | 60 | 50 | |
| $\rm Sc_2CO_2$ | (Metal) | 75 | (Metal) | 40 | (Metal) | 25 | |