Electronic Supplemental Information for

"Vibrational properties of Ti_3C_2 and $Ti_3C_2T_2$ (T = O, F, OH) monosheets by first-principles calculations: a comparative study"

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Table S1. Calculated lattice constant of Ti_3AlC_2 with present calculation scheme and available data from previous work

Lattice constants	a (Å)	c (Å)
This work	3.07885	18.6705
Available data	3.075[1],3.0816[2],3.0824[3]	18.58[1],18.6379[2],18.6522[3]

Table S2. Calculated wavenumbers (in cm^{-1}) of Raman active modes of Ti_3AlC_2 with present calculation scheme and available data from previous work

Modes	ω_1 (E_{2g})	ω_2 (E_{1g})	ω_3 (E_{2g})	ω_4 (E_{1g})	ω_5 (E_{1g} and E_{2g})	ω_6 (A_{1g})
Experimental[4]	——	182	——	270	——	658
Experimental[5]	——	183.4	201.5	270.2	632.2	663.2
Calculated[5]	125	182	197	268	620 and 621	655
Calculated, this work	126	181	197	268	615 and 617	657

[1] X. Wang and Y. Zhou, *J. Mater. Sci. Tech.*, 2010, **26**, 385.
[2] Y. Xie and P. R. C. Kent, *Phys. Rev. B*, 2013, **87**, 235441.
[3] I. R. Shein and A. L. Ivanovskii, *Computational Materials Science*, 2012, **65**, 104.
[4] H. Zhang, X. Wang, H. Xiang, Z. Li and Y. Zhou, *Appl. Phys. Lett.*, 2014, **104**, 131903.
[5] V. Presser, M. Naguib, L. Chaput, A. Togo, G. Hug and M. W. Barsoum, *J. Raman Spectrosc.*, 2012, **43**, 168.

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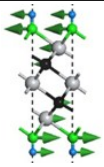
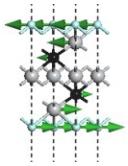
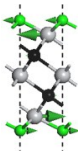
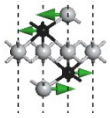
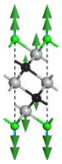
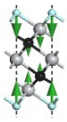
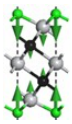
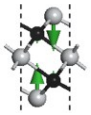
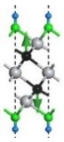
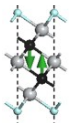
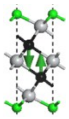
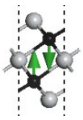
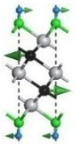
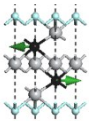
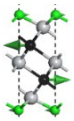
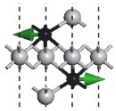
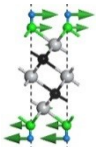
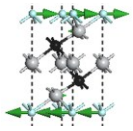
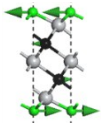
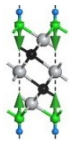
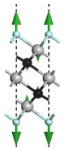
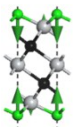
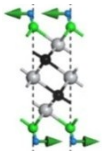
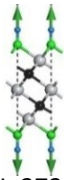
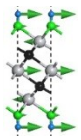
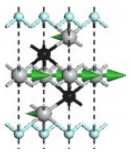
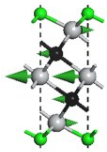
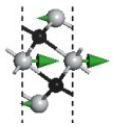
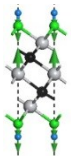
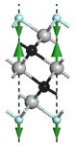
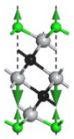
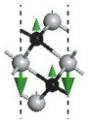
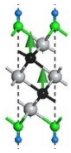
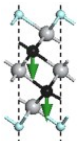
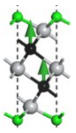
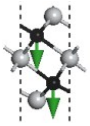
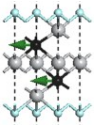
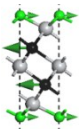
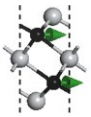
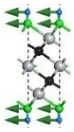
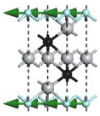
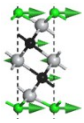
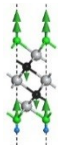
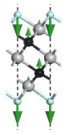
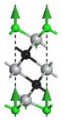
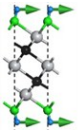
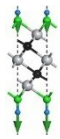
Table S3. Assignment of Raman active vibration modes of Ti_3C_2 and $Ti_3C_2T_2$ monosheets

Mode \ Formula	$Ti_3C_2(OH)_2$	$Ti_3C_2F_2$	$Ti_3C_2O_2$	Ti_3C_2
ω_1 (E_g)	 Ti2[a], C, O, H; 138[b]	 Ti2, C, F; 128	 Ti2, C, O; 107	 Ti2, C; 158
ω_2 (A_{1g})	 Ti2, C, O, H;218	 Ti2, C, F; 190	 Ti2, C, O; 208	 Ti2, C; 228
ω_3 (A_{1g})	 Ti2, C; 684	 Ti2, C; 694	 Ti2, C; 730	 C; 599
ω_4 (E_g)	 Ti2, C, H; 622	 Ti2, C, F; 612	 C, O; 523	 Ti2, C; 621
ω_5 (E_g)	 Ti2, C, O, H; 278	 Ti2, C, F; 231	 Ti2, C, O; 347	
ω_6 (A_{1g})	 Ti2, C,O, H; 514	 Ti2, C, F; 465	 Ti2, C, O; 586	
ω_7 (E_g)	 C,O, H; 437			
ω_8 (A_{1g})	 H; 3734			

[a] The main contributing atoms to the vibration mode are underlined.

[b] The number is the wave number (cm^{-1}) of the active mode.

Table S4. Assignment of IR active vibration mode of Ti_3C_2 and $Ti_3C_2T_2$ monosheets

Formula / Mode	$Ti_3C_2(OH)_2$	$Ti_3C_2F_2$	$Ti_3C_2O_2$	Ti_3C_2
ω_1 (E_u)	 Ti1[a],Ti2, C, O, H; 244[b]	 Ti1， Ti2, C, F; 225	 Ti1, Ti2, C; 179	 Ti1, Ti2, C; 277
ω_2 (A_{2u})	 Ti1,Ti2, C, O, H; 348	 Ti1， Ti2, C, F; 337	 Ti1,Ti2, C, O; 362	 Ti1, C, Ti2; 370
ω_3 (A_{2u})	 Ti1,Ti2,O,H,C; 577	 Ti2, C, F; 601	 Ti1,Ti2,O, C; 675	 C, Ti2, Ti1; 519
ω_4 (E_u)	 C, H, Ti1,Ti2; 637	 Ti1， Ti2, C, F; 633	 C, O , Ti1,Ti2; 473	 C, Ti1, Ti2; 625
ω_5 (E_u)	 Ti1,Ti2,C,O,H; 275	 Ti1， Ti2, C, F; 265	 Ti1, Ti2, C, O; 249	
ω_6 (A_{2u})	 C,Ti1,Ti2, O, H; 498	 Ti1， Ti2, C, F; 471	 Ti1,Ti2, C, O; 578	
ω_7 (E_u)	 O, H; 435			
ω_8 (A_{2u})	 H; 3732			

[a] The main contributing atoms to the vibration mode are underlined.

[b] The number is the wave number (cm^{-1}) of the active mode.

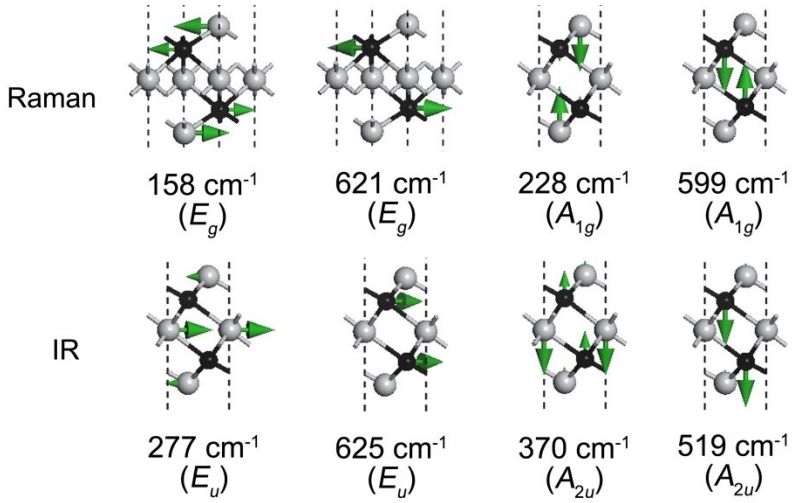


Fig. S1. Schematics of Raman and infrared active vibration modes of Ti_3C_2 monosheet.

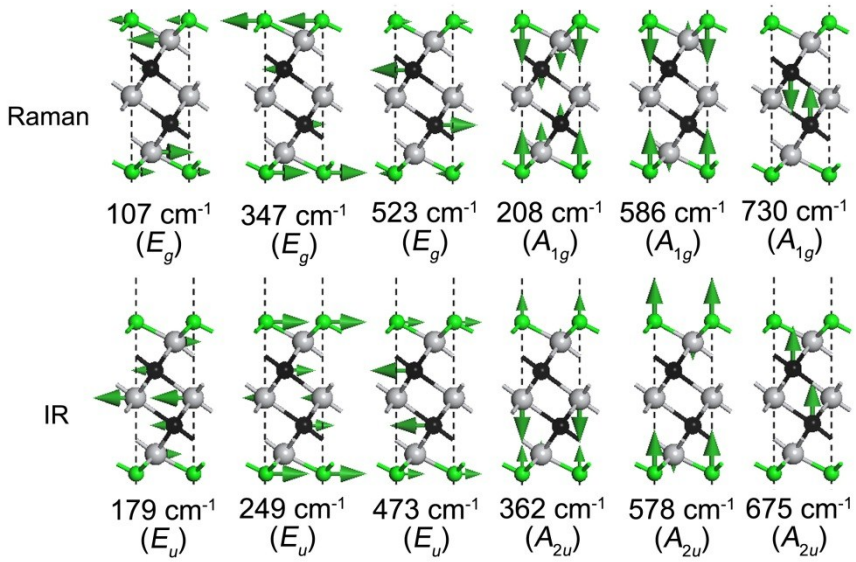


Fig. S2. Schematics of Raman and infrared active vibration modes of $Ti_3C_2O_2$ monosheet.

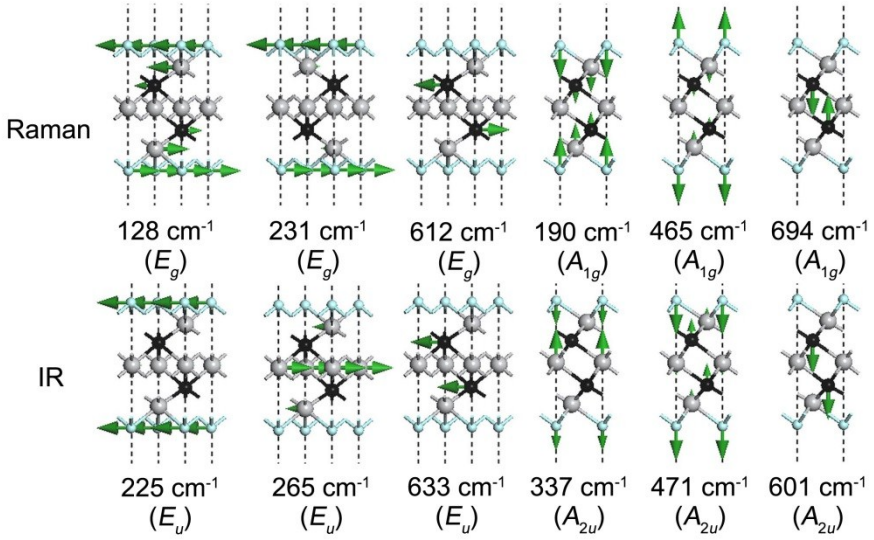


Fig. S3. Schematics of Raman and infrared active vibration modes of $Ti_3C_2F_2$ monosheet.

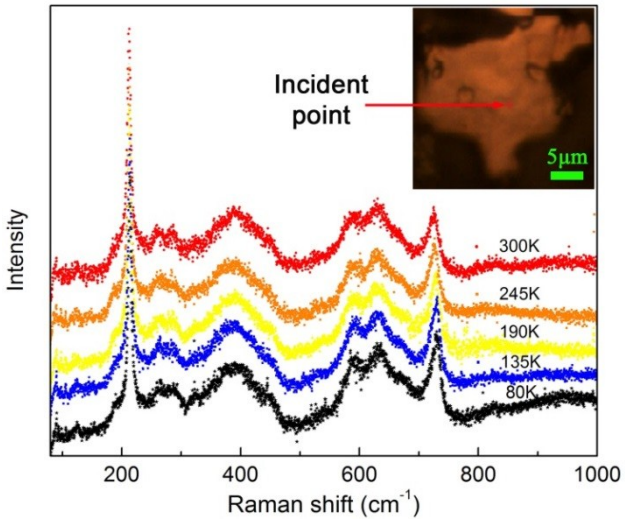


Fig. S4. Micro Raman spectra of exfoliated lamellae, collected at 80, 135, 190, 245 and 300 K. Inset shows image of lamellae.

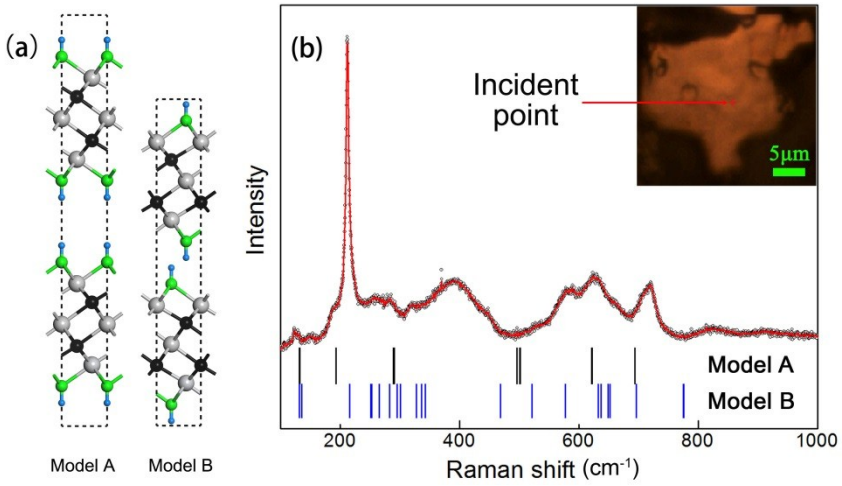


Fig. S5. (a) Two configurations of bulk $Ti_3C_2(OH)_2$; (b) Micro Raman spectrum of exfoliated lamellae, collected at 80 K. Calculated Raman active frequencies of bulk Ti_3C_2 $(OH)_2$ are also included. Inset shows image of lamellae.

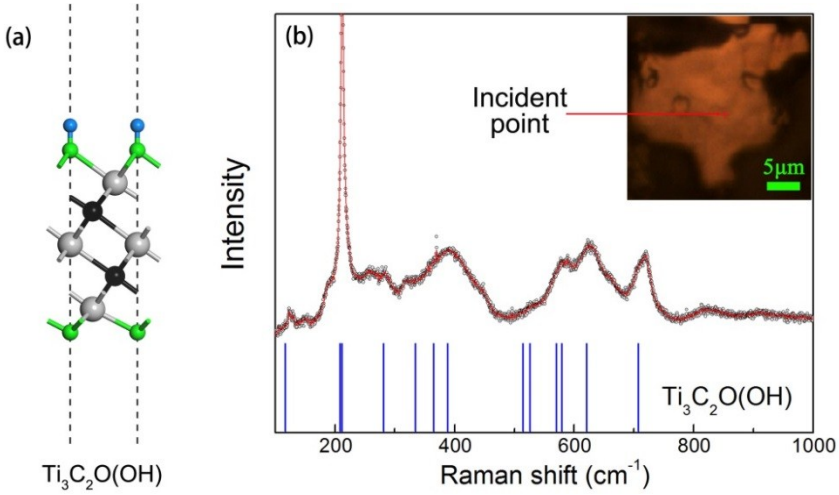


Fig. S6. (a) Crystal structure of $Ti_3C_2O(OH)$ monosheet; (b) Micro Raman spectrum of exfoliated lamellae, collected at 80 K. Calculated Raman active frequencies of $Ti_3C_2O(OH)$ monosheets are also included. Inset shows image of lamellae.