

Investigate the Effect of Surface Functionalization Halogen atoms by using the X-ray Absorption technique on the Two-dimensional Ti_3C_2 MXene

HESEB workshop on Soft X-ray

September 8-9, 2022



Saeid Khesali Azadi^{1*}, Mohammad Ali Fooladloo¹

¹Faculty of Physics, University of Tabriz, Tabriz, Iran

*Email: skhesali15@gmail.com



Introduction

MXene's characteristics, like those of other 2D materials, are sensitive to the type of functional group represented on the surface. Their surface chemistry, however, has been proven to be dependent on the synthesis circumstances, which affect the processing and characteristics of MXenes. In this calculation, the pristine Ti_3C_2 MXene and the functionalized ones are dynamically stable structures because there are not any imaginary frequencies in their phonon band dispersion curves.

In Two dimensional $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X}=\text{F}, \text{Cl}$) MXene the role of the surface termination groups in chemical bonding are directly apparent by applying electron energy-loss spectroscopy and simulations based on Density Function Theory (DFT). By concentrating on the 1s core electrons excitations of the C and Ti atoms, the effect of the termination atoms on the K-edge shift is determined.

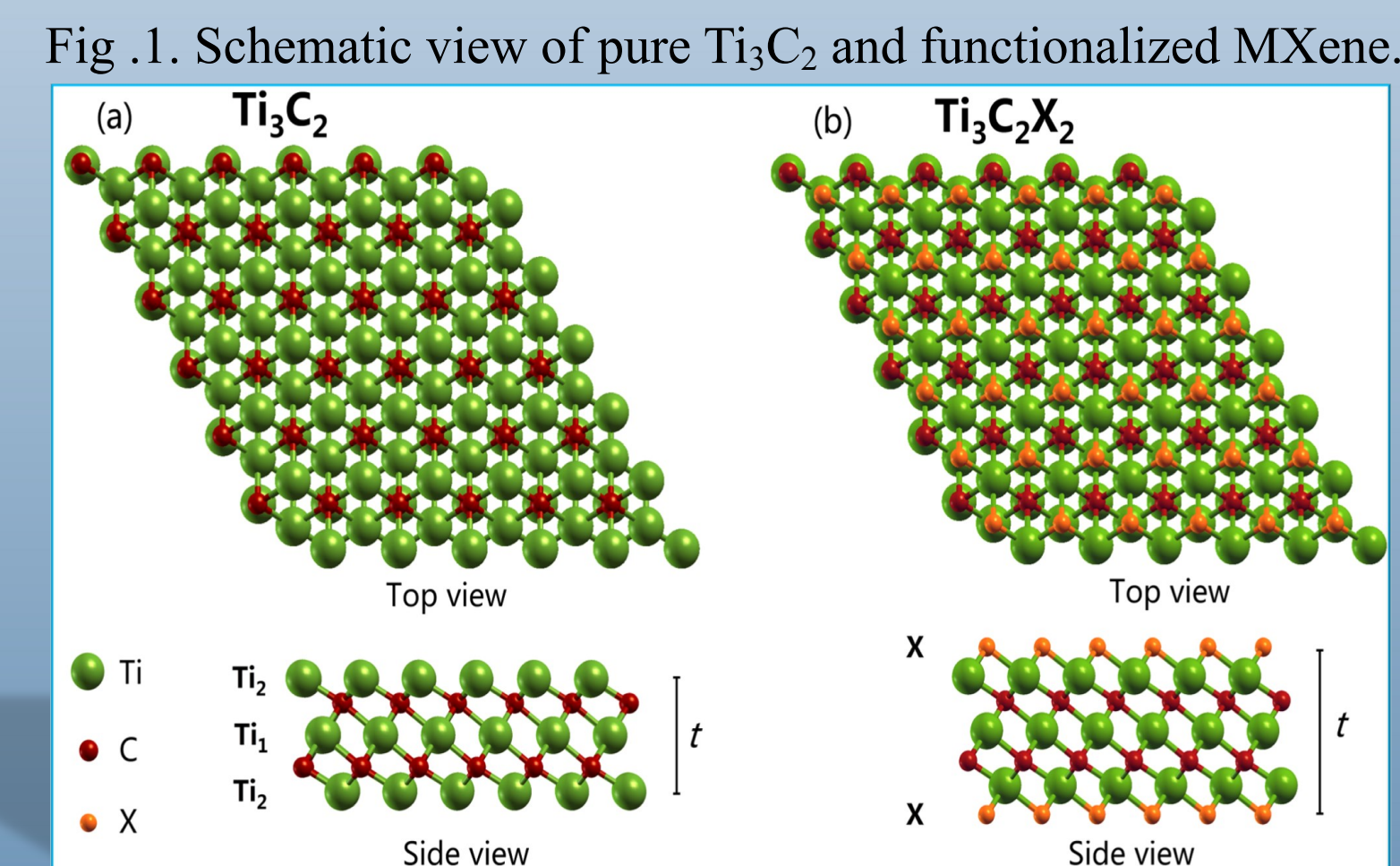
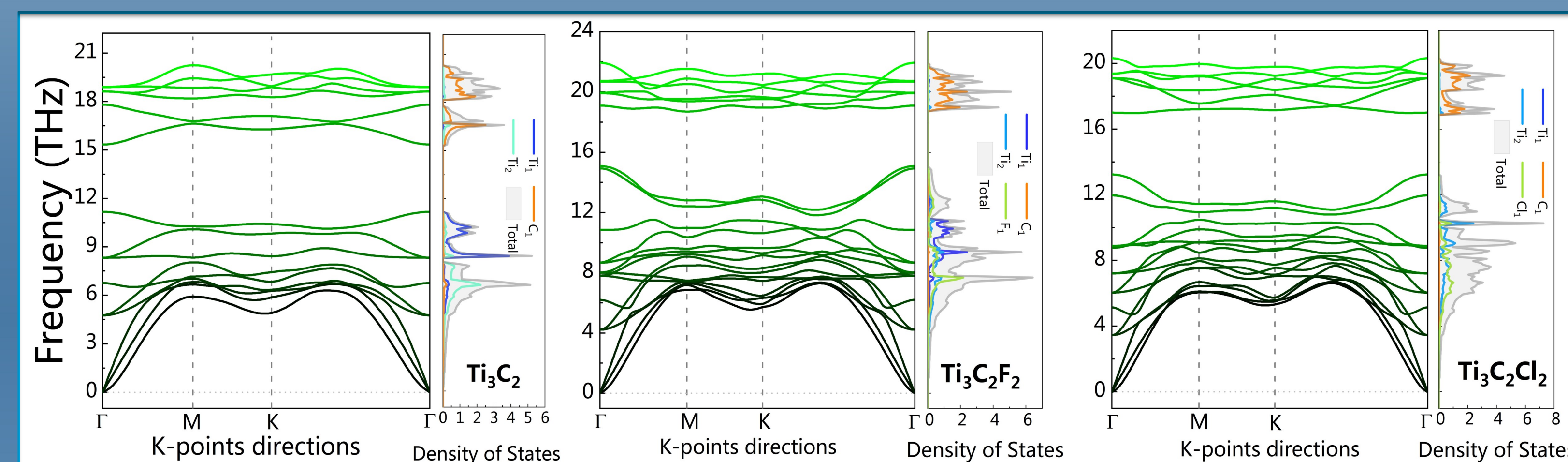


Fig. 2. The phonon dispersion and projected phonon density of states of pristine Ti_3C_2 and $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X}=\text{F}, \text{Cl}$) MXene.



We have done all our calculations based on density functional theory (DFT) using the projector augmented wave (PAW) potentials method by Quantum Espresso¹⁻³ (QE) code with an energy cut-off of 750 eV, and we concentrate on the electron energy-loss near edge structures (ELNES) at the C and Ti atoms K-edges. The experimental data were selected from Damien⁴. et al, To avoid unphysical mutual interactions between adjacent excited atoms, we used a $2 \times 2 \times 1$ supercell and the calculations were performed using a $10 \times 10 \times 2$ k-point sampling of the first Brillouin zone using a Monkhorst-Pack grid.

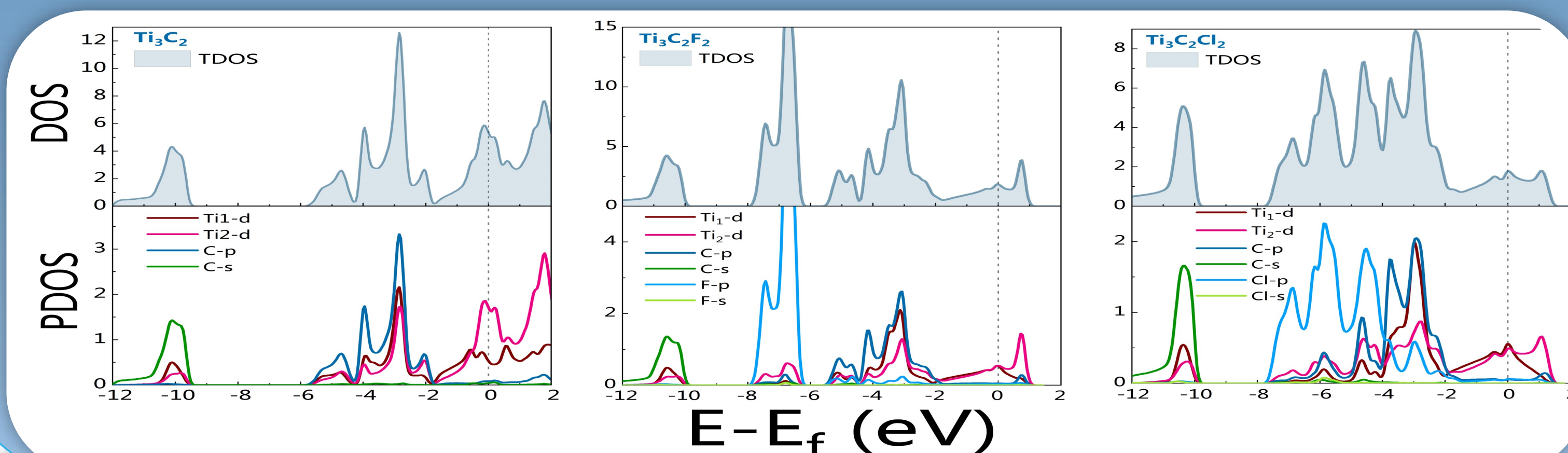


Fig. 3. DOS and PDOS of surface terminated $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X}=\text{F}, \text{Cl}$) monolayer.

Results

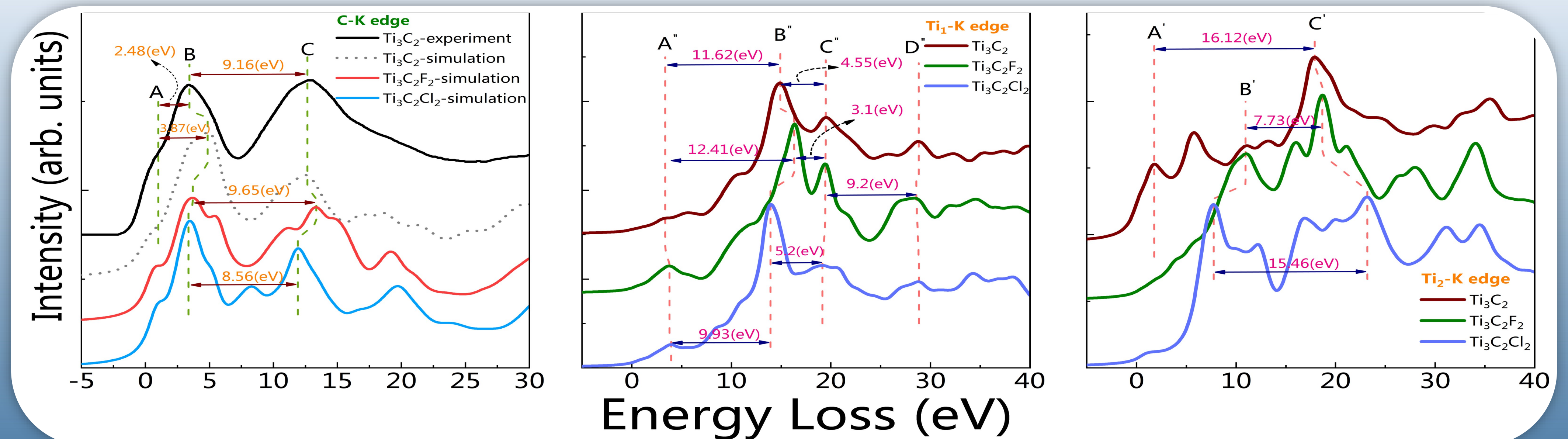


Fig. 4. Comparison between the experimental C-K edge and calculations performed for pristine Ti_3C_2 and its terminations ($\text{X}=\text{F}, \text{Cl}$). Also, the K-edge for the Ti_1 and Ti_2 atoms in the pure Ti_3C_2 and the functionalized one with halogen atoms is calculated.

It is obvious that in total density of state (TDOS) at around Fermi energy the dominant contribution is related to d orbitals of Ti atoms. The C-s states with little Ti-d states are the reason for the lowest valence bands contribution from -12 eV to around -10 eV. In the higher valence band from -5 eV to -2.5 eV for the Ti_3C_2 monolayer, the main share corresponds to a strong hybridization of C-p and Ti-d states (Ti-C bonds). However, applying the halogen atoms as surface functionalization has a diverge influence on these bands: for example, in the $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X}=\text{F}, \text{Cl}$) some bands shift into a lower energy range due to the hybridization among p electrons of terminated atoms and d electrons of Ti atoms, which correspond to the Ti-X bond.

The ELNES at the C-K edge is presented to be sensitive to the chemical nature and the location of the X termination atoms on the MXene's surface. Furthermore, the ELNES at the C-K edge is shown to be determined by the hybridizations of this atom with the Ti d bands: this edge is thus a relevant probe of the Ti d density of states close to the Fermi level which is of particular interest since it drives most of the $\text{Ti}_3\text{C}_2\text{X}_2$ electronic properties. Also, the ELNES for the Ti_1 -k and Ti_2 -k edge is demonstrated to be shifted for the functionalized with the halogen atom, because the Ti_2 -C bond length of the functionalized MXenes increases compared to the bare Ti_3C_2 , while the Ti_1 -C bond length for F and Cl terminated MXenes gets smaller.

Conclusion

The accounted DOS display that all the terminated monolayer structures sustain the metallic nature of Ti_3C_2 . Also, The electronic structure of multi-layer $\text{Ti}_3\text{C}_2\text{X}_2$ has been investigated using DFT calculations. The ELNES at the C-K edge is also shown to be highly sensitive to the chemical nature of the termination atoms. Considering that the C-K edge is to a good approximation a probe of the unoccupied C-p DOS. However, the K-edge for the other two Ti atoms (Ti_1 and Ti_2) was influenced due to the termination atoms. Considering the crucial role of X atoms in MXene's properties in general, these calculations can be applied to select the appropriate synthesis route regarding the desired applications.

Reference

- ¹ P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, and R.M. Wentzcovitch, Journal of Physics: Condensed Matter **21**, 395502 (2009).
- ² M. TAILLEFUMIER, D. CABARET, A.-M. FLANK, and F. MAURI, Physical Review B **66**, 195107 (2002).
- ³ C. Gougoussis, M. Calandra, A.P. Seitsonen, and F. Mauri, Physical Review B **80**, 075102 (2009).
- ⁴ D. Magne, V. Mauchamp, S. Célrier, P. Chartier, and T. Cabioch, Physical Chemistry Chemical Physics **18**, 30946 (2016).