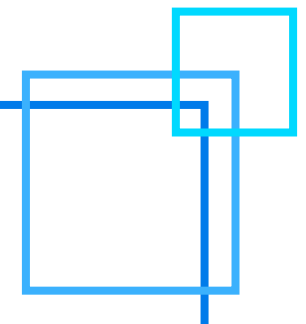
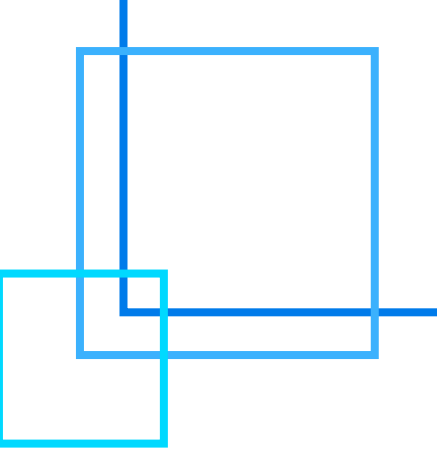


First-Principles Modeling of Temperature-Dependent Raman Spectra in 2H-MoS₂ via Machine Learning Potentials

Samuel Longo, Aloïs Castellano, Matthieu Verstraete
Nanomaterial group, QMAT, ULiège

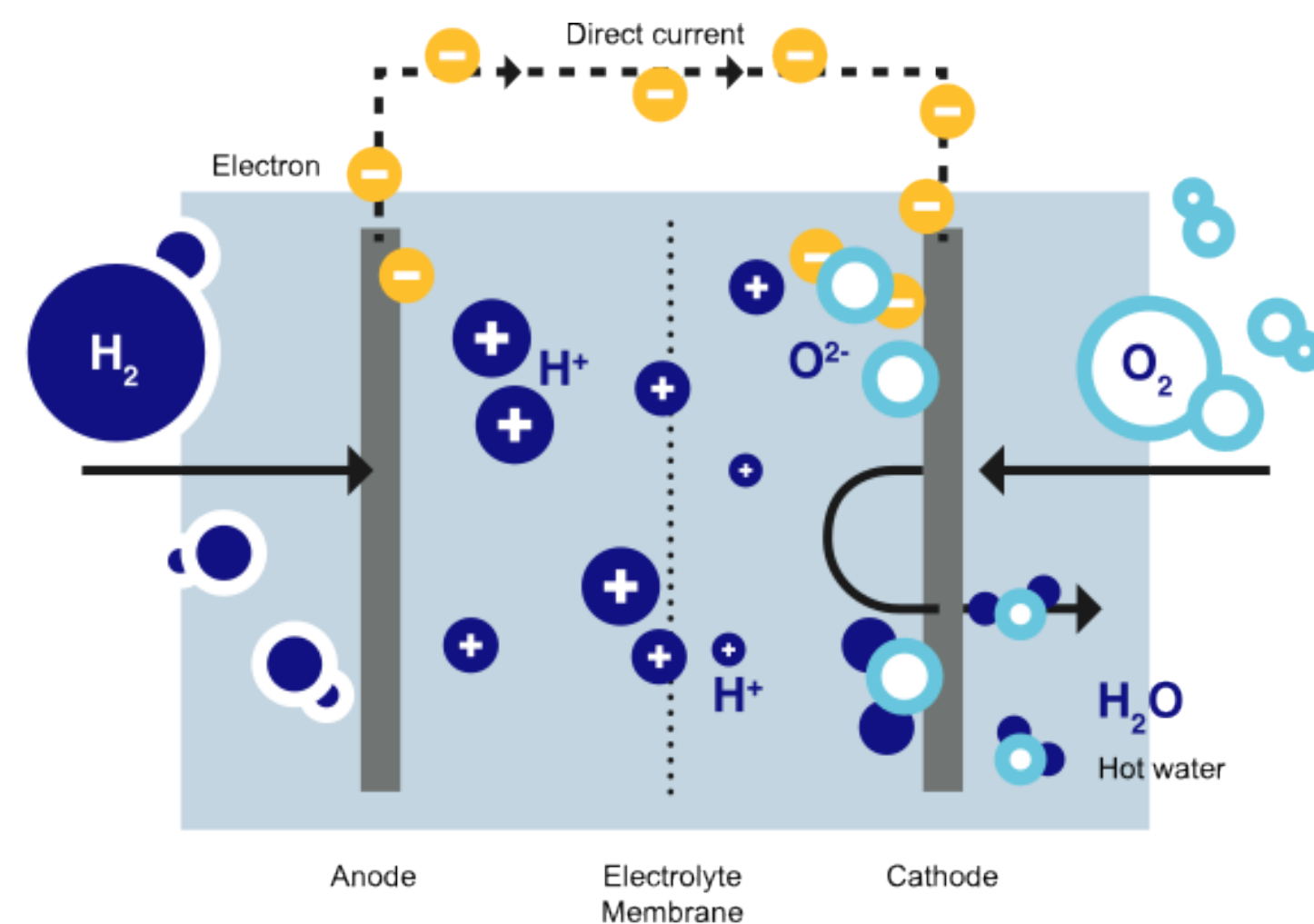
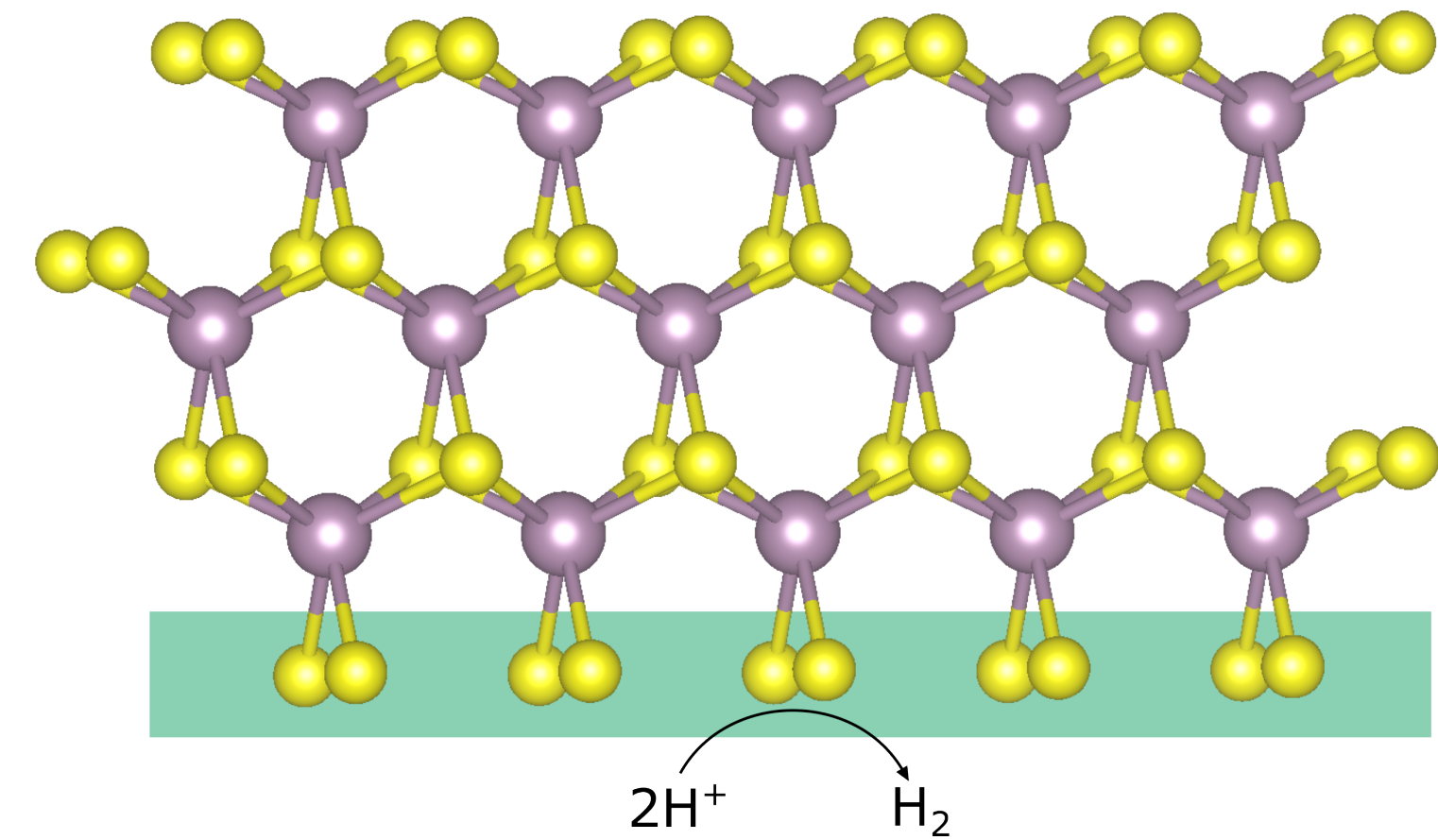
RACS 2026
Modena, 9/06/2026

Motivation: MoS_x as catalysts for HER



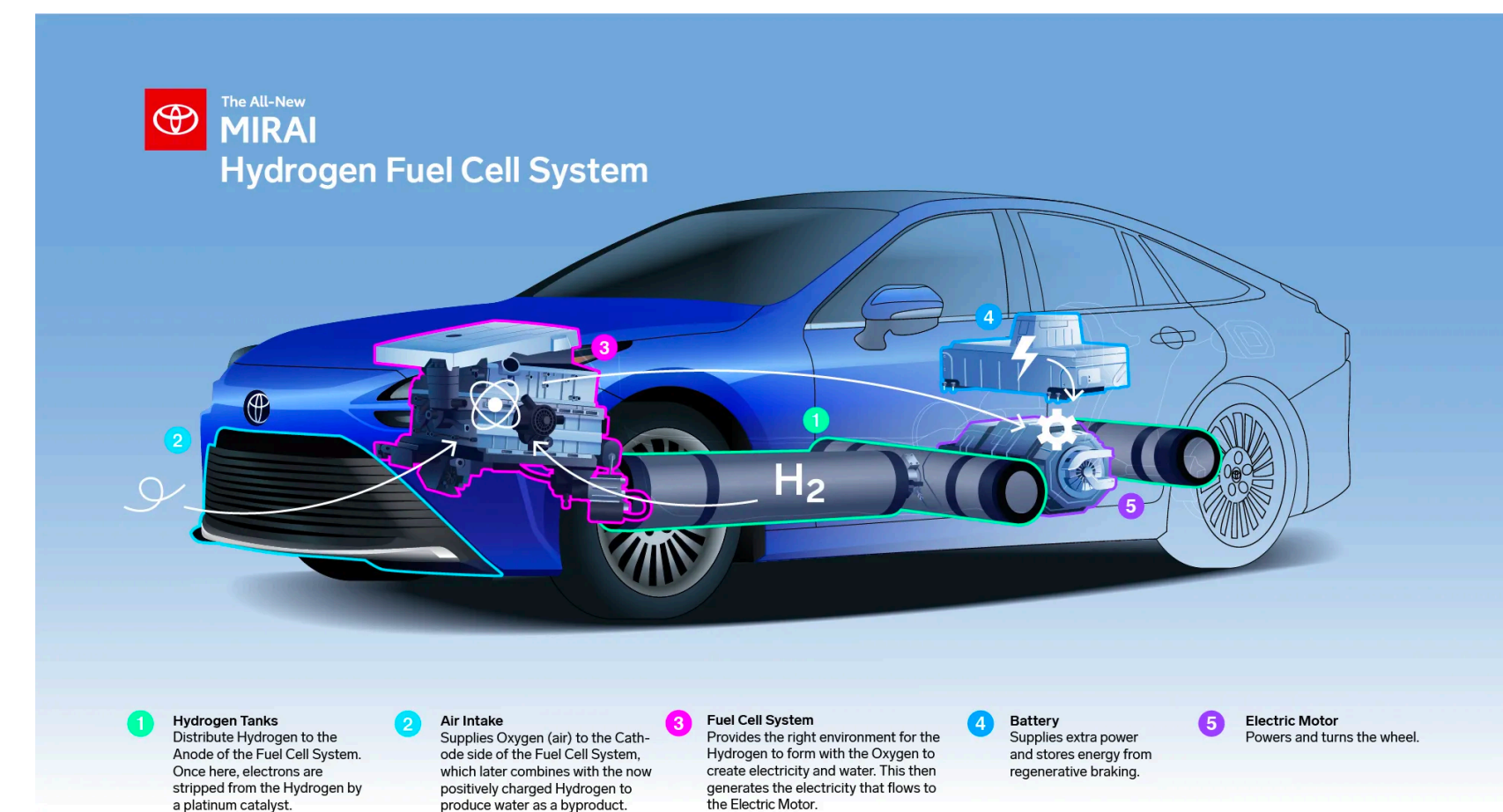
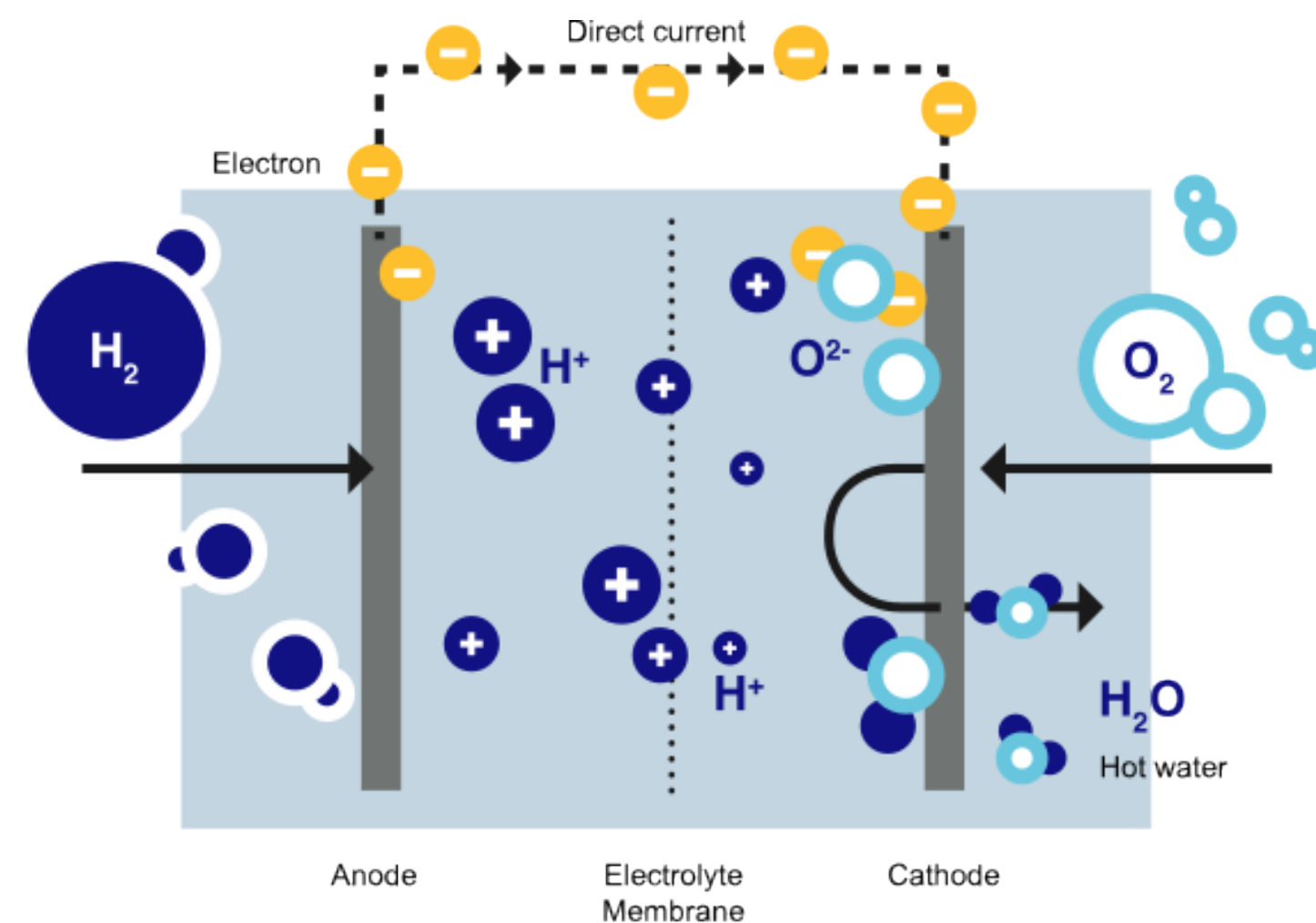
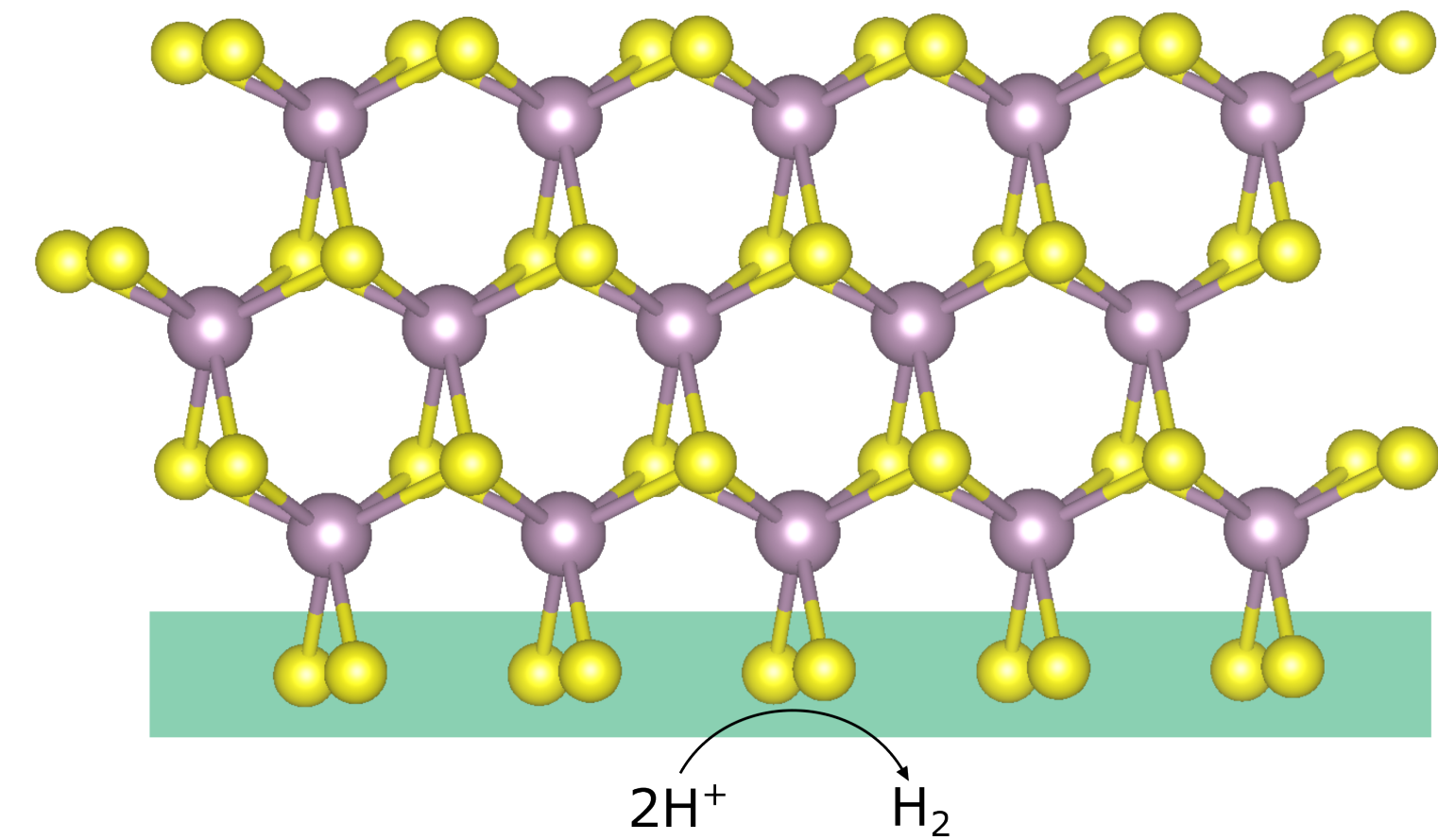
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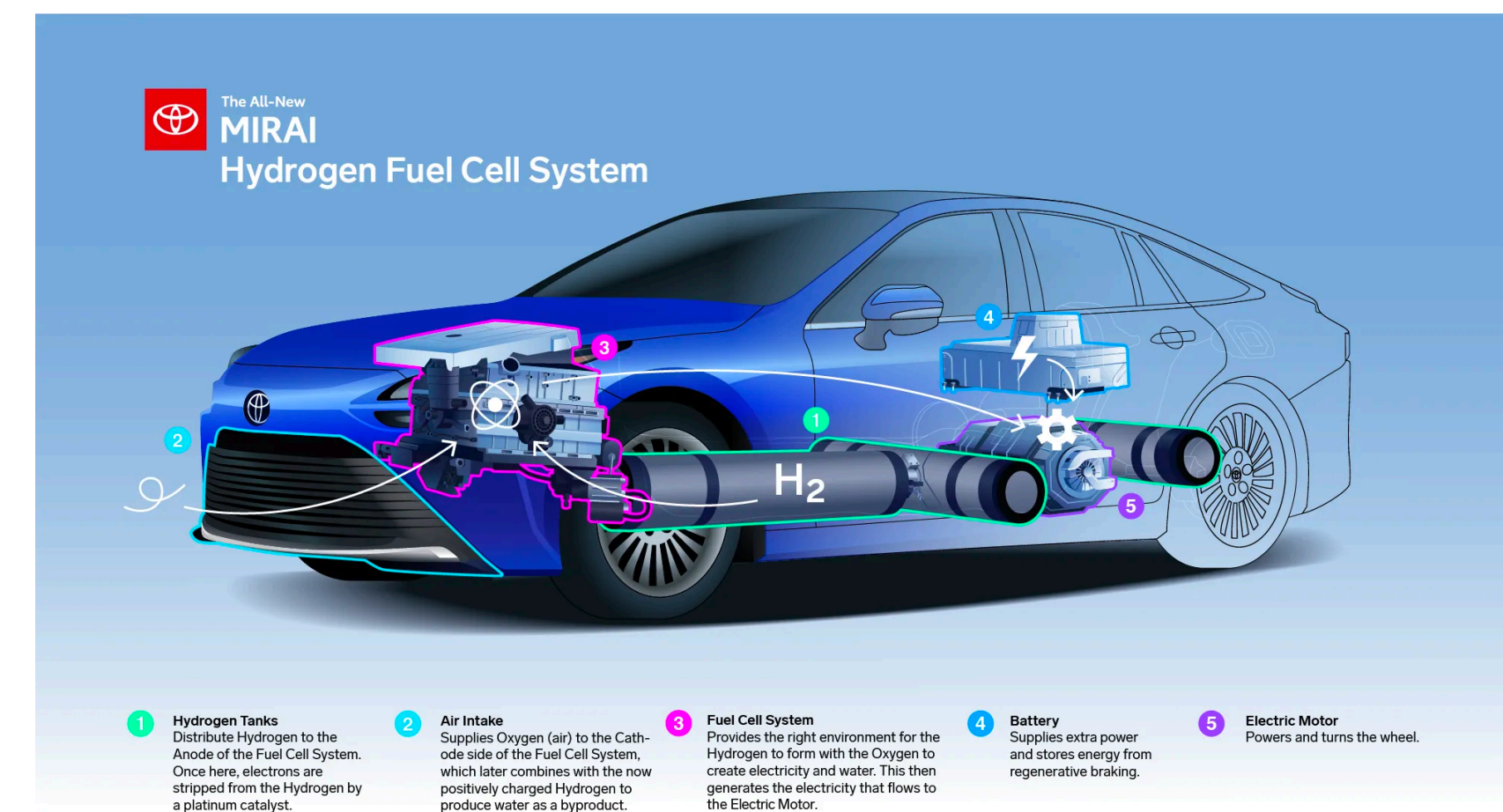
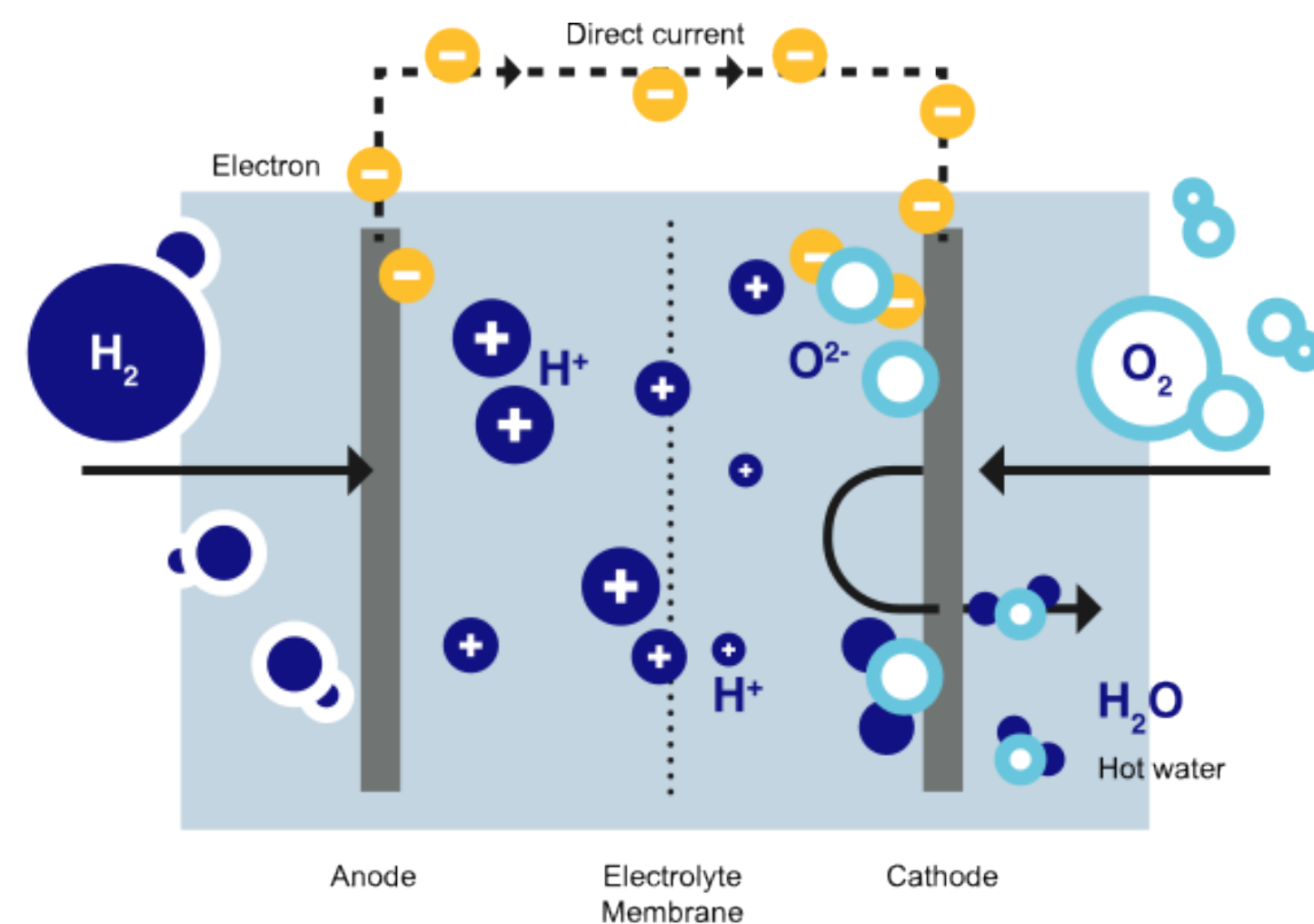
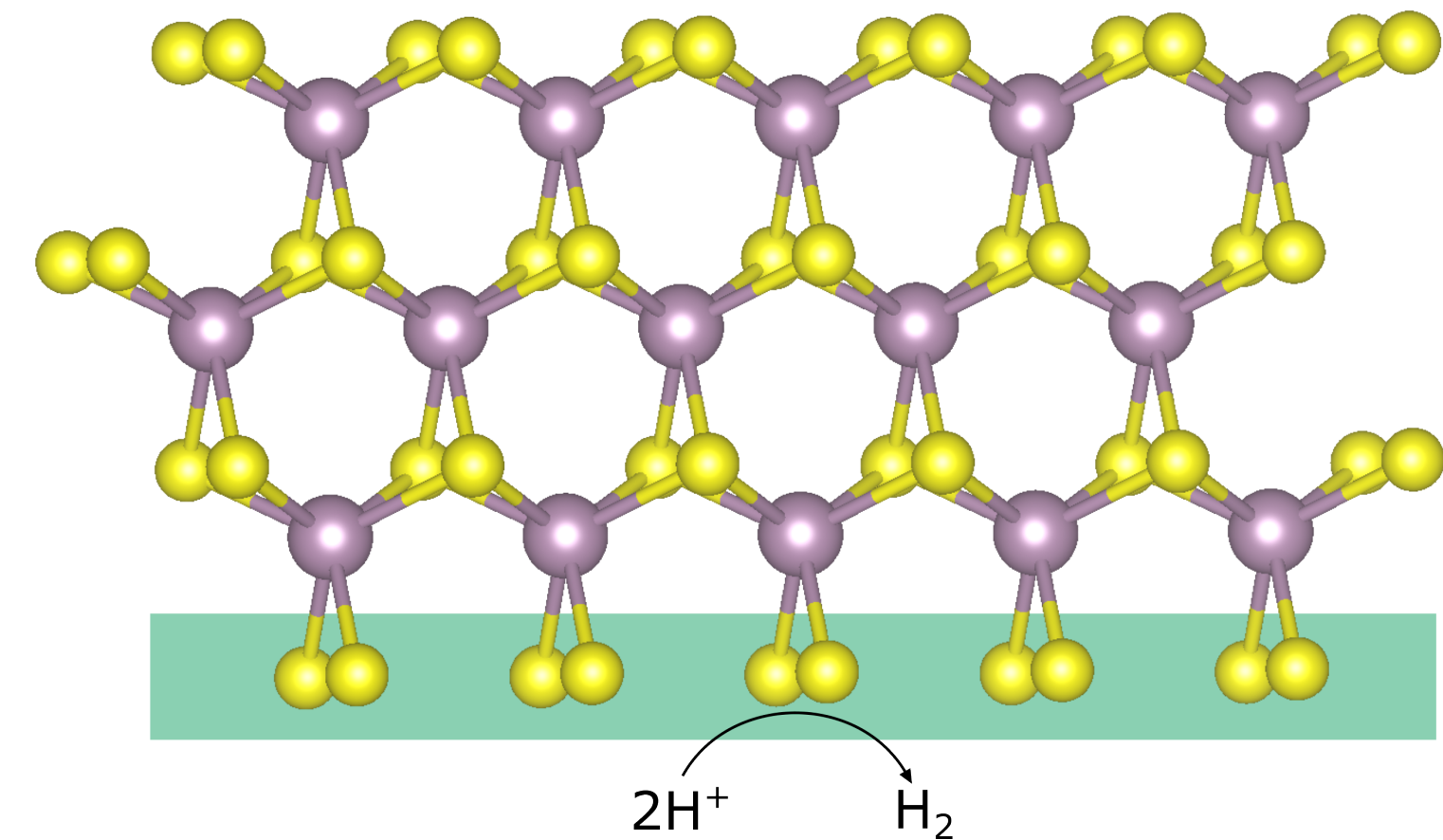
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 - Increasing general demand of Hydrogen



Motivation: MoS_x as catalysts for HER

- MoS_x exhibit catalytic activity in the **hydrogen evolution reaction (HER)**
 - Increasing general demand of Hydrogen
 - Unlike Pt-based catalysts, MoS_x are **non-toxic, cheap and eco-friendly**

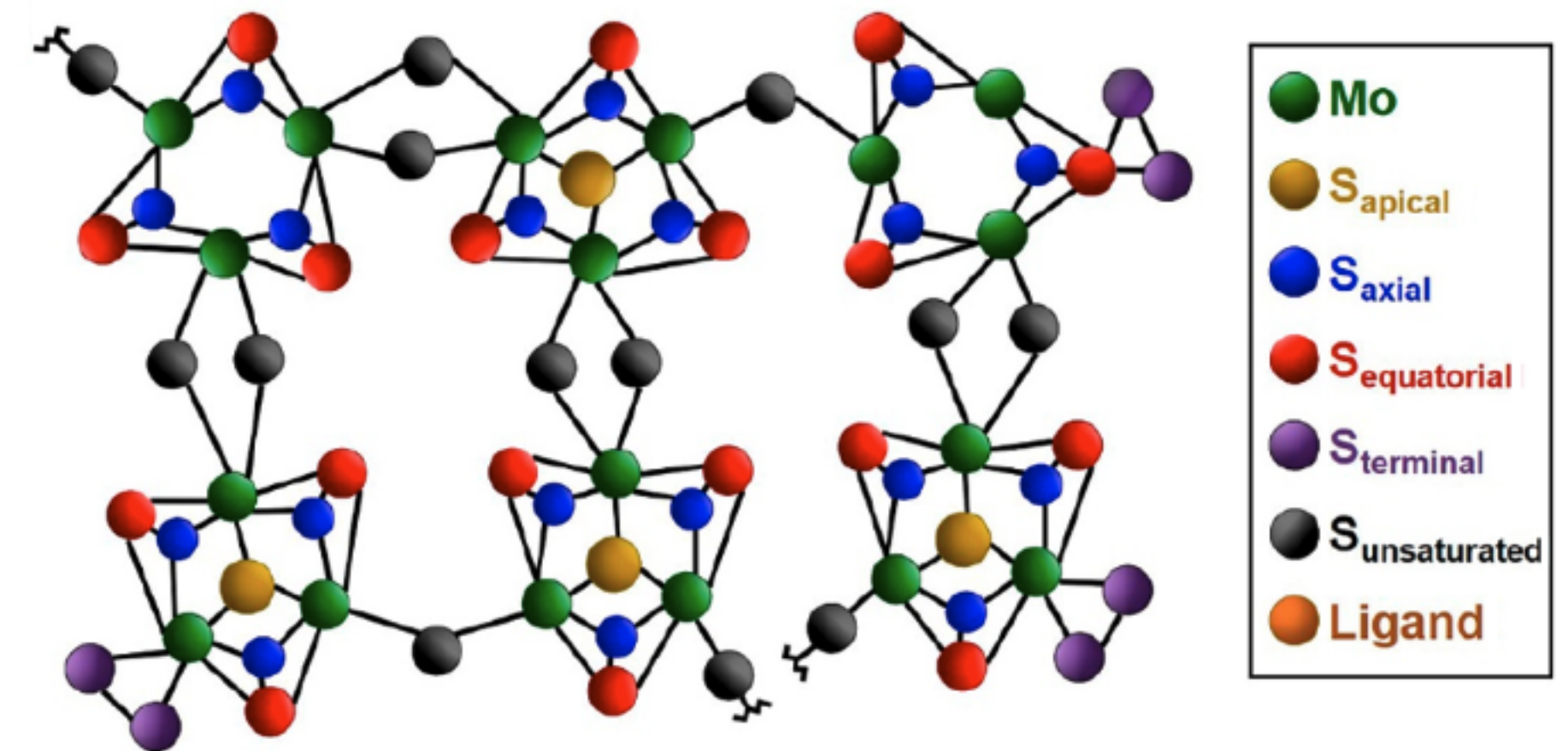
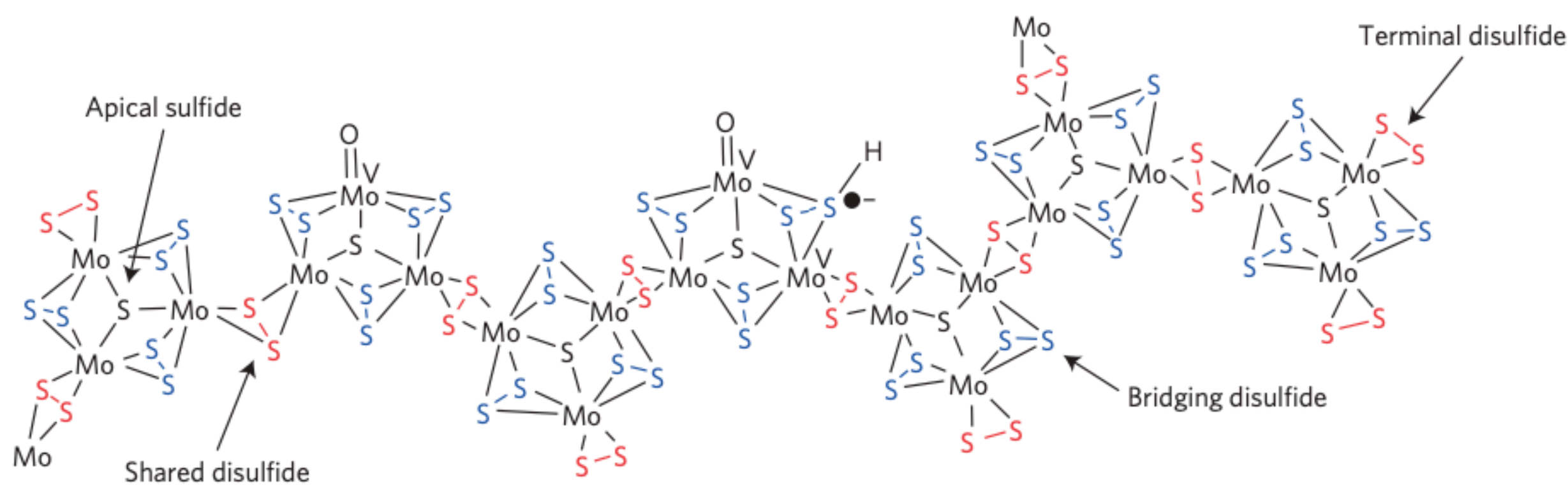


Molybdenum Sulphides: MoS_x

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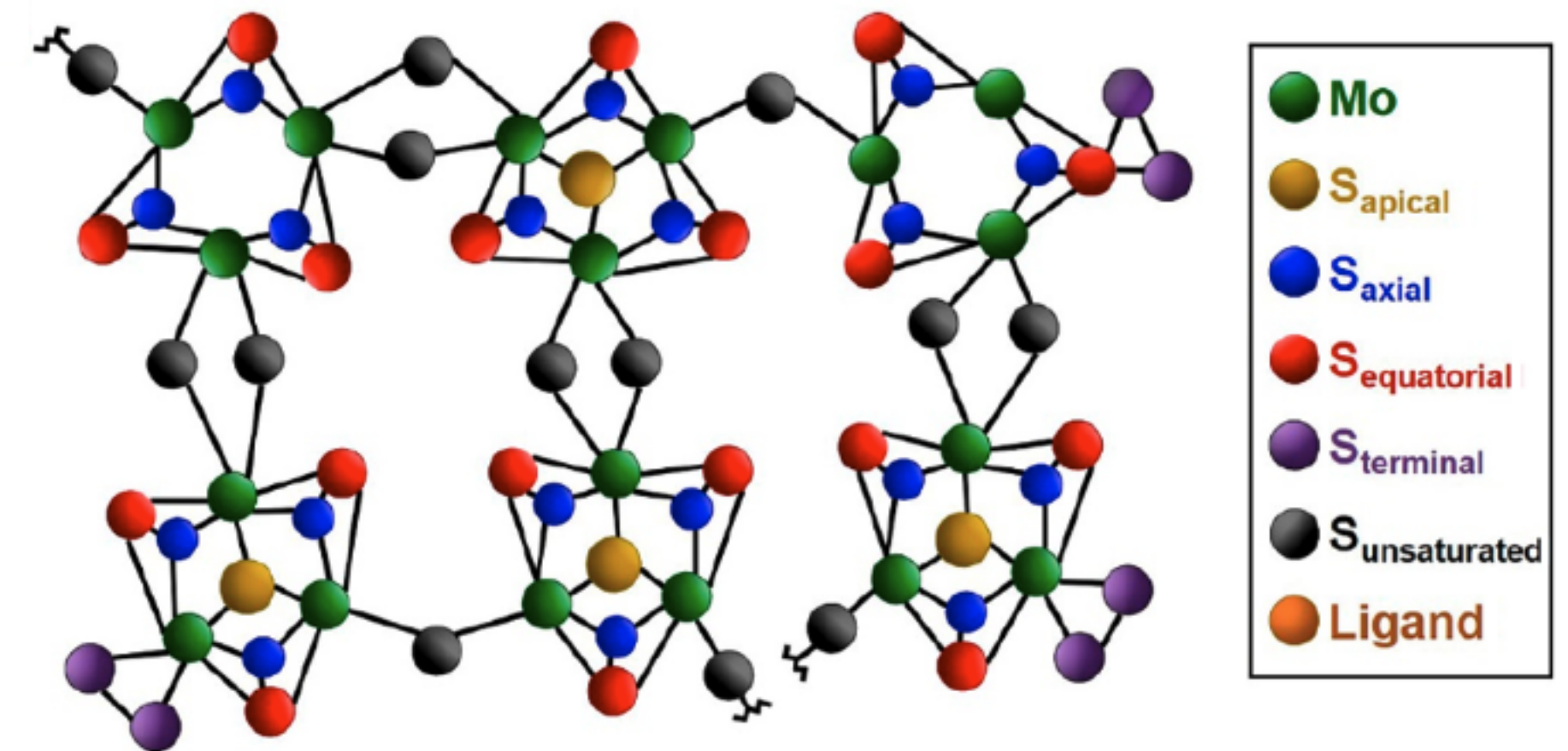
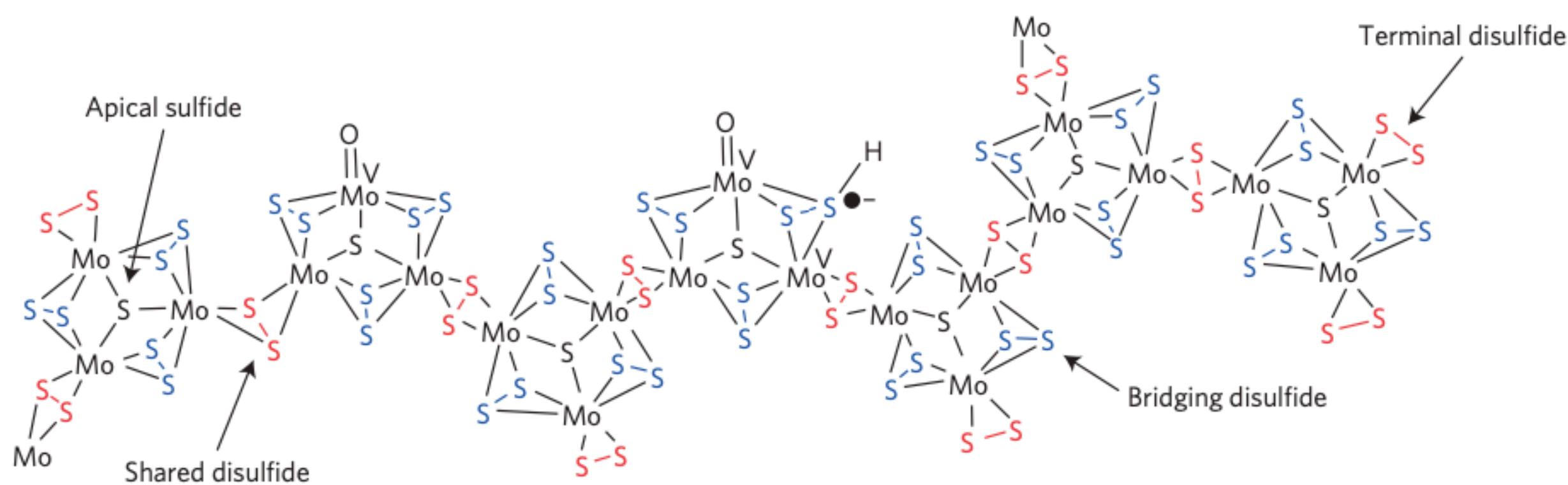
Molybdenum Sulphides: MoS_x

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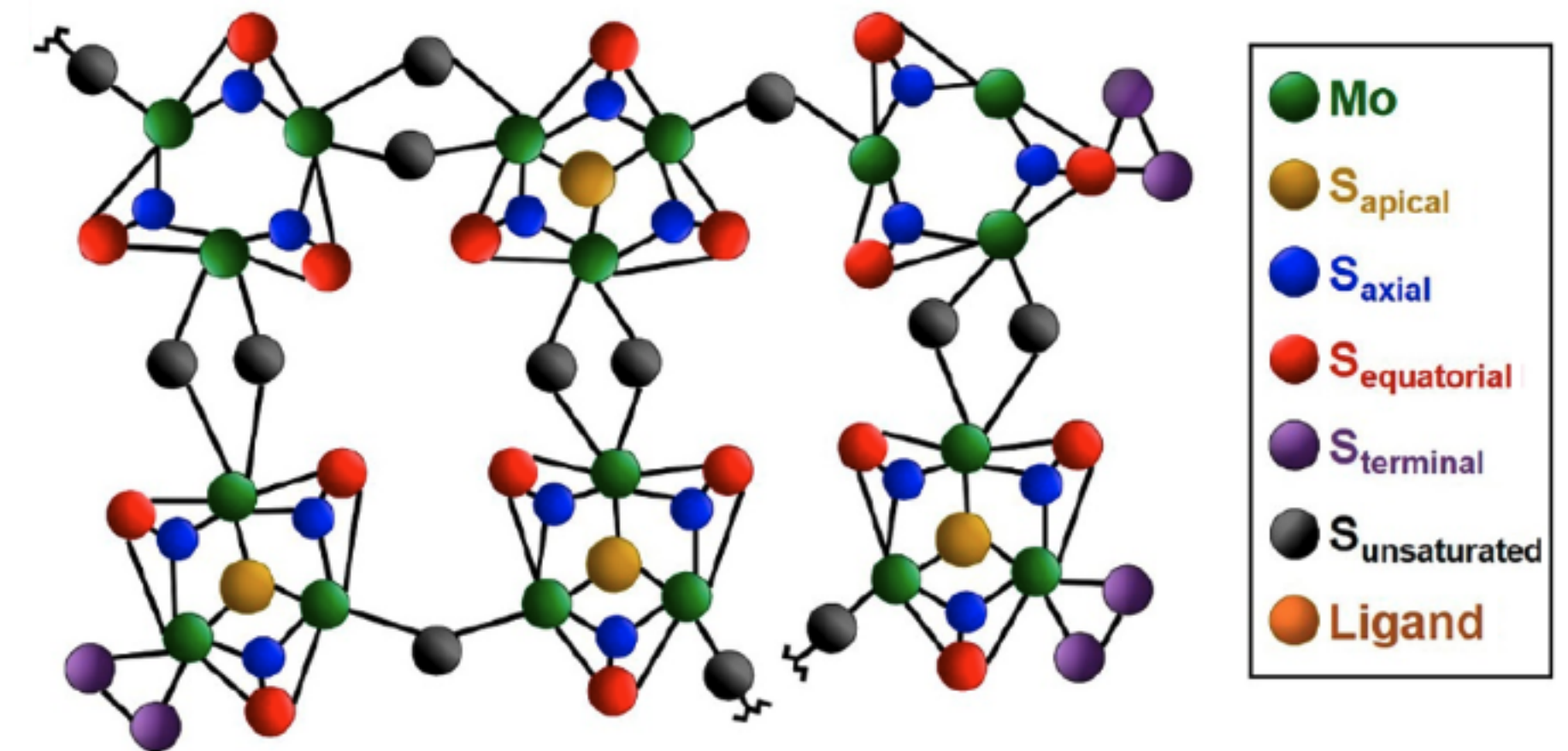
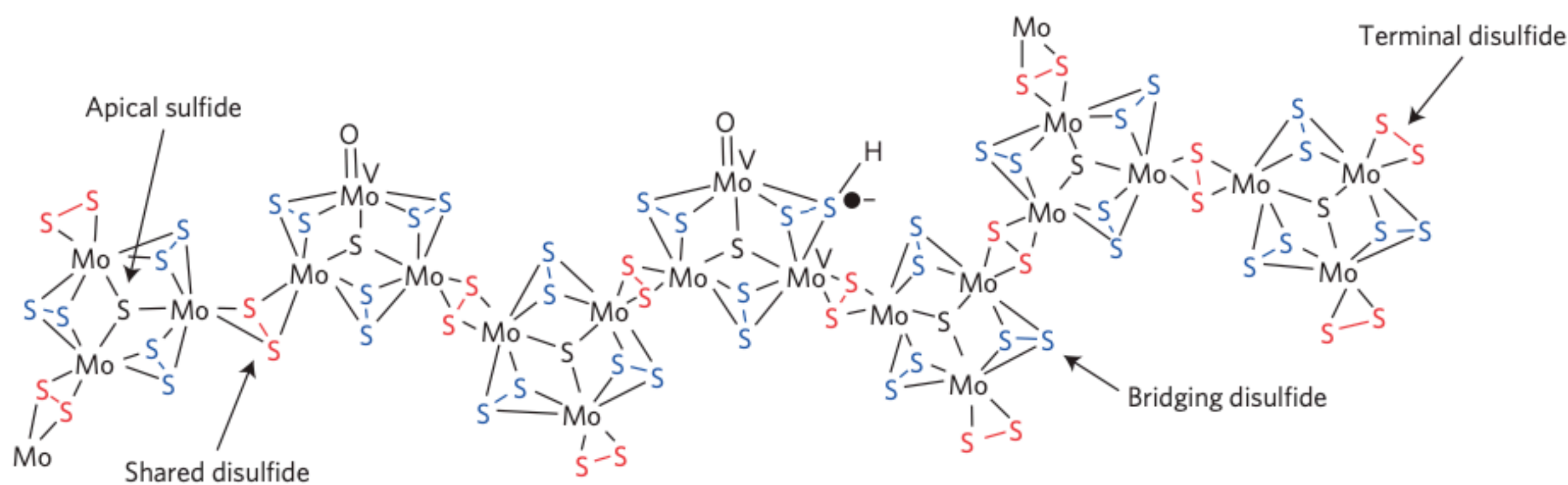
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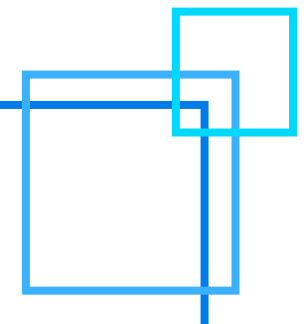
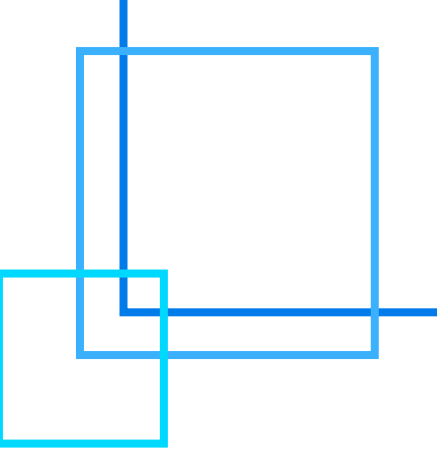


Molybdenum Sulphides: MoS_x

- MoS_x exhibit catalytic activity in the **hydrogen evolution reaction**
- Local structures still not known
- Catalytic mechanism not clear
- Vibrational spectra (IR and **Raman**) are related to the **local structure**



The way to the Raman spectrum

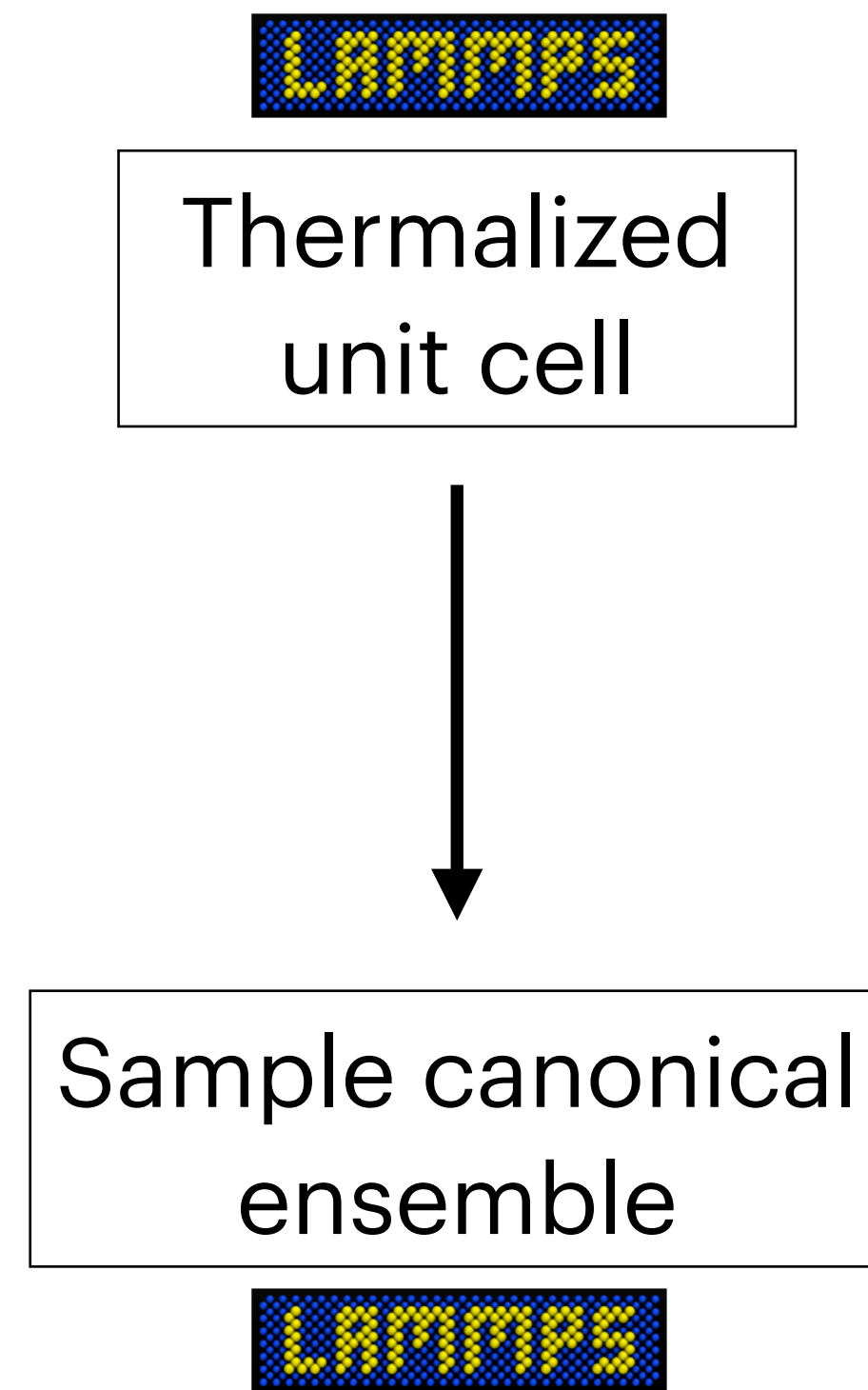


The way to the Raman spectrum

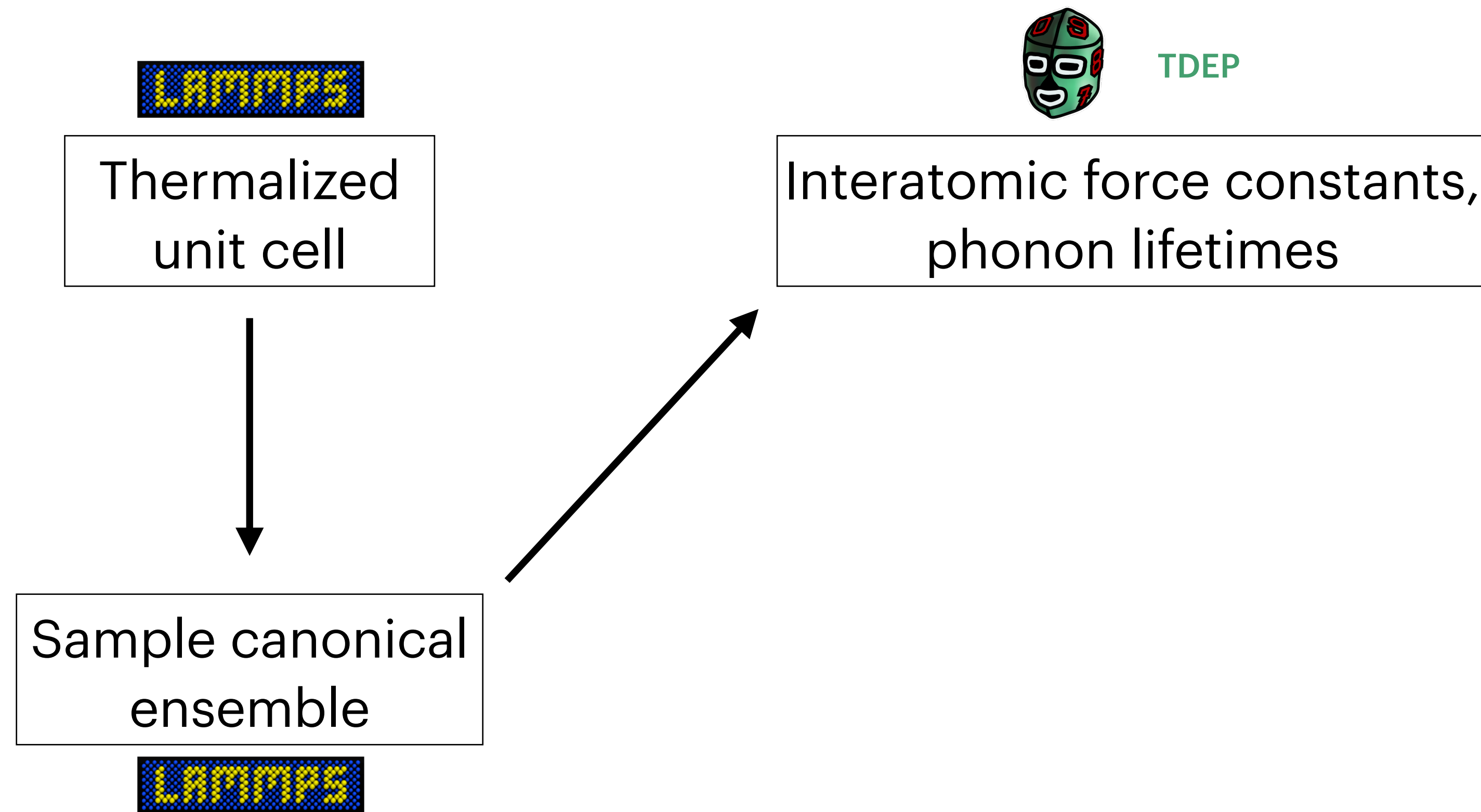
LAMMPS

Thermalized
unit cell

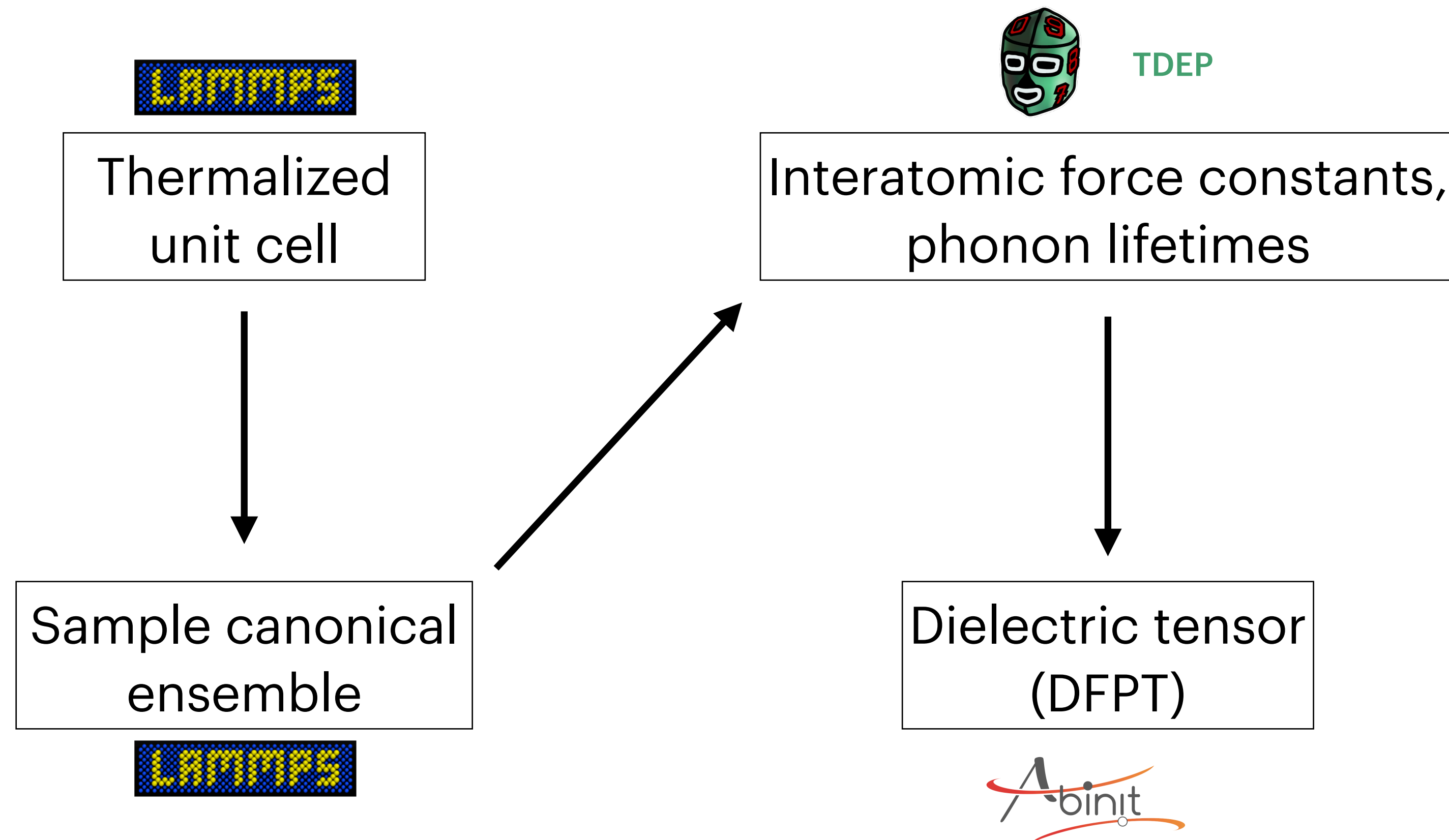
The way to the Raman spectrum



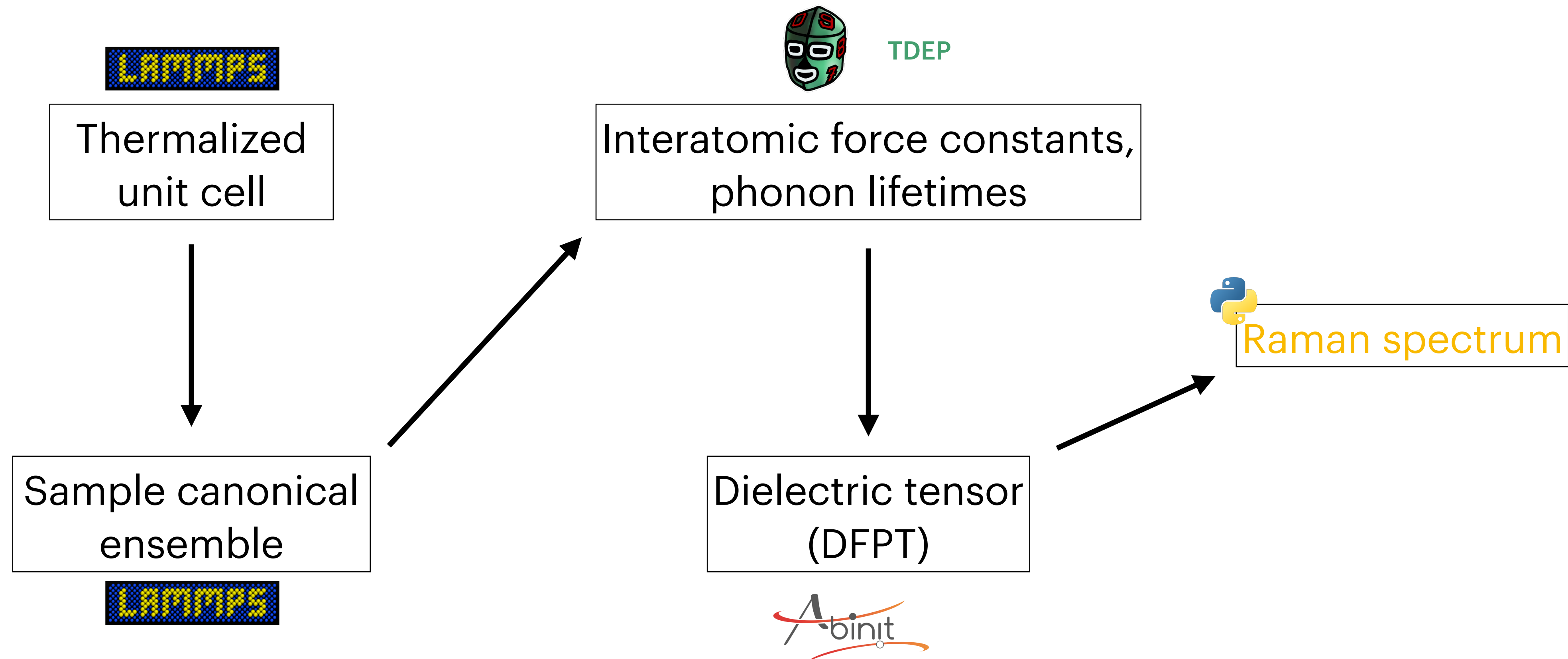
The way to the Raman spectrum



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The way to the Raman spectrum



Temperature Dependent Effective Potential

Describe the vibrational energy with the best n-order polynomial vs. atomic displacements at a fixed temperature



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$$U(\{u_i\}) = U(0) + \dots$$

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$$U(\{u_i\}) = U(0) + \frac{1}{2} \sum_i u_i \left[\sum_j \underbrace{\frac{\partial^2 U}{\partial u_i \partial u_j} \Big|_{eq}}_{\Phi_{ij}^{(2)}} u_j \right] + \dots$$

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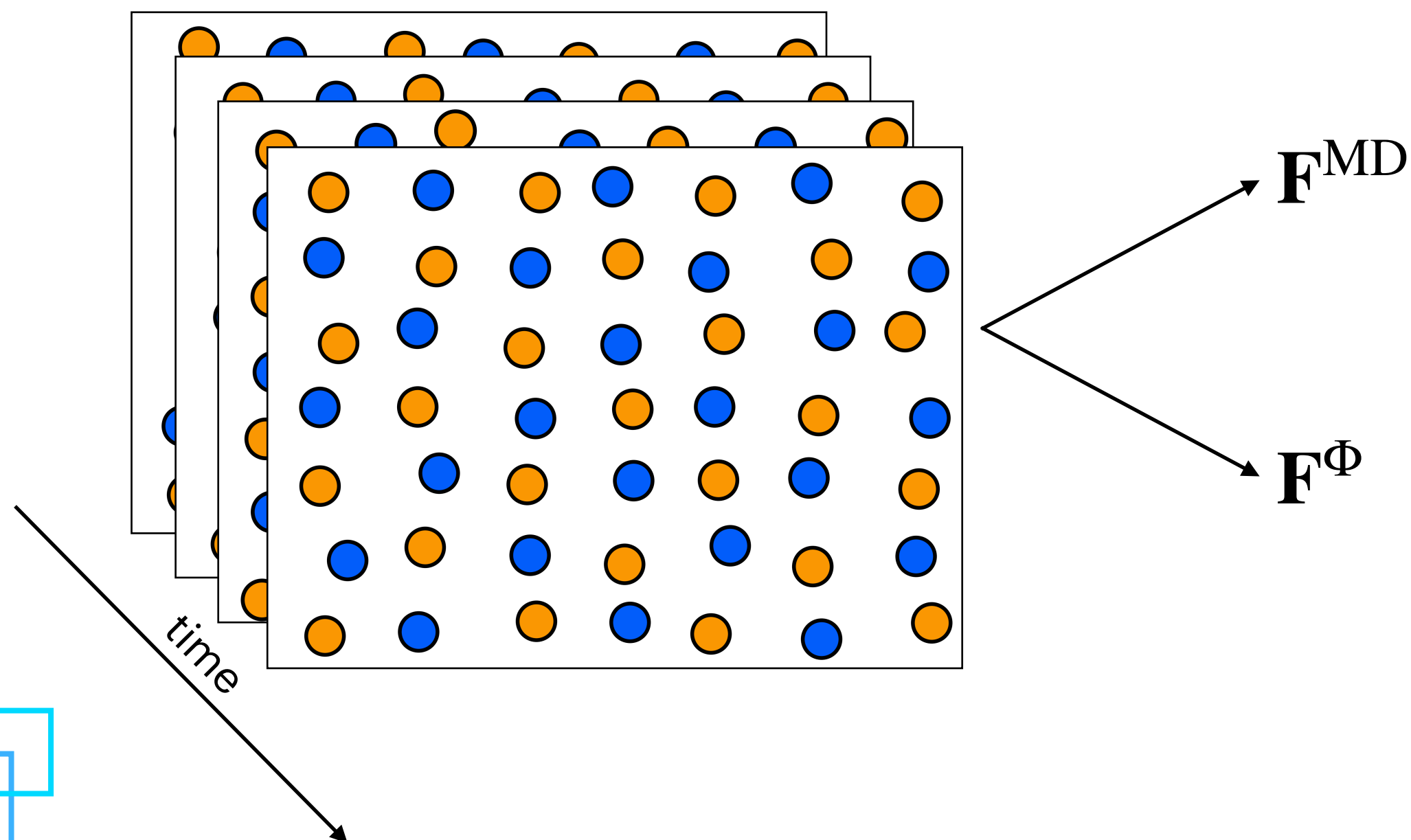
$$U(\{u_i\}) \approx U(0) + \frac{1}{2} \sum_i u_i \left[\sum_j \Phi_{ij}^{(2)} u_j \right]_{\equiv F_i^{(2)}} + \frac{1}{6} \sum_i u_i \left[\sum_{j,k} \Phi_{ijk}^{(3)} u_j u_k \right]_{\equiv F_i^{(3)}}$$

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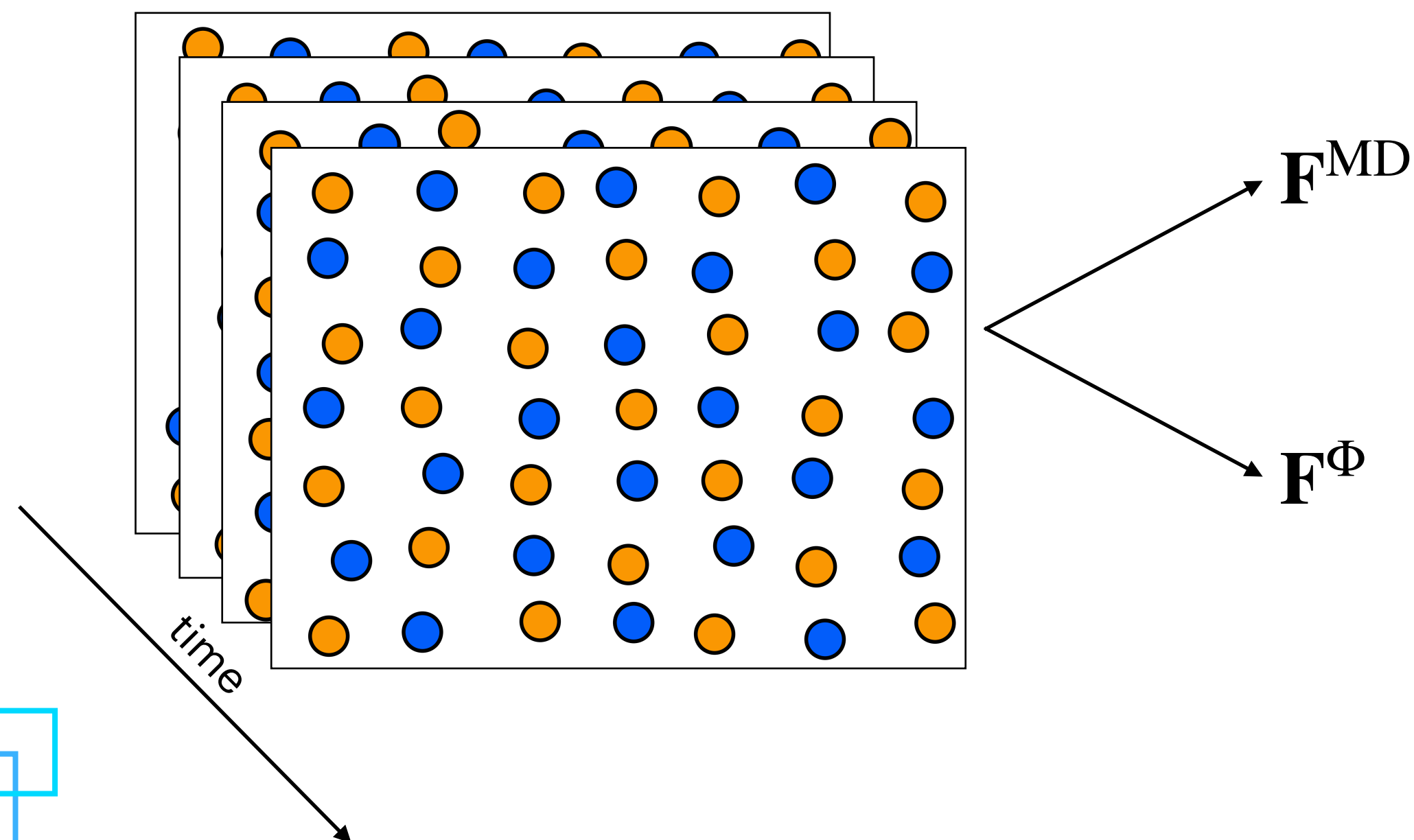


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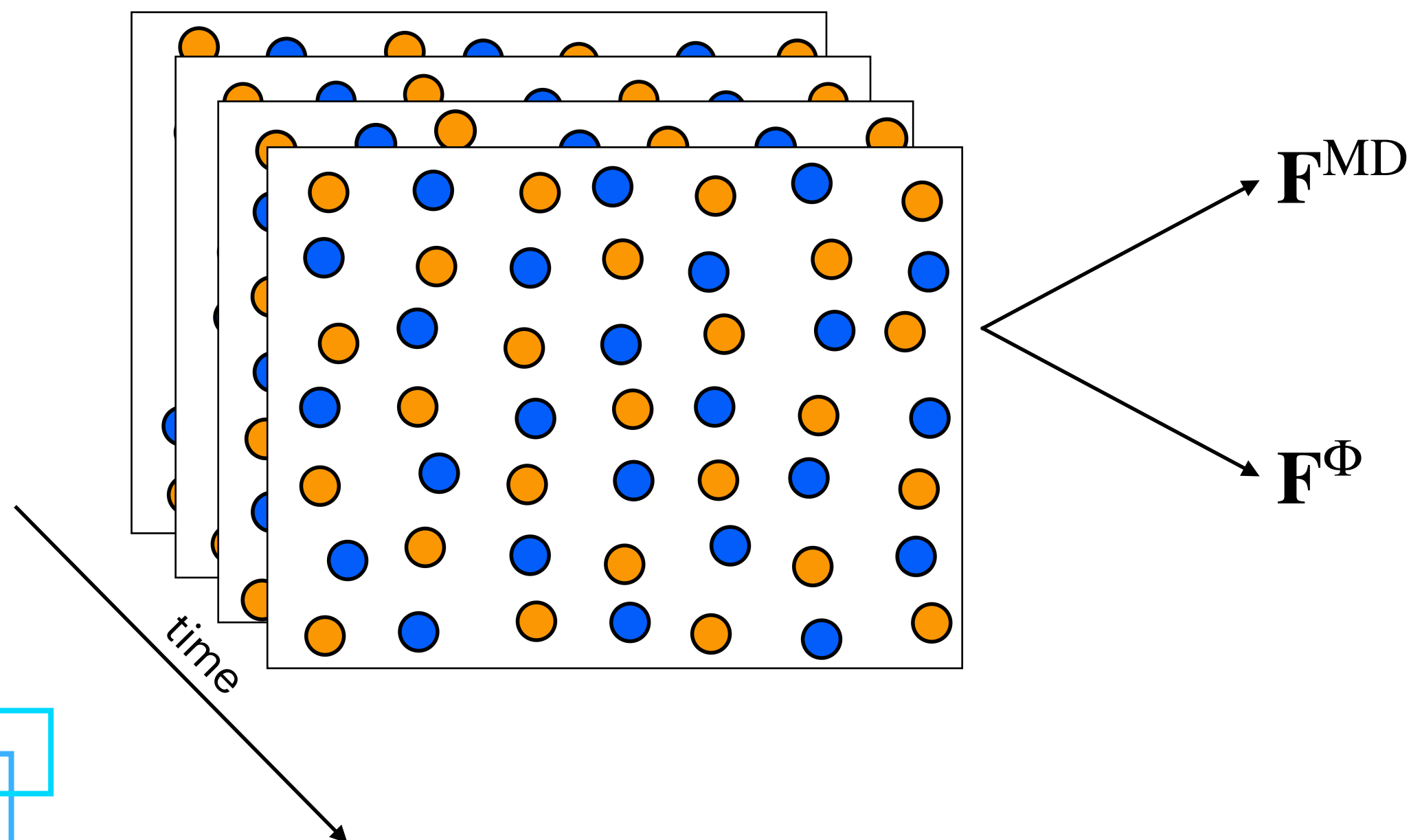
$$\min_{\Phi^{(2)}} (\Delta \mathbf{F}^{(2)}) = \min_{\Phi^{(2)}} \left(\frac{1}{N} \sum_{i,t} \left| F_{i,t}^{\text{true}} - F_{i,t}^{\Phi^{(2)}} \right|^2 \right) \longrightarrow \{\tilde{\Phi}^{(2)}\}$$

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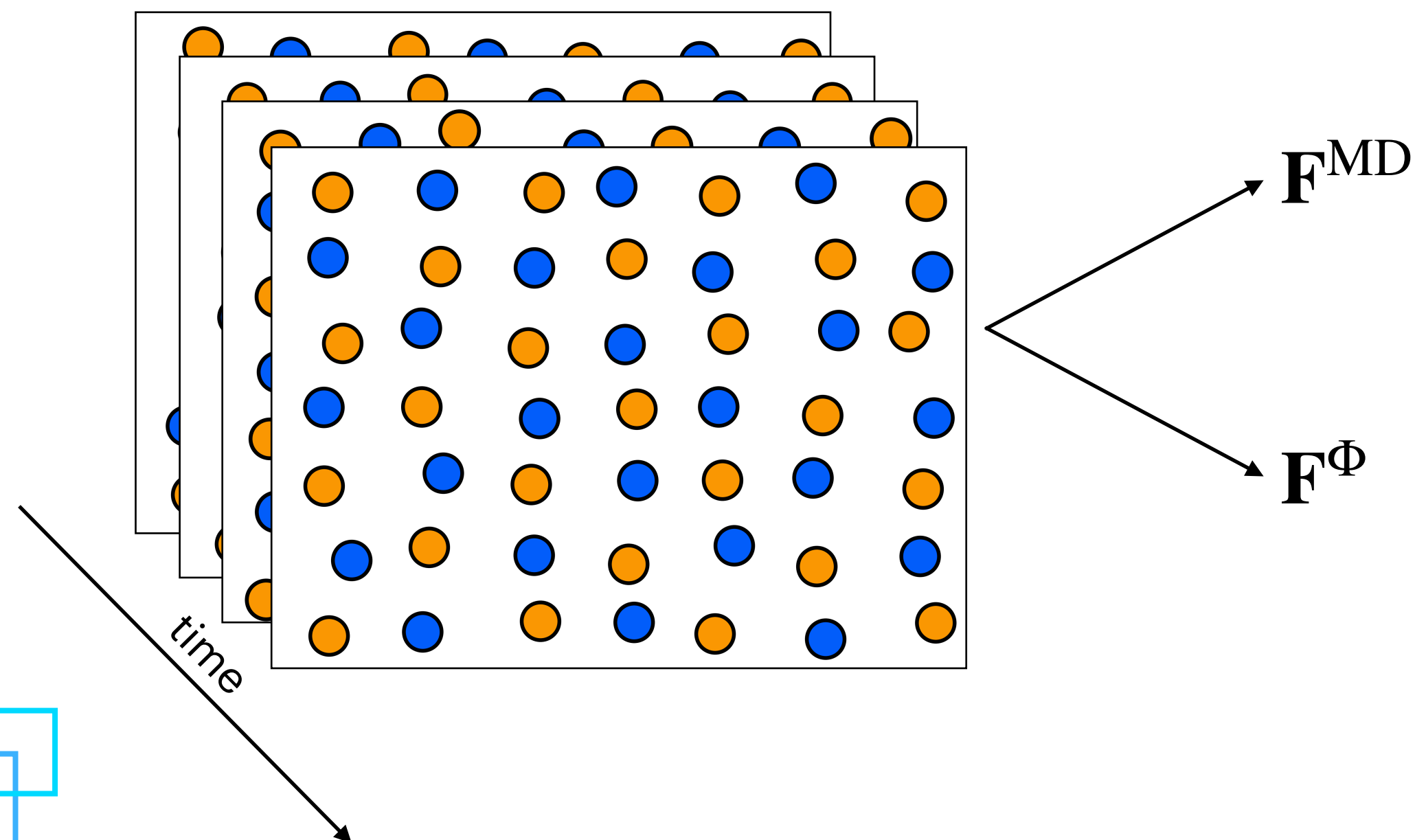
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$\{\tilde{\Phi}^{(3)}\} \longrightarrow$ Phonon lifetimes, spectral functions, thermal conductivity etc...

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$$\Gamma_m(\omega) \propto \sum_{m'm''} |\Phi_{mm'm''}^{(3)}|^2 \cdot \rho(\omega, \omega_{m'}, \omega_{m''})$$

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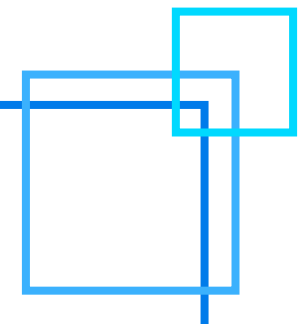
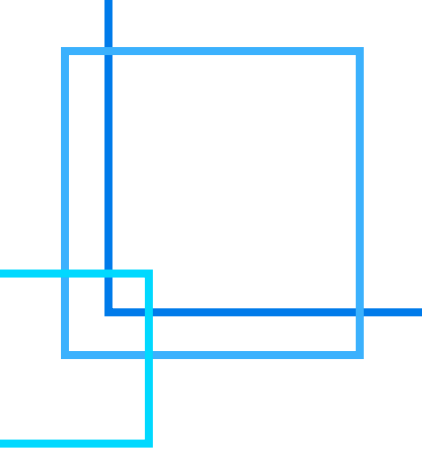
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TDEP: Raman calculation



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Raman spectra:

- Raman intensity for each mode at Γ

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$$I_m = |\mathbf{e}_i \cdot \alpha_m \cdot \mathbf{e}_o|^2$$

TDEP: Raman calculation

Raman spectra:

- Raman intensity for each mode at Γ
- Spectral function of each mode at Γ
 - Anharmonic frequencies
 - Phonon lifetimes

$$\left. \begin{array}{l} \text{Anharmonic frequencies} \\ \text{Phonon lifetimes} \end{array} \right] J_m(\omega)$$

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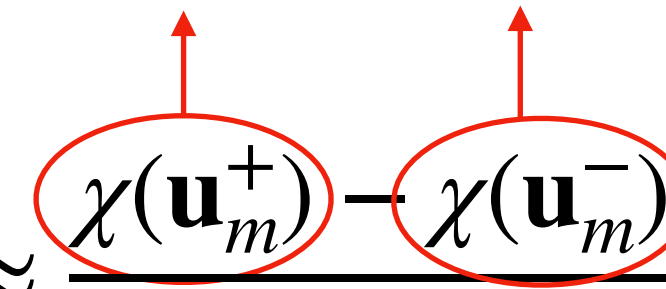
TDEP: Raman calculation

Raman spectra:

- Raman intensity for each mode at Γ
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- Spectrum = spectral function x intensity

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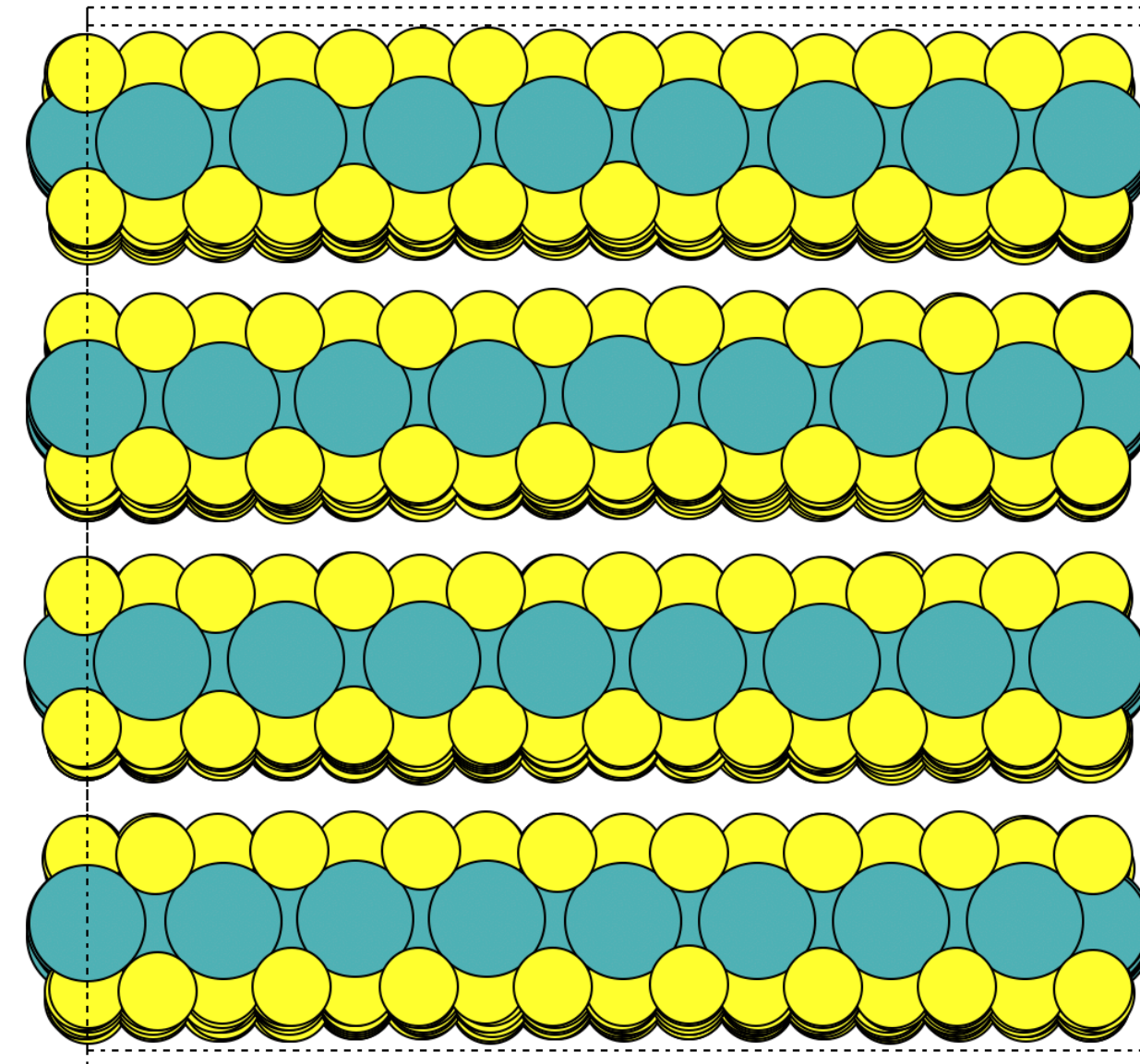
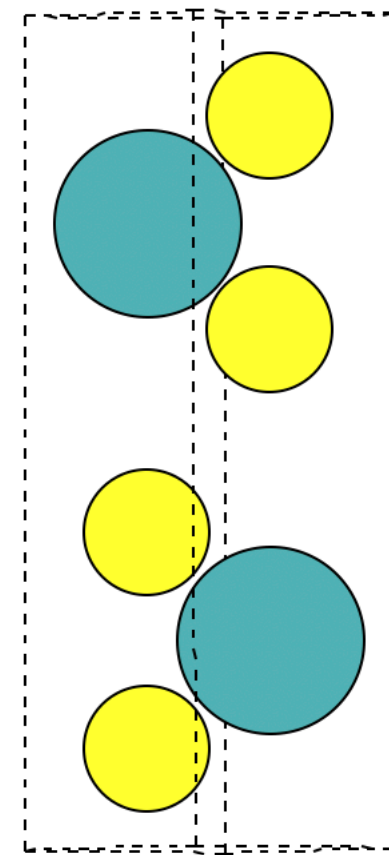
DFPT calculation



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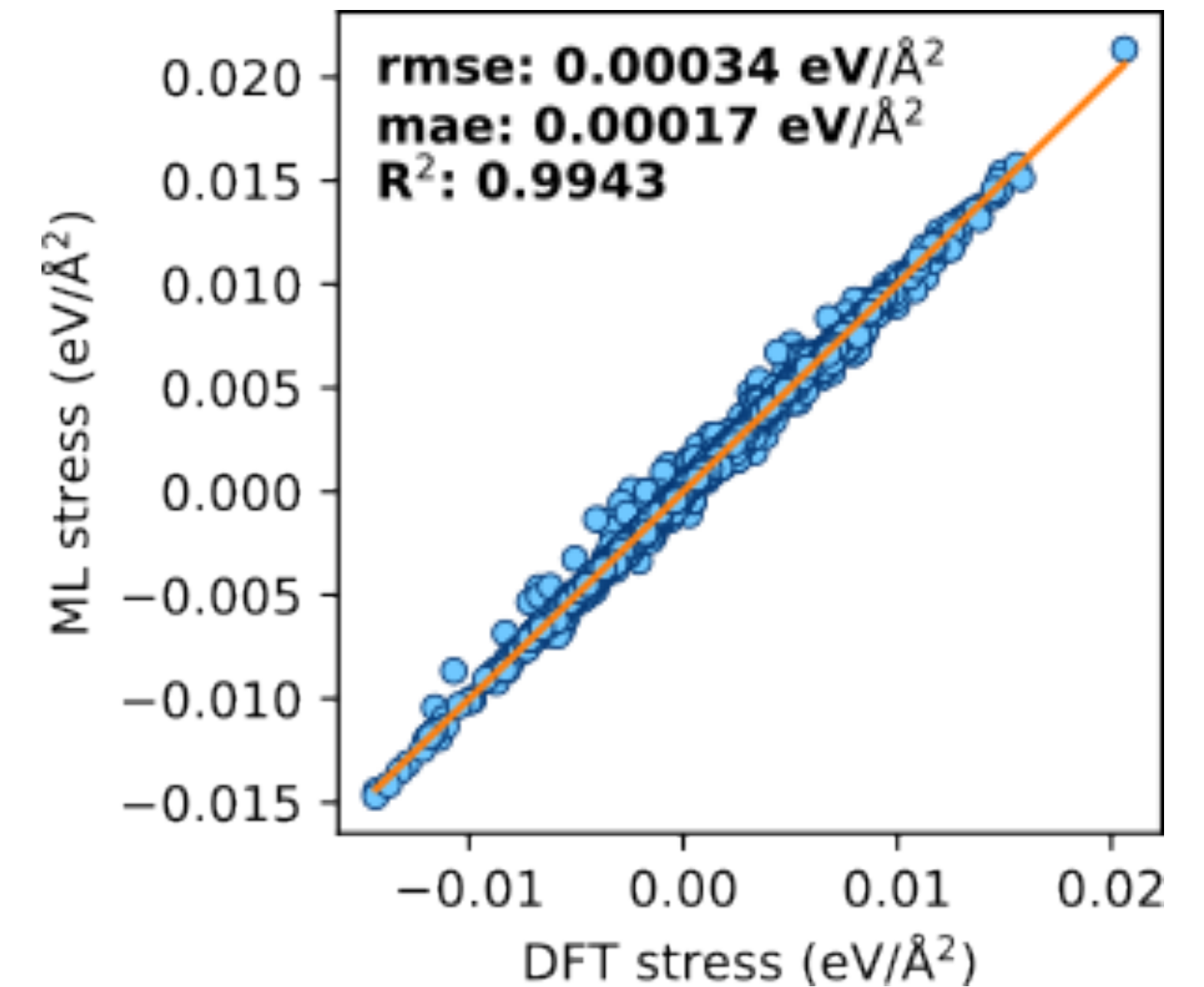
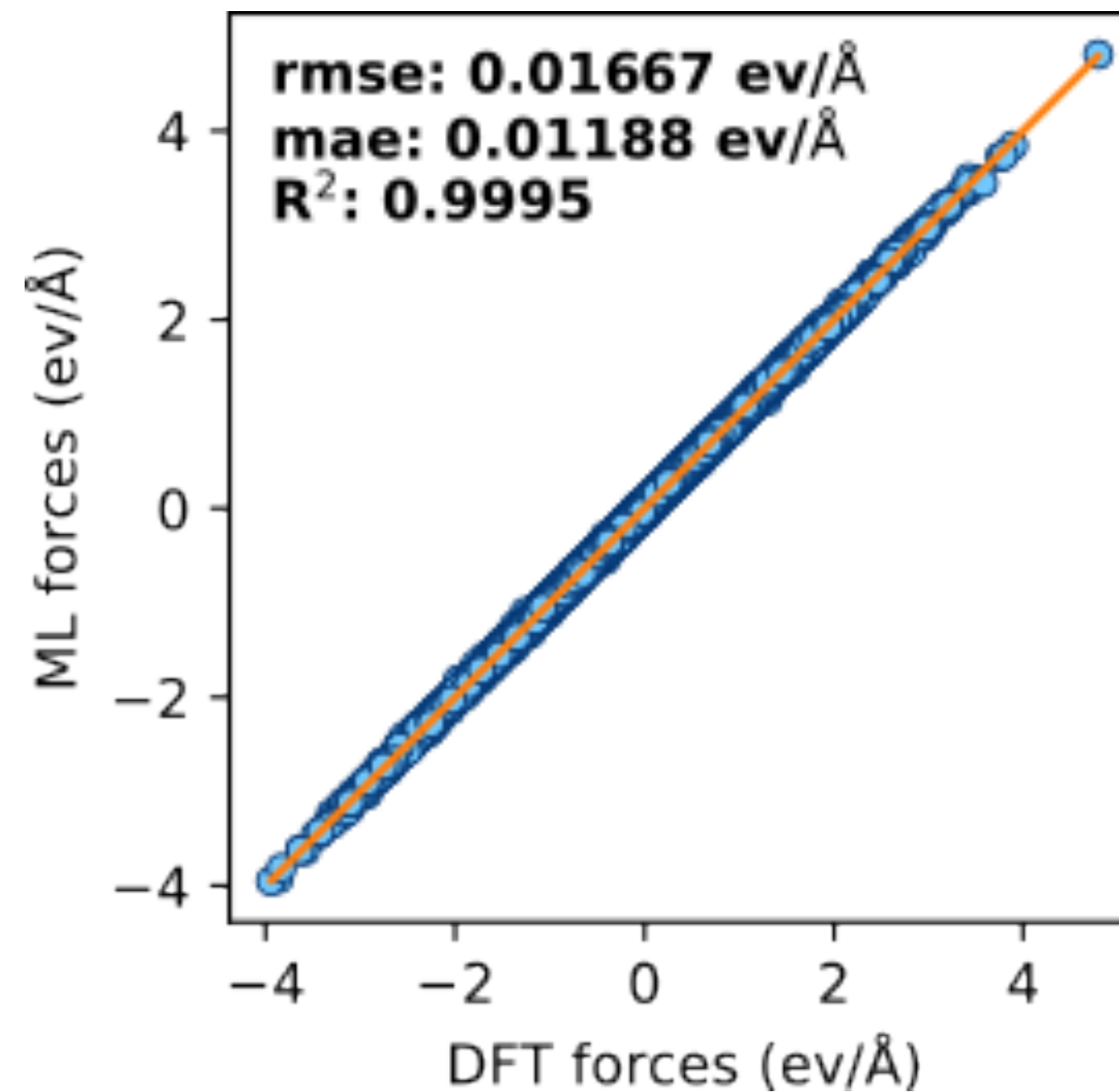
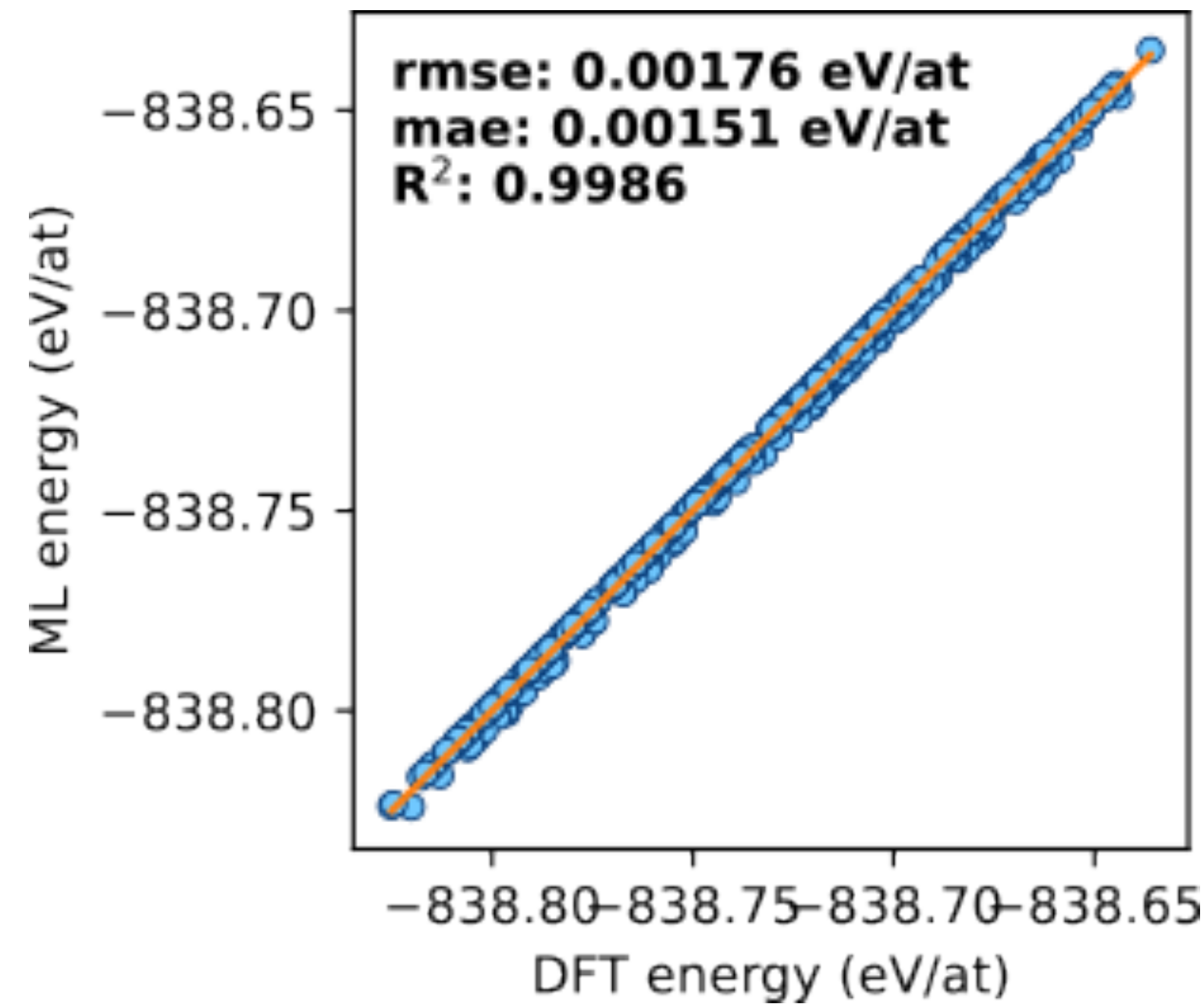
$$S(\omega) = \sum_m J_m(\omega) \cdot I_m$$

2H-MoS₂

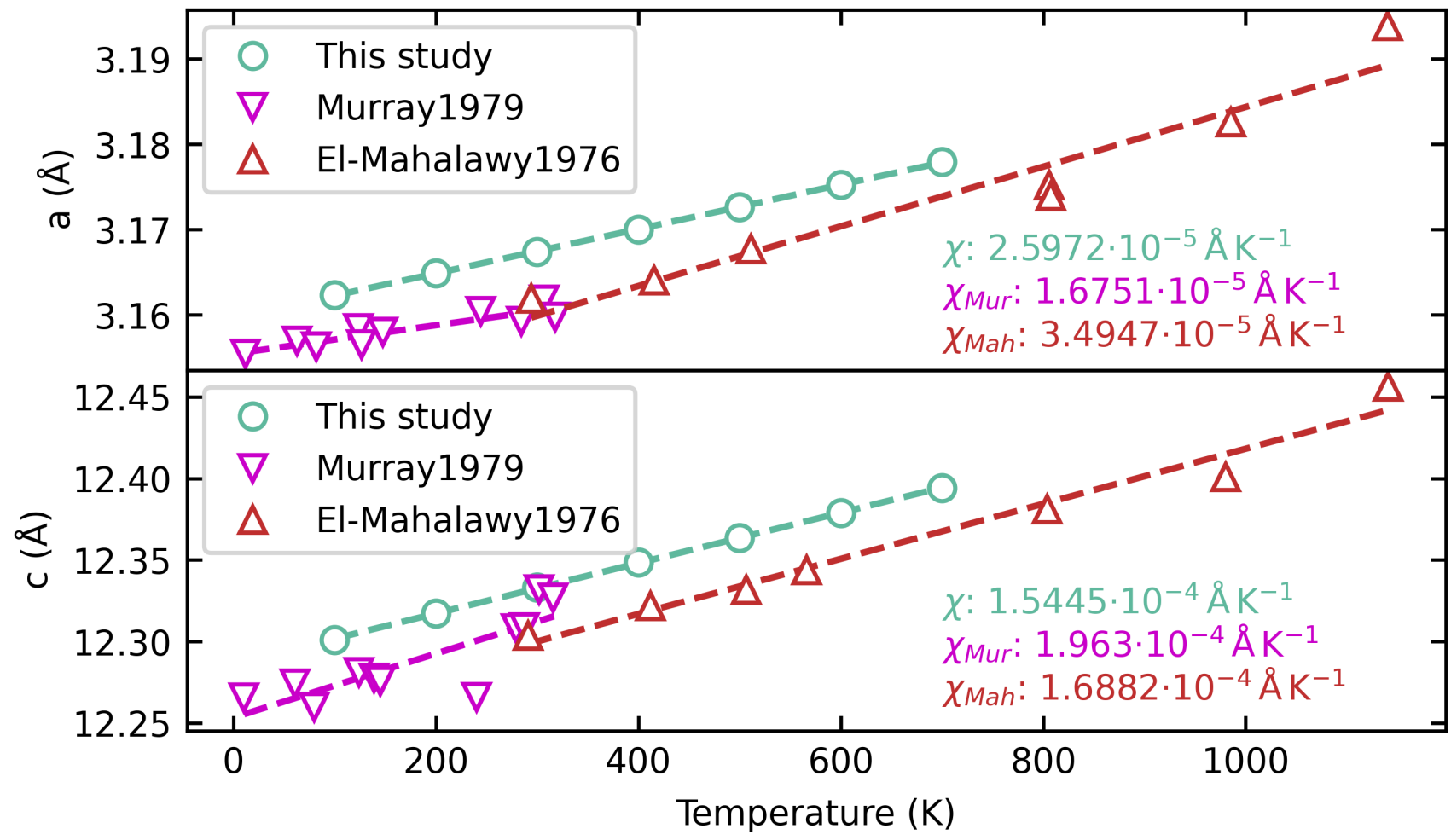
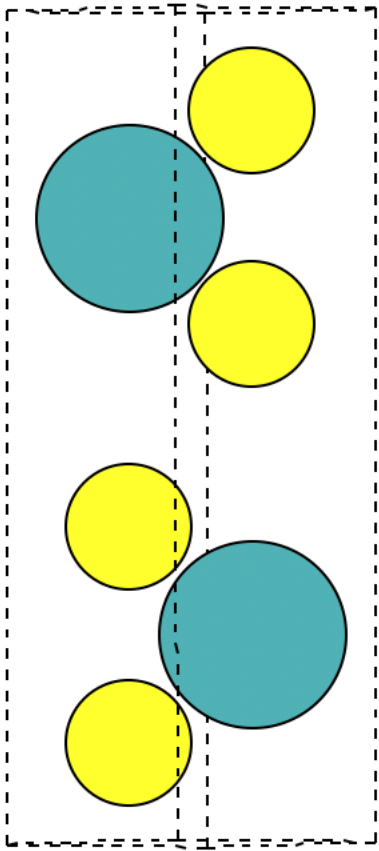


2H-MoS₂

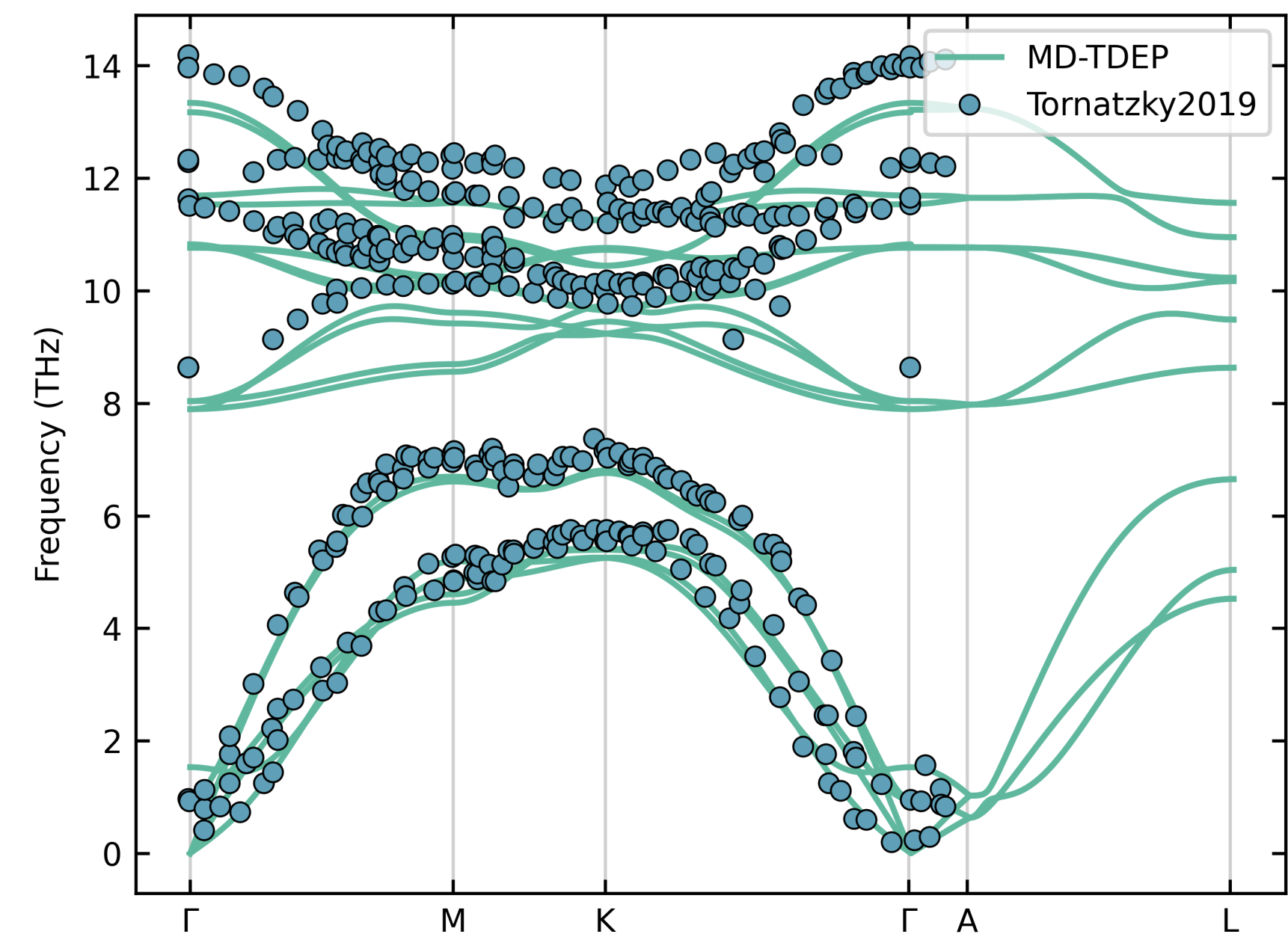
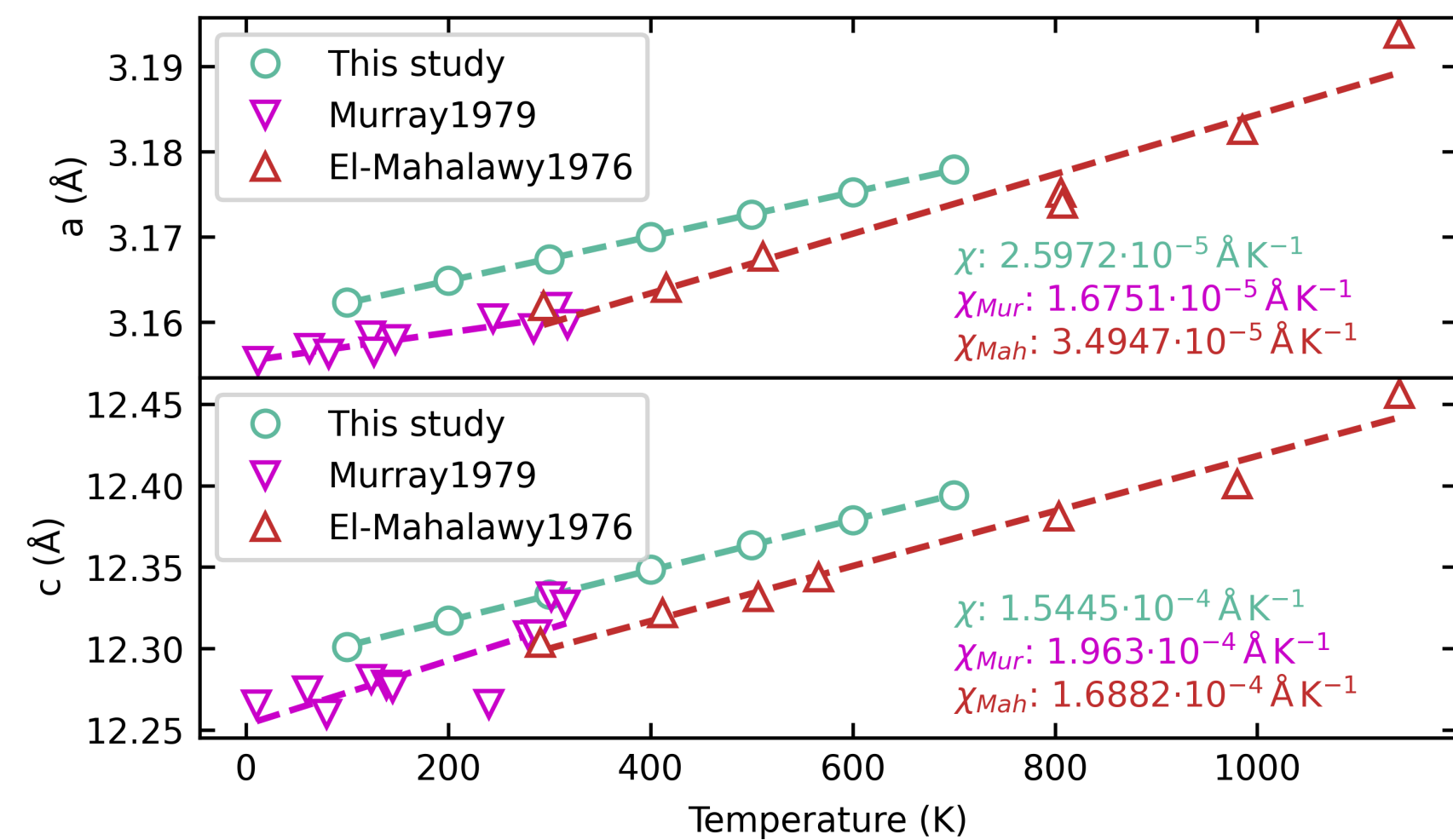
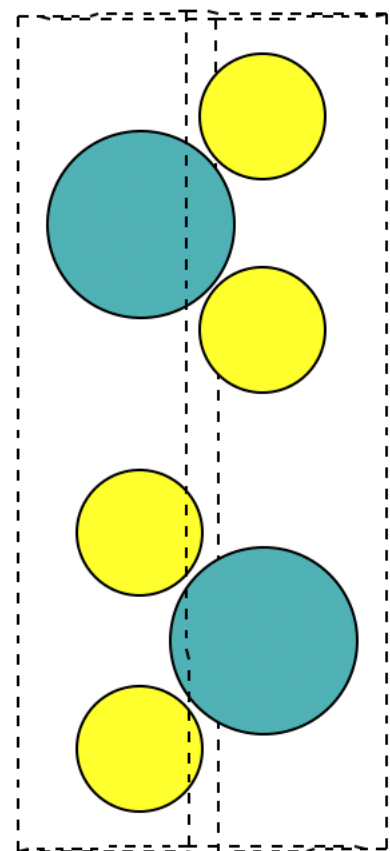
- Moment Tensor Potential
- Trained on ~330 2H-MoS₂ configurations
- From 100 to 700 K



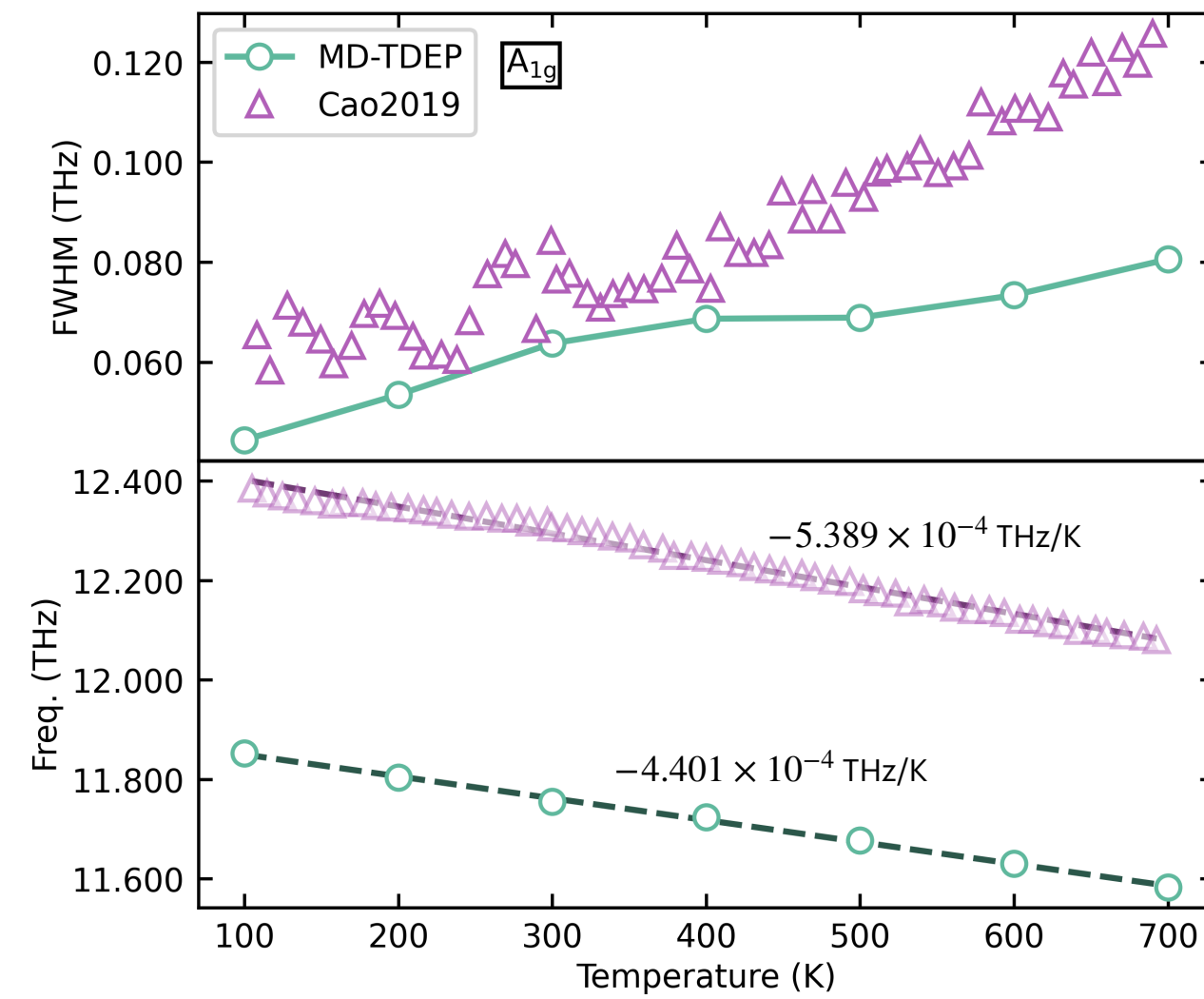
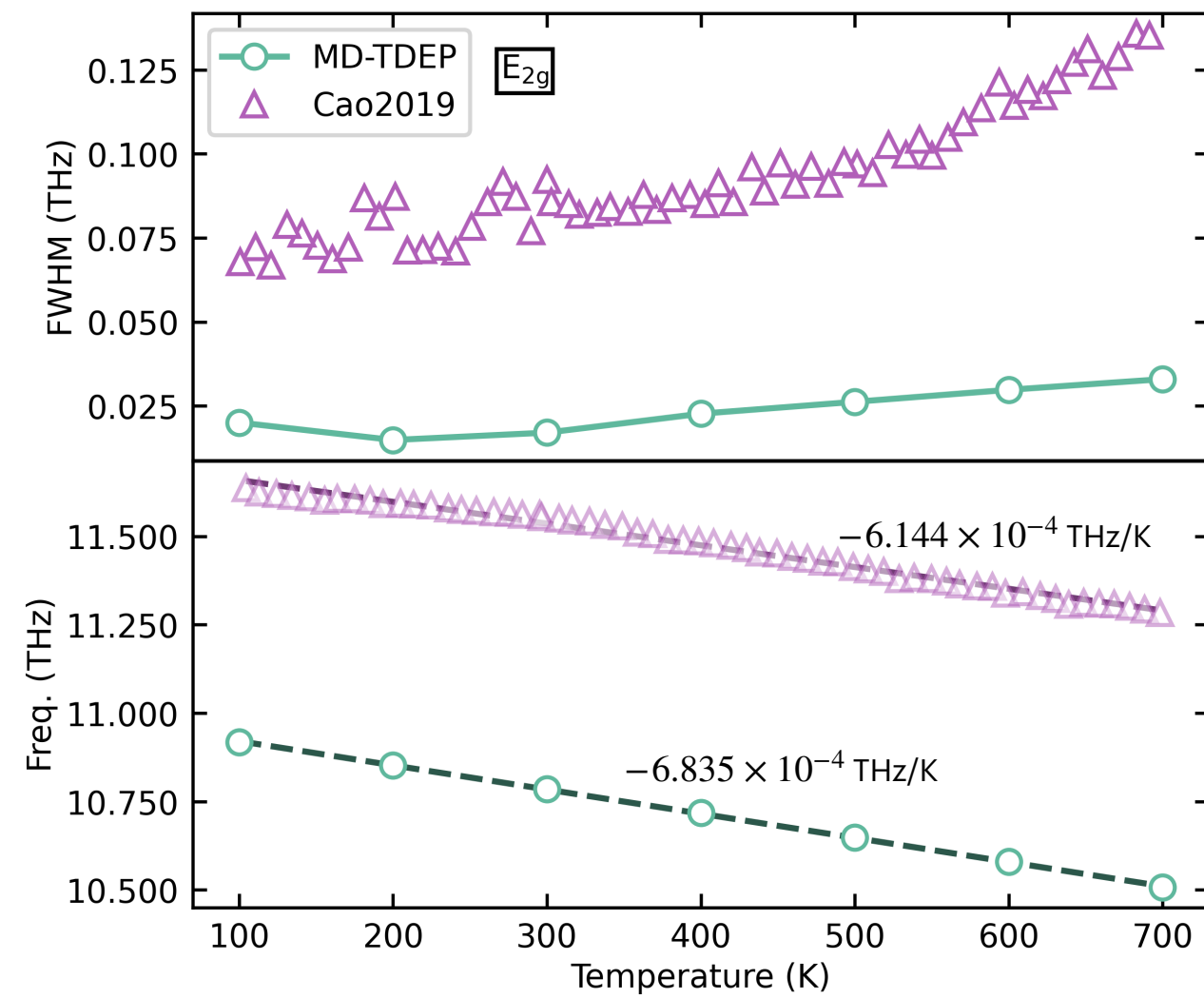
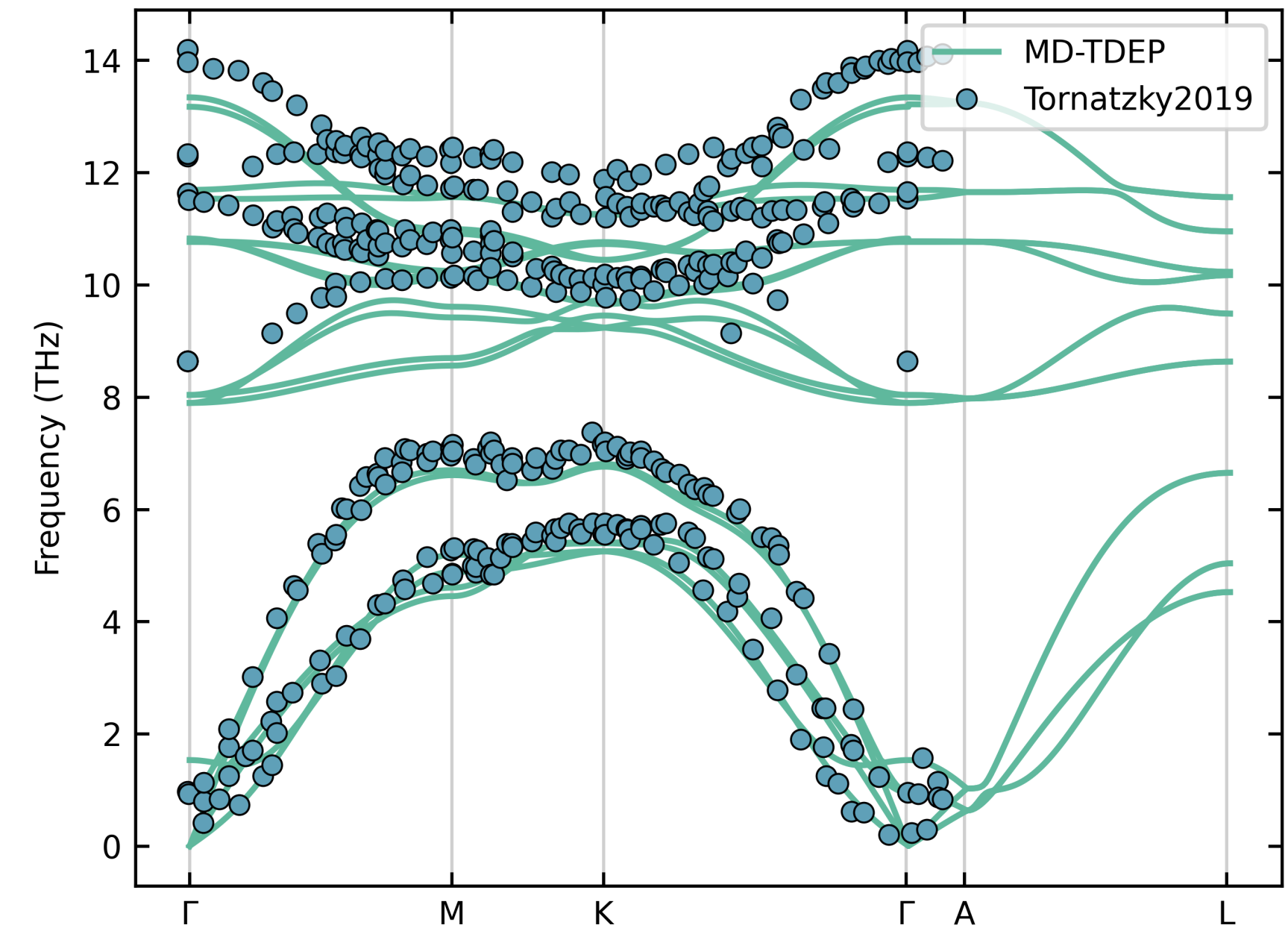
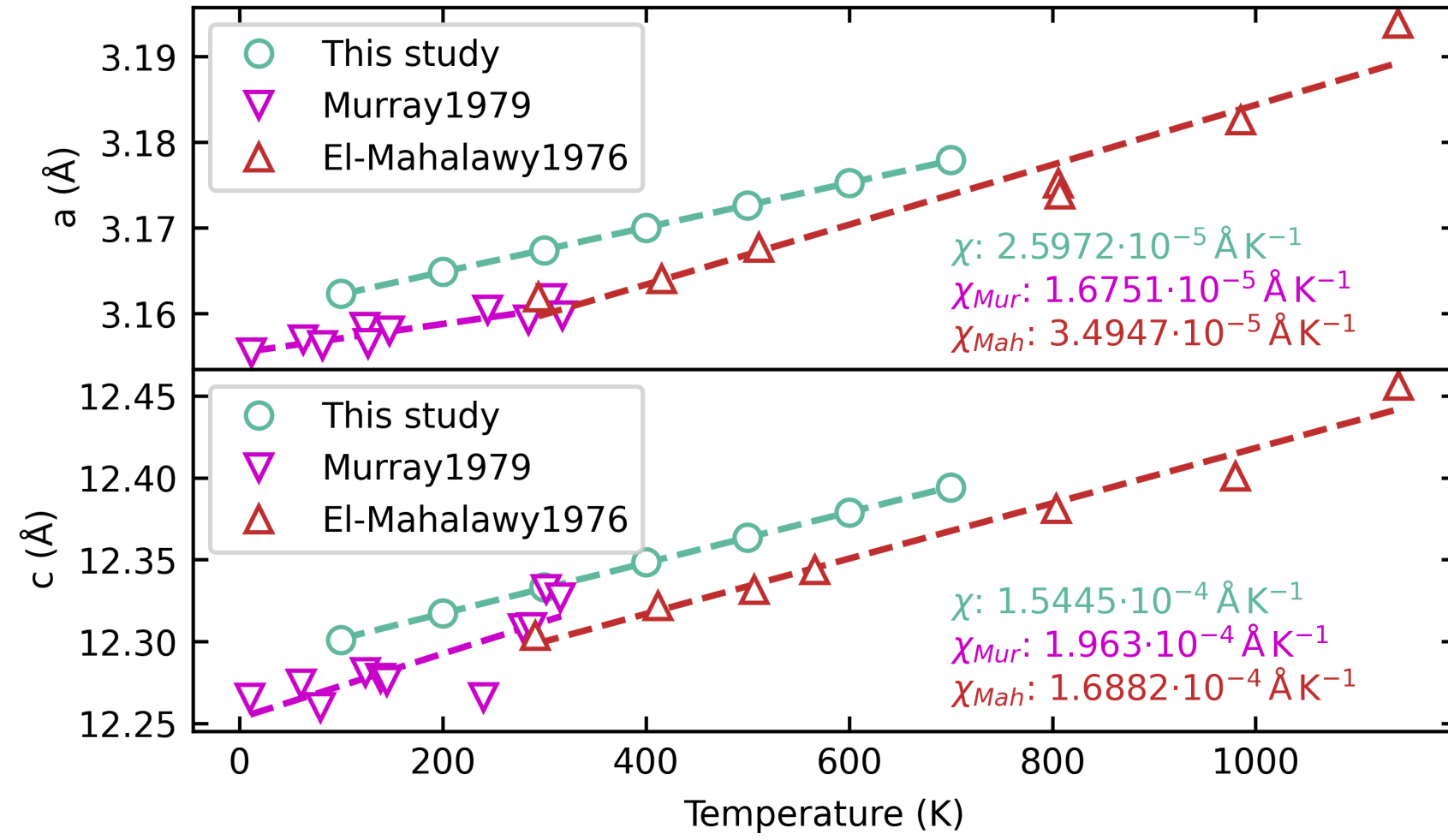
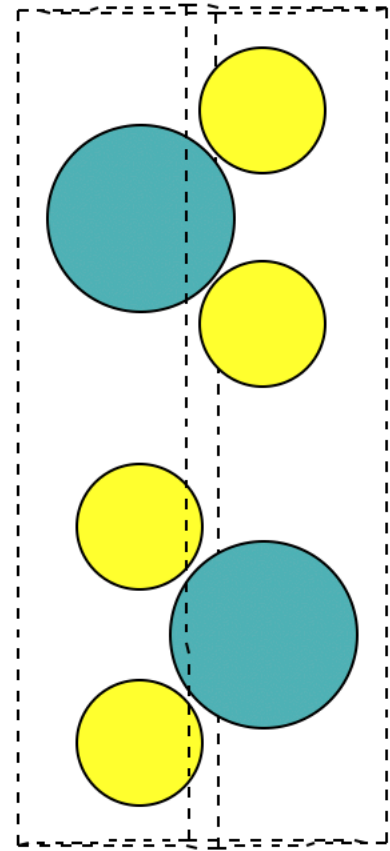
2H-MoS₂



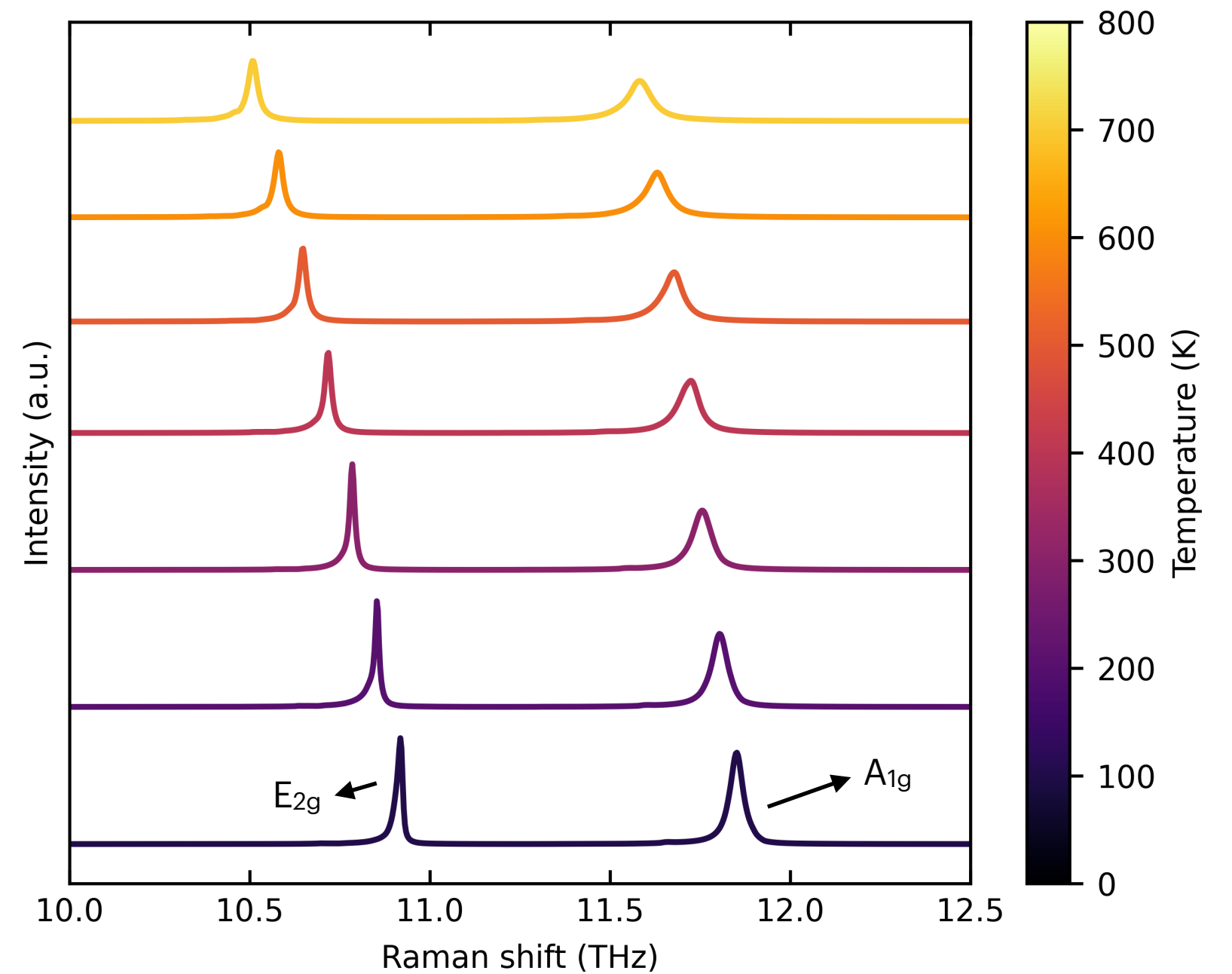
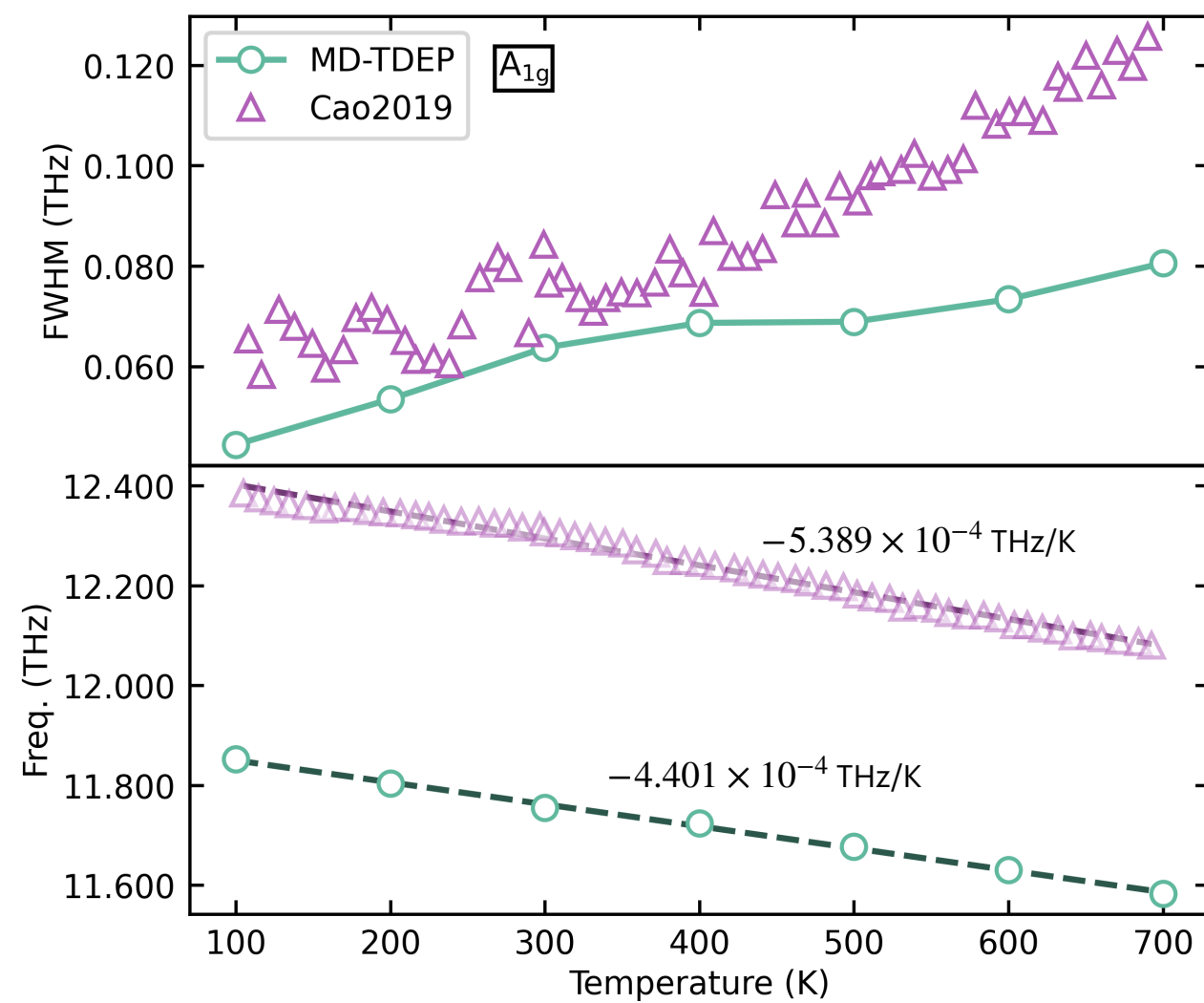
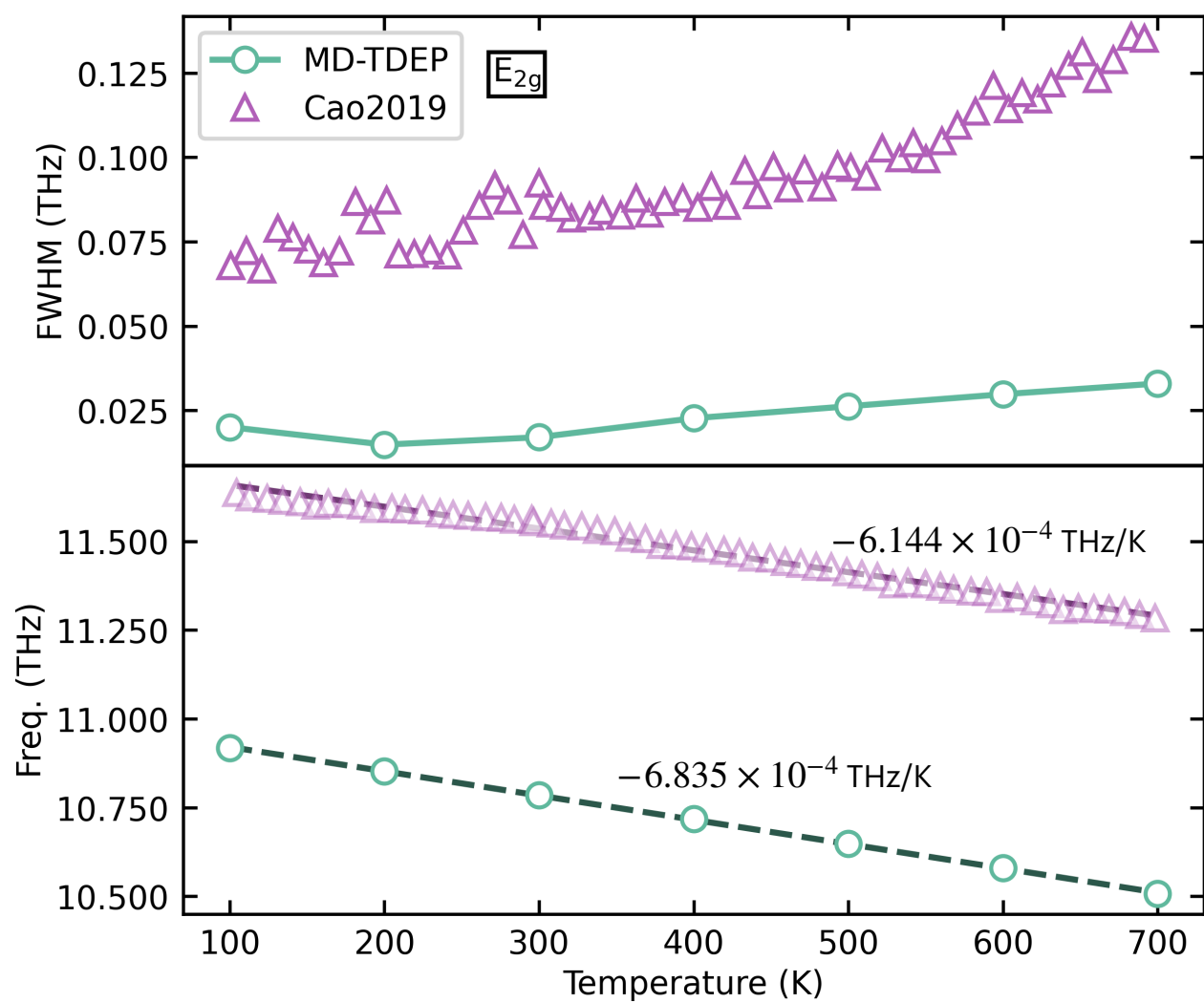
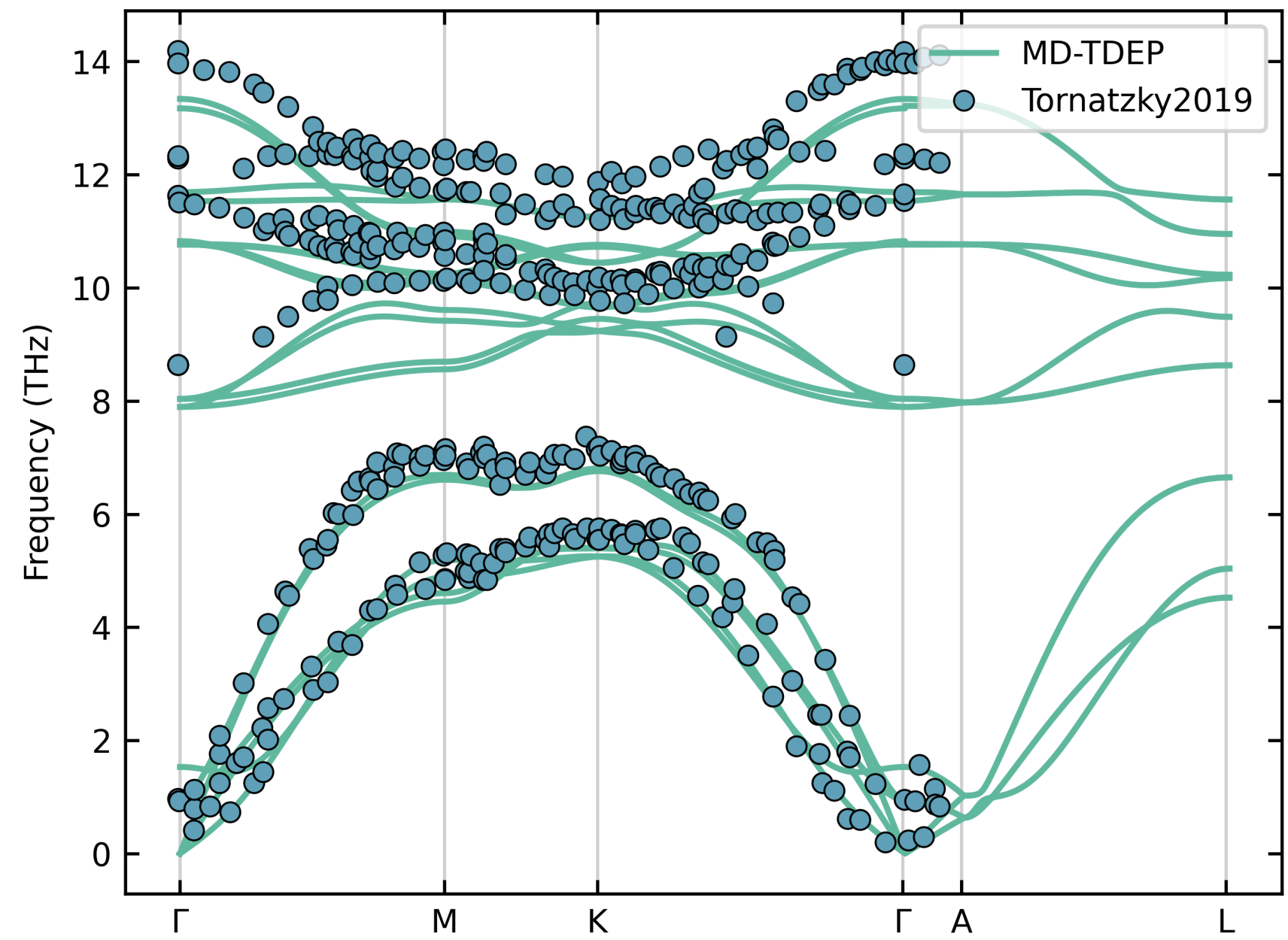
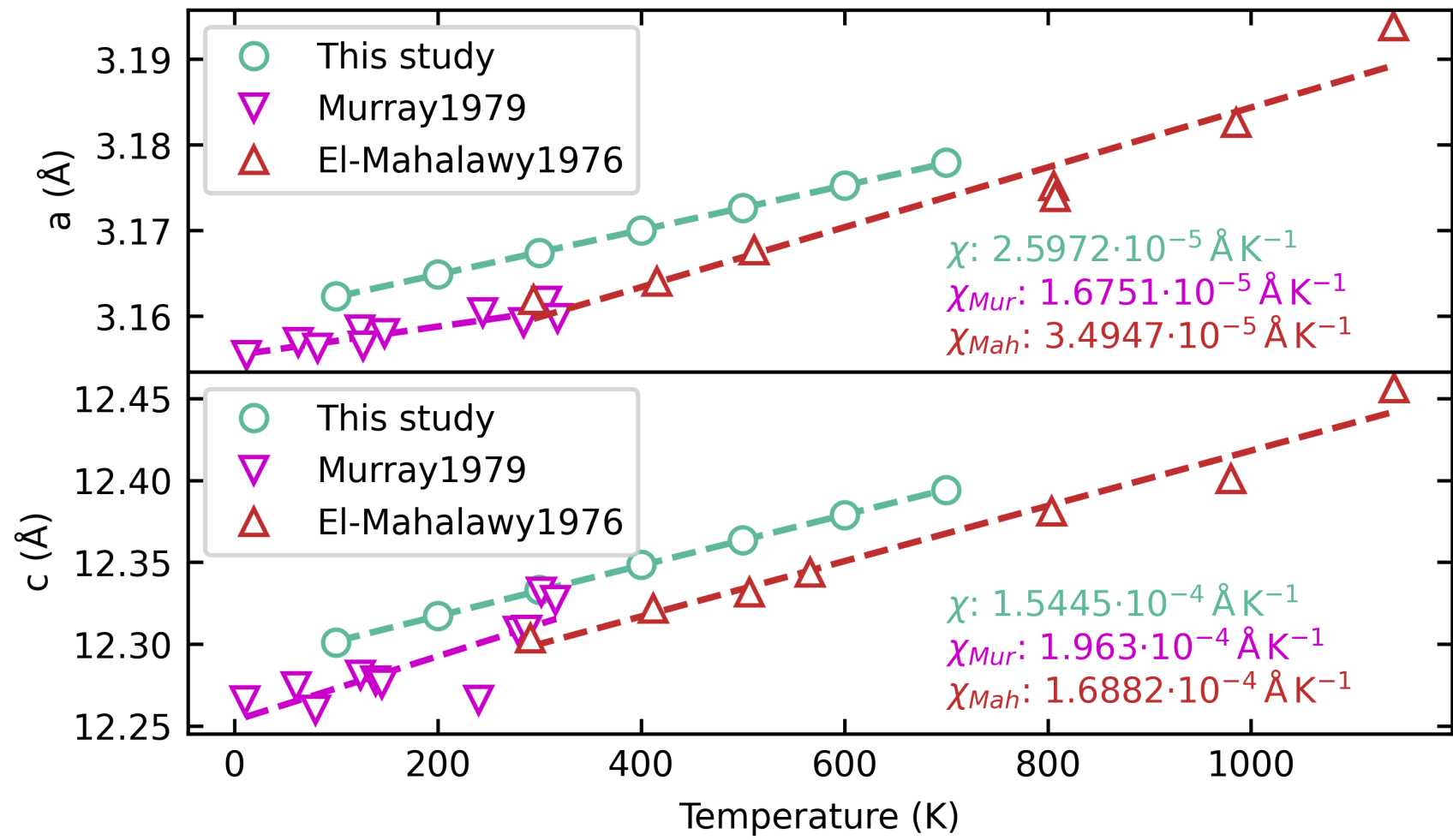
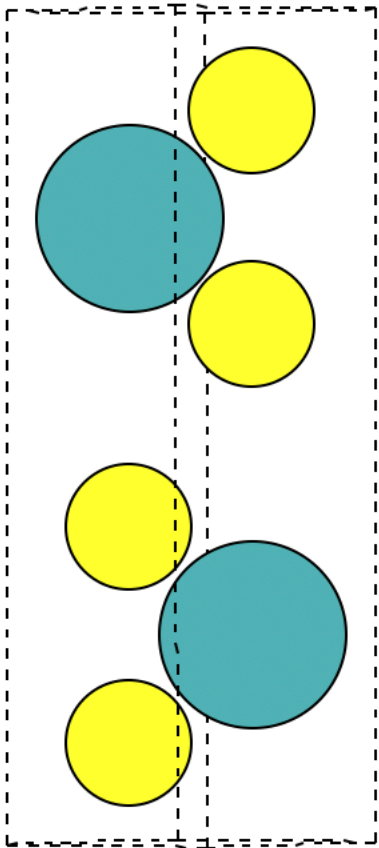
2H-MoS₂



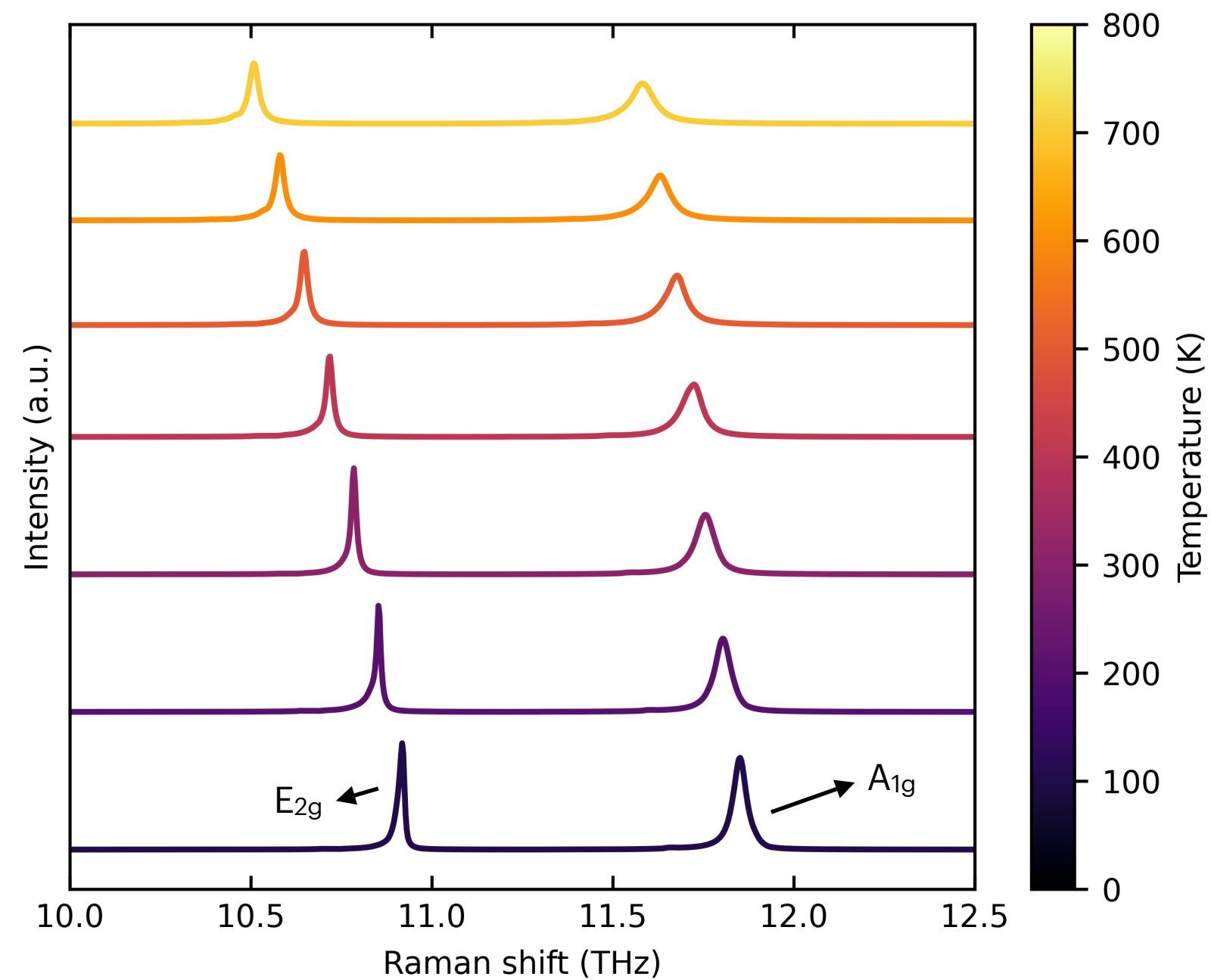
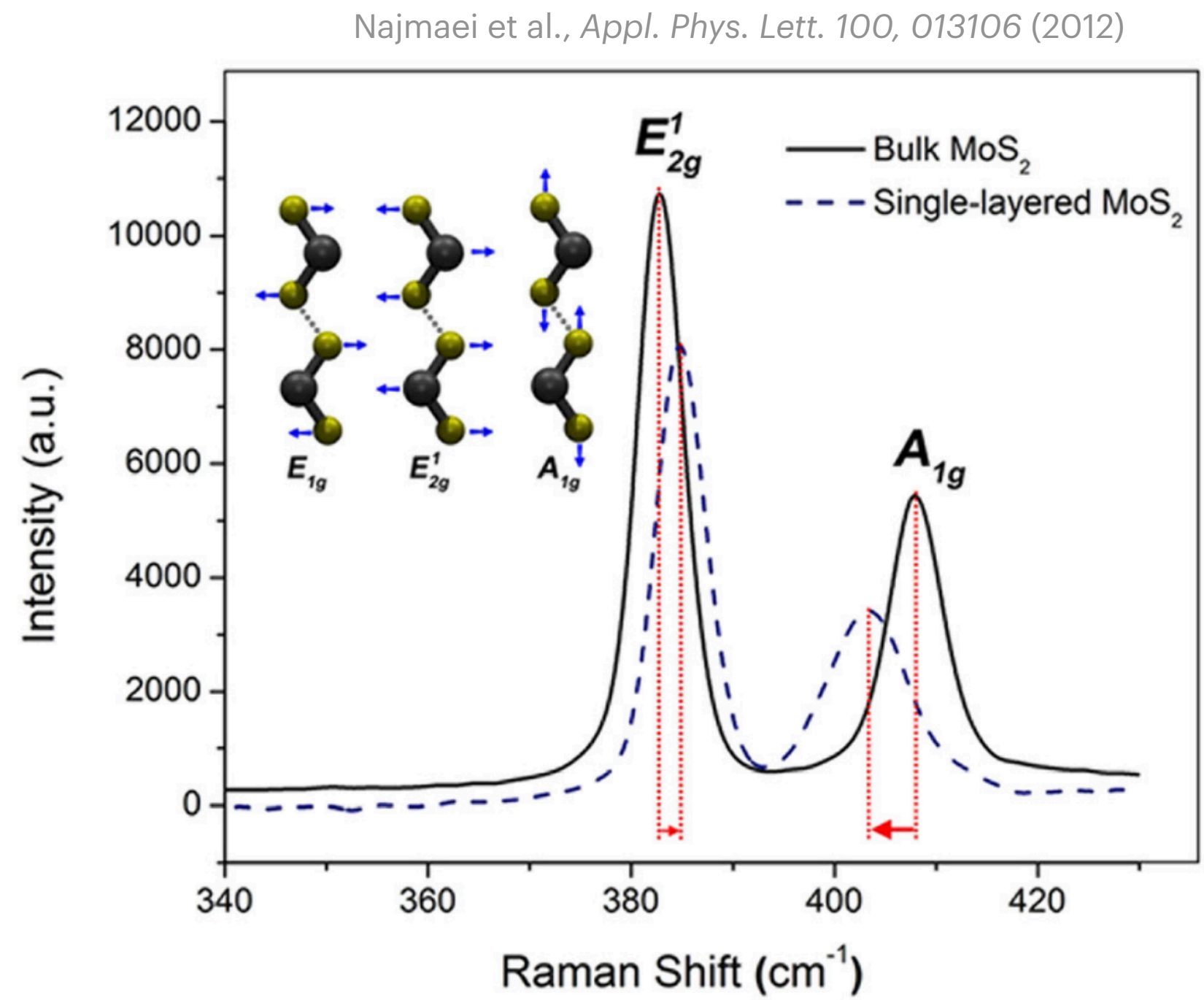
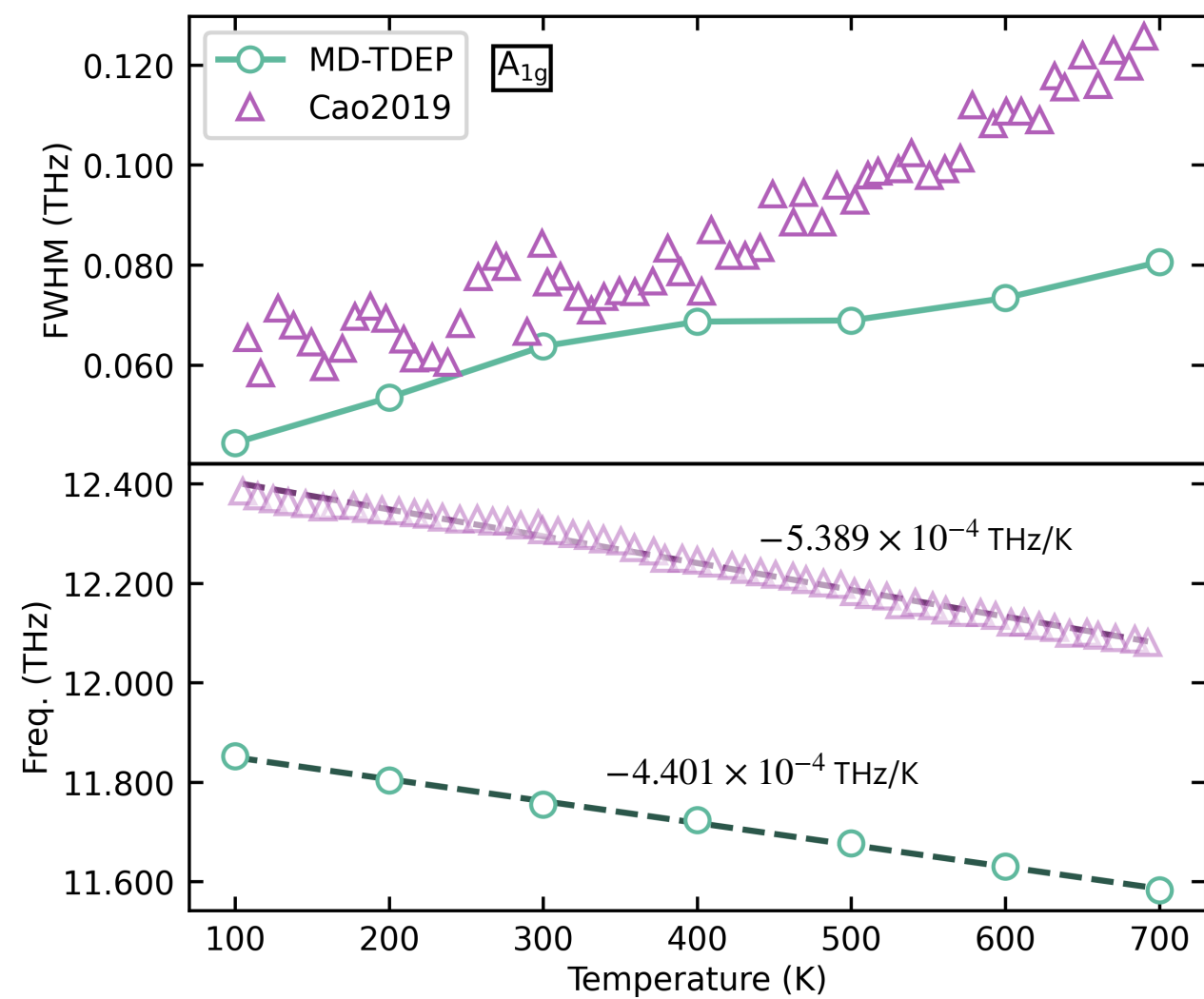
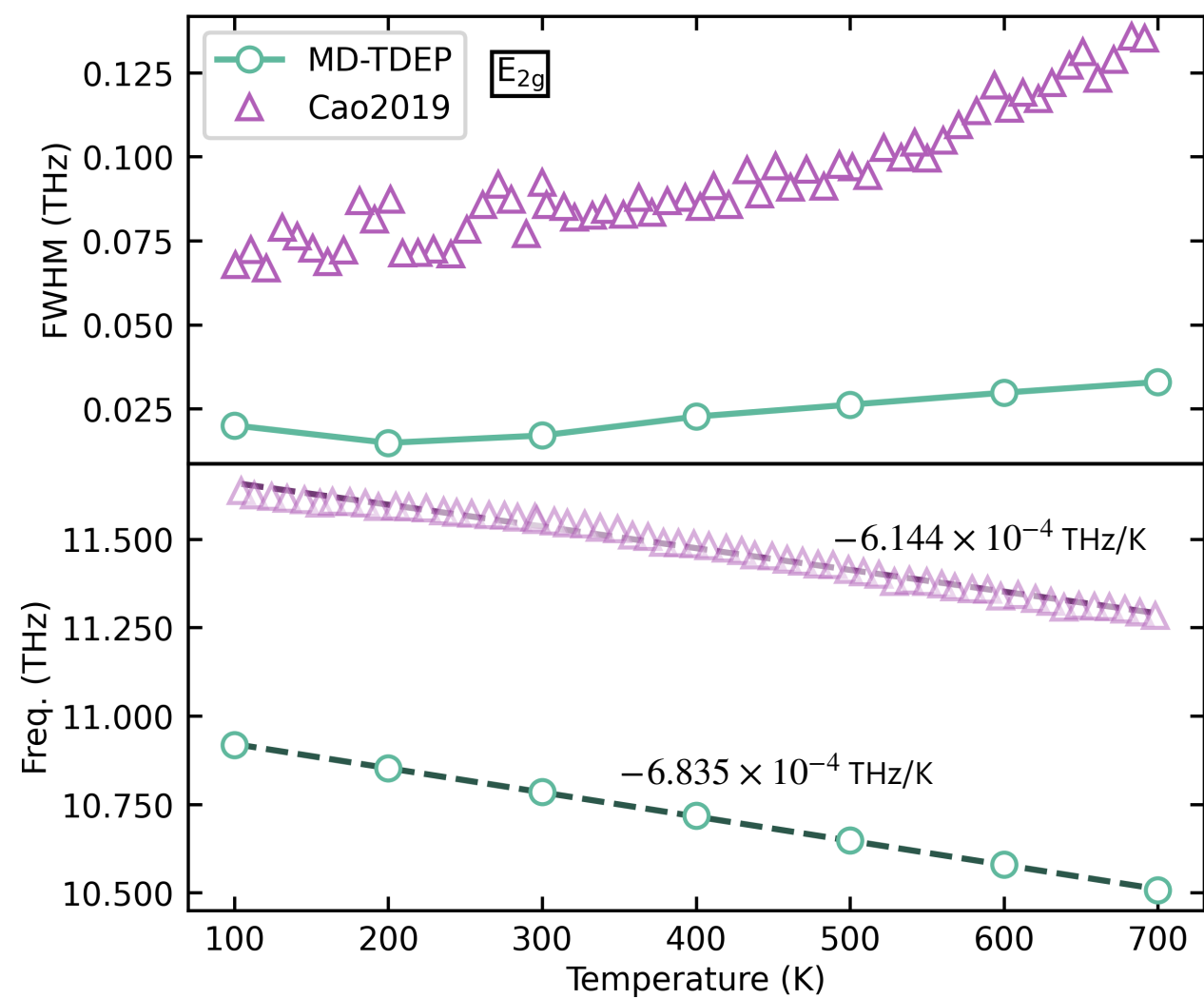
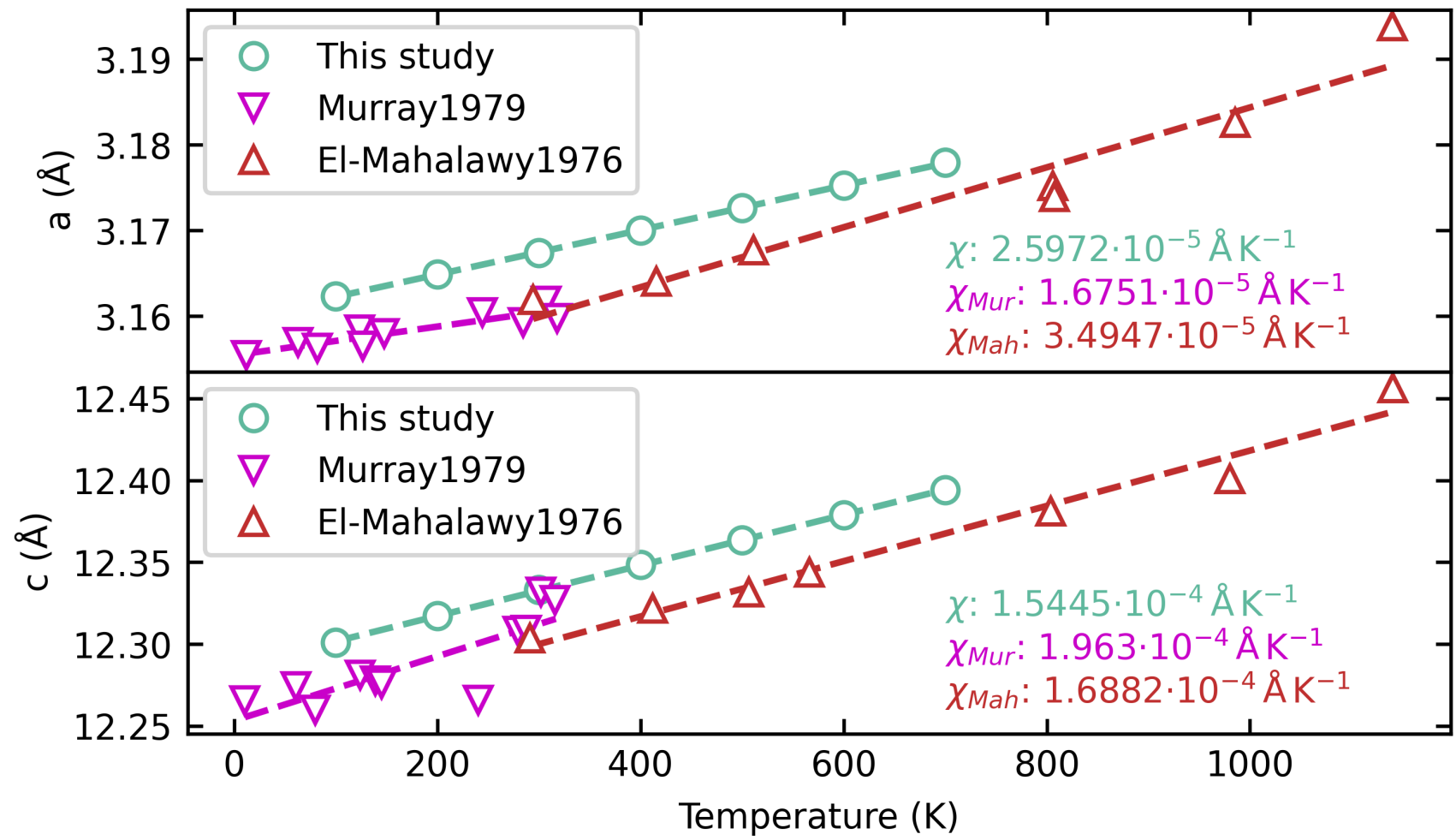
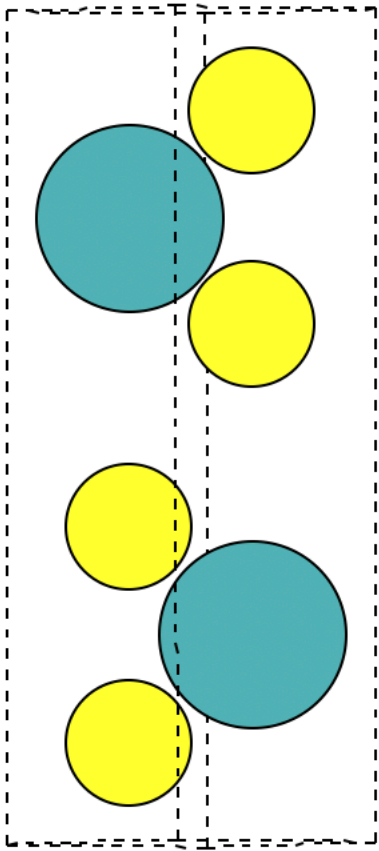
2H-MoS₂



2H-MoS₂



2H-MoS₂



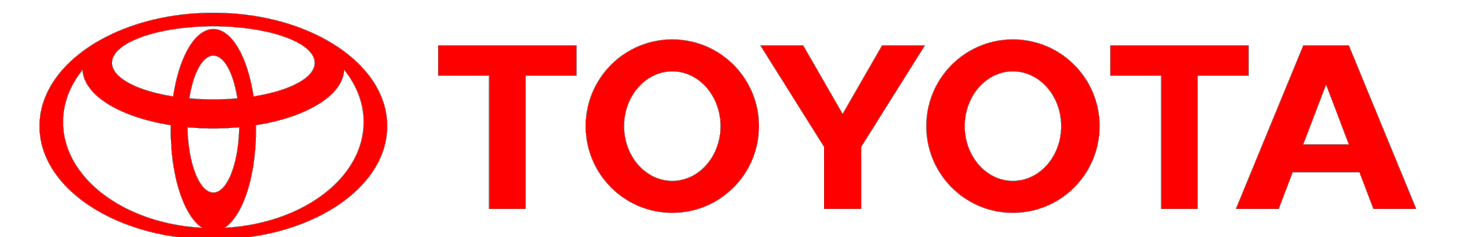
Conclusions and perspectives

- The ML model is able to accurately predict ground state properties and lattice parameters vs T
- TDEP method leads to results in good agreement with experiments
- 4th order to improve?
- Amorphous cases are being investigated now by melt & quench approach and generalized TDEP idea

Acknowledgements



LIÈGE
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The MTP model

- Moment Tensor Potential: the power of tensors

$$E(\mathbf{x}) = \sum_i^{atoms} V(\mathbf{x}_i) \quad V(\mathbf{x}_i) = \sum_{\alpha} \gamma_{\alpha} B_{\alpha}(\mathbf{x}_i)$$

$$\left[\begin{array}{c} \sum_{j \neq i}^{atoms} f_1(|\mathbf{r}_{ij}|, z_i, z_j) \underbrace{\mathbf{r}_{ij} \otimes \dots \otimes \mathbf{r}_{ij}}_{\nu_1 \text{ times}} \\ \vdots \\ \sum_{j \neq i}^{atoms} f_k(|\mathbf{r}_{ij}|, z_i, z_j) \underbrace{\mathbf{r}_{ij} \otimes \dots \otimes \mathbf{r}_{ij}}_{\nu_k \text{ times}} \end{array} \right] \xrightarrow[\{f_1, \dots, f_k, \nu_1, \dots, \nu_k\} \mapsto \alpha]{\text{tensorial contraction}} B_{\alpha}(\mathbf{x}_i)$$

atomic contribution

linear coefficient

descriptor

radial function

tensorial part

non-linear coefficient

$$f_{\mu} = \sum_{\beta}^{N_Q} c_{\mu, z_i, z_j}^{(\beta)} Q^{(\beta)}(|\mathbf{r}_{ij}|)$$