# Paving the way to unravelling Mars' regolith

**A systematic ab-initio vibrational spectra study of Mars' olivine solid solutions.**

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## In Short

- Mars' regolith is very complex, and further detection techniques, such as infra-red (IR) and Raman spectroscopy, can and must be exploited.
- The interpretation of measured spectra is difficult, and can be greatly accelerated employing theoretical DFT calculations.
- Here, we explore the full solid-solution of olivines, commonly present on Mars and other rocky astronomical objects.
- On-site self-consistent Hubbard corrections are applied to correctly and efficiently describe transition metals.
- A set of 7 van-der-Waals functionals is furthermore tested, to verify the accuracy on both geometry and spectra peak positions.

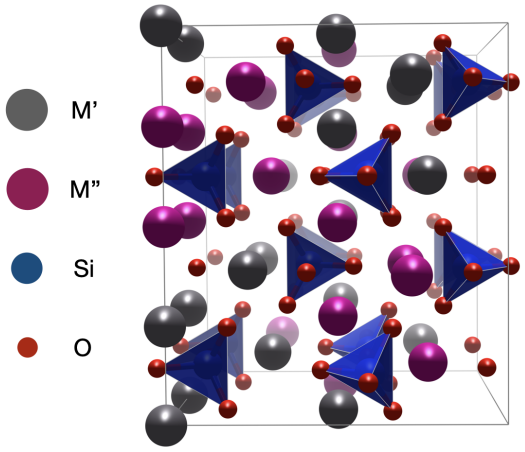


***Figure 1:*** *Example of a model structure of a general M'M"$SiO_4$ olivine solid solution.*

The second decade of our millennium has seen again an increased interest of Mars human exploration [1]. Technological advancements are required, and the actual possibility of humans surviving on the Red Planet environment is strictly bounded to the feasibility of using local resources, such as the regolith. This field has been developed under the name of *in situ resources utilization* (ISRU). The efficiency of these promising technologies will strongly depend on the composition of the soil, which can vary greatly depending on the landing site [2]. In addition, the employment of traditional XRD methods is not enough to reliably identify the structural composition, due to the amount of amorphous states present which can account up to $50\%$ of the mineral fraction [2]. A cheap, fast and accurate solution can be provided by vibrational spectroscopy, such as infrared (IR) and Raman. Although these techniques are very powerful, experimental results alone can have hard times in being interpreted, and atomistic first-principles simulations become an indispensable resource. Density functional theory, even in its most simple approximations, such as LDA and GGA, can already provide a very good sprettroscopic picture that can help unravelling such complexity. These simple approximations can be used jointly with ab-initio self-consistent Hubbard corrections, which is the method of choice when transition metals come into play. In fact, this is exactly the case on Mars, where the levels of iron oxides are very high [2], giving it its reddish hue.

In this study, we want to systematically characterize one of the main mineral present on Mars regolith, which is the olivine solid solution ($M_2SiO_4$, M=Mg,Fe,Mn, ...). Fig. 1 shows an approximate picture of how an olivine solid solution can be modelled. To date, despite the several studies on the Mg end-member, neither the transition metal nor the solid-solutions counter parts have not seen deep theoretical investigations yet. Exploiting new advancements in density functional perturbation theory (DFPT) for Hubbard parameters prediction [3], we can calculate on-site Hubbard values self-consistently, producing ground-state structures that can accurately and efficiently describe the vibrational spectra. Due to the known underestimation of higher frequency peaks in GGA functionals, we tested several van-der-Waals functionals on the forsterite structure ($Mg_2SiO4$), with the aim of correcting the tetrahedral-$SiO_4$ motions connected to these higher modes. In Fig. 2 we compare our theoretical results with the experimental spectra from a defect-free synthetic powder sample. As can be seen, theory is close to the experiments and the use of van-der-Waals corrections actually helped in restoring the higher frequency agreement. This test is absolutely promising and we plan to produce analogous spectra using the same set of functionals for the transition-metal end-members. The best functionals out of the 7 will then

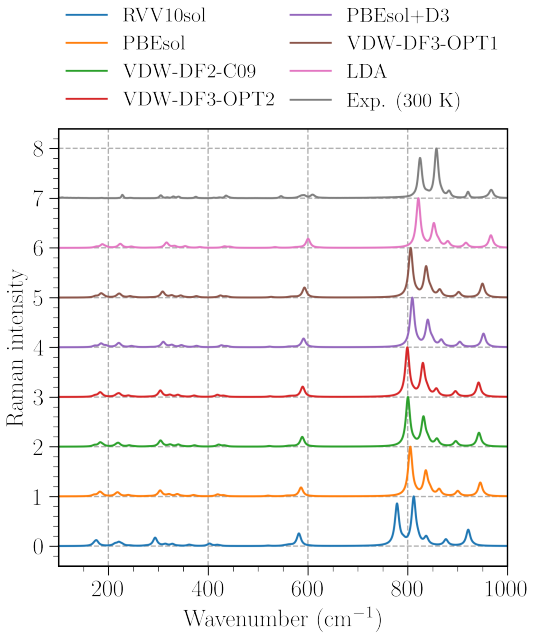


***Figure 2:*** *Raman spectra of forsterite ($Mg_2SiO_4$), where experimental measurement is compared to 7 theoretical results, each using a different DFT functional approximation.*

be applied to solid-solutions to obtain a full spectroscopic fingerprint of this important class of minerals.

## WWW

https://www.hmi.uni-bremen.de/

## More Information

[1] C. A. Platt, M. Jason, and C. J. Sullivan, *Space Policy*, **51** (2020)

[2] G. Certini et al., *Planetary and Space Science*, **186**, 104922, (2020). doi: doi.org/10.1016/j.pss.2020.104922

[3] I. Timrov, N. Marzari, and M. Cococcioni, *Phys. Rev. B*, **98**, 085127 (2018). doi: 10.1103/PhysRevB.98.085127

## Funding

U Bremen Excellence Chair

## DFG Subject Area

322-02