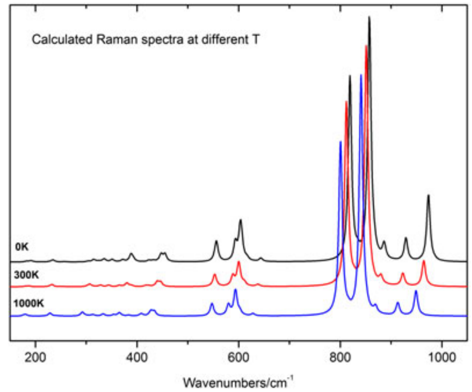
Thermal modeling of Raman spectra of forsterite in the framework of Phobos surface mineralogy: supporting science of RAX on the JAXA MMX mission. C. Stangarone[1], J. Helbert[1], M. Tribaudino[3], M. Prencipe[4], U. Böttger[2], M. Grott[1], A. Maturilli[1], [1]Institute of Planetary Research, Deutsches Zentrum für Luft- und Raumfahrt, Berlin, Germany (claudia.stangarone@dlr.de), [2]Institute of Optical Sensor Systems, Deutsches Zentrum für Luft- und Raumfahrt, Berlin, Germany, [3]Chemistry, Life and Environmental Sustainability Science Department, University of Parma, Italy, [4]Earth Sciences Department, University of Torino, Italy.

Introduction: Reconstructing the original mineralogy of early Mars is quite challenging if surveying only the current surface. Contrarily, the two Martian Moons Phobos and Deimos likely preserved records on the formation processes of the parent planet. The third sample return mission by JAXA, Martian Moons eXploration (MMX) [1], planned to be launched in 2024, will survey the two Martian moons and carry back samples from Phobos. The general science objectives of the mission are: 1) to settle the controversy on the origin of the Martian moons (weather caused by captured asteroids or via giant impacts), by close-up observations and sample return 2) to extract information on the rocky planet formation, 3) to reveal evolutionary processes of the Martian system in a unique circum-Martian environment [2].

On the payload of the rover, RAX – Raman Spectrometer for MMX serves the purpose of in-situ and sample analysis crucial to: 1) investigate the surface mineralogy on Phobos by spectroscopic identification, 2) study the surface heterogeneity by visiting different locations on Phobos by rover movement, 3) support the characterization of sampling site and the selection of samples for the return to Earth, 4) compare the measurements obtained from returned samples with Earth laboratories. The MiniRAD radiometer on the rover will independently provide surface temperatures and grain size information [1]. Moreover, MMX orbiter instruments will provide compositional, geological and morphological context for the landing site [3]. The MMX/RAX results will also be directly compared with Raman measurements obtained by the RLS instrument during ExoMars 2020 mission [4] as well.

Aim of the study: To support the science questions that RAX aims to answer, it is essential to build a solid scientific background in order to interpret any possible Raman shift due to the different environmental condition on Phobos. For instance, the temperature on the Martian moon decreases of 100 K during the night, dropping to a minimum ranging from 160 to 140 K [5]. The Raman measurements will be carried out during the night, therefore it is crucial to take into accounts the direct relationship between the crystal structure and the temperature (i.e. thermal expansion and thermal pressure), as the Raman peak will shift with the change of temperature [6]. In this study, we show the influence of temperature on Raman shifts by DFT simulations of Raman spectra of a common rocking form mineral, forsterite, Mg_2SiO_4, computed from first principles in three extreme temperature situations [6].

Method: The simulations of Raman spectra are performed by means of DFT calculations of the phonon frequencies employing the hybrid Hamiltonian WC1LYP, by means of CRYSTAL14 code [7]. The whole spectrum pattern is then modelled, calculating analytically for each frequency the second rank Raman tensor. The accuracy of the modeling is ensured by the comparison with the available experimental data [6, 8]. For instance with the experimental Raman spectra taken on a natural sample of olivine [6], carried out with the same environmental conditions at the Institute of Optical Sensor Systems, DLR in Berlin. The temperature factor is modelled including the zero point pressure and the vibrational pressure on the volume calculated for three extreme temperature situations (0K, ~ room T 300 K, high T 1000 K), in order to have a clear understanding on the Raman shift with temperature.



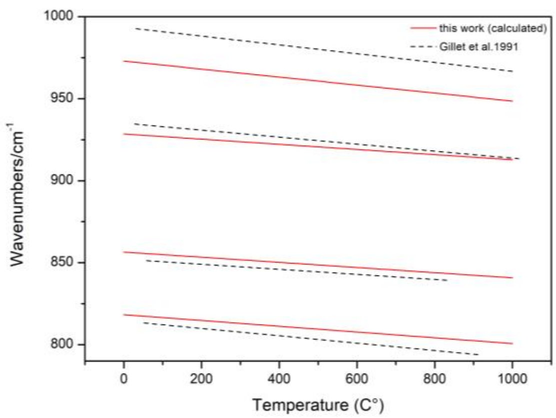


Figure 1: Figure 1: (top) calculated Raman spectra of forsterite respectively at 0, 300 and 1000 K (in offset for clarity); (bottom) $\Delta\nu_j/\Delta t$ slope comparisons between calculated and experimental for the most intense peaks.

Results: As shown in the figure 1 top panel, the temperature changing leads to a consistent peak shifting if compared to measurements taken at ca. room conditions (spectrum in red 300K). Moreover, we compared the slope of the wavenumber over temperature ($\Delta\nu\omega/\Delta T$) calculated from the difference of the calculated peak positions at 0 and 1000 K with the experimental $\delta\nu\omega/\delta T$ obtained by Gillet et al. [8] measured within the same range of temperature (Figure 1 bottom panel). Here are considered the strongest and best measured peaks at 819, 857, 929 and 974 cm^{-1}. The agreement is within experimental error, suggesting that calculated frequencies at different temperatures can be used to predict the actual changes in Raman peak positions.

Conclusions: DFT modelling is a reliable tool for improving Raman databases and theoretical background to deal with common issues in data interpretation of spectra. Here the reliability was shown by the comparison of the calculated data with the experimental ones available [6, 8]. Data analysis is still under process to extrapolate the exact Raman shift at the temperature expected on Phobos. However, it can be already inferred that with a dropping of 100K during the night, the Raman peaks will shift towards higher wavenumbers and therefore this effect must be considered for data interpretation. This method also provides valuable insights, which can be used to interpret or understand the macroscopic thermodynamic functions like heat capacity and bulk physical properties such as thermal expansion and compressibility. Therefore, the MMX/RAX measurements can complement the measurements of the thermophysical properties obtained by the MiniRAD instrument on the rover.

The work will also inform the preparation for the analysis of the returned samples in the new DLR Sample Analysis Laboratory [9].

Acknowledgments: this study was supported by a DLR/DAAD scholarship

References: [1] Campagnola, S., et al (2018). Acta Astronautica 146: 409-417. [2] Ulamec, S. et al. (2019) IAC-19-A3.4.8, [3] Lawrence, D. J, et al. (2019). Earth and Space Science. [4] Hagelschuer, T., et al. (2019) IAC-19-A3.4.9, [5] Ziese, R., et al. (2019) EPSC-DPS Joint Meeting 2019, [6] Stangarone et al. (2017) *J. Raman Spectrosc* 48-11, [7] Dovesi R. et al. (2014) CRYSTAL14 *User's Manual*, [8] Gillet, P. et al. (1991) *J. Geophys. Res. Solid Earth*, 96-11805. [9] Helbert, J et al. (2018) In European Planetary Science Congress (Vol. 12)