

## In situ Raman spectroscopy monitoring of material changes during proton irradiation

Mickael Baqué<sup>1</sup>, Frédéric Foucher<sup>2</sup>, Aurélien Canizarès<sup>3</sup>, Jean-Pierre de Vera<sup>4</sup>, Thierry Sauvage<sup>3</sup>, Olivier Wendling<sup>3</sup>, Aurélien Bellamy<sup>3</sup>, Paul Sigot<sup>3</sup>, Thomas Georgelin<sup>3</sup>, Frances Westall<sup>2</sup>,

<sup>1</sup>German Aerospace Center (DLR), Institute of Planetary Research, Department of Planetary Laboratories, Astrobiological Laboratories, Berlin, Germany

<sup>2</sup>CNRS, CBM, UPR 4301, rue Charles Sadron, CS80054, 45071 Orléans Cedex 2, France

<sup>3</sup>CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France

<sup>4</sup>German Aerospace Center (DLR), Space Operations and Astronaut Training, MUSC, Linder Höhe, Cologne, Germany.

**Introduction:** Organic molecules are prime targets for the search for life on other planetary bodies in the Solar System. Understanding their preservation potential and detectability after ionic irradiation, with fluencies potentially representing those received for several millions to billions of years at Mars or in interplanetary space, is a crucial goal for astrobiology research (Hassler et al. 2014). Particles of different energies and fluencies can indeed induce breaking of molecular bonds, depolymerization, and temperature increase among others. However, materials can evolve rapidly after irradiation and the changes, between the irradiation chamber and the ex situ laboratory analysis conditions (and environment), are hard to predict and time and sample consuming. The possibility to monitor changes in the sample in situ in the chamber thus constitutes an important breakthrough for the domain. In order to be able to perform in situ characterization of organic molecules under ionic irradiation, a feasibility experiment was performed with polymer test samples to validate the optical configuration and the irradiation chamber geometry (Fig. 1). Indeed, polymers are known to be sensitive to proton irradiation and they usually give Raman spectra with high signal to noise ratio (Samuel 2020). We present here a Raman in situ investigation of the evolution of a series of polymers during proton irradiation, for which a new type of Raman optical probe was designed.

**Material and methods:** In order to demonstrate the relevance of the coupling, a series of commercial polymers has been analyzed: polyvinyl chloride (PVC), polyamide (PA), polyethylene (PET), polystyrene (PS), and polypropylene (PP). The experiments were carried out in the Micro-beam line vacuum chamber with a 2.8 MeV proton ( $H^+$ ) beam at the CEMHTI Pelletron facility (<http://emir.in2p3.fr/CEMHTI>), CNRS, Orléans (Fig. 1). Samples were irradiated using a flux of  $5 \times 10^{10}$  protons. $cm^{-2}.s^{-1}$  to obtain different fluence values from  $5 \times 10^{12}$  to  $3 \times 10^{14}$  protons. $cm^{-2}$ . The probe is a 0.15 numerical aperture optic giving a 0.4 mm diameter spot size at the surface of the sample and a 1.5 mm depth of focus. The laser used was a 532 nm Excelsior Spectra Physics laser, and the spectrometer a Renishaw RA100 (1800 lines/mm grating, 250 mm focal length) with a spectral resolution 3.5-1.65  $cm^{-1}$ . The samples were alternately moved from the irradiation position to the Raman analysis position using a x,y goniometer.

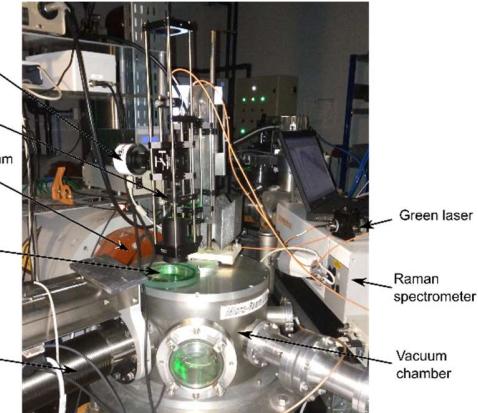


Fig. 1. Raman spectrometer probe interfaced with the Pelletron irradiation chamber, CEMHTI, CNRS, Orléans, France.

**Summary:** The coupling of particle irradiation with in situ Raman detection is particularly relevant for present and future missions to Mars like NASA Mars2020 and ESA/Roscosmos ExoMars2022 rovers carrying Raman instruments (Rull et al. 2017). Using a series of polymers as a proof of concept, we showed that the kinetics of alteration may vary drastically from one sample to another. Indeed, proton irradiation (with a final fluence of  $3.10^{14}$  protons. $cm^{-2}$ ) leads to an increase in the background level of the signal, potentially explained by the scission of the polymeric chains and by the atom displacements creating defects in the materials. Further improvements of the system are underway to reduce the Raman probe working distance, include a cooled sample holder, and allow for Raman mapping to apply to biomolecular samples of relevance for astrobiology.

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