Proposal Title and Acronym

Design and Construction of an X-Y-Z-motorized head to perform Deep-UV Raman measurements at microscopic level in cold environments from -30 to -5 ºC (CORaHE)

This proposal responds to challenge(s) in the following domain(s)
(Sensors)

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Consortium Composition Table

	Organization full name	Organization short name / PIC number	Organization type[1]	Contact person name	Contact person email
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[1] Research Infrastructure, University, SME, Large Corporation, Research & Technology Organization, Start-up. If other, please specify.

Project Public Summary

The main objective is to design and build the innovative CORaHE (**CO**ld **Ra**man **He**ad) sensor for Deep-UV Raman spectroscopy, to operate under cold environments between -30 and -5 ^{o}C. This portable sensor will perform non-destructive micro-Raman measurements of cold samples, without any limitation in size. The CORaHE sensor has been designed to cover the absence of technology to perform such measurements, either in laboratory or in the field, on sensitive samples having temperatures as low as -30 ^{o}C. Samples will not be destroyed like it is done currently with the use of cryocells. For laboratory analysis, the sensor will be placed inside a cold laboratory (-30 to -5 ^{o}C) while the Raman spectrometer and the computer control of the motorised X-Y-Z microscopy stage will be set outside, at room temperature. For field works in cold environments, the spectrometer will be placed in a thermic box at 15-20 ^{o}C.

The envisioned scientific and industrial applications for short-medium term include the characterisation of: Ice-core climate records, Snow and Permafrost samples, Clathrate hydrates, Organic trapped chemicals or Clays and other Hydrated Minerals, as well as industrial applications in the field of: Low-temperature molecular electronics, Frozen food, Protection from Ice or Future robotic missions to Icy Worlds.

The new CORaHE sensor can be used not only in cold environments but also at room temperature, enhancing its use to a broad areas of application. Such areas are those covered currently by Raman spectroscopy but with the enhanced capabilities of the Deep-UV excitation.

The detection and/or quantification of inorganic and organic chemical compounds with the new sensor will contribute to all of the societal challenges, with important benefits for the European society and their citizens, for example the new Deep-UV CORaHe sensor will be: (a) a more sensitive and healthy sensor than other Raman sensors currently used for diagnosis in Medicine, (b) a more powerful device in the detection of prohibited chemicals in surfaces of foods, agriculture soils and forestry products, (c) a standard for quality control of chemicals used in batteries and devices for energy accumulation, (d) the tool to check microelectronic based devices for control of the transport systems, (e) a critical technology to easily characterize environmental atmospheric particulate matter, biofilms, minerals and organics, (f) the tool to enhance Raman spectroscopy as the preferred analytical technique to diagnose the conservation state of Cultural Heritage materials, from both movable and immovable assets, due to its low impact on the precious surfaces under analysis, and (g) one of the best sensors to detect explosives and chemical hazards in public spaces.

The project has been structured in five steps, four of technical nature and the fifth to produce materials for dissemination. Three complementary partners will develop it: university, research organization and SME.

1. Project Description

The main objective of the project is to design and build the innovative CORaHE (**CO**ld **Ra**man **He**ad) sensor for Deep-UV Raman spectroscopy, to operate under cold environments between -30 and -5 °C. This portable sensor will perform non-destructive micro-Raman measurements on the original cold samples without any limitation in size of the sample and discard the need of cryostages, enabling direct microscopic measurements.

Raman spectroscopy is a vibrational spectroscopy technique that is used to identify chemical compounds (one or several present in the same sample) in different matrix and at different temperatures and humidities. Deep-UV Raman spectroscopy has been selected because it is the only excitation wavelength range that avoids the fluorescence background irrespective of the nature of the cold samples to be measured. Deep-UV lasers do not destroy the cold samples because the thermal heating is minimized to a minimum while maintaining the Raman scattering of molecules. Microscopic measurements have been selected to analyse the bubbles and inclusions in the surfaces of the cold samples due to their micrometric size. The selection of the areas of interest will be performed through a visible context camera. The spots of interest will be focused by software controlled high resolution motorised X-Y-Z translational stages. The bulk and microscopic spots will be measured by a simple change of the objectives in the rotating turret. The turret will be set in front of the cold (-30 and -5 °C) samples, irrespective of their size, avoiding the current use of cutting samples needed to be placed in cryostages. Thus, the new CORaHE sensor will measure cold samples non-invasively without destroying any part of them.

2. Technology Benchmark

Raman spectroscopy is a vibrational spectroscopic technique used to identify inorganic and organic chemical compounds, provided they are not 100% ionic (NaCl is not sensitive to Raman). This analytical technique has been applied in most of the current areas of interest in the field of fundamental and applied studies, especially when highly sensitive samples must be analyzed [L.A. Nafie, *J. Raman Spectrosc.*, 48 (2017) 1692]. The coordinator of this project have measured the organic compounds [L. Gomez-Nubla *et al.*, *Anal. Bioanal. Chem.*, 410 (2018) 6609] and inorganic gases [L. Gomez-Nubla *et al.*, *Anal. Bioanal. Chem.*, 409 (2017) 3597] present in micro bubbles and inclusions of geological materials using Confocal micro-Raman spectroscopy.

Raman measurements are performed currently at room temperature. But cold environments are generating more and more interest in several fields of research. Low-temperature Raman measurements are usually performed at room temperature with the help of cumbersome cryostages, often operated with liquid nitrogen, which generally limit the size of the sample to circa 1 cm^2 in surface area and some millimetres in thickness [C. Weikusat *et al.*, *J. Glaciol.*, 58 (2012) 761]. Since most cold samples are much bigger than available cryostage cells, such measurements are destructive, in the sense that they require a complicated selection and cutting procedure of a small piece from the original sample, which becomes ruined after the measurement, precluding reproducibility [T. Sakurai *et al.*, *Int. J. Spectrosc.*, (2010) 384956]. All these troubles hinder the use of Raman spectroscopy in the field, since cryostages and Raman instruments are usually not portable.

The new CORaHE sensor for measurements in cold environments has been designed to cover the absence of technology to perform non-destructive Raman measurements on sensitive samples having temperatures as low as -30 °C (ice cores, permafrost, frozen food, hydrated minerals, clathrates). The CORaHE sensor has been designed to be used in laboratory and field measurements. For laboratory analysis, the sensor will be placed inside IzotzaLab, the cold laboratory (-30 and -5 °C) of the BC3 partner, while the Raman spectrometer and the computer control of the motorised X-Y-Z microscopy stage will be set outside, at room temperature. For field works in cold environments (glaciers,..), the spectrometer will be placed in a thermic box at 15-20 °C.

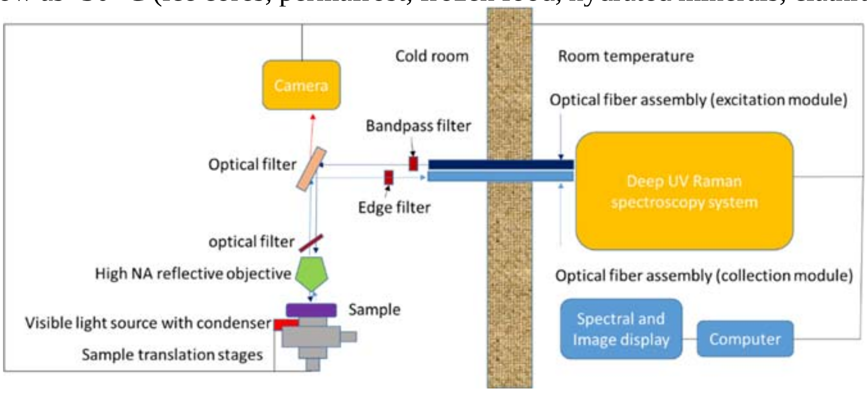

Fig 1.- Schematic of the Deep-UV Raman Sensor installed in a cold room and the Deep-UV Raman spectroscopy installed at room temperature.

The selection of Deep-UV excitation to promote the Raman scattering is derived from two characteristics of the sensitive cold samples and their interaction with the laser light of the Raman spectroscopy system.

The heat promoted by the use of some excitation lasers interacts with cold samples, changing the real composition of the chemical species present in the samples [S.H. Faria *et al.*, *Quatern. Sci. Rev.*, 29 (2010) 338]. The interaction is higher when using large wavelengths (i.e., 1064 or 785 nm) and is negligible when using deep ultraviolet ones (< 244 nm) [T. Frosch *et al.*, *Anal. Chem.*, 79 (2007) 1101]. Moreover, the power required to obtain Raman spectrum of a given sample is much lower for short wavelengths than for long ones.

Another problem related with the use of some lasers is the generation of high fluorescence background with the Raman signal of interest, lowering the sensitivity of Raman measurements of the chemical compounds. To avoid such background signal, Deep-UV lasers must be used [W.J. Abbey et *al.*, *Icarus*, 290 (2017) 201].

Our market research reveals that currently there are only three companies providing deep UV Raman spectroscopy systems. The market is led by Photon Systems Inc. (California, USA) with their "DUV Raman/PL 200", followed by Horiba Ltd. (Kyoto, Japan) with their optimised "LabRAM HR Evolution" working from 200 nm to 2100 nm. Finally, Nanophoton Corp. (Osaka, Japan) also claims having a product "RAMANtouch vioLa" to realise high spatial resolution and high-speed imaging from 200 nm to 800 nm. However, none of these companies have optimised their systems to be used in low temperature environments of -30 ^{o}C. Also, they do not market any Raman probe head that can be functional at these low temperatures and provide high spectral and spatial resolution and sample imaging capabilities, like our CORaHE sensor.

3. <u>Envisioned Innovation Potential</u>

The CORaHE sensor consists of special optical filters, optical fibre assemblies, confocal Raman signal collection head and imaging system that can operate at low temperature environments as shown in Fig 1. Following are the details of innovation inherent in each part of the new sensor:

3.1 Optical Filters

Optical filters used in Raman spectroscopy are interference based and their performance depends on the temperature at which they are designed to work. Currently Semrock Inc., USA offers optical filters (edge filters and bandpass filters) for Raman spectroscopy applications with the widest wavelength range and unmatched performance. But, these filters are designed to be used at room temperature. Variation in temperature shifts the central wavelength (CWL) and it is crucial in Raman spectroscopy to maintain constant CWL. Also, when cycled at different temperatures, or used with varying temperatures, optical coatings are subjected to mechanical stress, damaging the costly filters. PTI is already a preferred customer for some optical coating manufacturers and has obtained consent from one US based and another Japanese optical filter manufacturer, and they can manufacture optical filters specifically for use at low temperatures. These manufacturers use a production technique that increases the coating adhesion. They have also agreed to provide the optical filters at short notice to PTI and at a cost suitable for preferred customers.

3.2 Optical fibre assembly (Excitation module)

The Deep-UV Raman Spectroscopic system at 248.6 nm (which the consortium has already purchased for room temperature measurements on terrestrial and extra-terrestrial materials) will be kept at room temperature. The laser light will be transmitted to the cold room where temperature can be varied between -30 and -5 ^{o}C. To transmit Deep-UV light from laser room (room temperature) to the cold room, PTI will design an optical fibre assembly that contains the high OH optical fibre with a jacket. The selected optical fibre transmits more than 80% for 248.6 nm laser light through the core of the fibre, taking into account the coupling losses. The jacket and the optical fibre together form an assembly that can operate between -30 and +30 ^{o}C without the loss of transmission performance. We have particularly taken care that the bandpass optical filter design (see 3.1) filters out the background Raman signal from the optical fibre assembly.

3.3 Optical fibre assembly (Collection module)

The collected Raman signal will be focussed into an optical fibre, that will act as pin-hole to provide confocality. This optical fibre will form part of the optical fibre assembly (collection module) with edge filters and will deliver the Raman signal to the spectrometer and detector kept at room temperature.

3.4 Confocal Raman signal collection head and imaging system

PTI has designed a Deep-UV Raman signal collection head that can operate between -30 and -5 ^{o}C, providing images (visible light excitation) of the cold samples under investigation. The Piezo electric translation stages (PI GmbH & Co., Germany) have been selected with consortium partner UPV/EHU that can operate at these low temperatures with step size of < 1 micron. The novelty lies in the combination of visible light imaging and confocal Deep-UV Raman spectroscopy. High Nominal Aperture (NA>0.65) microscope objectives (all reflective, Schwarzschild configuration) that operate at low temperature and in Deep-UV have been selected. One objective will be used to provide the ~ 0.25-micron lateral resolution.

The coupling of the new CORaHE sensor with the existing portable spectrometer will provide the first portable Raman system for measurements under low-temperature conditions (cold environments) at micrometric scale, allowing the performance of non-destructive, fully reproducible Raman measurements of sensitive cold samples. The envisioned scientific and industrial applications for short-medium term include:

- *Ice-core climate records*: characterization of all kinds of climate-proxy inclusions, ranging from air bubbles to dust particles and salt/acid microinclusions derived from aerosols.
- *Snow and permafrost samples*: chemical analysis of snow (including black carbon, polen, dust, etc.), as well as organic and inorganic composition of permafrost.
- *Clathrate hydrates*: physical investigations of phase transitions and self-preservation, relevant for the oil and gas industry, permafrost engineering, carbon sequestration, climate research, and food industry.
- *Clays and other hydrated minerals*: characterization studies with important applications to planetary research. The next missions to Mars (Mars2020 from NASA and Exomars2020 from ESA) include Raman spectroscopy techniques implemented in the rovers for contact studies of the Martian surfaces; such surfaces have temperatures ranging from -30 till +10 ^{o}C during the working hours of instruments.
- *Low-temperature molecular electronics*: development and control of new electronic devices for low-temperature applications, including flexible organic components, with special applications in medical, sport, and aerospace technologies.
- *Frozen food*: inspection of the structural and chemical integrity of frozen foodstuff, with applications to food processing and preservation.
- *Protection from ice*: investigation of the mechanisms and efficiency of coatings for ice protection ("deicing") with applications to aerospace and textile industries.
- *Future robotic missions to icy worlds*: characterization of surface chemicals (robotic missions) on ice surfaces of non-terrestrial planets, moons and asteroids is a challenge for the coming near future. Deep-UV sensors coupled to Raman spectrometers will be certainly used for such purposes.

Moreover, the new CORaHE sensor can be used not only in cold environments but also at room temperature, enhancing its use to broad areas of application. Such areas are those covered currently by Raman spectroscopy but with the enhanced capabilities of the Deep-UV excitation. In particular, the detection and/or quantification of inorganic and organic chemical compounds with the new sensor will contribute to all of the societal challenges, with important benefits for the European society and their citizens,[2] for example:

- *Health, demographic change and wellbeing*: Raman spectroscopy is applied as a Medical Diagnostic Technique; the new Deep-UV sensor has higher sensitivity than the current Raman sensors.
- *Food security, sustainable agriculture and forestry, marine and maritime and inland water research, and the Bioeconomy*: Detection of prohibited chemicals in the surfaces of foods (vegetables, meat, etc.), in agriculture soils, forestry products or particulate matter in water systems.
- *Secure, clean and efficient energy*: quality control of chemicals (carbides, oxides, alloys) used in batteries and devices for energy accumulation.
- *Smart, green and integrated transport*: quality control of the microelectronic based devices for control of the transport systems.
- *Climate action, environment, resource efficiency and raw materials*: This challenge is the one with most applicability of portable Deep-UV Raman spectroscopy: characterization of atmospheric particulate matter, biofilms, minerals, etc.
- *Europe in a changing world - inclusive, innovative and reflective societies*: Portable Raman spectroscopy is the preferred analytical technique to diagnose the conservation state of Cultural Heritage materials, from both movable and immovable assets, and the Deep-UV excitation will enhance its current applicability due to its low impact on the precious surfaces under analysis.
- *Secure societies - protecting freedom and security of Europe and its citizens*: Detection of explosives and chemical hazards in public spaces, airports, train stations, harbors, etc.

4. Project Implementation, Budget Breakdown and Final Deliverables

The project will be developed in five steps (tasks), each with a given duration:

4.1 Procurement and testing of existing materials. (months 1-3) Materials in the market that can be used in the CORaHE sensor will be selected but only those with positive response at -30 ^{o}C will be used. Moreover, fibres, jackets, cables, filters and objectives will also be optically tested, measuring the transmission of Deep-UV light through the individual components, selecting the elements with the lower loss of energy.

4.2 Construction of the excitation and collection modules. (months 3-8) High OH quartz optical fibers with low-solarization and an attenuation < 350 dB/km will form the core of excitation and collection modules. These modules will enable transmission of deep UV light between the cold and normal temperature rooms. Fiber core size of 400 um and an NA of 0.22 will be selected, resulting in ultrahigh UV transmission at

[2] https://ec.europa.eu/programmes/horizon2020/en/h2020-section/societal-challenges

248.6 nm at very low temperatures such as -30ºC. Optical filters which can sustain this low temperature will also be used. The excitation and collection modules will combine the optical fibres, optical filters, deep UV optics for light coupling and collimation and an enveloping jacket of a suitable material. It has been taken care that those components which are not available off the shelf, can be procured to fit our design.

4.3 ***Integration of the CORaHE sensor in the BC3 cold room with the Raman spectrometer***. (months 8-11) The Deep-UV Raman spectrometer must be kept at room temperature for a proper performance of optical bandpass and edge filters. Additonally, the CCD camera for Deep-UV Raman is also not designed to work optimally at -30ºC. The reflective microscope objective, integrated in the high precision translation stage, will be coupled to the Raman excitation and collection modules and also to the context image acquisition system in cold room, forming the complete CORaHE sensor. Finally, the Deep-UV Raman spectrometer kept at room temperature will be coupled to the other end of the Raman excitation and collection modules.

4.4 ***Validation of the sensor for Deep-UV Raman measurements***. (months 10-12) The performance of the new sensor coupled to the Deep-UV Raman spectrometer will be validated at two levels. Raman spectra of cold hydrated minerals of known composition will be obtained with the new system in the BC3 cold room and compared with spectra obtained with a standard Deep-UV Raman spectrometer using a cryostage. Inclusions in ice samples will be measured using the current practice (slicing of ice, setting in the cryocell and micro-Raman measurements) and the new proposed method without destroying the ice samples.

4.5 ***Preparation of materials for dissemination***. (months 9-12) In the last four months of the project, the different dissemination materials described below will be prepared. All the materials purchased and tested in 4.1 and 4.2 will be documented and photographed. The integration of the sensor will be video recorded for dissemination as well as the validation procedures.

The **estimated budget** to develop, construct and validate the new CORaHE sensor and its dissemination is:

	UPV/EHU	**BC3**	**PTI**	**Sub-total**
Personal costs	10000	10500	14800	35300
Consumables (XYZ motors, filters, fibres, jacket and coupling, one objective, camera, mechanical and optical components)	28700	1500	500	30700
Travels (one person/org to a Congress + the ATTRACT meeting)	1500	1500	1500	4500
Others (materials for dissemination, couriers, fees, open access)	1500	1500	1500	4500
Overheads (25% of the Total)	13900	5000	6100	25000
TOTAL	55600	20000	24400	100000

We have detected some **risks/contingencies and** their respective **mitigation** actions:

No.	**Risk and/or contingency**	**Mitigation**
1	Attenuation in optical fiber results in higher loss in laser excitation power and also in collection Raman signal	Reducing the length of optical fibers will reduce attenuation loss
2	Condensation on the excitation and collection modules at the interface of cold and normal temperature rooms	Selection of thermally insulated jacket for the modules and appropriate wall plug
3	Long delivery time for customized optical filters	Designing and building the CORaHE sensor using off the shelf filters but installing at an angle to mimic low temperatures
4	Thermal or photo damage to sample	Increase acquisition time at low excitat. power

The expected results of the project are summarized in the next table, including the deliverables and dissemination products. All of these materials will be shared among the interested people, using different sites and repositories. The leader/coordinator of each item is also included although all the partners will contribute:

Result/Product	**Coordinator**
Deliverable: Procurement and testing of materials selected to construct the CORaHE sensor	UPV/EHU
Deliverable: Characteristics of the excitation and collection modules	PTI
Deliverable: Selection and preparation of the known samples for validation in the cold room	BC3
Product: The CORaHE sensor	PTI
Deliverable: Validation of the CORaHE sensor coupled to the Deep-UV Raman spectrometer	UPV/EHU
Dissemination: Preparation of a communication to an international congress	BC3
Dissemination: Preparation of a research paper to a high impact scientific journal	UPV/EHU
Dissemination: Preparation of a video with the key issues of the whole research development	PTI
Dissemination: Poster Preparation of the development and performance of the CORaHE sensor	BC3
Dissemination: Preparation of the final project summary	UPV/EHU