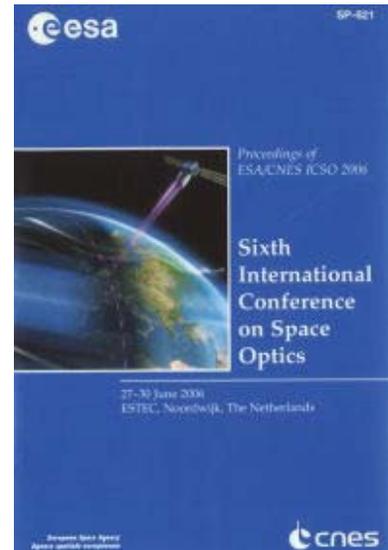


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Raman technology for future planetary missions

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RAMAN TECHNOLOGY FOR FUTURE PLANETARY MISSIONS

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ABSTRACT

Scientific experiments on mineral and biological samples with Raman excitation below 300nm show a wealth of scientific information. The fluorescence, which typically decreases signal quality in the visual or near infrared wavelength regime can be avoided with deep ultraviolet excitation. This wavelength regime is therefore regarded as highly attractive for a compact high performance Raman spectrometer for in-situ planetary research. Main objective of the MIRAS II breadboard activity presented here (MIRAS: Mineral Investigation with Raman Spectroscopy) is to evaluate, design and build a compact fiber coupled deep-UV Raman system breadboard. Additionally, the Raman system is combined with an innovative scanning microscope system to allow effective auto-focusing and autonomous orientation on the sample surface for high precise positioning or high resolution Raman mapping.

1. INTRODUCTION

Raman spectroscopy has great analytical potential for mineralogical and biological applications at the laboratory level. Due to these unique capabilities Raman spectroscopy has been recognized in the last few years as an extremely promising method for in-situ planetary analyses like mineralogy or the search for signs of extinct and/or extant life on Mars as well as identification of hazards for future human missions. Instruments with a fiber coupled optical head have the most flexible configuration with regard to accommodation and access to the planetary surface. A number of compact instrument configurations for in-situ planetary investigation have been proposed and developed in the last few years [1]. Most of these instruments use excitation lasers in the visual wavelength range (VIS) or even the near infrared wavelength range (NIR). The application of deep-ultraviolet excitation (deep-UV) below 300nm for such a compact instrument was proposed by Popp et al. [2].

Recent results on meteorite samples, achieved in the lab with research-grade UV Raman equipment show great potential and a very good signal to noise ratio (SNR) due to the absence of fluorescence [3].

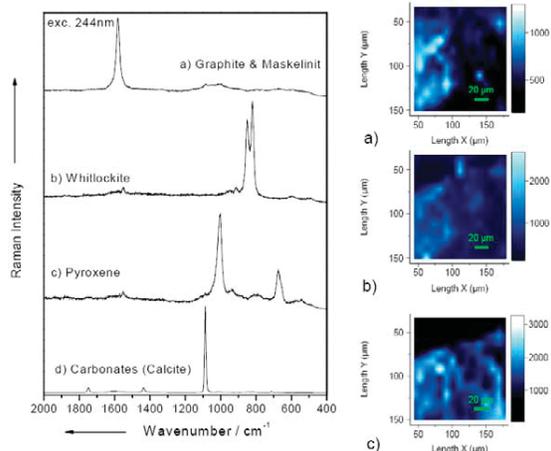


Fig. 1. Raman mapping experimental results on the Martian meteorite SAU060 measured with 244 nm excitation. Raman signatures of various minerals (left) and two dimensional maps representing the distribution of the most prominent constituents (right).

The technology developments, especially development of suitable compact deep-UV lasers, UV-resistant fibers and deep-UV filter technology recently opened this new wavelength regime for compact, high performance Raman instruments.

2. INSTRUMENT DESIGN

The current MIRAS II (Mineral Investigation with Raman Spectroscopy) instrument development activities at Kayser-Threde for an in-situ Raman instrument for planetary investigation are focused on the combination of a fiber coupled Raman optical head with deep-UV excitation and a high resolution deep-

UV spectrometer. An additional focus of this breadboard (BB) activity is to demonstrate a novel concept for positioning and focusing of the optics with a 3-D actuation stage, which also serves as scanning microscope and allows to measure the 3-D topology of the sample surface.

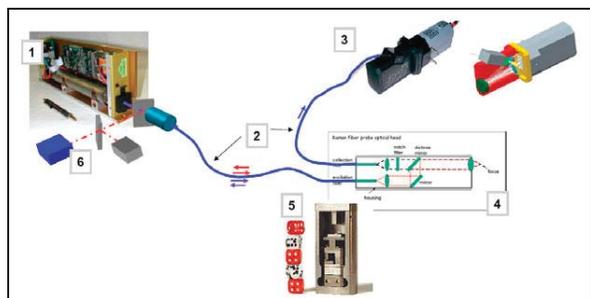


Fig. 2. The MIRAS II BB instrument concept.

The instrument as shown in Fig. 2 can be divided in two mayor subsystems, the actual Raman optical system containing laser (1), fiber coupling (2), spectrometer (3) and optical head (4), and the scanning microscope subsystem consisting of precision 3-D actuators (5), which carry the optical head and the optical auto-focus feedback system (6).

The scanning microscope system allows to position the optical head above the sample, perform a topography scan and to position the optical head with high accuracy for Raman point measurements or for 2-D mapping measurements.

2.1 Raman System

The following section describes the Raman system and its mayor subsystems. The technological challenges, which are specific for the deep-UV excitation and which are investigated in the MIRAS II study, are addressed. Results of design trade-offs or experimental tests performed on components and subsystems within the BB activity are presented.

2.1.1 Deep-UV Raman Laser

As mentioned above the scientific results demonstrated with deep-UV excitation show great detail and a good signal to noise ratio (SNR) compared to other excitation wavelength in the VIS or NIR wavelength range, mainly for two reasons:

- The Raman signal intensity scales with ω^4 . This means that the required laser output power to achieve a sufficient SNR can be lower than in the VIS or NIR wavelength ranges. This is

advantageous with regard to laser size and power consumption.

- No fluorescence background degrades the Raman signal.

The fluorescence, which is excited by the Raman excitation, is shifted to longer wavelength relative to the excitation wavelength (Stokes shift). As the spectral range of interest for Raman ($500\text{cm}^{-1} - 4000\text{cm}^{-1}$) is only a very small wavelength band in the deep-UV (about 40nm next to the excitation peak wavelength) the fluorescence is only present outside this spectral band and is therefore not overlapping with the spectral signatures in the Raman spectrum.

Within MIRAS II a very compact hollow cathode, quasi-continuous-wave (quasi-cw) laser was selected for the BB, after an extensive investigation and trade-off. The quasi-cw operation is a compromise between pure pulsed operation (laser damage of the sample and potentially the fiber optics) and cw-operation (large power consumption and active cooling required). These compact quasi-cw lasers allow operation without cooling over a large operational temperature range and the power consumption is compatible with an instrument for planetary exploration [4]. Raman measurements are reported with these lasers [5]. Very advantageous for these Raman measurements is the extremely narrow line width of $< 3 \text{ GHz}$ (0.0005 nm) and the wide operational temperature range ($-200^\circ\text{C} - +100^\circ\text{C}$) of these hollow cathode lasers. On the other hand, strong plasma lines within the wavelength region of interest have to be filtered out of the excitation path. A drawback of these multimode lasers is the relatively low beam quality, with an M^2 above 10. This is a mayor design driver for selecting the appropriate fiber to deliver this laser light to the sample and for the optical design of the Raman optical head. Improvement of the M^2 is required for a dedicated custom designed laser to relax the fiber coupling conditions.

2.1.2 Fiber Coupling

Due to the multimode excitation laser only multimode fibers can be used to deliver the light to the optical head and back to the spectrometer. The laser beam quality and beam diameter are design drivers for the numerical aperture (NA) and core diameter of the fiber. On the one hand a multimode fiber with a large core requires a more complex optical system in the optical head to achieve a small focus spot (imaging of the excitation fiber end on the sample). On the other hand large core multimode fiber is less critical in fiber coupling alignment tolerances and also less critical with regard to fiber bending (assuming that the full mode-field of the fibers is excited). An underfilled fiber would result in strong intensity variations when the fiber is moved during operation.

Due to the deep-UV excitation only special UV-enhanced fibers can be applied. Normal glass fibers would suffer from laser damage inside the fiber, which would cause irreversible attenuation increase. A number of fibers (UV-enhanced, solarisation resistant, different core diameters and NA) from different fiber manufacturers were tested within the project to identify the best possible coupling fiber, which ideally allows stable guidance of all of the laser light with a small core diameter and a low, constant attenuation. Additionally the compatibility of these fibers with regard to the space environmental conditions is investigated.

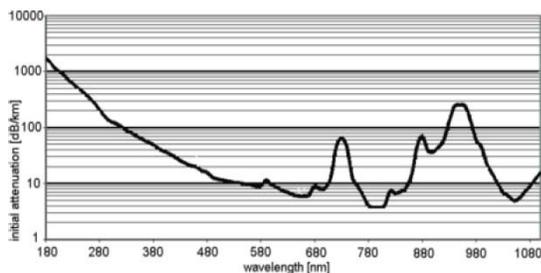


Fig. 3. Attenuation of a deep-UV enhanced all silica fiber (figure by FiberTech GmbH).

The typical attenuation of these UV-enhanced fibers is quite high compared to standard optical fibers like they are used in telecom industry. As the optical power budget of a Raman system is quite demanding and any losses within the optical train have to be minimized, the fiber length is a critical system parameter. At a wavelength of e.g. 250 nm the attenuation has reached about 0,5 dB/m, which means, that the cable length for a Raman system at these wavelength regime is restricted to a few meters.

2.1.3 Fiber Coupled Spectrometer

As mentioned above the spectral range of interest, which represents a Raman spectral range between 500cm^{-1} and 4000cm^{-1} covers just 40nm in the deep-UV. With the scientific goal to resolve spectral features down to 5cm^{-1} , a spectral resolution of 0,03 nm needs to be achieved. For the MIRAS II instrument BB a Hadamard transform spectrometer [6] was selected, which allows to achieve such a high resolution at a high optical throughput in an extremely small overall volume.



Fig. 4. MIRAS II spectrometer with commercial CCD detector (left) and schematic view of the folded optical path (right).

An alternative spectrometer concept which was evaluated in a former project [2], an acousto optical tunable filter (AOTF) spectrometer, was not further investigated, as such a scanning system is not the preferred approach with a pulsed excitation source. Currently the BB instrument uses a commercial, back-illuminated CCD detector with deep-UV antireflection coating. With regard to the quasi-cw pulsed operation of the laser, experiments with an intensified, UV sensitive CCD (ICCD) in gated operation mode (triggered by the laser pulses) were performed. These experiments indicate, that the ICCD is the preferred detector solution for the quasi-cw excitation laser, as signal intensities of the Raman signature are extremely low and a high number of laser pulses are required to accumulate enough photons for a significant spectral signature.

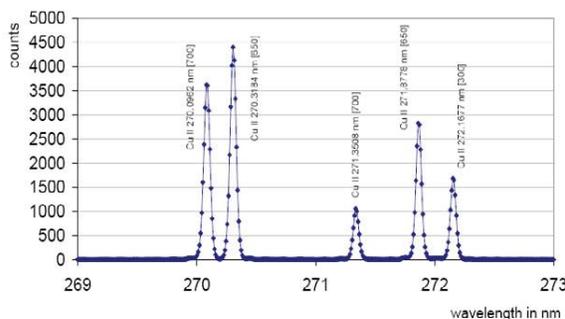


Fig. 5. Spectral data obtained with the deep-UV Hadamard spectral sensor (plasma lines of a tested deep-UV laser), demonstrating a resolution better than 0.1 nm.

2.1.4 Raman Optical Head

The Raman optical head has to fulfill the following functions and requirements (see also Fig. 6).

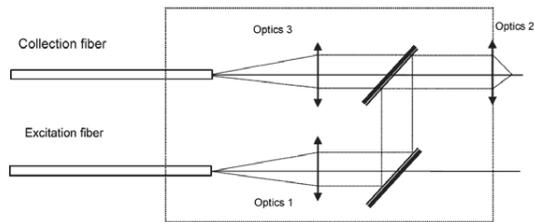


Fig. 6. Schematic of the Raman optical head (filters not shown).

The excitation light coming out of the excitation fiber needs to be collimated, fiber-Raman signature and laser plasma lines, have to be filtered. The pure excitation light has to be focused on the sample onto a relatively small spot by the front objective (optics 2). The same lens system then has to collect the Raman emission spectrum with a high efficiency, which means the collection NA should be as high as possible. As the excitation path (optics 1-2) mainly has to be optimized for effective focusing of the excitation wavelength, the reception path (optics 2-3) has to be achromatic for the Raman spectral range of about 50nm, to allow effective fiber coupling of the full spectrum. The beam-folding within the excitation path is also used to remove the plasma lines and the fiber Raman signature out of the excitation spectrum. As indicated in Fig. 6 two deep-UV edge filters with a very steep cut off are used for the beamfolding. The Raman spectrum can pass the edge filter on the way back. The beamsplitter and an additional filter (not shown) block the direct laser light with an optical density (OD) of 8. The remaining pure Raman spectrum needs to be focused on the core of the reception fiber.

The detailed optical design of the optics 1-3 is driven by several requirements and restrictions like small spot size, high reception NA to collect as much Raman light as possible, core diameter and NA of the excitation and reception fibers. Due to the operation wavelength range in the deep-UV the number of glasses to work with, is drastically limited to a few UV transparent materials. Additionally, only air-spaced designs for the optical systems 1-3 can be considered, as kitted optical systems might be permanently damaged by the deep UV laser light. All surfaces have to be coated for best UV transmission.

The overall optical design of the MIRAS II Raman optical head achieved a spot size of 6 μm , 2 mm working distance and a collection NA of 0,5. Especially the working distance has to be improved in future designs to allow access to samples with a rough topography. The spot size could be further reduced, however just by increasing the focal length and diameter of the optics, thus increasing volume and weight of the head. The opto-mechanical design of the head was optimized for these optical parameters to

reach a volume of 24x20x70 mm^3 (including beam-folding and edge filters, not including the fiber connectors) and a weight of just 100g.

2.2 Scanning Microscope System

In the ideal configuration for high resolution Raman spectroscopy, an optical microscope images the sample surface of interest and the Raman probe then is positioned above the same surface area of the sample. The required re-positioning limits the spatial resolution of the Raman measurements to the re-positioning tolerances. The fiber-coupled Raman instrument developed within the MIRAS II study uses an alternative, innovative confocal scanning microscope approach to measure the sample topology and to position and focus the Raman optical head with high precision. This approach not only allows an overview of the sample surface without the need for an additional classical optical microscope. Additionally, it allows to perform high resolution Raman mapping measurements on selected, small regions of interest on the sample surface with μm resolution, which is of high interest form the scientific point of view with interest in mineralogical microstructures or microfossiles. Fig. 7 shows the confocal scanning microscope setup as it is realized in the MIRAS II BB. Three slip stick actuators allow stepwise positioning of the optical head in x, y and z. The additional scanner allows continues movement in a much smaller volume but at extremely high spatial resolution. The objective indicated in Fig. 7 only shows the excitation path of the Raman head (optics 1-2 in Fig. 6). When the optical head is coarsely in focus, the excitation light if reflected back into the optical system. This light will be collimated inside the head and then focused back into the excitation fiber if the precise focus position is adjusted.

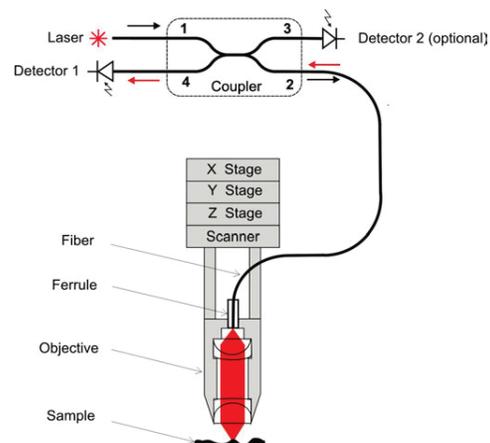


Fig. 7. Scanning microscope schematic setup.

This back-reflected light is split off the excitation fiber and monitored with a sensitive and fast pin diode detector. The back-reflection coupling efficiency is a function of the focus position, as indicated in Fig. 8. When operated, the z-actuator moves the optical head towards the surface and the back-reflected light is monitored continuously. Once the signal increases significantly a closed loop can derive and adjust the optimum focus position very fast.

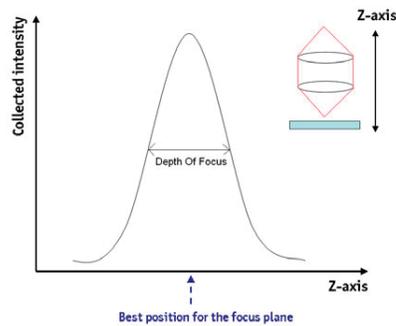


Fig. 8. Auto-focus control loop signal.

The “depth of view” range of this auto-focus system is a function of the focal length of the optics, their NA and the excitation fiber core diameter. In the current BB system the active control range has a depth of view of about 80 μ m. The piezo-actuators selected for the scanning microscope allow sub- μ m positional accuracy, while providing a large actuation range in each axis. That can be achieved by the slip-stick actuator principle [7].

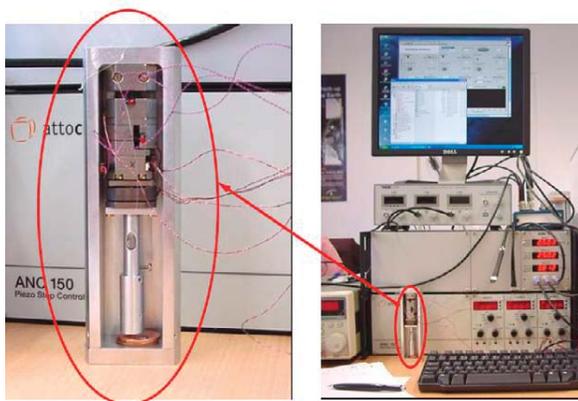


Fig. 9. MIRAS II scanning microscope test setup, actuator control system (right) and close-up of the actuator (left), the cylindrical housing just serves as a support and protection of the actual scanner-head; note the 2 €-Coin under the scanner as a scale.

The positioner/scanner as shown in Fig. 9 is capable of an actuation range of 6 mm in x, y and z (focus) with a sub- μ m step resolution. The integrated resistive encoders allow absolute repositioning in this 6x6x6mm³ volume of $\pm 2\mu$ m. The scanner itself is capable to move the optical head continuously in a volume of 70x70x40 μ m³ with sub- μ m resolution, which allows high resolution topography measurement or Raman mapping.

3. CONCLUSION

The presented scanning UV Raman microscope instrument BB is used to investigate a number of key technologies as preparation for designing a high performance instrument for in-situ planetary investigation. Within the MIRAS II project most of the deep-UV specific technological challenges are investigated and subcomponents designed, manufactured and tested to find the best possible subsystem combination and operational parameters for a compact Raman instrument in this advantageous wavelength regime.

The design experience gained in this BB activity will allow to design, specify or procure the relevant subsystems with higher maturity for future models of an instrument, which is dedicated to a specific mission. In this paper the combination of the Raman optical system with a scanning microscope is investigated as a promising instrument configuration. However, the results from the main subsystems investigation can be applied to alternative instrument scenarios such as a confocal combination with a classical microscope were the autofocus system investigated in MIRAS II can be applied for both optical trains.

The instruments fiber coupling design concept will allow operation scenarios inside of an instrument compartment or mounted on a robotic arm of a lander or rover. The instrument even will have the potential, due to the compact fiber-coupled optical head, to be integrated inside of a ground penetrating mole to investigate the mineral composition and to search for biomarkers below the planetary surface.

4. ACKNOWLEDGEMENTS

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