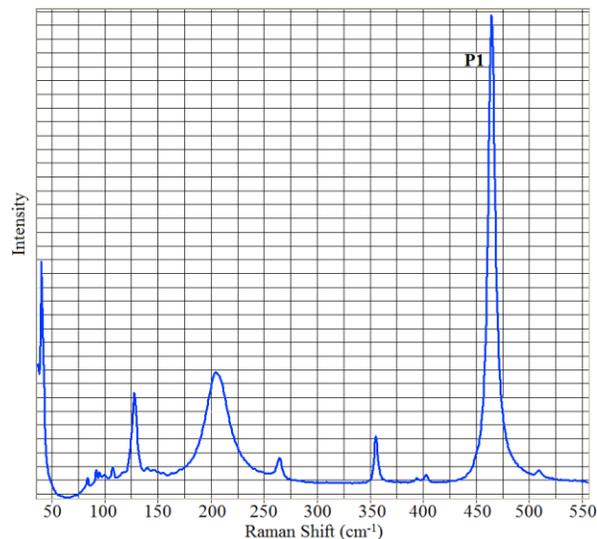


**THE EFFECTS OF TEMPERATURE ON THE RAMAN SPECTRUM OF HIGH PURITY QUARTZ CRYSTALS.** R. Hibbert<sup>1</sup>, M. C. Price<sup>1</sup>, T. M. Kinnear<sup>1</sup>, M. J. Cole<sup>1</sup> and M. J. Burchell<sup>1</sup>, <sup>1</sup>Centre for Astrophysics and Planetary Science, School of Physical Sciences, Univ. of Kent, Canterbury, CT2 7NH. (E-mail: rh443@kent.ac.uk).

**Introduction:** Quartz ( $\text{SiO}_2$ ) is known to be present on Mars and has been identified to be in its crystalline form near Antoniadi Crater on the northern edge of the Syrtis Major shield volcano [1]. The *ExoMars* rover, due to launch in 2018, will carry the first Raman spectrometer to be deployed on another planetary body [2, 3].

**Rationale:** Raman spectroscopy is generally regarded as a nondestructive technique; this statement is incorrect. Concentrated laser power can generate localized heating leading to devolatilisation, crystalline changes, and even melting of the sample [3]. These heating effects, coupled with the large fluctuation of Mars' surface temperature over the course of one Sol, could lead to misinterpretation of spectral data. This study aims to investigate how changes in temperature affect the Raman spectrum of quartz; either due to changes in the ambient temperature, and/or changes due to localized heating caused by the exciting laser. Further work is also ongoing [4] looking at how shock affects the Raman spectrum of quartz with the ultimate goal to being able to disentangle the two effects of heating and shock.



**Fig. 1:** Raman spectrum of quartz at 25°C with the main peak at 464  $\text{cm}^{-1}$  labelled as 'P1'

Raman spectroscopy uses monochromatic laser light to illuminate a sample. When the laser light strikes a molecule in the sample, most of the light is unaffected and can be detected at its original wave-

length. A very small amount of the light, however, shifts due to interaction with the molecule and can be detected at wavelengths specific to the composition of the sample. This is known as Raman scattering [5]. Because the Raman scattering is specific to the composition of the sample, Raman spectroscopy can be used to identify specific molecular bonds within the sample.

The University of Kent's Raman spectrometer is a Horiba LabRam-HR equipped with four lasers: near infrared (785 nm), red (633 nm), green (532 nm), and blue (473 nm). In addition, it has a *Linkam* temperature controlled stage which can be used to cool/heat samples to between -180°C and 600°C. The work carried out in this investigation used the 532 nm green laser that mimics the laser which will be carried on *ExoMars*. The Raman spectrum for quartz at 25°C can be seen in Fig. 1, with the main peak located at 464  $\text{cm}^{-1}$  labelled as 'P1'.



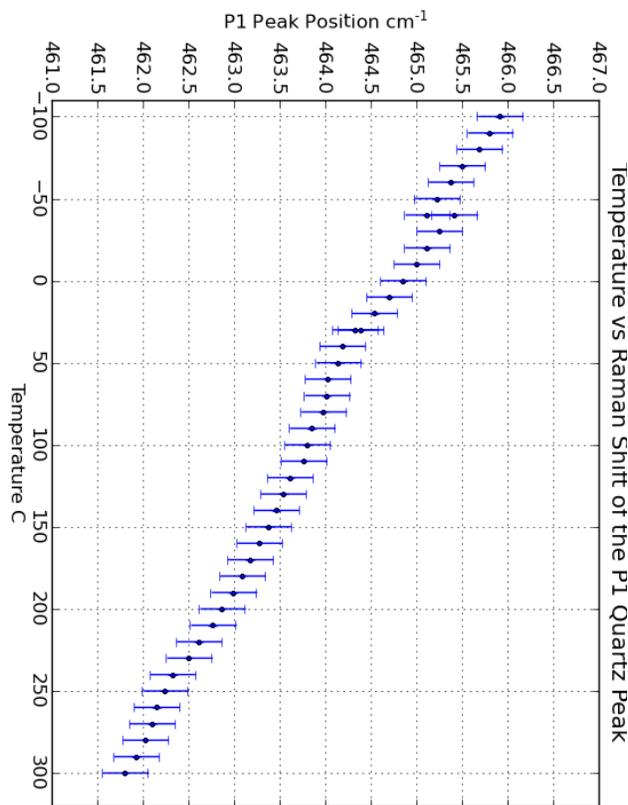
**Fig. 2:** 16 mm x 12mm 9.03 cts white quartz gemstone.

**Methodology:** A 9.03 ct quartz gemstone (Fig. 2) was placed in the *Linkam* temperature stage and heated to 30°C at a rate of 1°C per minute. Once 30°C had been reached the sample was allowed to stabilise for one hour before Raman spectra were obtained. The sample was then heated by 10°C at a rate of 1°C per minute and again allowed to stabilise for one hour before another spectrum was acquired. This process continued up to a maximum temperature of 300°C. To obtain data for temperatures below room temperature the quartz sample was cooled in the *Linkam* stage using a liquid nitrogen pump. At the beginning of this experimental run, the sample was first heated to 30°C (in the same manner as before) to allow for a comparison between the two experiments. Once this first datum was obtained, the sample was then cooled by 10°C at a rate of 1°C per minute and the sample was allowed

to stabilise for one hour before Raman data was obtained. This process continued down to  $-40^{\circ}\text{C}$  where a second datum point was obtained before the final run of experiments continued to a minimum temperature of  $-100^{\circ}\text{C}$ .

This Raman data were then processed using a Python script which uses the least-squares fitting routine to find the exact position of the P1 peak at each temperature and then plot this position against the sample temperature.

**Results:** The graph of temperature vs P1 position can be seen in Fig. 3. The plot shows a definite trend indicating that as the temperature of the sample is increased the P1 position decreases in wavenumber, while as the temperature decreases the position of P1 increases in wavenumber.



**Fig. 3:** A graph showing the P1 peak position when the quartz sample is subjected to varying temperatures.

The P1 position at  $-100^{\circ}\text{C}$  is  $466.92\text{ cm}^{-1}$ , while at  $300^{\circ}\text{C}$  it is  $461.80\text{ cm}^{-1}$ , giving a total variation of  $4.12\text{ cm}^{-1}$  across a  $400^{\circ}\text{C}$  temperature difference.

**Conclusion:** As can be clearly seen in Fig. 3, there is a strong negative trend showing the P1 position, decreasing in wavenumber as the temperature increases and the P1 position increasing in wavenumber as the temperature decreases. Further work will expand the temperature range to test the sample at temperatures

between  $-180^{\circ}\text{C}$  and  $600^{\circ}\text{C}$ . Using the Stokes and anti-Stokes ratio, the temperature of the sample itself will be calculated to compare with the ambient temperature of the stage to see how much laser heating has occurred.

**References:** [1] Bandfield J.L. et al (2004a) *J. Geophys. Res.*, 109, E10009 [2] Rull F. et al. (2011). 42<sup>nd</sup> LPSC abstract #2400. [3] Rull F. et al. (2013). 44<sup>th</sup> LPSC abstract #3110. [4] Hibbert R. et al (2015) LPSC (these proceedings) [5] Raman C.V. (1928). *Indian J. of Phys.*, 2, 387-389.

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