RAMAN (532 nm) SPECTROSCOPY OF POLYCYCLIC AROMATIC HYDROCARBONS. E.A. Cloutis[1], P. Szymanski[1], and D. Applin[1]. [1]Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, MB, Canada R3B 2E9 (e.cloutis@uwinnipeg.ca).

Background: Raman spectroscopy is becoming an analytical technique of increasing interest for planetary exploration. The first Raman system to fly on a planetary mission will likely be the Raman Laser Spectrometer (RLS) that is part of the Pasteur Payload Instrument onboard the ExoMars 2018 rover [1]. The RLS will be used to interrogate cuttings from the rover's subsurface sampling device which will have a penetration depth of up to 2 m [2]. Drill cuttings will be presented to the RLS, which will be mounted on the rover body [1, 3]. The RLS will operate with a continuous excitation wavelength of 532 nm with a laser spot size of ~50 µm on the target, resulting in an on-target irradiance between 0.8 and 1.2 kW/cm^2. The upper limit is fixed to remain below the threshold of powder grain thermal damage mainly in oxides and hydroxides. The spectrometer will cover the spectral shift from ~150 to 3800 cm^{-1}. The Raman spectral resolution goal is ~6 cm^{-1} in the fingerprint spectral region below 2000 cm^{-1}, and higher above this limit [1, 3].

Due to the inclusion of a Raman spectrometer on the ExoMars rover and possibly on future missions such as MSL 2020, we are investigating the utility of a 532 nm Raman system for detection and characterization of polycyclic aromatic hydrocarbons (PAHs), as such phases are expected to be present on Mars, at least from meteoritic infall [4].

Methodology. The University of Winnipeg's HOSERLab is equipped with a BWS415-532S iRaman spectrometer that uses a 532 nm excitation source. It covers the Raman shift region from 4000 to 175cm^{-1}, with a spectral resolution of 4 cm^{-1} at 614 nm. Integration time can be controlled between 5 and 65535 msec, and power levels can also be adjusted between 1 and 50 mW; spot size is on the order of 80 µm. A suite of 48 synthetic PAHs that occur as solids at terrestrial ambient conditions were characterized for this study, most in two different grain sizes. They include PAHs with different numbers of benzene rings, functional groups, and heteroatomic substitutions. Power levels were kept low enough to avoid thermally-induced sample damage [5]. The spectrometer was wavelength calibrated using a polystyrene standard. Laser power levels and integration times were adjusted for optimal SNR. Each sample was measured five times and the spectra were averaged to enhance SNR.

Fluorescence results overview. Space precludes a detailed discussion of individual PAHs, but some general trends have been observed. Laser-induced fluorescence is nearly ubiquitous in the PAH spectra, but the strongest Raman peaks associated with specific PAHs are generally still resolvable for approximately half of the samples (e.g., Figs. 1 and 2). The number and wavelength position(s) of the fluorescence peak(s) can be very variable for different PAHs, providing an additional means of PAH discrimination. This would be useful in situations where Raman peaks may not be detected. Even when PAHs have similar structures, such as phenoxathiin and phenoxazine (NH substituting for S in the middle ring), fluorescence peak positions can vary widely (~1400 cm^{-1} for phenoxathiin vs. ~2000 cm^{-1} for phenoxazine: Fig. 3 and 4).

Raman results overview. An understanding of how ring system arrangement and functional groups affect peak shifts was achieved by first noting the positions of certain peaks in the Raman spectrum of naphthalene (Fig. 1) which correspond to specific molecular vibrations. The recurrence of these peaks in the Raman spectra of similar PAHs allowed shifts in their positioning to be determined and possible causes to be elucidated. The direction and extent of these shifts was indicative of differences in conjugation among these related molecular structures. Shifts were found to occur both to lower energies (bathochromic shifts) and higher energies (hypsochromic shifts). Relative to naphthalene (2 rings), anthracene (3 linear rings) displayed bathochromic shifts for the peaks which corresponded to uncoupled C-C and in-phase C=C stretching as well as ring breathing. However, hypsochromic shifts were observed for the Raman peaks which corresponded to C-C stretching coupled with C-H bending and ring deformation. Also, the Raman peaks which corresponded to C-C-C bending, uncoupled C=C stretching and out-of-phase C-H stretching did not appear to greatly shift in either direction (Fig. 1 vs. Fig. 2).

If peak comparison is extended to include phenanthrene (3 rings, offset connected) and chrysene (4 rings, offset connected), the difference in conjugation between linear and non-linear ring systems becomes evident. When the Raman spectra of anthracene and phenanthrene are compared, the latter displayed greater bathochromic shifts for the peaks which corresponded to ring breathing and in-phase C=C stretching. Also, the shift observed for the Raman peak of uncoupled C-C stretching was bathochromic for anthracene, but hypsochromic for phenanthrene. In contrast, the shifts observed for the Raman peaks of C-C stretching coupled with C-H bending and ring deformation were hyp-

sochromic for anthracene, but bathochromic for phenanthrene. The position of the peaks corresponding to C-C-C stretching, out-of-phase C-H stretching, and uncoupled C=C stretching did not appear to greatly differ in the Raman spectra of naphthalene and anthracene. However, the first two of these peaks displayed hypsochromic shifts while a bathochromic shift was observed for the third in the Raman spectra of phenanthrene.

Discussion. Laser-induced fluorescence often interferes with the analysis of Raman spectra because electron emission bands can sometimes occur over wavelength ranges in which Stokes shifts are commonly observed [6]. If this happens, Raman peaks of low intensity may become indiscernible [7]. However, fluorescence interferences can be minimized by gating the detector to detect Raman peaks, followed by fluorescence [8].

Summary. Collectively our results suggest that:

- The number and position(s) of fluorescence peak(s) varies among different PAHs, providing an additional means of PAH discrimination (in addition to Raman peak positions).
- Most PAHs display multiple Raman peaks in the 200 - 4000 cm^{-1} region, whose positions vary as a function of PAH type.
- Raman and fluorescence peaks can display wavelength shifts as a function of the type and position of functional groups, how rings are connected, and heteromatic substitutions in rings

It appears that the combination of Raman and 532 nm induced fluorescence spectra allow a wide range of PAHs to be uniquely identified. Separation of Raman from fluorescence spectra will allow for even weak Raman emitters to be identified [8].

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References: [1] Rull, F., et al. (2011) *LPSC 42*, abstract #2400. [2] Magnani, P., et al. (2010) *61st IAC*, paper #7208. [3] Rull, F., et al. (2013) *LPSC 44*, abstract #3110. [4] Benner, S. A. et al. (2000) *PNAS, 97,* 2425-2430. [5] Som, S.M., et al. (2012) *Int. J. Astrobio., 11,* 177-186. [6] Smith, E., Dent, G, (2005) *Modern Raman Spectroscopy: A Practical Approach.* Wiley. [7] McCreery, R.L. (2000) *Chemical Analysis: Raman Spectroscopy for Chemical Analysis.* Wiley. [8] Bozlee, B.J., et al. (2005) *Spectrochim. Acta A, 61,* 2342-2348.

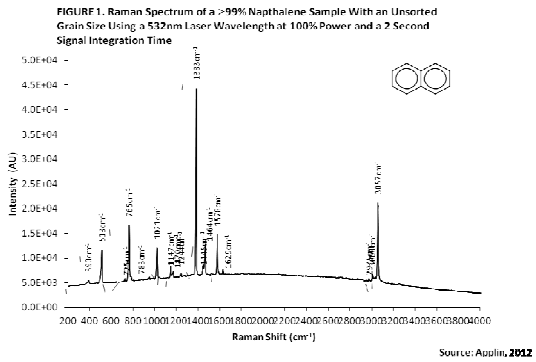

FIGURE 1. Raman Spectrum of a >99% Napthalene Sample With an Unsorted Grain Size Using a 532nm Laser Wavelength at 100% Power and a 2 Second Signal Integration Time

Source: Applin, 2012

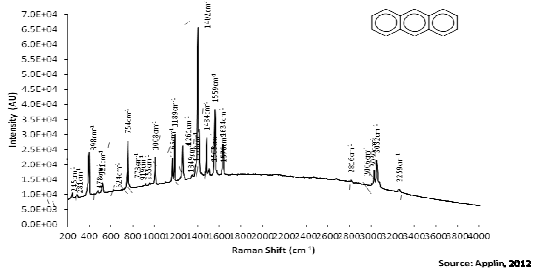

FIGURE 2. Raman Spectrum of a 99% Anthracene Sample With a <45µm Grain Size Using a 532nm Laser Wavelength at 100% Power and a 2 Second Signal Integration Time

Source: Applin, 2012

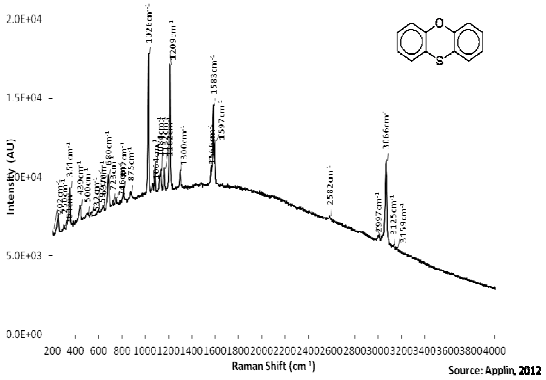

Figure 3. Raman Spectrum of a 97% Phenoxathiin Sample With a <45µm Grain Size Using a 532nm Laser Wavelength at 100% Power and a 2 Second Signal Integration Time

Source: Applin, 2012

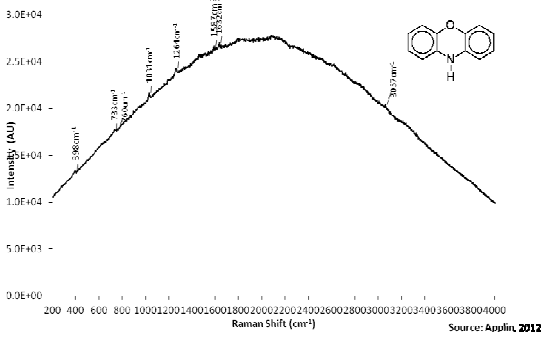

Figure 4. Raman Spectrum of a >99% Phenoxazine Sample With an Unsorted Grain Size Using a 532nm Laser Wavelength at 100% Power and a 2 Second Signal Integration Time

Source: Applin, 2012