

ULTRAVIOLET REFLECTANCE AND FLUORESCENCE SPECTROSCOPY OF SOLID STATE POLYCYCLIC AROMATIC HYDROCARBONS. D. M. Applin^{1*}, M. R. M. Izawa¹, and E. A. Cloutis¹

¹Hyperspectral Optical Sensing for Extraterrestrial Reconnaissance Laboratory, Department of Geography, University of Winnipeg, 515 Portage Ave., Winnipeg, Manitoba, Canada, R3B 2E9. *daniel.m.applin@gmail.com

Introduction: Polycyclic aromatic hydrocarbons (PAHs) are the most common organic compounds in the universe. Within our solar system PAHs are known to occur in a wide variety settings including, icy satellites [1], Titan's hazes [2], carbonaceous meteorites [3, 4], and comets [5-7]. The infall of that latter two leads to the expectation that PAHs are present in the near surface of planets, particularly Mars, even in the absence of endogenic sources.

Ultraviolet absorbance and laser induced fluorescence (LIF) have been studied for some of these compounds in solution and in the gas state [8-11], but PAHs are expected to exist in the solid state within the settings mentioned above.

Methods: A series of 47 high-purity solid state PAH compounds were used for this study. Samples include variations in number aromatic of rings, ring connectivity, heterocycles, and side groups. Ultraviolet reflectance spectra were measured with an Ocean Optics Maya2000 Pro spectrometer equipped with a grating that provides coverage from 200 to 1100 nm with spectral resolution between 0.48 nm (at 200 nm) and 0.46 nm (at 400 nm). Illumination was provided by an Analytical Instrument Systems Inc. Mini-DTA light source with output from a 30 W deuterium lamp directed through a bifurcated fibre optic bundle consisting of six illumination fibres surrounding a central pick-up fibre feeding into the detector array, producing a biconical geometry with i and e centered on $\sim 0^\circ$ and detector and illumination fields of view of 25.4° . Measurements for each sample were made by first acquiring a dark current spectrum, a reference spectrum of a Spectralon standard, followed by measurement of the samples. The spectra were corrected for irregularities in the Spectralon standard using a calibrated deep UV mirror as described by [12].

Fluorescence spectra measured with the same spectrometer. Illumination was provided by two lasers: a 75 mW, 405 nm (Wicked Lasers, Tsim Sha Tsui, Kowloon, Hong Kong) and a 50 mW, 532 nm (B&WTek; Newark, DE); and one spot light: UVP (Upland, CA) Blak-Ray® B-100AP 100 W spotlight with a 365 nm bandpass filter. All were separately directed into the other end of the bifurcated cable, giving a viewing geometry of $i=0^\circ$ and $e=0^\circ$. Integration times were optimized for 1,2-benzanthracene (strongest fluorescence) to avoid detector saturation. Additional fluorescence spectra were collected simultaneously with

Raman spectra collection with a 532 nm laser; these spectra were not calibrated to a single sample.

Results and Discussion: The solid state PAHs show a wide range of ultraviolet-visible absorption and fluorescence features (Figs. 1-3).

PAHs have characteristic UV reflectance spectra. In general, the addition of side groups only alters these spectra slightly but uniquely (Fig. 3). Many PAHs exhibit either weak fluorescence in the UV spectrum or highly variable reflectance. Several clearly fluoresce <365 nm. The wide variation in UV reflectance has broad potential applicability as a tool for the detection and discrimination of PAHs on planetary bodies.

Some features induced by the 365 nm spotlight are not induced by the 405 nm laser (Figs. 3). Heterocyclic substitution changes the fluorescence spectrum completely (Fig. 3). The addition of side groups generally reduces fluorescence by interfering with ring aromaticity. Only one PAH we studied (naphtho[2,3-a]pyrene) fluoresces significantly (much stronger than Raman scattering) when illuminated with a 532 nm laser. Fifteen of the PAHs fluoresce with resolvable peaks in Raman spectra, with similar intensities as Raman scattering (Fig. 2), and 5 of these are methylated. Higher energy excitation yields considerably stronger fluorescence, and thus indicates that identification of solid state PAHs can be made at much lower abundances with excitation wavelengths <532 nm.

Although some PAHs show upwards of 20 absorption bands in the ultraviolet region, most that clearly lead to visible de-excitation are in the 350-450 nm range. These absorption bands do not need to be within the excitation wavelength range, but fluorescence intensity increases by up to multiple orders of magnitude if this occurs [9].

Implications for Surface Exploration: We propose that frequency multiplexing of a 1064 nm Nd:YAG laser (potentially offering 532, 355, 266 nm excitation) will be ideal for coupling time-resolved Raman and fluorescence detection and characterization of PAHs (with the possibility of additional LIBS and LIDAR capabilities). Utilizing the 355 nm wavelength will induce most fluorescence features and is close to many of the absorption bands that lead to strong visible de-excitation. An alternative would be the use of an InGaN 405 nm diode laser to measure both time resolved Raman and fluorescence spectra. The differences from a 532 nm system would be considerable more intense fluorescence, much larger range of diag-

nostic features, and the capability of hyperspectral reflectance spectroscopy over a different portion of the visible spectrum. Both of these methods can be enhanced by exciting a dye laser, allowing resonance Raman spectroscopy (excitation wavelengths equal to the absorption bands we show in the UV reflectance spectra) [13], and lower detection limits to the ppb level without solvents.

A further enhancement of these methods would be solvent (e.g., cyclohexane) extraction prior to analyses. By extracting organics and analyzing via hyperspectral LIF, PAHs should be detectable at the zeptomole level (<ppq, assuming ~0.5 g sample) with an excitation wavelength <450 nm [9].

Acknowledgements: This study was supported by the Canadian Space Agency (CSA) through various programs, NSERC, and the U. of Winnipeg. HOSERLab was established with funding from CSA, the Canada Foundation for Innovation, the Manitoba Research Innovations Fund, and the University of Winnipeg.

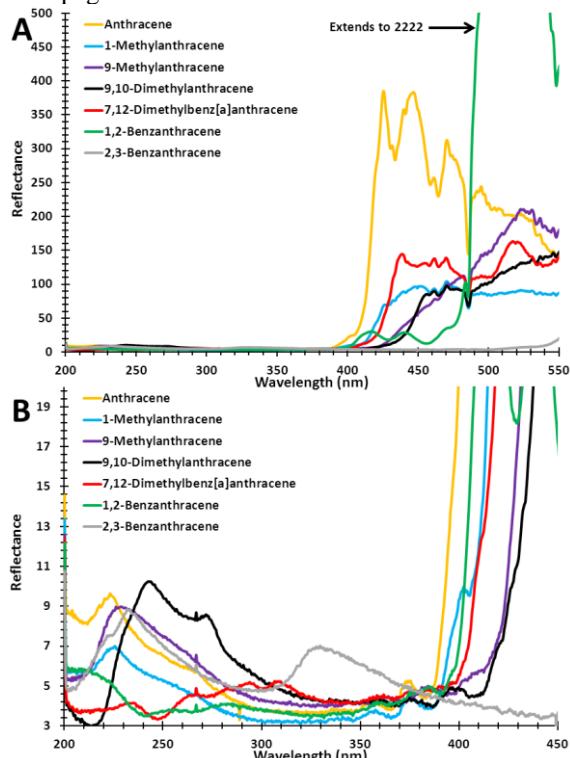


Figure 1. Effects of methyl side-groups ultraviolet-visible reflectance on anthracene and 1,2-benzanthracene structures. (A) The deuterium bulb emission covers all absorption bands in this region, and therefore intense fluorescence is superimposed on reflectance. (B) UV reflectance spectra.

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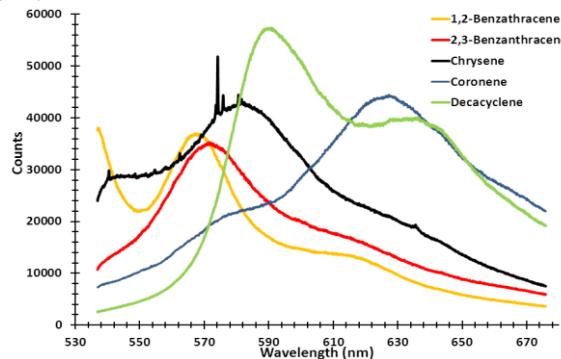


Figure 2. PAH fluorescence during collection of Raman spectra with a 532 nm laser. Five of 15 PAHs that fluoresce at similar intensities to Raman scattering.

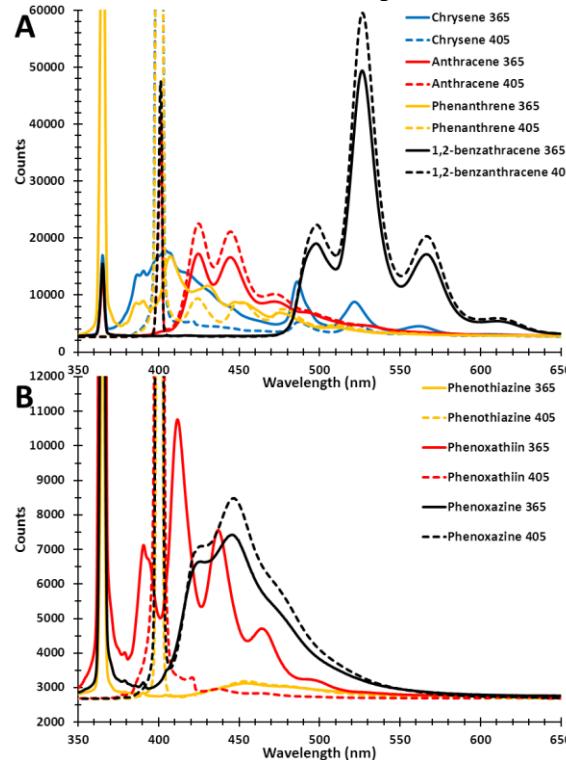


Figure 3. (A) Fluorescence spectra of low molecular weight PAHs. (B) Effect of different heterocycle substitutions on fluorescence spectra. Both spectra collected with a 365 nm and 405 nm laser are shown.