

THE “INFRARED-ULTRAVIOLET CONNECTION” IN REFLECTANCE SPECTROSCOPY. M. R. M.

Izawa¹ D. M. Applin², E. A. Cloutis², ¹Institute for Planetary Materials, Okayama University – Misasa, 827 Yamada, Misasa, Tottori 682-0193, Japan, ²Hyperspectral Optical Sensing for Extraterrestrial Reconnaissance Laboratory, Dept. Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9

Introduction: A number of planetary exploration missions have flown instruments with sensors covering the ultraviolet (UV) wavelength range. The interpretation of those measurements in terms of surface composition and properties has been hampered by two major impediments: A lack of extensive databases of UV reflectance measurements of relevant materials, and shortcomings in the underlying theoretical framework for interpreting surface reflectance spectral measurements at ultraviolet wavelengths; compared to the visible and infrared.

The Infrared-Ultraviolet Connection: The UV, like the mid-infrared, is a region of “strong” scattering, that is, the extinction coefficient (imaginary component of the complex refractive index) is much larger than ~ 0.1 . By adapting the framework developed for interpreting absorptions due to molecular vibrational processes in the near-infrared to electronic phenomena in the UV, it is possible to understand the UV reflectance phenomena in a unified manner.

Large changes in the complex refractive indices (denoted n and k) of a material over small wavelength intervals occur due to ‘strong’ absorption bands (Fig. 1). This is commonly termed *anomalous* dispersion, because n will decrease with decreasing wavelength within the band, in contrast with the typical increase in n with decreasing wavelength. Weak absorptions such as overtones and combinations of molecular fundamental vibrations, or $d-d$ orbital “crystal field” transitions typically do not cause anomalous dispersion. Anomalous dispersion causes the appearance of specific features in reflectance, emittance, and transmittance spectra. We advocate the adoption by the UV spectroscopy community of the terminology of infrared (IR) spectroscopy: reststrahlen band, Fresnel peak, Christiansen feature, transparency feature, and transition minimum. The rationale for making this connection between UV and IR wavelengths is that the values of the complex refractive indices underlying both the IR and UV phenomena are similar, despite the very different physical causes of absorption (i.e., vibrational dipole moments vs. electronic excitons, charge transfers, and interband transitions).

Reststrahlen band: Reststrahlen bands (RB), (German “residual rays”), are regions of strong absorption where incident light is strongly attenuated and reflected [1]. At the center of RBs, surface scattering dominates leading to a local maximum in reflectance (a Fresnel

peak, see below). We will refer to the RB as the entire absorption envelope that may contain Christiansen features, Fresnel peaks, and transition minima.

Fresnel peak: A Fresnel peak (FP) occurs near the center of RB where the value of k becomes large, causing ‘mirror-like’ or coherent reflectance from the grain surfaces. The maximum is generally offset to the short wavelength side of the maximum in k (Fig. 2).

Christiansen feature: While IR *emission* spectra are not perfectly analogous to UV reflectance spectra, but we highlight the useful parallels between spectral behaviors in these two “strong” surface scattering wavelength domains. Many RBs have a Christiansen feature (CF) on the short wavelength side of the FP and offset on the short wavelength side of the Christiansen frequency (where $n=1$). Here, the Christiansen feature refers to a minimum in reflectance, associated with this short-wavelength transition minimum of a strong absorption band.

Transparency feature: A transparency feature is a maximum in reflectance, or minimum in emissivity that appears most prominently in IR reflectance spectra of fine powders. They are generally located between RBs in wavelength and are attributed to enhanced volume scattering due to low k in the absence of absorption bands.

Transition minimum: Where strong absorption bands are surrounded by transparency features, or volume scattering regions, a minimum in reflectance can also occur on the long-wavelength side of the reststrahlen band. This is the long-wavelength transition minimum, where surface scattering begins to strongly dominate over volume scattering with decreasing wavelength.

Laboratory spectroscopy of carbonaceous phases:

Ultraviolet (UV) wavelengths (approximately ~ 70 -350 nm) are highly sensitive to the presence and chemistry of carbonaceous materials. We have systematically analyzed reflectance spectra of carbonaceous materials in the 200-500 nm spectral range, and found spectral-compositional-structural relationships that suggest this wavelength region could distinguish between otherwise difficult-to-identify phases. In particular (and by analogy with the infrared spectral region), large changes over short wavelength intervals in the refractive indices associated with the trigonal $sp^2 \pi-\pi^*$ transition of carbon can lead to reststrahlen bands with Fresnel peaks and

Christiansen-like features in reflectance. Previous studies extending to shorter wavelengths also show that anomalous dispersion caused by the σ - σ^* transition associated with both the trigonal sp^2 and tetrahedral sp^3 sites causes these features below $\lambda = 200$ nm. The peak wavelength positions and shapes of π - π^* and σ - σ^* features contain information on sp^3/sp^2 , structure, crystallinity (Fig. 3), and powder grain size.

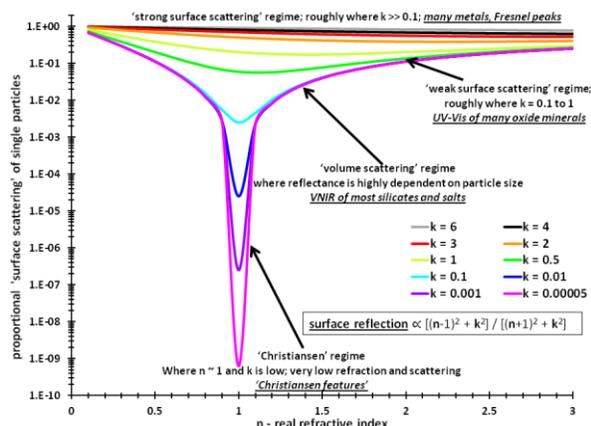


Figure 1: Relationship between proportional scattering intensity from grain boundaries of single large spherical particles at normal incidence, with refractive indices. This plot demonstrates how reflectance spectra are affected by high k and changes in n from the Christiansen frequencies ($n=1$). Typical behavior of some common geological materials are also noted.

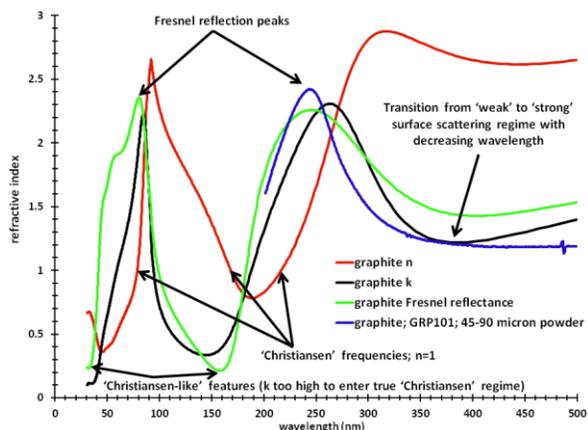


Figure 2: Ordinary-ray refractive indices of graphite from [2] compared to a derived Fresnel reflectance spectrum. Fresnel peak maxima are typically offset to shorter wavelengths than the corresponding maximum in k .

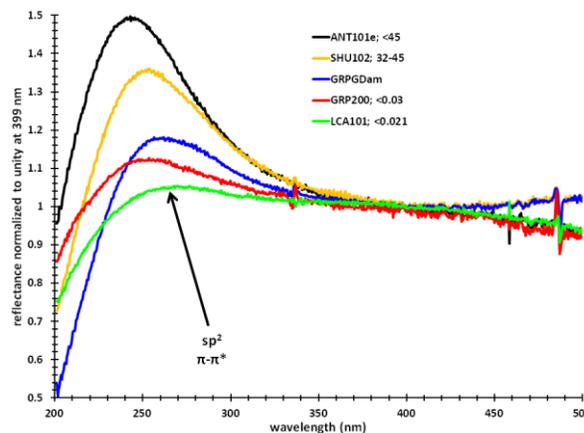


Figure 3: Ultraviolet reflectance spectra of various carbon powders of different crystallinities normalized to unity at 399 nm, showing a Fresnel peak from sp^2 -bonded carbon. Nanophase graphite (GRP200), shungite (SHU102) and anthraxolite (ANTI01) show FP positions at shorter wavelengths than amorphous-carbon (GRPDam) and amorphous, nanoscopic carbon lampblack (LCA101).

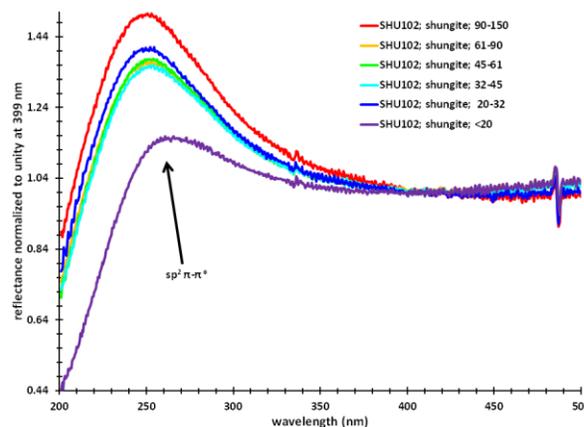


Figure 4: Grain size effects in UV spectra of shungite, an amorphous carbon phase characterized by a glassy appearance and low H/C ratio. Decreasing grain size leads to a reduction in the intensity of the Fresnel peak.

References: [1] Hapke, B., Theory of Reflectance and Emittance Spectroscopy pp. 469. Cambridge University Press (2012); [2] Djurišić, A.B., Li, E.H., *J. Appl. Phys.* 85, 7404-7410 (1999).

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