



## Ultraviolet spectral reflectance of carbonaceous materials

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### ABSTRACT

A number of planetary spacecraft missions have carried instruments with sensors covering the ultraviolet (UV) wavelength range. However, there exists a general lack of relevant UV reflectance laboratory data to compare against these planetary surface remote sensing observations in order to make confident material identifications. To address this need, 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 carbon 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 Fresnel peaks and Christiansen-like features in reflectance. Previous studies extending to shorter wavelengths also show that anomalous dispersion caused by the  $\sigma$ - $\sigma^*$  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  $\pi$ - $\pi^*$  and  $\sigma$ - $\sigma^*$  features contain information on  $sp^3/sp^2$ , structure, crystallinity, and powder grain size. A brief comparison with existing observational data indicates that the carbon fraction of the surface of Mercury is likely amorphous and submicroscopic, as is that on the surface of the martian satellites Phobos and Deimos, and possibly comet 67P/Churyumov-Gerasimenko, while further coordinated observations and laboratory experiments should refine these feature assignments and compositional hypotheses. The new laboratory diffuse reflectance data reported here provide an important new resource for interpreting UV reflectance measurements from planetary surfaces throughout the solar system, and confirm that the UV can be rich in important spectral information.

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### 1. Introduction

The ultraviolet (UV) wavelength range ( $\lambda = \sim 10$ –400 nm) has historically been largely used to study planetary atmospheres and gas production ratios from comets (e.g., Krasnopolsky et al., 2004). The application of this wavelength range to planetary surface reflectance spectra is relatively underexplored and underutilized, but interest and applications have been rapidly increasing, because a number of planetary missions have carried and will carry instruments with sensors covering at least some portion of this spectral

range, including the following spacecraft and satellites: Mariners 6, 7, 9, and 10, Voyagers 1 and 2, Galileo, the International Ultraviolet Explorer (IUE), Cassini, the Hubble Space Telescope, the Mercury Surface Space ENvironment GEochemistry and Ranging (MESSENGER), the Mars Atmosphere and Volatile Evolution Mission (MAVEN), Mars Express, Dawn, Rosetta, New Horizons, and the Mercury Planetary Orbiter (MPO). There exists a general lack of UV laboratory reflectance data that is relevant to conducting comparative analysis of planetary surface reflectance spectra. The limited studies that have been performed in this wavelength region generally find the far-UV to near-UV (FUV-NUV) spectrum to be a potentially powerful and an important spectral range for detection and discrimination of minerals and volatile compounds on airless bodies (e.g., Wagner et al., 1987; Cloutis et al., 2008). Hence, recent efforts (e.g., Cloutis et al., 2015; Liu et al. 2016) are focusing on building new FUV-NUV laboratory datasets for analyses

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of the Moon, comets, asteroids, Mercury, Phobos, Deimos, Iapetus, and other airless bodies. In the context of carbonaceous materials, which appear to be present on a number of planetary surfaces, we expect that these materials exert a strong influence on UV diffuse reflectance spectra due to their wide wavelength range opacity and highly absorbing behavior (Cloutis et al., 2011a, 2012).

### 1.1. UV detection and discrimination of carbonaceous material on planetary bodies

Ultraviolet spectral features have been identified in observational spectra for several bodies expected to contain significant surficial carbon fractions and which are not highlighted in laboratory analyses of inorganic materials. For example, Parker et al. (2002) and Li et al. (2009) demonstrated that the surface of Ceres exhibits unusual UV spectral behavior, with reflectance increasing with decreasing wavelengths toward  $\lambda = 150$  nm. To date, no other planetary surface has shown this spectral behavior. This was confirmed by Hendrix et al. (2016a) using data from the Hubble Space Telescope STIS instrument, finding that a peak in reflectance exists near  $\lambda \sim 160$  nm, and they ascribed it to a spectrally local increase in volume scattering due to a highly concentrated ( $\sim 85$ – $90\%$ )  $\sim 0.5$   $\mu\text{m}$  thick veneer of a material similar to demineralized anthracite termed “graphitized carbon” by Hendrix et al. (2016a, 2016b). This material was noted to not contribute to the near-UV-visible spectral shape.

Bertaux et al. (2011, 2016, pers. comm., 2016), using Mars Express Spectroscopy for Investigation of Characteristics of the Atmosphere of Mars (SPICAM) data, showed that UV reflectance spectra of Phobos exhibit a sharp peak in reflectance near  $\lambda \sim 280$  nm with an I/F value at or below  $\sim 1\%$  depending on phase angle, but were unable to attribute this feature to a specific cause. They suggested that an associated minimum in reflectance near  $\lambda = 220$  nm could be due to an absorption band in solid, dehydrogenated coronene-like polycyclic aromatic hydrocarbons (PAHs), citing work from Duley and Lazarev (2004), who measured absorption spectra of plasma-deposited carbon in gases and vacuum from XeCl laser ablation of graphite. Duley and Lazarev (2004) found that absorption spectra of the plasma-deposited carbon in gas that had been subsequently heated exhibited an extinction maximum to occur near  $\lambda = 220$  nm, and showed that this is analogous to previous calculations of the spectroscopic properties of coronene-like gas phase molecules. Bertaux et al. (2016) also showed that the Deimos spectrum may exhibit a weak peak at  $\lambda \sim 260$  nm, when ratioed against the spectrum of Phobos.

Roettger and Buratti (1994) compiled all measured reflectance spectra from the IUE of 45 asteroids, co-added and recalibrated these spectra for maximum signal-to-noise (S/N) and photometric accuracy, and presented and analyzed these spectra. They concluded that many of the 45 asteroids exhibited spectral slopes shortward of  $\lambda = 260$  nm that were consistent with organic material, but that S/N was not sufficient to be conclusive.

Stern et al. (2015) presented the first extreme UV (EUV) and FUV reflectance spectra of a cometary nucleus, 67P/Churyumov-Gerasimenko. The spectra show an overall I/F of  $\sim 0.02$ , a peak in reflectance near  $\lambda \sim 90$  nm, minima near  $\lambda \sim 170$  nm, from which they concluded that the spectra are consistent with carbon and tholin-like materials, and possible contribution from Rayleigh scattering.

Hendrix et al. (2016b), using HST/FOS data (from Noll et al., 1997) and Cassini UVIS data (from Hendrix and Hansen, 2008), found that the dark leading hemisphere of Iapetus may exhibit a peak in reflectance near  $\lambda = 190$ – $205$  nm, and suggested that this feature could be consistent with reflectance peaks in matrix-isolated phases (spectra of pentacene and acenaphthylene were shown) of polycyclic aromatic hydrocarbons (PAHs), as computed photo-absorption cross sections produced by Mallocci et al.

(2004) showed absorption maxima near this wavelength for pentacene. Hendrix et al. (2016b) also indicated that many condensed PAH films show an absorption peak near  $\lambda = 200$  nm, citing work from Steglich et al. (2010), who showed that thin film transmission spectra of coronene exhibit strong extinction features near  $\lambda = 300$  nm and 200 nm. Steglich et al. (2010) also showed that film transmission spectra of two solvent extracts of soot exhibited extinction features near  $\lambda = 200$  nm, and that the feature moves to longer wavelengths as PAHs become larger. Hendrix et al. (2016b) indicated that mixtures of many aromatic molecules will generally lead to the presence of only the  $\pi$  band near  $\lambda = 200$  nm, citing Papoular et al. (1993) who showed that as coal rank decreases, the  $\pi$ – $\pi^*$  band weakens, widens, and shifts to longer wavelengths from  $\lambda = 250$  nm. The presence of organic materials on the surface of both of Iapetus’ hemispheres was previously suggested from infrared spectral data (Cruikshank et al., 2008, 2014), who found partially resolved, overlapping absorption bands near  $\lambda = 3.30$   $\mu\text{m}$  and ascribed them to aromatic and aliphatic C–H bonding.

### 1.2. Detection of carbonaceous material on planetary bodies using albedo

The evidence for the widespread presence of carbonaceous material on other planetary bodies is both direct and implied from reflectance spectra collected at longer wavelengths. Much of this evidence points to the fact that carbonaceous materials have an exponential impact on the spectroscopic properties of assemblages within which they are contained, due to the strong nonlinear effect of “dark” (i.e. highly absorbing) materials in the presence of multiple scattering in powders.

High S/N disk-averaged UV spectra from the surface of Mercury have previously been acquired with the Mercury Atmospheric and Surface Composition Spectrometer (MASCS) instrument on the MESSENGER spacecraft (McClintock et al., 2008). They found that Mercury’s reflectance spectrum relative to that of the lunar far-side exhibits lower albedo and a progressive increase in relative reflectance with decreasing wavelength from  $\lambda = 1400$  nm to  $\lambda \sim 320$  nm, with an abrupt downturn at  $\lambda = 300$  nm, with a suggestion that the UV feature could be due to oxygen-metal charge transfers in  $\text{Fe}^{2+}$ - and/or  $\text{Ti}^{4+}$ -bearing silicates. A non FeO-bearing material, which would be opaque over a wide spectral range, is required for the darkening and suppression of silicate near-infrared (NIR) absorption bands in reflectance spectra collected from the surface of Mercury (e.g., Robinson and Lucey, 1997). Low iron (Weider et al., 2015; Peplowski et al., 2011) and titanium (Peplowski et al., 2011) abundances do not support the hypothesis that opaque oxides of these elements contribute substantially to Mercury’s low and variable surface reflectance. As such, the presence of carbon at concentrations of multiple wt.% on Mercury has been deduced on the basis of this and elemental data acquired by the MESSENGER spacecraft (Syal et al., 2015; Peplowski et al., 2016), but the source and specific phase is not yet uniquely resolved, because there are not diagnostic features in the VNIR. Trang et al. (2017) were able to successfully model the VNIR reflectance spectra of Mercury by adding wt.% concentrations of nanophase and microphase iron and amorphous carbon to a silicate matrix.

Diverse carbonaceous phases are present at up to only the few percent level in the various classes of carbonaceous chondrite meteorites, yet the spectral properties of carbonaceous chondrites are very strongly influenced by those of the carbonaceous fraction (e.g., Cloutis et al., 2011a, 2011b). Carbonaceous phases are also important constituents of some differentiated meteorites, such as ureilites and certain iron meteorites (e.g., Brearley and Jones, 1998; Mittlefehldt and Lindstrom, 1998; Cloutis et al., 2010; Cloutis et al., 2012), but they also do not show direct evidence of specific car-

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