Optical Constants of Outer Solar System Materials and Radiative Transfer Modeling

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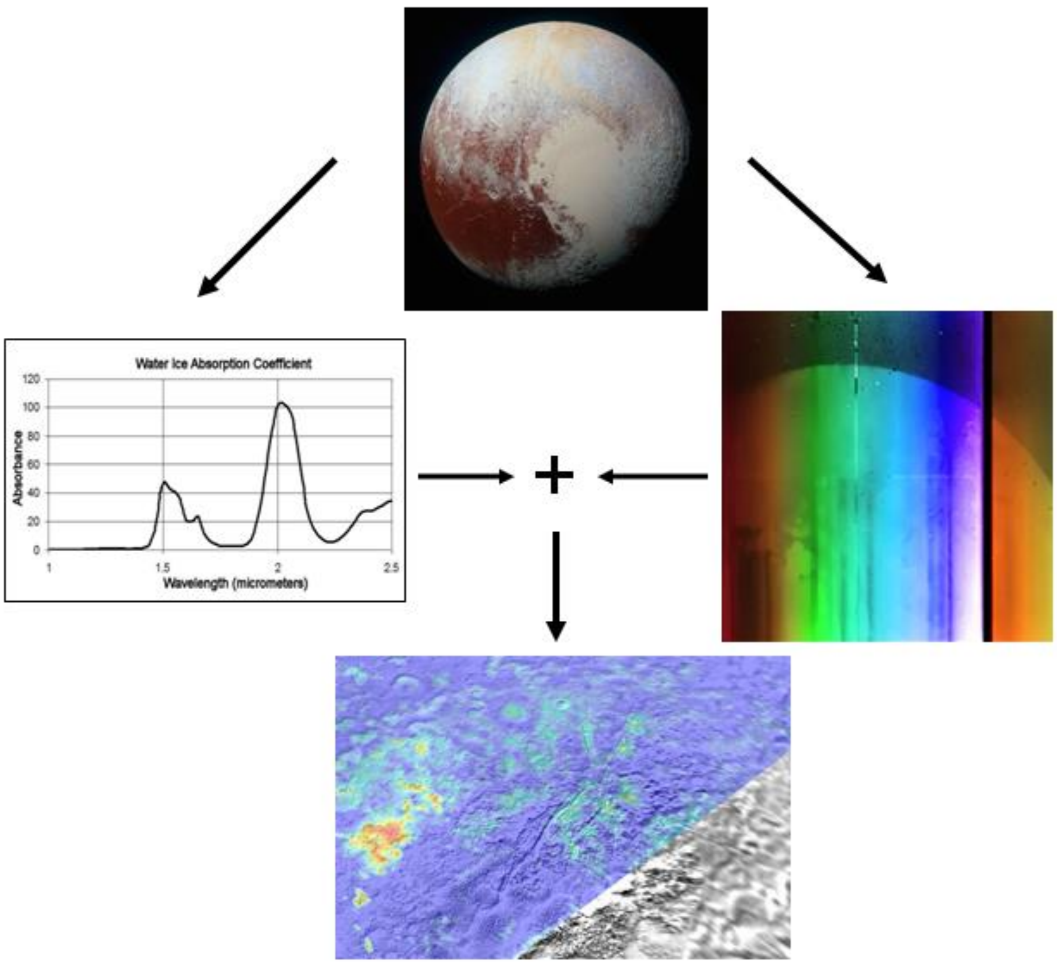

Figure 1: Stages of the exploration of an icy world: New Horizons *enhanced color image of Pluto*(top), the absorption coefficient of an H_2O ice sample versus wavelength†(left), a visual-color representation of an image from the* New Horizons *LEISA mapping spectrometer (right)‡, and a map of the Mwindo Fossae and Kiladze crater region on Pluto§ (bottom).*

*Image credits: NASA/Johns Hopkins University Applied Physics Laboratory/Southwest Research Institute, †Data provided by R. M. Mastrapa, ‡Still image from video credits: NASA/Johns Hopkins University Applied Physics Laboratory/Southwest Research Institute/Alex Parker, §Figure courtesy of B. Schmitt

1. Introduction and Motivation

The dramatic scientific discoveries of the *Cassini* and *New Horizons* missions to the Saturn and Pluto systems have greatly increased interest in the exploration of small outer Solar System bodies. The surfaces and atmospheres of these bodies — giant planet moons, comets, Centaurs, outer Solar System dwarf planets, and trans-Neptunian objects — reflect the location and conditions of their formation, their geological evolution and recent geological activity, their collisions and interactions with other bodies, and the cumulative effects of chemistry and radiation processing. New measurements of the wavelength-dependent complex indices of refraction, or *"optical constants,"* of outer Solar System materials paired with advances in radiative transfer modeling techniques are **urgently** needed to better investigate these processes and to maximize the number of scientific discoveries that will be made.

NASA has a historical and long-term major commitment to planetary science and outer Solar System exploration. Recent observatories and planetary missions such as *Galileo*, *Juno, Cassini*, *New Horizons*, *Rosetta*, *SOFIA*, *Spitzer,* and *Dawn* have already provided an extensive body of observations of thermal emission (≥10 μm), reflected sunlight (0.3–5 μm), and absorbed sunlight (0.3–150 μm) for a wide range of objects. In addition, the *James Webb Space Telescope* (*JWST*) will provide a comprehensive program of observations of Solar System bodies as part of its "planetary systems and the origin of life" science theme with instruments covering the entire spectrum from 0.6 to 28.8 μm [1]. NASA and other research agencies are also developing future missions and observatories that will generate an enormous wealth of additional Solar System observations (see Table 1).

Experimentally measured optical constants are fundamental input parameters used in the radiative transfer models that are essential for interpreting this observational data and determining properties such as surface composition maps, surface temperature maps, or atmospheric opacities.

Table 1: Some upcoming telescopes and missions with imaging and spectroscopic capabilities and with planned observations of outer Solar System bodies

Mission (Launch Date)	**Observing Instruments with Spectral Ranges above 5 μm**	**Ref.**
JWST (2021)	MIRI (5.0–28.8 μm)	1
Mission (Launch Date)	**Observing Instruments with Spectral Ranges below 5 μm**	**Ref.**
JWST (2021)	NIRCam (0.6–5.0 μm), NIRSpec (0.6–5.0 μm), NIRISS (0.9–5.0 μm)	1
JUICE (2022)	JANUS (0.36–1.1 μm), MAJIS (0.5–5.5 μm), UVS (55–210 nm)	2
SPHEREx (2024)	Spectrophotometer (0.75–5.0 μm)	3
Europa Clipper (2024)	MISE (0.8–5 μm), EIS (390–700 nm), Europa-UVS (55–210 nm)	4
LUVOIR (Late 2030s)	HDI (0.2–2.5 μm), LUMOS (0.1–1 μm), ECLIPS (0.2–2.0 μm), POLLUX (100–400 nm)	5
Telescope (First Light)	**Selected Observing Instruments and Spectral Ranges**	**Ref.**
TMT (2027)	MOBIE (0.31–1.1 μm), IRIS (0.84–2.4 μm), IRMS (0.95–2.45 μm)	6
GMT (2029)	G-CLEF (0.35–1.0 μm), GMTNIRS (1.15–5.3 μm)	7
E-ELT	CODEX (0.37–0.71 μm), HARMONI (0.47–2.45 μm), MICADO (0.8–2.5 μm), METIS (2.9–14 μm)	8

Optical constants have been measured for the most important ices and ice mixtures, some refractory organics, and some minerals in limited spectral regions and with widely different spectral resolutions. There is an urgent need for new, more accurate, and more complete optical constants measured across the UV to far-IR spectral range at resolutions of *R*=100,000 or better (to meet or exceed capabilities of the LUMOS spectrograph on *LUVOIR* or the HIRMES instrument on *SOFIA*).

Experimental measurements are needed for both pure components and mixtures since molecular interactions in a mixture can produce spectral features that are not simply related to the optical constants of the individual components. These improved optical constants will also greatly benefit studies of exoplanet atmospheres and studies of astrophysical sources with ice-covered dust grains such as protoplanetary environments and dense interstellar clouds.

Here we identify areas where progress in the measurement of optical constants will support observations of past, current, and in-development observatories and missions. In sections 2 through 4, we provide an overview of several phenomena that require new optical constants measurements for their full investigation, and we refer readers to comprehensive historical reviews of optical constants of ices [9,10] and aerosol analog studies [11–12] for in-depth detail. Section 5 briefly details radiative transfer modeling and directions for improvements for these models. In section 6, we conclude that coordinated efforts to measure optical constants should be organized along with the provision of a dedicated NASA Planetary Data System (PDS) node or a PDS-equivalent repository for long-term data accessibility.

2. Optical Constants of Outer Solar System Ices

There are several broad areas where new optical constants of ices are needed to support analysis of specific outer Solar System processes, some with implications for the search for compounds of biological interest and the search for extraterrestrial life.

Ammonia and ammonium compounds: An absorption feature at approximately 2.2 µm identified in reflectance spectra of a variety of icy bodies in the outer Solar System is associated with the $\nu_1 + \nu_4$ infrared band of ammonia or an ammonium compound. This is surprising since the lifetime of primordial ammonia on the surfaces of outer Solar System bodies is too short for maintaining an appreciable surface abundance due to removal via UV photons, magnetospheric charged particles, cosmic rays, and other sources of irradiation [13].

Emplacement of cryovolcanic deposits, sourced from subsurface liquid ammonia/water mixtures, is a natural ammonia replenishment mechanism for explaining observations of the 2.2 µm band [14]. Another possible source of ammonia on the surface of small outer Solar System objects is ammonia emplaced by cometary bombardment, since recent evidence suggests that ammonia salts are present in cometary comae [15]. Ammonia-rich deposits in an icy body’s subsurface could then be exposed by tectonism, mass wasting, or impact events.

Geological activity such as cryovolcanism could be an important indicator for ocean worlds with subsurface ammonia/water oceans, with liquid water also representing a tempting target for the search for life. Optical constants of ammonia, ammonia hydrates, ammonium salts, and other relevant ammonium compounds are therefore needed for resolving the identity of this 2.2 µm feature and for better using it as a tracer for ocean world processes.

Small Hydrocarbons: Sublimated methane is well known for supplying carbon and hydrogen within the complex, energetically driven atmospheric chemistry of Pluto, Titan, and Triton. An initial population of small hydrocarbon radicals formed from the dissociation of methane can recombine to form larger molecules such as alkanes, nitriles (by incorporating available N atoms), and benzene. Optical constants of ices of small hydrocarbons are needed because these molecules can condense on and mix with surface ices of bodies with haze-producing atmospheres and because hydrocarbon ice clouds were observed in Titan's atmosphere by the *Cassini* ISS*,* CIRS, and VIMS instruments. Depending upon the species, optical constants from the far-UV up to wavelengths of 2–5 µm are needed for modeling surface ices and optical constants from 0.6 µm to 150 µm are needed for better fitting of *Cassini* observations.

An atmospheric chemistry capable of forming benzene might also be able to form small, polycyclic aromatic hydrocarbons (PAHs) with sizes presumably on the order of 10–20 carbon atoms. Reflectance spectra of small, functionalized PAHs that might be forming in the haze layers indicate that these molecules can often have strong visual absorptions [16]. Optical constants of these species are also needed since they could contribute to the strong visual pigmentation of icy surfaces described below.

Complex Organic Molecules: Methanol is an abundant component of cometary and interstellar ices that plays an important role in the formation of complex organic molecules (COMs). Methanol is destroyed by energetic radiation, leading to the creation of radicals ($CH_3^\bullet$, $^\bullet OH$, $^\bullet CH_2OH$, $CH_3O^\bullet$), ions, and photoproducts (CO, H_2CO). These species contribute to the formation of more complex organics with longer carbon chains, in particular when the temperature in the ice matrix increases enough for these species to diffuse and react. For example, the polymerization of formaldehyde (H_2CO) results in the formation of polyoxymethylene $(CH_2O)_n$, which is found in the coma of comets [17]. CH_3OH and H_2CO are also the precursors of polyols, i.e., sugar derivatives [18]. CH_3OH ice was also shown to be an important precursor for the formation of a wide range of amino acids when mixed with NH_3 ice [19], and it is believed to be a precursor for the formation of fatty acids and other lipids.

Optical constants for determining the presence of abiotically produced COMs and biomolecules on icy bodies are important because these molecules will be the primary targets of future missions that are focused on the search for current or past life on icy satellites such as Europa and Enceladus. A better characterization of (i) the chemical and physical environments in which methanol ice is present, and (ii) the products resulting from the energetic processing of methanol-containing ices is needed to better distinguish between biologically produced molecules and COMs arising from energetically processed methanol.

3. Optical Constants of Tholins

Complex, refractory organic materials can be produced from the processing of ices on planetary surfaces and gaseous species in planetary atmospheres. On Titan and Pluto, the complex atmospheric chemistry is initiated by the dissociation and ionization of N_2 and CH_4. Small radicals, ions, and neutrals form and their chemical interactions result in the formation of increasingly larger molecules, leading to the production of aerosol particles that contribute to the observed haze layers and can settle onto the surface.

The refractory materials resulting from surface or atmospheric chemistry often have a strong visual pigmentation that is readily observed in the orange aerosol haze in Titan's atmosphere, the dark-red Cthulhu region of Pluto's surface, and throughout the outer Solar System. Optical constants of these materials are critically needed as input parameters for modeling spectra of planetary atmospheres and surfaces and for the radiative transfer component of the global circulation models used to study the thermal structure of atmospheres.

"Tholins" are laboratory analogues of these materials that can be synthesized from N_2/CH_4 gas and ice mixtures when exposed to various energy sources. In general, tholins are disordered, polymer-like materials made of repeating chains of linked aromatic and aliphatic subunits with complex combinations of carbon-bearing functional groups. Nitrogen and other elements can be incorporated into the aromatic and aliphatic subunits to varying degrees.

Tholins have been extensively synthesized and studied [12,20–22]. However, few measurements of their optical constants have been achieved due to the difficulty in producing satisfactory samples for quantitative spectroscopic measurements across a wide wavelength range [12]. The optical constants obtained by Khare et al. [23] for a "Titan tholin" produced by UV photolysis of a N_2:CH_4 (9:1) gas mixture have been widely used in models of planetary surfaces and atmospheres, not because they are the most representative, but because they cover a broad range of wavelengths from X-rays to microwaves. **More optical constants of tholins are needed, covering a broad spectral range and with production in different experimental conditions (pressure, temperature, gas mixture, energy source)**, that are more representative of the different planetary environments where refractory materials have been detected. Multiple experimental results are needed for attributing common features to chemical pathways, reaction mechanisms, and experiment-specific phenomena.

4. Optical constants of exoplanetary cloud and haze particle analogs

A major result from the previous 15 years of exoplanet atmospheric characterization is that all exoplanetary atmospheres have aerosols, including clouds and photochemical hazes. Understanding the properties of planets therefore requires us to understand cloud and haze formation. A key problem is that we do not have well-constrained optical properties for the plethora of species that could condense, based upon a planet's temperature, composition, and irradiation by the host star. Without knowing how these materials absorb and scatter light, it is impossible to model spectra of cloudy exoplanets accurately.

To make progress in understanding clouds and hazes in exoplanets, **we need a uniform, broad wavelength-coverage (0.4–28 µm) set of optical constants for all potential condensates and for exoplanetary aerosol analogs** — silicates, sulfur and phosphorous species, complex organic haze analogs for cooler exoplanets, and refractory minerals for hot exoplanet applications [24].

5. Radiative Transfer Modeling

One of the primary tools used by planetary astronomers and spectroscopists to interpret the composition of planetary surfaces and atmospheres involves the generation of synthetic spectra with radiative transfer (RT) models. Light–solid interactions are influenced by the composition of the solids, their grain size distributions, relative abundances, mixing regimes, viewing geometries, surface structures, and other factors. Molecular interactions in solids of mixed composition can make the optical constants of the mixture difficult to predict even with knowledge of the optical constants of the components.

Consequently, deconvolving reflectance spectra to assess the identity and abundance of the individual constituents that comprise the regoliths of icy satellites, dwarf planets, and other icy bodies is difficult. Multiple scattering theories, e.g., the Hapke [25] and Shkuratov et al. [26] theories, can be used in the models to generate approximate solutions to RT in a planetary regolith. Most importantly, **RT models all require the optical constants of the candidate materials as input for the calculations.**

Although the Hapke and Shkuratov models can provide useful approximations for planetary surfaces, these approaches do have some key drawbacks. For example, regoliths composed of grains with diameters comparable to or smaller than the incident light wavelength violate the principle of geometrical optics, which forms the basis of Hapke and Shkuratov scattering theories [27]. More recent work has attempted to mitigate these small grain size drawbacks using Mie scattering [28] or Rayleigh scattering [29] theories to calculate the single scattering albedos for each modeled constituent. RT modeling of two or more discrete compositional layers in a regolith represents additional complexity, requiring further modifications to the traditional spectral modeling approaches [30]. **Continued fine tuning of scattering theories is needed as tools evolve to match our ever-increasing knowledge of the composition and structure of planetary regoliths.**

6. Conclusions

The enormous interest and investment in new science missions that will be exploring the outer Solar System must be provided with the optical constants of ices, surface material and aerosol analogues such as tholins, and cloud or haze-forming species in exoplanetary atmospheres that are necessary for maximizing the scientific knowledge and discoveries that will be made. **A first, necessary recommendation is to support a comprehensive and coordinated effort among laboratory groups specializing in optical constants measurements to address the full scope of these data needs**. A comprehensive and coordinated effort by experienced researchers would be able to make rapid progress and produce reliable optical constants measurements.

Although there are several repositories that provide a limited quantity of optical constants and other spectral data, there is no overall comprehensive and authoritative database for optical constants for planetary science and exoplanetary applications. **The most important subsequent recommendation is to support the creation and maintenance of a PDS node or a PDS-equivalent repository,** as defined by NASA's yearly ROSES solicitation for proposals, as the authoritative archive for optical constants relevant to planetary and exoplanetary applications. A repository that fulfills these requirements would ensure that optical constants are archived for long-term and public accessibility and that the stored optical constants are searchable, citable, and peer-reviewed for reliability. **This repository would strongly support the data management plans proposed by optical constants researchers responding to solicitations for proposals, ensure that the science community has access to the most reliable optical constants available, and allow researchers to rapidly identify unmet needs for new optical constants measurements.**

We also expect that an increase in the volume and detail of observations of icy bodies and exoplanets will necessarily entail an increased demand for the associated RT modeling techniques. **The third recommendation is to support a community effort to develop and advance RT modeling techniques,** which will complement laboratory measurements of optical constants and ongoing observations.

7. References

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