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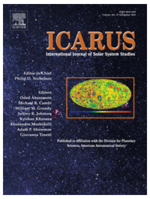

The optical and chemical properties of discharge generated organic haze using in-situ real-time techniques

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ABSTRACT

Organic hazes formed from methane are present in many planetary and satellite atmospheres and influence surface and atmospheric processes. Here we examine the compositional and optical properties of laboratory generated hazes, or tholins, formed with varying amounts of methane using spark discharge excitation. By studying the optical and chemical properties together as a function of methane precursor concentration, the radiative impact of haze can be better understood. To determine the complex refractive index of tholin, we combine two spectroscopic techniques: photoacoustic spectroscopy and cavity ring-down spectroscopy (PASCaRD). The refractive indices are retrieved at $\lambda = 405$ and 532 nm. Quadrupole aerosol mass spectrometry is used along with a technique that utilizes isotopically labeled and unlabeled methane gas to quantify elemental composition. Tholin optical and compositional measurements are performed within a flow system, eliminating the need for tholin collection on a substrate and possible post-collection changes. We observe n values within the range of n values from most previous studies. However, the observed k values, like most others from recent studies, are significantly lower than the values from Khare et al. (1984) (Khare, B.N., Sagan, C., Arakawa, E.T., Suits, F., Callcott, T.A., Williams, M.W. [1984]. Icarus 60, 127–137) that are commonly used in data retrieval programs and models. In addition, comparing the tholin k values to their approximate nitrogen and aromatic content suggests both chemical constituents are important factors for increased aerosol absorption.

1. Introduction

Any planetary body with a reduced atmosphere containing methane has the potential to form an organic atmospheric haze. In our solar system, organic hazes have been reported for Titan, Jupiter, Saturn, Uranus, Neptune and, most recently, Pluto (Gladstone et al., 2016; Pyror and Hord, 1991; Wagener et al., 1986). Additionally, haze could possibly have formed in the atmosphere of the ancient Earth (Sagan and Chyba, 1997). Hazes can greatly impact atmospheric and surface properties, including the radiative balance (McKay et al., 1989; 1991) and surface albedos (Griffith et al., 2003; 2012; Hirtzig et al., 2013; Negrão et al., 2006). Thus, hazes can significantly influence surface and atmospheric temperatures (Pavlov et al., 2001; Haqq-Misra et al., 2008). In order to calculate or model many of these impacts, knowledge of the complex refractive index of the haze, m, is required. The complex refractive index is defined as $m = n + ki$, where the real part, n, describes scattering, and the imaginary part, k, describes absorption. Ideally, measurements of chemical composition would accompany the complex refractive index retrievals since chemical composition fundamentally determines how the haze will interact with light. A review by Brassé et al. (2015) provides an in depth analysis of previous work on haze analog complex refractive indices.

The most comprehensive study of tholin optical constants is reported in Khare et al. (1984). In that study, haze was produced by the direct current (DC) electrical discharge of 10% CH_4 in N_2 and was collected on a substrate. The optical constants of the tholins over a wide wavelength range were determined by the combination of transmittance, reflectance, interference, ellipsometric polarization and Brewster angle measurements. The cold plasma energy source, the collection of haze produced from gas mixtures of CH_4 and N_2 on a substrate and the spectrophotometric and ellipsometric methods used by Khare et al. (1984) are similar to the

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experimental procedures and methods used by most studies that determined the full complex refractive index of haze analogs decades later (Imanaka et al., 2012; Mahjoub et al., 2012; Ramirez et al., 2002; Sciamma-O'Brien et al., 2012, Studies that report only the imaginary refractive index are not referenced).

Studies that differ from Khare et al. (1984) include Khare et al. (1987), Tran et al. (2003) and Hasenkopf et al. (2010). While Khare et al. (1987) used similar experimental methods as Khare et al. (1984), they produced tholin from various combinations of methane, hydrogen and helium. Additionally, both Tran et al. (2003) and Hasenkopf et al. (2010) used ultraviolet excitation to produce tholin. Tran et al. (2003) irradiated methane and nitrogen mixtures that included hydrogen, acetylene, ethylene and cyanoacetylene using wavelengths at 185 and 254 nm. Hasenkopf et al. (2010) produced tholin from Lyman-α excitation of methane and nitrogen and used cavity ring-down spectroscopy to determine the tholin optical constants. Cavity ring-down spectroscopy allows for the measurement of the complex refractive index in situ on freely flowing aerosol. However, that study was performed only at 532 nm.

Despite the many studies that have determined the optical constants of tholin produced from methane and nitrogen, there is still great variation in the reported k values. Experimental differences resulting in different k values, like initial gas mixture compositions, energy source (including temperature changes resulting from the energy source) and pressure during tholin formation, have been discussed in detail by Sciamma-O'Brien et al. (2012). And while most tholin optical constant studies have synthesized tholin at room temperature, a study by Mahjoub et al. (2014) has shown that the complex refractive indices of tholin are different when produced in a colder environment. Further, experiments that use the same energy source and experimental setup can measure different imaginary refractive index values by simply changing the type of substrate used to collect the tholin (Mahjoub et al., 2012; Sciamma-O'Brien et al., 2012). Substrates can influence the flux of the energy source used to produce tholin (Mahjoub et al., 2012), possibly impacting the chemical properties of the tholin.

In addition to the variation in the imaginary refractive index of these tholins between studies, there is also high uncertainty in the reported k values in the visible and ultraviolet wavelength range (at least 30% uncertainty) (Hasenkopf et al., 2010; Khare et al., 1984; Ramirez et al., 2002), which can result from experimental effects like the retrieval method used (Hasenkopf et al., 2010), tholin substrate uncertainties; nonuniform film thickness and aerosol porosity (Ramirez et al., 2002), and sample variations (Khare et al., 1984). Imanaka et al. (2012) reports an uncertainty of $< 10\%$ in their tholin k values, but that experiment focused on the infrared range, solving for complex refractive indices between 2.5 and 25 µm. Having precise k values are important for understanding the radiative forcing of an aerosol (Zarzana et al., 2014). Zarzana et al. (2014) shows that even small uncertainties in k can exacerbate radiative forcing uncertainties, where they show that a 150 nm sized particle with an uncertainty of $\pm$ 0.01 in k can result in approximately $\pm$ 20% uncertainty in forcing.

Although there is variation and high uncertainty in the optical constants of tholins, many planetary studies use the complex refractive indices of the particles produced by Khare et al. (1984) in data retrieval programs and algorithms to calculate other parameters, including the single-scattering albedo of Titan aerosol (Tomasko et al., 2005; 2008). In addition to Titan studies, ancient Earth studies, like those of Sagan and Chyba (1997) and Pavlov et al. (2001), have used the optical constants determined by Khare et al. (1984) to study the impact of potential haze on the paleoclimate. Even some past studies of Pluto and Jupiter have used the optical constants from Khare et al. (1984) in their atmospheric models (Grundy and Buie, 2001; Irwin et al., 1998).

In the study presented here, three different hazes have been produced with a spark discharge source using different initial methane concentrations in nitrogen. The resulting particles were produced in a flow system, and their compositions were determined in situ using quadrupole aerosol mass spectrometry (Q-AMS) with the aid of isotopically labeled precursor gas. The complex refractive indices at wavelengths of 405 and 532 nm were determined in situ using photoacoustic spectroscopy coupled to cavity ring-down spectroscopy (PASCaRD). The addition of photoacoustic spectroscopy to the optical measurements allows for the direct measurement of particle absorption, which can enhance precision and accuracy in the imaginary refractive index term k. While photoacoustic spectroscopy and cavity ring-down spectroscopy have been used together before in studies of the optical properties of Earth aerosol (Atkinson et al., 2015; Cappa et al., 2016; Lack et al., 2006, 2012a,b; Lambe et al., 2013; Radney et al., 2013, 2014; Zarzana, 2014; Zhang et al., 2016), this is the first study that uses this technique for planetary haze analogs. Like previous work by Imanaka et al. (2004) and Mahjoub et al. (2012), this study will use the chemical properties of haze analogs formed under different experimental conditions to help explain their optical properties.

2. Experimental

2.1. Aerosol production

Tholins were produced with varying initial ultra-high purity methane (Airgas, 99.99%) concentrations of 0.1, 2 and 10% by volume in ultra-high purity nitrogen (Airgas, 99.999%). These specific concentrations of CH_4 have been chosen in order to study the optical and chemical properties of haze analogs produced with a concentration of CH_4 covering two orders of magnitude. The first two concentrations, 0.1 and 2% CH_4, were included because they are at the peak aerosol production rate for our experimental setup using the UV (Trainer et al., 2006) and spark discharge (Hörst and Tolbert, 2013) energy sources, respectively. In addition, 10% CH_4 was also included in this study as a point of comparison since it is a common precursor methane concentration used in previous organic haze analog studies that determine the complex refractive index of haze analogs produced by methane in nitrogen only (Khare et al., 1984; Imanaka et al., 2004, 2012; Mahjoub et al., 2012).

The haze generation system has been described in detail previously (Trainer et al., 2004, 2006). Briefly, methane and nitrogen flow into a mixing chamber where they mix for at least 8 hours. Then, using a mass flow controller (MFC; Mykrolis, FC-2900), the gas mixture flows at 60 sccm to the reaction cell where a spark discharge energy source (Electro Technic Products) operating between 30–35 kV initiates chemistry to form tholin at ambient conditions (~620 Torr and 20 °C). The tholin particles then flow to either analysis method used in this study, Q-AMS or PASCaRD. The tholin particles are always suspended in the gas flow so no deposition onto a substrate is needed. Additional pre-purified nitrogen gas flow after the reaction cell is added, 40 and 240 sccm to the Q-AMS and PASCaRD, respectively, due to instrument requirements.

2.2. Photoacoustic spectroscopy and cavity ring-down spectroscopy (PASCaRD)

Fig. 1 shows a schematic of the PASCaRD system used to determine the complex refractive index of tholin. In these experiments, two channels, one at 405 nm and one at 532 nm, are used. When using PASCaRD, the polydisperse particles first flow to a differential mobility analyzer (DMA; TSI, 3081) to be size selected. The DMA was calibrated using five different sizes of polystyrene latex