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Electron-molecule chemistry and charging processes on organic ices and Titan's icy aerosol surrogates

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ABSTRACT

Electron-induced polymerization processes and charging events that can occur within Titan's atmosphere or on its surface were simulated using electron irradiation and dissociative electron attachment (DEA) studies of nitrogen-containing organic condensates. The DEA studies probe the desorption of H^- from hydrogen cyanide (HCN), acetonitrile (CH_3CN), and aminoacetonitrile (NH_2CH_2CN) ices, as well as from synthesized tholin materials condensed or deposited onto a graphite substrate maintained at low temperature (90–130 K). The peak cross sections for H^- desorption during low-energy (3–15 eV) electron irradiation were measured and range from 3×10^{-21} to 2×10^{-18} cm^2. Chemical and structural transformations of HCN ice upon 2 keV electron irradiation were investigated using X-ray photoelectron and Fourier-transform infrared spectroscopy techniques. The electron-beam processed materials displayed optical properties very similar to tholins produced by conventional discharge methods. Electron and negative ion trapping lead to 10^{11} charges cm^{-2} on a flat surface which, assuming a radius of 0.05 μm for Titan aerosols, is ~628 charges/radius (in μm). The facile charge trapping indicates that electron interactions with nitriles and complex tholin-like molecules could affect the conductivity of Titan's atmosphere due to the formation of large negative ion complexes. These negatively charged complexes can also precipitate onto Titan's surface and possibly contribute to surface reactions and the formation of dunes.

1. Introduction

Titan, the largest satellite of Saturn, has a complex atmosphere that is continually bombarded with energetic radiation, including ultraviolet photons, soft X-rays, solar wind, galactic cosmic rays, and particle precipitation from Saturn's magnetosphere (Sagan and Reid Thompson, 1984). The energy flux provided by these photons, electrons, and ions, ranges from a few eV to over 1 GeV, and drives a multitude of chemical processes in the atmosphere and down to the surface. In Titan's upper atmosphere, measurements from the Cassini mission indicate that solar radiation is the primary source of molecular dissociation and ionization events (Lavvas et al., 2011a). Electrons produced during such photoionization processes have an energy distribution ranging from very low kinetic energy for photons corresponding to energies very close to the ionization threshold of the molecules, up to a few keV for X-ray photons (Lavvas et al., 2011a). In the lower stratosphere and on the surface, galactic cosmic rays (GCR) are the primary energy source that can interact with molecules and generate secondary electrons. These can then collide with neutral species producing more secondary ionization events. This cascade of secondary low-energy electron (LEE) production continues until their energies become less than the ionization energy of the surrounding neutral molecules. In this energy range, transient negative ions (TNIs) and atomic and molecular dissociation products contribute to the formation of the complex molecules and organic-rich aerosols referred to as Titan haze particles (Cravens et al., 2006; Sittler et al., 2010; Vuitton et al., 2007).

Various chemical pathways leading to aerosol formation from simple gas-phase molecules or icy grains may exist depending on the composition, altitude and temperature profile within the atmosphere (e.g. Cabane and Chassefière, 1995; Lebonnois et al., 2002). The Cassini Plasma Spectrometer (CAPS) has discovered large negative ion populations in Titan's atmosphere (Coates et al., 2009; Crary et al., 2009) and the Cassini Ion and Neutral Mass Spectrometer (INMS) observations have confirmed the presence of molecular hydrogen, argon and numerous stable carbon-nitrile compounds (Cui et al., 2009; Magee et al., 2009; Waite Jr. et al., 2005).

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The carbon-nitrile species can be precursors or by-products of complex chemical reaction schemes. In addition, seasonal changes may affect atmospheric gas condensation processes in generating icy clouds were they are not, a priori, expected. For instance, a large cloud mainly composed of micrometer-sized particles of frozen hydrogen cyanide (HCN) was observed in May 2012 (de Kok et al., 2014) at an altitude of 300 km. Cassini observations revealed the presence of aerosols from the thermosphere (~1000 km) to the troposphere (Lavvas et al., 2013 and references therein), while the Visual and Infrared Mapping Spectrometer (VIMS) indicated that the reflectance of the lower albedo Titan regions matches the spectrum of water ice contaminated with a darker material (McCord et al., 2006). Temperature variations are observed with altitude, having peaks at 186 K and 70 K at 250 and 44 km, respectively, and a temperature of about 94 K at the surface (Fulchignoni et al., 2005). Secondary LEEs, also present at low altitudes and in the near surface regions of Titan (where organics freeze), are probably involved to some degree in the formation of organic condensates, polymerization reactions, and negative charging of the haze particles. Of note, here the notion of 'polymerization' does not refer necessarily to the repetition of the same monomeric unit, but rather to the formation of heteropolymers possessing various organic functional groups that are not necessarily repetitive.

Low-energy electron-molecule scattering resulting from exposure to extreme ultraviolet (EUV) photons, electrons or ions is known to induce electronic excitations. This opens numerous dissociative decay channels leading to the production of negative ions and radicals, in both the gas phase and in the condensed phase. One major fragmentation channel accessible at incident electron energies lower than the ionization potential of the molecule is dissociative electron attachment (DEA) (Sanche, 1990). DEA is initiated by electron capture into short-lived resonances, followed by molecular dissociation into neutral and negative ion fragments. Resonances are either low-energy single particle shape resonances or higher-energy core-excited (1-hole 2-electron) Feschbach resonances. DEA of HCN or other carbon-nitrile compounds present in Titan's upper atmosphere was found to initiate the formation of CN^- and other larger negative ions, likely to be the precursors to aerosol formation (Vuitton et al., 2009).

Laboratory experiments have been performed to simulate the growth of Titan haze particle surrogates from simple precursors (methane and nitrogen gases). The resulting polymer is referred to as "tholins" (e.g. (He and Smith, 2013). Synthesized tholins are highly varied in their production methods and properties, and are generally unsaturated molecules consistent with highly asymmetric polycyclic aromatic nitrogenated hydrocarbons (PANHs), conjugated imines and nitriles with some degree of aromaticity (Cable et al. (2011) and references therein). As an example, the following formula $(C_{11}N_4H_{14})_n$ is believed to be a good surrogate for Titan's tholins, as its optical properties compare well with the haze's (Buckingham et al., 2011; Coll et al., 1999). Tholin-like aerosols could eventually rain down to the surface and influence the composition of the bulk atmosphere as they act as condensation nuclei for species in the troposphere, including hydrogen cyanide and methane (Lavvas et al., 2011b). Because aerosols interact with free electrons and acquire charge (Borucki and Whitten, 2008; Michael et al., 2011), a decrease in the electron population can be observed in the presence of negatively charged aerosols (Lavvas et al., 2013).

In order to investigate the polymerization processes and charging events that are occurring within Titan's troposphere and on the surface, we have performed DEA experiments on nitrogen-containing organic condensates. This study focuses on the desorption yield of H^- from organic materials during bombardment of 3–15 eV incident electron energies. This is typical of secondary electron energy distributions. The H^- channel acts as a proxy for maximum electron damage since H^- is the lightest fragment and has the highest desorption probability. Specifically, we probed the desorption of H^- from hydrogen cyanide (HCN), acetonitrile (CH_3CN), and aminoacetonitrile (NH_2CH_2CN) ices as well as from synthesized tholin materials (Imanaka et al., 2004) condensed or deposited onto a graphite substrate maintained at low temperature (90–130 K). In addition, chemical and structural transformations of HCN upon 2 keV electron irradiation were investigated at 90 K using X-ray photoelectron (XPS) and Fourier-transform Infrared (FT-IR) spectroscopies. Further, information regarding the charging properties of these condensates was obtained. Specifically, experiments presented and discussed are organized in 3 sections as follows. In Section 3.1, surface organic materials and aerosol production upon electron irradiation of HCN ice is presented, and the molecular complexity of the resulting residue is characterized via XPS and FT-IR. In Section 3.2, DEA experiments of organic ices are presented and H^- desorption cross-sections determined. Finally, in Section 3.3, charging effects are investigated and implications with respect to Titan are discussed.

2. Experimental methods

For the purpose of clarity, experimental details corresponding to the 3 different sections are summarized in Table 1. Experiments involving electron irradiation were performed in an ultrahigh vacuum (UHV) system with a base pressure of $\sim 10^{-10}$ Torr. The experimental setup shown in Fig. 1 consists of a temperature-controlled sample mount attached to a rotatable XYZ manipulator. The temperature of the sample is measured with a Type K thermocouple, and a resistive heater is used to clean the graphite substrate. Instruments available on the experimental setup and used in the forthcoming sections are: a quadrupole residual gas analyzer (Pfeiffer, Prisma 80) and a custom time-of-flight (ToF) mass spectrometer, an Auger spectrometer (PHI 15-255G, double pass CMA), and a low-energy tunable electron gun (Kimball Physics, ELG2; energy resolution ~0.5 eV FWHM). The high energy electron beam was supplied by the Auger system.

Reagents CH_3CN (Sigma Aldrich, anhydrous, 99.8%) and NH_2CH_2CN (Sigma Aldrich $\geqslant$98%) were vapor-deposited by backfilling at 10^{-7} Torr onto a 2 cm^2 graphite substrate (Alpha Aesar, 99.8%). The graphite was used as a proxy for carbonaceous grains. HCN was synthesized under vacuum from melting (350 K) an equimolar amount of stearic acid ($CH_3(CH_2)_{16}COOH$) powder with KCN powder, as described in (Gerakines et al., 2004). HCN was then purified by annealing cycles, from 77 K (liquid nitrogen bath) to 178 K (acetone slush bath), in order to sublimate other side products while keeping HCN frozen. This HCN gas purity (>99%) was checked using quadrupole mass spectrometry.

The tholin material (provided by M.A. Smith, e.g., Imanaka et al., 2004) we used for comparison was synthetized from a N_2/CH_4 mixture exposed to an alternative current (AC) discharge, and subsequently stored in a vial closed under argon. This material is referred to as 'discharge-generated tholin' in the rest of the manuscript.

For the experiments described in Section 3.1, HCN was condensed on the bare graphite sample (90 K) at a pressure of 10^{-7} Torr using a 100 Langmuir (L) exposure (1 L = 10^{-6} Torr $\times$ 1 s). Electron irradiation (50 s) of this overlayer was performed at 2 keV (fluence of $\sim 1 \times 10^{15}$ cm^{-2} s^{-1}) using the electron gun of the Auger spectrometer (Section 3.1). The polymer resulting from the 2 keV electron irradiation and the enhanced secondary electrons was then analyzed *ex-situ* by means of XPS and FT-IR spectroscopies, as well as observed through a fluorescence microscope.