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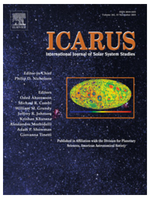

The effect of like-charge attraction on aerosol growth in the atmosphere of Titan

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ABSTRACT

The formation of aerosols in the atmosphere of Titan is based extensively on ion-neutral chemistry and physical condensation processes. Herein it is shown that the formation of aerosols may also occur through an alternative pathway that involves the physical aggregation of negatively charged particles, which are known to be abundant in the satellite's atmosphere. It is shown that, given the right circumstances, like-charged particles with a dielectric constant characteristic of nitrated hydrocarbons have sufficient kinetic energy to overcome any repulsive electrostatic barrier that separates them and can subsequently experience an attractive interaction at very short separation. Aerosol growth can then unfold through a charge scavenging process, whereby nitrated aggregates preferentially grow by assimilating smaller like-charged particles. Since hydrocarbon aerosols have much lower dielectric constants, it is shown that a similar mechanism involving hydrocarbon particles will not be as efficient. As a consequence of this proposed growth mechanism, it is suggested that the lower atmosphere of Titan will be enriched in nitrogen-containing aerosols.

1. Introduction

Since the discovery of Titan by the Dutch astronomer Christiaan Huygens in 1655, Saturn's largest moon has been subject of considerable interest and curiosity. Remarkably, Titan is the only satellite in the Solar System known to display a dense atmosphere (Flasar et al., 2005), harbouring several organic compounds and particular conditions that led some authors to consider the presence of different life forms (Benner et al., 2004; McKay and Smith, 2005; Raulin et al., 2012; Stevenson et al., 2015). Over the past few decades, a significant amount of new information about Titan has been acquired through the Voyager program and, latterly, with the Cassini–Huygens mission. While Voyager represented a breakthrough in exploration of the Solar System and, particularly, Titan, it was only with arrival of the Cassini–Huygens spacecraft in 2004 at Saturn and its moons that Titan's atmosphere and surface could be studied in greater detail, through *in situ* measurements made by the lander Huygens and the Cassini orbiter.

The atmosphere of Titan is known to stage a series of chemical and physical processes that are ultimately responsible for the formation of a characteristic orange haze. Composed primarily of nitrogen (N_2) and methane (CH_4) (Flasar et al., 2005; Coates et al., 2007; Cable et al., 2012), Titan's atmosphere is constantly bombarded by energy sources such as solar ultraviolet radiation and energetic particles from Saturn's magnetosphere. This irradiation triggers the dissociation and ionization of the simple primordial molecules and subsequently leads, through a series of chemical and physical processes, to the formation of charged aerosol particles with an average mass of 500 Da (Lavvas et al., 2013) at altitudes between 950 and 1150 km (upper atmosphere) (Coates et al., 2007; Cable et al., 2012; Waite Jr. et al., 2007; Wahlund et al., 2009; Ågren et al., 2012). With decreasing altitude, these particles grow spherically until they reach the detached haze layer at

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520 km in Titan's mesosphere, from where they start to form fractal aggregates (Cable et al., 2012; Lavvas et al., 2009; 2010; 2011).

Several studies have already shown the crucial role of ion-neutral chemistry and physical aggregation in the production of aerosols in Titan's atmosphere (Cable et al., 2012; Lavvas et al., 2013; Waite Jr. et al., 2007; Lavvas et al., 2009; 2010; 2011; Vuitton et al., 2007; Skorov et al., 2008; Coates et al., 2009; Vuitton et al., 2009; Imanaka and Smith, 2010; Skorov et al., 2010; Sittler Jr. et al., 2009). In this paper, we present a theoretical investigation of a particular aspect of aerosol growth that has not previously been considered. New calculations have been undertaken for the case of like-charged particle interactions in vacuum, which, under certain circumstances, can be counterintuitively attractive. Interactions between neutral and charged particles as well as between oppositely charged particles are not considered since these are already taken to be attractive under similar conditions. The calculations examine how differences in the dielectric constants of particles could lead to a preferential concentration of nitrogen-containing aerosols in the lower atmosphere of Titan.

Depending on the assumed mass density, particles produced in the upper atmosphere of Titan have an estimated radius of either 0.6 nm or 6 nm if 1 elementary charge per particle and densities of 1000 $\mathrm{kg \cdot m^{-3}}$ (Lavvas et al., 2013) or 1 $\mathrm{kg \cdot m^{-3}}$ (Tomasko and West, 2010; Michael et al., 2011), respectively, are considered. Regardless of their initial size, these particles grow as they sink towards lower altitudes eventually forming large particles with radii of 40–50 nm, which have been identified as being present in the detached haze layer (Lavvas et al., 2009; 2010; Tomasko et al., 2008; 2009). Since the amount of charge on the embryonic particles cannot be independently measured, actual sizes could be larger than those estimated above (Coates et al., 2007; Waite Jr. et al., 2007). For example, a particle bearing 5 elementary charges would have a radius 1.7 greater than the same particle carrying just 1 charge. To take into account this degree of uncertainty, the calculations presented here consider charge per particle values that range from 1 to 5 e.

2. Origin of like-charge attraction

In Titan's atmosphere it is generally assumed that like-charged particles will repel one another and so any such interactions will make no contribution to the growth of aerosols (Lavvas et al., 2013). Whilst this concept is generally true, if the particles are sufficiently polarizable, attraction can occur at small separations. Bichoutskaia et al. (2010) showed that for two interacting dielectric particles in vacuum, the electrostatic force can be expressed as a sum of two contributions - a repulsive contribution described by Coulomb's law and an attractive polarization contribution. If the particles are non-polarizable, namely if their dielectric constants, k_i $(i = 1, 2)$, are close to unity, the attractive term tends to zero and the total force is described by Coulomb's law. Conversely, if the particles have dielectric constants that are much greater than unity then the attractive polarization term gains in magnitude and, under certain circumstances, can even overcome the repulsion. As presented, the formalism (Bichoutskaia et al., 2010) is able to treat a broad range of dielectric materials, and is able to differentiate between particles with very different polarizabilities, ranging from oils ($k \approx 2$) through to water ($k \approx 80$), and on to particles of metallic character ($k \geq 1000$).

Fig. 1 shows how the electrostatic force (a) and potential energy (b) varies as a function of particle separation for three different cases of interacting like-charged dielectric particles. Each particle has been assigned a dielectric constant of $k_i = 20$, since this value is comparable to that of many hydrocarbon-nitrile compounds (Wohlfarth, 2016), and so should be representative of nitrile-rich aerosols. Charges, q_i, and radii, a_i, were also selected in order to represent emerging particles in the region between the upper atmosphere and the detached haze layer of Titan's atmosphere. The curve depicting an unstable interaction (dotted line) corresponds to a scenario where the particles repel one another at all values of interparticle separation, which means the potential energy increases as two particles approach each other during a collision. The metastable (dashed line) and stable (solid line) cases are similar in that a repulsive potential energy barrier occurs before they achieve close separation; however, once over the barrier, the energy decreases rapidly as the particles approach touching point. The reason for the observed decrease in potential energy is the onset of an overall polarization induced attractive interaction at sufficiently close interparticle separations. Accordingly, it can be proposed that particles interacting under a stable or even metastable electrostatic regime may provide an important contribution to the growth of aerosol particles and production of the 40–50 nm radius aerosols found in the detached haze layer. It is especially significant when it is considered that charged particles, particularly those carrying a negative charge, are present in high abundance in Titan's atmosphere (Lavvas et al., 2013). The circumstances where such stabilising interactions occur and how the interacting particles are able to overcome the repulsive Coulomb barrier are discussed below. Details of the calculations can be found in the Theory section, where a description is given of the steps taken to achieve a rapid convergence of the electrostatic multipole terms that arise in the formalism describing charged particle interactions. It has recently been shown that a failure to include sufficient terms can lead to a very considerable underestimate in the magnitude of polarization interactions (Lindgren et al., 2016).

3. Discussion

Table 1(a–e) shows values of potential energy barriers (eV) calculated for different cases where two like-charged particles interact. These examples have been chosen to represent the process of particle growth that may occur within Titan's upper atmosphere, leading to the production of aerosol monomers in the detached haze layer. In each sub-table, the radius a_2 and charge q_2 of sphere 2 have been allowed to vary from 5 to 50 nm and 1 to 5 e, respectively, whilst the equivalent parameters a_1 and q_1 for sphere 1 have remained fixed.

As can be seen from Table 1, examples of unstable interactions occur at or near the point where the interacting particles have identical characteristics, i.e. $a_1 = a_2$ and $q_1 = q_2$, and in general they extend across points where a_2/a_1 and q_2/q_1 increase concurrently. Cases of stable interaction occur when the particles have sufficiently dissimilar sizes, and are more generally favoured when the smaller of the two particles carries more charge. Metastable interactions fall between these two scenarios. The magnitude of the energy barrier varies inversely with particle radii and increases with the amount of charge. Broadly speaking, as interacting particles increase in size, the free charge on one becomes, on average, more distant from the free charge on the second particle, which then contributes to a decrease in Coulomb repulsion and, consequently, a decrease in the energy barrier. In contrast, for a fixed particle size, an increase in the amount of free charge on one or both particles means that more charge occupies a fixed area, which then contributes to an increase in Coulomb repulsion and, consequently, an increase in the magnitude of the energy barrier.

Fig. 2a shows a Maxwell–Boltzmann distribution of the kinetic energy of particles calculated for the upper and lower average temperatures, 112 K and 175 K (Snowden et al., 2013), as identified for Titan's thermosphere. The calculations presented in Table 1 suggest that at the beginning of the aerosol growth process, when particles are particularly small, the Coulomb repulsion barrier, generally greater than kT, is high enough to reduce the coagulation rates

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