The Development of a Probabilistic Model for Tholin Aggregation in Titan's Atmosphere

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***Abstract*—Tholin is an organic aerosol produced in Titan's atmosphere. The resulting reddish opaque haze characteristic of the satellite is now known to be the dominating factor in Titan's climate through its influence in temperature control, atmospheric circulation, and hydrocarbon production. Because of the diverse interest to understand the tropospheric activities on Titan, it is of growing importance to understand the various processes involving tholin in different layers of the atmosphere, especially those concerning the actual production and growth of tholin itself. It is the purpose of this study to model the formation of tholin molecules in the lower atmospheric regions of Titan, roughly 80 to 300 kilometers in altitude above the surface, using two different charging classes for daytime and nighttime ion production. A thorough discussion of the model and method used are presented. Then preliminary results are given and discussed for the first generation of aggregates produced. These results are consistent with expected behavior with the exception of two constant inconsistencies at aggregate sizes 10 and 15 monomers where there are abrupt changes in the fractal aggregate growth and charging patterns.**

***Index Terms*—Titan, tholin production, fractal aggregates, dust coagulation**

I. INTRODUCTION

AMONG the many moons of Saturn exists Titan, one of the more distinctive bodies in our solar system. In addition to being the largest of Saturn's moons, interest to study this apparently hazy orange satellite is generated by its uniquely thick atmosphere [1] and in Titan's apparent similarities and differences with Earth [2]. Like Earth, Titan possesses both a terrestrial surface in addition to an atmosphere, but evidence suggests that Titan's crust harbors volcanoes which erupt liquid water instead of lava, a topographical feature known as cryptovolcanism [3]. Then in the lower atmosphere, there are clouds composed of condensed methane which precipitate centimeter sized rain drops [2]. This rain forms lakes and rivers of liquid methane and ethane which erodes away and shapes the surface, much like water does on Earth, before evaporating back up into the atmosphere [2]. However, in order to model weather patterns on Earth, parameters, such as temperature, pressure, and wind speed must be considered with equal importance. But on Titan, only one dominating factor controls the weather, and that is the organic molecule known as tholin.

A broad and diverse interest in tholin production (from atmospheric dynamics, chemistry, to climatology) spurred the study of the organic aerosol beginning in the late 1970's [4]. One of the scientists involved in such studies was Carl Sagan, who was the first to propose in 1974 the complexity of the aerosols contained in atmospheric haze; later in a paper published in 1979, he coined the name, "tholin," for the now configured organic aerosol responsible for the unique characteristics of Titan's atmosphere. The hazy material that appears orange to red in color was appropriately named using a derivation of the Greek word for mud, *tholós* [2].

Since then much research has been conducted on the material, including a myriad of observation hours, the development of theoretical models and laboratory synthesis [5]. Finally on January 14, 2005, the Huygens probe associated with the Cassini spacecraft descended 1500 km through the atmosphere to the ground collecting valuable information about the atmosphere [6], which is now being used to strengthen and improve tholin associated model [7].

II. THE THOLIN PRODUCTION

Tholin is a polycyclic aromatic hydrocarbon formed by photolysis by its chemical description [8]. A subsequent description for its formation begins about 1000 kilometers above Titan's surface [9]. The atmosphere at this altitude contains a concentration of diatomic nitrogen and methane, which are bombarded and charged by incident solar ultraviolet radiation, galactic cosmic rays, and energetic particles [10]. The intensity of the energetic particles increases particularly when Titan passes through Saturn's magnetosphere. These charged molecules then partake in chemical reactions with other molecules present in the atmosphere and form four different species of organic compounds which are further photolyzed by long wave UV rays. The end result is a polymerization of C_2H_2 and HCN producing benzene [9]. Benzene continues to react with the remaining organic compounds, during which time these compounds become more negatively charged though interactions with free electrons and other ions [11]. These aerosols are then further processed into tholin [8]. Tholins will begin to form at about 400 to 500 kilometers above the surface [11]. In Fig. 1 presented below, the steps in the upper atmospheric development of tholin are illustrated beginning with the initial collision of ultraviolet rays with the molecular nitrogen and ethane atoms.

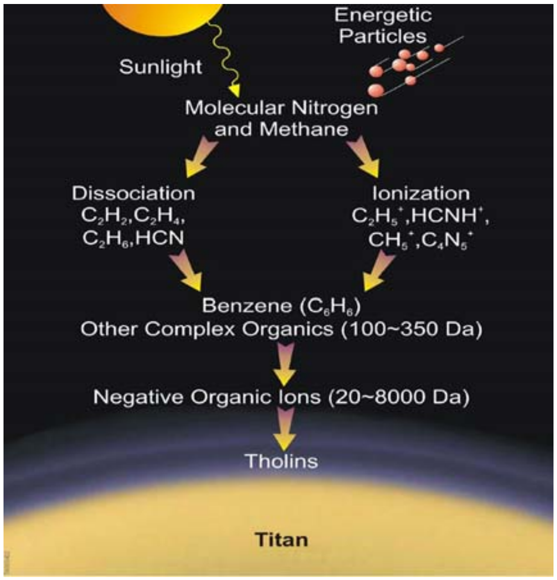

Fig. 1 An illustration of the chemical process in the upper atmosphere leading to the formation of tholin. [http://www-stage.jpl.nasa.gov/]

Although the chemical process conveys vital information about the tholin formation process, this study is concerned with the associated physical process. Following the model outlined by Bar-Nun (2008), let us consider the development of tholin with respect to altitude and the aggregate's mass. As such, the formation of tholin molecules is presented in three primary groups based on size as defined by the number of components contained in the aggregate.

The first group is referred to as *embryos*. Embryos are the original product of the nucleation of the newly formed aerosols and are present in all levels of the atmosphere from about 1000 kilometers and down. In this work, the term 'aerosol' is interchangeable with the term *monomer*. Monomers are characterized as spherical masses and, in this work, are assumed to be about 0.04 to 0.05 microns in diameter [5]. Embryos usually consisted of about 10 to 40 such monomers.

As the embryos grow in radius and mass, they naturally begin to settle lower in the atmosphere and collide with other embryos forming larger and heavier aggregates. These aggregates continue to collide and coagulate with other aggregates eventually forming the last two classes: at an altitude of about 500 km, medium or second generation aggregates form up to about 800 to 1,800 monomers. Finally, the third generation starts collecting up to size 1,500 to 5,000 monomers at an altitude of roughly 200 km. It should be noted that others would suggest that the primary production zone for tholin is about 270±40 kilometers [5].

Ultimately, once the third and final tholin generation has settled into the lower atmosphere, it condenses into a thick layer at about 80 kilometers where is dominates the atmospheric activity by filtering the incoming UV rays (thus regulating the temperature) and controlling the atmospheric circulation [8]. Since tholin also heavily influences the amount of methane present in the atmosphere, methane clouds are influenced by the distribution of tholin concentrations. The diagram in Fig. 2 shows the atmospheric activity in Titan's lower atmosphere with respective altitude, temperature, and pressure.

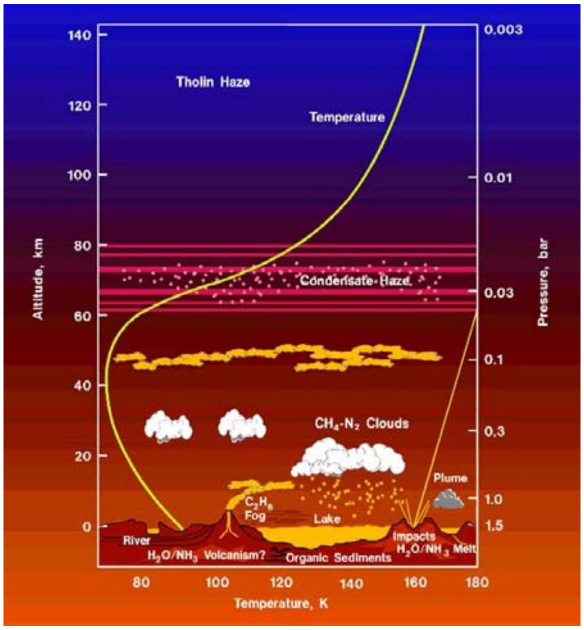

Fig. 2 A diagram illustrating atmospheric temperature and pressure with respect to altitude. Also shown are the tholin concentration zones for the lower altitudes, types of atmospheric activity in the troposphere, and suspected topographical features of the surface. [http://www.jpl.nasa.gov/]

III. Numerical Model

The model used to simulate the growth process, Tholin Builder, is a modified version of Aggregate Builder, a computer model developed by Matthews to investigate early stages of planetesimal formation [12]. Tholin Builder follows the same algorithm as Aggregate Builder but uses different plasma parameter values, velocities, and general particle characteristics appropriate to modeling tholin development on Titan.

The general process for the program algorithm follows a simple procedure. An aggregate or monomer with a fixed mass and charge is placed at the origin defined by its center of mass. An incoming aggregate or monomer is then introduced into the frame with similar set characteristics such as mass, charge and velocity but with a randomly determined position and a predetermined time step, which is dependent on velocity.

If the particles connect, then the new aggregate's characteristics including the fractal dimension and charge are calculated. The fractal dimension is calculated using the Hansdorff method; thereby, the aggregate is placed in a subsectioned cube, and the fractal dimension is calculated by dividing the logarithmic values of the number of subboxes containing portions of the aggregate by the logarithmic value of the quotient of the original cube length with the length of the subboxes.

Then for the charge calculation, a modified orbital motion limited theory is used with a line-of-sight approximation (OML_LOS). This technique is employed to accommodate the fractal aggregate structure, which can not be approximated by a spherical shape. Orbital motion limited theory is founded in the "assumption that energy and momentum are conserved for impinging current species and that ions and electrons that have encountered potential barriers… have been removed from the background Maxwellain distribution" [13].

But then, as the fractal aggregates grow, OML requires more computation time creating the need for the line-of-sight approximation. LOS works by reducing an amount of surface area to be analyzed in OML. Since aggregates are charged through collisions with ions, it is unnecessary to consider the areas on a fractal aggregate structure where charging is not possible, because the part of the aggregate is blocked by another part of the structure. LOS determines these irrelevant areas and thus reduces the total surface area OML analyzes [13].

Once the charge and fractal dimension are calculated for the newly formed aggregate, another particle is initialized as the next incoming particle. The process repeats until either an aggregate of the specified size forms or the number of missed collisions maxes out.

In order to determine the velocity involved in the current density coefficient calculations, the mass of the ions and their respective percent abundance was needed for the given altitudes. These were calculated by taking the molecular mass of the compounds within the three most prevalent cation groups (nitrogenerated cations, short chain hydrocarbons and long chain hydrocarbons) and averaging the mass for each of the three subcategories. Then the percent abundances are acquired from taking the percentage of the mass of the group with respect to the entire positive ion mass. Then using these values, the positive ion mass calculation is built into the following velocity equation [14],

$$\theta = \alpha\sqrt{\frac{kT}{m_1}}+\beta\sqrt{\frac{kT}{m_2}}+\gamma\sqrt{\frac{kT}{m_3}}\ , \qquad (1)$$

where k is Boltzmann's constant, T is temperature, α, β, and γ are the percent abundances for m_1, m_2, and m_3, respectively. Note that this velocity is related to the coefficient of current density calculation, not the relative velocity of the incoming particle.

The relative velocities between aggregate and the incoming particle assuming Brownian motion [15] is

$$v' = \sqrt{\frac{8kT}{\pi\mu}}\ , \qquad (2)$$

where μ is the reduced mass for the two masses, m_1 and m_2, defined as

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)}\ . \qquad (3)$$

IV. METHOD

Using Tholin Builder, aggregates are made in three generations. Beginning with 40 to 50 nanometer sized monomers, the first generation of aggregates is built up to 10 to 15 monomers in size. This growth is considered to take place at about 270 kilometers in altitude with an atmospheric temperature of 175 Kelvin. Assuming an increased gravitational force, monomer charge and plasma parameters are updated for the next generation of aggregates. This second generation consists of about 200 to 300 monomers and is grown at 200 kilometers and 158 Kelvin. Repeating the general process, the final generation is assumed to be at 100 kilometers with a temperature of 140 Kelvin and built up to 2000 to 3000 monomers in size. In all cases, the plasma parameters, including ion masses and densities, are calculated from data given by Molina-Cuberos (1999), and the temperatures are given by Bar-Nun (2008).

Furthermore, the three generations of aggregates are built in two different classes: a nighttime charging class and a daytime charging class. The difference between these resides in the initial charge on the monomers and the charging method used in OML_LOS.

During the nighttime, only charging due to incident galactic cosmic rays is considered, whereas the daytime charging accounts for the resulting photon flux created by the incoming solar ultraviolent radiation. The photon flux in the lower atmosphere was calculated to be $1.29 * 10^9$ $(sm^3)^{-1}$ by only considering the wavelength range of 155-287 nanometers [10] and the solar irradiance given by Woods (1996).

Finally, the collision data collected from the aggregate formations are then used to calculate the coagulation kernel in the Smoluchowsky coagulation equation,

$$Q(m) = -\int_0^\infty K(m,m')\, f(z,m)\, f(z,m')\, dm' + \frac{1}{2}\int_0^m K(m',m-m')\, f(z,m')\, f(z,m-m')\, dm' \quad , \qquad (4)$$

which describes the evolution of particles with a given mass at a specific altitude. Here, f is a function for the density of particles with given masses at certain altitudes, and K is the coagulation kernel. The coagulation kernel is important since it gives the probability of particles with masses, m and m', coagulating [5]. Calculating this kernel is the ultimate goal of this study.

V. RESULTS

As of yet in the overall progress of the study, only the first generations for each of the charging classes have been produced. In order to evaluate the general accuracy of the model, the radius, charge, and collision probability of the aggregates are considered. The subsequent preliminary data is presented below in Fig. 3, 4, and 5 all with respect to the number of monomers present in the aggregate.

Consider first the radial growth of the aggregates as portrayed in Fig. 3. A pleasing linear trend is demonstrated with two discontinuities when the monomer number reaches 10 and 15 in size. With the exception of the abrupt increases, the general pattern is as expected, since adding monomers to an aggregate would increase the volume of the structure, but these inconsistencies show a rapid increase in radius length when the tenth and fifthteenth monomers are added to the structure. In other words, the radius becomes suddenly more linear, and the aggregate becomes less compact at these points.

Similarly, the overall trend for the charge development on the aggregates is consistent with the expected behavior. As more negatively charged monomers are incorporated into the aggregate, the more negatively charged the aggregate itself should become. Also, since the daytime charging is one hundred times smaller in magnitude than the nighttime charging class, it appears constant in comparison; therefore, a close-up graph is provided in Fig. 4. In this secondary graph, the same cumulative growth of negative charge is demonstrated. In both cases, two sudden drops in charge occur at size 10 and 15 monomers, but this would result form the OML_LOS calculation for charge which is dependent on the distance between monomers, which is reflected in the structure's radius.

Finally, as shown in Fig. 5, the collision probability follows a similar trend as the previous two data sets. The percentages for the probability for incoming monomers to coagulate with the central aggregate increase as the aggregate itself increases. This is easily explained by the differences in the electric potential between the two structures. When two monomers or a monomer and a smaller aggregate are attempting to collide, the small difference between their charges allows for the monomer to be repelled. But when the aggregate is more heavily charged, the difference between the potentials is greater, and monomers are more readably able to collide. Furthermore, the collision data is also consistent with the rapid increases at 10 and 15 monomers, which may be due to the sudden jumps in aggregate charge.

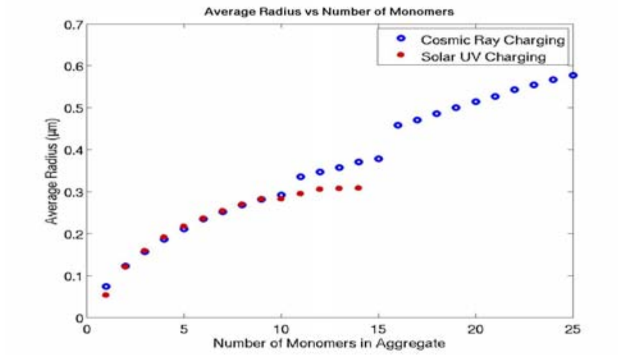

Fig. 3 A graph of the first generation of aggregates' radius versus the number of monomers contained in the aggregate

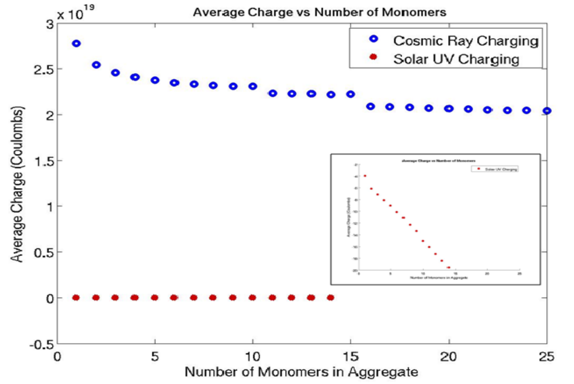

Fig. 4 A graph of the first generation of aggregates' charge given with respect to the number of monomers contained in the aggregate

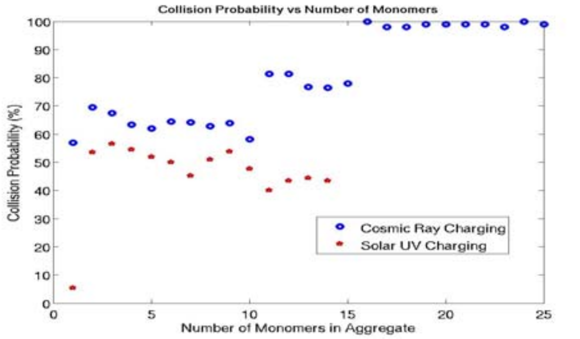

Fig. 5 A graph of the percent collision probability for the first generation of aggregates with respect to the number of monomers contained in the aggregate

Thus far, the discontinuities in the radius data set are unexplainable. It has been suggested by Matthews that this behavior may be related with the fractal dimension. In future works, the correlation between the fractal dimension and the sudden increase in radial length of the aggregates will be discussed or the subsequent error will be corrected.

VI. CONCLUSION

Tholin is an interdisciplinary study in which further research must be done to understand the role it plays in Titan's tropospheric activities. So far in this study, only the first generations in both the nighttime and daytime charging classes have been produced. In future works, the final two remaining generations will be built, and the data collected from their formations will be used to calculate the coagulation kernel in the Smoluchowsky equation.

VII. ACKNOWLEDGMENT

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