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Unraveling the Composition of Tholins Using Very High Resolution Mass Spectrometry

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Abstract

1. Introduction

The destruction of N_2 and CH_4 and subsequent complex chemical processes lead to the formation of organic aerosols in Titan's atmosphere. The CAPS (CAssini Plasma Spectrometer) detection of molecules in Titan's ionosphere with masses in excess of hundreds of u (negative ions with m/z up to 10,000 u/q at 950 km [1], positive ions with m/z up to 400 u/q [2]) suggests that production of aerosols begins in the upper atmosphere [3]. Although CAPS is able to detect these very large molecules and a few of the molecules have been identified [4] it does not have the mass resolution necessary to infer their chemical composition. The ability to create large organic molecules in the upper atmosphere of Titan, or any planet, is of significant astrobiological interest.

2. Sample Production and Analysis

To further our understanding of the formation and composition of these aerosols, laboratory experiments have been designed to produce aerosols under Titan atmospheric conditions. We have characterized Titan aerosol analogues or "tholins" generated by the PAMPRE (Production d'Aérosols en Microgravité par Plasma REactifs) experiment, which uses capacitively coupled RF plasma discharge to initiate the chemistry between N_2 and CH_4 that leads to the production of submicron size solid particles [5]. The tholins form and grow while levitated in the plasma, which minimizes any possible wall effects. Tholins were generated using N_2/CH_4 gas mixtures that range from 2-10% CH_4.

The samples were characterized using an LTQ-Orbitrap XL mass spectrometer, which has a resolving power of better than 10^5 up to 400 u and accuracy in exact mass determination of ± 2 ppm. Custom computer software allows for rapid and accurate assignment of molecular formulas to the spectral peaks. Thousands of molecular formulas have been identified ranging in mass from 50 to 800 u.

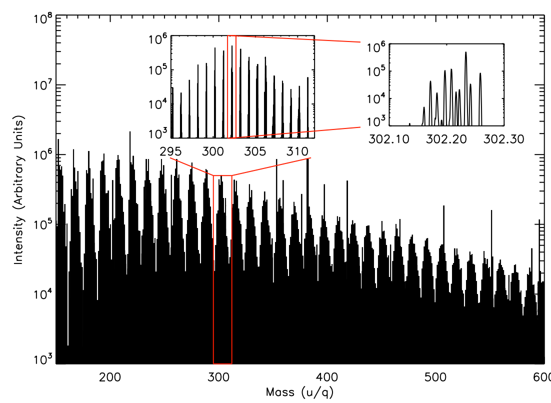

Figure 1: Typical tholin Orbitrap positive ion mode mass spectrum for a 90/10 tholin sample. The inset panels demonstrate the resolution of the Orbitrap and complexity of the tholin samples. In this particular sample, 11 peaks with a nominal mass of 302 are seen above the noise level in the data. There are groups of peaks in the mass spectrum that exhibit very regular spacing of ∼13.5 u.

3. Summary and Conclusions

Groups of peaks with mass spacing of ∼13.5 are observed in all of the tholin spectra. Analysis of the Orbitrap tholin measurements indicates that these groups can be defined by molecules that have a constant number of heavy atoms (C+N). The average number of C, N, and H atoms in each group increases linearly as a function of increasing mass. These trends can therefore be extrapolated to the higher masses observed in the CAPS measurements as a first estimate of the possible composition of those molecules. The spacing appears to be a consequence of the degree of saturation of the molecules. The INMS spectra and the CAPS-IBS (positive ions) spectra exhibit groups of very regularly spaced peaks as well. The spacing in the INMS data is $\sim$12.5 but seems to increase towards 13.5 for the heavier masses in the CAPS-IBS data. The spacing change may be indicative of the transition from gas phase molecules to aerosols.

References

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