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Structural Analysis of Titan's Tholins by Very-High Resolution Mass Spectrometry

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The structure, composition and formation processes of the aerosols constituting Titan's haze are largely unknown. As a consequence, analogs (called tholins) produced in laboratories have been extensively studied with various analytical methods (IR, UV and Raman spectroscopy, NMR, pyrolysis-GC/MS, etc.) and appear to be hydrogenated carbon nitrides with a very complex structure [1,4].

While the techniques mentioned above provide some information on the bulk composition, very-high resolution mass spectrometry (HRMS) with accurate mass measurements is necessary to determine the elemental composition of each individual molecule making up the samples. Moreover, tandem mass spectrometry (MS/MS) experiments can provide complementary information on the functional group inventory in tholins [2]. Based on previous work performed in the positive ionization mode, we propose here a systematic very-high resolution tandem mass spectrometry analysis (HR-MS/MS) of tholins in the negative ionization mode.

Our tholin sample is synthesized at the University of Arizona in a ultra-high vacuum (UHV) reactor by exposing a N2 / CH4 (95% / 5%) gas mixture kept at 195 K to an AC electrical discharge. The tholins soluble fraction is analyzed with two Fourier Transform mass spectrometers: a LTQ-Orbitrap in Grenoble and a 9.4 T FT-ICR in Tucson. The sample is introduced in both mass spectrometers with an ElectroSpray Ionization (ESI) source. Selected ions are submitted to two low-energy collision induced dissociation (CID) methods: collision activated dissociation with He (CAD) in the Orbitrap and Sustained Off Resonance Irradiation CID (SORI-CID) in the FT-ICR. Infrared multiphoton dissociation (IRMPD) MS/MS experiments were also carried out on the FT-ICR instrument.

Spectra obtained in the negative ionization mode are much simpler than the spectra obtained in the positive one. Below m/z 400, they are typically constituted of one or two peaks at each nominal m/z while the positive mode spectra can present up to five or six peaks at each m/z. This is easily understandable as many of the molecules identified as positive ions cannot be easily deprotonated and, as a consequence, do not appear in the negative mode spectra. However, negative mode data reveal highly unsaturated (H poor) molecules with large N content (C/N $\approx$ 1.0) that were not previously observed in the positive ionization mode. This shows the importance of studying tholins ionized in both polarities in order to have a more representative picture of the classes of molecules present in those samples.

HR MS/MS of complex mixtures are extremely difficult to disentangle because of intricate parent/fragment combinations [3]. However, the relative simplicity of the negative mode data allows a more straightforward analysis of the HR MS/MS data. They confirmed the role of the C2N3- anion as a major building block of tholins [4] from which several families of ions can be identified. Iterative HR MS/MS on members of a given family allows retrieving likely structures for those ions.

In the context of a return to Titan, development of very-high resolution ($m/\Delta m > 105$) mass spectrometers for spaceflight capable of in situ sampling of the atmosphere is mandatory, i.e. adding the ability to analyze both positive and negative ions would be very beneficial.

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