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Structural Characterization of Laboratory Made Tholins by IRMPD Action Spectroscopy and Ultrahigh Resolution Mass Spectrometry

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Introduction

The complex organic material that is found on the surface and within the haze layer of Titan is attributed to chemistry occurring in its thick N_2/CH_4 atmosphere. Although several groups are producing in various laboratory setting the so-called tholins which have been investigated by using analytical methods including UV/Vis, fluorescence, IR, and MS[1-5], these very complex organic mixtures still hold many unanswered questions, especially related to the potentiality for their prebiotic chemistry. In addition to tholins characterization and analysis, we recently investigated quantitatively the hydrolysis kinetics of tholins in pure and NH_3 containing water at different temperatures.[7-8] Our groups at UJF (Grenoble) and at U of Arizona (Tucson) have been collaborating on mass spectral analyses of tholins samples for several years.[9] Here, we report our most recent results on the structural characterization of tholins by infrared multiphoton dissociation (IRMPD) action spectroscopy[10] and ultrahigh resolution MS. IRMPD action spectroscopy is a recently developed technique that uses IR photons of variable wavelengths to activate ions trapped inside an ion trap. When photons are absorbed at a given wavelength, the selected ion fragments and this fragmentation is monitored as a function of wavelength, analog to an absorption spectrum (impossible to record otherwise because of the much reduced density). This technique can, therefore, be used to determine IR spectra of ions in the gas phase, and provides with very acute structural information. IRMPD action spectroscopy is often used to distinguish between structural isomers of isobaric ions. The drawback is that it requests for high power lasers. Only two Free Electron Lasers (FEL) are available in the world and allow to record spectra with reasonable resolution (20-25 cm^{-1}). IRMPD action spectra of selected ions from tholins will be presented and discussed together with observed fragmentation processes that reveal structural features of the ions. We have studied ions in the mass range from 60 to 160 u, corresponding to particularly interesting species already characterized by other (e.g. tandem MS/MS) methods.

Methods

Tholin samples were prepared by exposing a mixture of 5% methane and 95% nitrogen to a high frequency electrical discharge under slow flow (6 atm L h-1 and a pressure of 10^{-2} bar) at a temperature of 195 K in a recently designed ultra-high vacuum reaction chamber. Positively and negatively charged ions were generated by electrospray ionization (ESI) from laboratory made tholin samples dissolved in MeOH:ACN 1:1. Ions were selected with the quadrupole mass analyzer and they were then trapped in the ion-cyclotron resonance (ICR) cell of a Bruker Apex Qh 7T FT-ICR instrument. The trapped ions were exposed to laser irradiation for a time of 1-10 s and the mass spectra were collected as a function of IR wavelength (with 5 cm^{-1} increments). IRMPD action spectroscopy measurements were carried out at CLIO[10] (Université Paris-Sud, Orsay, France).

Results

To illustrate the usefulness of IRMPD action spectroscopy a representative spectrum is shown in Figure 1. The spectrum shows all the fragment ions generated by IR irradiation. This representation is rather complex but it is clear that fragmentation ("activity") occurs only in the ca. 1450-1650 cm^{-1} region.

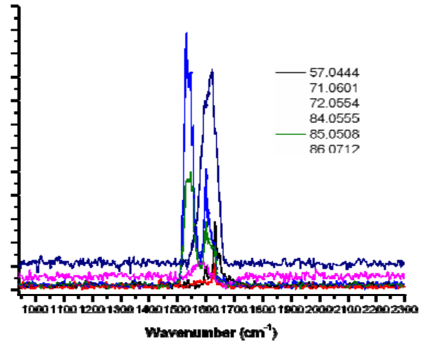

Figure 1 IRPMD action spectrum obtained for positively charged ions at m/z 114 and 113.

The high resolution capability of the FT-ICR instrument allows us to individually select and correlate precursor ion/fragment ion relationships with high mass accuracy as a function of wavelength. Two mass spectra obtained at different IR wavelengths are shown in Figure 2. The upper spectrum (recorded at $\lambda \approx 1550$ cm^{-1}) shows primarily the fragmentation of the positively charged ion at m/z 114.07738 ($C_3H_8N_5$) leading to fragments at m/z 85.05087 ($C_2H_5N_4$, loss of CH_2NH) and m/z 72.05544 (($C_2H_6N_3$, loss of CH_2N_2). The bottom spectrum (recorded at $\lambda \approx 1610$ cm^{-1}) is related to the fragmentation of the ion at m/z 113.08206 ($C_4H_9N_4$) leading to the fragment at m/z 86 ($C_3H_8N_5$, loss of HCN).

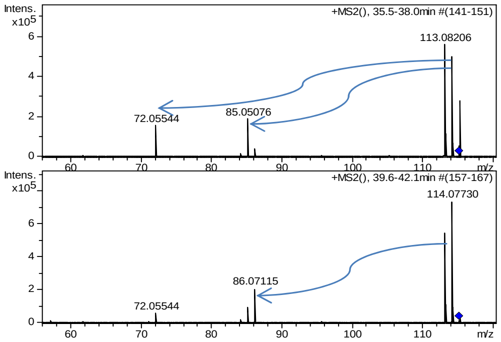

Figure 2 IRMPD fragmentation spectra of m/z 114 ($C_3H_8N_5$) and 113 ($C_4H_9N_4$)

The precursor/fragment correlation can also be presented by monitoring the changes in the appropriate intensities as illustrated in Figure 3 for the 1400-1800 cm^{-1} (active) region.

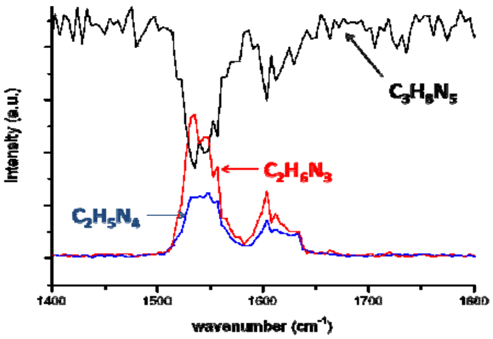

Figure 3 Changes in relative intensities as a function of wavelength of the m/z 114 ($C_3H_8N_5$) precursor ion and two of its fragments (m/z 85 and 72, $C_2H_5N_4$ and $C_2H_6N_3$, respectively).

Together with quantum chemical calculations of theoretical IR spectra, other experimental IRMPD spectra for representative positively and negatively charged ions will be shown and structural features will be discussed. Among others, we were able to detect IR absorption bands corresponding to the cyano group (around 2300 cm^{-1}) and also for a carboxyl group (for a hydrolyzed sample, at around 1620 cm^{-1}). In agreement with the theoretical prediction, an IR absorption band was also detected at 1689 cm^{-1} for the protonated guanidino group at m/z 60 (CH_6N_3). The IRMPD results presented provide strong evidence for the presence of chemical groups of great biological potential.

Conclusion

IRMPD action spectroscopy of mass selected tholin ions has been recorded on a series of species. These results will be interpreted with the help of quantum calculations, in order to extract structural information on these species and will serve as benchmark to help interpret extensive series of structural measurements performed with Collision Induced Dissociation Tandem mass spectrometry (CID MS/MS).

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