

CHEMICAL STRUCTURE AND OPTICAL PROPERTIES OF TITAN'S THOLINS AND "HCN POLYMER". IMPLICATIONS FOR THE ANALYSIS OF CASSINI-HUYGENS OBSERVATIONS AND REFRACTORY ORGANICS IN COMETARY GRAINS. E. Quirico, J-M Bernard, G. Montagnac, J-N Rouzaud, C. Szopa, G. Cernogora, B. Reynard, P. Mc Millan, N. Fray, B. Schmitt, P. Coll and F. Raulin. ¹Laboratoire de Planétologie 38041 Grenoble Cedex France (eric.quirico@obs.ujf-grenoble.fr), ²Laboratoire de Sciences de la Terre ENS-Lyon 69364 Lyon Cedex 7 France, ³Laboratoire de Géologie ENS-Paris 75 Paris France, ⁴Service d'Aéronomie 91371 Verrières le Buisson Cedex France, ⁵University College of London UK, ⁶Laboratoire Interdisciplinaire des Systèmes Atmosphériques 94010 Créteil France.

Introduction: Tholins and "HCN polymer" are used as analogs of Titan's aerosols and N-rich cometary refractory organics, respectively [1,2]. The chemical structure of these compounds is up to now not elucidated, as well as the identification of the parameters which do control their optical properties.

This study provides new clues on the chemical structure of these compounds, and we discuss some implications for 1) the analysis of spectral data of the CASSINI-HUYGENS mission and 2) the analysis of organic N-rich compounds in cometary grains.

Experimental: Raman experiments were performed using visible and UV Jobin-Yvon LabRaman spectrometers, and an Ar+ laser (514 nm) and a frequency-doubled Ar+ laser (244 nm) for excitation, respectively. The size of the laser spot onto the sample was around ~ 2-3 μm in the visible, and slightly more in UV. Most of UV Raman spectra were recorded with a 600 gr/mm grating in order to optimize the acquisition time, and great care was taken for avoiding thermal and photolysis damage on the samples.

Samples: Tholins were produced from two different experiments located in Service d'Aéronomie (Verrières-le-buisson - France), and in LISA (Créteil France). The first uses a cold plasma capacitively coupled to a radio-frequency power source [3], the second is coupled to an electric discharge [4]. The same HCN polymers (poly-HCN) used in the earlier study [1] were also analyzed. All samples are mostly insoluble in polar (Me-OH) and apolar (Cl_2CH_2) organic solvents, evidencing a covalent macromolecular structure. Optical observations reveal that SA tholins (SA-tholins) are optically homogeneous, unlike poly-HCNs and tholins produced at LISA (L-tholins) which are optically heterogeneous at the micrometric scale [5].

SA-tholins were selected because of their optical and textural homogeneity. Samples produced from three initial $\text{N}_2:\text{CH}_4$ mixtures (1:99, 2:98 and 10:90) were studied: SA99, SA98 and SA90. The color of the two first ones is dark-brown, the latter is yellow. Infrared spectra of these samples are consistent with those of L-tholins, and tholins formed by other groups [2, 5].

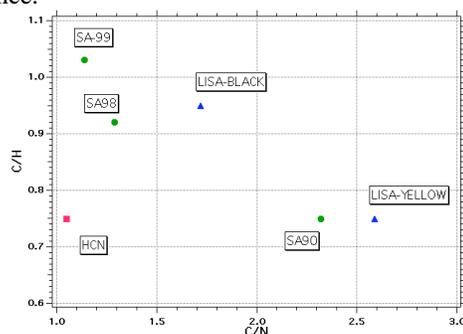


Fig. 1: Elemental compositions of studied samples: SA90/98/99, the two L-tholins studied in [5], and poly-HCN. Note the lack of straightforward correlation between sample color and elemental composition.

LIF and UV Raman spectroscopy: Laser Induced Fluorescent (LIF) measurements were achieved with a 514 nm excitation. The spectra reveal that SA-tholins are chemically homogeneous at the micrometric scale, whereas L-tholins are not. SA99 and SA98 exhibit rather similar fluorescence spectra. Using a UV excitation, the Raman signal is revealed in the absence of fluorescence and provides clues on the solid structure, mostly sp^2 ordering and clustering [6].

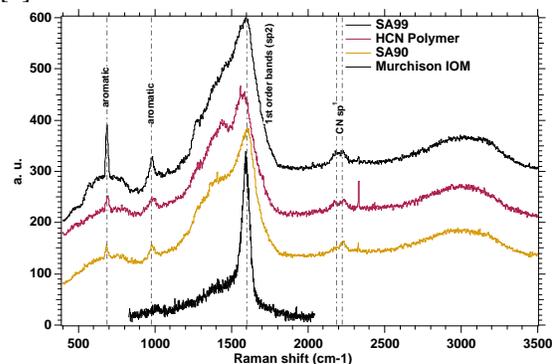


Fig.2: UV Raman spectra of SA99, poly-HCN, SA90 and Murchison IOM. Note the unambiguous discrimination between the amorphous vs. polyaromatic structure in Murchison IOM, valuable for analyzing cometary grains.

Spectra of SA-tholins are consistent with the earlier study of L-tholins by [5], and exhibit the same spectral features. They do reveal an amorphous structure, consisting of a macromolecular network,

with small inserted aromatic units and terminating sp^1 CN functions. The sp^2 clustering thus consists of aromatic rings, probably N-substituted, and conjugated chains as evidenced by the broad first-order carbon bands. Spectra were fitted using a LBWF model for fitting the G and D bands[6], supplemented by a Lorentzian profile for the aromatic breathing mode at $\sim 980\text{ cm}^{-1}$ (called A band). The data point out a much higher sp^2/sp^3 ratio and in particular a higher abundance of small aromatic units in SA99/SA98 than in SA90 (Fig. 3). Differences in the sp^2 chemical structure among SA-tholins is also clearly evidenced, by the spectral profile of the $\sim 2200\text{ cm}^{-1}$ of the CN band, and the spectral parameters of the G and D bands. Note that the Raman data of SA99 and SA98 are rather similar, though slight differences may be pointed out.

Poly-HCN exhibits Raman spectra very similar to those of tholins, while their IR spectra are slightly different. These solids should be considered as amorphous hydrogenated carbon nitrides, with a sp^2 structure similar to that of tholins, but with a significantly different chemical composition. We suggest that the term “polymer” is misleading to qualify these complex solids.

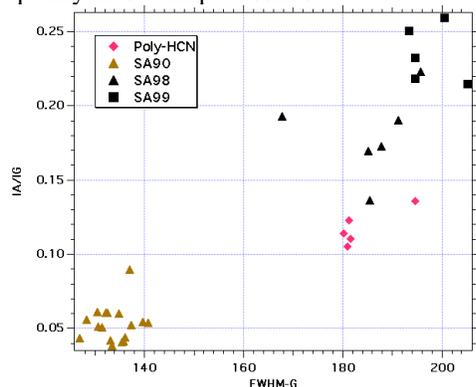


Fig. 3: Ratio of the intensities of the A and G bands, versus the width of the G band. The former reveals the lower abundance of small aromatic units in SA90 than SA99/98 and poly-HCN.

HRTEM analysis: HRTEM images first reveal the texture of the samples, as homogeneous sub-micrometric spheres. Images in 002 lattice mode point out very disordered samples, consistently with the amorphous structure evidenced by UV Raman spectroscopy (Fig. 4). 002 images were treated using a dedicated numerical method, providing semi-quantitative structural information [7]. SA99/SA98 appear slightly more organized than SA90: smaller d (0.40 vs 0.42 nm), larger correlation domain diameter L_c (0.30 vs 0.25 nm), height of stacked

layer L_c (0.53 vs. 0.47 nm) and weaker amount of stacked layer (45 vs. 75 %).

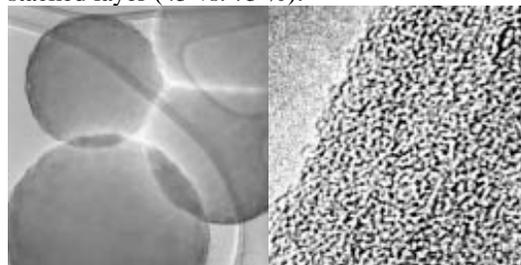


Fig. 4: Tholin SA90 as observed by HRTEM. Left : bright field mode (1.1x1.1 μm); right : 002 lattice mode (19x19 nm), evidencing the amorphous structure and the low size of the aromatic units.

Implications : Tholins produced by two different experiments, P-tholins and L-tholins, are rather similar but exhibit differences with important consequences on the use of the sample for interpreting observational spectral data. There is no straightforward correlation between the color and the elemental compositions, demonstrating that there is no univocal relationship between optical properties and chemical composition. Optical properties in the Vis-NIR range are indeed mostly controlled by the sp^2 (C,N) structure, through $\pi-\pi^*$ electronic transitions. Different sets of experimental conditions may lead to samples with very similar sp^2 structure, but with variations of their composition. It thus appears very unlikely to derive such chemical parameters from remote sensing data in this spectral range, as well as physical parameters relevant to the formation conditions (e.g. pressure) [2].

This structural study by combined UV Raman, IR spectroscopy and HRTEM reveals that the so-called HCN polymer is an amorphous carbon nitride solid, and should not be termed as a “polymer”. It has a sp^2 (C,N) structure rather similar to that of tholins, but slight differences in the chemical composition. Our results demonstrate that the identification and characterization of this compound in cometary grains (IDPs, STARDUST samples), and any N-rich refractory organics, is possible with UV Raman spectroscopy (Fig. 2).

References:

- [1] Fray N. et al. (2004) MPS, 39, 581-587. [2] Imanaka et al (2004). Icarus, 168, 344-366. [3] Szopa et al. (2003) EGS-AGU, Abstract 8523 ; Szopa et al. (2006) Planet. Spa Sci. In press [4] Coll et al. (1999) Planet. Spa Sci, 47, 1331-1340. [5] Bernard et al. Icarus Submitted. [6] Ferrari and Robertson (2000) PhysRevB, 61, 14095-14107 [7] Rouzaud and Clinard (2002) Fuel ProcTech, 77-78, 229-235