

USE OF THE LINEAR ABSORPTION COEFFICIENT FOR ABSOLUTE COMPARISON OF PLASMA FILMS IN THE MID-IR RANGE

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In this work, we present the mid-infrared analysis of analogues of Titan's aerosols produced in a radio frequency capacitively coupled plasma (RF-CCP). The influence of the gas mixture on aerosols spectra is also studied through the analysis of the carbonaceous bands of the spectra, and its Gaussian deconvolution.

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INTRODUCTION

Titan's atmosphere is the place of a complex organic chemistry initiated from dissociation of its main constituents, *i.e.* N₂ and CH₄. This chemistry leads to the formation of solid aerosols and can be simulated in laboratory using a RF-CCP setup [1].

In this work we propose a method for infrared analyses that allows direct comparison of different samples. This method is used for the analysis of the carbon-hydrogen bonding in the organic material produced with the plasma.

1. THE PAMPRE EXPERIMENT

Fig. 1 present the experimental setup. The reaction chamber is a stainless-steel cylinder 30 cm in diameter and 40 cm in height. The plasma is confined in a metallic box 13.7 cm in diameter and with a 4...5 cm inter-electrode gap (Confining Box CB). The bottom of the box is meshed to allow sweeping the dust out. On the side of the box, two 1 cm-wide apertures, covered with a thin grid, allow studying the plasma using optical emission spectroscopy (OES) using a -UV-VIS-NIR Monochromator (SP) fitted with a - Photomultiplier; (PM) and a Picoampmeter (PA) [2]. This configuration, already used in the GREMI laboratory [3] is known to produce dust in a reactive gas mixture [4]. Other available diagnosis are, FTIR, mass spectrometry [5], cryogenic trapping associated to gas chromatography-mass spectrometry [6], the electron density measurements using the confining box as a resonant microwave cavity and the self-bias voltage (Vdc).

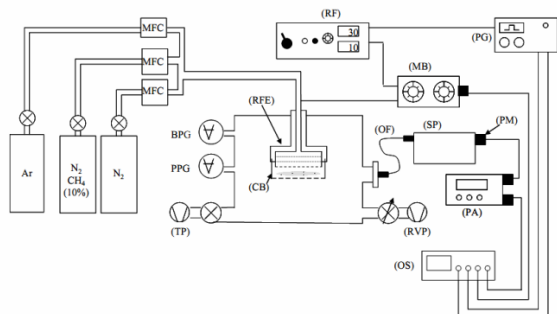


Fig. 1. Experimental setup of the PAMPRE experiment

Before production of samples, the reactor is heated and pumped with a turbo molecular pump (TP) down to a secondary vacuum measured with a penning gauge (PG).

Reactive gas (*i.e.* mixture of N₂ and CH₄) is injected through a shower head located above the top electrode using mass flow controllers (MFC) and pumped by a rotary vane pump (RVP). Pressure is measured with a capacitance gauge (BPG). Organic solid material are produced at room temperature, with a pressure of 90 Pa and a gas mixture varying from 1 to 10 % of CH₄ in N₂.

Samples can be produced either as bulk dust or deposited as thin films on substrates placed on the confining box, directly inside the plasma. Tholins analyzed in this work were deposited as thin film on low-emissivity infrared mirror (MirrIR™).

2. SAMPLE ANALYSIS AND DISCUSSION

Analyses of organic film absorption in the Infrared were performed at the SMIS beamline of SOLEIL synchrotron facility, France [7]. We used a NicPlan microscope coupled to a Nicolet Magna System 560 Fourier Transformed Infrared spectrometer. The Infrared source was the synchrotron radiation and the detector was a Mercury-Cadmium Telluride (MCT) detector. Infrared spectra were performed in double transmission mode.

Spectra were recorded at a spectral resolution of 4 cm⁻¹ after co-adding 512 scans at a Michelson mirror velocity of 1.26 cm·s⁻¹. Spectra cover the full mid and far infrared range, from 50 cm⁻¹ (200 μm) up to 4500 cm⁻¹ (2.2 μm). This work will focus on the 2800...3000 cm⁻¹ wavenumber range, corresponding to the aliphatic carbons bands.

In order to compare several samples, it is needed to calibrate absorption spectra according to the thickness of the films. Indeed, after absorption in the sample, the intensity of the beam follows the Beer-Lambert law that can be established as:

$$I_t = I_0 \times \exp(-\epsilon \times d).$$

Where d is the sample thickness, I_t the intensity of the transmitted beam, I_0 the initial intensity and ϵ is the linear absorption coefficient of the material.

As film thickness d (a few hundreds nanometers) varies with discharges conditions, d is measured for each sample by ellipsometry [8].

The full spectra in the mid-infrared of tholins is presented Fig. 2.

The different curves correspond to spectra of tholins produced with different gas mixtures (respectively 1, 2, 5 and 10 % of CH_4 in N_2). These spectra present common tholins absorption features in the mid-infrared, widely described in literature [9-11].

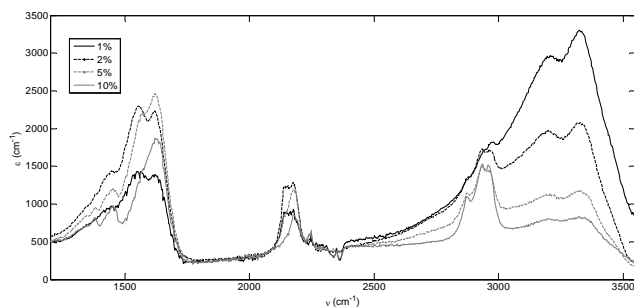


Fig. 2. Spectra of tholins produced with different gas mixture. Full black curve: 1 % CH_4 ; Dashed black: 2 % CH_4 ; Dashed grey: 5% CH_4 ; Full grey: 10% CH_4 . Adapted from [11]

Two broad bands coming from amine ($-\text{NH}$ and $-\text{NH}_2$) stretching modes are visible at high wavenumber (3200 and 3330 cm^{-1}). Close to these bands is the pattern attributed to aliphatic carbons ($-\text{CH}_2$ and $-\text{CH}_3$) stretching modes, around 2900 cm^{-1} . This pattern will be discussed in details later. The three bands observed around 2200 cm^{-1} can be attributed to nitriles ($-\text{C}=\text{N}$), isocyanides ($-\text{N}=\text{C}$) and carbodiimide ($-\text{N}=\text{C}=\text{N}-$) stretching modes. Finally, the intense bands at 1560 and 1630 cm^{-1} cannot be unambiguously attributed since they could correspond to several functional groups bending modes such as $-\text{NH}_2$, $\text{C}=\text{C}$, $\text{C}=\text{N}$ or aromatics.

To study the impact of methane percentage in the experiment on aliphatic carbon content, we used a poly-Gaussian deconvolution (performed with fityk software) of the 2900 cm^{-1} pattern as proposed in [9].

In order to study this pattern, it was first necessary to remove the component due to the presence of amines bands at higher wavenumbers, considering this amine band as a baseline for the aliphatic carbons bands. This means that the pattern visible on Fig. 2 is only due to the contribution of aliphatic carbons ($-\text{CH}_2$ and $-\text{CH}_3$) bands. This $2800\text{--}2900\text{ cm}^{-1}$ pattern is fitted by a combination of Gaussian functions. In this spectral range, there are up to five possible stretching modes for C-H bonding, corresponding to $-\text{CH}_3$ asymmetric ($\sim 2970\text{ cm}^{-1}$); $-\text{CH}_2$ asymmetric ($\sim 2930\text{ cm}^{-1}$); $-\text{CH}$ ($\sim 2900\text{ cm}^{-1}$); $-\text{CH}_3$ symmetric ($\sim 2870\text{ cm}^{-1}$) and $-\text{CH}_2$ symmetric ($\sim 2850\text{ cm}^{-1}$).

The fitting process was thus initialized with five Gaussians at these positions. Figs. 3 and 4 present the fit for samples produced with 1 and 10 % CH_4 . Dots are the experimental spectra, dashed lined are the Gaussians used for the fit, and full line is the resulting model.

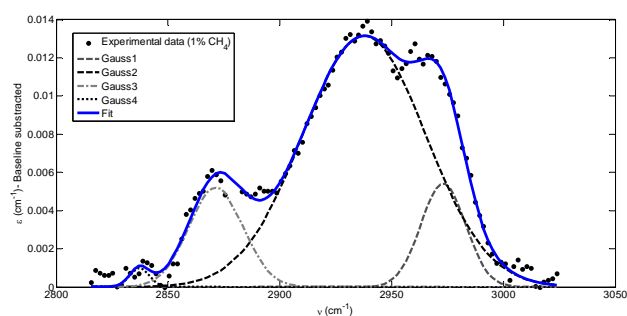


Fig. 3. Deconvolution of films 1% CH_4 -spectrum

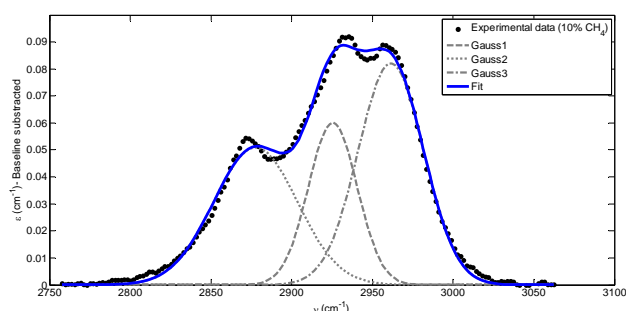


Fig. 4. Deconvolution of films 10 % CH_4 -spectrum

The first information in this plot is the global intensity of this pattern, which regularly increases with the methane percentage in the experiment. Indeed, ϵ''_{max} is around 1.10^{-2} cm^{-1} for 1 % CH_4 , 4.10^{-2} cm^{-1} for 2 % CH_4 , 6.10^{-2} cm^{-1} for 5 % CH_4 and 9.10^{-2} cm^{-1} for 10 % of CH_4 in the experiment. This means that the global amount of aliphatic carbon in tholins increases with the percentage of methane in the mixture used to produce tholins. This is also consistent with the decrease of amines bands when CH_4 increases in the experiment, visible on Fig. 2.

Secondly, as visible on these figures, most part of the signal comes from only three of the Gaussians, corresponding to $-\text{CH}_2$ asymmetric and $-\text{CH}_3$ symmetric and asymmetric stretching. Looking to the respective weight of these three Gaussians in the fit, one can see that the $-\text{CH}_2$ are the predominant bonding in tholins produced with 1 % of CH_4 . But when methane percentage increases, $-\text{CH}_3$ become slightly more abundant than $-\text{CH}_2$. This augmentation is consistent with elemental analysis performed previously on tholins [12] which showed that the H/C ratio in tholins increases with methane percentage.

CONCLUSIONS

In the present work, the proposed method for infrared analysis of organic thin film allows quantitative comparison of different samples.

The comparison of spectra of thin film produced with different methane percentage shows the decreases of amine bands and increases of carbon bands, and also the evolution of the 2900 cm^{-1} pattern.

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ИСПОЛЬЗОВАНИЕ ЛИНЕЙНОГО КОЭФФИЦИЕНТА ПОГЛОЩЕНИЯ ДЛЯ АБСОЛЮТНОГО СРАВНЕНИЯ ПЛАЗМЕННЫХ ПЛЕНОК В СРЕДНЕМ ИК-ДИАПАЗОНЕ

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Представлен анализ в среднем инфракрасном диапазоне аналогов титановых аэрозолей, которые производятся в радиочастотных источниках плазмы с емкостной связью (РЧ-ЕСС). Также изучено влияние газовой смеси на спектры аэрозолей с помощью анализа углеродсодержащих полос спектра и ее гауссовой деконволюции (обратная свертка).

ВИКОРИСТАННЯ ЛІНІЙНОГО КОЕФІЦІЕНТА ПОГЛИНАННЯ ДЛЯ АБСОЛЮТНОГО ПОРІВНЯННЯ ПЛАЗМОВИХ ПЛІВОК У СЕРЕДНЬОМУ ІЧ-ДІАПАЗОНІ

T. Gautier, N. Carrasco, A. Mahjoub, I. Stefanovic, C. Szopa, G. Cernogora, E. Hadamcik, J. Winter

Представлено аналіз у середньому інфрачервоному діапазоні аналогів титанових аерозолів, які проводяться в радіочастотних джерелах плазми з ємнісним зв'язком (РЧ-ЕСС). Також вивчено вплив газової суміші на спектри аерозолів за допомогою аналізу вуглецевмісних смуг спектра і її гауссової деконволюції (зворотня згортка).