UV/Vis-IR-THz spectroscopy for conservation studies of ancient paper

M. Missori[1*], A. Mosca Conte[2], J. Bagniuk[3], M. Clerici[4,6], J. Łojewska[3], M. C. Misiti[5], R. Morandotti[6], M. Peccianti[1,7], O. Pulci[2], L. Teodonio[1,2,5], C. Violante[2]

[1]ISC-CNR, via Salaria km 29.300, 00015 Monterotondo Scalo (Rome), ITALY
[2]ETSF, Università di Roma Tor Vergata, via della Ricerca Scientifica 1, 00133 Rome, ITALY
[3]Jagiellonian University, Ingardena 3, 30-060 Kraków, POLAND
[4]Heriot‑Watt University, Edinburgh EH14 4AS, UK
[5]ICRCPAL, MIBACT, via Milano 76 00184, Rome, ITALY
[6]INRS-EMT, University of Quebec, 1650 Blvd. Lionel-Boulet, Varennes, Quebec J3X 1S2, CANADA
[7]University of Sussex, Falmer (Brighton) BN1 9QH, UK

***Abstract*—We developed UV/Vis-IR-THz theoretical and experimental spectroscopic approaches for non-destructive diagnostic analysis of ancient paper. Important paper artefacts such as the Leonardo da Vinci's self-portrait were studied.**

I. INTRODUCTION

PAPER has been widely used as convenient vehicle for the acquisition, storage and dissemination of human knowledge. For centuries, a growing number of cultural resources have been accumulating in archives, libraries and museums. The preservation of these cultural properties poses the significant challenge of limiting the deterioration of ancient paper. An advanced knowledge of the microscopical characteristics of paper and its degradation processes is indispensable in order to fulfill this objective.

Paper sheets are mostly constituted of cellulose, the most abundant biopolymer on Earth. The increasing fragility and yellowing that are commonly observed in the ancient paper-based artifacts have been explained by the increasing fragmentation of cellulose polymers (depolymerization) and their oxidation.

In order to recover chemical information, we applied a theoretical-experimental approach based on ultraviolet/visible (UV/Vis) spectroscopy. In this way we were able to obtain non-invasive measurements of the concentration of oxidized functional groups in cellulose acting as chromophores and responsible of paper yellowing [1]. In this presentation we will shortly review this method [2] and show an application to the Leonardo da Vinci's self-portrait [3]. Moreover, more detailed information on depolymerization and oxidation mechanisms of ancient paper has been recently obtained by infrared (IR) and THz spectroscopies, supported by theoretical *ab-initio* computational simulations.

II. RESULTS

Our UV/Vis spectroscopy studies allowed us to explore the formation kinetics of chromophores in aged cellulose. Studies were performed on modern reference paper samples artificially aged in several environmental conditions. Results clearly showed that chromophores transform in not UV/Vis active oxidized forms as paper degradation proceeds. A quantitative but non-destructive approach for the measurement of the overall concentration of oxidized functional groups in cellulose was therefore developed. It is based on the comparison of experimental IR spectra of samples without water IR signal, with theoretical computational simulation based on the density functional theory (DFT) including Van der Walls interactions.

The experimental and theoretical IR analyses have been extended up to the THz region [4] which is dominated by collective atomic vibrational modes (Fig. 1). These modes are directly correlated to cellulose crystallinity which, in turn, depend on the depolymerization of cellulose polymers. Noteworthy our investigations via THz Time-Domain Spectroscopy provided access to the average optical density spectrum. This information is in general not available in other frequency ranges, although its relation with the molecular morphology of the sample is still under investigation.

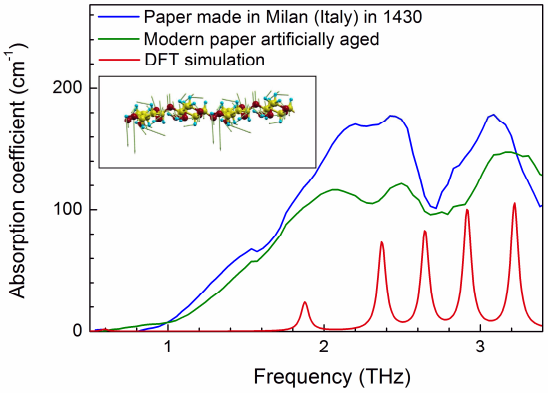

Fig. 1. THz experimental spectra of paper samples acquired at INRS- EMT facility compared with *ab-initio* theoretical computational simulations. In the inset atomic displacement vectors of cellulose polymer for 1.9 THz mode are represented.

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(*) Corresponding author. E-mail address: mauro.missori@isc.cnr.it