

FT-Raman Spectra of Cellulose and Lignocellulose Materials: “Self-Absorption” Phenomenon and its Implications for Quantitative Work

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ABSTRACT

The phenomenon of “self-absorption” was found to exist in the FT-Raman spectra of cellulose and thermomechanical pulp (TMP), but not in the spectrum of milled wood lignin. For cellulose and TMP, the effect was responsible for reducing the intensity of the Raman bands in the C-H stretch region. Several factors including sampling position, sample thickness, and moisture content of the sample affected the band suppression due to self-absorption. The intensity reduction, detected only in the C-H stretch region, was largely due to the fact that the aliphatic- and water- hydroxyl groups have non-fundamental vibration transitions in the near-IR frequency range that are coincident with the C-H Raman frequency shifts in FT-Raman. In light of these findings, ways are discussed to minimize or avoid the impact of self-absorption in quantitative work.

INTRODUCTION

Although cellulose and lignocellulose materials have been studied using conventional Raman spectroscopy, availability of the FT-Raman instrumentation has made studying these materials more convenient [1]. Especially because the problem of laser induced fluorescence can be avoided or minimized. Many FT-Raman studies of such materials have been published including studies of quantitative nature [2-4].

In FT-Raman spectroscopy, self-absorption (defined as absorption of Raman scattered photons by the sample itself) has been studied before [5, 6] and it was reported that its influence in a Raman spectrum is manifested in the spectral region where the sample absorbs (sample absorption due to overtone and combination vibration bands). The net result being that the Raman band intensity (ies) will be diminished. Previously, for samples that have electronic absorption in visible, researchers have pointed out the occurrence of self-absorption in resonance Raman spectroscopy [7, 8]. Although only a small number of samples have strong electronic absorption in visible, in near-IR, many more are expected to have overtone and combination vibration transitions. Additionally, in near-IR Raman, because

sampling occurs deeper into the sample, the self-absorption, if present, can be more problematic.

METHODS AND MATERIALS

Cellulose filter paper Whatman # 1 sheets were used as cellulose samples. Milled wood lignin (MWL) was isolated from black spruce wood using the previously reported isolation procedure [9]. Thermomechanical pulp (TMP) was a gift from Consolidated Papers, (now Stora Enso North America).

The FT-Raman instrument used was Bruker’s RFS-100 which is capable of producing 1 W of laser power output at 1064 nm. Samples were analyzed in the 180° scattering geometry and a sample stage micrometer was used to position the sample along the optical axis of the spectrometer. Spectra were obtained from several sample positions around the focal plane. In some of the acquisitions a front-surface coated mirror was positioned behind the sample to determine how band intensities, relative to one another, in a spectrum were affected. Sample thickness and moisture changes were two other variables that were investigated. Samples were either thin strip (Whatman # 1) or pressed pellets of varying thickness (MWL and TMP). Near-IR measurements were carried out on the Bruker’s IFS66 that was equipped with a Spectra-Tech diffuse Reflectance accessory.

RESULTS AND DISCUSSION

Effect of sample position

It has been reported that when self-absorption is present, band heights in a Raman spectrum depend upon the sample position [10]. Samples of cellulose, MWL, and TMP were studied at various sampling positions (distance from focus in Fig. 1, MWL data not shown) and, for the TMP and cellulose, the band peak heights were calculated after normalizing spectra on the 1098 cm^{-1} Raman band. It was found that, between spectra, except for the 2890 cm^{-1} band the intensity of all other bands were similar indicating that the C-H stretch band intensity was suppressed due to self-absorption. In Fig. 1, the 2890 cm^{-1} band intensity decline (%) is plotted against the sample position. The choice of the reference band at 1098 cm^{-1} was based on the fact that this band is moderately intense and occurs at 8300 cm^{-1} (absolute frequency) where no absorption is detected in the near-IR spectra of cellulose, MWL, and TMP (Fig. 2). One of the other lower frequency (lower than 1098 cm^{-1}) bands of cellulose can also be used as a reference band for spectra normalization purposes.

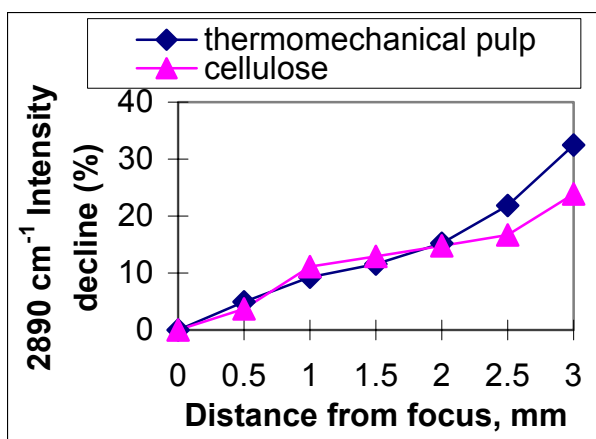


Fig. 1. 2890 cm^{-1} band intensity decline in the FT-Raman spectra of cellulose and thermomechanical pulp. The decline is higher for sampling positions that are farther from the focal plane.

In case of MWL, after normalizing at 1600 cm^{-1} band [9], all spectra showed similar peak intensities and therefore, indicated that self-absorption was not an important consideration for quantitative analysis of MWL by FT-Raman spectroscopy.

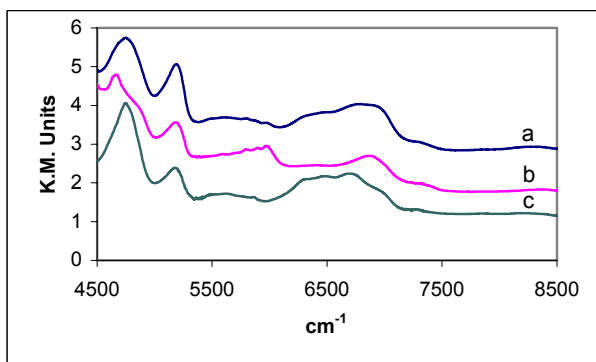


Fig. 2. Near-IR diffuse reflectance spectra of (a) thermomechanical pulp, (b) MWL, and (c) Whatman #1 cellulose; In (a), (b), & (c), no absorption is seen at 8300 cm^{-1} (corresponding to a Raman shift of 1098 cm^{-1}) but in (a) & (c) significant absorption is observed at 6500 cm^{-1} (corresponding to 2890 cm^{-1} Raman shift).

Effects of sample thickness and mirror positioning

Effect of sample thickness on self-absorption was evaluated by studying TMP pellets of varying thickness or in case of cellulose, by analyzing several Whatman # 1 sheet portions together. For a given sample position, it was found that the thicker the sample the larger the decline in the relative peak intensity of the band at 2890 cm^{-1} . These results can be understood in

terms of higher absorption of the Raman scattered photons in a thicker sample. Fig. 3 and Table 1 show results for the cellulose paper sample.

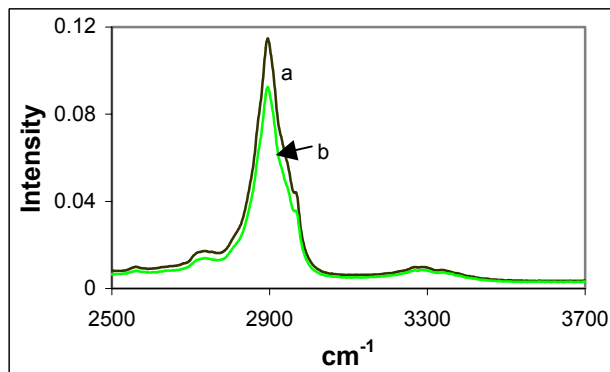


Fig. 3. Effect of sample thickness on the suppression of the 2890 cm^{-1} band; (a) single sheet and (b) 3 sheets of cellulose Whatman # 1 sample. Spectra were normalized on the 1098 cm^{-1} band (not shown).

Table 1: Peak height of 2890 cm^{-1} band, after normalizing on 1098 cm^{-1} band, in the spectrum of cellulose (Whatman # 1)

Sample	I_{2890}	% Decline
Control, single sheet	111	—
Thick, 3 sheets	91	18.02
Mirror behind the control	100	9.9
Control plus 25 μl H ₂ O	76	31.5
Control plus water, after evaporation	100	9.9

In FT-Raman, often, to increase signal, a front-surface coated mirror is put behind the thin samples. Based on our analysis of the spectra of thin and thick samples of cellulose and TMP, having a mirror resulted in the 2890 cm^{-1} band being suppressed only in the thin samples (Fig. 4 & Table 1). This is explained by the fact that using a mirror is equivalent to increasing the sample thickness because the laser beam makes an additional pass, after being reflected from the mirror, from the back of the sample to the front. For thick samples, on the other hand, the beam is already diffused and weak, and therefore, it is reflected negligibly from the mirror.

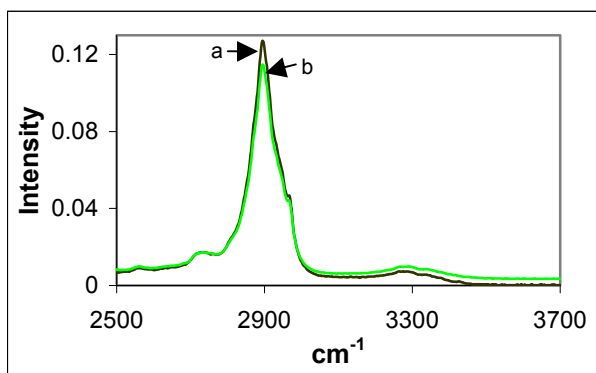


Fig. 4. Role of mirror causing the suppression of the 2890 cm^{-1} band; (a) without mirror and (b) with mirror; single sheet of cellulose Whatman # 1 sample. Spectra were normalized on the 1098 cm^{-1} band (not shown).

Role of water

In near-IR, water absorbs strongly in the $9500\text{--}5500\text{ cm}^{-1}$ range [5]. Comparing the near-IR absorption spectra of water, cellulose and TMP, it can be concluded that the hydroxyl groups in the samples are to a large part responsible for the suppression of the bands in the C-H stretch region. To further evaluate the role of water and carbohydrate O-H groups, cellulose Raman spectra were obtained both before and after adding a small amount ($25\text{ }\mu\text{l}$) of water (Fig. 5). As expected, after adding water the 2890 cm^{-1} band intensity declined substantially (Fig. 5b & Table 1) but as water evaporated, the band intensity recovered (Fig. 5c & Table 1). Clearly presence of water diminished the intensity of the 2890 cm^{-1} C-H stretch band in the cellulose sample.

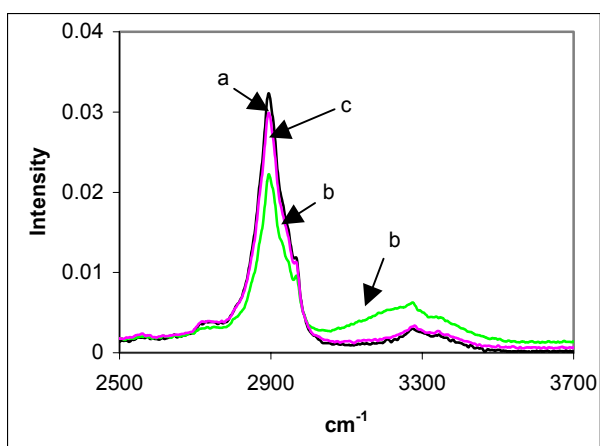


Fig. 5. Effect of small amount of water on the cellulose sample; (a) control, (b) with $25\text{ }\mu\text{l}$ H_2O added, and (c) after most H_2O has evaporated

Implications for quantitative work

In FT-Raman analysis of a sample, one simple way to determine whether or not self-absorption is likely to be a problem is to obtain a near-IR spectrum of the sample (or obtain it from the literature if available) and determine if over the range of Raman measurement any near-IR absorption is present. In case near-IR absorption is present and self-absorption is predicted in FT-Raman, wherever possible, thin samples ought to be used because thin samples are less prone to showing band suppression. Also, using samples with identical thickness may be warranted, as the effect will then not vary from one sample to the next. Lastly, in quantitative work, one could avoid self-absorption problems by avoiding peaks in the C-H stretch region. In case a study uses H_2O replacing it with D_2O should be considered.

CONCLUSIONS

Self-absorption effect was found to be present in cellulose and TMP but not in MWL. The effect suppressed the intensity of the 2890 cm^{-1} band in the C-H stretch region of the FT-Raman spectra. In pulp and cellulose, the hydroxyl groups - present both in carbohydrates and water, cause the suppression effect. Although, in quantitative work, certain precautions can be taken to minimize the detrimental effect of this phenomenon, it is best to choose a band that is not in the C-H stretch region of the spectrum.

DISCLAIMER

The use of trade or firm names in this publication is for reader information and does not imply endorsement by U.S. Department of Agriculture of any product or service.

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