FT-Raman Study of Dehydrogenation Polymer (DHP) Lignins

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ABSTRACT

Compared to conventional Raman spectroscopy where samples are excited using visible light lasers, 1064 nm-excited FT-Raman technique has the single most important advantage that the sample-fluorescence is significantly suppressed for samples that are strongly fluorescent. DHPs are difficult to analyze in conventional Raman because small amounts of chromophores present in their structures make them highly fluorescent. An FT Raman study of S-, GS-, G-, HG-, and H-DHPs along with two deuterated analogues of G-DHP was carried out with the objectives of understanding the similarities and differences in their Raman spectra and to use such information towards interpreting and identifying lignin contributions in the Raman spectra of lignins and lignin-containing materials.

INTRODUCTION

Raman spectroscopy is being increasingly used in the analysis of lignin containing materials [1]. Although earlier Raman studies, performed using visible laser excitation, were useful in some ways, significantly more useful information has been obtained using FT-Raman technique. This is largely due to the fact that, for most lignin-containing samples, laser-induced fluorescence is no longer a problem. FT-Raman studies of woods, pulps, and milled wood lignins have been published.

Before Raman information belonging to lignin can be deciphered, basic knowledge needs to exist that will facilitate such an analysis. Although, already, for some lignins the Raman bands have been identified [2]. Additionally, spectra need to be analyzed for similarities and differences and interpreted in terms of molecular structure. In the present work, a number of DHPs - including two deuterated analogues of guaiacyl DHP, have been studied.

METHODS AND MATERIALS

Some of the DHP samples were a gift from John Obst (Forest Products Laboratory). These were synthesized using the conventional DHP lignin preparation procedure. Deuterated G-DHPs were synthesized in one of the co-author's laboratory. The lignin composition of G-DHP was mostly guaiacyl whereas that of GS-DHP was more-guaiacyl-than-syringyl. Similarly, whereas the H-DHP was made from 100 % coumaryl units, HG-DHP had more-coumaryl-than-guaiacyl structures.

FT-Raman Spectra were obtained using the Bruker RFS-100 instrument that is equipped with a 1 watt 1064 nm Nd:YAG diode laser. Samples were analyzed in the 180° scattering geometry and the power at the sample was about 100 mW. Two sequential spectra of each sample were obtained to ensure the laser was not modifying the sample. The 1600 cm^{-1} band was used to normalize the spectra: this permitted intensity comparison of bands between the spectra. It was assumed that, to a first approximation. the 1600 cm^{-1} band intensity did not differ significantly among the DHP lignins.

RESULTS AND DISCUSSION

The FT Raman spectra of the DHPs are shown in Fig. 1 and the vibrational band positions are listed in Table 1. A cursory look at the spectra indicates that there are significant differences in the intensities of the bands. Irrespective of the significant intensity variations between DHPs, the total number of bands detected did not change all that much. Although, at 23, H-DHP spectrum contained the least number of bands, other DHPs had somewhat higher number of bands (S-DHP 29, GS-DHP 34, G-DHP 32, and HG-DHP 33). To compare bands in the spectra, each band was assigned an intensity designation (Table 1; very strong vs, strong s, medium m, weak w, and very weak vw). For band assignment information in a lignin Raman spectrum, the reader is advised to consult the literature [1].

250 - 1550 cm^{-1} region

A large number of bands are detected in this region (Table 1) but except for the bands at 371, 1041, 1333, and 1456 cm^{-1}, in the spectra of S- and GS-DHPs, most bands are weak. After considering the intensities of these four bands in the spectra of G-, HG- and H-DHPs, it can be concluded that these band intensities are a reflection of syringyl lignin content in the sample. This observation is supported further by earlier study of MWLs [3] where the same four bands were found to be stronger in the spectra of hardwood MWLs (syringyl rich). On the other hand, in the spectrum of G-DHP (Fig. 1 c), the band detected at 1276 cm^{-1} has higher intensity then its intensity in the spectra of other DHPs. This is supported by the previous report on MWLs that showed that the band at 1272 cm^{-1} was more intense in the spectra of black spruce and loblolly pine (both contain guaiacyl lignin) [3]. Therefore, 1276 cm^{-1} band intensity is dependent upon how much guaiacyl lignin is present. Also in this region, the only band due to HG- and H-DHPs that had medium intensity and was weaker in the spectra of the other DHPs was detected at 832 cm^{-1} (Table 1, 4th column). The other bands, in the spectra of HG- and H-DHPs, which could be better detected were 1133, 1266, 1305, 1335, and 1445 cm^{-1}. One of lignin's aromatic-ring stretch mode, detected in the DHPs between 1501 - 1510 cm^{-1}, has very weak scattering cross section in Raman. This is due to the selection rules. The same vibration mode absorbs strongly in IR.

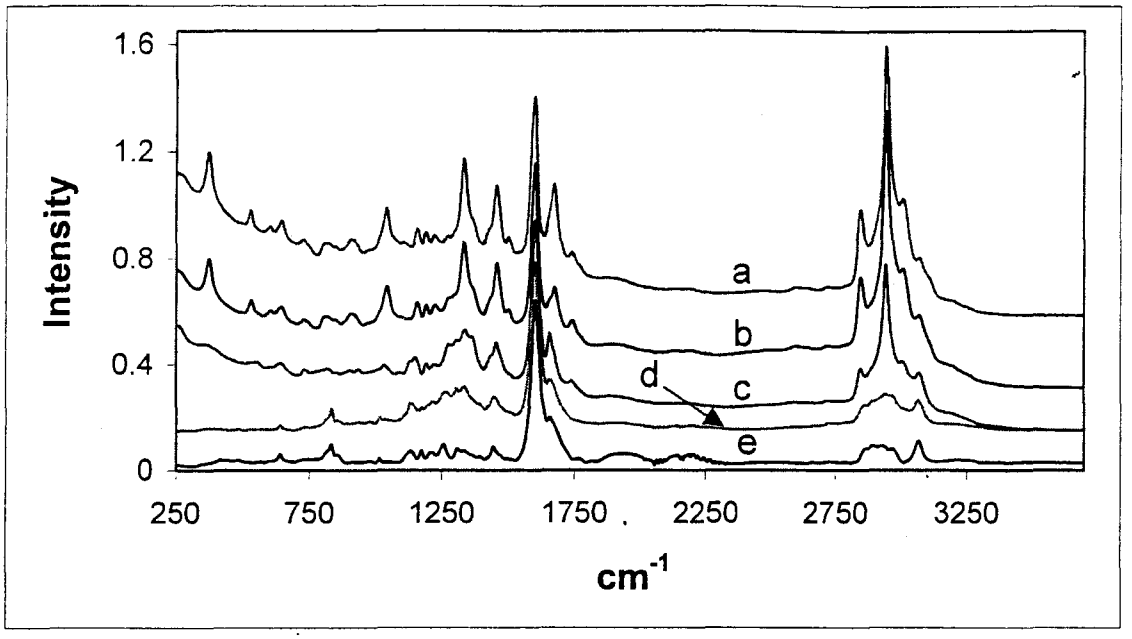

Fig. 1. FT-Raman spectra of DHP lignins; (a) S-DHP, (b) GS-DHP, (c) G-DHP, (d) HG-DHP, and (e) H-DHP; Spectra were normalized on the 1600 cm^{-1} band and, for display purposes, have been shifted on the intensity scale. Significant fluorescence was only detected for the H-DKP sample and most of this background was subtracted out (spectrum e). Other spectra were not modified in any way.

1550 - 1850 cm^{-1} region

Although a much smaller spectral interval, this is the most important and most analyzed region in the Raman spectra of lignins and lignocellulosics [1]. Besides contributions of aromatic ring modes, this region contains vibrational modes of C=C, C=O, COOR, and COOH groups. The region is sensitive to chemical changes in lignin and has been used in the studies of pulp bleaching, photoyellowing, and aging of paper, to name just a few. In the DHP spectra, the symmetric benzene-ring stretch mode produced an intense band at about 1600 cm^{-1}. A small difference in the frequency of this band (Table 1), seen among the spectra of the DHPs, is believed to be within the experimental error and is not necessarily indicative of various lignin types. The band (or shoulder) present at about 1657 cm^{-1} in all but the spectrum of S-DHP has been assigned to the aromatic-ring conjugated C=C bonds and to the C=O groups (of coniferaldehyde and/or sinapaldehyde units in lignin) [1]. The 1672 cm^{-1} band was clearly seen in the spectra of S-, GS-, and G-DHPs and is due to non-hydrogen bonded C=O groups in coniferaldehyde and/or sinapaldehyde groups [4].

2700 - 3100 cm^{-1} region

Spectra of S- GS-, and G-DHPs showed five peaks whereas six bands were present in the spectra of HG- and H-DHPs. Compared to the syringyl and guaiacyl DHPs, both the HG- and H-DHPs showed weak bands in the aliphatic C-H stretch region. This is likely to be due to the fact that in these DHPs there were not many lignin units with $-OCH_3$ groups. In the spectra of the HG- and H-DHPs, it is likely that the additional peak at 2961 cm^{-1} became visible because compared to the spectra of other DHPs the intensity of the 2939 cm^{-1} is much weaker. The aromatic C-H stretch is seen at about 3065 cm^{-1} and its intensity does not seem to vary a great deal. However, considering that, in the S-, GS, and G-DHP spectra, this band overlaps with the decaying wing of the 2939 cm^{-1} band, the intensity estimation may not be accurate. Based on the structures of the syringyl and guaiacyl units, one would expect the 3065 cm^{-1} C-H band intensity to be lower compared to DHPs where more aromatic C-H bonds are present (H- and HG-DHPs).

Table 1. Raman Frequencies of DHP Lignins

S-DHP, cm^{-1}	GS-DHP, cm^{-1}	G-DHP, cm^{-1}	HG-DHP, cm^{-1}	H-DHP, cm^{-1}
371 s[a]	372 m	367 vw	366vw	—
—	—	—	413 vw	418 w
—	—	—	451 vw	—
—	—	—	486 w	488 w
530 w	531 w	542 vw	523 vw	—
603 vw	605 vw	602 vw	595 vw	—
646 w	644 w	638 w	639 w	640 w
—	687 vw	—	—	—
727 w	729 w	731 w	730 w	—
820 w	806 m	818 w	814 sh	—
—	—	—	832 s	831 m
845 sh	846 sh	—	852 m	857 w
906 w	906 m	904 w	—	—
—	933 sh	934 w	930 w	—
969 vw	966 vw	970 vw	976 w	978 vw
—	—	1006 sh	1013 m	1013 w
1041 m	1042 w	1032 w	1034 w	—
—	1042 vw	—	—	—
1103 w	1082 vw	1092 vw	—	—
1115 sh	1127 sh	1132 sh	1133 s	1134 m
1157 w	1155 w	1148 m	—	—
—	—	—	1173 w	1173 m
1192 w	1191 vw	1192 w	1195 sh	—
1224 w	1223 wv	1224 vw	1217 w	1216 w
—	—	—	1266 m	1257 m
1272 vw	1278 sh	1276 m	—	—
—	—	1303 w	1305 m	1307 m
1333 s	1332 m	1337 m	1335 m	1333 sh
1366 sh	1366 sh	1364 sh	—	—
—	—	—	1391 vw	1393 w
1431 sh	1434 sh	1433 sh	1445 m	1443 m
1456 s	1456 s	1454 m	—	—
1501 w	1501 vw	1510 vw	1508 sh	—
1599 vs	1602 vs	1603 vs	1600 vs	1602 vs
—	1657 sh	1657 s	1658 m	1655 m
1672 s	1674 s	1673 sh	—	—
1739 w	1740 w	1738 w	—	—
2717 vw	2718 vw	2722 vw	2725 w	2724 w
2845 s	2845 m	2845 m	—	—
—	—	—	2861 w	2864 w
—	—	—	2894 sh	2891 w
2939 vs	2940 vs	2938 vs	2939 w	2926 w
—	—	—	2961 w	2964 w
3006 w	3005 sh	3005 sh	—	—
3067 w	3066 w	3068 m	3065 m	3063 m

[a]The peak intensity designations are relative to the 1600 cm^{-1} intensity in the spectrum. Intensities between columns can be compared because the spectra have been normalized.

Effect of aromatic-ring deuteration

Two deuterated analogues of G-DHPs were synthesized. One had deuterium atom at the 2nd carbon in the ring (G[r-2-^{2}H]-DHP) whereas the other had it at position 5 (G[r-5-^{2}H]-DHP). Obtained spectra indicated that for some unknown reason the fluorescence for the G[r-2-^{2}H]-DHP sample was quite high and limited the number of peaks that could be observed (Table 2).

When the three G-DHP spectra were compared, a number of new bands were detected (in bold in Table 2) in the deuterated lignins (bands were classified as new/different if a band position differed more that 4 wavenumbers). Those bands that shifted to lower frequency upon deuteration are likely to be associated with the aromatic-ring vibrations. Even the most intense band at 1603 cm^{-1} showed a shift to 1595 cm^{-1} wavenumber. More analysis is presently underway to use this information in lignin band assignment work.

Table 2. Effect of selective aromatic-ring deuteration on the G-DHP Raman spectrum

G-DHP	G[r-2-^{2}H]-dDHP	G[r-5-^{2}H]-DHP
367 vw	—	**360** vw
—	—	**487** vw
542 vw	—	543 w
602 vw	—	**591** w
638 w	—	—
731 w	—	731 w
—	—	**751** vw
—	—	**770** vw
818 w	—	—
—	**833** m	**832** s
—	—	**852** w
904 w	**892** vw	**898** vw
934 w	932 vw	930 w
970 vw	—	972 w
1006 sh	1016 vw	**1013** m
1032 w	—	—
—	—	**1050** w
1092 vw	—	1098 vw
1132 sh	—	1136 s
1148 m	—	—
1192 w	1196 w	1191 w
1224 vw	1220 w	**1217** w
—	—	**1237** vw
1276 m	1272 w	1280 sh
1303 w	1306 w	1305 m
1337 m	1336 w	1334 s
1364 sh	1364 w	—
—	—	**1392** w
1433 sh	—	—
1454 m	1453 m	1452 m
1510 vw	—	—
1603 vs	**1589** s	**1595**vs
—	—	1620 sh
1657 s	—	1656 s
1673 sh	—	—
1738 w	—	—
2722 vw	2723 vw	2727vw
2845 m	**2856** m	**2852** m
—	**2891** w	**2890** w
2938 vs	2939 m	2940 m
3005 sh	—	3006 sh
3068 m	—	**3060** sh

CONCLUSIONS

FT Raman study of various DHPs clearly showed differences in intensities of bands that originated due to the differences in structures. Based on such differences it was straightforward to distinguish between S-, G-, and H-DHPs. Several of the previously reported characteristics of hardwood and softwood MWLs were reproduced in the Raman spectra of DHPs indicating that the study of the latter can provide further insights for understanding Raman spectra of real lignins. Analysis of the deuterated G-DHPs data suggested that peak shifts information may be helpful in the lignin band assignment work.

DISCLAIMER

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