Raman spectra of lignin model compounds

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ABSTRACT

To fully exploit the value of Raman spectroscopy for analyzing lignins and lignin-containing materials, a detailed understanding of lignins' Raman spectra needs to be achieved. Although advances made thus far have led to significant growth in application of Raman techniques, further developments are needed to improve upon the existing knowledge. Considering that lignin's heterogeneous structure consists not only of inter-phenylpropane-unit linkages of carbon-to-carbon and carbon-to-oxygen, but also of side chains with various substituent and functional groups, a study of a large number of representative models is essential. In the present work, 40 lignin models were investigated in the neat state (near-IR FT-Raman and FT-IR), in solution (near-IR FT-Raman), and on cellulose (near-IR FT-Raman). These models represent a large number of substituent/functional groups and sub-structures in lignin - aliphatic and phenolic OH, C=O, CHO, COOH, CH_3, OCH_3, α,β C=C, furan, and interunit C-O-C and C-C linkages. Raman band positions associated with various groups were identified and Raman frequencies and intensities were compared between the models. For example, for the phenyl group, some of the noteworthy findings were as follows. The intensities of the 1600 (aromatic ring stretch) and 3070 (aromatic C-H stretch) cm^{-1} bands varied significantly between the models. The position of the 1600 cm^{-1}-Raman-mode was found to be only minimally sensitive to substituents because in about 70 % of the models, including those containing more than 1 phenyl group, the vibrational frequency was confined between 1594 and 1603 cm^{-1}. Similar information was obtained on other functional groups as well. It is hoped that the findings from this study will greatly aid in developing a better understanding of the Raman spectra of lignins and lignocellulosic materials.

INTRODUCTION

Raman spectroscopy is increasingly used to analyze lignin containing materials [1-8]. Although significant progress has been made in interpreting the contribution of lignin to a spectrum [9], the need exists to further improve upon this understanding. This can be accomplished by carrying out a systematic broad-based investigation of lignin models. Earlier work in this area focused on a few models that were deemed relevant to the study at hand. However, such investigations and resultant advances in understanding were not sufficient. Considering that lignin is a heterogeneous polymer that consists of many different types of inter-unit linkages, substituents, and side chains with various functional groups, a study incorporating a large number of representative models is essential In the present work, using near-IR FT-Raman and FT-IR techniques, 40 lignin models (nearly half of them tri-substituted aromatics) were investigated in neat state. Additionally, near-IR FT-Raman was used to study these models in solution and on cellulose.

EXPERIMENTAL

Chemicals

A large number of lignin models (Fig. 1) were purchased from Aldrich, Eastman, Fluka, and Lancaster. Additionally, a significant number were synthesized by an FPL staff chemist (Larry Landucci). Model structures and their ID numbers are shown in Fig. 1

Raman- and IR– neat

Near-IR FT-Raman and FT-IR spectra of the pure models were obtained, respectively, using the RFS 100 (Bruker) and Galaxy-5000 (Mattson) instruments.

Raman– solution

Appropriate amounts of compounds were weighed in 1, 2 or 3 mL Class A volumetric flasks and dissolved in methanol, dioxane:water or dimethyl sulfoxide (DMSO) with most solutions near 0.5 M. For solution studies, most models were dissolved in methanol. For those few that were not soluble, dioxane:water or DMSO was used. The solvent background was subtracted from the raw data prior to determining peak positions and intensities. Peak intensity was calculated on a molar basis and for those models that contained more than one group per molecule the band intensity was adjusted by ratioing to the appropriate number of such groups.

Raman– cellulose

Solutions used above (with exceptions: 10, 16 and 19) were measured in a 1 mL GlenCo Precision Bore ampoule and &luted with the appropriate solvent to make 0.5 mL of 0.1 M solutions. This was poured onto a 55 mm round Whatman #1 filter paper and allowed to evaporate for 2-5 days. The papers were folded into 16 layers and placed on the sampling bench in the instrument with a mirror behind them. Model peaks that occurred in essentially the same place as cellulose peaks were not included in the results because there would be significant uncertainty regarding the peak position and amplitude

	R_1	R_2	R_3	R_4
1	-COOH	-H	$-OCH_3$	-H
2	-COOH	$-OCH_3$	$-OCH_3$	-H
3	-CH=CHCHO	-H	$-OCH_3$	-H
4	-H	$-OCH_3$	-OH	$-OCH_3$
5	O $-CCH_3$	$-OCH_3$	$-OCH_3$	-H
6	O $-CCH_3$	$-OCH_3$	-OH	-H
7	*figure*	-H	-H	-H
8	-CH=CHCOOH	-H	$-OCH_3$	-H
9	-H	$-OCH_3$	$-OCH_3$	-H
10	O $-CCH_3$	$-OCH_3$	O -OCCH3	-H
11	O $-CCH_3$	-H	-H	-H
12	-CHO	$-OCH_3$	$-OCH_3$	-H
13	O $-CCH_3$	-H	-OH	-H
14	-CH=CHCOOH	$-OCH_3$	-OH	-H
15	O $-CCH_3$	$-OCH_3$	$-OCH_3$	$-OCH_3$
16	*figure*	$-OCH_3$	-OH	-H
17	-CH=CHCOOH	$-OCH_3$	-OH	$-OCH_3$
18	$-CH_2OH$	-H	-OH	-H
19	*figure*	-H	*figure*	-H
20	O $-CCH_3$	-H	*figure*	-H

	R_1	R_2	R_3	R_4
21	O $-CCH_2CH_3$	$-OCH_3$	-OH	$-OCH_3$
22	*figure*	$-OCH_3$	$-OCH_3$	-H
23	*figure*	$-OCH_3$	-OH	-H
24	*figure*	$-OCH_3$	$-OCH_3$	-H
25	OH $-CHCH_3$	$-OCH_3$	$-OCH_3$	-H
26	$-CH_3$	$-OCH_3$	-OH	-H
27	$-CH_2OH$	$-OCH_3$	$-OCH_3$	-H
28	$-CH_3$	$-OCH_3$	O $-OCCH_3$	-H
29	$-CH_2OH$	-H	$-OCH_3$	-H
30	$-CH_2CH_2CH_3$	$-OCH_3$	-OH	-H
31	$-CH=CHCH_3$	$-OCH_3$	-OH	-H
32	-COOH	$-OCH_3$	-OH	-H
33	-CHO	-OH	$-OCH_3$	-H
34	-CHO	$-OCH_3$	-OH	-H
35	-COOH	$-OCH_3$	-OH	$-OCH_3$
36	-CHO	$-OCH_3$	-OH	$-OCH_3$
37	-CH=CHCOOH	-H	-OH	-H
38	-COOH	-H	-OH	-H
39	-CHO	$-OCH_3$	$-OCH_3$	$-OCH_3$
40	O $-CCH_3$	$-OCH_3$	-OH	$-OCH_3$

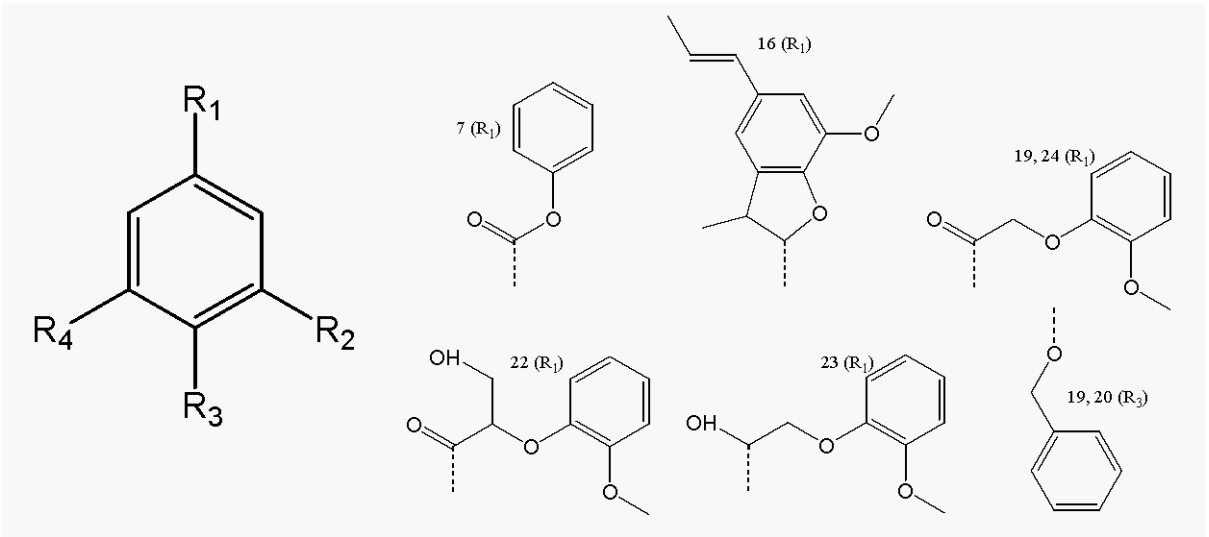

Fig. 1: Molecular structures of 40 lignin models used in the present study

Table 1: Raman band positions of lignin models in 3 environments - neat, in solution, and on cellulose

Sample		Most prominent bands																
1	Neat WN[a]		824	1134	1180		1270	1291	1452	1581	1609		3029	3079				
	Cell WN	634	823		1181		1269	1290	1452	1580	1608		3029	3078				
	Soln WN	634	819			1258					1607	1695						
2	Neat WN	357		745	771		1268	1296	1352		1438	1454	1598			3088		
	Cell WN	353	628	744	770	1253	1273		1354	1414			1599			3089		
	Soln WN				767		1271		1342				1603	1694	1717			
3	Neat WN	568			1131	1174	1250		1406	1570	1600	1621	1664	1675				
	Cell WN	568	639	767	1136	1176	1251			1571	1599	1623	1660					
	Soln WN	568			1137	1177	1251	1327	1395	1573	1603	1625	1664					
4	Neat WN	368	531	708	823	1084		1297	1460	1592			3075	3090				
	Cell WN									1599	1622	1652						
	Soln WN			705	828		1187	1298		1594			3079					
5	Neat WN		765	979	1082	1266			1347	1418	1446		1587	1671	3080			
	Cell WN	677	768			1271				1419	1452		1595	1667	3083			
	Soln WN	677	768		1082	1272	1294	1335	1347	1420			1597	1665				
6	Neat WN	342	366	684					1079	1162	1188	1288			1577	1606	1659	
	Cell WN			685	794							1287			1591		1660	3077
	Soln WN			685	794	886	981	1028				1287	1427	1454	1592		1661	
7	Neat WN	263		856	1003	1028	1170	1194	1264	1600	1727		3070					
	Cell WN									1599								
	Soln WN		616	854	1002		1162	1198	1268	1601	1721	1743	3074					
8	Neat WN		815		1178			1241	1273		1433	1464		1602	1629		3061	3079
	Cell WN	775		861	1174	1194	1213		1265	1307	1422			1604	1638			
	Soln WN	771			1175		1210	1250	1269		1424		1576	1605	1637	1691		
9	Neat WN	380	581	753	1053	1163	1255	1332	1457	1594	3078							
	Cell WN									1605								
	Soln WN		582	754		1162	1255	1331		1595	3072							
10	Neat WN	314	355	667		747	804			1291	1328			1607	1625		3086	
	Cell WN				727			904	1276			1453	1593	1606		1673	3070	
	Soln WN			667	727				1274					1599		1701	3072	
11	Neat WN	288			722	1000	1029	1150	1279	1597	1650		3059	3068				
	Cell WN			618	721	1001		1151		1598	1655			3065				
	Soln WN		568	617	721	1001		1152	1280	1599	1650	1665		3069				
12	Neat WN	377	643	734		773		1198	1278	1350		1445	1599	1672	3079			
	Cell WN		643	734	765	774			1269	1349		1453	1595	1674				
	Soln WN		642			775	1138	1197	1271	1349	1425	1455	1598	1678				
13	Neat WN	638		842	962	1077	1165	1219	1276	1575	1604	1660						
	Cell WN	638	825	840	962	1077	1171		1278	1585	1602	1659	3068					

	Soln WN	638	823	842	962	1076	1171		1279	1584	1606	1663	3073				
14	Neat WN	396	673	815		1178	1241	1273	1433	1464	1602	1629					
	Cell WN			810		1188		1276	1430	1452	1600	1630	1679	3070			
	Soln WN			812	1162	1191	1223	1274	1431	1455	1603	1633	1687				
15	Neat WN	376		752	890	980	995	1035	1093		1322	1452	1586	1681			
	Cell WN		608	751	889	980	995			1216	1325	1451	1585	1680			
	Soln WN			743					1098		1333		1585	1669			
16	Neat WN		790		913	1075			1274	1322	1338	1386	1455	1597	1654		
	Cell WN			811							1336		1450	1603	1654		
	Soln WN	756					1145	1191			1338	1379		1601	1654	3070	
17	Neat WN		1160	1209	1271	1305	1336	1425	1459	1516	1595	1644					
	Cell WN	814								1514	1594	1632	1676	1688			
	Soln WN		1161				1337				1595	1635		1688			
18	Neat WN	406	644	827	853	995	1172	1211	1599	1613	3065						
	Cell WN		642	828	849				1600	1614	3063						
	Soln WN		642	824	849		1170	1209		1617	3063						
19	Neat WN	754	767	1007	1192	1248	1264	1346	1451	1596	1687						
	Cell WN	753	771	1003						1594	1690	3066					
	Soln WN	755	771	1002	1201		1267	1334		1594	1691	3062					
20	Neat WN			863		1005	1077	1173	1250		1303		1600	1672	3058	3080	
	Cell WN	806	832	858		1003	1077	1175				1576	1599	1670	3064		
	Soln WN	805			959	1002	1077	1175	1249	1275			1600	1677	3065		
21	Neat WN	372			873	1033	1089	1170	1200		1320	1450		1590	1655		
	Cell WN			791	872	1318							1519	1591	1657		
	Soln WN		689	792	873		1087	1171	1197		1319			1593	1662		
22	Neat WN	767		1092	1249	1265	1354	1422	1446	1593	1684	3074					
	Cell WN	768	952			1262			1450	1593	1677	3078					
	Soln WN	768								1595	1684	3080					
23	Neat WN	772	1058	1163	1221	1253	1326	1456	1590	1607	3076						
	Cell WN	775							1594	1611	3076						
	Soln WN	775	1054						1594	1613	3077						
24	Neat WN		753	766	1203	1262	1348	1420	1453	1593	1686	3080					
	Cell WN	735		766	1203	1265	1336	1421		1594	1689	3078					
	Soln WN			767		1273	1347			1595	1695	3081					
25	Neat WN	703	766	872	1028	1188	1267	1315	1454	1608	3077						
	Cell WN		766	871			1265		1454	1608	3076						
	Soln WN	702	766	868		1193	1270	1317	1456	1611							
26	Neat WN	359	465	560	713	792	921	1288	1379	1616	3065						
	Cell WN				713	791	922			1614	3062						
	Soln WN		464	566	713	793	924	1288	1380	1616							
27	Neat WN	374			739	765	1027	1189	1265	1335	1455	1609	3076				
	Cell WN			720	739	765					1456	1608	3076				

	Soln WN		554	716	739	766			1263	1326		1611								
28	Neat WN	326	373	497	547	726	791		1291	1381	1607		3068							
	Cell WN				547	725	790				1606	1760	3065							
	Soln WN			497	546	726	790	904	1290	1380	1609	1760	3071							
29	Neat WN	637	820	844	1178	1211	1247		1461		1613	3012	3072							
	Cell WN	637	820	843	1178					1587	1611		3066							
	Soln WN	637	819	845	1178	1210	1249	1302			1614		3072							
30	Neat WN	306	386	561				796	1037	1271	1450	1614	3019	3065						
	Cell WN						777	795			1449	1613		3063						
	Soln WN			567	699	736	778	797		1275		1614		3063						
31	Neat WN	370	559		748	796	1184	1293	1452	1614	1639	3067								
	Cell WN			649	747	796				1612	1638	3069								
	Soln WN		568		747	796		1293		1613	1640									
32	Neat WN	345	386	741	807	918	1181	1206	1286	1426	1601	1639			3083					
	Cell WN			741	800						1599		1689		3080					
	Soln WN			742	799	920			1281		1599		1690	1717						
33	Neat WN	354	503		761		1117		1248	1277	1345			1578	1607	1671				
	Cell WN			640	762	789				1278		1443	1460	1588	1607	1675				
	Soln WN		520	640	763		1132	1159		1281					1609	1677	1693			
34	Neat WN	430				813	1154	1172		1267		1431	1453	1589	1604	1664				
	Cell WN		634	732	784	811			1186			1435	1455	1593		1670		3071		
	Soln WN	416	633	731		812			1191	1273	1294			1595		1673	1695			
35	Neat WN	292	384		803	1033	1198	1321	1369	1446		1592		1699						
	Cell WN			702	805			1334			1516	1595	1647	1688						
	Soln WN			700	803			1329				1596		1693	1716					
36	Neat WN	430			1106	1143	1251	1276	1333	1460	1512	1586	1670							
	Cell WN			812					1331	1460	1512	1588	1675							
	Soln WN	416	521	812		1146			1332		1514	1589	1674	1692						
37	Neat WN		799	864	1171	1212	1259	1281	1306	1447		1606	1635							
	Cell WN	643	800	861	1172	1207	1264			1444		1604	1629	1676						
	Soln WN		801	860	1171	1206	1264				1587	1607	1631	1688	3068					
38	Neat WN	309	391			842	1131	1166	1287	1314		1600	1612			3085				
	Cell WN			639	830	846					1521	1592	1608	1689		3075				
	Soln WN			639	828	847	1165		1285			1593	1611	1693	1716	3074				
39	Neat WN	364	397	523			993	1148	1221	1332	1456		1585	1684						
	Cell WN				756	786				1331	1456	1503	1585	1683						
	Soln WN					785		1146		1331			1589	1682	1697					
40	Neat WN	382	798		988	1096	1203	1278	1336		1517	1578	1656							
	Cell WN		796						1332	1455	1517	1586	1662							
	Soln WN		796	894	980	1093			1333			1584	1662							

[a]WN is wavenumber

RESULTS AND DISCUSSION

Structures of models shown in Fig. 1 consist of various inter-unit linkages, substituents and functional groups found in lignin. The models collectively represent aliphatic and phenolic OH, C=O, CHO, COOH, CH_3, OCH_3, α,β C=C, furan, and interunit C-O-C and C-C linkages. In addition, there are models that contain more than 1 group of the same kind in their structure (e.g., models 7, 16, 19, 20, 22-24 contain at least 2 phenyl groups).

In neat state, model spectra were obtained using both near-IR Raman and FT-IR, whereas models in solution and on cellulose were analyzed only by Raman. From the model spectra obtained in three different environments, 10 most prominent Raman bands were selected for listing in Table 1. In general, due to low concentration of the models, sampling in the solution and on cellulose resulted in fewer than 10 bands.

Raman vs. IR

As is well known, Raman and IR are complementary vibrational spectroscopic techniques. This aspect was illustrated in the present study as well. In neat state, of the total detected Raman bands, only about 60% were also detected in the IR, implying that 40% of the bands could only be detected by Raman. Moreover, there were band intensity differences between the two techniques. Therefore, to obtain the most detailed chemical information, both IR and Raman analyses should to be carried out.

Effect of the Environment

When models were sampled in solution and on cellulose, several Raman band positions shifted compared to the value in the neat state. A Table summarizing this data is not shown here due to lack of space but bands were classified according to the extent of the shift. Shifts between 3 and 5 cm^{-1} were designated as small, 5 and 9 cm^{-1} as medium and more than 9 cm^{-1} as large. Total numbers of bands in small, medium, and large categories were, respectively, 48, 47 and 24. Considering that some of the functional groups are capable of H-bonding in solution and with cellulose, shifts associated with the bands of such groups can be readily explained. On the other hand, there were several instances where band shifts are not easily interpreted.

Band Intensity Differences

1510, 1600, and 3070 cm^{-1} phenyl group modes

In the Raman spectra of models in neat state, a weak 1510 cm^{-1} band was detected. However, in solution, for most models, this band was not detected. On the contrary, the 1600 cm^{-1} band was strong in both states. The intensities of the 1600 (aromatic ring stretch) and 3070 (aromatic C-H stretch) cm^{-1} bands varied significantly among the models (Figs. 2 and 3). Bar-plot in Fig. 2 shows the variation of the molar intensity of the 1600 cm^{-1} band. The intensities are plotted with respect to the 1600 cm^{-1} band intensity of model 26 which had the lowest non-zero value.

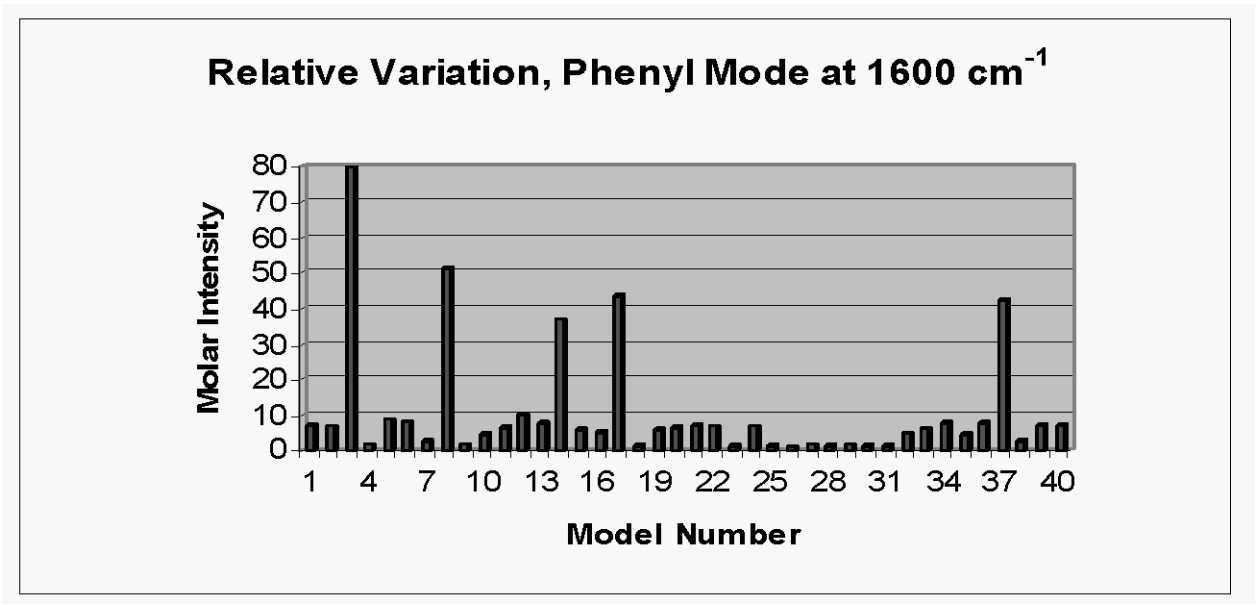

Fig. 2: Relative variation of molar intensity of the ≈ 1600 cm^{-1} phenyl mode in lignin models. Intensity variation is with respect to model 26 whose intensity was set to 1. See Fig. 1 for identifying various lignin models.

Previously, such intensity variation was observed [9] when a number of models were investigated by conventional Raman spectroscopy (514.5 nm laser excitation). As discussed earlier [9], the 1600 cm^{-1} band intensity enhancement was reported to be due to both pre-resonance Raman and conlugation effects. Considering the long wavelength nature (1064 nm) of the laser excitation in the present work, which makes excitation far removed from any electronic absorption in the models, the pre-resonance Raman is not expected to play a role in intensity enhancement. Therefore, the intensity of the aromatic band at 1600 cm^{-1} is affected solely by the π-electron conlugation between the phenyl ring and its substituents. More conlugation and consequently, more conjugation-enhancement is usually present in the absence of steric hindrance from substituents on the 2 and 6 positions of the phenyl ring.

While the intensity was very sensitive to the model structure, the position of the 1600 cm^{-1} Raman band was found to be only minimally sensitive. In about 70% of the models, including those containing more than one phenyl group, the vibrational frequency was confined between 1594 to 1603 cm^{-1} (Table 1).

A similar molar intensity variation plot was generated for the 3070 cm^{-1} band. For this aromatic C-H stretch mode, the intensities were calculated relative to that of model 29, which had the lowest non-zero intensity in solution. The models with missing data in the plot are those whose spectra did

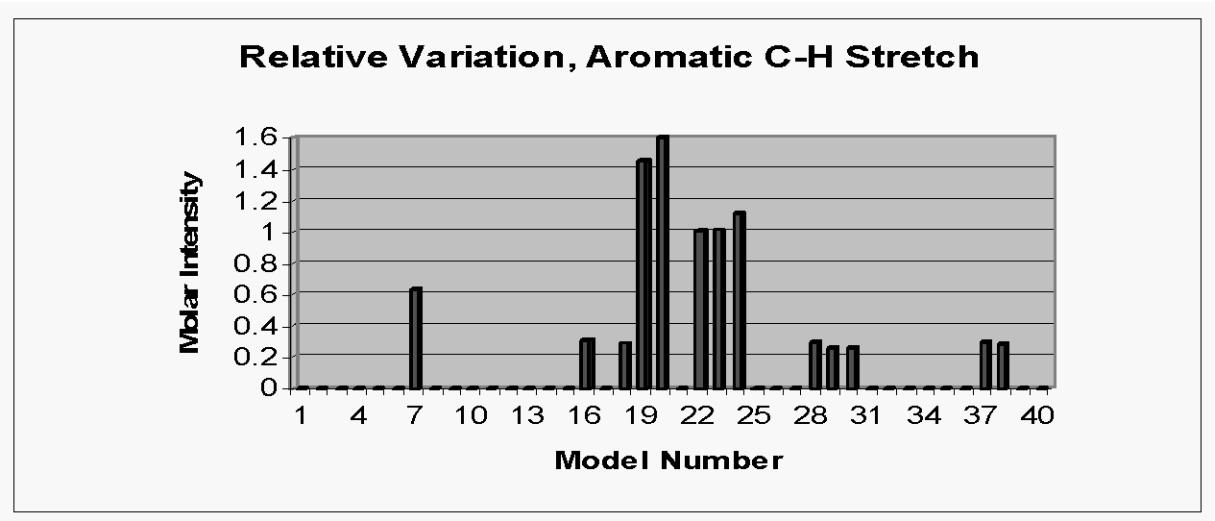

Fig. 3: Relative variation of molar intensity of the ≈ 3070 cm^{-1} C-H stretch in lignin models. Intensity variation is with respect to model 29 whose intensity was set to 1. See Fig. 1 for identifying various lignin models.

When Figs. 2 and 3 are compared, it is noted that the two model sets that produced intensity enhancements are different. This suggests that the mechanisms underlying the 1600 and 3070 cm^{-1} band enhancements are not the same.

Raman Frequencies and Band Assignment

Making assignments of characteristic Raman frequencies of the model compounds is a complex task and the already available information in the literature is extremely helpful [9-11]. Using existing knowledge, bands in model spectra were identified that were characteristic of various sub-structures/groups (Table 2). Column 1 in Table 2 identifies the group, and corresponding Raman frequencies are listed in the subsequent columns according to various model characteristics. For instance, depending upon the substitution pattern of the phenyl group (mono, di, tri or tetra) aromatic bands may or may not be seen in specific regions of the spectrum. On the other hand, functional and substituent groups have no such limitation and they are usually detected in their respective regions.

In lignin models, there are some phenyl group modes of vibrations that are substituent sensitive and others that are not. The former are coupled to the motions of the substituent group and their frequencies move about significantly depending upon the nature of the substituent. These modes are not useful in characterizing the phenyl group. However, the substituent-insensitive frequencies show variation that is much more limited and these can be taken to be the characteristic vibrations of the phenyl group.

Table 2: Raman Frequencies of selected sub-structures in models

Group	Model Characteristics/Vibrational Modes			
Phenyl	Mono-sub.	Di-sub.	Tri-sub., all are 1, 3, 4 type	Tetra-sub., 1, 3, 4, 5 type
	615-618 1000-1003 Both are in plane ring deformations (IPRD) 1449-1454 CC stretch 1597- 1600 CC stretch	Ortho, 639-643 (IPRD) Para, 635-673 (IPRD) Ortho, 1053-1058 (C-H **i**n **p**lane **b**ending **m**ode) Para, 995-1023 (C-H IPBM) Ortho, 1430-1465, CC str Para, 1400-1420, CC str Ortho, 1455-1510, CC str Para, 1480-1525, CC str ortho & para, 1580-1605 CC stretch	616-727 (IPRD) 1141-1198 (C-H IPBM) 1261-1293, CC stretch 1426-1464, CC stretch 1498-1520, CC stretch 1570-1590, CC stretch 1590-1614, CC stretch	609-629 (IPRD) 1148-1203 (IPBM) 1332-1432 CC stretch 1452-1517 CC stretch 1578-1597 CC stretch
Aromatic C-H	3061-3090, C-H str			
C=O[a] C=O stretch	α (e.g., **5**)	α-O-1 (e.g., **7**)	β-O-1 (**22**)	4-O-C (**10**)
	1650–1681	1727	1684–1687	1740, 1763
HC=O C=O stretch	1 (**12**)	β (**3**)		
	1664-1684	1664, 1675		
HO-C=O C=O stretch	1 (**1**)	β (**8**)		
	≈1695 (soln)	≈1690 (soln)		
α,β HC=CH	899-982 Trans C-H wag	1271-1313 Trans C-H sym. rock	1621-1654 C=C stretch	3017-3035 C-H stretch
H_2C-OH	373-463 C-C-O bend	767-922 In phase C-C-O stretch	995-1053 Out of phase C-C-O stretch	1247-1433 C-O-H bend
HC-OH	516-519 C-C-O bend	845-872 In phase C-C-O stretch	1027, 1028 Out of phase C-C-O stretch	1157-1163 1267-1315 C-O-H bend
O-CH_3	1143-1209 Rock	1426-1470 Deformation		
Furan	1430 C-O-C in phase stretch	1498 In phase C=C stretch	1597 Out of phase C=C stretch	

[a]Location of the C=O is indicated by the α, α-O-1, β-O-1, and 4-O-C, model example is in parentheses

Considering the limitation of space, a detailed discussion of the Raman frequencies and their assignments is not possible here. Nevertheless, it is important to note that a large number of previously identified lignin and DHP Raman bands were detected in the spectra of this current set of models.

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In: Proceedings of the 59th APPITA Annual Conference and Exhibition incorporating the 13th ISWFPC (International Symposium on Wood, Fibre, and Pulping Chemistry), held in Auckland, New Zealand (May 16-19, 2005). [Carlton, Victoria, Australia]: APPITA, c2005. Both print and CD versions are available. pp. 1-8.