

**XXV Galyna Puchkovska International School-Seminar
“Spectroscopy of Molecules and Crystals”
(XXV ISSSMC)**

**The Quantum-Chemical
Investigation
of the IR Absorption
Characteristics for Structural
Fragments of Lignin
Macromolecules**



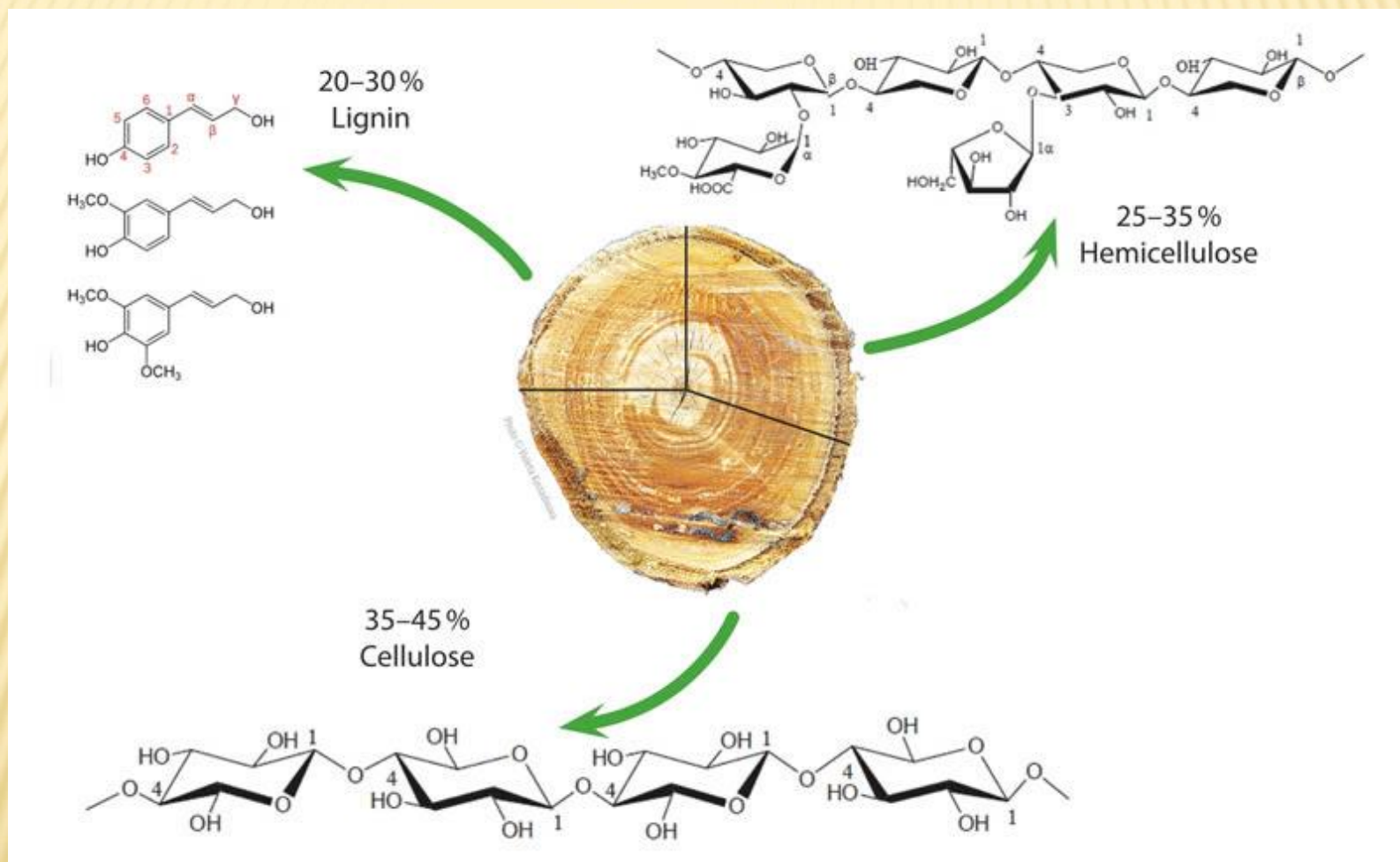
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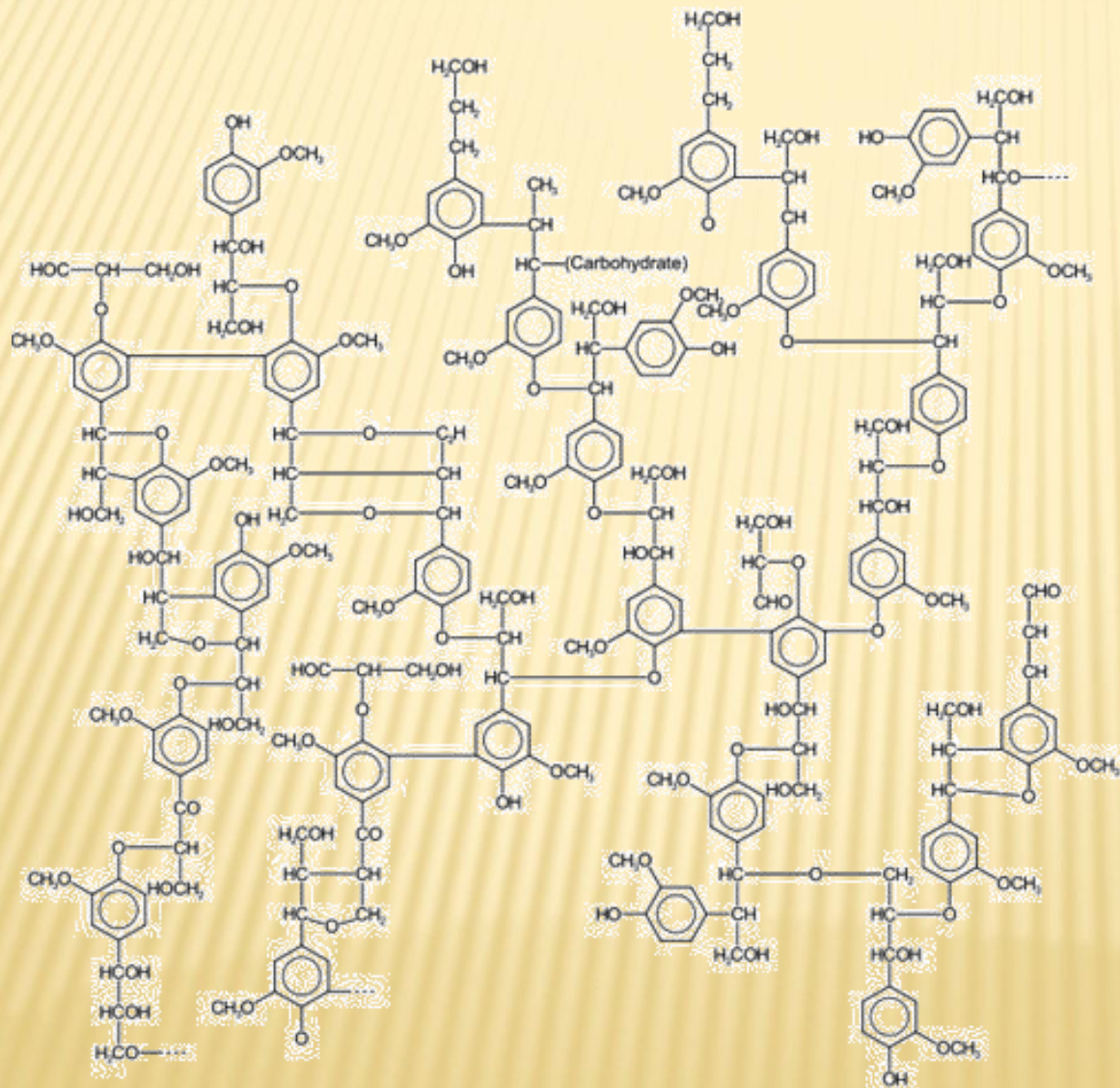
Introduction

Lignin is a complex phenolic polymer that provides mechanical strength to plant cell walls and protects from decay or invasion by pests and pathogens. Wood is typically composed of about **25% lignin**, ranging between **15%** and **40%** across species, and can increase after biomass storage due to the decay of the readily available carbohydrate fraction. Bark usually contains higher levels of lignin than wood, but this depends on the age, region of the tree, and species, but it does contain far higher levels of extractives, which include low molecular weight organic compounds, including fatty acids, waxes, terpenes and tannins.

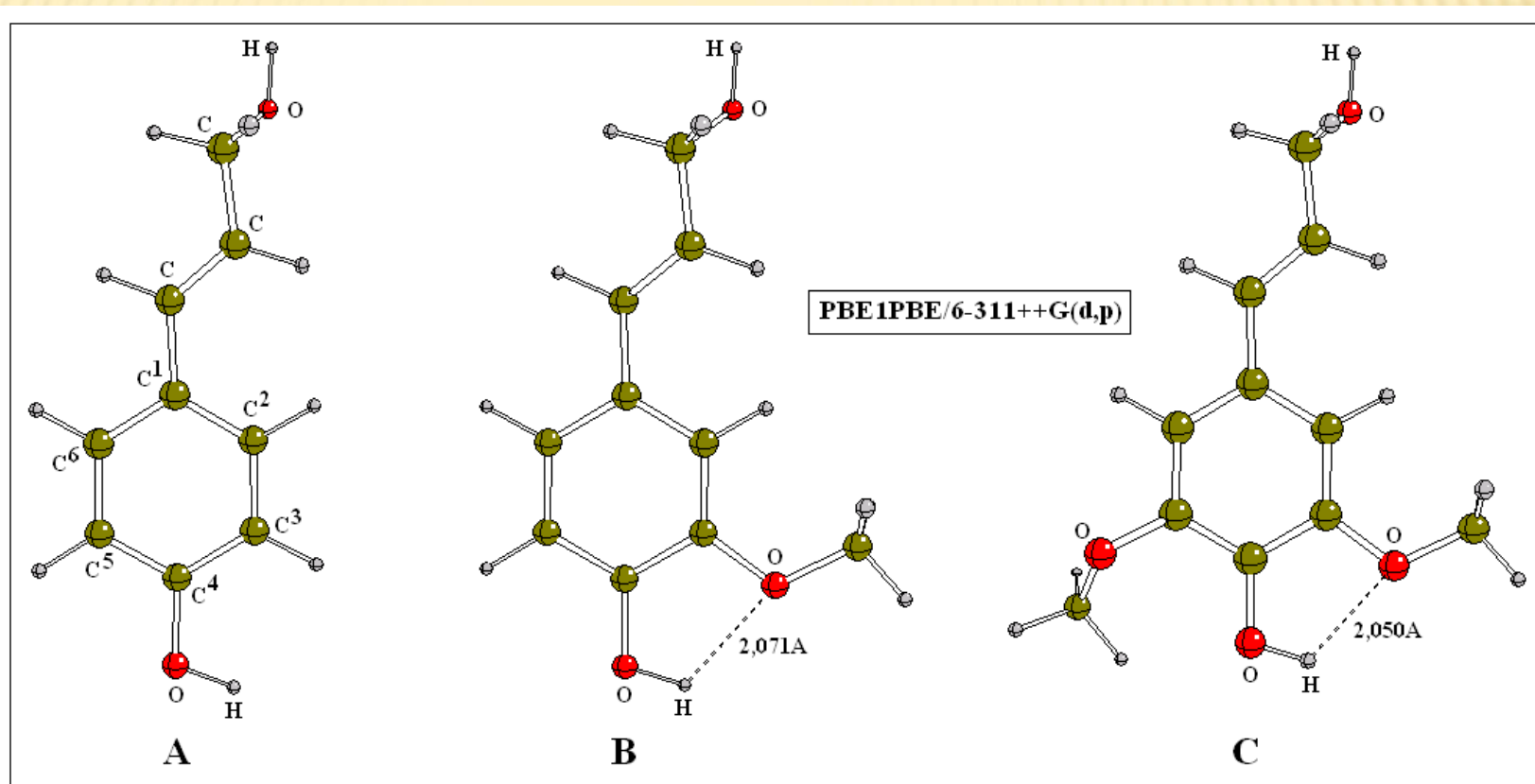
The main purpose of this work is to investigate some individual fragments of lignin macromolecules structure with their infrared absorption spectra interpretation at high *ab initio* level of theory.



Some typical wood components with their chemical structures



The investigation of native lignin structure with methods of IR absorption spectroscopy as well as some *ab initio* quantum-chemical calculations have a great importance from the point of view about searching of appropriate precursor compounds for this irregular biopolymer building. For the first step of our consideration some model structures have been chosen as the typical building blocks, such as (A-C) alcohols with *trans*-configuration of double carbon-carbon bond.



The structure of model compounds, namely p-coumaryl (A), coniferyl (B) and sinapyl (C) alcohols as well as their spectral characteristics have been established at *DFT-PBE1PBE/6-311++G(d,p)* level of theory.

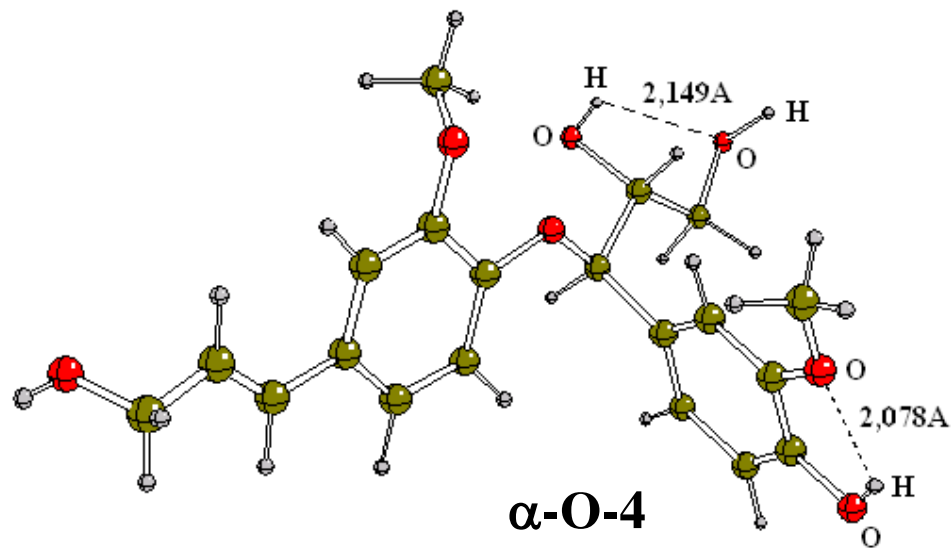
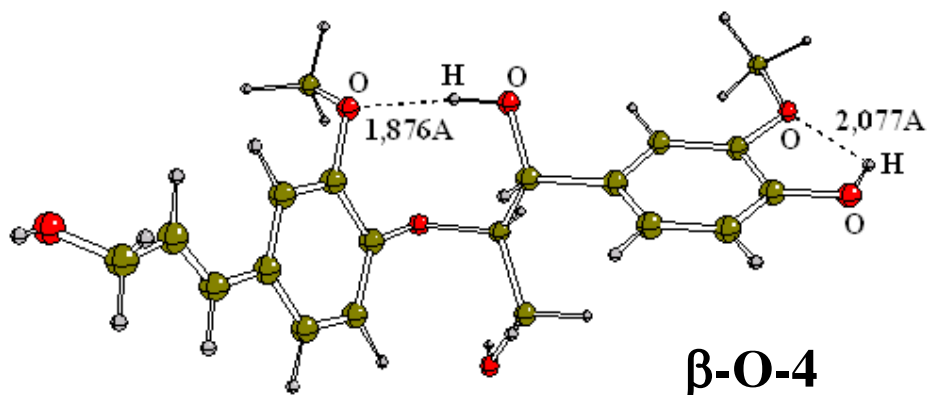
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Model (A)		Model (B)		Model (C)		Interpretation
ν, cm^{-1}	$T_{\text{calc.}}$	ν, cm^{-1}	$T_{\text{calc.}}$	ν, cm^{-1}	$T_{\text{calc.}}$	
3879	29	3878	28	3877	29	ν_{OH} (alcohol)
3871	96	3801	135	3793	143	ν_{OH} (phenolic)
-	-	3084	28	3087	27	ν_{CH_3} (OCH ₃)
-	-	3016	37	3017	40	
3016	40	3015	42	3016	43	ν_{CH_2} (OH)
2971	64	2970	67	2970	66	
1729	14	1728	21	1729	20	$\nu_{\text{C=C}}$
1674	106	1671	52	1664	7	ν_{CC} (Ar)
1644	22	1655	24	1661	122	
1552	<u>145</u>	1559	<u>282</u>	1555	237	
-	-	1499	82	1497	100	δ_{CH_3} (OCH ₃)
-	-	1461	42	1453	47	
1384	29	1329	252	1363	<u>313</u>	$\delta_{\text{CC}}, \delta_{\text{CH}}$ (Ar)
-	-	1064	83	1064	86	ν_{CO} (etheric)
994	50	991	44	991	49	δ_{CH} (C=C)

For the second step of our consideration some thermodynamic parameters such as **an Enthalpy, Entropy and Gibbs free energy for dimmers formed through coupling of coniferyl alcohol radicals have also been evaluated.** It should be noted, that the **most stable ones correspond to (α -O-4), (β - β) and (5-5) models.**

It is well known, that the harmonic vibrational frequencies calculated by means of quantum-chemical methods are usually more than their analog parameters achieved experimentally. The main source of faults is ignoring the anharmonicity effects as well as lack of full description of electron correlations constrained with use of the limited sets of basis functions.

To increase data calculation accuracy in their simulation of the main spectral characteristics of observed system, we used some additional values of the scale factors being 0.9580 and 0.9688 for the 6-311+G(d) and 6-311+G(d,p) basis sets respectively. The results of calculations are represented below.



β -O-4 (7.2 kJ/mol)

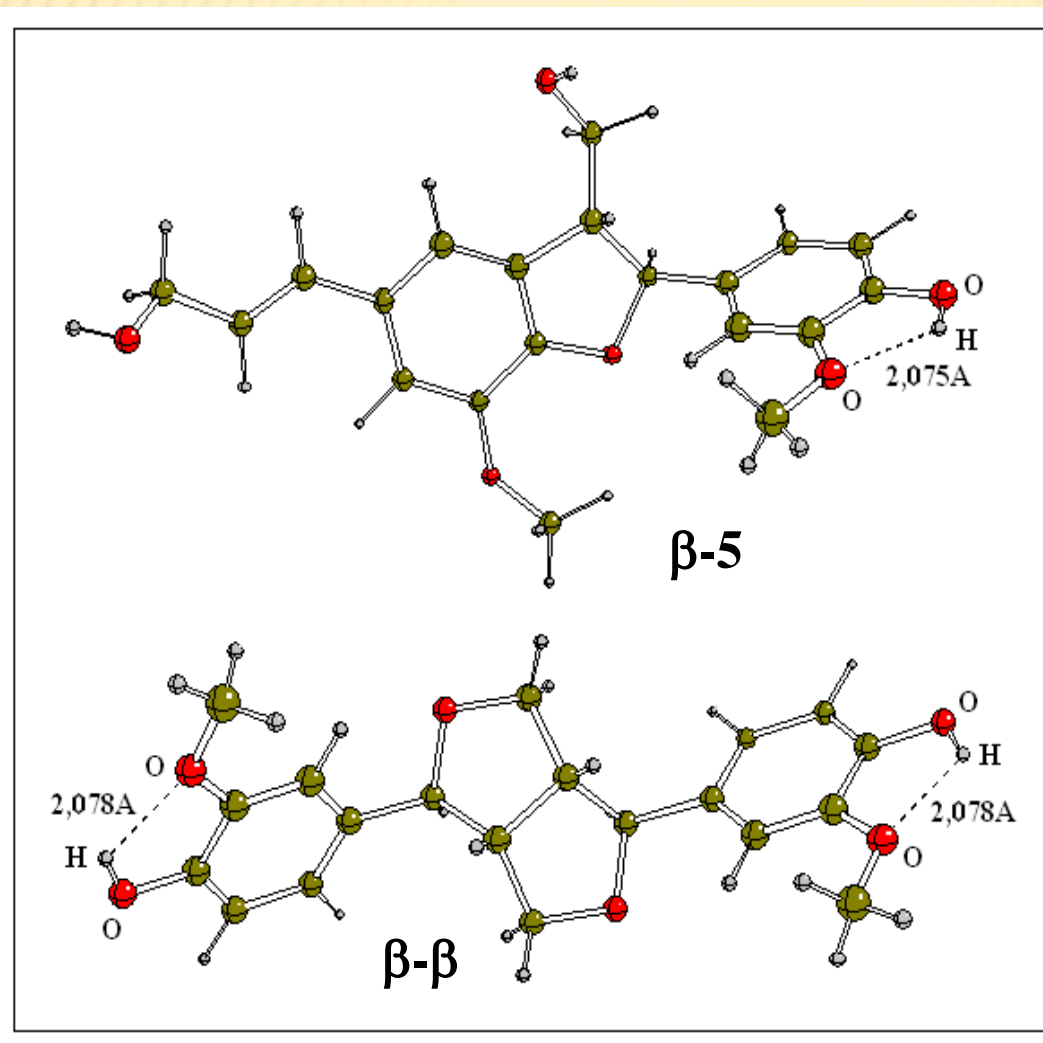
α -O-4 (0.0 kJ/mol)

$\Delta H_{\text{calc.}} = 6.8 \text{ kJ/mol}$

$\Delta S_{\text{calc.}} = -4.8 \text{ J/mol}\cdot\text{K}$

$\Delta G_{\text{calc.}} = 8.2 \text{ kJ/mol}$

ν, cm^{-1}	$T_{\text{calc.}}$	Interpretation
β-O-4		
3879	35	ν_{OH} (alcohol)
3868	36	ν_{OH} (alcohol)
3804	129	ν_{OH} (phenolic)
3666	626	ν_{OH} (alcohol)
α-O-4		
3879	28	ν_{OH} (alcohol)
3868	43	ν_{OH} (alcohol)
3801	121	ν_{OH} (phenolic)
3791	108	ν_{OH} (alcohol)



β -5 (56.7 kJ/mol)

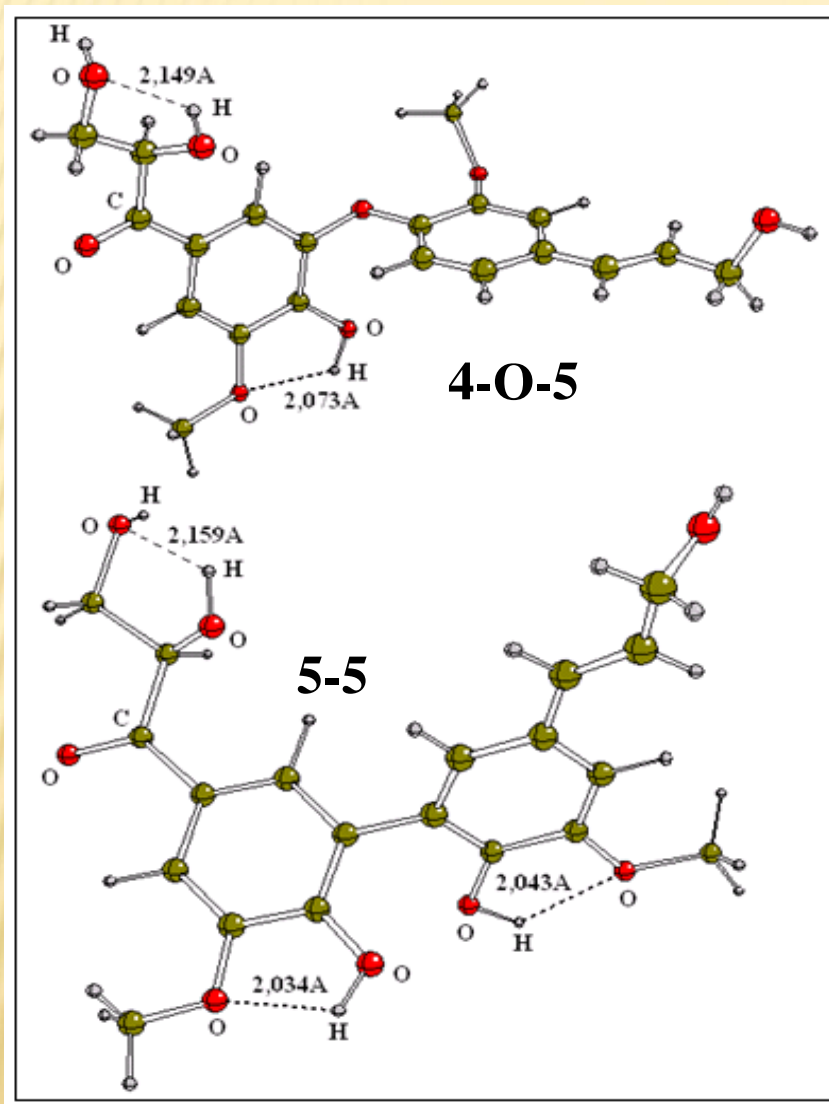
β - β (0.0 kJ/mol)

$\Delta H_{\text{calc.}} = 62.9 \text{ kJ/mol}$

$\Delta S_{\text{calc.}} = +37.9 \text{ J/mol}\cdot\text{K}$

$\Delta G_{\text{calc.}} = 51.6 \text{ kJ/mol}$

ν, cm^{-1}	$T_{\text{calc.}}$	Inter-pretation
β-5		
3803	123	ν_{OH} (phenolic)
1060	71	ν_{CO} (etheric)
1011	99	ν_{CO} (etheric)
β-β		
3805	114 133	ν_{OH} (phenolic)
1126	235	ν_{CO} (etheric)
1011	61	ν_{CO} (etheric)



4-O-5 (75.4 kJ/mol)

5-5 (0.0 kJ/mol)

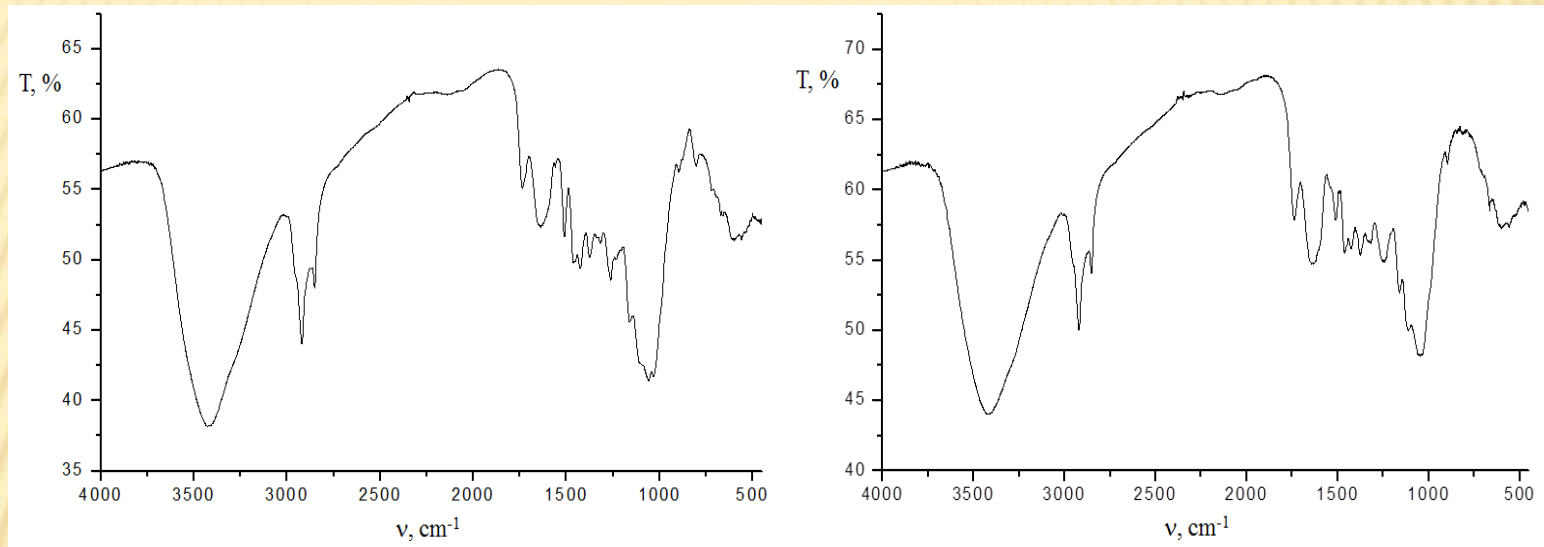
$\Delta H_{\text{calc.}} = 75.6 \text{ kJ/mol}$

$\Delta S_{\text{calc.}} = +15.2 \text{ J/mol}\cdot\text{K}$

$\Delta G_{\text{calc.}} = 71.0 \text{ kJ/mol}$

ν, cm^{-1}	$T_{\text{calc.}}$	Inter-pretation
4-O-5		
3870	46	ν_{OH} (alcohol)
3787	164	ν_{OH} (phenolic)
3772	112	ν_{OH} (alcohol)
1756	252	$\nu_{\text{C=O}}$
5-5		
3869	41	ν_{OH} (alcohol)
3798	160	ν_{OH} (phenolic)
3784	172	ν_{OH} (phenolic)
3776	102	ν_{OH} (alcohol)
1750	292	$\nu_{\text{C=O}}$

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Some typical infrared absorption spectra of native lignin were recorded by means of **SPECTRUM ONE (PerkinElmer)** instrument.

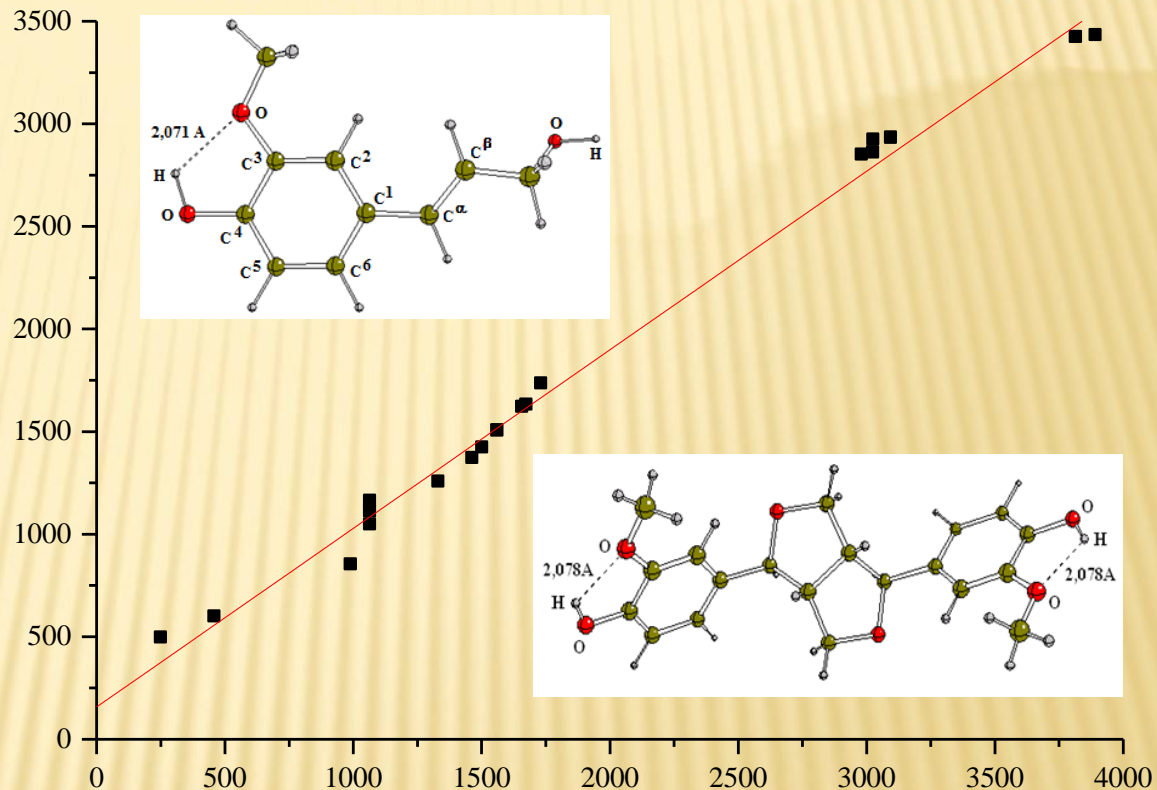
The samples for recording were prepared due to the standard procedure with **KBr**. The effective diameter of the pellets was about **12 mm** with a thickness of nearly **1 mm**. In this case not more than **3 wt%** of wood powder in the pills was appropriate. Some statistical processing of data was carried out using **ORIGIN Professional 6.0**.

By comparative analysis of theoretical and experimental results, it has been shown that the most intensive absorption bands are in area **3400–3430** and **1038–1070** cm^{-1} . For the first one, mainly deals with the stretching vibrations of sterically hindered hydroxyl groups of alcohol or phenolic type with the strength hydrogen bonding between some other structural fragments of macromolecules. There are also two typical stretching vibrations of benzene rings at **1625** and **1510** cm^{-1} . As to the area **1731–1755** cm^{-1} , there is only one not very intensive fringe giving by the stretching vibrations of double carbon-carbon bonds. Finally, some interesting results have also been achieved for **pinoresinol molecular system** (β - β) mainly because of the rigid cage fragment presentation. The most typical bands in this case correspond to the methylene groups with neighboring oxygen atom stretching vibrations of the rings in area **2846–2863** and **1038–1070** cm^{-1} .

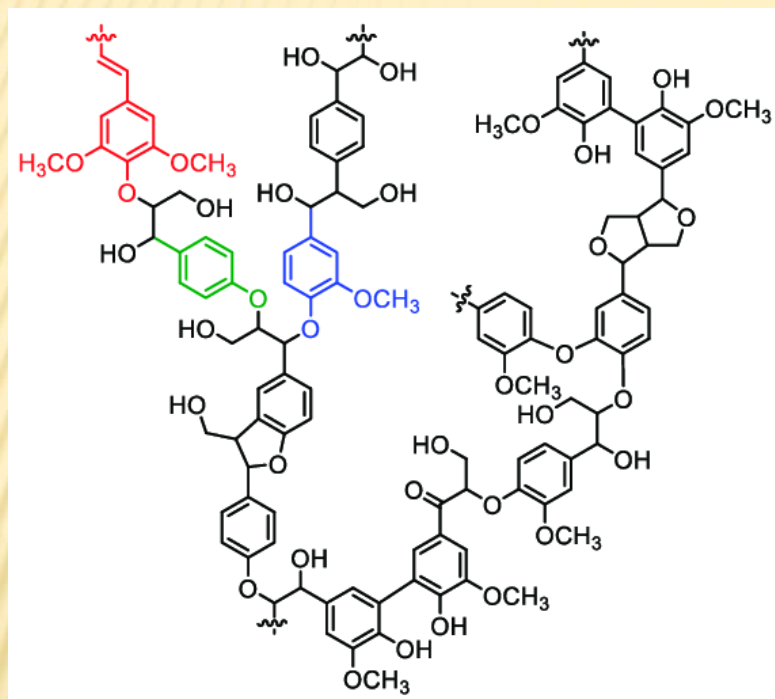
The proposed theoretical models are validated in reflection of spectral and energetic parameters for investigating systems.

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Theory	Experiment
3878 3801	3417, 3427, 3438
3084 3016	2917, 2927, 2938
3015 2970	2833, 2844, 2854
1728	1719, 1729
1671 1655	1615, 1625
1559	1480, 1500, 1510
1499	1408, 1417, 1427
1461	1365, 1375, 1378
1329	1245, 1250
1064	1153, 1156 1092, 1104 1041, 1052
991	844, 847, 865
462	582, 594
255	479, 490, 500



$$v.\delta(\text{Experiment}) = (0.87 \pm 0.02) \cdot v.\delta(\text{Theory}) + (157.89 \pm 39.00); r=0.996; s_0=88.50; n=19$$



Conclusions

Finally, the given results of the quantum-chemical studies show the possibility in principle to use methods and techniques of the quantum chemistry to study features of internal and intermolecular interactions at the single areas level – the structural fragments of lignin macromolecules.

The results of calculations are in good agreement with the spectral data for this irregular biopolymer building and could be critical with regard to the preestimation of identity of single components while producing some nanocomposite materials based on them.

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