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Electronic Supplementary Information

Spectroscopic and Theoretical Study in the Near-Infrared Region of Low Concentration Aliphatic Alcohols

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Part I. TABLES

Table S 1. PED table for methanol (CPCM-B2PLYP-D/SNST). Negative value of a percentage of a coordinate indicates opposite phase of vibration.

Mode	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int [km mol^{-1}]	Coordinate	Contrib. [%]	Coordinate	Contrib. [%]	Coordinate	Contrib. [%]
1	3839.7	3659.8	32.62	νOH	100				
2	3154.7	3013.0	22.86	νas CH_3	90				
3	3089.4	2927.9	48.35	νas’CH_3	100				
4	3030.3	2843.7	59.55	νsCH_3	100				
5	1524.0	1479.5	5.12	δas’CH_3	64	δas CH_3	21	$\delta_{\mathrm{rock}}CH_3$	-12
6	1513.8	1473.8	2.85	δas CH_3	70	δas’CH_3	-24	δ_{rock}’CH_3	-6
7	1490.2	1458.2	3.64	δs CH_3	95				
8	1372.8	1323.2	23.42	OH ip bend.	63	$\delta_{\mathrm{rock}}CH_3$	30	δas’CH_3	5
9	1182.1	1153.5	0.39	δ_{rock}’CH_3	95				
10	1081.9	1067.0	3.67	$\delta_{\mathrm{rock}}CH_3$	52	OH ip bend.	-30	νCO	-16
11	1045.7	1016.1	116.1	νCO	76	OH ip bend.	-15	$\delta_{\mathrm{rock}}CH_3$	8
12	291.6	236.4	105.52	τCO (OH oop bend.)	99				

Table S 2. Calculated first overtones of fundamental modes of methanol (B2PLYP-D/SNST).

1st Overtone of mode	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int [km mol^{-1}]	Main coordinate
1	7679.4	7148.2	3.66	νOH
2	6309.4	5923.9	0.39	νas CH$_3$
3	6178.7	5823.7	0.45	νas’CH$_3$
4	6060.5	5729.0	0.03	νsCH$_3$
5	3048.0	2977.2	0.26	δas’CH$_3$
7	2980.4	2944.9	1.23	δas CH$_3$
6	3027.6	2929.5	0.81	δs CH$_3$
8	2745.7	2633.0	1.06	OH ip bend.
9	2364.2	2302.2	0.03	δ_{rock}’CH$_3$
10	2163.8	2131.9	0.43	δ_{rock}CH$_3$
11	2091.3	2019.5	1.79	νCO
12	583.1	410.8	2.90	τCO (OH oop bend.)

Table S 3. Calculated combination modes of methanol (CPCM-B2PLYP-D/SNST). Intensities in [km mol^{-1}].

Modes	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int	Modes	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int	Modes	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int
2+1	6994.4	6670.3	0.03	7+4	4520.5	4330.4	0.06	9+5	2706.1	2624.5	0.13
3+1	6929.1	6606.8	0.01	8+3	4462.2	4271.4	0.03	9+6	2695.9	2621.1	0.12
4+1	6870.0	6548.1	0.10	8+4	4403.1	4215.3	0.15	9+7	2672.3	2604.4	0.16
3+2	6244.0	5949.5	0.22	9+2	4336.8	4164.8	0.02	10+5	2605.9	2543.6	0.18
4+2	6184.9	5874.0	0.05	9+3	4271.5	4099.3	0.07	10+6	2595.7	2537.9	0.01
4+3	6119.6	5723.5	0.37	10+2	4236.6	4080.2	0.03	10+7	2572.1	2520.1	0.00
5+1	5363.7	5139.0	0.04	9+4	4212.4	4037.4	0.22	11+5	2569.7	2491.7	0.03
6+1	5353.5	5132.3	0.00	11+2	4200.4	4029.6	0.21	11+6	2559.5	2487.8	0.01
7+1	5329.9	5116.6	0.19	10+3	4171.3	4011.6	0.14	11+7	2535.9	2467.3	0.00
8+1	5212.5	4975.2	0.75	11+3	4135.0	3968.0	0.53	9+8	2554.9	2465.3	0.03
9+1	5021.8	4812.1	0.01	10+4	4112.2	3954.8	0.17	10+8	2454.8	2381.4	0.69
10+1	4921.6	4720.5	0.14	11+4	4075.9	3908.1	0.63	11+8	2418.5	2328.4	0.49
11+1	4885.4	4673.8	0.01	12+1	4131.3	3902.0	0.29	10+9	2264.0	2216.4	0.01
5+2	4678.7	4486.0	0.29	12+2	3446.3	3240.0	0.04	11+9	2227.8	2161.6	0.13
6+2	4668.5	4473.6	0.22	12+3	3380.9	3192.0	0.39	11+10	2127.6	2075.1	0.65
7+2	4644.9	4465.3	0.50	12+4	3321.8	3128.9	0.11	12+6	1805.4	1713.5	0.08
6+3	4603.1	4410.5	0.34	6+5	3037.8	2971.0	0.12	12+5	1815.6	1711.8	0.00
7+3	4579.6	4401.8	0.39	7+5	3014.2	2935.4	0.46	12+7	1781.8	1696.6	0.02
5+3	4613.3	4401.6	0.47	7+6	3004.0	2927.1	1.80	12+8	1664.4	1540.8	0.03
6+4	4544.0	4346.4	0.62	8+5	2896.8	2797.6	0.84	12+9	1473.7	1396.8	2.18
5+4	4554.2	4345.7	0.29	8+6	2886.6	2791.6	0.34	12+10	1373.5	1319.4	0.00
8+2	4527.5	4333.9	0.22	8+7	2863.1	2774.8	0.53	12+11	1337.2	1252.4	0.36

Table S 4. Calculated DFT-B3LYP and DFT-B2PLYP frequencies of selected overtones and combination modes of methanol. All values in [cm^{-1}].

	B2PLYP/aVDZ	**B2PLYP/aVTZ**	**B2PLYP/aVQZ**	**B2PLYPD/aVDZ**	**B2PLYPD/aVTZ**	**B2PLYPD/aVQZ**	**B2PLYPD3/aVDZ**	**B2PLYPD3/aVTZ**	**B2PLYPD3/aVQZ**
ν_{02}OH	7134.4	7170.6	7184.7	7135.2	7171.2	7185.4	7133.6	7170.2	7185.0
ν_{as} CH$_3$ + νOH	6660.1	6674.0	6682.3	6650.7	6664.2	6672.6	6656.5	6670.8	6678.6
ν_s CH$_3$ + νOH	6537.4	6555.9	6563.0	6527.8	6544.9	6551.9	6533.7	6552.1	6558.8
(1) δ_{as}CH$_3$ + νOH and (2) δ_sCH$_3$ + νOH	5087.5	5126.2	5136.6	5087.5	5125.7	5136.0	5086.9	5125.8	5135.1
δ_{ip}OH + νOH	4964.2	4984.2	4994.5	4963.3	4983.3	4993.6	4963.3	4983.7	4993.1
δ_{rock}CH$_3$+ νOH	4705.2	4730.9	4741.6	4705.3	4731.8	4742.7	4705.0	4731.0	4740.5
δ_{as}CH$_3$ + ν_{as}CH$_3$	4380.8	4396.3	4397.7	4369.1	4383.5	4385.0	4377.6	4392.3	4391.7
νC-O + ν_{as}CH$_3$	3965.8	3965.1	3969.2	3952.4	3951.8	3956.4	3960.3	3959.3	3961.5
(1) νC-O + ν_{as}CH$_3$ and (2) τC-O + νOH	3900.9	3910.4	3915.2	3889.4	3897.4	3912.5	3894.9	3905.8	3907.6
RMSD	37.7	51.5	58.8	32.8	46.1	54.8	35.3	49.4	56.1

	B3LYP/aVDZ	**B3LYP/aVTZ**	**B3LYP/aVQZ**	**B3LYPD3/aVDZ**	**B3LYPD3/aVTZ**	**B3LYPD3/aVQZ**	**Exp. val.**
ν_{02}OH	7106.8	7136.4	7143.7	7104.9	7135.4	7142.5	7118.3
ν_{as} CH$_3$ + νOH	6609.5	6622.2	6622.9	6602.9	6616.7	6617.1	6582.1
ν_s CH$_3$ + νOH	6499.0	6508.1	6507.9	6492.0	6501.4	6500.8	6476.6
(1) δ_{as}CH$_3$ + νOH and (2) δ_sCH$_3$ + νOH	5062.6	5101.7	5104.7	5060.9	5101.0	5103.5	5088.0
δ_{ip}OH + νOH	4942.1	4962.5	4965.3	4940.5	4961.3	4963.8	4961.0
δ_{rock}CH$_3$+ νOH	4686.2	4711.0	4712.4	4685.0	4710.8	4711.5	4706.2
δ_{as}CH$_3$ + ν_{as}CH$_3$	4325.4	4343.9	4339.8	4313.8	4337.4	4332.6	4390.4
νC-O + ν_{as}CH$_3$	3924.7	3921.1	3916.3	3914.5	3911.6	3906.1	3958.4
(1) νC-O + ν_{as}CH$_3$ and (2) τC-O + νOH	3877.8	3885.2	3870.2	3866.8	3875.2	3858.1	3849.8
RMSD	31.5	29.7	30.5	34.2	29.7	31.3	

Table S 5. Frequency errors (ν_{exp}/ν_{calc}) calculated on the basis of selected overtones and combination modes of methanol.

Vibrational mode	**Group$^{a)}$**	**MP2/ aVTZ**	**MP2/ aVQZ**	**MP2/ SNST**	**MP2/ 6-31G(d,p)**	**B3LYP/ 6-31G(d,p)**	**B3LYP/ N07D**	**B3LYP/ SNST**	**B3LYP-D3/ SNST**	**B2PLYP/ N07D**	**B2PLYP/ SNSD**	**B2PLYP/ SNST**	**B2PLYP-D/ SNST**
ν_{02}OH	1	0.9833	0.9817	0.9921	0.9776	1.0016	0.9955	1.0007	1.0009	0.9895	0.9905	0.9958	0.9959
ν_{as} CH$_3$ + νOH	1	0.9746	0.9722	0.9786	0.9631	0.9938	0.9912	1.0054	0.9983	0.9812	0.9839	0.9868	0.9883
ν_s CH3 + νOH	1	0.9751	0.9749	0.9819	0.9692	0.9985	0.9930	0.9970	1.0003	0.9836	0.9854	0.9891	0.9908
(1) δ_{as}CH$_3$ + νOH and (2) δ_sCH$_3$ + νOH	1	0.9847	0.9840	0.9908	0.9725	0.9962	0.9959	1.0003	1.0008	0.9885	0.9909	0.9944	0.9947
δ_{ip}OH + νOH	1	0.9880	0.9871	0.9943	0.9754	0.9968	0.9975	1.0025	1.0032	0.9907	0.9929	0.9972	0.9975
δ_{rock}CH$_3$+ νOH	1	0.9860	0.9845	0.9933	0.9765	0.9987	0.9974	1.0022	1.0023	0.9909	0.9930	0.9970	0.9970
	Group 1 average	**0.982**	**0.9807**	**0.9885**	**0.9724**	**0.9976**	**0.9951**	**1.0013**	**1.001**	**0.9874**	**0.9895**	**0.9934**	**0.9940**
δ_{as}CH$_3$ + ν'_{as}CH$_3$	2	0.9827	0.9785	0.9810	0.9665	1.0090	1.0086	1.0110	1.0166	0.9927	0.9979	0.9975	1.0004
νC-O + ν'_{as}CH$_3$	2	0.9811	0.9760	0.9813	0.9661	1.0064	1.0041	1.0099	1.0168	0.9903	0.9947	0.9976	1.0011
(1) νC-O + ν'_{as}CH$_3$ and (2) τC-O + νOH	2	0.9581	0.9716	0.9769	0.9581	0.9898	0.9898	0.9905	0.9948	0.9785	0.9853	0.9887	0.9859
	Group 2 average	**0.9739**	**0.9754**	**0.9797**	**0.9635**	**1.0017**	**1.0008**	**1.0038**	**1.0094**	**0.9872**	**0.9926**	**0.9946**	**0.9958**

a) Arbitrary grouping of bands for comparison purposes. Group 1 includes selected combination bands involving νOH mode; group 2 includes selected combination bands without νOH mode.

Table S 6. PED table for *gauche* conformer of ethanol (CPCM-B2PLPY-D/SNST).Negative value of a percentage of a coordinate indicates opposite phase of vibration.

	Freq. [cm^{-1}]		Natural Coordinate Contribution (>5%)															
Mode	Harm	Anh.	Coordinate	C.	Coordinate	C.	Coordinate	C.	Coordinate	C.	Coordinate	C.	Coordinate	C.	Coordinate	C.	Coordinate	C.
21	259.9	257.6	OH ip bend.	90%	C-C tors.	7%												
20	279.1	233.3	C-C tors.	86%	OH ip bend.	-9%												
19	422.2	423.9	CH2 sciss.	76%	CH3 rock.	-17%												
18	805.1	808.6	CH2 rock.	44%	CH3 rock.'	-40%	CH2 twist.	11%										
17	884.0	867.0	C-O str.	35%	C-C str.	29%	CH3 rock.	27%	CH2 wagg.	5%								
16	1062.5	1027.7	C-O str.	57%	C-C str.	-37%												
15	1069.0	1052.0	C-O tors. (OH oop bend.)	31%	CH3 rock.	22%	C-C str.	-10%	CH2 rock.	9%	CH3 rock.'	9%	CH2 twist.	-8%				
14	1134.8	1111.2	CH3 rock.	25%	CH2 rock.	-19%	CH3 rock.'	-13%	CH2 sciss.	9%	C-O str.	-9%	CH2 twist.	7%	C-O tors. (OH oop bend.)	-6%	C-C str.	-6%
13	1286.2	1254.7	CH2 twist.	36%	C-O tors. (OH oop bend.)	-22%	CH3 rock.'	19%	CH2 rock.	13%	CH3 asym.def.	5%						
12	1374.8	1334.0	CH2 twist.	38%	C-O tors. (OH oop bend.)	27%	CH2 wagg.	23%										
11	1406.3	1378.9	CH3 sym. def.	71%	CH2 wagg.	17%												
10	1424.6	1392.8	CH2 wagg.	53%	CH3 sym. def.	-21%	C-C str.	-10%	C-O tors. (OH oop bend.)	-7%								
9	1489.3	1451.7	CH3 asym.def.	57%	CH3 asym.def.'	-32%	CH3 rock.'	-9%										
8	1493.8	1454.0	CH3 asym.def.'	47%	CH3 asym.def.	26%	CH2 sciss.	-17%	CH3 rock.	-5%								
7	1522.1	1486.9	CH2 sciss.	82%	CH3 asym.def.'	8%												
6	3029.1	2884.7	CH2 symm. str.	95%														
5	3032.4	2932.7	CH2 as. str.	95%														
4	3100.5	2960.2	CH3 symm. str.	95%														
3	3117.6	2976.8	CH3 as.' str.	97%														
2	3128.9	2984.7	CH3 as. str.	96%														
1	3813.0	3628.5	O-H str.	100%														

Table S 7. PED table for *trans*conformer of ethanol (CPCM-B2PLPY-D/SNST). Negative value of a percentage of a coordinate indicates opposite phase of vibration.

Mode	Freq. [cm^{-1}]		Natural Coordinates Contributions (>5%)							
	Harm.	Anh.	Coordinate	C.	Coordinate	C.	Coordinate	C.	Coordinate	C.
21	232.5	226.9	OH ip bend.	51%	C-C tors.	46%				
20	275.2	264.9	C-C tors.	51%	OH ip bend.	-45%				
19	419.9	415.3	CH2 sciss.	78%	CH3 rock.	-15%				
18	818.3	815.6	CH3 rock.'	43%	CH2 rock.	-40%	CH2 twist.	-13%		
17	893.9	877.4	C-O str.	41%	CH3 rock.	27%	C-C str.	23%	CH2 wagg.	6%
16	1038.3	1009.2	C-C str.	50%	C-O tors. (OH oop bend.)	19%	C-O str.	-16%	CH3 rock.	-9%
15	1091.0	1070.0	C-O str.	49%	CH3 rock.	-32%	C-O tors. (OH oop bend.)	6%	CH2 sciss.	-5%
14	1185.1	1160.2	CH2 rock.	54%	CH3 rock.'	28%	CH2 twist.	-11%		
13	1266.3	1235.6	C-O tors. (OH oop bend.)	58%	CH2 wagg.	-17%	CH3 rock.	10%	CH2 sciss.	5%
12	1305.9	1276.1	CH2 twist.	84%	CH3 rock.'	12%				
11	1408.1	1375.5	CH3 sym. def.	83%	CH2 wagg.	12%				
10	1455.2	1403.3	CH2 wagg.	59%	C-O tors. (OH oop bend.)	13%	C-C str.	-12%	CH3 sym. def.	-9%
9	1485.7	1445.4	CH3 asym.def.	68%	CH3 asym.def.'	-23%	CH3 rock.'	-9%		
8	1500.2	1461.4	CH3 asym.def.'	57%	CH3 asym.def.	19%	CH2 sciss.	-10%	CH3 rock.	-6%
7	1532.0	1490.1	CH2 sciss.	87%	CH3 asym.def.'	5%				
6	3017.0	2895.8	CH2 symm. str.	100%						
5	3043.7	2945.8	CH2 as. str.	100%						
4	3056.7	2917.3	CH3 symm. str.	96%						
3	3127.0	2984.1	CH3 as.' str.	100%						
2	3130.3	2985.9	CH3 as. str.	98%						
1	3825.6	3649.0	O-H str.	100%						

Table S 8. Calculated first overtones of fundamental modes of *gauche* conformer of ethanol (CPCM-B2PLYP-D/SNST).

1st overtone of mode	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int [km mol^{-1}]
1	7625.9	7084.4	2.43
2	6257.7	5919.1	0.13
3	6235.2	5913.1	0.16
4	6201.0	5882.4	0.04
5	6064.8	5783.0	0.00
6	6058.1	5700.9	0.42
7	3044.1	2982.4	0.99
8	2987.7	2911.5	0.10
9	2978.5	2863.3	0.33
10	2849.1	2765.7	0.67
11	2812.5	2743.4	0.06
12	2749.7	2654.7	0.54
13	2572.4	2505.9	0.19
14	2269.6	2223.1	0.04
15	2137.9	2102.6	0.26
16	2124.9	2046.6	0.36
17	1767.9	1731.8	0.20
18	1610.1	1627.7	0.11
19	844.4	849.4	0.03
20	558.1	405.5	3.05
21	519.8	507.3	0.06

Table S 9. Calculated first overtones of fundamental modes of *trans* conformer of ethanol (CPCM-B2PLYP-D/SNST).

1st Overtone of mode	ν_{harm} [cm^{-1}]	ν_{anh} [cm^{-1}]	Int [km mol^{-1}]
1	7651.1	7127.0	2.88
2	6260.6	5920.7	0.24
3	6254.0	5894.8	0.24
4	6113.3	5765.8	0.60
5	6087.4	5804.0	0.00
6	6034.0	5707.0	0.05
7	3064.0	2993.2	0.22
8	3000.5	2907.1	5.01
9	2971.4	2864.7	0.02
10	2910.4	2797.2	0.69
11	2816.2	2737.2	0.07
12	2611.9	2547.3	0.01
13	2532.6	2463.2	0.64
14	2370.2	2309.4	0.05
15	2182.1	2132.7	0.09
16	2076.6	2011.9	0.19
17	1787.8	1752.5	0.33
18	1636.5	1640.8	0.10
19	839.9	830.9	0.01
20	550.3	521.6	0.96
21	464.9	447.5	2.22

Table S 10. Calculated combinational modes of *gauche* conformer of ethanol (CPCM-B2PLYP-D/SNST). Order of columns: modes in combination, anharmonic frequency [cm^{-1}], intensity [km mol^{-1}].

2	1	6612.6	0.01
3	1	6604.0	0.00
3	2	5921.4	0.14
4	1	6587.0	0.03
4	2	5903.0	0.43
4	3	5870.9	0.48
5	1	6535.9	0.00
5	2	5843.3	0.04
5	3	5840.7	0.01
5	4	5819.0	0.10
6	1	6528.1	0.03
6	2	5869.8	0.08
6	3	5863.2	0.13
6	4	5843.5	0.15
6	5	5796.4	0.01
7	1	5114.5	0.03
7	2	4466.5	0.02
7	3	4460.9	0.16
7	4	4443.8	0.35
7	5	4391.1	0.02
7	6	4367.2	0.33
8	1	5083.0	0.00
8	2	4427.9	0.16
8	3	4428.3	0.10
8	4	4408.3	0.05
8	5	4349.1	0.09
8	6	4352.1	0.06
8	7	2952.0	0.33
9	1	5081.4	0.04
9	2	4430.7	0.08
9	3	4419.4	0.06
9	4	4406.4	0.12
9	5	4344.9	0.12
9	6	4355.1	0.01
9	7	2938.0	1.92
9	8	2905.3	0.30
10	1	5016.8	0.29
10	2	4374.0	0.01
10	3	4364.6	0.03
10	4	4350.4	0.01
10	5	4305.6	0.03
10	6	4303.1	0.03
10	7	2874.6	0.48
10	8	2841.8	0.42
10	9	2839.9	0.39
11	1	5004.3	0.20
11	2	4357.0	0.26
11	3	4349.6	0.13
11	4	4333.3	0.27
11	5	4295.5	0.22
11	6	4279.5	0.02
11	7	2862.8	0.11
11	8	2828.8	0.41
11	9	2828.3	0.14
11	10	2752.3	0.53
12	1	4955.6	0.25
12	2	4317.8	0.11
12	3	4309.9	0.02
12	4	4293.2	0.02
12	5	4241.7	0.06
12	6	4234.7	0.01
12	7	2817.7	0.42
12	8	2787.6	0.18
12	9	2786.9	0.02
12	10	2715.3	0.59
12	11	2708.4	0.17
13	1	4878.2	0.11
13	2	4237.6	0.33
13	3	4229.2	0.25
13	4	4213.6	0.01
13	5	4161.4	0.22
13	6	4152.7	0.26
13	7	2737.5	0.10
13	8	2705.2	0.01
13	9	2705.0	0.07
13	10	2636.7	0.04
13	11	2628.4	0.01
13	12	2583.0	0.36
14	1	4740.4	0.04
14	2	4094.9	0.14
14	3	4089.5	0.04
14	4	4072.9	0.03
14	5	4019.6	0.12
14	6	4010.1	0.42
14	7	2596.3	0.02
14	8	2565.2	0.02
14	9	2563.8	0.09
14	10	2500.6	0.03
14	11	2488.2	0.04
14	12	2439.3	0.16
14	13	2365.6	0.06
15	1	4675.3	0.06
15	2	4036.0	0.05
15	3	4028.2	0.07
15	4	4010.8	0.01
15	5	3958.9	0.09
15	6	3952.7	0.09
15	7	2538.1	0.03
15	8	2505.9	0.02
15	9	2503.4	0.02
15	10	2439.5	0.09
15	11	2427.1	0.05
15	12	2381.8	0.33
15	13	2303.4	0.20
15	14	2165.0	0.09
16	1	4656.9	0.02
16	2	4014.6	0.04
16	3	4006.3	0.05
16	4	3990.5	0.01
16	5	3937.1	0.01
16	6	3932.3	0.17
16	7	2514.1	0.04
16	8	2482.9	0.05
16	9	2481.4	0.01
16	10	2412.2	0.04
16	11	2402.5	0.20
16	12	2357.9	0.10
16	13	2278.3	0.03
16	14	2136.0	0.10
16	15	2077.1	0.15
17	1	4495.0	0.01
17	2	3851.7	0.04
17	3	3842.5	0.06
17	4	3827.0	0.01
17	5	3774.1	0.05
17	6	3767.7	0.10
17	7	2352.2	0.02
17	8	2319.8	0.01
17	9	2318.1	0.01
17	10	2254.4	0.33
17	11	2241.5	0.06
17	12	2198.4	0.01
17	13	2119.8	0.02
17	14	1977.1	0.01
17	15	1917.0	0.01
17	16	1888.7	1.24
18	1	4437.2	0.00
18	2	3790.8	0.01
18	3	3782.9	0.02
18	4	3765.9	0.13
18	5	3715.4	0.03
18	6	3706.4	0.06
18	7	2292.7	0.04
18	8	2258.5	0.09
18	9	2259.9	0.03
18	10	2198.9	0.02
18	11	2185.9	0.09
18	12	2143.3	0.03
18	13	2061.3	0.07
18	14	1922.8	0.07
18	15	1862.1	0.04
18	16	1835.6	0.01
18	17	1675.6	0.00
19	1	4052.6	0.01
19	2	3408.7	0.05
19	3	3400.5	0.16
19	4	3384.3	0.07
19	5	3332.0	0.00
19	6	3325.1	0.02
19	7	1910.0	0.01
19	8	1878.2	0.00
19	9	1878.2	0.01
19	10	1812.5	0.06
19	11	1801.6	0.03
19	12	1757.8	0.06
19	13	1679.1	0.02
19	14	1537.7	0.03
19	15	1479.8	0.03
19	16	1450.6	0.31
19	17	1289.5	0.29
19	18	1232.2	0.02
20	1	3868.2	0.95
20	2	3216.2	0.02
20	3	3207.4	0.04
20	4	3190.8	0.07
20	5	3141.4	0.01
20	6	3138.1	0.09
20	7	1721.6	0.01
20	8	1688.9	0.01
20	9	1688.9	0.05
20	10	1623.2	0.02
20	11	1612.4	0.05
20	12	1566.6	0.19
20	13	1493.3	0.28
20	14	1350.0	0.73
20	15	1301.1	0.03
20	16	1257.9	0.96
20	17	1099.4	0.02
20	18	1045.6	6.81
20	19	655.1	0.63
21	1	3885.5	0.11
21	2	3241.5	0.19
21	3	3235.0	0.18
21	4	3219.1	0.20
21	5	3162.7	0.02
21	6	3158.4	0.02
21	7	1745.1	0.02
21	8	1713.5	0.05
21	9	1711.7	0.11
21	10	1649.1	0.01
21	11	1635.9	0.01
21	12	1589.5	0.01
21	13	1508.7	0.01
21	14	1372.9	0.09
21	15	1311.7	0.05
21	16	1286.8	0.30
21	17	1130.2	0.38
21	18	1073.4	0.03
21	19	687.0	0.06
21	20	486.6	0.74

Table S 11. Calculated combinational modes of *trans* conformer of ethanol (B2PLYPD/SNST). Order of columns: modes in combination, anharmonic frequency [cm^{-1}], intensity [km mol^{-1}].

2	1	6634.9	0.00
3	1	6632.8	0.00
3	2	5931.5	0.24
4	1	6566.6	0.00
4	2	5895.1	0.13
4	3	5900.9	0.03
5	1	6567.9	0.00
5	2	5833.1	0.07
5	3	5828.4	0.07
5	4	5834.4	0.07
6	1	6532.7	0.10
6	2	5865.3	0.00
6	3	5867.5	0.04
6	4	5673.7	0.73
6	5	5802.4	0.03
7	1	5138.9	0.01
7	2	4473.2	0.01
7	3	4473.8	0.01
7	4	4392.1	0.78
7	5	4406.8	0.00
7	6	4348.4	0.37
8	1	5111.8	0.00
8	2	4432.4	0.18
8	3	4442.9	0.15
8	4	4377.9	0.00
8	5	4367.7	0.10
8	6	4353.9	0.03
8	7	2962.2	0.09
9	1	5094.2	0.00
9	2	4422.5	0.15
9	3	4411.3	0.13
9	4	4363.2	0.04
9	5	4346.5	0.13
9	6	4328.7	0.01
9	7	2933.8	0.46
9	8	2905.5	0.16
10	1	5058.6	0.09
10	2	4400.2	0.03
10	3	4397.2	0.01
10	4	4332.6	0.01
10	5	4337.7	0.03
10	6	4295.6	0.02
10	7	2901.5	0.49
10	8	2869.5	3.81
10	9	2857.1	0.14
11	1	5023.8	0.00
11	2	4356.1	0.36
11	3	4352.1	0.29
11	4	4291.5	0.08
11	5	4307.5	0.18
11	6	4261.6	0.04
11	7	2865.0	0.18
11	8	2834.5	0.63
11	9	2818.0	0.18
11	10	2778.2	0.96
12	1	4924.0	0.00
12	2	4261.2	0.25
12	3	4259.5	0.06
12	4	4191.0	0.03
12	5	4194.6	0.14
12	6	4151.9	0.11
12	7	2762.2	0.00
12	8	2734.8	0.04
12	9	2719.8	0.01
12	10	2677.0	0.60
12	11	2648.4	0.07
13	1	4874.5	0.50
13	2	4220.2	0.08
13	3	4218.8	0.12
13	4	4151.4	0.04
13	5	4153.6	0.14
13	6	4119.8	0.12
13	7	2724.6	0.12
13	8	2697.3	0.05
13	9	2678.4	0.00
13	10	2639.0	0.44
13	11	2608.8	0.00
13	12	2511.4	0.02
14	1	4804.2	0.00
14	2	4139.2	0.12
14	3	4138.3	0.05
14	4	4074.4	0.11
14	5	4073.6	0.15
14	6	4035.3	0.30
14	7	2634.4	0.30
14	8	2616.0	0.00
14	9	2598.5	0.14
14	10	2570.4	0.02
14	11	2527.8	0.02
14	12	2430.9	0.04
14	13	2385.2	0.00
15	1	4715.4	0.16
15	2	4055.2	0.07
15	3	4051.0	0.01
15	4	3989.1	0.28
15	5	3987.5	0.10
15	6	3954.6	0.34
15	7	2558.5	0.01
15	8	2531.1	0.05
15	9	2513.7	0.00
15	10	2478.4	0.21
15	11	2443.7	0.00
15	12	2341.8	0.00
15	13	2303.7	0.46
15	14	2222.1	0.06
16	1	4653.7	0.03
16	2	3993.8	0.00
16	3	3993.7	0.07
16	4	3928.5	0.01
16	5	3927.3	0.06
16	6	3894.1	0.07
16	7	2497.9	0.04
16	8	2471.4	0.00
16	9	2452.7	0.01
16	10	2415.5	0.09
16	11	2380.9	0.35
16	12	2279.1	0.00
16	13	2235.8	0.36
16	14	2161.3	0.00
16	15	2075.1	0.43
17	1	4525.4	0.02
17	2	3863.3	0.03
17	3	3858.6	0.07
17	4	3796.4	0.12
17	5	3795.1	0.03
17	6	3762.0	0.14
17	7	2365.7	0.02
17	8	2338.3	0.01
17	9	2320.7	0.01
17	10	2288.1	0.07
17	11	2250.9	0.12
17	12	2152.3	0.01
17	13	2110.3	0.14
17	14	2030.9	0.00
17	15	1942.2	0.42
17	16	1882.4	0.82
18	1	4465.0	0.00
18	2	3798.3	0.05
18	3	3797.4	0.00
18	4	3729.9	0.16
18	5	3733.3	0.01
18	6	3696.2	0.09
18	7	2300.5	0.01
18	8	2274.2	0.06
18	9	2258.3	0.06
18	10	2229.1	0.02
18	11	2191.3	0.06
18	12	2092.1	0.06
18	13	2053.2	0.00
18	14	1968.3	0.17
18	15	1887.5	0.01
18	16	1823.5	0.00
18	17	1693.5	0.01
19	1	4063.4	0.12
19	2	3401.1	0.00
19	3	3398.9	0.20
19	4	3333.8	0.00
19	5	3334.2	0.01
19	6	3299.7	0.01
19	7	1904.5	0.03
19	8	1878.6	0.00
19	9	1860.4	0.00
19	10	1827.5	0.06
19	11	1790.7	0.03
19	12	1693.4	0.00
19	13	1650.0	0.19
19	14	1570.2	0.00
19	15	1486.0	0.09
19	16	1421.4	0.21
19	17	1291.1	0.01
19	18	1229.8	0.01
20	1	3921.9	0.57
20	2	3250.9	0.12
20	3	3247.8	0.13
20	4	3188.7	0.04
20	5	3181.6	0.00
20	6	3154.4	0.02
20	7	1753.8	0.03
20	8	1727.9	0.04
20	9	1709.3	0.05
20	10	1674.3	0.00
20	11	1639.8	0.02
20	12	1540.8	0.04
20	13	1503.7	0.03
20	14	1432.0	0.26
20	15	1336.9	0.06
20	16	1277.1	0.00
20	17	1138.2	0.07
20	18	1082.1	10.36
20	19	679.8	0.10
21	1	3884.8	0.59
21	2	3212.1	0.07
21	3	3210.1	0.24
21	4	3150.7	0.15
21	5	3142.6	0.00
21	6	3116.3	0.02
21	7	1715.0	0.00
21	8	1689.3	0.04
21	9	1671.5	0.05
21	10	1638.9	0.06
21	11	1600.7	0.00
21	12	1504.9	0.30
21	13	1464.5	0.23
21	14	1381.7	3.16
21	15	1304.9	0.05
21	16	1238.7	0.01
21	17	1106.4	0.16
21	18	1041.5	3.45
21	19	643.0	0.01
21	20	469.1	2.67

Table S 12. Calculated and experimental position of components of first overtone band of OH stretching mode of ethanol. Calculation results with CPCM solvent model applied. Experimental values resolved by second derivative and independently by band fitting.

	Position [cm^{-1}]				
	Calculated			Experimental	
	CPCM-B3LYP/SNST	CPCM-B3LYP-D3/SNST	CPCM-B2PLYP-D/SNST	2nd deriv.	Band fitting
A (*trans*)	7105.8	7105.4	7127.0	7106.1	7105.9
B (*gauche*)	7055.4	7077.9	7084.4	7082.4	7083.1
Frequency error (calc./exp.)					
A	1.000	1.000	1.003		
B	0.996	0.999	1.000		
Avg.	0.998	1.000	1.002		

Note, that for 1-propanol we do not present the PED tables nor detailed calculated data for overtones and combinational modes because of the excessive volume of the dataset involved (almost 500 calculated vibrational modes for each of 5 conformational isomers of 1-propanol). These datasets are available from corresponding authors upon request.

Table S 13. Energy difference between *gauche* and *trans* conformational isomers of ethanol ($\Delta E=E_{\text{gauche}}-E_{\text{trans}}$) calculated with the use of exemplary quantum methods.

Quantum method	$\Delta E=E_{\text{gauche}}-E_{\text{trans}}$ [kcal/mol]
B3LYP/SNST	0.08
B2PLYP-D/SNST	0.09
B2PLYP/SNST	0.15
B2PLYP/SNSD	0.23
MP2/aVTZ	0.20

Table S 14. Accuracy of three different implementations of VPT2 method on the frequency of selected NIR modes of methanol. Results obtained on B2PLYP-D/SNST level; no solvent model was applied here.

		Peak position [cm^{-1}]		
mode	**Experimental**	**GVPT2**	**DCPT2**	**HDCPT2**
ν_{02}OH	**7118.3**	7147.7	7056.3	7146.9
ν_{as} CH$_3$ + νOH	**6582.1**	6659.9	6613.2	6658.5
ν_s CH$_3$ + νOH	**6476.6**	6536.7	6519.1	6563.7
(1) δ_{as}CH$_3$ + νOH and (2) δ_sCH$_3$ + νOH	**5088.0**	5115.2	5057.4	5102.7
δ_{ip}OH + νOH	**4961.0**	4973.5	4927.5	4972.9
δ_{rock}CH$_3$+ νOH	**4706.2**	4720.4	4674.5	4719.8
$\delta_{as'}$CH$_3$ + $\nu_{as'}$CH$_3$	**4390.4**	4388.7	4412.4	4411.6
νC-O + $\nu_{as'}$CH$_3$	**3958.4**	3954.1	3961.2	3960.4

		ν_{exp}/ν_{calc}		
		GVPT2	**HDCPT2**	**DVPT2**
ν_{02}OH		0.9959	1.0088	0.9960
ν_{as} CH$_3$ + νOH		0.9883	0.9953	0.9885
ν_s CH$_3$ + νOH		0.9908	0.9935	0.9867
(1) δ_{as}CH$_3$ + νOH and (2) δ_sCH$_3$ + νOH		0.9947	1.0061	0.9971
δ_{ip}OH + νOH		0.9975	1.0068	0.9976
δ_{rock}CH$_3$+ νOH		0.9970	1.0068	0.9971
	Avg. val.	**0.9940**	**1.0029**	**0.9938**

Table S 15. Frequency difference calculated for ν_{02} OH stretching band of ethanol isomers with and without solvation model. Comparison of different solvation models (CPCM, IEF-PCM, SMD) applied for DFT-B3LYP and DFT-B2PLYP methods. All values in [cm^{-1}].

	B2PLYP/SNST				B3LYP/SNST			
	no solv. mod.	CPCM	IEF-PCM	SMD	no solv. mod.	CPCM	IEF-PCM	SMD
trans	7142.8	7127.0	7139.8	7106.1	7116.1	7105.8	7111.6	7068.3
gauche	7104.4	7084.4	7089.8	7062.2	7074.3	7055.4	7050.3	7053.0
ν_{trans}- ν_{gauche}	38.4	42.6	50.0	43.9	41.8	50.5	61.3	15.2

	B3LYP-D3/SNST			
	no solv. mod.	CPCM	IEF-PCM	SMD
trans	7119.2	7105.6	7109.0	7051.3
gauche	7071.4	7050.5	7047.8	7054.4
ν_{trans}- ν_{gauche}	47.8	55.0	61.2	-3.0

Table S 16. Comparison of computational time required for frequency job, including anharmonic VPT2 calculation of NIR spectra of methanol, for selected quantum methods. Values sorted by CPU time in increasing order. Relative ratio in accordance with real time, where the quickest method has arbitrary value of 1.

		CPU time [s]	Real time [hh:mm:ss]	Real time [s]	Relative ratio
B3LYP/6-31G(d,p)		117	0:05:53	353	1
B3LYP/6-31G(d,p)	CPCM	135	0:06:15	375	1.1
B3LYP/6-31G(d,p)	IEF-PCM	147	0:06:49	409	1.2
B3LYP/6-31G(d,p)	SMD	151	0:07:02	422	1.2
B3LYP/N07D		157	0:07:46	466	1.3
B3LYP/SNST		246	0:22:25	1345	3.8
B3LYP-D3/SNST		246	0:22:31	1351	3.8
B2PLYP/N07D		370	0:17:40	1060	3.0
B2PLYP/SNSD		660	0:31:00	1860	5.3
B2PLYP/SNST		886	0:42:14	2534	7.2
B2PLYP-FC/SNST		887	0:40:48	2448	6.9
B2PLYP-D/SNST		891	0:42:00	2520	7.1
B2PLYP/SNST	CPCM	928	0:41:55	2515	7.1
B2PLYP-D/SNST	CPCM	938	0:44:04	2644	7.5
B2PLYP/SNST	SMD	957	0:43:00	2580	7.3
B2PLYP/SNST	IEF-PCM	971	0:43:43	2623	7.4
MP2/aVTZ		2512	1:49:13	6553	18.6
MP2/aVQZ		46083	33:08:08	119288	337.9

Part II. FIGURES

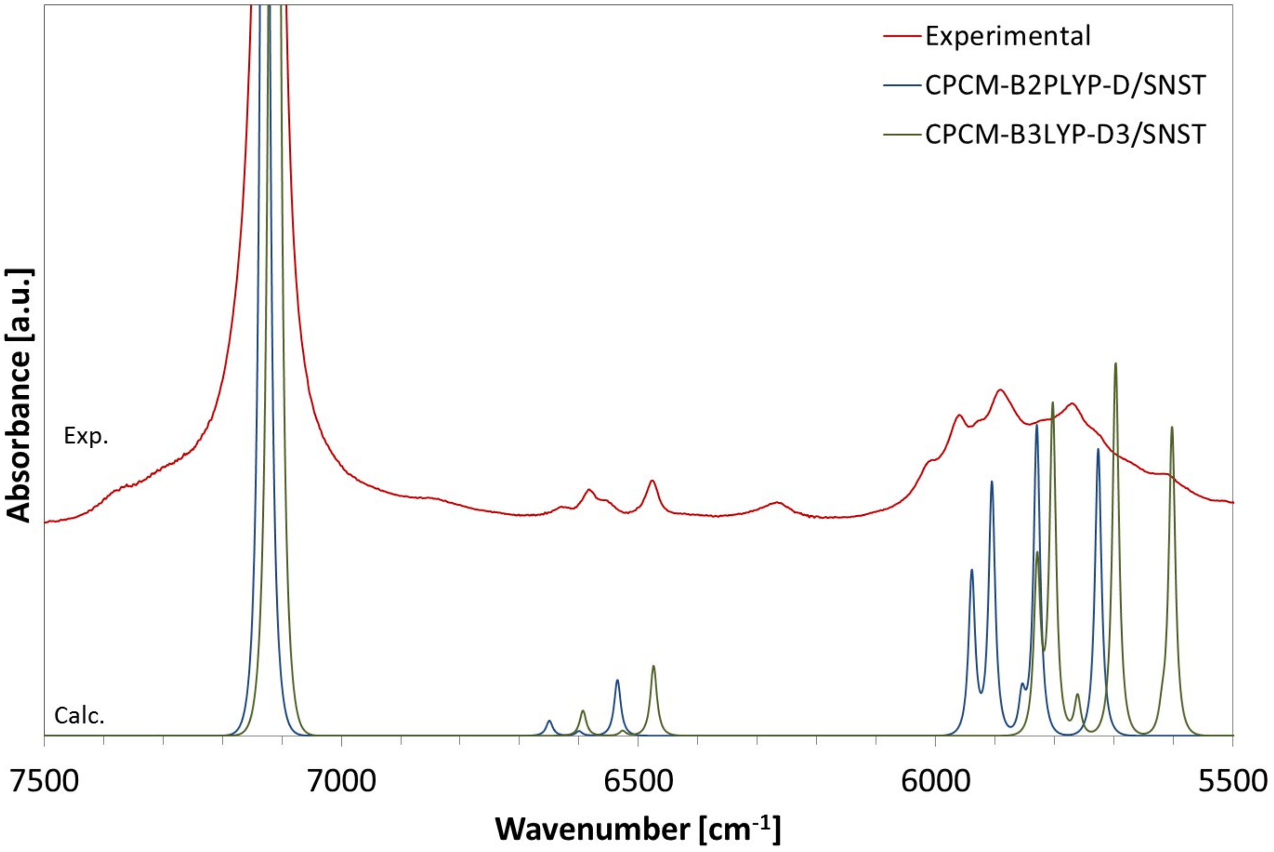

Figure S 1. Experimental and calculated (B2PLYP-D/SNST and B3LYP-D3/SNST; both applied with CPCM solvent model of CCl_4) NIR spectra of methanol. Details of the spectra in the 7500 – 5500 cm^{-1} region.

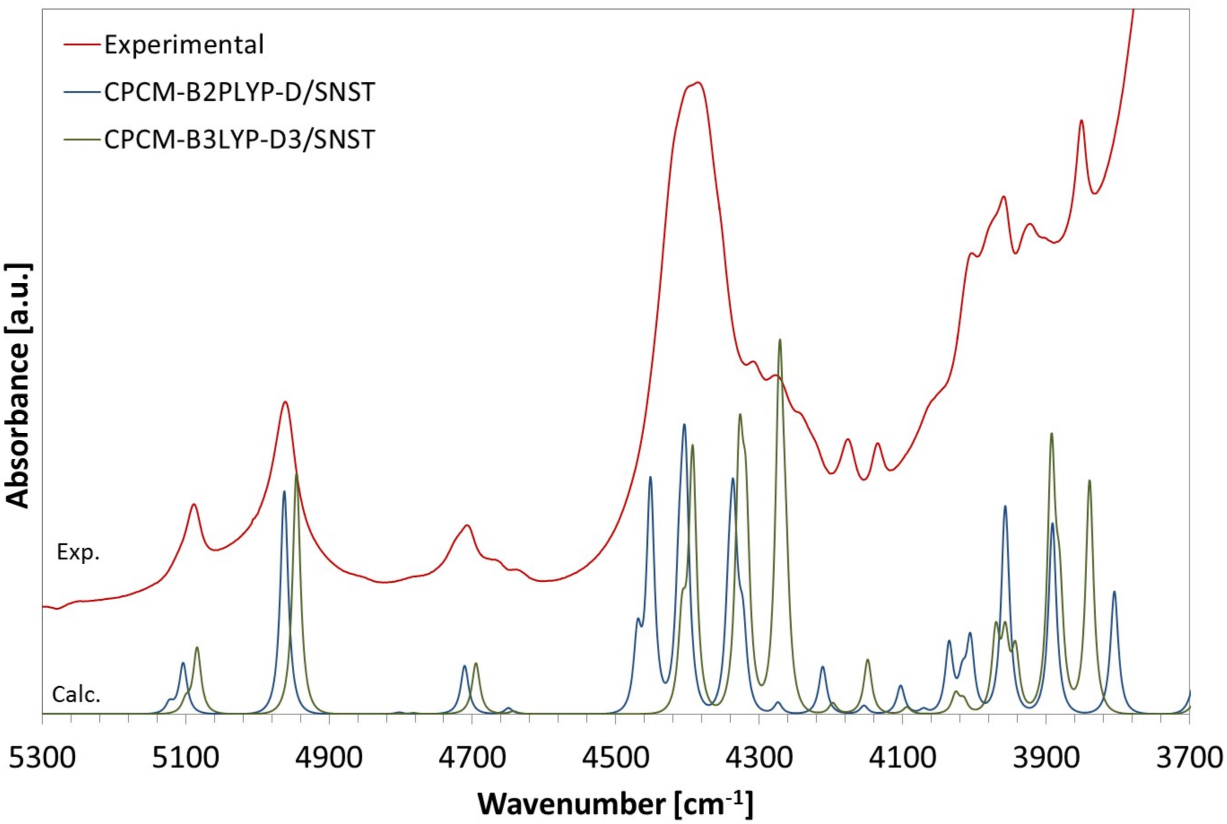

Figure S 2. Experimental and calculated (B2PLYP-D/SNST and B3LYP-D3/SNST; both applied with CPCM solvent model of CCl_4) NIR spectra of methanol. Details of the spectra in the 5300 – 3700 cm^{-1} region.

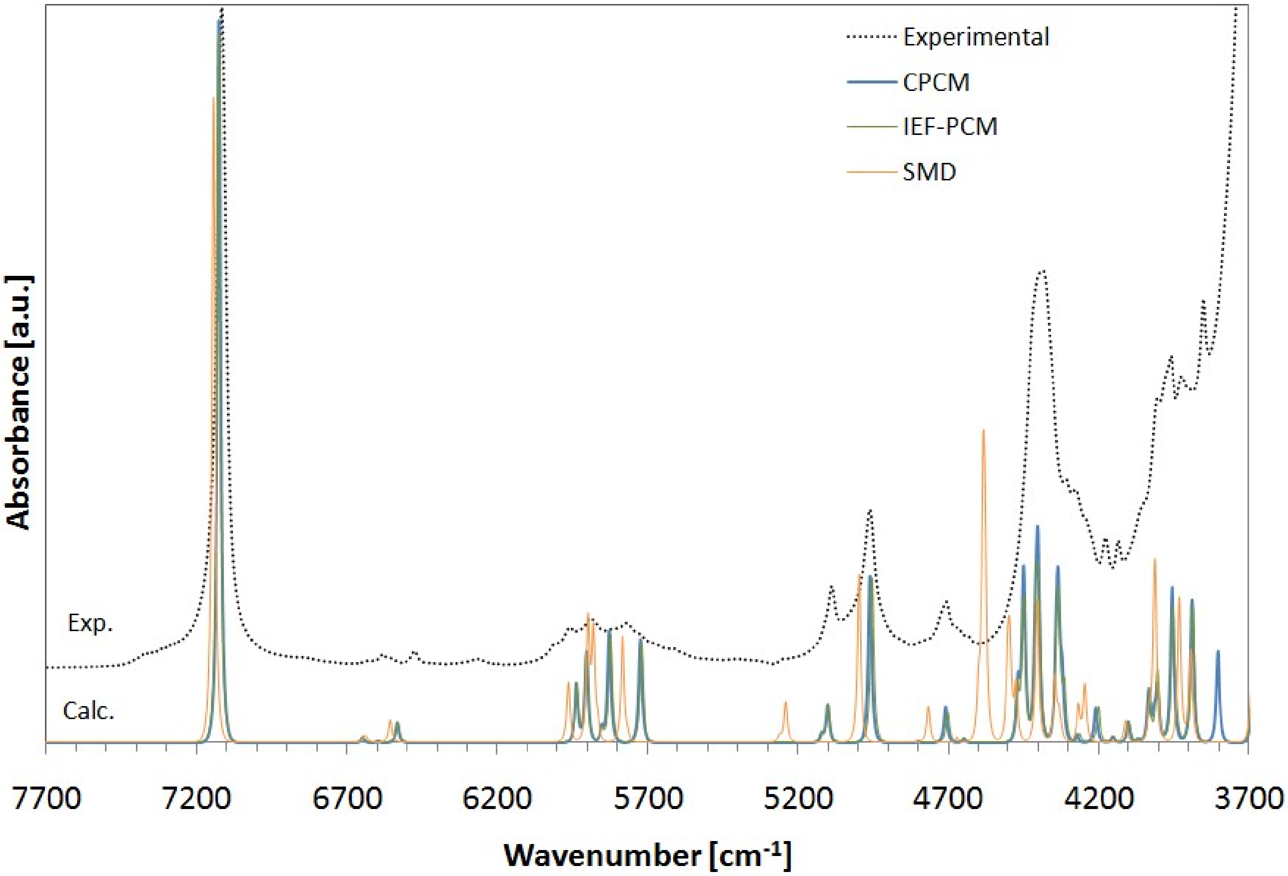

Figure S 3. Experimental spectrum of (CCl_4) diluted methanol and B2PLYP-D/SNST calculated spectra with three different solvation models applied (CPCM, IEF-PCM and SMD).

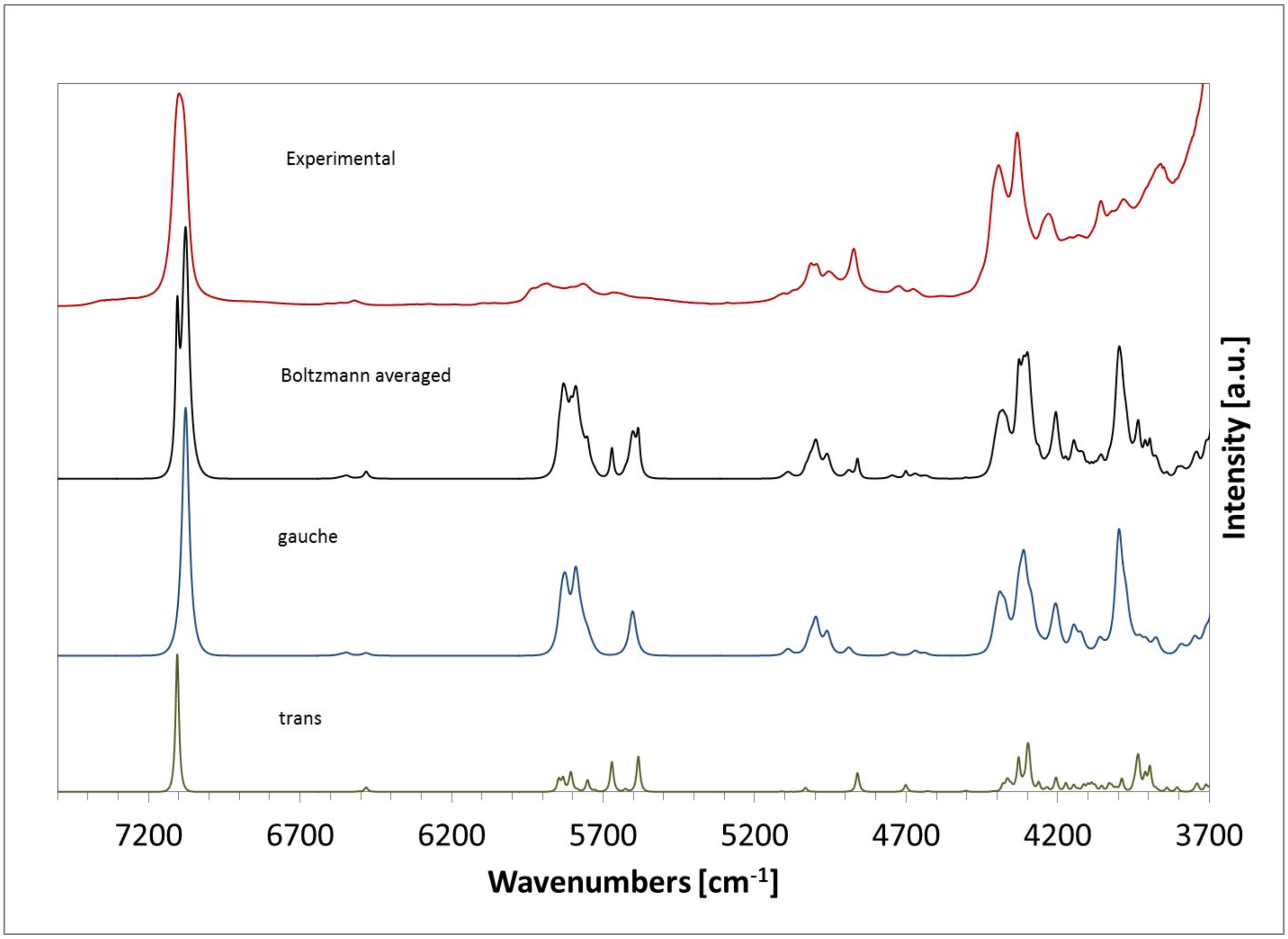

Figure S 4. Experimental and calculated NIR spectra of ethanol. CPCM-B3LYP-D3/SNST spectra of *gauche* and *trans* isomers and Boltzmann averaged final predicted spectrum presented. Relative intensities of spectra of isomers are presented in accordance to relative abundances.

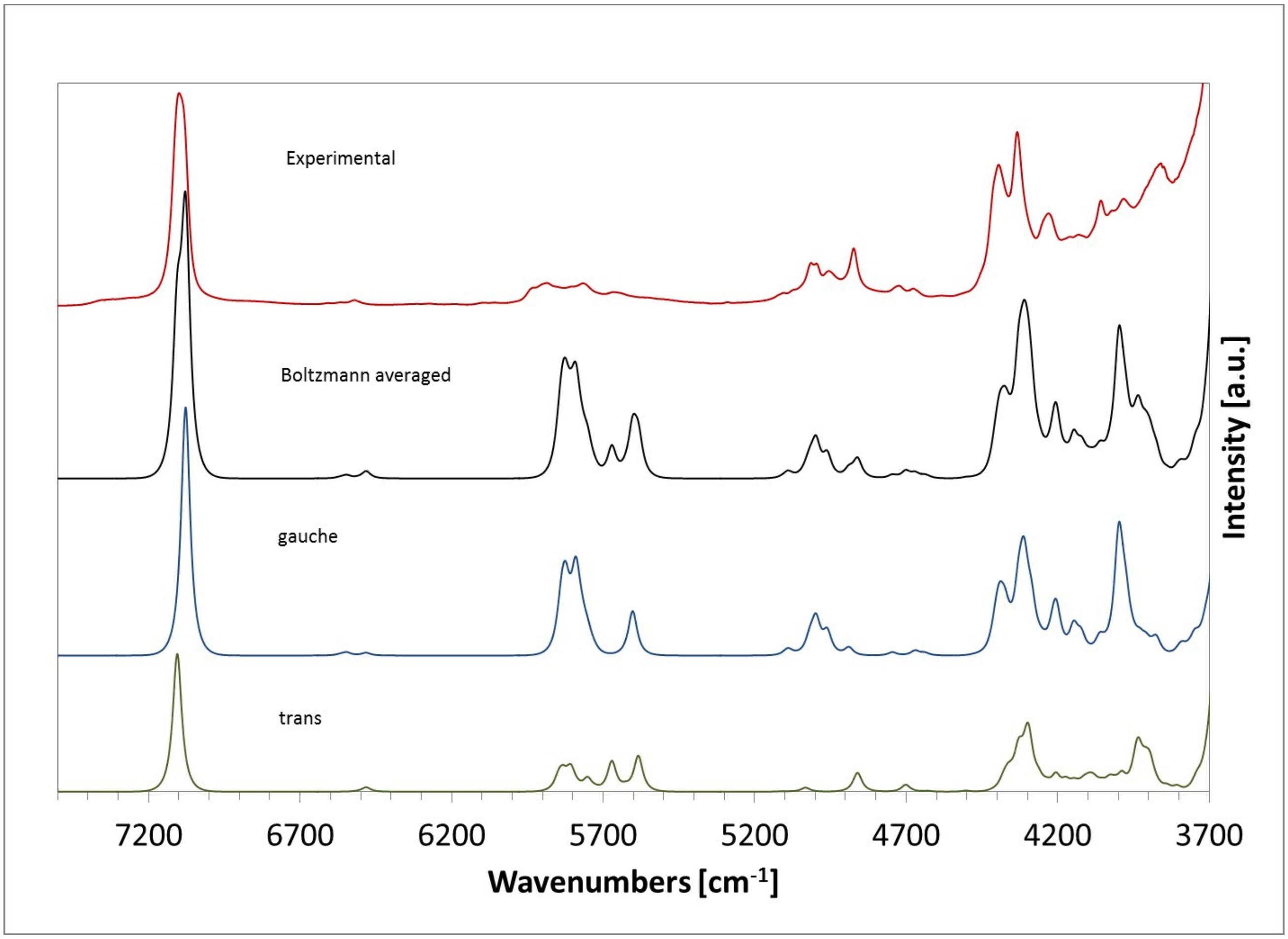

Figure S 5. Experimental and calculated NIR spectra of ethanol. CPCM-B3LYP-D3/SNST spectra of *gauche* and *trans* isomers and Boltzmann averaged final predicted spectrum presented. Relative intensities of spectra of isomers are presented in accordance to relative abundances (wider bands).

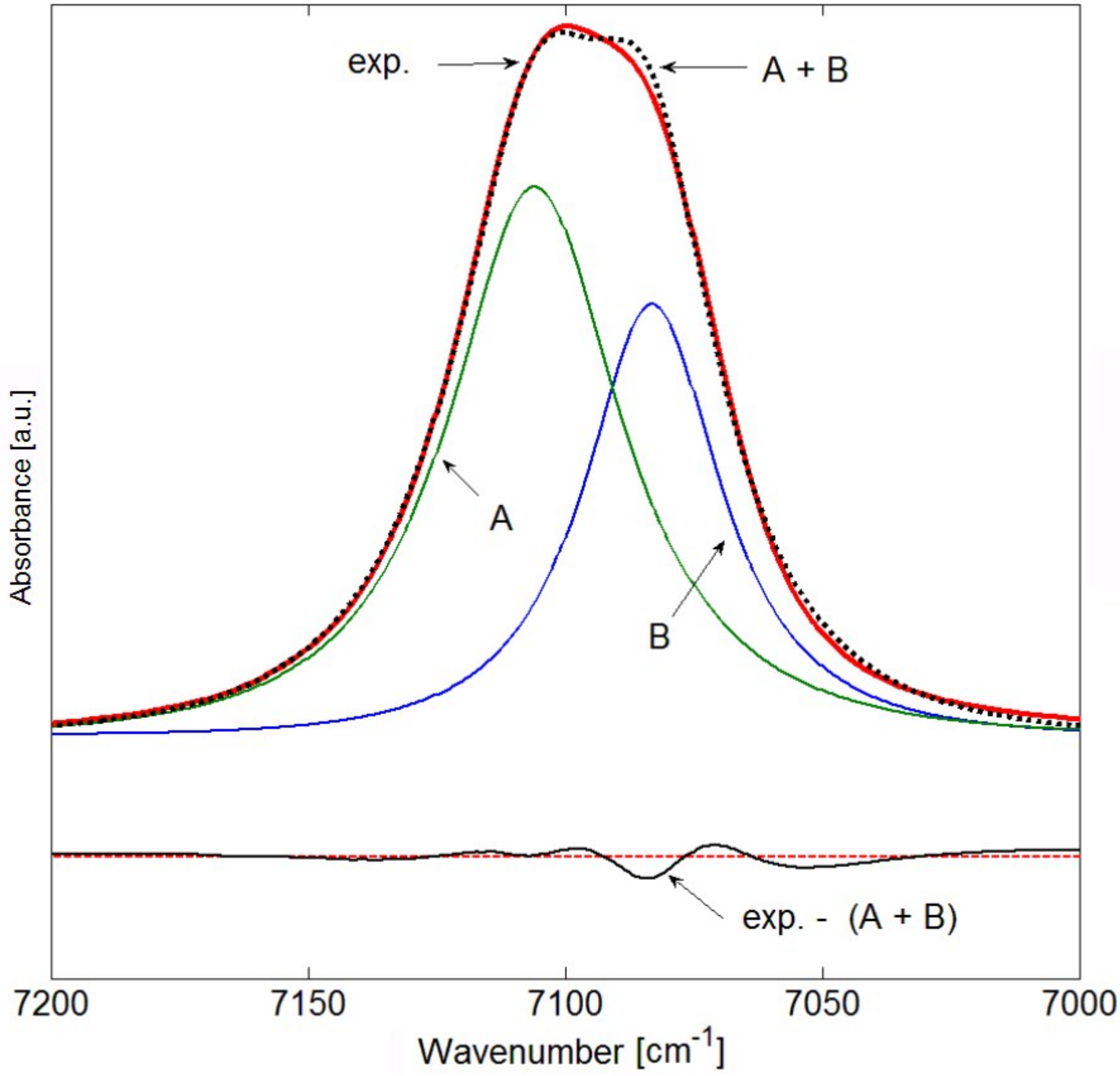

Figure S 6. Result of two-component band fitting (Cauchy-Gauss Product Function, Least Squares Regression, Powell gradientless optimization algorithm) for 1st overtone band of OH stretching mode in the experimental NIR spectrum of ethanol. Position of resolved components: 7105.9 and 7083.1 cm^{-1}.

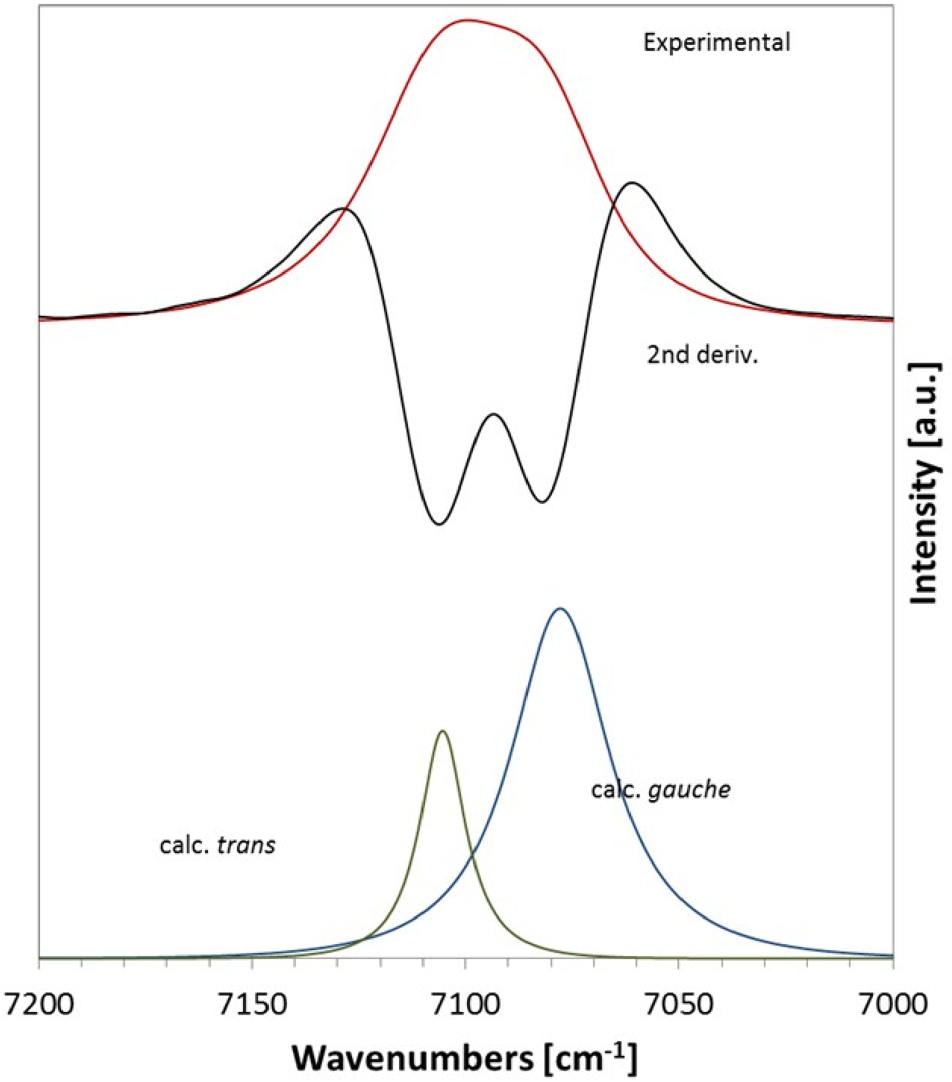

Figure S 7. Details of ethanol spectrum in the spectral range covering first overtone band of OH stretching mode. Experimental, 2nd derivative and calculated (CPCM-B3LYP-D3/SNST) components of ν^1OH band.

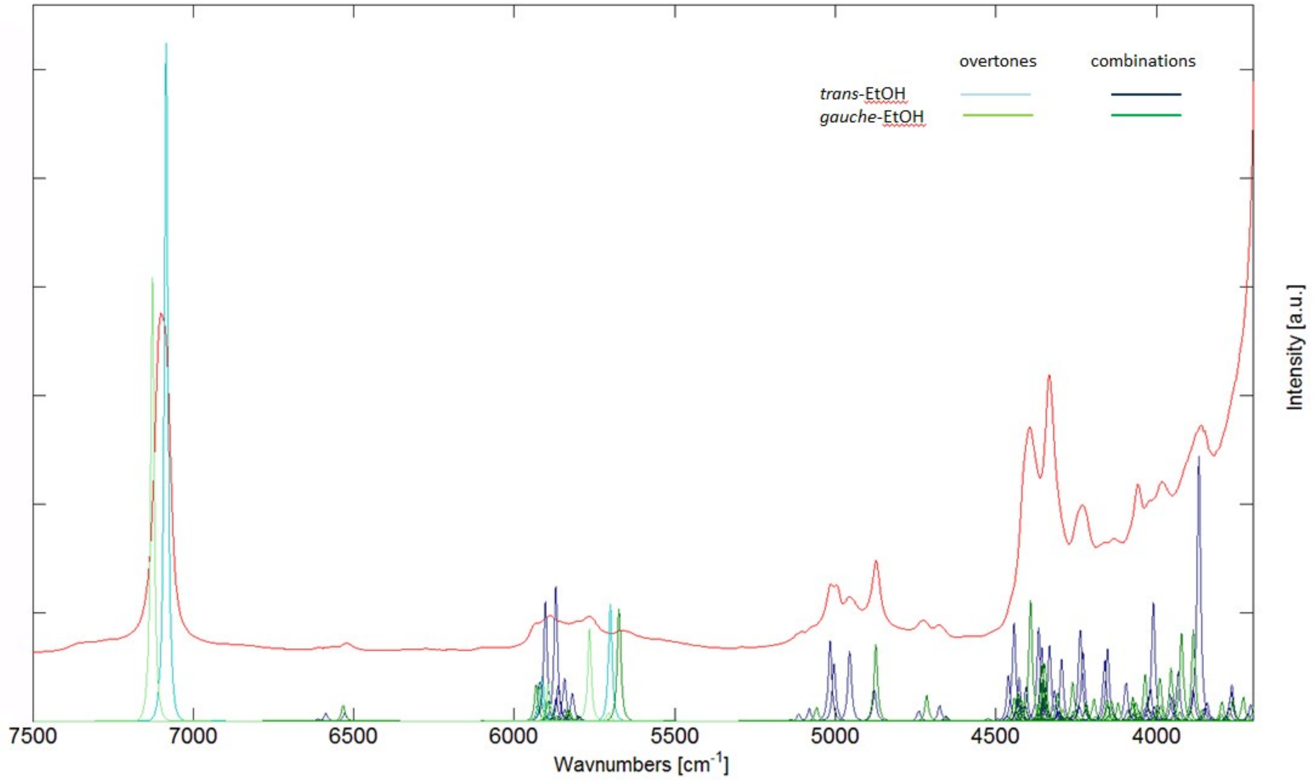

Figure S 8. Details of calculated NIR spectrum of ethanol. Individual calculated overtones and combinational bands of both conformers (CPCM-B3LYP-D3/SNST).

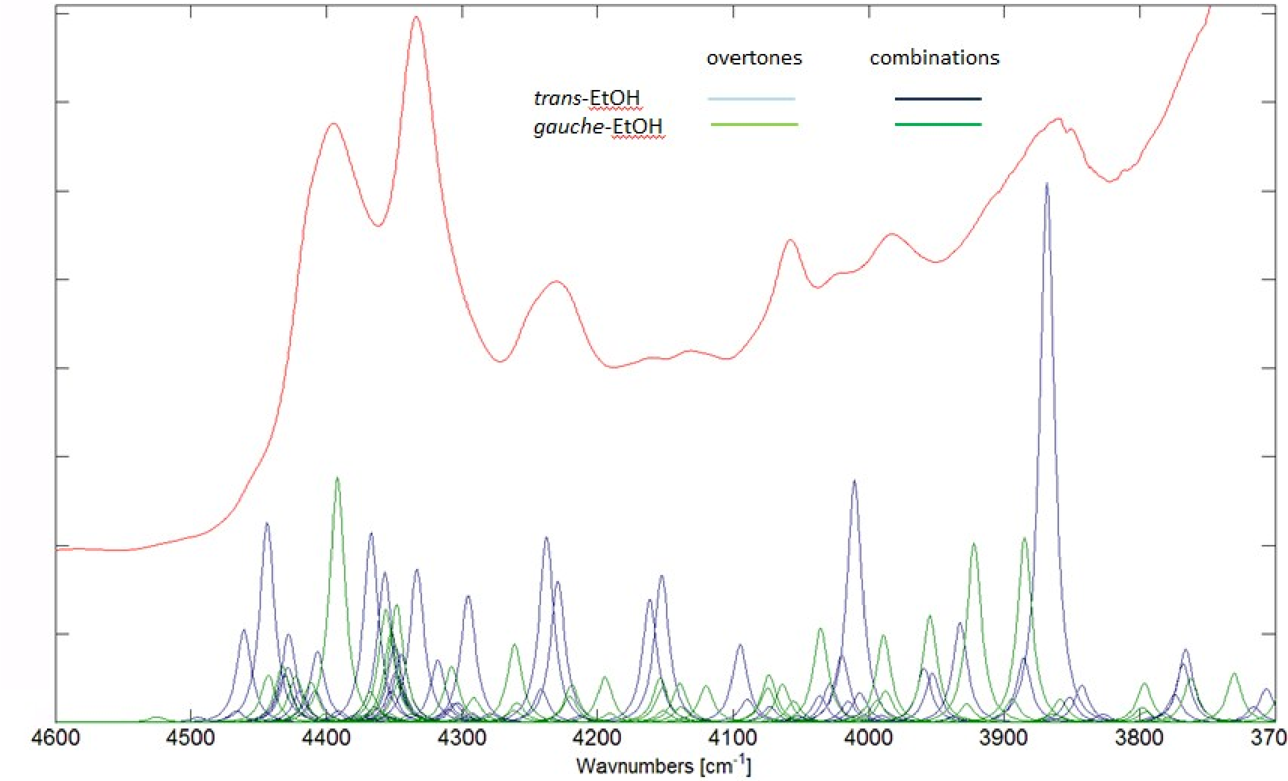

Figure S 9. Details of calculated NIR spectrum of ethanol – lower NIR range. Individual calculated overtones and combinational bands of both conformers (CPCM-B3LYP-D3/SNST).

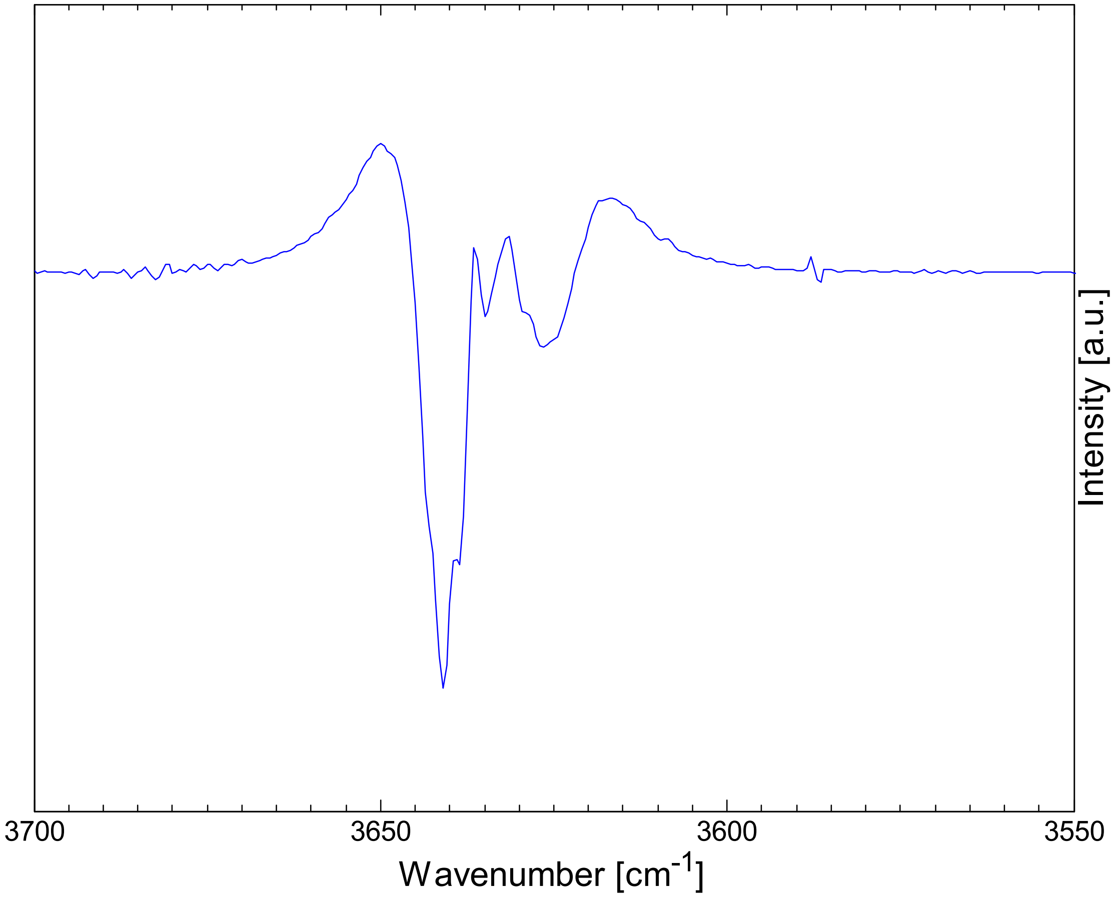

Figure S 10. Second derivative of fundamental band of OH stretching mode of 1-propanol.

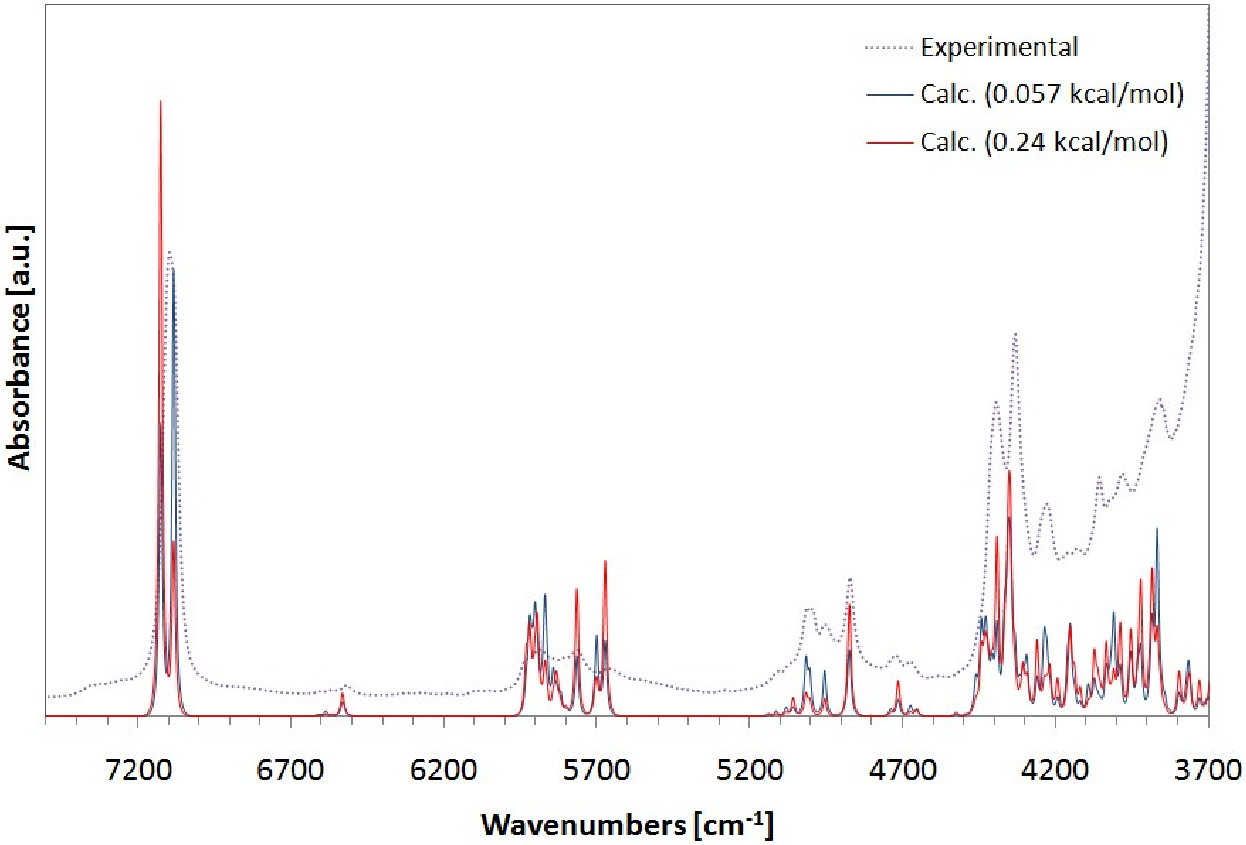

Figure S 11. **Comparison of calculated (CPCM-B2PYP-D/SNST) NIR spectra of ethanol obtained with use of different two values of ($\Delta E = E_{gauche}-E_{trans}$); 0.057 kcal/mol and 0.24 kcal/mol.**

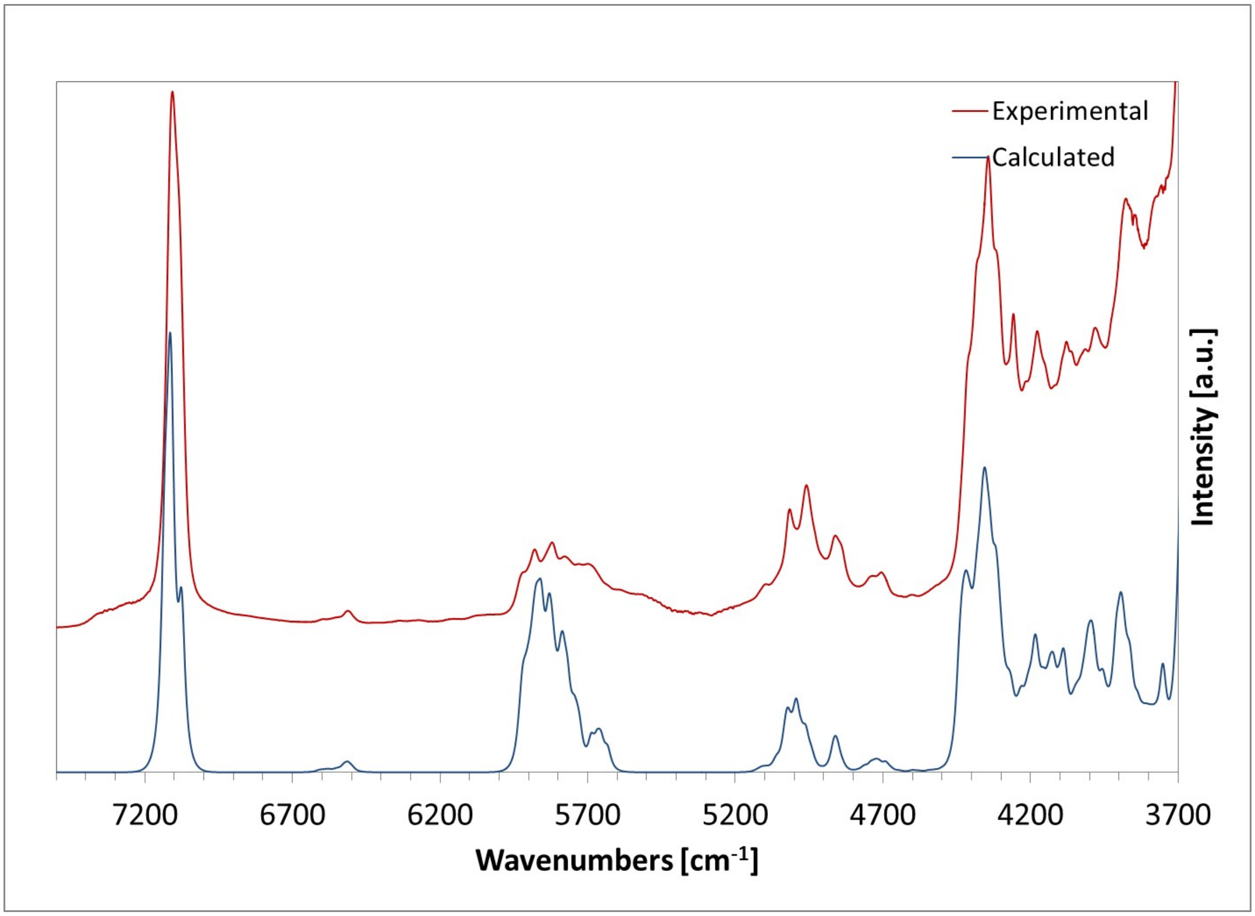

Figure S 12. Experimental and calculated (CPCM-B2PLYP-D/SNST) of 1-propanol. Wider FWHH of model bands applied.

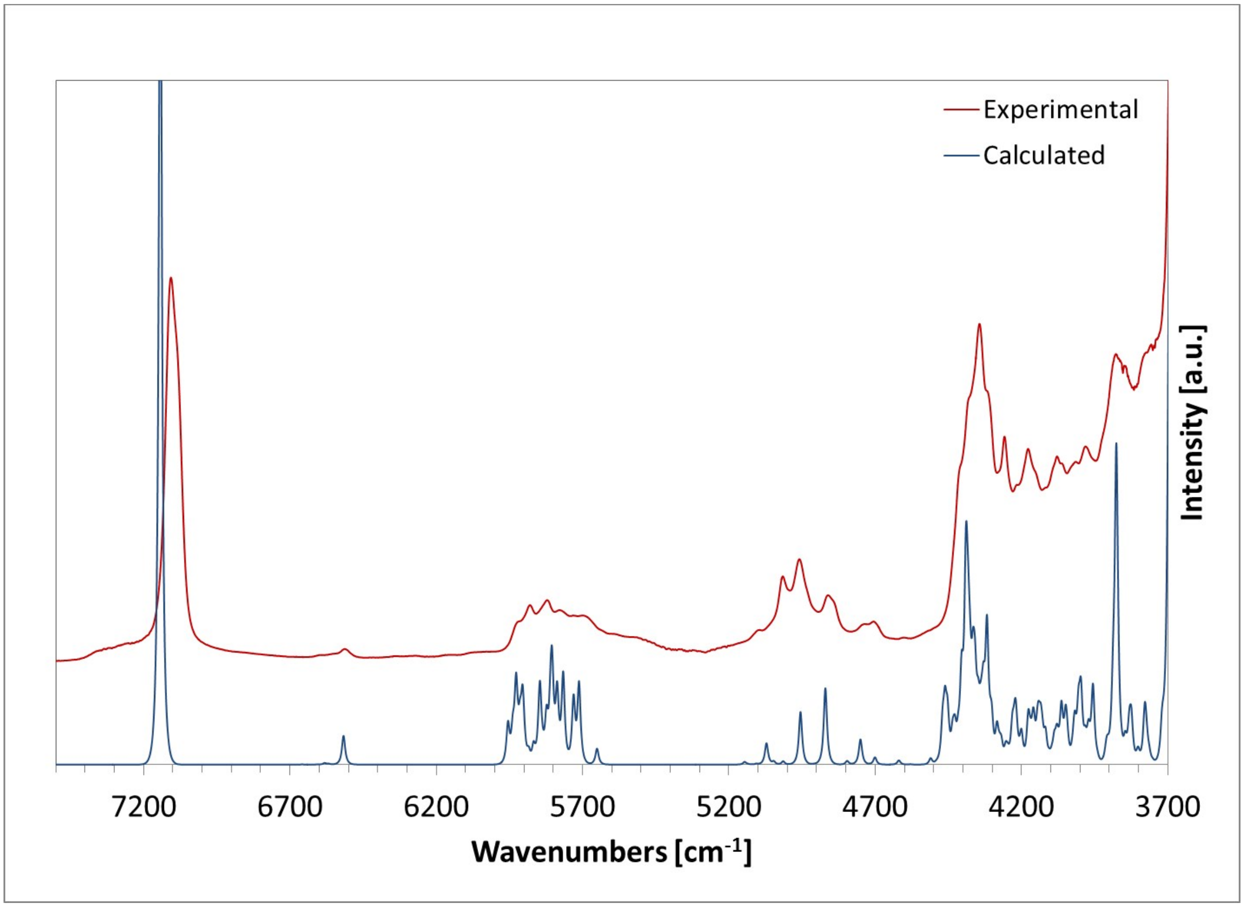

Figure S 13. Experimental and calculated (CPCM-B2PLYP-D/SNST) NIR spectra of 1-propanol. Only dominant conformer *Tg* of 1-propanol used in calculated spectrum.

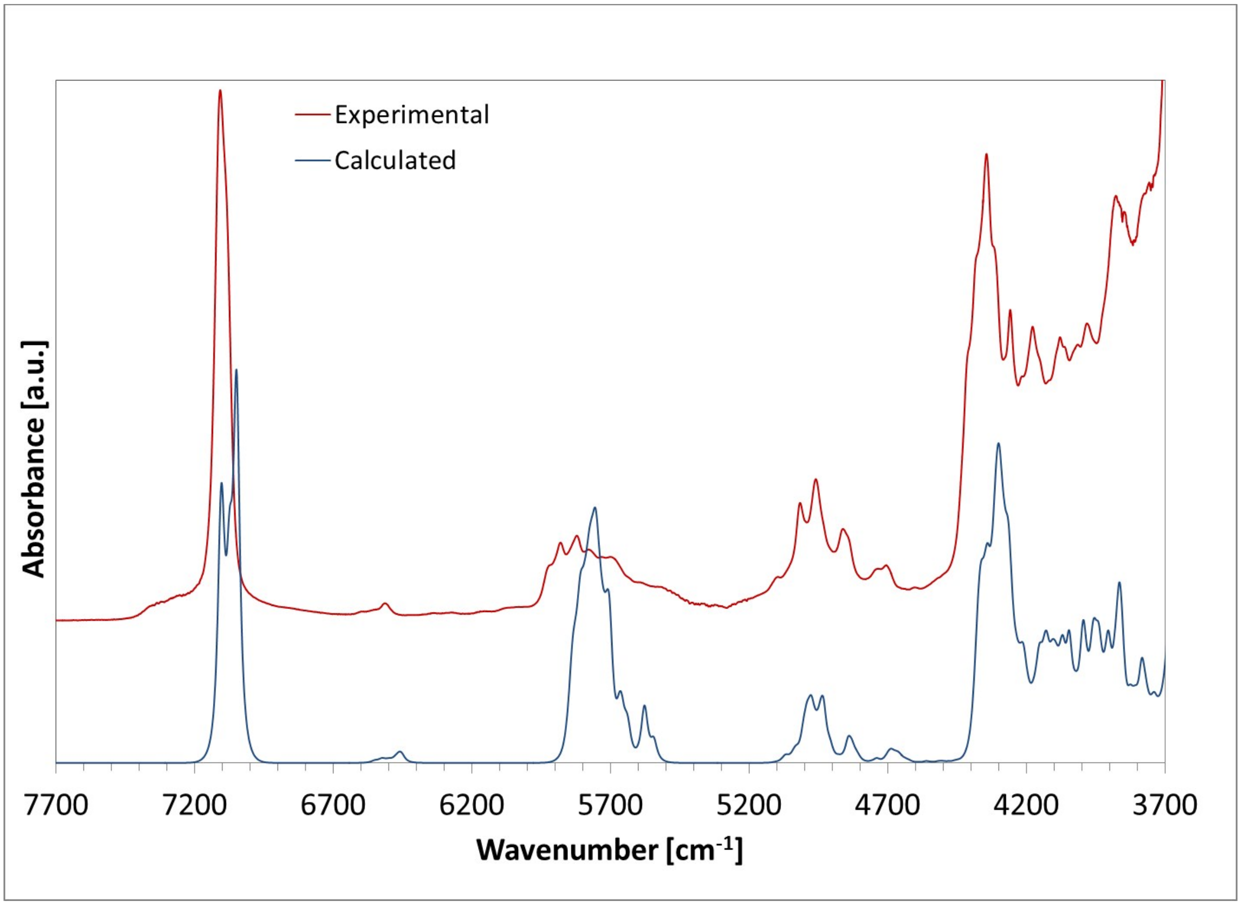

Figure S 14. Experimental and calculated (CPCM-B3LYP-D3/SNST) of 1-propanol.

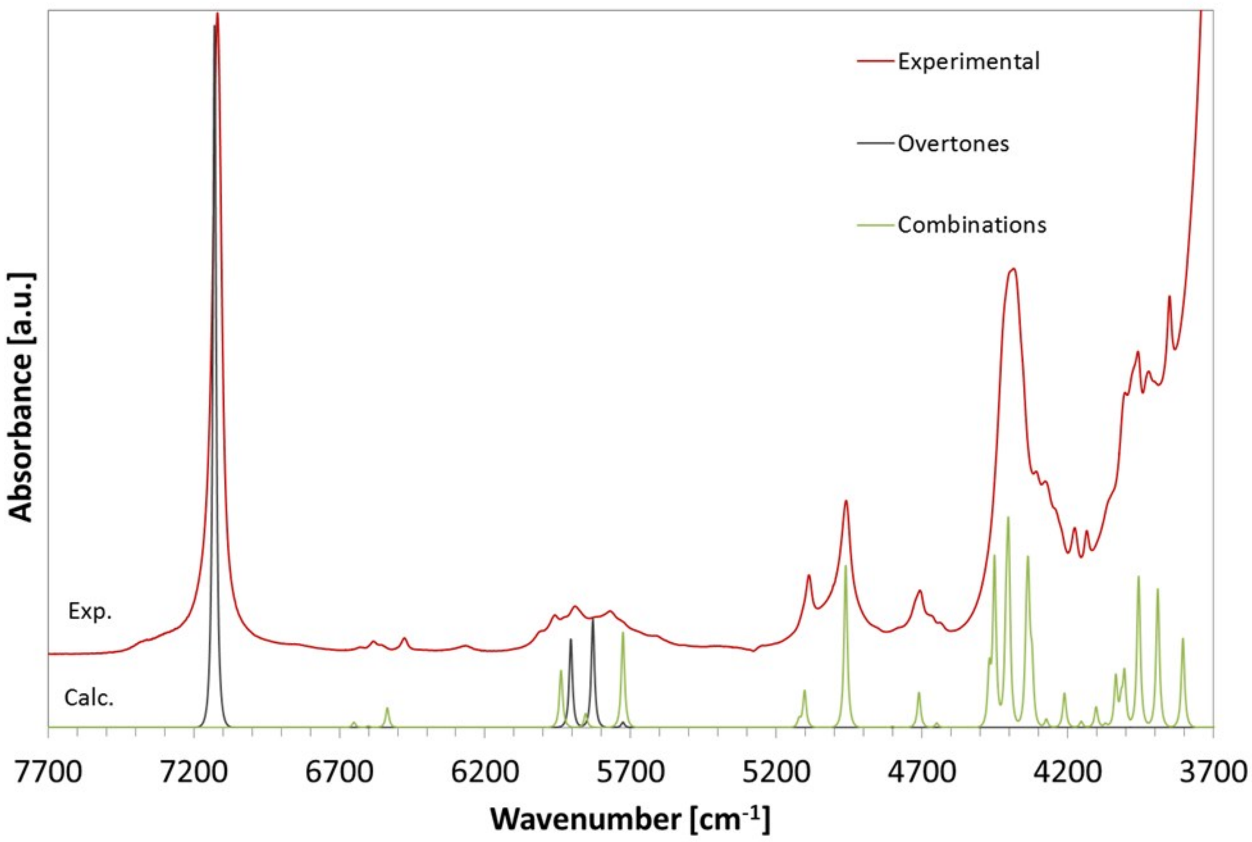

Figure S 15. Contributions of overtones and combination bands into NIR spectra of methanol calculated on CPCM-B2PLYP-D/SNST level of theory.

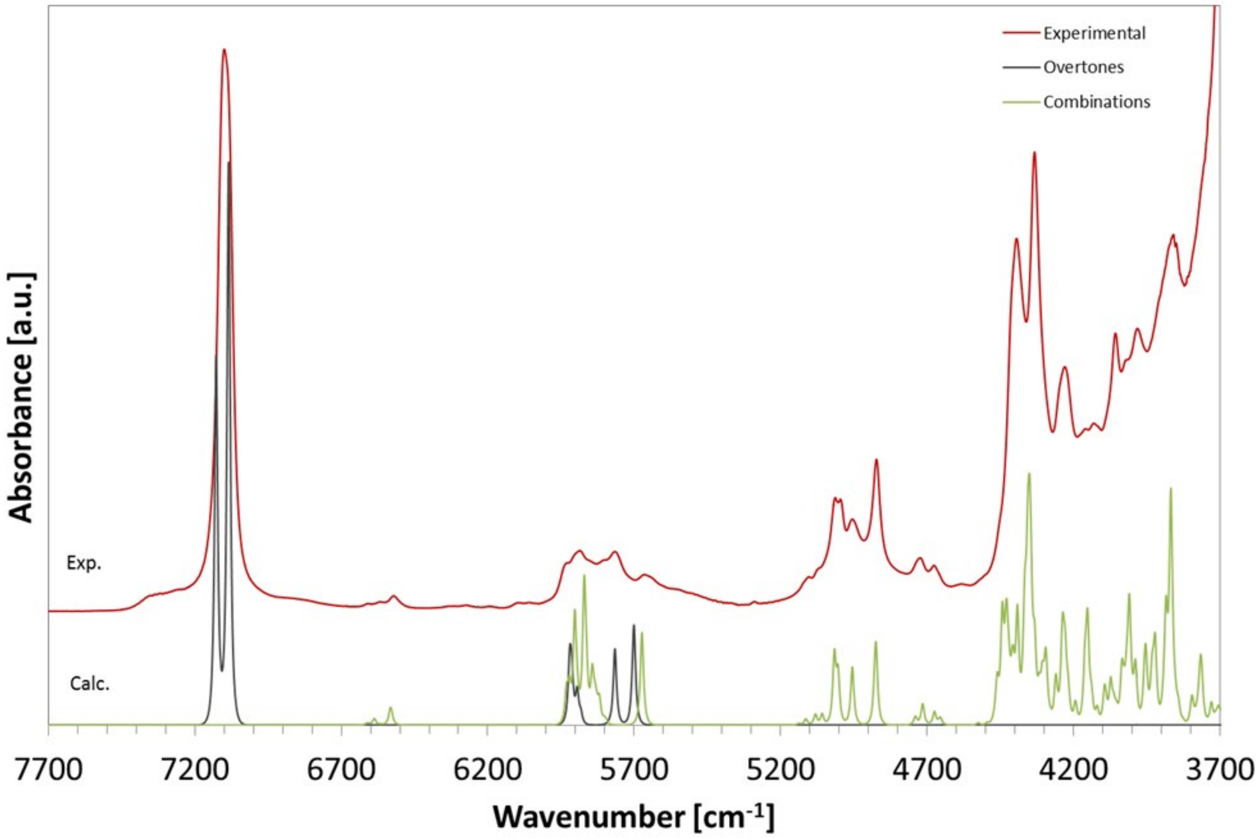

Figure S 16. Contributions of overtones and combination bands into NIR spectra of ethanol calculated on B2PLYP-D/SNST level of theory with additionally applied CPCM solvent model of CCl_4. Final contribution of overtones and combination modes presented; detailed contributions of gauche and trans isomers of ethanol not shown here.

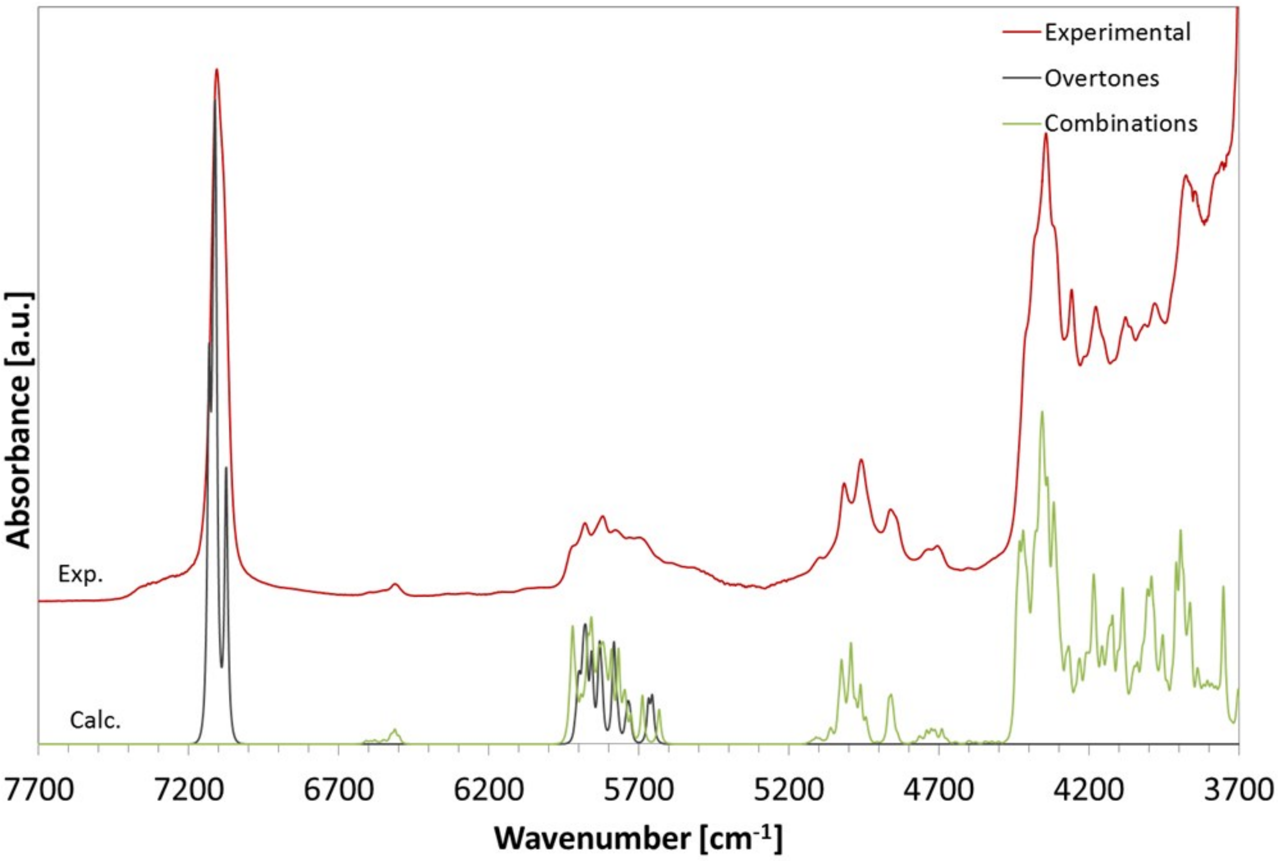

Figure S 17 **Contributions of overtones and combination bands into NIR spectra of 1-propanol calculated on B2PLYP-D/SNST level of theory with additionally applied CPCM solvent model of CCl_4. Final contribution of overtones and combination modes presented; detailed contributions of isomers of 1-propanol not shown here.**