IINS, MIR, and DFT Investigations of Vibrational Spectra of 3,3-Dimethyl-1-Butanol and 3,3-Dimethyl-2-Butanol

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Dedicated to Professor Jerzy Janik on the occasion of his 80th birthday

Molecular vibrational spectra in 3,3-dimethyl-1-butanol, $(CH_3)_3CCH_2CH_2OH$, and 3,3-dimethyl-2-butanol, $(CH_3)_3CCHOHCH_3$, were measured by the inelastic incoherent neutron scattering and mid infrared spectroscopy and for 3,3-dimethyl-2-butanol additionally by the far infrared absorption method. Experimental results were discussed and compared with the results of the quantum chemical calculations performed by the density functional theory (DFT/B3LYP/6-311G**) and semi-empirical PM3 calculation methods assuming the isolated molecule approximation.

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1. Introduction

The 3,3-dimethyl-1-butanol (3,3-DM-1B) and 3,3-dimethyl-2-butanol (3,3-DM-2B) are the branched primary and secondary alcohols, respectively. These substances are isomers of neohexanol with the general chemical formula $C_6H_{13}OH$. Their solid phase polymorphism has been identified by the differential scanning calorimetry (DSC) and adiabatic calorimetry methods [1, 2]. For 3,3-DM-1B on cooling down to 13 K glass of isotropic liquid was formed and it softened

during heating at 156 K. At 196 K the crystallization of the supercooled liquid occurred and at 234 K melting of the stable crystal was observed. On cooling of 3,3-DM-2B to liquid nitrogen temperatures a crystallization of the orientationally disordered plastic crystal C1 (ODIC) occurs at 260 K and it transforms into glass of plastic crystal at 210 K. On heating the ODIC phase C1 appeared at 210 K, and next solid–solid phase transitions took place at 245 K and 271 K, and at 275 K melting was observed [2]. At 20 K in 3,3-DM-1B glass of isotropic liquid phase (on fast cooling) or crystal phase (on slow cooling) were identified by the inelastic incoherent neutron scattering (IINS) spectra obtained using different temperature treatment of the sample [3, 4] and only glassy crystal in 3,3-DM-2B.

This paper presents the results of the observations of the vibrational modes in 3,3-DM-1B and 3,3-DM-2B with help of the inelastic incoherent neutron scattering method as well as of the mid infrared (MIR) absorption spectroscopy and the far infrared (FIR) spectroscopy (for 3,3-DM-2B only). The IINS and FIR spectra measured at 20 K and MIR spectra measured at room temperature are interpreted in terms of the bands of the normal modes obtained by quantum chemical calculations.

2. Experimental details

The investigated samples have been purchased from the Aldrich Chemical Company. The IINS measurements of 3,3-DM-1B and 3,3-DM-2B have been carried out in the energy range up to 1600 cm^{-1} and the temperatures from 20 to 290 K using the inverted geometry time-of-flight (TOF) spectrometer NERA-PR at the IBR-2 flux pulsed reactor at JINR described in [5].

The FIR absorption measurements have been carried out with the DIGILAB FTS-14 spectrometer in the 40–500 cm^{-1} frequency range; the resolution has been 2 cm^{-1}. The temperature dependence of the FIR absorption spectra of 3,3-DM-2B has been measured in the temperature range 25–290 K.

The MIR spectra of 3,3-DM-1B and 3,3-DM-2B have been measured at room temperature in the liquid phase in the frequency range of 400–4000 cm^{-1}. The measurements have been carried out with the Excalibur FTS 3000 spectrometer. The resolution of our spectra is close to 2 cm^{-1}.

3. Calculations of structure and dynamics of free molecules

The geometry of isolated molecule has been optimized in the first step by the semi-empirical PM3 method because its conformational structure is unknown. In the second step, the structure has been optimized using the Gaussian'03 program [6] by the density functional B3LYP (Becke 3-Lee–Yang–Parr correlations) [7, 8] with the basis set 6-311 G**. The structures of the lowest energy conformers of 3,3-DM-1B and 3,3-DM-2B calculated on the B3LYP/6-311G** level are displayed in Fig. 1. The parameters of geometry of both isomers studied are shown in detail in Table I. One can see that the results of PM3 method are close to these of density

functional theory (DFT) method. The optimized molecular structure of isolated molecule is dependent on the level of the calculation methods. The structure of the 3,3-DM-1B and 3,3-DM-2B molecules is characterized by C_1 symmetry confirmed by DFT calculations with the electronic energy (E_e) of –312.38 Hartree* and -312.39 Hartree, respectively.
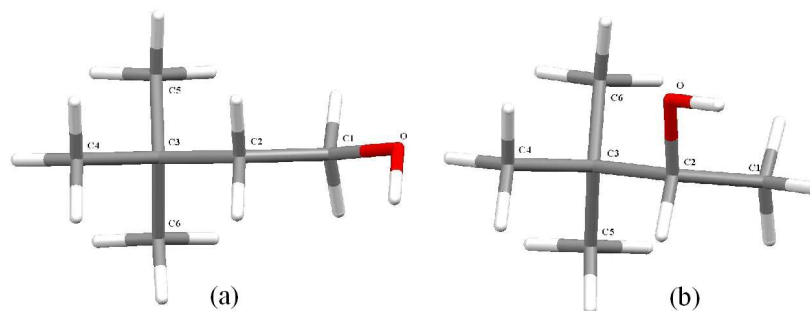

Fig. 1.   Geometry of the lowest energy conformers: 3,3-dimethyl-1-butanol (a) and 3,3-dimethyl-2-butanol (b). Numbering scheme of carbon atoms is given.

Additionally, the potential energy of the molecule as a function of reorientation angle of t-butyl group around C2–C3 bond for an isolated molecule has been calculated by the semi-empirical PM3 method (see Fig. 2). The heights of three potential barriers for 3,3-DM-1B are equal to 3.45 kcal/mol, 3.79 kcal/mol, and 3.36 kcal/ mol for angles 60°, 180°, and 300°, respectively. For 3,3-DM-2B the potential barriers of reorientation of t-butyl group around C2–C3 bond are higher — they are equal to 4.69 kcal/mol, 4.93 kcal/mol, and 4.84 kcal/ mol for the same angles.

Calculations by the DFT method performed by Gaussian'03 program [6] allow to establish the frequencies of normal modes, ν_j, and displacements $A_n(\nu_j)$ in corresponding normal mode j of a molecule of n atoms, as well as the IR intensities of normal modes. Neutron scattering intensities $G(\nu)$ defined as

$$G(\nu) = \sum_j \sum_n \left[A_n(\nu_j)\right]^2 \delta(\nu - \nu_j) \tag{1}$$

have been calculated using the α-Climax program [9]. Next, using the program RES [10], neutron scattering intensities were convoluted with the resolution function of the NERA spectrometer in order to obtained calculated phonon density of states $G_{\mathrm{cal}}(\nu)$. The calculated neutron scattering intensities $G_{\mathrm{cal}}(\nu)$ for 3,3-DM-1B and 3,3-DM-2B in form of the Dirac delta at the calculated frequencies are presented in Figs. 3 and 4 together with their convolution with the NERA resolution function and compared with the experimental $G_{\mathrm{exp}}(\nu)$ spectra (in the

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*1 Hartree = 4.359 744 17(75) × 10^{-18} J = 27.211 3845(23) eV = 2 Ry = 627.509 391 kcal/mol.

Optimized geometry of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol. DFT — DFT/B3LYP/6-311G**.

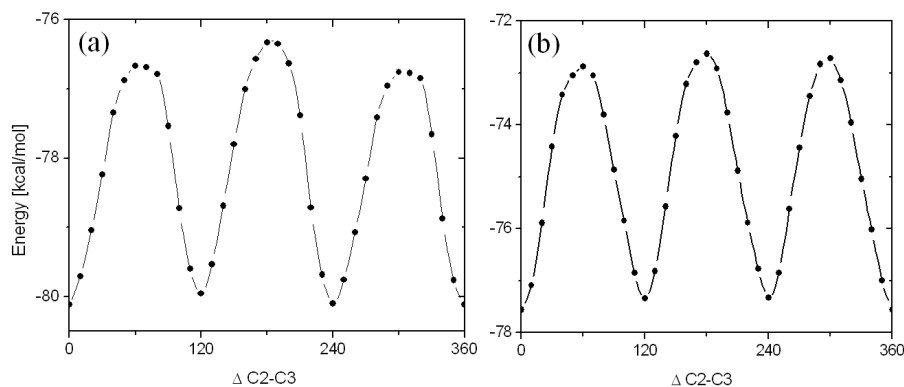| 3,3-dimethyl-1-butanol			3,3-dimethyl-2-butanol		
Internal bond length [Å] of isolated molecule					
	DFT	PM3		DFT	PM3
H-O	0.95009	0.94931	H-O	0.95005	0.94931
O-C(1)	1.46994	1.40182	O-C(2)	1.47157	1.40182
C(1)-C(2)	1.52515	1.53084	C(1)-C(2)	1.52591	1.53084
C(2)-C(3)	1.52877	1.53748	C(2)-C(3)	1.53093	1.53738
C(3)-C(4)	1.52830	1.52920	C(3)-C(4)	1.52585	1.52920
C(3)-C(5)	1.52542	1.52759	C(3)-C(5)	1.52504	11.52759
C(3)-C(6)	1.52477	1.52714	C(3)-C(6)	1.52902	11.52714
Internal angles [degree] isolated molecule					
	DFT	PM3		DFT	PM3
H-O-C(1)	109.501	110.966	O-C(2)	109.434	106.256
O-C(1)-C(2)	111.192	113.105	O-C(1)-C(2)	108.999	111.182
O-C(2)-C(3)-C(4)	107.860	108.565	O-C(2)-C(3)	109.983	108.208
C(6)-C(3)-C(5)	108.512	109.652	C(2)-C(3)-C(4)	111.045	111.623
C(1)-C(2)-C(3)	109.382	112.998	C(6)-C(3)-C(5)	108.459	108.548
C(5)-C(3)-C(4)	108.233	109.160	C(1)-C(2)-C(3)	113.536	112.627
C(6)-C(3)-C(4)	108.531	108.820	C(5)-C(3)-C(4)	109.147	109.342

Fig. 2. Energy of molecule as a function of reorientational angle around C2–C3 bond for 3,3-dimethyl-1-butanol (a) and for 3,3-dimethyl-2-butanol (b).

frequency range up to 800 cm^{-1}). Calculated IR intensities are presented in Figs. 5 and 6 together with optical spectroscopy results.

Fig. 3. Comparison of the experimental IINS low-temperature phonon density of states $G_{exp}(\nu)$ of crystal phase of 3,3-DM-1B and $G_{cal}(\nu)$ calculated by DFT method using the B3LYP/6-311G** level.
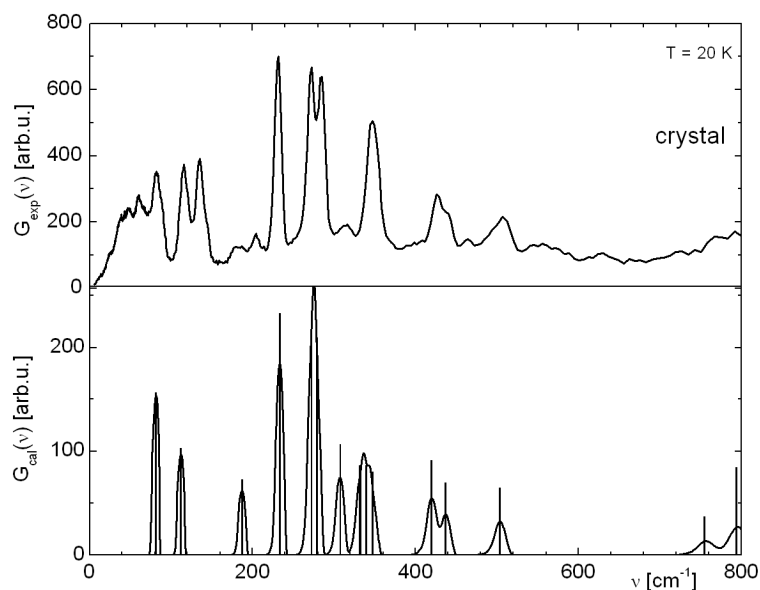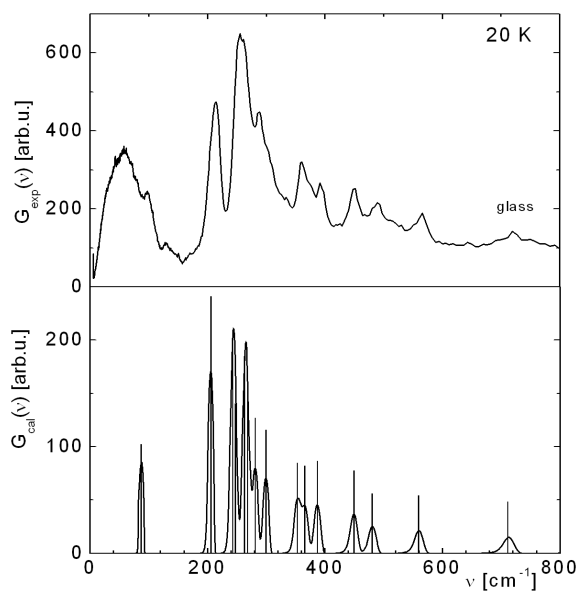

Fig. 4. Comparison of the experimental IINS low-temperature phonon density of states $G_{exp}(\nu)$ of glassy crystal of 3,3-DM-2B and $G_{cal}(\nu)$ calculated using the B3LYP/6-311G** level.
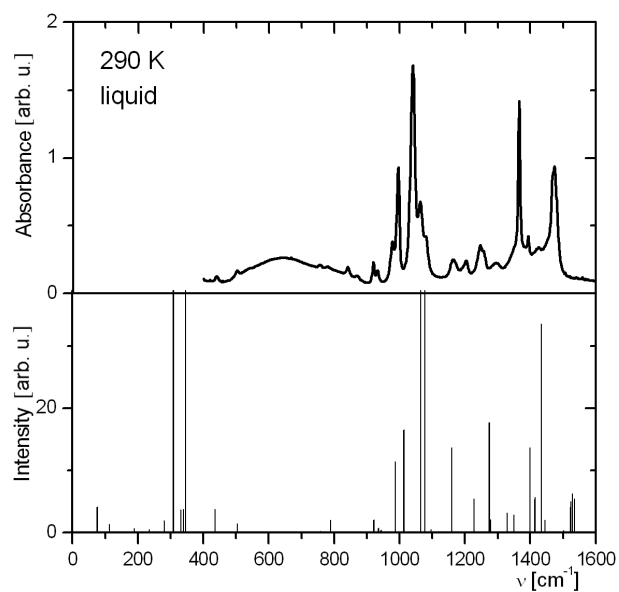
Fig. 5.   Comparison of the experimental MIR and calculated spectra of 3,3-DM-1B.
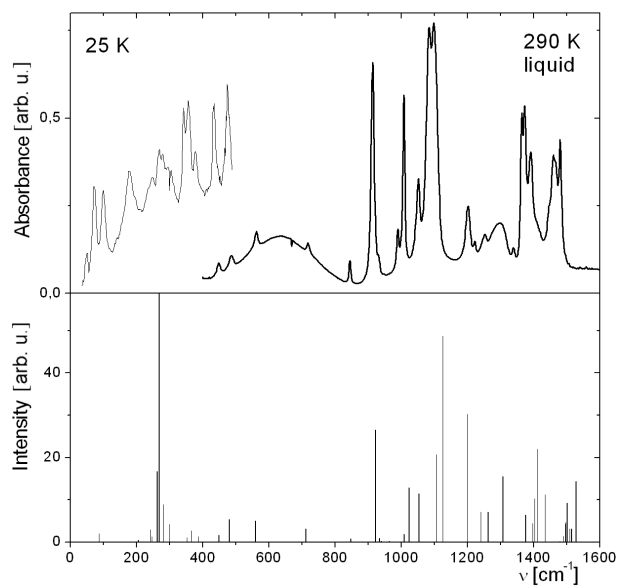
Fig. 6.   Experimental FIR and MIR spectra for 3,3-DM-2B in glassy crystal and liquid phase, respectively, compared with the spectra calculated by DFT method using the B3LYP/6-311G** basis set.

Using the gOpenMol program [11] visualization of vibrational motions of atoms in molecule and interpretation of each mode was performed.

4. Comparison of experimental and calculated spectra

In Table II the frequencies of normal vibrational modes obtained experimentally by IINS, MIR, and FIR methods are compared with calculated frequencies for 3,3-DM-1B and 3,3-DM-2B. It occurs that $G_{\text{cal}}(\nu)$ spectra calculated in the one-phonon scattering approximation for the isolated molecule are in relatively good agreement with the $G_{\text{exp}}(\nu)$ experimental ones above *ca.* 180 cm^{-1}. In a solid phase, vibrational bands interpreted as torsional modes around C2–C3 bond appear at the lower energy transfer on smooth background of lattice phonons. The bands responsible for librational modes of methyl groups and deformational vibrations of skeleton appear in the frequency range from about 180 cm^{-1} to 600 cm^{-1} while methyl and methylene wagging modes appear near 800 cm^{-1}.

TABLE II

Calculated frequencies for isolated molecules and experimental results of MIR and $G_{\text{exp}}(\nu)$ for 3,3-dimethyl-1-butanol and FIR, MIR and $G_{\text{exp}}(\nu)$ for 3,3-dimethyl-2-butanol. MIR — MIR 290 K, G(ν) — $G_{\text{exp}}(\nu)$ 20 K, IR — FIR 25 K and MIR 290 K, Exp. freq. — Experimental frequencies [cm^{-1}], Cal. freq. — Calculated frequencies [cm^{-1}], Ass. — Assignment and potential energy distribution ((%) > 10%).

3,3-dimethyl-1-butanol			3,3- dimethyl-2-butanol			
Exp. freq.	Cal. freq.		Ass.	Exp. freq.		Cal. freq.		Ass.
G(ν)	DFT	PM3		IR	G(ν)	DFT	PM3	
82	80.9	80.7	χ[C1-C2]80%	95.5	97.5	83.8	90.8	χ[C2-C3]74%
116	111.8	113	χ[C3-C2]71%	122.4	130	205.7	162.9	χ[C1-C2]]35%
135			χ[C6-C3]]12%	195	170			χ[C3-C5]30%
					215			χ[C3-C6]21%
								χ[C3-C4]10%
179	187.0	174.8	χ[C3-C4]52%			245.0	196.1	χ[C3-C4]33%
			χ[C6-C3]29%					χ[C1-C2]26%
								χ[C2-O]24%
186		199.4	χ[C6-C3]52%			247.3	199.4	χ[C2-O]144%
204			χ[C3-C4]36%					χ[C3-C4]25%
232	233.5	211.8	χ[C3-C5]65%	265	256	261.0	205.7	χ[C2-O]33%
			δ[C3-C2-C1]13%					χ[C3-C5]7%
								χ[C1-C2]16%
273	272.4	250.8	χ[C3-C5]20%			270.6	227.1	χ[C3-C6]60%
285	278.6		δ[C4-C3-C2]12%					χ[C1-C2]13%
			δ[C3-C2-C1]10%					
			δ[C2-C1-O]10%					
316	307.4	308.2	χ[C1-O]82%	286	287	282.8	283.9	δ[C2-C3-C5]34%
				297				δ[C2-C3-C4]24%
								δ[C1-C2-C3]13%
	331.9	340.1	δ[C6-C3-C4]31%	320		301.5	301.7	δ[O-C2-C3]24%
			δ[C2-C3-C5]26%					δ[C2-C3-C4]17%
			δ[C6-C3-C2]19%					δ[C2-C3-C6]15%
	339.4	365.5	δ[C6-C3-C5]39%			352.9	361.0	δ[C6-C3-C5]27%
			δ[C2-C1-O]15%					δ[C4-C3-C5]21%
			δ[C6-C3-C2]12%					δ[O-C2-C3]15%
								δ[C2-C3-C6]15%

TABLE II (cont.)

3,3-dimethyl-1-butanol					3,3-dimethyl-2-butanol				
Exp. freq.		Cal. freq.		Ass.	Exp. freq.		Cal. freq.		Ass.
MIR	G(ν)	DFT	PM3		IR	G(ν)	DFT	PM3	
	347	347.2	386.5	δ[C4-C3-C5]26%	358	361	366.4	417.7	δ[C4-C3-C6]41%
	370			δ[C2-C3-C5]17%	371				δ[C4-C3-C5]17%
				δ[C3-C2-C1]14%					δ[C6-C3-C5]16%
				δ[C4-C3-C2]10%					δ[C1-C2-O]12%
	425	419.4	448.8	δ[C4-C3-C5]25%	392	391	386.8	443.3	δ[C1-C2-C3]36%
				δ[C6-C3-C4]24%					δ[C4-C3- C6]12%
				δ[C2-C3-C5]22%					δ[C2-C3- C4]11%
				δ[C6-C3-C2]16%					
438	440	436.6	481.3	δ[C4-C3-C2]31%	446.5	452	449.8	484.5	δ[C2-C3-C6]35%
	464			δ[C6-C3-C5]23%	488.9				δ[C4-C3-C5]20%
				δ[C2-C1-O]15%					δ[C1-C2-C3]17%
500	507	503.4	537.5	δ[C2-c3-C5]16%	488.9	489	481.2	504.2	δ[C1-C2-O]27%
643				δ[C3-C2-C1]16%					δ[C2-c3-C4]20%
				δ[C2-C1-O]11%					δ[O-C2-C3]19%
				δ[C6-C3-C4]11%					δ[C6-C3-C5]16%
				δ[C4-C3-C5]11%					
756	766	754.5	780.8	δ[C1-C2-H]29%	563.2	567	560.3	584.0	δ[C2-C3-C5]23%
777				δ[C2-C1-H]28%		576			δ[C1-c2-O]11%
					635	668			δ[O-C2-C3]11%
842	792	793.3	886.3	ν[C6-C3]28%	718		713.2	801.0	ν[C2-C3]52%
868	818			ν[C3-C5]24%					
	875			ν[C3-C2]18%					
				ν[C3-C4]13%					
919		915.9	934.3	δ[C3-C4-H]22%	845		853.1	920.9	ν[C3-C6]22%
				δ[C3-C6-H]16.5%	913		930.6		ν[C3-C5]20%
				ν[C3-C5]12%					ν[C3-C4]12%
933		931.1	938	δ[C3-C6-H]26%		938	939.4	939.1	δ[C3-C5-H]54%
				δ[C3-C4-H]15%					ν[C3-C4]13%
				ν[C3-C2]12%					
	943	939.9	939.5	δ[C3-C5-H]37%			945.0	940.8	δ[C3-C5-H]21%
				δ[C3-C6-H]30%					ν[C3-C5]17%
									δ[C3-C4-H]14%
									δ[C3-C6-H]21%
	949	960.3	946.1	δ[C3-C4-H]36%				950.0	δ[C3-C4-H]23%
				ν[C6-C3]10%					δ[C3-C6-H]37%
978		985.3	951	δ[C3-C5-H]22%			967.2	969.0	δ[C2-C1-H]35%
				δ[O-C1-H]10%					δ[C3-C4-H]12%
				ν[C3-C4]10%					ν[C2-O]10%
996	996	1007.8	979.7	δ[C3-C6-H]19%				981.2	δ[C3-C4-H]31%
				δ[C3-C5-H]29%					δ[C3-C5-H]25%
				δ[C3-C4-H]17%					δ[C3-C6-H]10%
1040	1020	1056.8	1003.6	δ[C3-C5-H]39%	990		1011.8	994.2	δ[C3-C6-H]32%
				δ[C3-C6-H]10%	1008		1031.1		δ[C2-C1-H]22%
							1057.7		δ[C3-C6-H]11%
1064		1069.5	1035.2	δ[O-C1-H]23%			1115.0	1025	δ[C2-C1-H]43%
				δ[C2-C1-H]16%					δ[C3-C6-H]10%
				δ[C3-C2-H]11%					
				δ[C1-O-H]10%					

TABLE II (cont.)

3,3-dimethyl-1-butanol					3,3-dimethyl-2-butanol				
Exp. freq.		Cal. freq.		Ass.	Exp. freq.		Cal. freq.		Ass.
MIR	G(ν)	DFT	PM3		IR	G(ν)	DFT	PM3	
1079	1072	1090.3	1083.9	ν[C2-C1]65%	1052 1084 1098		1136.7	1059.2	δ[O-C2-H]52% δ[C1-C2-H]17% ν[C2-O]12%
1163	1099	1161.0	1102.8	δ[C1-C2-H]25% δ[C2-C1-H]21% δ[C1-C2-H]19%	1202		1204.2	1087.5	ν[C1-C2]43% δ[C2-C1-H]17%
1203 6	1202	1222.0	1150.6	ν[C1-O6]31% δ[O6-C1-H]26% δ[C2-C1-H]17%	1223	1235	1249.4	1152.5	δ[C3-C2-H]25% δ[C1-C2-H]21% δ[C2-O-H]17%
1247		1266.0	1207.3	δ[C3-C2-H]23% ν[C3-C4]12% δ[C1-C2-H]21%	1254		1269.9	1252.5	ν[C2-C3]22% δ[C2-O-H]18%
1256	1251	1272.1	1289.7	ν[C3-C5]11% ν[C3-C4]10%	1299		1311.6	1263.3	ν[C3-C6]25% ν[C2-O]16% ν[C3-C4]12%
1294		1324.7	1291.1	ν[C6-C3]16%	1340	1321	1384.5	1289.5	ν[C3-C5]17%
		1346.1	1299.7	ν[C3-C2]17% δ[H-Cl-H]11%	1364		1405.8	1317.2	ν[C2-O]31%
1365		1394.0	1331.7	δ[H-C1-H]20% ν[C3-C2]15% δ[C1-O-H]12%			1410.9	1348.5	δ[H-C1-H]58% δ[H-C6-H]14%
1394		1401.8	1337	δ[C1-O-H]48% δ[H-C1-H]15% δ[H-C2-H]15%			1415.1	1352.8	δ[H-C5-H]37% δ[H-C4-H]32%
		1403.6	1353	δ[H-C6-H]71%			1424.0	1353.7	δ[H-C5-H]40% δ[H-C6-H]22% δ[H-C1-H]10%
1425		1431.0	1355.2	δ[H-C4-H]36% δ[H-C5-H]25% δ[H-C4-H]12%		1358	1447.2	1355.9	δ[H-C6-H]29% δ[H-C1-H]18%
		1433.2	1358.6	δ[H-C2-H]19% δ[H-C4-H]12% δ[H-C5-H]12%			1491.8	1358.9	δ[H-C4-H]35%
1473		1483.2	1358.9	δ[H-C4-H]65% δ[H-C6-H]14%			1502.2	1360.7	δ[H-C4-H]52% δ[H-C6-H]13%
		1484.7	1361.2	δ[H-C6-H]23% δ[H-C4-H]12%			1507.5	1362.3	δ[H-C6-H]37% δ[H-C1-H]19% δ[H-C4-H]11%
		1491.2	1364.5	δ[H-C2-H]31% δ[H-C5-H]20% δ[H-C6-H]12%			1511.0	1364.7	δ[H-C6-H]25% δ[H-C4-H]17% δ[H-C1-H]12%
		1493.0	1368.6	δ[H-C4-H]23% δ[H-C5-H]31% δ[H-C6-H]20%			1513.5	1370.6	δ[H-C6-H]14%
		1511.0	1377.7	δ[H-C4-H]15% ν[C3-C4]14%	1373		1522.3	1375.2	δ[H-C4-H]13% ν[C3-C6]10%
		1512.6	1379	ν[C6-C3]25% ν[C3-C4]12%			1526.8	1380.0	ν[C3-C5]29% δ[H-C5-H]10%

TABLE II (cont.)

	3,3-dimethyl-1-butanol				3,3-dimethyl-2-butanol				
Exp. freq.		Cal. freq.		Ass.	Exp. freq.		Cal. freq.		Ass.
MIR	G(ν)	DFT	PM3		IR	G(ν)	DFT	PM3	
		1518.4	1390.3	ν[C1-O]15% ν[C2-C1]11% ν[C3-C5]10%	1392	1417 1479	1539.4	1397.8	δ[C2-O-H]27% ν[C1-C2]11% ν[C2-C3]11%
	1521	1524.6	1404	δ[H-C5-H]23% δ[C3-C5-H]11%	1460 1480			1432.4	δ[H-C6-H]27% δ[H-C1-H]23% δ[C2-C1-H]12% δ[C3-C6-H]10%
2869		2987.4	2784.9	ν[C1-H]95%	2654 2712 2873 2909		2953.7 3034.1	2716.5	ν[C2-H]99%
2908		2991.6	2846.4	ν[C2-H]99%			3038.3	2944.4	ν[C6-H]66% ν[C1-H]16%
		3013.8	2914.8	ν[C1-H]96%			3041.4	2956.5	ν[C1-H]76% ν[C6-H]15%
		3017.3	2919.4	ν[C2-H]99%			3047.8	2969.6	ν[C5-H]98%
2957		3025.0	2944.3	ν[C5-H]95%	2950		3097.2	2972.1	ν[C4-H]93%
		3042.2	2971.2	ν[C6-H]91%			3103.4	2975.9	ν[C5-H]23% ν[C1-H]32% ν[C6-H]26%
		3075.9	2974.2	ν[C4-H]89%			3106.6	2976.8	ν[C1-H]57% ν[C6-H]37%
		3078.0	2975.2	ν[C4-H]44% ν[C6-H]31%			3107.4	2977.3	ν[C4-H]91%
		3079.7	2975.9	ν[C4-H]48% ν[C6-H]44%			3116.3	2977.9	ν[C5-H]58% ν[C6-H]33%
		3084.1	2978.6	ν[C5-H]60%			3136.4	3049.9	ν[C6-H]98%
		3085.3	3049.4	ν[c5-H]99%			3140.8	3052.9	ν[C1-H]96%
		3090.6	3058.5	ν[C6-H]85%			3142.9	3058.2	ν[C5-H]89%
		3094.9	3060.2	ν[C4-H]87%				3060.2	ν[C4-H]90%
3339		3823.4	3747.4	ν[O-H]100%	3392		3820.4	3764.0	ν[O-H]100%

χ — torsion mode, δ — deformational mode, ν — stretching mode.

For 3,3-DM-1B using the B3LYP/6-311G** (PM3) method of calculations the torsional out-of-plane χ [C1–C2] and χ [C2–C3] modes were localized at 80.9 cm^{-1} and 111.8 cm^{-1} (80.7 cm^{-1} and 113 cm^{-1}), while in the $G_{\exp}(\nu)$ experimental spectra they were observed at 82 cm^{-1} and 116 cm^{-1}. The librational modes of methyl groups are visible in $G_{\exp}(\nu)$ at 135 cm^{-1}, 179 cm^{-1}, 186 cm^{-1}, 204 cm^{-1}, 232 cm^{-1}, and 273 cm^{-1}.

Deformational in-plane δ [C–C–C] modes were predicted by DFT (PM3) in the range from 331.9 cm^{-1} to 503.4 cm^{-1} (340.1 cm^{-1} to 537.5 cm^{-1}) and observed in the IINS spectra in frequencies from 347 cm^{-1} to 507 cm^{-1}. The deformational in-plane [C-C-H] modes of methyl groups were calculated by DFT (PM3) method between 915.9 cm^{-1} and 1266 cm^{-1} (934.3 cm^{-1} to 1207.3 cm^{-1}) and were identified with bands between 919 cm^{-1} and 1247 cm^{-1} in MIR spectra.

The deformational [H-C-H] mode was found by DFT (PM3) in the range from 1346 cm^{-1} to 1511 cm^{-1} (1299.7 cm^{-1} to 1377.7 cm^{-1}) and by MIR method in the range from 1365 cm^{-1} to 1473 cm^{-1}.

Stretching ν [C3–C2], ν [C3–C4], ν [C3–C5], and ν [C3–C6] modes calculated by DFT (PM3) method at 793.3 cm^{-1} (886.3 cm^{-1}) correspond to three bands around 820 cm^{-1} in IINS spectra and two bands between 842 cm^{-1} and 868 cm^{-1} in MIR spectra. The symmetric and asymmetric stretching ν [C-H] modes of methyl groups calculated between 2987.4 cm^{-1} and 3094.9 cm^{-1} (2784.9 cm^{-1} and 3060.2 cm^{-1}), when the DFT (PM3) method was used, were found in range from 2869 cm^{-1} to 2957 cm^{-1} in the MIR spectra.

For 3,3-DM-2B the torsional out-of-plane χ [C2–C3] modes were found at 83.8 cm^{-1} by B3LYP/6-311G** method and at 90.8 cm^{-1} by PM3 method. It corresponds to the mode observed in $G_{\exp}(\nu)$ at 97.5 cm^{-1} and in FIR at 95.5 cm^{-1}. The librational modes of methyl groups are visible at 130 cm^{-1}, 170 cm^{-1}, 215 cm^{-1}, and 256 cm^{-1} in IINS spectra and at 122.4 cm^{-1}, 195 cm^{-1}, and 265 cm^{-1} in FIR spectra.

The vibrational modes predicted by DFT (PM3) in the range from 282.8 cm^{-1} to 560.3 cm^{-1} (283.9 cm^{-1} to 584 cm^{-1}) were ascribed to the deformational in-plane δ [C–C–C] modes observed from 287 cm^{-1} to 567 cm^{-1} in the $G_{\exp}(\nu)$ spectra and from 286 cm^{-1} to 563.2 cm^{-1} in the FIR spectra. The deformational in-plane δ [C–C–H] modes were identified in calculated DFT (PM3) spectra between 939.4 cm^{-1} and 1249.4 cm^{-1} (from 939.1 cm^{-1} to 1152.5 cm^{-1}). They were observed between 990 cm^{-1} and 1202 cm^{-1} in MIR spectra and between 938 cm^{-1} and 1230 cm^{-1} in IINS spectra, i.e. above the frequency range chosen for presentation. The deformational δ [H–C–H] modes were found by DFT (PM3) method in the range from 1405 cm^{-1} to 1539.4 cm^{-1} (1348.5 cm^{-1} to 1432.4 cm^{-1}) and from 1364 cm^{-1} to 1480 cm^{-1} by MIR method. In IINS spectra the corresponding band was found in the range from 1321 cm^{-1} to 1600 cm^{-1}.

Frequencies of the stretching modes: ν [C3–C2] and ν [C3–C4], ν [C3–C5], ν [C3–C6] calculated by DFT are equal to 713.2 cm^{-1} and 853 cm^{-1}. Those calculated by PM3 are equal to 801 cm^{-1} and 920.9 cm^{-1}. In MIR spectra they were observed at 718 cm^{-1} and 845 cm^{-1} and additionally at 913 cm^{-1}. The symmetric and asymmetric stretching ν [C–H] modes of methyl groups appeared between 2953.7 cm^{-1} and 3142.9 cm^{-1} (2716.5 cm^{-1} and 3060.2 cm^{-1}) in spectra calculated by DFT (PM3) method and from 2654 cm- 1to 2950 cm^{-1} in MIR spectra.

In IINS method a contribution of the O–H mode to the density of states function is small when compared to contribution of modes connected to thirteen other hydrogen atoms in the molecule. In MIR spectra of 3,3-DM-1B (3,3-DM-2B) shown in Fig. 5 (Fig. 6) the following characteristic vibrations of hydroxyl group are well pronounced: torsional out-of-plane χ [O–H] modes at 646 cm^{-1} (635 cm^{-1}), stretching ν [C–O] mode at 1040 cm^{-1} (1084 cm^{-1}), deformational

in-plane [C–O–H] mode at 1365 cm^{-1} (1392 cm^{-1}) and stretching ν [O–H] mode which appeared near 3350 cm^{-1} (3392 cm^{-1}). The corresponding frequency values calculated by both methods used are presented in Table II. The hydroxyl group modes were observed to be overlapped by weak C–H group vibrations. It is important to note that frequency of modes in the experimental MIR spectra and those calculated by DFT method and also by PM3 method are similar.

5. Final remarks

This work presents results of DFT (B3LYP/6-311G**) calculations for 3,3-DM-1B and 3,3-DM-2B isomers of neohexanol. They were undertaken to reproduce the vibrational density of states $G_{exp}(\nu)$ obtained using IINS method and the experimental FIR and MIR spectra. Calculated frequencies of stretching C–C and C–H modes as well as of deformational C–C–H modes agree well with those found in the experimental MIR spectra of liquid phase in both substances. The main features of $G_{exp}(\nu)$, i.e. torsional out-of-plane modes of t-butyl group and methyl groups around C–C bond and deformational C–C–C modes, detected in the frequency range up to 600 cm^{-1} were satisfactorily identified by $G_{cal}(\nu)$ calculated in terms of isolated molecule approximation. Threefold symmetry potential for rotations of t-butyl group around C–C axis was confirmed in both substances studied. DFT calculations for dimer and higher order molecular clusters are in preparation, in order to investigate influence of hydrogen bonds on hydroxyl groups dynamics and other vibrational modes of free molecule.

Acknowledgments

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