

# Equilibrium Structures and Vibrational Assignments for Isoamyl Alcohol and *tert*-Amyl Alcohol: A Density Functional Study

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We have calculated the vibrational spectra of isoamyl alcohol and of *tert*-amyl alcohol using Density Functional Theory (DFT) with the Becke-3 Lee Yang Parr (B3LYP) functional and a 6-311+G\*\* atomic basis set. The energies of the conformers were also calculated with *ab initio* Perturbation Theory of second (MP2) and fourth order restricted to single, double and quadruple excitations (MP4 SDQ) with the same basis set. We found rather complicated equilibria of four conformations in each case, counting only those with appreciable abundancies. PED data were compared with GAUSSVIEW animations. The calculated wavenumbers agree rather well with the experimental ones when the *gauche-trans* conformer is assumed as the most important one for isoamyl alcohol, and the *gauche-gauche* one for *tert*-amyl alcohol. However, some of the experimental bands had to be assigned also to other conformers, indicating their presence in the equilibrium mixture. Due to sterical reasons both the CO and the OH bonds appear to be weaker in the tertiary alcohol, considering the wavenumbers of the CO and OH bond stretching vibrations. The bond lengths point into the same direction, however, the OH bond in the tertiary alcohol is only slightly longer than that in the primary alcohol.

**Key words:** Isoamyl Alcohol, *tert*-Amyl Alcohol, Vibrational Assignments, Molecular Structures, DFT Study

## Introduction

Vibrational assignments of infrared and Raman lines in the respective spectra are a very important tool, both for detection of the presence of chemicals in reaction mixtures and for the study of atomic motions in molecules. The best way to perform such assignments are potential energy distribution (PED) calculations [1] which yield not only the presence of a group coordinate (the symmetry coordinates, when symmetry is present), but also quantitatively its degree of admixture in a normal mode. In this work we study both PED calculations and the results of the more qualitative GAUSSVIEW program [2]. We find that although GAUSSVIEW yields no quantitative information at all, it works rather well as long as the degree of mixing of different group coordinates in a normal mode is not too large, *i. e.* in relatively small molecules. Further we discuss structures and PEDs as obtained from Density Functional Theory (DFT) calculations.

To this end we were looking for molecules which are both relatively small but also of some chemical and/or biological importance. Thus we have chosen isoamyl alcohol (3-methylbutan-1-ol) and *tert*-amyl alcohol (2-methylbutan-2-ol) as our systems. These molecules allow a look at the different behavior of primary and tertiary OH groups. We have also calculated amyl-alcohol, but because of it being a primary alcohol like isoamyl alcohol we did not expect anything new from this system, which turned out to be the case and thus we restrict our discussion to *tert*- and isoamyl alcohol.

Isoamyl alcohol has some biological significance and because we are not aware of any literature about the vibrational spectroscopy or about any calculations of structural equilibria, we think that this should be mentioned in the Introduction. For example there is even a gene for isoamyl alcohol oxidase in *Aspergillus oryzae* [3], and it is known that there are differences in metabolism and DNA ethylation between it and ethanol [4]. Further there is decarboxylation of  $\alpha$ -

ketoisocaproate to isoamyl alcohol formation [5] and isoamyl alcohol-induced morphological change [6] in *Saccharomyces cerevisiae*. A sake yeast mutant produces isoamyl alcohol [7]. Finally there is a fragrance materials review on isoamyl alcohol [8]. On the chemical side there is for example a catalytic study of isoamyl alcohol dehydrogenation [9] and a kinetic study of the esterification of acetic acid with isoamyl alcohol [10].

*tert*-Butylalcohol (being a tertiary alcohol as our system, *tert*-amyl alcohol) is reported to undergo microbial biodegradation [11], the solubility of fuel oxygenates in water is studied as a function of its concentration [12], and in reactive distillation it is used in glycerol ether synthesis [13]. In a thermodynamic study excess enthalpies of binary and ternary mixtures containing *tert*-amyl alcohol were determined [14]. Again in reactive distillation it was etherized with ethanol [15], and further phenol was alkylated with *tert*-amyl alcohol using a superacidic mesoporous catalyst [16]. Tertiary alcohols were used as reaction media in nucleophilic fluorinations [17, 18] and finally a kinetic study of the liquid phase synthesis of *tert*-amyl ethyl ether was performed [19].

### Experimental Spectra

The sample of liquid isoamyl alcohol with about 98 % purity was purchased from BDH Chemicals. The mid-infrared spectrum ( $4000\text{--}500\text{ cm}^{-1}$ ) of the chemical was obtained with a Perkin Elmer 16F PC FTIR spectrometer using an NaCl window. Finally further experimental spectra of the two molecules had to be retrieved from the official Japanese vibrational spectroscopy link <http://www.aist.go.jp/RIODB/SDBS>, no. 541 in case of the Raman spectrum of isoamyl alcohol and no. 1709 in case of the infrared and Raman spectra of *tert*-amyl alcohol to compare our calculated wavenumbers with the experimental ones.

### Theoretical Calculations

For our DFT calculations we used the GAUSSIAN 03 program system and the 6-311+G\*\* atomic basis set [20]. We set up internal and group (symmetry) coordinates which are given in Tables S1 and S2 (S before a figure or table number indicates that it is part of the Supporting Information available online; see note at the end of the paper for availability), while the structures of the molecules as calculated with DFT as well as the atom numbering

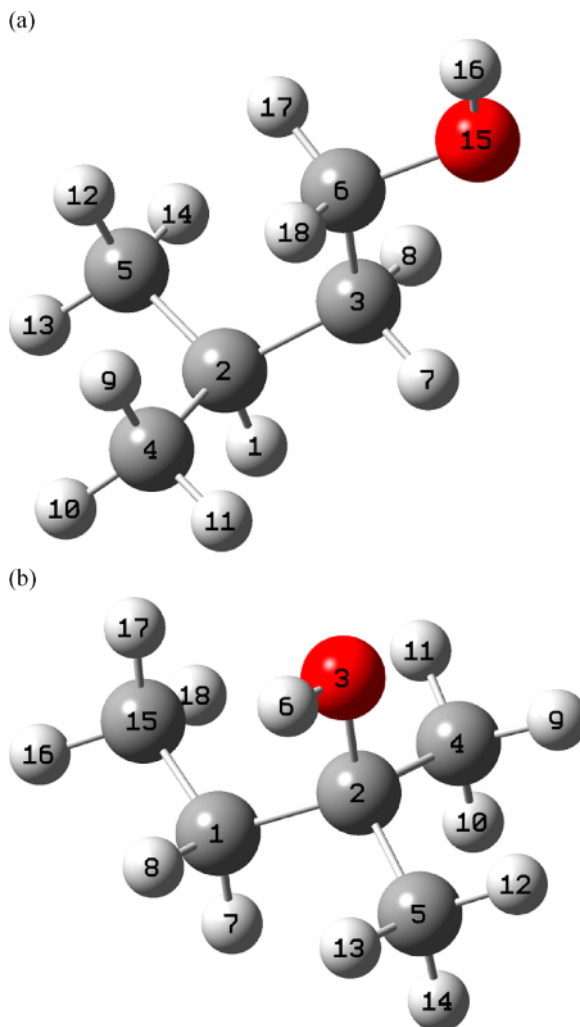


Fig. 1. Atom numbering of the *trans-trans* structure of isoamyl alcohol (upper panel) and the *gauche-gauche* structure of *tert*-amyl alcohol (lower panel).

used are drawn in Fig. 1. With the help of these coordinates and the GAUSSIAN output we were able to calculate the PEDs using our program [1].

### Conformational Equilibria and Structural Data

Isoamyl alcohol exists in a conformational equilibrium of four conformers at 25 °C. The relative energies of the conformers for both alcohols are listed in Table 1. Due to the fact that *gauche* conformers are degenerate, the conformer lowest in energy, the

Table 1. Relative energies  $E_r$  (kcal mol<sup>-1</sup>) for the different conformers of isoamyl alcohol (torsion angles  $T_c = C_6C_3C_2H_1$ ,  $T_o = O_{15}C_6C_3C_2$  and  $T_{oh} = H_{16}O_{15}C_6C_3$ ) and of *tert*-amyl alcohol (torsion angles  $T_o = C_{15}C_1C_2O_3$  and  $T_{oh} = H_6O_3C_2C_1$ ). DFT denotes Density Functional Theory with Becke 3 Lee Yang Parr functional, MP2 Moeller Plesset Perturbation Theory of second order, and MP4 SDQ Moeller Plesset Perturbation Theory of fourth order with single, double and quadruple excitations. Abundancies are based on MP4 SDQ energies.

Isoamyl alcohol				
	$T_o$ (deg)	$T_c$ (deg)	$T_{oh}$ (deg)	$E_r$ (kcal mol <sup>-1</sup> )
<i>trans-trans</i> (24 % abundance)				
DFT	180.0	180.0	180.0	0.00
MP2	180.0	180.0	180.0	0.10
MP4 SDQ	180.0	180.0	180.0	0.00
<i>gauche-gauche</i> (32 % abundance)				
DFT	65.7	172.2	61.5	0.42
MP2	61.4	166.8	59.0	0.25
MP4 SDQ	62.0	167.7	59.2	0.25
<i>gauche-trans</i> (43 % abundance)				
DFT	170.2	67.4	177.5	0.42
MP2	164.3	61.7	175.7	0.00
MP4 SDQ	165.2	62.3	176.0	0.07
<i>trans-cis</i> (2 % abundance)				
DFT	180.0	180.0	0.0	1.30
MP2	180.0	180.0	0.0	1.59
MP4 SDQ	180.0	180.0	0.0	1.49
<i>tert</i> -Amyl alcohol				
	$T_o$ (deg)	$T_{oh}$ (deg)	$E_r$ (kcal mol <sup>-1</sup> )	
<i>gauche-gauche</i> (52 % abundance)				
DFT	58.6	64.4	0.00	
MP2	61.1	64.1	0.00	
MP4 SDQ	60.9	63.8	0.00	
<i>cis-cis</i> ( $5 \times 10^{-4}$ % abundance)				
DFT	0.0	0.0	5.76	
MP2	0.0	0.0	6.57	
MP4 SDQ	0.0	0.0	6.43	
<i>cis-trans</i> ( $10^{-2}$ % abundance)				
DFT	0.0	180.0	4.14	
MP2	0.0	180.0	4.75	
MP4 SDQ	0.0	180.0	4.55	
<i>trans-cis</i> (2 % abundance)				
DFT	180.0	0.0	1.37	
MP2	180.0	0.0	1.45	
MP4 SDQ	180.0	0.0	1.50	
<i>trans-gauche</i> (33 % abundance)				
DFT	177.2	59.1	0.23	
MP2	177.4	57.1	0.22	
MP4 SDQ	177.6	57.5	0.26	
<i>trans-trans</i> (13 % abundance)				
DFT	180.0	180.0	0.29	
MP2	180.0	180.0	0.22	
MP4 SDQ	180.0	180.0	0.39	

Table 2. Observed and calculated wavenumbers in isoamyl alcohol (most observed wavenumbers fit well with the calculated ones of the *gauche-trans* conformation) and *tert*-amyl alcohol (most observed wavenumbers fit nicely with the calculated ones of the *gauche-gauche* conformation). However, both alcohols seem to exist in a mixture of several low-energy conformers.

Isoamyl alcohol (mostly gt)			
IR (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	calcd. (DFT) (cm <sup>-1</sup> )	obs./calcd.
3335 vs		3843	0.87
3326 sh,vs		still OH stretch	
	2966 s	3075	0.96
2959 s		3024	0.98
2931 s		3016	0.97
	2921 s	3016	0.97
	2875 s	3005	0.96
2874 m		2987	0.96
	2727 w	2982	0.91
1465 s	1469 m	1487	0.99
	1456 m	1470	0.99
1426 m		1425	1.00
1384 s		1402	0.99
1368 s		1372	1.00
	1340 w	1354	0.99
	1310 w	1316	1.00
1262 w		1231	1.03
1214 m		1201	1.01
1169 m		1173 (tt)	1.00
1125 s	1133 w	1131	0.98
1059 vs		1044	1.01
1012 s		1024	0.99
967 s	973 w	990	0.98
939 sh,w		966	0.97
921 vw		933	0.99
899 w		892	1.01
	867 w	891 (gg)	0.97
	855 w	848	1.01
836 m		845 (gg)	0.99
772 m	769 m	742	1.04
760 sh		794 (tt)	0.96
669 br,s		no match found	
	448 w	415 (gg)	1.08

*trans-trans* one, has only an abundance of 24 %, while the abundance of *gauche-gauche* is 32 % and that of *gauche-trans* is 43 %. The abundance of the high-energy conformer *trans-cis* is only 2 %. Here the first label indicates the position of the C–O bond relative to the neighboring H<sub>2</sub>C–C bond, while the second label indicates the position of the O–H bond relative to the H<sub>2</sub>C–C bond. Interestingly the MP2 minimum is actually *gauche-trans*, the same which comes out as the one with highest abundance in DFT and MP4 SDQ calculations. Consequently we base all our following discussions on the *gauche-trans* conformer

Table 2. Continued.

<i>tert</i> -Amyl alcohol (mostly <i>gg</i> )			
IR (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	calcd. (DFT) (cm <sup>-1</sup> )	obs./calcd.
3614 sh		3816	0.94
3371 vs		still OH stretch	
2971 s	2973 s	3035	0.98
2941 s	2944 vs	3032	0.97
2928 m	2920 s	3018	0.97
2883 m		2997	0.96
1466 s		1475	0.99
1446 m		1422	1.02
1379 m		1412	0.98
1374 m		1403	0.98
1365 s		1377	0.99
1330 vs		1361	0.98
1277 s		1293	0.99
1188 m		1209	0.98
1167 m		1150	1.01
1060 s	1063 w	1079	0.98
1053 s		1057	1.00
1019 s		1007	1.01
1003 s		1001	1.00
985 s		993 (tg)	0.99
940 w	943 w	931	1.01
881 w	884 w	879	1.00
786 s		788	1.00
727 m	730 vvs	723	1.01
636 m, broad		no match found	
479 sh		488 (tt)	0.98
474 sh		466 (tt)	1.02

which has by far the highest abundance. The comparison between observed and calculated wavenumbers for both alcohols is given in Table 2. Obviously there is a good agreement between observed and calculated wavenumbers. However, for three of the observed wavenumbers no matches in the calculated spectrum could be found. It seems that the samples used to record the spectra contained some traces of impurities. Furthermore, the conformational equilibrium mixture for isoamyl alcohol obviously contains the *trans-trans*, the *gauche-gauche* and the *gauche-trans* conformers, because some wavenumbers had to be assigned to the calculated ones of those conformers.

The conformational equilibrium of *tert*-amyl alcohol contains six conformers, however, only three of them in appreciable abundancies. Those are the *gauche-gauche* conformer with 52% abundance, the *trans-gauche* conformer with 33% abundance and the *trans-trans* one with 13% abundance, all three having lines in the spectrum which is dominated by the one

lowest in energy (*gauche-gauche*). Here the first label indicates again the position of the C–O bond relative to the neighboring C<sub>2</sub>C–C bond, while the second label indicates the position of the O–H bond relative to one of the neighboring H<sub>2</sub>C–H bonds.

Table S3 lists the geometrical parameters calculated by DFT and MP2 for the two alcohols. Obviously the DFT and MP2 values do not differ too much from each other. The C–O bond length is 1.433 Å in isoamyl alcohol while with 1.444 Å it is considerably longer in *tert*-amyl alcohol, indicating that the environment of the CO bond, crowded with methyl groups in the latter, obviously forces the OH group away from the methyl group, thereby making the CO bond weaker. This is indicated by the PED (Table 3) of the two alcohols which shows the CO stretch at 1044 cm<sup>-1</sup> in isoamyl alcohol and considerably lower at 942 cm<sup>-1</sup> in *tert*-amyl alcohol.

### Discussion of Spectra

Table 3 lists the contributions of the group coordinates (symmetry coordinates in case of symmetry) to all the normal modes of the two alcohols. Note that not all of these modes show up in the spectra which are shown in Figs. 2–4. In Table 3 the wavenumbers observed in the spectra are highlighted as bold face. Some of the normal modes, a few in isoamyl alcohol, more of them in *tert*-amyl alcohol, are seen in GAUSSVIEW as having just a localized contribution in one methyl group, while in the in-phase and out-of-phase group coordinates they are present with equal magnitude in two methyl groups. However, the PED in such cases shows the same phenomenon, by having entries of the same percentage numbers of both of these group coordinates, which in the corresponding normal mode cancels one of the methyl group vibrations out. Thus the localization shows up equally well in the PED and in the GAUSSVIEW animation. If in a normal mode there are an in-phase and an out-of-phase linear combination of the methyl group vibrations superimposed, then this superposition determines in which one of the two methyl groups the corresponding localized methyl group motion takes place. This is not in all cases obvious in the GAUSSVIEW animations, if there is a large number of group coordinates mixed in the same normal mode. Then these other coordinates might mask the localized methyl group motion in the animation. This is a clear shortcoming of GAUSSVIEW. The normal

Table 3. Calculated wavenumbers (all of them, bold face italic ones seen in the experimental spectra, DFT), Potential Energy Distributions (PED), only entries larger or equal 5% are listed, together with (for comparison) the GAUSSVIEW results<sup>a</sup> for *gauche-trans* isoamyl alcohol and *gauche-gauche tert*-amyl alcohol.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
<i>gauche-trans</i> isoamyl alcohol		
<b>3843</b>	100% OH str (S <sub>28</sub> )	yes
3111	76% CH <sub>3</sub> as str iph (S <sub>2</sub> )	yes
	40% CH <sub>3</sub> as str oph (S <sub>11</sub> )	loc
3081	36% CH <sub>3</sub> as str oph (S <sub>11</sub> )	yes
	35% CH <sub>3</sub> as str iph (S <sub>3</sub> )	masked
	24% CH <sub>3</sub> as str iph (S <sub>2</sub> )	loc
3077	59% CH <sub>3</sub> as str iph (S <sub>3</sub> )	yes
	19% CH <sub>3</sub> as str oph (S <sub>12</sub> )	masked
	19% CH <sub>3</sub> as str iph (S <sub>2</sub> )	masked
<b>3075</b>	76% CH <sub>3</sub> as str oph (S <sub>12</sub> )	yes
	9% CH <sub>3</sub> as str oph (S <sub>11</sub> )	masked
	8% CH <sub>3</sub> as str iph (S <sub>2</sub> )	masked
	6% CH <sub>3</sub> as str iph (S <sub>3</sub> )	masked
3049	88% CH <sub>2</sub> as str (S <sub>39</sub> )	yes
	6% CH <sub>2</sub> s str (S <sub>26</sub> )	masked
<b>3024</b>	73% CH <sub>3</sub> s str iph (S <sub>1</sub> )	yes
	13% CH <sub>3</sub> s str oph (S <sub>10</sub> )	masked
	7% CH <sub>2</sub> s str (S <sub>26</sub> )	masked
<b>3016</b>	39% CH <sub>2</sub> as str (S <sub>40</sub> )	yes
	38% CH <sub>2</sub> s str (S <sub>26</sub> )	yes
	10% CH <sub>3</sub> s str iph (S <sub>1</sub> )	yes
	8% CH <sub>2</sub> as str (S <sub>39</sub> )	masked
<b>3016</b>	80% CH <sub>3</sub> s str oph (S <sub>10</sub> )	yes
	8% CH <sub>2</sub> s str (S <sub>26</sub> )	masked
	8% CH <sub>3</sub> s str iph (S <sub>1</sub> )	masked
<b>3005</b>	53% CH <sub>2</sub> as str (S <sub>40</sub> )	yes
	27% CH <sub>2</sub> s str (S <sub>26</sub> )	masked
	6% <i>tert</i> -CH str (S <sub>47</sub> )	yes
	6% CH <sub>3</sub> s str iph (S <sub>1</sub> )	yes
<b>2987</b>	85% <i>tert</i> -CH str (S <sub>47</sub> )	yes
	7% CH <sub>2</sub> s str (S <sub>26</sub> )	yes
<b>2982</b>	88% CH <sub>2</sub> s str (S <sub>27</sub> )	yes
	6% CH <sub>2</sub> s str (S <sub>26</sub> )	yes
1525	78% CH <sub>2</sub> scissor (S <sub>31</sub> )	yes
	11% CH <sub>3</sub> as def iph (S <sub>7</sub> )	masked
	7% CH <sub>3</sub> as def oph (S <sub>16</sub> )	masked
1513	65% CH <sub>3</sub> as def iph (S <sub>7</sub> )	indist
	15% CH <sub>3</sub> as def iph (S <sub>5</sub> )	indist
	7% CH <sub>3</sub> rock (S <sub>8</sub> )	hard
	6% CH <sub>2</sub> scissor (S <sub>31</sub> )	indist
1506	66% CH <sub>3</sub> as def iph (S <sub>5</sub> )	indist
	12% CH <sub>3</sub> as def iph (S <sub>7</sub> )	indist
	8% CH <sub>2</sub> scissor (S <sub>31</sub> )	indist
	7% CH <sub>3</sub> rock iph (S <sub>6</sub> )	indist
1494	73% CH <sub>3</sub> as def oph (S <sub>16</sub> )	indist
	8% CH <sub>2</sub> scissor (S <sub>31</sub> )	indist
	7% CH <sub>3</sub> as def oph (S <sub>14</sub> )	indist
	5% CH <sub>3</sub> rock oph (S <sub>31</sub> )	indist
<b>1487</b>	83% CH <sub>3</sub> as def oph (S <sub>14</sub> )	indist
	9% CH <sub>3</sub> as def oph (S <sub>16</sub> )	indist

Table 3. Continued.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
	6% CH <sub>3</sub> rock oph (S <sub>15</sub> )	indist
<b>1470</b>	92% CH <sub>2</sub> scissor (S <sub>30</sub> )	yes
1447	67% CH <sub>2</sub> wag (S <sub>33</sub> )	yes
	13% C-OH ipl bend (S <sub>34</sub> )	yes
<b>1425</b>	81% CH <sub>3</sub> s def iph (S <sub>4</sub> )	yes
	10% CH <sub>2</sub> wag (S <sub>32</sub> )	hard
<b>1402</b>	90% CH <sub>3</sub> s def iph (S <sub>13</sub> )	yes
1392	46% CH <sub>2</sub> wag (S <sub>32</sub> )	yes
	19% CCC bend (S <sub>22</sub> )	yes
	15% CH <sub>3</sub> s def iph (S <sub>4</sub> )	yes
	10% CH <sub>2</sub> wag (S <sub>33</sub> )	yes
<b>1372</b>	36% CC <sub>2</sub> rock (S <sub>25</sub> )	yes
	17% CH <sub>2</sub> twist (S <sub>41</sub> )	indist
	15% CC <sub>2</sub> twist (S <sub>24</sub> )	hard
	6% CH <sub>3</sub> s def iph (S <sub>13</sub> )	hard
<b>1354</b>	26% CCC bend (S <sub>22</sub> )	hard
	16% CC <sub>2</sub> wag (S <sub>23</sub> )	hard
	12% CH <sub>2</sub> twist (S <sub>42</sub> )	indist
	10% CH <sub>2</sub> wag (S <sub>32</sub> )	indist
	6% CC <sub>2</sub> rock (S <sub>25</sub> )	hard
	6% CC <sub>2</sub> as str (S <sub>35</sub> )	hard
<b>1316</b>	38% CH <sub>2</sub> twist (S <sub>41</sub> )	yes
	16% C-OH ipl bend (S <sub>34</sub> )	yes
	15% CH <sub>2</sub> twist (S <sub>42</sub> )	indist
	8% CC <sub>2</sub> twist (S <sub>24</sub> )	hard
	6% CC <sub>2</sub> rock (S <sub>25</sub> )	hard
1256	58% CH <sub>2</sub> twist (S <sub>42</sub> )	hard
	9% CH <sub>2</sub> twist (S <sub>41</sub> )	hard
	9% CH <sub>2</sub> rock (S <sub>45</sub> )	indist
	6% CH <sub>2</sub> wag (S <sub>32</sub> )	hard
<b>1231</b>	35% C-OH ipl bend (S <sub>34</sub> )	yes
	11% CH <sub>2</sub> wag (S <sub>33</sub> )	hard
	8% CH <sub>2</sub> twist (S <sub>41</sub> )	hard
	7% CH <sub>3</sub> rock iph (S <sub>6</sub> )	hard
	6% CC <sub>2</sub> twist (S <sub>24</sub> )	hard
	6% CH <sub>2</sub> rock (S <sub>44</sub> )	hard
<b>1201</b>	24% CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
	17% CH <sub>3</sub> rock iph (S <sub>6</sub> )	indist
	12% CC <sub>2</sub> scissor (S <sub>21</sub> )	yes
	10% CC <sub>2</sub> s str (S <sub>19</sub> )	yes
	8% C-OH ipl bend (S <sub>34</sub> )	yes
	6% CCC as str (S <sub>35</sub> )	yes
1152	20% CH <sub>2</sub> rock (S <sub>45</sub> )	yes
	19% CH <sub>3</sub> rock iph (S <sub>6</sub> )	indist
	11% CC <sub>2</sub> as str (S <sub>35</sub> )	yes
	11% CC <sub>2</sub> bend (S <sub>22</sub> )	indist
	10% CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
	8% CCC ipl bend (S <sub>38</sub> )	yes
<b>1131</b>	18% CCC as str (S <sub>20</sub> )	yes
	15% CO str (S <sub>29</sub> )	yes
	11% CH <sub>2</sub> rock (S <sub>44</sub> )	yes
	10% CH <sub>3</sub> rock oph (S <sub>17</sub> )	yes
	8% C-OH ipl bend (S <sub>34</sub> )	hard
	7% CH <sub>2</sub> twist (S <sub>41</sub> )	hard
	5% CC <sub>2</sub> twist (S <sub>24</sub> )	indist
<b>1044</b>	41% CO str (S <sub>29</sub> )	yes

Table 3. Continued.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
<b>1024</b>	18 % CCC as str (S <sub>35</sub> )	yes
	12 % CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
	7 % CCC s str (S <sub>36</sub> )	indist
	6 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	indist
	35 % CH <sub>2</sub> rock (S <sub>45</sub> )	indist
	9 % CH <sub>2</sub> wag (S <sub>32</sub> )	indist
	8 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	indist
	8 % CCC as str (S <sub>35</sub> )	indist
	5 % CCC s str (S <sub>36</sub> )	indist
	5 % CH <sub>3</sub> rock iph (S <sub>8</sub> )	indist
<b>990</b>	5 % CCC as str (S <sub>20</sub> )	indist
	19 % CCC as str (S <sub>20</sub> )	yes
	19 % CCC as str (S <sub>35</sub> )	yes
	17 % CO str (S <sub>29</sub> )	yes
	11 % CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
	11 % CH <sub>2</sub> rock (S <sub>44</sub> )	yes
	6 % CH <sub>2</sub> twist (S <sub>41</sub> )	hard
966	45 % CH <sub>3</sub> rock oph (S <sub>17</sub> )	indist
	26 % CC <sub>2</sub> as str (S <sub>20</sub> )	yes
	17 % CH <sub>3</sub> rock oph (S <sub>15</sub> )	indist
<b>933</b>	57 % CH <sub>3</sub> rock oph (S <sub>15</sub> )	indist
	20 % CH <sub>3</sub> rock oph (S <sub>17</sub> )	yes
<b>892</b>	9 % CC <sub>2</sub> rock (S <sub>25</sub> )	hard
	41 % CC <sub>2</sub> s str (S <sub>19</sub> )	yes
	21 % CC <sub>2</sub> s str (S <sub>36</sub> )	yes
	11 % CH <sub>2</sub> rock (S <sub>45</sub> )	yes
	10 % CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
<b>848</b>	43 % CH <sub>2</sub> rock (S <sub>44</sub> )	yes
	18 % CO str (S <sub>29</sub> )	yes
	7 % CC <sub>2</sub> as str (S <sub>35</sub> )	indist
	50 % CC <sub>2</sub> s str (S <sub>36</sub> )	yes
<b>742</b>	33 % CCC s str (S <sub>19</sub> )	yes
	29 % CC <sub>2</sub> wag (S <sub>23</sub> )	yes
566	25 % CCC ipl bend (S <sub>38</sub> )	yes
	13 % CCO ipl bend (S <sub>37</sub> )	yes
	8 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	yes
	7 % CH <sub>2</sub> rock (S <sub>45</sub> )	indist
	6 % CH <sub>2</sub> rock (S <sub>44</sub> )	indist
410	39 % CCO ipl bend (S <sub>37</sub> )	yes
	13 % CCC scissor (S <sub>21</sub> )	yes
	11 % CH <sub>2</sub> rock (S <sub>44</sub> )	yes
	8 % CCC wag (S <sub>23</sub> )	indist
	7 % CCC rock (S <sub>25</sub> )	indist
	7 % CCC twist (S <sub>24</sub> )	indist
	57 % CC <sub>2</sub> scissor (S <sub>21</sub> )	indist
	11 % CC <sub>2</sub> twist (S <sub>24</sub> )	indist
371	10 % CC <sub>2</sub> rock (S <sub>25</sub> )	indist
	19 % CC <sub>2</sub> twist (S <sub>24</sub> )	indist
	17 % CCC rock (S <sub>23</sub> )	indist
	16 % CCO ipl bend (S <sub>37</sub> )	indist
343	14 % CCC rock (S <sub>25</sub> )	indist
	14 % CC <sub>2</sub> scissor (S <sub>21</sub> )	indist
	72 % OH torsion (S <sub>43</sub> )	yes
	29 % CH <sub>3</sub> torsion oph (S <sub>18</sub> )	yes
289	21 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	indist
	19 % OH torsion (S <sub>43</sub> )	yes
265		

Table 3. Continued.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
251	12 % CCC ipl bend (S <sub>38</sub> )	hard
	6 % CO torsion (S <sub>46</sub> )	hard
	63 % CH <sub>3</sub> torsion oph (S <sub>18</sub> )	yes
	6 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	indist
	6 % CH <sub>3</sub> as def oph (S <sub>24</sub> )	indist
231	5 % CCC ipl bend (S <sub>38</sub> )	indist
	55 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	yes
	26 % CC <sub>2</sub> ipl bend (S <sub>38</sub> )	hard
	7 % CCC wag (S <sub>23</sub> )	hard
	5 % CCO ipl bend (S <sub>37</sub> )	yes
152	53 % CO torsion (S <sub>46</sub> )	yes
	24 % isopropyl torsion (S <sub>46</sub> )	hard
	12 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	yes
	5 % CCC ipl bend (S <sub>38</sub> )	yes
43	71 % isopropyl torsion (S <sub>48</sub> )	yes
	28 % CO torsion (S <sub>46</sub> )	yes
<i>gauche-gauche tert-amyl alcohol</i>		
<b>3816</b>	100 % OH str (S <sub>45</sub> )	yes
3118	36 % CH <sub>3</sub> as str oph (S <sub>12</sub> )	yes
	34 % CH <sub>3</sub> as str iph (S <sub>3</sub> )	loc
	14 % CH <sub>3</sub> as str iph (S <sub>2</sub> )	loc
	12 % CH <sub>3</sub> as str oph (S <sub>1</sub> )	loc
	66 % CH <sub>3</sub> as str iph (S <sub>2</sub> )	yes
3106	19 % CH <sub>3</sub> as str oph (S <sub>12</sub> )	loc
	9 % eth CH <sub>3</sub> as str (S <sub>38</sub> )	yes
3103	76 % eth CH <sub>3</sub> as str (S <sub>38</sub> )	yes
	11 % CH <sub>3</sub> as str iph (S <sub>2</sub> )	yes
3098	10 % eth CH <sub>3</sub> as str (S <sub>30</sub> )	masked
	82 % CH <sub>3</sub> as str oph (S <sub>11</sub> )	yes
3089	12 % CH <sub>3</sub> as str iph (S <sub>3</sub> )	loc
	5 % CH <sub>3</sub> as str iph (S <sub>2</sub> )	loc
	86 % eth CH <sub>3</sub> as str (S <sub>30</sub> )	yes
	11 % eth CH <sub>3</sub> as str (S <sub>38</sub> )	indist
	48 % CH <sub>3</sub> as str iph (S <sub>3</sub> )	yes
3079	41 % CH <sub>3</sub> as str oph (S <sub>12</sub> )	loc
	51 % CH <sub>3</sub> s str iph (S <sub>1</sub> )	yes
3040	31 % CH <sub>3</sub> s str oph (S <sub>10</sub> )	loc
	8 % CH <sub>2</sub> as str (S <sub>37</sub> )	yes
<b>3035</b>	71 % CH <sub>2</sub> as str (S <sub>37</sub> )	yes
	10 % CH <sub>2</sub> s str (S <sub>26</sub> )	yes
	9 % CH <sub>3</sub> s str iph (S <sub>1</sub> )	yes
	6 % CH <sub>3</sub> s str oph (S <sub>10</sub> )	loc
	92 % eth CH <sub>3</sub> s str (S <sub>29</sub> )	yes
<b>3032</b>		
<b>3018</b>	60 % CH <sub>3</sub> s str oph (S <sub>10</sub> )	yes
<b>2997</b>	33 % CH <sub>3</sub> s str iph (S <sub>1</sub> )	loc
	83 % CH <sub>2</sub> s str (S <sub>26</sub> )	yes
	13 % CH <sub>2</sub> as str (S <sub>37</sub> )	indist
	33 % eth CH <sub>3</sub> as def (S <sub>41</sub> )	yes
	29 % CH <sub>3</sub> as def oph (S <sub>16</sub> )	yes
1517	20 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	indist
	5 % CH <sub>3</sub> as def iph (S <sub>7</sub> )	indist
	33 % eth CH <sub>3</sub> as def (S <sub>41</sub> )	yes
	20 % eth CH <sub>3</sub> as def (S <sub>34</sub> )	indist
	15 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	yes
1510	14 % CH <sub>2</sub> scissor (S <sub>27</sub> )	yes
	8 % CH <sub>3</sub> as def oph (S <sub>16</sub> )	indist

Table 3. Continued.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
1501	46 % CH <sub>3</sub> as def oph (S <sub>16</sub> )	yes
	18 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	indist
	8 % eth CH <sub>3</sub> as def (S <sub>34</sub> )	yes
	6 % eth CH <sub>3</sub> as def (S <sub>41</sub> )	indist
	5 % CH <sub>3</sub> as def iph (S <sub>7</sub> )	indist
1499	58 % eth CH <sub>3</sub> as def (S <sub>34</sub> )	yes
	13 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	yes
	9 % CH <sub>3</sub> as def oph (S <sub>14</sub> )	loc
	7 % CH <sub>2</sub> scissor (S <sub>27</sub> )	yes
1492	37 % CH <sub>3</sub> as def iph (S <sub>7</sub> )	yes
	28 % CH <sub>2</sub> scissor (S <sub>27</sub> )	yes
	21 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	indist
1485	35 % CH <sub>3</sub> as def oph (S <sub>14</sub> )	yes
	30 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	indist
	15 % CH <sub>2</sub> scissor (S <sub>27</sub> )	yes
	8 % eth CH <sub>3</sub> as def (S <sub>41</sub> )	yes
1475	45 % CH <sub>3</sub> as def oph (S <sub>14</sub> )	yes
	34 % CH <sub>2</sub> scissor (S <sub>27</sub> )	yes
	10 % CH <sub>3</sub> as def iph (S <sub>7</sub> )	loc
1422	72 % CH <sub>3</sub> s def iph (S <sub>4</sub> )	yes
	5 % CH <sub>2</sub> wag (S <sub>28</sub> )	yes
1412	90 % eth CH <sub>3</sub> s def (S <sub>33</sub> )	yes
1403	69 % CH <sub>3</sub> s def oph (S <sub>13</sub> )	yes
	13 % CH <sub>3</sub> s def iph (S <sub>4</sub> )	loc
	6 % CC <sub>2</sub> as str (S <sub>20</sub> )	yes
1377	38 % CH <sub>2</sub> wag (S <sub>28</sub> )	yes
	18 % CH <sub>3</sub> s def oph (S <sub>13</sub> )	yes
	10 % C–OH ipl bend (S <sub>46</sub> )	yes
	9 % CH <sub>3</sub> as def oph (S <sub>14</sub> )	indist
	6 % CH <sub>2</sub> twist (S <sub>39</sub> )	indist
1361	31 % CH <sub>2</sub> wag (S <sub>28</sub> )	yes
	18 % C–OH ipl bend (S <sub>46</sub> )	yes
	11 % CH <sub>2</sub> twist (S <sub>39</sub> )	indist
	7 % eth CCC as str (S <sub>32</sub> )	yes
	5 % CH <sub>3</sub> s def oph (S <sub>13</sub> )	yes
1293	51 % CH <sub>2</sub> twist (S <sub>39</sub> )	yes
	14 % eth CH <sub>3</sub> rock (S <sub>42</sub> )	yes
	13 % C–OH ipl bend (S <sub>46</sub> )	yes
1231	38 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	yes
	13 % CC <sub>2</sub> wag (S <sub>23</sub> )	yes
	8 % eth CCC as str (S <sub>32</sub> )	yes
	7 % CH <sub>3</sub> as def iph (S <sub>5</sub> )	loc
	6 % CH <sub>2</sub> wag (S <sub>28</sub> )	yes
	6 % eth CCC s str (S <sub>31</sub> )	indist
1209	29 % CH <sub>3</sub> rock oph (S <sub>17</sub> )	yes
	11 % CH <sub>2</sub> rock (S <sub>40</sub> )	yes
	10 % eth CCC rock (S <sub>42</sub> )	yes
	8 % CO str (S <sub>44</sub> )	yes
	7 % CC <sub>2</sub> scissor (S <sub>21</sub> )	yes
	7 % CC <sub>2</sub> s str (S <sub>19</sub> )	yes
1150	34 % C–OH ipl bend (S <sub>46</sub> )	yes
	14 % eth CH <sub>3</sub> rock (S <sub>35</sub> )	yes
	11 % CC <sub>2</sub> as str (S <sub>20</sub> )	yes
	8 % CH <sub>3</sub> rock oph (S <sub>15</sub> )	yes
	7 % eth CCC ipl bend (S <sub>36</sub> )	yes
	6 % CC <sub>2</sub> rock (S <sub>25</sub> )	hard

Table 3. Continued.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
	6 % CH <sub>2</sub> rock (S <sub>40</sub> )	hard
1079	24 % CH <sub>3</sub> rock oph (S <sub>17</sub> )	yes
	17 % eth CH <sub>3</sub> rock (S <sub>42</sub> )	yes
	15 % eth CCC as str (S <sub>32</sub> )	yes
	12 % CH <sub>2</sub> rock (S <sub>40</sub> )	hard
	12 % CH <sub>2</sub> twist (S <sub>39</sub> )	indist
1057	19 % eth CH <sub>3</sub> rock (S <sub>35</sub> )	yes
	18 % CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
	18 % CC <sub>2</sub> as str (S <sub>20</sub> )	yes
	11 % eth CCC as str (S <sub>32</sub> )	yes
	8 % C–OH ipl bend (S <sub>46</sub> )	yes
	7 % eth CCC s str (S <sub>31</sub> )	indist
1007	42 % eth CCC as str (S <sub>32</sub> )	yes
	18 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	yes
	10 % CH <sub>2</sub> wag (S <sub>28</sub> )	yes
	8 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	yes
1001	72 % CH <sub>3</sub> rock oph (S <sub>15</sub> )	yes
	11 % eth CH <sub>3</sub> rock (S <sub>35</sub> )	yes
942	34 % CO str (S <sub>44</sub> )	yes
	27 % eth CCC s str (S <sub>31</sub> )	yes
	18 % CH <sub>3</sub> rock oph (S <sub>17</sub> )	yes
	6 % eth CH <sub>3</sub> rock (S <sub>42</sub> )	yes
931	52 % CH <sub>3</sub> rock iph (S <sub>8</sub> )	yes
	6 % CC <sub>2</sub> wag (S <sub>23</sub> )	indist
	5 % CH <sub>3</sub> rock oph (S <sub>15</sub> )	indist
879	31 % CO str (S <sub>44</sub> )	yes
	25 % eth CCC s str (S <sub>31</sub> )	yes
	24 % CH <sub>3</sub> rock iph (S <sub>6</sub> )	yes
	11 % CC <sub>2</sub> s str (S <sub>19</sub> )	yes
788	55 % CH <sub>2</sub> rock (S <sub>40</sub> )	yes
	31 % eth CH <sub>3</sub> rock (S <sub>42</sub> )	yes
723	37 % CC <sub>2</sub> s str (S <sub>19</sub> )	yes
	27 % eth CCC s str (S <sub>31</sub> )	yes
	14 % CO str (S <sub>44</sub> )	yes
	9 % eth CCC as str (S <sub>32</sub> )	masked
	6 % eth CH <sub>3</sub> rock (S <sub>35</sub> )	hard
528	23 % CCC ipl bend (S <sub>22</sub> )	yes
	20 % CC <sub>2</sub> rock (S <sub>25</sub> )	indist
	18 % eth CCC ipl bend (S <sub>36</sub> )	yes
	8 % CC <sub>2</sub> as str (S <sub>20</sub> )	yes
	6 % CC <sub>2</sub> s str (S <sub>19</sub> )	indist
	6 % CC <sub>2</sub> wag (S <sub>23</sub> )	indist
454	42 % CC <sub>2</sub> rock (S <sub>25</sub> )	yes
	17 % CCC ipl bend (S <sub>22</sub> )	yes
	7 % CC <sub>2</sub> scissor (S <sub>21</sub> )	indist
	7 % CC <sub>2</sub> wag (S <sub>23</sub> )	indist
	6 % CC <sub>2</sub> as str (S <sub>20</sub> )	indist
415	67 % CC <sub>2</sub> wag (S <sub>23</sub> )	yes
	10 % CC <sub>2</sub> scissor (S <sub>21</sub> )	indist
	6 % CH <sub>3</sub> rock oph (S <sub>17</sub> )	yes
367	41 % CC <sub>2</sub> twist (S <sub>24</sub> )	yes
	21 % CC <sub>2</sub> scissor (S <sub>21</sub> )	indist
	17 % eth CCC ipl bend (S <sub>36</sub> )	yes
	7 % eth CCC s str (S <sub>31</sub> )	no
345	38 % CC <sub>2</sub> scissor (S <sub>21</sub> )	yes
	9 % CC <sub>2</sub> twist (S <sub>24</sub> )	hard

Table 3. Continued.

Wavenumber (DFT, cm <sup>-1</sup> )	PED <sup>b</sup> (DFT)	GAUSSVIEW (DFT)
298	17 % CC <sub>2</sub> twist (S <sub>24</sub> )	indist
	79 % <i>tert</i> OH torsion (S <sub>47</sub> )	yes
270	18 % CH <sub>3</sub> torsion oph (S <sub>18</sub> )	yes
	34 % CH <sub>3</sub> torsion oph (S <sub>18</sub> )	yes
	22 % eth CH <sub>3</sub> torsion (S <sub>43</sub> )	yes
	10 % CC <sub>2</sub> twist (S <sub>24</sub> )	indist
255	9 % eth CCC ipl bend (S <sub>36</sub> )	hard
	8 % <i>tert</i> OH torsion (S <sub>47</sub> )	yes
	6 % CC <sub>2</sub> rock (S <sub>25</sub> )	indist
	35 % CH <sub>3</sub> torsion oph (S <sub>18</sub> )	yes
	32 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	loc
	11 % eth CCC ipl bend (S <sub>36</sub> )	yes
227	9 % CC <sub>2</sub> twist (S <sub>24</sub> )	hard
	5 % <i>tert</i> OH torsion (S <sub>47</sub> )	yes
	42 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	yes
	22 % eth CCC ipl bend (S <sub>36</sub> )	yes
207	10 % CC <sub>2</sub> twist (S <sub>24</sub> )	indist
	8 % CCC ipl bend (S <sub>22</sub> )	indist
	6 % CC <sub>2</sub> rock (S <sub>25</sub> )	indist
	60 % eth CH <sub>3</sub> torsion (S <sub>43</sub> )	yes
	20 % CH <sub>3</sub> torsion iph (S <sub>9</sub> )	yes
111	8 % CH <sub>3</sub> torsion oph (S <sub>18</sub> )	hard
	91 % hydr. isopr. tors. (S <sub>48</sub> )	yes
	6 % eth CH <sub>3</sub> torsion (S <sub>43</sub> )	yes

<sup>a</sup> “hard” means hard to see, almost invisible, “masked” means invisible because of a similar coordinate with much larger amplitude motion, “yes” means clearly visible, “no” means invisible, “indist” means indistinguishable from others, “loc” localization of motion in one side of the molecule; <sup>b</sup> abbreviations: str: stretch, def: deformation, s: symmetric, as: antisymmetric, iph: in phase, oph: out of phase, ipl: in plane, opl: out of plane.

mode with the highest calculated wavenumber is the one at 3843 cm<sup>-1</sup> in isoamyl alcohol and at 3816 cm<sup>-1</sup> in *tert*-amyl alcohol, both being OH stretches with 100% PED in both alcohols, S<sub>28</sub> in isoamyl alcohol and S<sub>45</sub> in *tert*-amyl alcohol. As usual these OH stretches show up at lower wavenumbers in the infrared spectra, namely at 3335 cm<sup>-1</sup> in isoamyl alcohol and at 3614 cm<sup>-1</sup> in *tert*-amyl alcohol. In both spectra at 3326 and at 3371 cm<sup>-1</sup> there are shoulders which have no counterparts among the calculated normal modes. Most probably these are due to OH stretches, either hydrogen bonded ones or from crystal water. The next lower calculated wavenumber in isoamyl alcohol is at 3075 cm<sup>-1</sup> and has a highly mixed PED with a leading contribution of 76 % out-of-phase methyl antisymmetric stretch (S<sub>12</sub>). In the GAUSSVIEW animation three of the four PED entries are masked by the leading one and cannot be identified. There is no counterpart to this mode in the experimental spectra of

*tert*-amyl alcohol. For isoamyl alcohol the line is observed in the Raman spectrum at 2966 cm<sup>-1</sup> as a strong one. The CH stretches in isoamyl alcohol continue at 3024 cm<sup>-1</sup> with a leading term of 73 % symmetric in-phase CH<sub>3</sub> stretch (S<sub>1</sub>), at 3016 cm<sup>-1</sup> with two lines, one being highly mixed with leading terms of 39 % CH<sub>2</sub> antisymmetric stretch (S<sub>40</sub>) and of 38 % CH<sub>2</sub> symmetric stretch (S<sub>26</sub>), the other one being more pure with a leading 80 % out-of-phase methyl symmetric stretch (S<sub>10</sub>), at 3005 cm<sup>-1</sup> with 53 % CH<sub>2</sub> antisymmetric stretch (S<sub>40</sub>), at 2987 cm<sup>-1</sup> with 85 % *tert*-CH stretch (S<sub>47</sub>), and finally at 2982 cm<sup>-1</sup> with 88 % CH<sub>2</sub> symmetric stretch (S<sub>27</sub>). These lines are observed between 2966 and 2727 cm<sup>-1</sup>, all strong, some even very strong bands, besides the last one which is a medium one. In the GAUSSVIEW animation most of the smaller PED entries cannot be seen. In *tert*-amyl alcohol the line at 3035 cm<sup>-1</sup> has a PED of 71 % CH<sub>2</sub> antisymmetric stretch (S<sub>37</sub>). Below that at 3032 cm<sup>-1</sup> there is a mode with 92 % ethyl CH<sub>3</sub> symmetric stretch (S<sub>29</sub>), at 3018 cm<sup>-1</sup> there is a mixed mode with 60 % out-of-phase methyl symmetric stretch (S<sub>10</sub>) and 33 % in-phase methyl symmetric stretch (S<sub>1</sub>), which cannot be seen in the GAUSSVIEW animation, and finally at 2997 cm<sup>-1</sup> 83 % CH<sub>2</sub> symmetric stretch (S<sub>26</sub>). These lines are observed between 2971 and 2883 cm<sup>-1</sup> in the infrared and Raman spectra with most being strong or even very strong features.

In the lower wavenumber region we want to focus on the intense and characteristic lines. The next strong line in the infrared spectrum of isoamyl alcohol is one at 1465 cm<sup>-1</sup> which is calculated at 1487 cm<sup>-1</sup> with 83 % PED for an out-of-phase methyl antisymmetric deformation (S<sub>14</sub>). In the infrared spectrum of *tert*-amyl alcohol there is a similar strong band observed also at 1466 cm<sup>-1</sup> and calculated at 1475 cm<sup>-1</sup>. Because *tert*-amyl alcohol is *gauche-gauche*, there are fewer symmetry restrictions for the mixing of group coordinates in a normal mode, and thus in the PED of this mode the leading contribution (same as above, S<sub>14</sub>) has only 45 %, while there is a PED entry of 34 % for the methylene scissor (S<sub>27</sub>) motion. Note that the Raman spectra contain, besides the CH stretches, only medium and weak intensity lines, except for a very strong one in *tert*-amyl alcohol (see below).

In the infrared spectrum of isoamyl alcohol one sees a group of five strong to weak bands at 1262, 1214, 1169, 1125, and 1059 cm<sup>-1</sup>, which are calculated



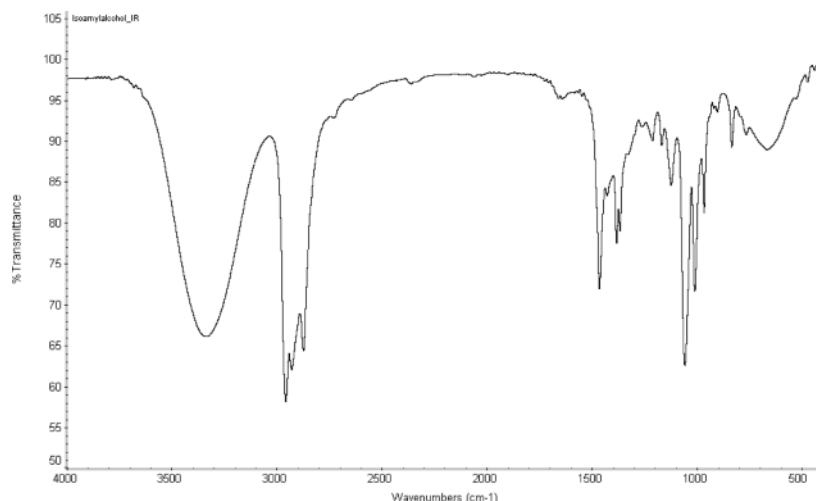


Fig. 2. Infrared spectrum of liquid isoamyl alcohol as obtained in our laboratory.

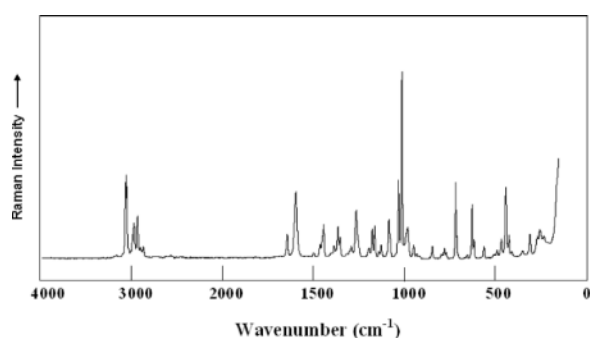


Fig. 3. Raman spectrum of isoamyl alcohol retrieved from <http://www.aist.go.jp/RIODB/SDBS>; no. 541 (accessed March 20, 2013).

between 1231 and 1044  $\text{cm}^{-1}$ , where the 1214  $\text{cm}^{-1}$  band has to be assigned to the calculated mode at 1201  $\text{cm}^{-1}$  in the *trans-trans* conformer. Of these bands the one with highest wavenumber has a PED of 58% methylene twist ( $S_{42}$ ), while the band calculated at 1231  $\text{cm}^{-1}$  is highly mixed with 35% C–OH in plane bend ( $S_{34}$ ) and 11% methylene wag ( $S_{33}$ ). The band calculated at 1201  $\text{cm}^{-1}$  is again highly mixed with leading terms of 24% in-phase methyl rock ( $S_8$ ) and 17% of also in-phase methyl rock ( $S_6$ , another coordinate describing also in phase methyl rock). These two cannot be seen separately in the GAUSSVIEW animation. The next lower calculated bands at 1131, 1044 and 1024  $\text{cm}^{-1}$  are all highly mixed again as can be seen from the rather low leading contributions, which are 18% CCC antisymmetric stretch ( $S_{20}$ ) in the 1131  $\text{cm}^{-1}$  band, followed by 15% CO stretch

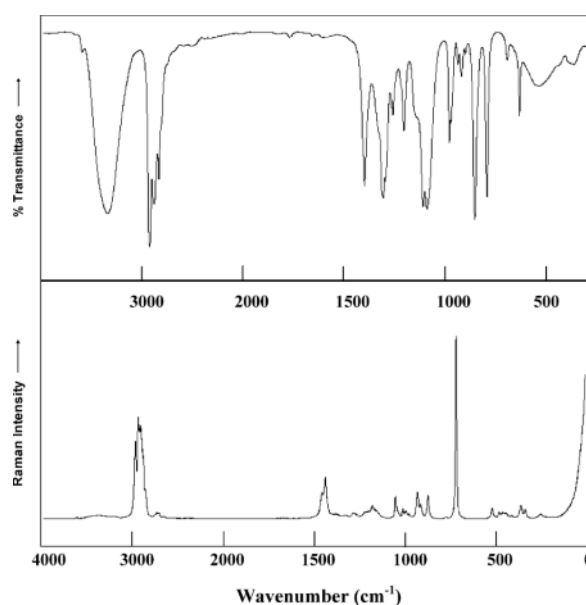


Fig. 4. Infrared (upper) and Raman (lower) spectra of liquid *tert*-amyl alcohol retrieved from <http://www.aist.go.jp/RIODB/SDBS>; no. 1709 (accessed March 20, 2013).

( $S_{29}$ ), 41% CO stretch ( $S_{29}$ ) in the 1044  $\text{cm}^{-1}$  band, and 35% methylene rock ( $S_{45}$ ) in the 1024  $\text{cm}^{-1}$  band. For *tert*-amyl alcohol this series of neighboring strong and very strong bands in the infrared spectrum is interrupted by two bands of medium intensity observed at 1188 and 1167  $\text{cm}^{-1}$ . The strong and very strong bands in the infrared spectrum of *tert*-amyl alcohol are observed at 1365, 1330, 1277, 1060, 1053, 1019,

1003, and  $985\text{ cm}^{-1}$  and calculated between  $1377$  and  $1001\text{ cm}^{-1}$ , while the  $985\text{ cm}^{-1}$  band has to be assigned to the calculated  $993\text{ cm}^{-1}$  band in the *gauche-trans* conformer. The degree of mixing of group coordinates in these normal modes in *tert*-amyl alcohol is even larger than in isoamyl alcohol, so that we list only the leading PED entries in the corresponding calculated normal modes. These are 38 % methylene wag ( $S_{28}$ ) in the  $1377\text{ cm}^{-1}$  band and 31 % of the same coordinate ( $S_{28}$ ) in the  $1361\text{ cm}^{-1}$  band. The calculated  $1293\text{ cm}^{-1}$  band is more pure and has 51 % methylene twist ( $S_{39}$ ) as leading PED entry. The leading PED entry in the band calculated at  $1079\text{ cm}^{-1}$  is of only 24 % out-of-phase methyl rock ( $S_{17}$ ), as much as in the case of the corresponding bands in isoamyl alcohol. For *tert*-amyl alcohol, in the band at  $1057\text{ cm}^{-1}$  the leading PED term is even smaller, namely 19 % ethyl-methyl rock ( $S_{35}$ ), while the one in the  $1007\text{ cm}^{-1}$  band is 42 % ethyl CCC symmetric stretch ( $S_{32}$ ). The  $1001\text{ cm}^{-1}$  band is much more pure with a leading PED term of 72 % out-of-phase methyl rock ( $S_{15}$ ).

Below this group of strong features, there is only one more strong band observed in the infrared spectrum of isoamyl alcohol at  $772\text{ cm}^{-1}$ , calculated at  $742\text{ cm}^{-1}$ . This is a relatively pure normal mode with 50 % and 33 % CCC symmetric stretch (different coordinates:  $S_{19}$  and  $S_{36}$ ). For *tert*-amyl alcohol only one more remarkable feature is observed, namely the very strong Raman line at  $730\text{ cm}^{-1}$ , calculated at  $723\text{ cm}^{-1}$ . With 27 % CCC symmetric stretch ( $S_{19}$ ) and 27 % ethyl CCC symmetric stretch ( $S_{31}$ ) this line has a similar PED as the lowest strong infrared band in isoamyl alcohol observed at  $772\text{ cm}^{-1}$ . Note that “CCC symmetric stretch” denotes the symmetric combination of the two C–C stretches in the  $\text{CH}_3\text{--CH--CH}_3$  subgroup in isoamyl alcohol and the corresponding stretches in the  $\text{CH}_3\text{--COH--CH}_3$  subgroup in *tert*-amyl

alcohol, while “ethyl CCC symmetric stretch” denotes the symmetric combination of the two C–C stretches in the  $\text{C}_2\text{C}_3\text{C}_6$  subgroup in isoamyl alcohol and in the  $\text{C}_2\text{C}_1\text{C}_{15}$  subgroup in *tert*-amyl alcohol.

## Conclusion

The spectra of isoamyl alcohol and *tert*-amyl alcohol are rather similar with straightforward assignments of lines. The calculated lines in both cases fit nicely to the experimental ones. The calculated spectra of amylalcohol, as a primary alcohol like isoamyl alcohol, contain not much new data, and thus we refrain from discussing them here in any detail. Both the CO and the OH bond appear to be weaker in the tertiary than in the primary alcohol. This is indicated by the CO stretch wavenumbers which are lower in the tertiary alcohol ( $879$  and  $942\text{ cm}^{-1}$ ) than in the primary alcohol ( $990$  and  $1044\text{ cm}^{-1}$ ). The OH stretch in the latter case is also higher ( $3843\text{ cm}^{-1}$ ) than in the former ( $3816\text{ cm}^{-1}$ ). The corresponding bonds are longer in the tertiary than in the primary alcohol (although the difference in bond length of the OH bond in *tert*-amyl alcohol is very small). We attribute that to steric effects in the tertiary alcohol.

## Supporting information

Internal coordinate definitions, group coordinates, and calculated (DFT and MP2) structural parameters, dipole moments and rotational constants are given as Supporting Information available online (DOI: 10.5560/ZNB.2013-3003).

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