

## Long-wave Raman spectra of some normal alcohols



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### ABSTRACT

Long-wave Raman spectra of some normal alcohols (from *n*-pentanol to *n*-decanol) in the liquid phase were registered. The regularities in the dependencies of Raman bands frequencies on the number of carbon atoms in the hydrocarbon chain were deduced. The calculations of Raman spectra of the studied molecules, their equilibrium structures and possible conformers were carried out in the approximation B3LYP/cc-pVDZ. These results in combination with the analysis of literature data allowed to explain the observed regularities in Raman band positions in the spectral range of 200–600 cm<sup>-1</sup> and their shifts upon increasing length of the chains. It was found that the plane configurations dominate in the liquid phase for molecules with short- and moderate-chain lengths. The elongation of the chain leads to the decrease of the fraction of plane conformers and in *n*-decanol the plane structure is completely absent.

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### 1. Introduction

Alcohol molecules attract investigators by their ability to form various cluster structures. Studying of such structures allows tracing in detail the gradual transition from individual molecules in gas phase to liquid media, as well as the changes of spectral characteristics during this transition [1–3]. Liquid monohydric alcohols are partly ordered systems. Partial ordering in liquid alcohols is due to the formation of the specific intermolecular interaction – hydrogen bonding [4] – between their molecules, which mainly determines the structure of these liquids as well as kinetic processes in them. The energy of the hydrogen bonding noticeably exceeds the energy of the usual van der Waals interactions and lower than the energy of the strong chemical bonding by only one order [5]. Investigation of the influence of the environment on hydrogen-bonded systems also attracts the attention of researchers [6,7]. Liquids with intermolecular hydrogen bonding are very significant in chemistry and biology, ranging from the unique properties of water to their role in the formation of the biomolecule structure. But despite of their great significance, the depth of our understanding of the structure and dynamics of these molecular systems is poor.

Vibrational spectroscopy (infrared absorption and Raman scattering) is a very productive method for the investigation of the

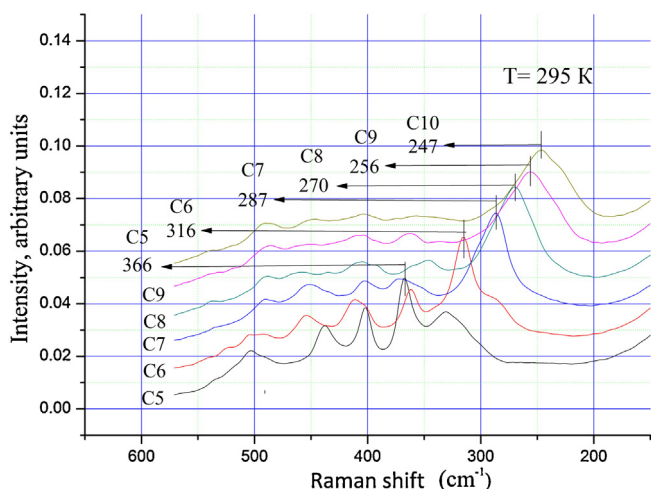
systems with hydrogen bonding [8–11]. This method is a fine instrument for studying of microscopic state of the substance, combining the high sensitivity and ability to provide the information on the system at the molecular scale. Raman spectroscopy is a powerful method for studying liquids, because Raman spectra are sensitive to the molecular interactions and to the changes inside molecules. In spite of the fact that the vibrational spectra of studied alcohols have been investigated for a long time (first systematic study was made in 1932 [12]) it is worth to note that the long-wave region has not received enough attention. As a rule, IR spectra of alcohols are registered from 400 cm<sup>-1</sup>. The data on systematic analysis of the long-wave spectra of the series of normal alcohols (other than the above-cited work [12]) are unknown for us. In this relation the main goal of our work was to obtain Raman spectra and explain some features in the behavior of the intense Raman lines of normal alcohols in spectral range 200–600 cm<sup>-1</sup>.

### 2. Experimental

Using a Bruker MultiRAM FT-Raman spectrometer, the long-wave Raman spectra of a series of liquid monohydric alcohols – pentanol (C5), hexanol (C6), heptanol (C7), octanol (C8), nonanol (C9), and decanol (C10) – were registered. The excitation wavelength and the intensity of the laser beam were, respectively, 1064 nm and 500 mW. The scattering geometry was such that back scattered light was collected, acquisition mode: double-side, forward–backward, zero filling factor—2. Raman spectra were

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**Fig. 1.** Raman spectra of the series of normal alcohols in spectral region 200–600  $\text{cm}^{-1}$ . (The excitation wavelength was 1064 nm. Raman spectra were registered at 295 K with resolution 4  $\text{cm}^{-1}$ , the low wavenumber cut-off value is 70  $\text{cm}^{-1}$ .)

registered at 4  $\text{cm}^{-1}$  resolution, with low wavenumber cut-off at 70  $\text{cm}^{-1}$ . In total, 800 scans were averaged for each spectrum. Standard 5-mm NMR glass tubes were used as cells for preparing samples of liquid alcohols. Liquid phase samples of normal alcohols with purity >99.9% from Fluka were used as received. The temperature of the samples was 295 K. The registered Raman spectra are presented in Fig. 1.

### 3. Calculation details

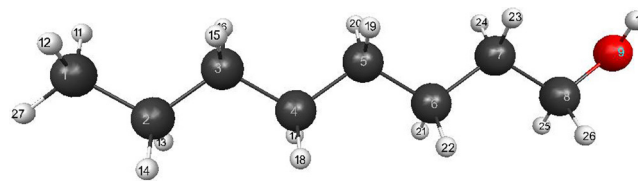
The calculations of the structure and spectral properties of all alcohol molecules were carried out using program set GAMESS [13] in the approximation B3LYP/cc-pVDZ. When choosing the approximation the large volume of the needed calculations – equilibrium configurations and frequencies of normal modes of six molecules containing from 18 to 33 atoms – was taken into account. Moreover, for some of them the same calculations should be carried out for several conformers. On the other hand it was shown earlier [14] that in case of organic molecules this approximation is quite acceptable for calculations of harmonic vibrations, and the most part of the vibrations in the interval 200–600  $\text{cm}^{-1}$  in alcohol molecules can be undoubtedly related to this type of vibrations. Additional calculations of geometries and Raman spectra were performed in the approximation B3LYP/cc-pVQZ for some conformers of pentanol molecules.

To obtain the relative intensity of Raman lines from Raman activity of the vibrations obtained directly from the quantum chemical program set [13], the additional calculations were performed in accordance with [15,16].

## 4. Discussion of the results

### 4.1. Qualitative analysis of Raman spectra

The main feature in the comparative analysis of the registered spectra of the series of alcohols is the monotone red shift of the intense Raman line and the increasing of its half-width with the increasing of the number of carbon atoms. Formally one can assume that this is a general vibration for all molecules and it is related to the hydrogen bond formation. In particular, this can be the intermolecular vibration in alcohol dimers. Then the observed red shift with the increasing of the molecule size can be related to the increasing of the reduced masses involved in the vibrations.



**Fig. 2.** The energetically preferable plane configuration of  $n$ -octanol molecule.

According to the results of the calculations of normal vibrations of methanol and ethanol dimers, the frequency of the hydrogen bond vibrations for methanol is in fact lower than the corresponding frequency for ethanol. However, the frequencies of both vibrations are lower than 200  $\text{cm}^{-1}$  (182.6 and 154.4  $\text{cm}^{-1}$ , respectively). That is why this hypothesis was excluded from consideration.

Next assumption on the nature of the analyzed Raman lines concerns the structure of the molecules of the investigated alcohols. For those configurations of the conformers of normal alcohols, which correspond to minimal energy, the chain location of carbon atoms in one plane (plane configuration) is typical, as is shown in Fig. 2 for normal alcohol  $\text{C}_8\text{H}_{17}\text{OH}$  ( $n$ -octanol).

One can suppose that the investigated Raman lines are due to the vibrations like standing waves on the strings. Even closer mechanical analogue is the spring with the length that increases and decreases owing to tension and compression of the chain at the synchronous increasing of the angles C–C–C. Note that in this case the maximal wavelength of the vibration turns out to be equal to the double length of carbon chain of the molecule including oxygen atom. On the assumption of this model we have

$$\lambda_n = 2l_{n+1} \quad (1)$$

where  $n$  is the number of carbon atoms in the molecule of  $n$ -alcohol,  $l_{n+1}$  – the length of the molecule. Since the wavenumber is determined as

$$\tilde{\nu}_n = \frac{1}{\lambda_n} \quad (2)$$

then taking into account (1) one can obtain:

$$\tilde{\nu}_n = \frac{1}{2l_{n+1}}. \quad (3)$$

In absolute terms these wavenumbers, of course, have no sense. Assuming that,

$$l_{n+1} = c(n+1), \quad (4)$$

where  $c = l_{n+1}/n+1 = l_1$  is the distance between  $\text{CH}_2$  groups, we obtain:

$$\tilde{\nu}_n = \frac{1}{2c(n+1)}. \quad (5)$$

Now we have series of the frequencies for normal alcohols of the following type:  $\tilde{\nu}_{10}$ ;  $\tilde{\nu}_9$ ;  $\tilde{\nu}_8$ ;  $\tilde{\nu}_7$ ;  $\tilde{\nu}_6$ ;  $\tilde{\nu}_5$ ; ... Let us divide all of them by  $\tilde{\nu}_{10}$ . We obtain: 1;  $\tilde{\nu}_9/\tilde{\nu}_{10}$ ;  $\tilde{\nu}_8/\tilde{\nu}_{10}$ ;  $\tilde{\nu}_7/\tilde{\nu}_{10}$ ;  $\tilde{\nu}_6/\tilde{\nu}_{10}$ ;  $\tilde{\nu}_5/\tilde{\nu}_{10}$ ; Taking into account (5) we obtain the series: 1; 11/10; 11/9; 11/8; 11/7; 11/6 or 1; 1.1; 1.2; 1.38; 1.57; 1.83. From the experiment we have the following frequency values:  $\tilde{\nu}_{10} = 247$ ;  $\tilde{\nu}_9 = 256$ ;  $\tilde{\nu}_8 = 270$ ;  $\tilde{\nu}_7 = 287$ ;  $\tilde{\nu}_6 = 316$ ;  $\tilde{\nu}_5 = 366$ . Dividing them by  $\tilde{\nu}_{10}$  we obtain the following numbers: 1; 1.04; 1.09; 1.16; 1.28; 1.48. It is not difficult to notice that there is a correlation between these two number sequences. Of course, there is no perfect analogy between the considered model and the molecules. The spring is assumed to be the homogeneous one, while the molecules contain the end groups. Based on the proposed analogy, we can use well-developed methods of oscillation theory of one-dimensional crystal or polymer chain [17–20]. In doing so, one can see that if

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