



# Cluster structure changes during melting of 1-decanol: FTIR study and DFT calculations



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## ABSTRACT

Temperature dependence of 1-decanol FTIR spectra is studied from both sides of melting point with a step of 0.5 °C near the phase transition. Using *ab initio* quantum-chemistry calculations of different cluster structures, authors show, that solid phase of alcohol is formed by clusters consisting of 3 molecules and liquid phase – by clusters consisting of 5 molecules. Unlike small alcohols, 1-decanol is formed by chain-like clusters. Gradual changes of spectral bands in process of heating are interpreted as a feature of amorphous phase.

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## 1. Introduction

Substances with hydrogen bonds are interesting for scientists in different fields – physics, chemistry, biology, medicine and other. They are also important for industrial and technical applications. The list of such substances includes water, alcohols and many other partially ordered liquids.

Alcohols are widely used and studied when it comes to methanol [1–4], ethanol [4–5], propanol [4,6–9] and butanol [7,10–13], but their “bigger brothers” with larger number of atoms in molecule are less spread in scientific and technical fields. Another reason for such a neglect of bigger alcohols is more complicated structure of their molecules, that leads to complexity of experimental, theoretical and analytical investigation. Thus, there is no much information about structure of “big” alcohols with >3–4 carbon atoms in molecule. Some progress in studying such substances was achieved in works [14–19]. One of the first studies of cluster formation in dilute decanol was presented in [20].

There are many experimental and theoretical technics for alcohols investigations. One of the most effective technics for molecular structure investigation is vibrational spectroscopy (FTIR [2,3,5–7,9–11,15–18], Raman [7,8,11]) – it can be used to study intra- and intermolecular hydrogen bonds. Among theoretical methods of investigation quantum-

chemistry calculations can be allotted [1,2,4–13,15–18]. Semiempirical PM3 method was used in [21] for quantum chemical analysis of 2D cluster formation of some fatty alcohols including 1-decanol at the air/water interface, the formation of stable tetramers for 1-decanol was predicted. Interfacial behavior of 1-decanol was also studied in [22].

The important part of structure investigation is to study not only the substance under certain conditions, but also a dependence of its behavior on some parameters. Temperature is an important parameter for investigation of condensed alcohols [2,3,5,6,15–18]. The article presented is devoted to studying of cluster structure changes during melting process of 1-decanol.

## 2. Experiment

Each FTIR absorption spectrum was measured using a Bruker Vertex 70 spectrometer with temperature control (A147-L01, A147/Q). Spectrometer was equipped with mercury cadmium telluride (MTC) detector cooled with liquid N<sub>2</sub>. Every spectrum was registered as averaged 128 scans with resolution of 1 cm<sup>-1</sup> in the 500–4000 cm<sup>-1</sup> regions. Thermostabilization was provided by a LINKAM cryostat (model FTIR 600).

Liquid 1-decanol (Fluka, purity >99.9%) was used as received. Temperature measurements were performed from –10 to +7 °C by gradual heating. The chosen temperature range includes the temperature of 1-decanol melting (+5 till +7 °C [18–20]).

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### 3. Experimental FTIR spectra

The temperature evolution of the registered FTIR spectra of 1-decanol in the spectral region of O—H stretching vibrations ( $3100\text{--}3700\text{ cm}^{-1}$ ) is presented in Fig. 1. The stretching vibrations of hydroxyl groups is the most sensitive to hydrogen bonds formation [2].

As seen from Fig. 1, spectra of 1-decanol in this region have one narrow vibrational band at  $3417\text{ cm}^{-1}$  and one wide band with peak at  $3367\text{ cm}^{-1}$  in solid phase ( $-10\text{ }^{\circ}\text{C}$ ). The lowest absorbance rate between these two bands is at  $3388\text{ cm}^{-1}$ . Structure of spectra remains the same during heating from  $-10$  to  $+5\text{ }^{\circ}\text{C}$ . After  $+5\text{ }^{\circ}\text{C}$  some changes in the registered spectra are observed. From  $5.5$  to  $7\text{ }^{\circ}\text{C}$  one can observe a wide vibrational band from  $3150$  to  $3500\text{ cm}^{-1}$ .

In order to study changes in cluster structure of 1-decanol during the phase transition one needs to consider spectral changes occurring between different temperatures. Thus, transition spectra of 1-decanol were calculated. Each transition spectrum can be calculated as a difference between intensity in  $\mu$  spectrum and  $(\mu - 1)$  spectrum. Such spectral differences are presented in Fig. 2.

As seen from Fig. 2, significant changes in spectra occur near the phase transition point. To highlight the required range, we can check a dependency of spectra deviation from temperature. For such analysis, variance formula for deviation was used:

$$\sigma = \frac{1}{n} \sum (x - \bar{x})^2$$

where  $\sigma$  is variance,  $n$  – number of points (wavenumbers),  $x$  – difference between two temperatures at the same wavenumber,  $\bar{x}$  can be found as  $\bar{x} = \frac{1}{n} \sum x$ .

Such approach avoids including for consideration of transition spectra with steady background growth. Variance was calculated only in the spectral region  $3100\text{--}3700\text{ cm}^{-1}$  – the region of stretching O—H vibrations [1–4].

In Fig. 3 the dependency of spectra deviation from temperature is shown. The temperature axis in Fig. 3 represents final temperature of transition. Temperature of transition beginning can be found as a previous point on this axis.

Obviously, temperature of phase transition should be between  $5$  and  $5.5\text{ }^{\circ}\text{C}$ , that corresponds to known data on 1-decanol [23–25]. For further consideration, we have chosen the temperature range from  $2$  to  $7\text{ }^{\circ}\text{C}$ , that is presented in Fig. 4.

In Fig. 4 one can observe bands at  $3417$ ,  $3388$  and  $3367\text{ cm}^{-1}$ . Besides, wide vibrational bands with maxima at  $\sim 3265\text{ cm}^{-1}$  and

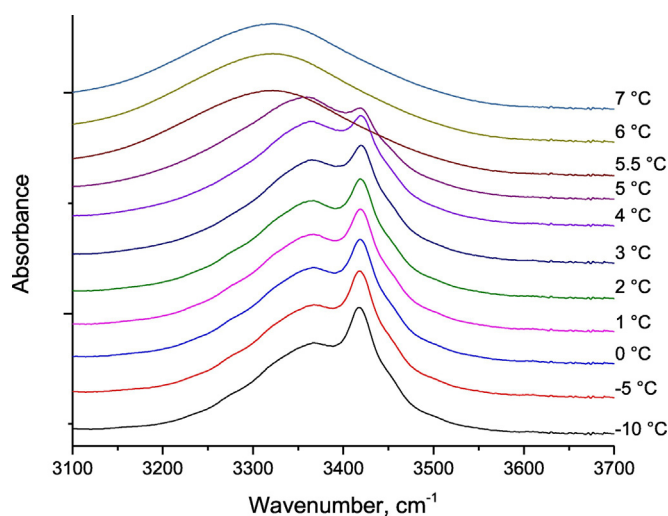


Fig. 1. Temperature evolution of FTIR spectra of 1-decanol at temperatures from  $-10$  to  $+7\text{ }^{\circ}\text{C}$  in the spectral region  $3100\text{--}3700\text{ cm}^{-1}$ .

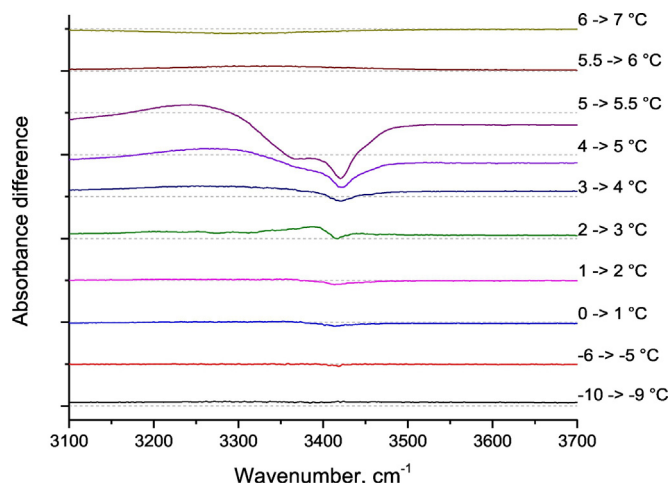


Fig. 2. Difference FTIR spectra of 1-decanol in the temperature range from  $-10$  to  $+7\text{ }^{\circ}\text{C}$  in the spectral region  $3100\text{--}3700\text{ cm}^{-1}$ .

$\sim 3240\text{ cm}^{-1}$  are present in difference spectra from  $4$  to  $5\text{ }^{\circ}\text{C}$  and from  $5$  to  $6\text{ }^{\circ}\text{C}$ . These bands will be used for further analysis.

### 4. Ab initio calculations

For interpretation of experimental FTIR spectra and determining which cluster structures exist in condensed 1-decanol, quantum-chemistry simulation with Gaussian [26] software was carried out. We considered cluster structures of two types: cyclic ( $\theta$ ) and chain-like ( $\xi$ ) ones. Each cluster has its own designation:  $\theta_N$  for cyclic and  $\xi_L$  for chain-like; where  $N$  and  $L$  – number of molecules in cluster of each type. For each cluster structure, optimal geometry and its FTIR spectra were firstly calculated using density functional theory (DFT) with B3LYP functional and 6-31g(d,p) basis set. Calculations were carried out taking into account an influence of the media using 1-decanol as a solvent in frame of polarizable continuum model (PCM). Calculated cluster structures are presented in Fig. 5. Their energies and some geometrical parameters are listed respectively in Tables S1 and S2 of Supplementary Materials.

Our calculations have shown that plain cyclic structures  $\theta_3$  and  $\theta_4$  are not stable structures in such conditions. At least we failed to find any corresponding configurations without negative frequencies in

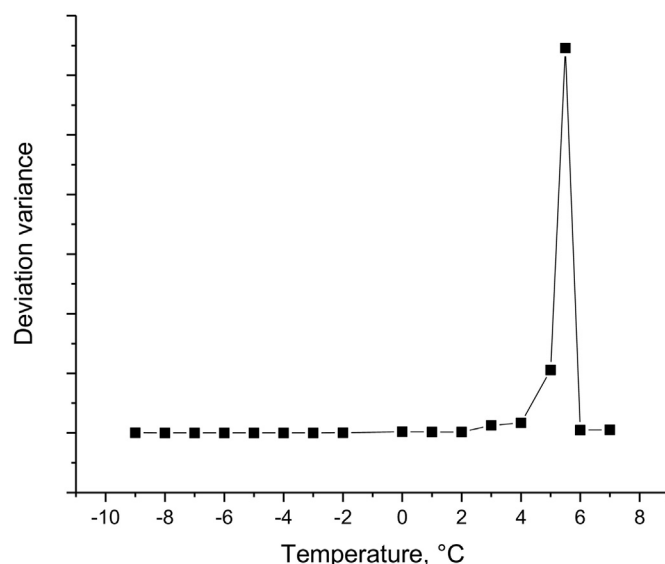


Fig. 3. Deviation variance of transition spectra depending on the temperature.

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