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FTIR SPECTRA OF N-PENTANOL AND N-OCTANOL IN LIQUID AND SOLID STATES

Alcohol molecules can form hydrogen bonds and arrange in different structures named clusters. The aim of this work is to study the behavior of a cluster structure of alcohols at phase transitions and to elucidate the structure of clusters in the solid and liquid states.
The objects of investigation are monohydric alcohols n-pentanol $(CH_2)_4CH_3$–OH and n-octanol $(CH_2)_7CH_3$–OH. For the structural analysis of the clusters, the matrix isolation FTIR spectroscopy is used, while the spectroscopic studies of the behavior of different clusters at the solid-liquid phase transition are performed in the liquid and solid states. In order to interpret the experimental spectra, the quantum-chemical calculations with the use of Gaussian03 software (approximation DFT/B3LYP, 6–31G (d, p) are carried out.

Keywords: FTIR Spectra, n-pentanol, n-octanol, cluster structure of alcohols, Gaussian03 software.

1. Introduction

Liquids with hydrogen-bonded molecules play an important role in the Nature and are intensively studied by various methods [1–7]. Monohydric alcohols, being partially ordered liquids with intermolecular hydrogen bonding, are of great interest [8–10]. For studies of such liquids, both experimental and theoretical methods are used; the common approach is a combination of these methods [11, 12]. Our work is devoted to the investigation of a cluster structure of alcohols in the solid and liquid states.

Alcohol dimers and other small clusters are products of the first steps of the association reaction from a monomeric alcohol molecule to large aggregates present in liquid alcohols. The matrix isolation infrared spectroscopy has been used for studying the molecular conformations and weak intermolecular interactions [13]. The main idea of this method is to isolate the molecules of a substance from each other using the solid matrix of an inert gas cooled to cryogenic temperatures. The commercial software Gaussian 03 was used for the theoretical simulation of various cluster structures.

2. Experimental

Commercial alcohol samples were previously purified from water molecules (using molecular sieves during 48 h) and degassed. The FTIR spectra of n-pentanol and n-octanol in the condensed state were registered using a Bruker FTIR spectrometer VERTEX 70. A Bruker FTIR spectrometer IFS 113 was used for the registration of the spectra of n-pentanol isolated in an Ar matrix (matrix ratio 1:1000). For the thermal stabilization, a LINKAM cryostat (model FTIR 600) was used. The IR spectra were registered in the spectral range from 500 to 4000 cm^{-1} with a spectral resolution of 1 cm^{-1}. In order to increase the signal-

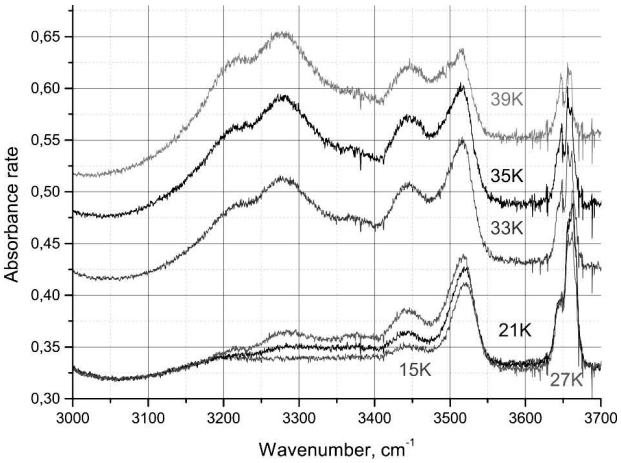

Fig. 1. FTIR spectra of n-pentanol trapped in an Ar matrix

Fig. 2. Optimized structures of different clusters of n-pentanol

Table 1. **Average intermolecular distances O···H, average angles O···H–O, and the energy of a hydrogen bond for pentanol clusters calculated in the B3LYP/6-31G (d, p) approximation**

Cluster	O···H–O	O···H_O, Å	Energy of H-bond, kcal/mol	Energy of H-bond, kJ/mol
Dimer	166.1	1.89	–7.73	–32.35
Trimer	152.6	1.85	–7.88	–33.00
Tetramer	167.8	1.74	–9.58	–40.07
Pentamer	174.9	1.70	–10.33	–43.22

to-noise ratio, each spectrum was taken as the average of 128 scans.

3. FTIR Spectra of n-Pentanol in an Ar Matrix

Hydroxyl group plays a major role in the formation of a hydrogen bond. Therefore, in the spectral investigations of the formation of hydrogen bonds between alcohol molecules, a special attention is paid to the region of stretching vibrations of OH-groups (3000–3700 cm^{-1}). The registered FTIR spectra of n-pentanol isolated in an Ar matrix in the spectral region of the O–H stretching vibrations are presented in Fig. 1. The spectra were registered in the temperature interval 15–39 K.

As is seen from Fig. 1, two intense peaks at 3660 cm^{-1} and 3518 cm^{-1} are observed at 15 K. At 27 K, three intense peaks at 3658, 3516, and 3439 cm^{-1} are observed. Then, upon a gradual increasing of the temperature, the intense bands appear in the low-frequency region, and the intensity of the bands in the high-frequency region gradually decreases. For the interpretation of experimental data, a quantum-chemical simulation with the use of Gaussian 03 software was carried out.

4. Computer Simulation

The geometry optimization for different clusters of the title compounds was carried out, by using the DFT method (B3LYP/6–31(d, p)). The corresponding IR spectra were calculated at the same level of theory. The optimized structures of various pentanol and octanol clusters are presented in Figs. 2 and 3, respectively.

Average intermolecular distances (O···H), average angles (O···H–O), and the energy of a hydrogen bond for different clusters of n-pentanol and n-octanol were calculated. The obtained data are listed in Tables 1 and 2, respectively.

As is seen from Tables 1 and 2, the average intermolecular distance O···H decreases with the growing of the number of molecules in clusters for both alcohols. Large clusters are tighter, so the energy of a hydrogen bond for n-pentanol and n-octanol increases with the number of molecules in clusters.

The calculated IR spectra of pentanol clusters are presented in Fig. 4. The number of peaks increases

Fig. 3. Optimized structures of monomer, dimer, trimer, and tetramer of n-octanol

with the number of molecules in a cluster. So, one peak is observed for monomer, two peaks – for dimers, *etc.* Similar results were obtained for other alcohols [4, 11].

The calculated spectra were compared with the results of matrix isolation experiments. Now, we can assign the observed absorption bands (Fig. 1) as follows: the spectral bands near 3660 cm^{-1} are assigned to monomers, 3518 cm^{-1} – to dimers, 3439 cm^{-1} – to trimers, 3250 cm^{-1} – to tetramers, *etc.* So, at 15 K, small clusters (monomers, dimers, and trimers) are dominant. At higher temperatures, molecules begin to interact with each other, and bigger clusters are formed. This is confirmed by the fact that the intensity of the bands in the low-frequency region increases, while the intensity of the bands in the high-frequency region decreases, as the temperature increases to 39 K.

5. FTIR Spectra of n-Pentanol and n-Octanol in Condensed State

FTIR spectra of the investigated alcohols in the condensed state were obtained over a wide temperature range: from –130 °C to + 30 °C for n-pentanol and from –50 °C to –9 °C for n-octanol. A special attention is paid to the behavior of alcohol molecules at the temperatures near the phase transition liquid – solid state. This temperature is –78.4 °C for n-pentanol and –16 °C [14] for n-octanol.

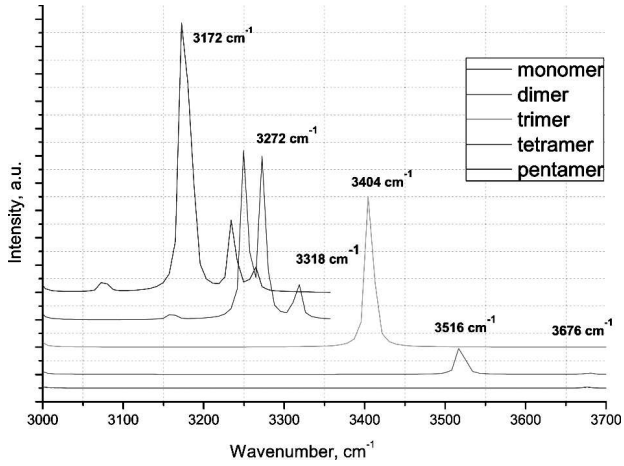

Fig. 4. Calculated IR spectra of different clusters of n-pentanol

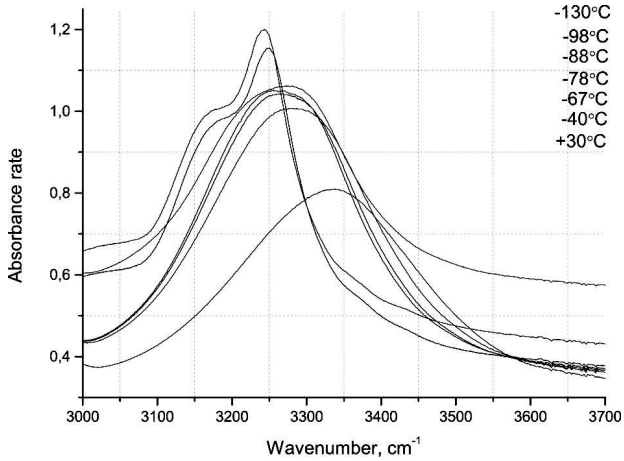

Fig. 5. FTIR spectra of n-pentanol in the condensed state

Table 2. **Average intermolecular distances O···H, average angles O···H-O, and the energy of a hydrogen bond for octanol clusters calculated in the B3LYP/6-31G approximation**

Cluster	O···H–O	O···H_O, Å	Energy of H-bond, kcal/mol	Energy of H-bond, kJ/mol
Dimer	166.7	1.78	–9.76	–40.82
Trimer	149.2	1.74	–9.85	–41.19
Tetramer	165.6	1.60	–12.56	–52.54

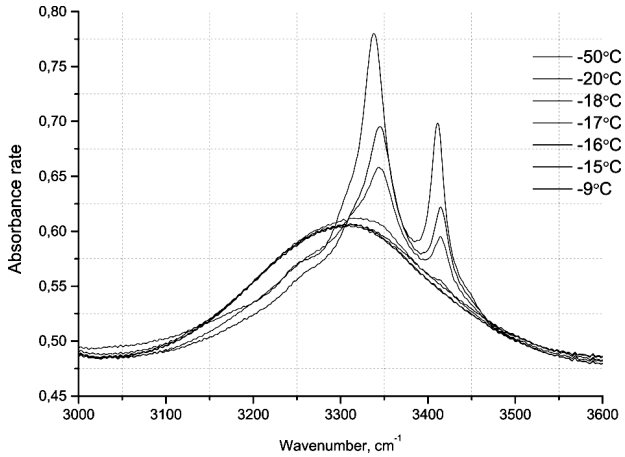

Fig. 6. FTIR spectra of n-octanol in the condensed state

The FTIR spectra of n-pentanol in the spectral region of OH stretching vibrations are registered, by using the radual cooling of the sample from + 30 °C to –130 °C are presented in Fig. 5.

At the temperature +30 °C, the band at 3335 cm^{-1} with a width of ≈250 cm^{-1} is observed. As the temperature decreases, this band becomes narrower and shifts to 3265 cm^{-1}. After the phase transition temperature (–78.4 °C), a wide structureless band shifts toward the low-frequency region. After –88 °C, one can observe the splitting and the narrowing of the spectral band of OH stretching vibrations, as in the crystalline phase. We can assume that, in the temperature range from –78.4 °C to –88 °C, n-pentanol exists in a vitreous phase. After the phase transition vitreous phase – solid state, the spectral band of OH stretching vibrations becomes structured: two bands at 3169 cm^{-1} and 3241 cm^{-1} appear. Having compared these results with matrix isolation data for n-pentanol, we can assume that, in the liquid state, trimers, tetramers, and pentamers are the dominant structures. But, in the solid state, tetramers and bigger clusters dominate.

The analysis of the spectra of n-octanol in the region of OH stretching vibrations was carried out as well. The FTIR spectra of n-octanol were registered during the gradual cooling of the sample from –9 °C to –50 °C and are presented in Fig. 6.

As is seen from Fig. 6, no changes are observed between –9 °C and –16 °C. There is one band at 3312 cm^{-1} with the width ∼200 cm^{-1}. As the temperature decreases, two intense bands at 3314 cm^{-1} and at 3345 cm^{-1} are observed. In contrast to the case of n-pentanol, the spectral band assigned to the OH stretching vibrations in n-octanol shifts toward higher frequencies upon the temperature lowering. Therefore, we can assume that small clusters (probably, dimers and trimers) dominate in n-octanol at these temperatures.

6. Conclusions

The matrix isolation FTIR spectroscopy was used for structural studies of individual H-bond clusters of n-pentanol. The transformation of the registered spectra of isolated monomers and dimers upon the temperature increasing was observed. At the highest temperature of the Ar matrix, the spectra became similar to those of liquid pentanol. Using the results of quantum-chemical calculations, the assignment of the observed bands to different pentanol clusters was made.

The FTIR spectra of n-pentanol and n-octanol in the liquid and solid states over a wide temperature range were registered. As the temperature decreases (below the melting point), the spectral band of OH stretching vibrations becomes structured (two intense bands appear for both alcohols). In the case of n-pentanol, bigger clusters (tetramers, pentamers, and, probably, hexamers) dominate in the disordered (glassy) solid state. While, in the case of n-octanol, smaller clusters (dimers and trimers) dominate.

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ІЧ СПЕКТРИ Н-ПЕНТАНОЛУ
І Н-ОКТАНОЛУ В РІДКОМУ І ТВЕРДОМУ СТАНАХ

Р е з ю м е

Молекули спиртів утворюють водневі зв'язки і можуть об'єднуватись у різноманітні структури, які звуться кластерами. Метою цієї роботи є дослідження поведінки кластерної структури спиртів при фазових переходах та визначення структури кластерів у твердому і рідкому станах.

Об'єктами дослідження є одноатомні спирти н-пентанол $(CH_2)_4CH_3$–OH і н-октанол $(CH_2)_7CH_3$–OH. Для аналізу структури кластерів використовувався метод матричної ізоляції та ІЧ фур'є-спектроскопія. Спектроскопічні дослідження поведінки різних кластерів при фазовому переході тверде тіло–рідина проводились у рідкому і твердому станах. Для інтерпретації експериментальних спектрів було виконано квантово-хімічне моделювання з використанням програмного пакета Gaussian03 (у наближенні DFT/B3LYP, 6-31G (d, p)).

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ИК СПЕКТРЫ Н-ПЕНТАНОЛА И Н-ОКТАНОЛА
В ЖИДКОМ И ТВЕРДОМ СОСТОЯНИЯХ

Р е з ю м е

Молекулы спиртов образуют водородные связи и могут объединяться в разнообразные структуры, которые называются кластерами. Цель данной работы – исследование поведения кластерной структуры спиртов при фазовых переходах и определение структуры кластеров в твердом и жидком состояниях.

Объектами исследования являются одноатомные спирты н-пентанол $(CH_2)_4CH_3$–OH и н-октанол $(CH_2)_7CH_3$–OH. Для анализа структуры кластеров использовался метод матричной изоляции и ИК фурье-спектроскопия. Спектроскопические исследования поведения различных кластеров при фазовом переходе твердое тело–жидкость проводились в жидком и твердом состояниях. Для интерпретации экспериментальных спектров было выполнено квантово-химическое моделирование с использованием программного пакета Gaussian03 (в приближении DFT/B3LYP, 6-31G (d, p)).