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CONFORMATIONAL ANALYSIS OF SMALL ETHANOL CLUSTERS TRAPPED IN A LOW-TEMPERATURE ARGON MATRIX

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This work presents a conformational analysis of ethanol molecules and their clusters isolated in a low-temperature argon matrix using FTIR spectroscopy and quantum-chemical calculations. Optimal geometry, energy parameters and vibrational frequencies for trans and gauche conformations of ethanol, as well as for various possible combinations of conformers in dimers, trimers and tetramers, were calculated. Temperature-dependent FTIR spectra reveal distinct bands corresponding to the O–H stretching vibrations of both conformers. As the matrix temperature increases from 20 to 50 K, ethanol monomers progressively form hydrogen-bonded clusters. Quantum-chemical modelling confirms the presence of all theoretically predicted cluster configurations in the matrix at temperatures about 40 K.

Keywords: ethanol, conformers, argon matrix, FTIR spectroscopy, hydrogen bonding

1. Introduction

Ethanol, a simple alcohol with the molecular formula C_2H_5OH, exhibits conformational isomerism due to rotation around its single bonds. These conformers are different spatial arrangements of the molecule that result from rotation around the C–C and C–O bonds, leading to variations in the relative positions of the hydroxyl group (–OH) and the ethyl group. In the case of a trans conformer, the dihedral angle CCOH is 180°, which means that the –OH group is opposite the ethyl group. In a gauche conformer, the –OH group is staggered relative to the ethyl group and the dihedral angle CCOH is 60°. The energy barrier for rotation around the C–C and C–O bonds is relatively low (a few kcal/mol), allowing a rapid interconversion between conformers at room temperature, and their relative populations depend on factors like temperature and a solvent [1]. However, in low-temperature matrices, the heights of energy barriers between gauche and trans conformers change [2, 3]. Higher barriers mean a slower or inhibited interconversion between conformers. At cryogenic temperatures (10–30 K), thermal energy is insufficient to overcome the barrier, so each conformer becomes effectively trapped in its local minimum. This allows individual conformers to be studied spectroscopically, as they do not rapidly equilibrate.

The aim of this work is to determine the conformational composition of ethanol trapped in a cryogenic argon matrix using FTIR spectroscopy and quantum-chemical calculations. When the matrix temperature gradually increases from 10 to 40 K, the isolated ethanol molecules form hydrogen-bonded clusters consisting of several molecules [4–8]. Structure parameters of the clusters formed depend on the initial conformational composition of the sample and possible interconversion between the conformers with matrix heating.

If we denote the gauche conformer by g and the trans conformer by t, then for dimers the following combinations are possible: tt, tg, gt and gg, where the first letter represents a molecule that acts as a proton donor during hydrogen bond formation, and the second letter is a molecule which is a proton acceptor. For the cyclic trimer, configurations ttt, ttg, tgg and ggg are considered, and for the cyclic tetramer, tttt, tgtg, ttgg and gggg.

2. Methods

FTIR spectra of ethanol in an Ar matrix was registered using a FTIR spectrometer IFS 113 (*Bruker*) in the laboratory of molecular spectroscopy at Vilnius University. The matrix was prepared as a mixture of argon (*Elme Messer*, purity >99.995) and ethanol. Liquid ethanol (purity >99.9) was dried by keeping the sample on molecular sieves (grade 3Å) for 48 h. Degassing of the alcohol was performed just before the preparation of the gas mixture for the matrix deposition by multiple repetitions of the freezing, evacuation and freezing-out cycle for a sample with the use of a standard vacuum assembly. The molecular ratio of ethanol and argon, coming to 1:1000, was determined by a standard manometer technique. The gas mixture was deposited on the substrate (CsI) cooled down to 20 K in a closed-cycle helium cryostat (*Laybold-Hareus* RW2). The gas flow in the cryostat was controlled with the help of a needle valve. The deposition rate was about 2 mmol/h to provide the formation of a partially crystallized argon matrix.

The spectral data were recoded with the resolution 0.5 cm^{-1} in the region from 500 to 4000 cm^{-1}. Each spectrum was averaged over 128 scans in order to improve the signal/noise ratio. The spectra were recorded at different temperatures ranging from 20 to 50 K. The experimental conditions are described in detail in our previous works [8, 9].

The calculation of structural and spectral characteristics of ethanol conformers was carried out using the Gaussian 09 software [10]. The DFT method with the B3LYP/cc-pVTZ basis was used. The optimized structures were calculated for different conformations of monomers (g, t), dimers (tt, tg, gt, gg), trimers (ttt, ttg, tgg, ggg) and tetramers (tttt, gggg, tgtg, ttgg). After the geometry optimization of the clusters, the total cluster energy and the dissociation energy per hydrogen bond were calculated. Having obtained the optimized geometries of monomers and clusters, the infrared absorption spectra were calculated. The vibrational frequencies were computed within the harmonic approximation using the cc-pVTZ basis set.

3. Results and discussion

The calculated optimal structures of ethanol trans and gauche conformers are presented in Fig. 1. The values of their geometry parameters and dipole moments are listed in Table 1.

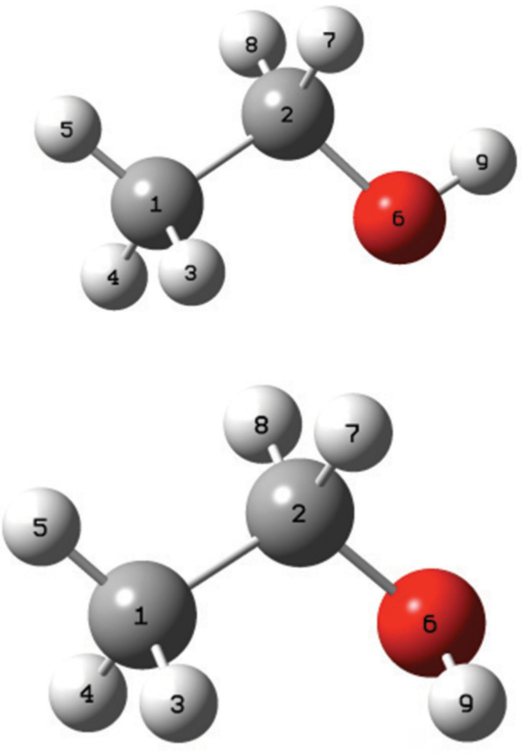

Fig. 1. Optimal geometries of ethanol conformers.

Table 1. Calculated geometry parameters and dipole moments of trans and gauche conformers of ethanol.

Parameter	Trans (t)	Gauche (g)
C–O, Å	1.42	1.43
O–H, Å	0.97	0.96
C–C, Å	1.52	1.52
C–H (in CH_3 group), Å	1.10	1.09
C–H (in CH_2 group), Å	1.11	1.09
C–O–H, °	107.8	108.4
C–C–H (in CH_3 group), °	110.4	111.0
C–C–H (in CH_2 group), °	109.8	110.3
Dipole moment, D	1.53	1.60

The calculated at the same level of theory energies of the conformers differ in 0.3 kcal/mol, with the gauche conformer having higher energy. This result is in good agreement with the results of calculations presented in Refs. [1, 10–12], where the values of the energy difference close to 0.5 kcal/mol were obtained.

The calculations of vibrational spectra of the conformers were also carried out. Since the main difference between trans and gauche conformers lies in the position of the O–H bond, their vibrational spectra differ mainly in the location and intensity of the O–H stretching vibration band. Moreover, the process of hydrogen bond formation is most prominently manifested in the region of the hydroxyl group's stretching vibrations, so we will focus only on the spectral region of the O–H stretching vibrations going forward.

The calculated frequency of the O–H stretching vibration for the trans conformer is 3670 cm^{-1}, while for the gauche conformer it is 3682 cm^{-1}. This indicates that the O–H stretching frequency is higher in the gauche conformer compared to the trans conformer. This observation is consistent with the data presented in Table 1, which shows that the O–H bond length in the gauche conformer is shorter than in the trans conformer. The registered FTIR spectra of ethanol trapped in an Ar matrix at 20–40 K temperatures in the spectral region of free O–H stretching vibrations (3630–3680 cm^{-1}) are presented in Fig. 2.

In several works, the bands of the O–H stretching vibrations of trans conformer in ethanol in low-temperature argon matrices were registered at 3660 [2], 3657 [13, 14], 3660 and 3655 [15], 3653 cm^{-1} [16], and the corresponding bands of the gauche conformer at 3655 [2], 3662 [13, 16] and 3649 cm^{-1} [14, 15]. Thus, we assign the bands observed in the FTIR spectra of ethanol at 3656 and 3659 cm^{-1} to the O–H stretching vibrations of trans and gauche conformers of ethanol, respectively.

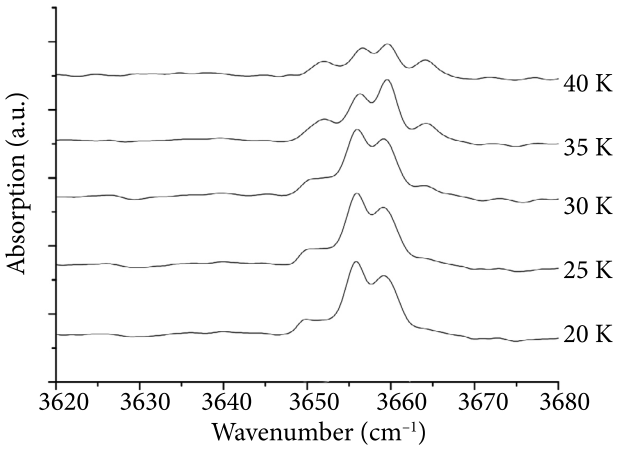

Fig. 2. FTIR spectra of ethanol trapped in an Ar matrix at temperatures 20–40 K in the spectral region of free O–H stretching vibrations.

As one can see, at 20 K the intensity of the trans conformer band is higher, meaning that trans conformers are present in the sample in greater amounts. With the matrix heating, a redistribution of intensity between the bands is observed and already at 35 K the band of the gauche conformer becomes stronger. This may indicate a conformational transition from the trans to the gauche form. However, since the energy of the gauche conformer is higher and the trans conformer is the more energetically favourable structure, such a redistribution may be associated with the fact that trans conformers more actively participate in cluster formation as the matrix temperature increases, which leads to a decrease in their relative amount. At 40 K, the intensity of both bands begins to decrease, since, at this temperature, ethanol monomers combine into clusters consisting of two or more molecules [4, 8, 9].

In addition, in the same spectral region (Fig. 2), two weaker bands are observed at 3649 and 3664 cm^{-1}. These can be attributed to the vibrations of free hydroxyl groups in ethanol dimers, as their intensity increases with rising matrix temperature.

The calculated spectra of various dimeric combinations of ethanol conformers in the spectral region of O–H stretching vibrations contain two bands: the higher-frequency one corresponds to vibrations of the free hydroxyl group (proton acceptor molecule), while the lower-frequency one corresponds to vibrations of the hydroxyl group involved in hydrogen bond formation (proton donor molecule). The calculated vibrational frequencies are presented in Table 2.

From these data, it is evident that when the gauche conformer acts as the acceptor, the vibrational band appears at a lower frequency than when the trans conformer serves as the acceptor. The difference between these frequencies is 15 cm^{-1}, which matches the experimentally observed difference between the bands at 3649 and 3664 cm^{-1}. Thus, it can be concluded that in the argon matrix there are dimers in which both gauche and trans conformers act as acceptors.

In the region of the bonded O–H vibrations in ethanol dimers, a series of absorption bands

Table 2. Calculated frequencies of O–H stretching vibrations in ethanol dimers, as well as their dissociation energies and dipole moments.

Dimer configuration	Frequency of the O–H stretching vibrations in proton donor molecule, cm^{-1}	Frequency of the O–H stretching vibrations in proton donor molecule, cm^{-1}	Dissociation energy, kcal/mol	Dipole moment, D
tt	3531	3674	4.47	2.7
tg	3527	3659	4.42	2.41
gt	3526	3674	4.40	2.64
gg	3519	3659	4.52	2.26

is observed at 3516, 3521, 3524 and 3531 cm^{-1}, which are most intense at temperatures above 35 K (Fig. 3). Comparing these frequencies with the calculated values of the corresponding vibrational frequencies of donor molecules allows us to conclude that all the considered types of dimers are present in the matrix.

For all possible dimer configurations, the dissociation energy and dipole moments were calculated. The results are also presented in Table 2. According to the calculations, the most energetically favourable configuration is the gg dimer, in which both the donor and acceptor are gauche conformers. Conversely, the least favourable configuration is the gauche–trans (gt) arrangement.

Assuming an equal number of gauche and trans conformers in the sample, the Boltzmann distribution can be used to determine the ratio of individual conformers at a given temperature. Thus, at 35 K temperature, the percentage ratio of conformers is

$$\mathrm{gg : tt : tg : gt} \approx 49 : 26 : 14 : 11.$$

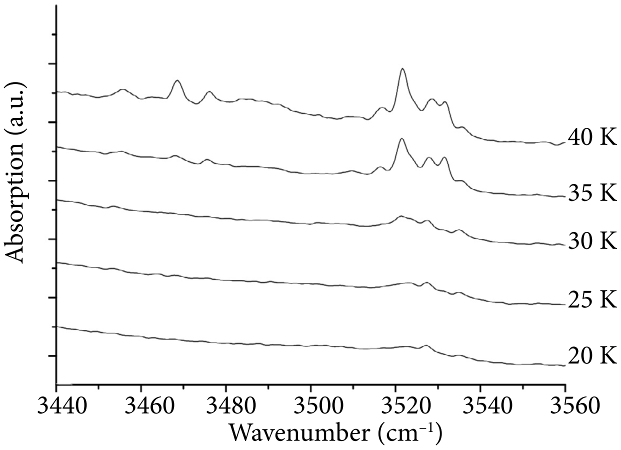

Fig. 3. FTIR spectra of ethanol trapped in an Ar matrix at temperatures 20–40 K in the spectral region of bonded O–H stretching vibrations in dimers and trimers.

Similar theoretical results for the relative distribution of dimers were obtained in Ref. [17]:

$$\mathrm{gg > tt > tg} \approx \mathrm{gt}.$$

Quantum-chemical calculations of optimal geometry and IR spectra were performed for possible ethanol trimers. According to the simulation results [18], the most probable structures are cyclic trimers. In the case of a cyclic trimer, all hydroxyl groups participate in hydrogen bonding. The calculated vibrational frequencies in the region of the O–H stretching vibrations as well as their dissociation energies and dipole moments are presented in Table 3. As is seen, the dissociation energy per hydrogen bond in a trimer is slightly higher than the corresponding value in a dimer, but the difference is small – approximately 0.19 kcal/mol. This slight increase is explained by the fact that the strength of a hydrogen bond increases as the angle $\angle(\mathrm{O}\cdots\mathrm{H{-}O})$ approaches 180°. According to the simulation results, this angle is approximately 151° in trimers, whereas in dimers it is around 170°.

According to the calculation results, the least energetically favourable structure is ggg. The configurations ttt and tgg have equal probabilities of occurrence. At 35 K temperature, the approximate percentage distribution of trimers is as follows:

$$\mathrm{ttt : ttg : tgg : ggg} \approx 31 : 24 : 31 : 14.$$

In the spectra presented in Fig. 3, one can also observe the bands of ethanol trimers in the range

Table 3. Calculated frequencies of O–H stretching vibrations in ethanol trimers, as well as their dissociation energies and dipole moments.

Trimer configuration	Frequencies of the O–H stretching vibrations, cm^{-1}	Dissociation energy, kcal/mol	Dipole moment, D
ttg	3405 (very weak), 3459, 3463	4.65	1.01
ttt	3405 (very weak), 3450, 3482	4.67	0.87
tgg	3404 (very weak), 3456, 3463	4.67	0.87
ggg	3410 (very weak), 3459, 3466	4.61	0.86

3450–3500 cm^{-1} [4–6], which are most noticeable at 40 K temperature. They are the ones at 3455, 3461, 3468, 3476 and 3483 cm^{-1}. Comparing these frequencies with the calculated values of the corresponding vibrational frequencies of trimers (Table 3), we can conclude that all the considered types of trimers can be present in the matrix.

Modelling of tetramer structures also predicts a high likelihood of forming cyclic associates consisting of four ethanol molecules. Table 4 presents the results of calculations of vibrational frequencies, dissociation energies, and the dipole moments of tetramers. As the simulation results show, the binding energy in tetramers is higher than in smaller clusters. This is due to the geometry of the tetramer (the hydrogen bond angle is closer to the value of a linear angle) as well as the denser arrangement of molecules within the cluster.

Figure 4 presents the FTIR spectra of ethanol in an Ar matrix in the region of the O–H stretching vibrations in tetramers. As one can see, at temperature 40 K several bands appear in this region: 3355, 3362, 3366, 3371, 3372, 3376 and 3383 cm^{-1}. This series of bands correlates with the calculated frequencies of the O–H stretching vibrations in ethanol tetramers (Table 4). Thus, we observe the presence of various types of tetramers in the matrix at 40 K.

When the matrix temperature increases to 50 K, the bands of monomers, dimers, trimers and tetramers disappear, and the spectrum in the range from 3100 to 3600 cm^{-1} contains only one very broad band with the maximum near 3250 cm^{-1}, which is very similar to that in liquid ethanol and corresponds to large hydrogen-bonded structures consisting of five and more molecules [4–6].

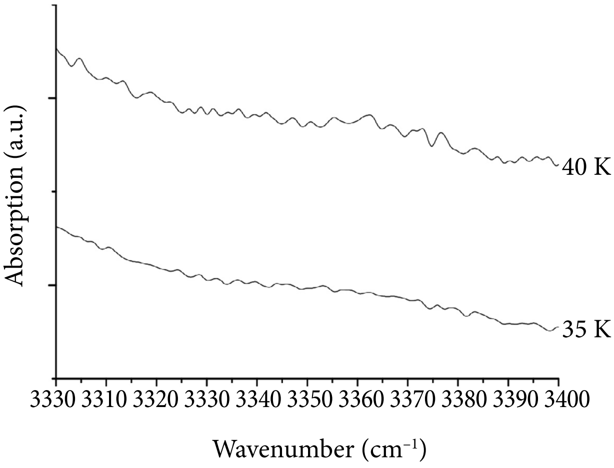

Fig. 4. FTIR spectra of ethanol trapped in an Ar matrix at temperatures 35–40 K in the spectral region of bonded O–H stretching vibrations in tetramers.

4. Conclusions

A detailed conformational analysis of ethanol molecules and small clusters isolated in a low-temperature argon matrix was made using FTIR spectroscopy and quantum-chemical modelling.

Table 4. Calculated values of the O–H stretching frequencies, dissociation energy and dipole moments of ethanol tetramers.

Tetramer configuration	Frequencies of the O–H stretching vibrations, cm^{-1}	Dissociation energy, kcal/mol	Dipole moment, D
tttt	3336, 3377 (weak)	6.19	0.0003
ttgg	3303 (weak), 3325, 3360, 3382	6.07	1.2
tgtg	3342, 3345, 3380 (weak)	6.14	0.07
gggg	3341, 3350, 3388 (weak)	6.16	0.13

The results demonstrate that ethanol exists in both trans and gauche conformations, with the trans conformer being energetically more favourable, while the gauche conformer exhibits a slightly higher dipole moment and a shorter O–H bond length.

Temperature-dependent FTIR spectra reveal distinct bands corresponding to the O–H stretching vibrations of both trans and gauche conformers at 20 K. As the matrix temperature increases, the redistribution of vibrational band intensities suggests conformational transitions and the progressive formation of hydrogen-bonded clusters.

Quantum-chemical calculations confirm the presence of all theoretically predicted configurations of dimers, trimers and tetramers at higher temperatures (35–40 K), each exhibiting characteristic vibrational features. Among dimers, according to the calculation results, the gg configuration is the most stable, while gt is the least favourable one. Cyclic trimers and tetramers dominate at higher temperatures, with tetramers showing the highest dissociation energies due to more linear hydrogen bonding and compact molecular arrangements. At 50 K, the disappearance of discrete spectral bands and the emergence of a broad absorption feature near 3250 cm^{-1} indicate the formation of larger hydrogen-bonded aggregates, resembling the structure of bulk liquid ethanol.

These findings provide additional insights into the conformational behaviour and clustering dynamics of ethanol in cryogenic environments, contributing to a deeper understanding of molecular interactions in low-temperature matrices.

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MAŽŲ ETANOLIO KLASTERIŲ ŽEMOS TEMPERATŪROS ARGONO MATRICOJE KONFORMACINĖ ANALIZĖ

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