STRUCTURE OF VALERIC ACID MONOMERS AND DIMERS. MATRIX ISOLATION INFRARED SPECTROSCOPY STUDY

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Carboxylic acids are often studied using vibrational spectroscopy because they serve as excellent model systems for understanding processes involved in more complex molecular structures [1]. While the hydrogen bonding properties of saturated carboxylic acids have been studied for decades, there are still unanswered questions about the structure of such systems and the hydrogen bonds formed between these molecules. Research has shown that the first three carboxylic acids of the homologous series can form at least two types of dimers [2]. Valeric acid, also known as pentanoic acid ($C_5H_{10}O_{10}$), is described as a straight, saturated chain alkyl carboxylic acid [3]. Recent calculations predict another stable conformers of valeric acid monomer with non-linear alkyl chain. The main objective of this work is to identify experimentally observable structures of valeric acid (refer to Figure 1) using matrix isolation infrared spectroscopy in conjunction with theoretical calculations. The second goal is to determine structure of valeric acid dimers. The questions of possibility to observe open type dimers similar as in the lighter acids of valeric acid will be addressed.

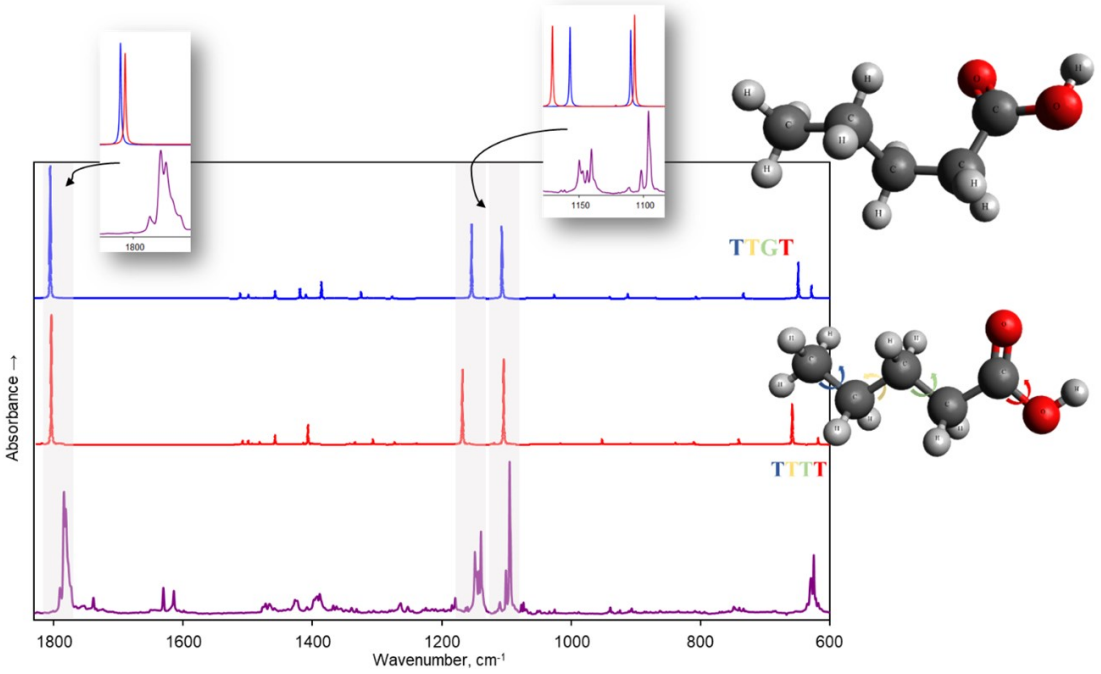

Fig. 1. FTIR absorption spectrum (lower curve) of valeric acid, isolated in neon 3 K matrix. The figure also shows the theoretically predicted spectra of conformers TTGT (upper curve) and TTTT (middle curve). The calculations were performed using MP2/cc-pVTZ theory level.

The theoretical calculations were carried out using the MP2 - Møller-Plesset expansion extension which contains truncated second orders, supplemented with the Dunning correlation matched basis set (triple zeta). The MP2 calculations show that the TTGT conformation has the lowest energy, which is Δ E = - 0.3 k J/mol. The experimental FTIR absorption spectra of valeric acid isolated in a neon matrix, together with the theoretical spectra of the two most stable conformers, are shown in Figure 1. Comparison of the experimental spectra with calculated ones of the two lowest energy conformers (see fig. 1) allowed us to identify bands belonging to the both conformers. The band corresponding to C=O stretching vibration at 1802 cm $^{-1}$ for TTTT and 1803 cm $^{-1}$ for TTGT conformer. These results demonstrate that in low-temperature matrices there are two valeric acid monomer conformers at different concentrations. The results on dimer structure and stability will be demonstrated from matrix isolation infrared spectroscopy results.

[1] J. Ceponkus et al. Lithuanian Journal of Physics, Vol. 49, No. 1, pp. 53–62 (2009)
[2] V. Sablinskas et al. Journal of Molecular Structure 976 (2010) 263–269
[3] Schaechter M. Encyclopedia of Microbiology. 3rd ed. Amsterdam: Elsevier/Academic Press; (2009)