

Association of Water with Small Monocarboxylic Acids. Matrix Isolation Infrared Absorption Study.

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Water is very important in many chemical, physical and biological processes. Single water molecule is rather simple system, consisting from three atoms. Nevertheless, due to its structure water molecules are able to form hydrogen bonds. Thus water molecules could form very complicated associates with organic and inorganic substances.

There are a number of reasons to study hydrogen bond complexes between water and carboxylic acids. Small carboxylic acids are abundant in the environment therefore it is important to know how water changes the properties of such substances. On the other hand carboxylic acids are one of the smallest organic compounds capable of forming hydrogen bonds therefore they could serve as very good model compounds for the understanding of more complicated systems in biology and biochemistry.

There only two attempts experimentally characterize structure of formic acid and water complexes [1-2]. Due to the complicity of the system there are no experimental studies on the complexes of water with higher carboxylic acids. In order to have full picture of hydrogen bonding between water and organic compounds it is very important to understand how this interaction is influenced by the length of the radical chain of the substance under study.

Infrared absorption spectroscopy is one of the most suitable methods to study molecular systems. From the structure of vibrational and rotational bands one can obtain direct information about molecules and molecular clusters. Matrix isolation technique extends possibility of the infrared spectroscopy, to study isolated molecules and molecular complexes.

Vapor of carboxylic acid and water were mixed in the vacuum system using standard manometric technique. Such mixtures afterwards were diluted with argon (matrix gas). In order to identify spectral bands associated with different possible clusters a wide number of ratios carboxylic acid:water:argon was used. Matrix mixtures were deposited on the spectroscopic window cooled down to 10 K, in the close cycle helium cryostat. Approximately 2 moles of the matrix mixture were deposited in all experiments.

Quantum chemistry calculations of possible water carboxylic acid complexes were performed at HF 6-311++(3df, 3pd) and B3LYP 6-311++(3df, 3pd) calculation levels. Based on theoretical calculations and experimental observations C=O stretch vibrations are the most sensitive to the formation of the hydrogen bond, therefore spectral region corresponding to those vibrations were chosen for the detail examination.

Spectral bands were attributed to the water carboxylic acid complexes based on results of experiments performed using different acid:water:argon ratios and matrix annealing experiments. Our theoretical calculations support such assignment. Strength of the hydrogen bond and the structure of the most stable complexes between water and carboxylic acid were estimated from the theoretical and experimental data. In this work structural and energetic parameters of acetic acid – water, propionic acid – water and butyric acid – water were obtained for the first time.

- [1] D. Priem, T.-K. Ha, and A. Bauder, *The Journal of Chemical Physics* 113 (2000) 169-175.
[2] L. George, W. Sander, *Spectrochimica Acta A* 60 (2004) 3225–3232.