

## PD Research Report for the 2015 year

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Research Theme	Spectroscopic studies of the chiral discrimination effect in optically active aliphatic alcohols
Research Period	06, 01, 2015 ~ 02, 28, 2016
Research Results	

The proposed research focused on investigation of chiral aliphatic alcohols by Two-Dimensional Correlation (2D-COS) FT-NIR spectroscopy and anharmonic quantum chemical calculations. However, due to previously unexpected imperfect condition of the Perkin Elmer FT-NIR spectrometer, the research plan was modified. The experimental condition were deemed not good for application of 2D-COS. The observed background instability of the spectrometer was investigated and it was found, that a complex spectrometer service is needed. Therefore my research work focused on other, previously unplanned, research topics. The research topics that I worked on are listed below.

### **1. Spectroscopic and Theoretical Study in the Near-Infrared Region of Low Concentration Aliphatic Alcohols**

This research topic focused on application of the novel and powerful quantum chemical methods for the NIR spectroscopy. The theoretical prediction of vibrational spectra has widely been used as a strong support for interpreting IR spectra for many years. However, NIR spectroscopy has been unable to benefit fully from advances in quantum chemistry because of not enough reliability to predict entire NIR spectra of molecules of reasonable size and high computational cost of theoretical approaches. Recent (2014 year) introduction of second-order vibrational perturbation theory (VPT2), allows for prediction of overtones and combination modes and for modeling of NIR spectra. In this project we used novel DFT methods (including double hybrid B2PLYP functional, with empirical dispersion correction) and innovative “spectroscopic” basis sets (SNSD and SNST) with VPT2-based calculation of NIR spectra of aliphatic alcohols in diluted phase (methanol, ethanol, 1-propanol). Additionally, other methods were used for comparison and evaluation (DFT-B3LYP, MP2), polarized continuum (PCM) solvent models were tested as well. The results allowed for a very accurate prediction of entire NIR spectra of the studied systems, in the region of  $7500 - 3700 \text{ cm}^{-1}$ . For the first time prediction of entire NIR spectra was reported, also this is the first time of application of VPT2 method to the spectra of aliphatic alcohols. Thermodynamics data and rotational isomerism of aliphatic alcohols were taken into account as well. The obtained results enabled us for a very deep and insightful analysis of the NIR spectra of studied molecules, to the point where bands originating from individual conformational isomers could be identified. Decomposition of the major band in this region, the first overtone of the OH stretching band, could be also supported by the results of quantum calculation. This research allowed for a significant improvement of the current knowledge about NIR spectra of aliphatic alcohols. The results

were submitted to Physical Chemistry Chemical Physics journal (K. B. Beć, Y. Futami, M. J. Wójcik and Y. Ozaki, Spectroscopic and Theoretical Study in the Near-Infrared Region of Low Concentration Aliphatic Alcohols; currently under review).

## **2. Hydrogen bonding in the acetic acid dimer by FT-NIR spectroscopy and anharmonic quantum chemical calculation study**

In this project we focused on quantum chemical study of NIR vibrational modes (overtone, combinations) of hydrogen bonded acetic acid. In particular, the properties of double hydrogen bond bridge formed in acetic acid dimer, was studied in detail. The acetic acid is an important system for studies of hydrogen bonding, due to high hydrogen bond stabilization energy and formation of dimer, which exhibits interesting properties. In this work, acetic acid (acac), deuterated acetic acid (acac-d) and trifluoroacetic acid (acac-3F) were chosen as objects of the study. The experimental work was focused on measuring NIR spectra of these systems in a wide range of concentrations (solution in CCl<sub>4</sub>), both a single compound and mixed systems (acac:acac-d; acac:acac-3F; acac-d:acac-3F; in each case with varying concentrations of both ingredients; wide range of concentration was studied to elucidate the formation of dimeric forms). The experimental was supported by extensive quantum chemical calculation. Again, novel DFT methods (double hybrid B2PLYP functional) and basis set (SNSD, “spectroscopic” basis set) were employed; novel VPT2 method was used for the prediction of NIR spectra of monomeric and dimeric species. It was found that the observed broad spectral feature, mainly determining the NIR spectra of acetic acids, should be contributed to the combination mode of the two stretching modes of the double-hydrogen-bonded bridge in dimeric species; this is in contrast with previously accepted explanation, indicating that the broad structure originates from OH first overtone band. The results of this project are now being prepared as a manuscript (K. B. Beć, Y. Futami, M. J. Wójcik and Y. Ozaki, Hydrogen bonding in the acetic acid dimer by FT-NIR spectroscopy and anharmonic quantum chemical calculation study; in preparation).

## **3. Quantitative FT-NIR spectroscopy of polyphenolic compounds in the rosemary extract**

In this project NIR spectroscopy, chemometrics and quantum chemical methods were applied for the analysis of polyphenolic compounds in the extract of rosemary medicinal plant. The polyphenolic compounds that can be found in medicinal plants (gallic acid, ellagic acid, rosmarinic acid, carnosol and carnosic acid). A large number of rosemary extract samples (over 40 samples) was measured by diffuse reflectance Fourier transform NIR spectrometer (DRIFT) and the results were analyzed by PLS regression chemometrics method. Additionally, the theoretical spectra of the polyphenols were calculated by quantum chemical methods. DFT-B3LYP/SNSD method was applied and anharmonic infrared spectroscopy was obtained by VPT2 method. Due to large size of studied molecules, and their polycrystalline phase, approximations were necessary. Yet, our calculated spectra were accurate enough to allow for identification of major bands in the rosemary samples. This project was carried out in collaboration with Professor Christian W. Huck from University of Innsbruck. A manuscript, to which this research contributed, is currently being prepared.