

# PROGRAM

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## Material Science 4

Tuesday, 13:30 - 14:50  
Chair: Yukio Furukawa

HS5

13:30 **Recent Advances in Micro and Macro ATR-FTIR Spectroscopic Imaging**  
TU506-inv Sergei Kazarian

The most recent developments in ATR-FTIR spectroscopic imaging and its applications will be summarized here. Two complementary approaches have been used, providing flexibility with field of view and spatial resolution: micro ATR-FTIR imaging using a microscope objective with a Ge crystal, and macro ATR-FTIR imaging using a single-reflection ATR accessory, the latter provides many opportunities for studying dynamic chemical systems. Recent advances in ATR-FTIR imaging include control of the angles of incidence for depth profiling.

13:50 **ATR-IR-based Molecular-Scale Thermometer Reflecting Free Volume Changes due to Azobenzene Photoisomerization**  
TU507

Jaana Vapaavuori, Audrey Laventure, Jérémie Bourotte, Olivier Lebel,  
C. Geraldine Bazuin, Christian Pellerin

By correlating IR wavenumber shifts upon heating to shifts upon illumination, we show that the free volume created by the photoisomerization of azobenzene derivatives in glassy materials is unevenly distributed. A concept of apparent temperature reflecting the free volume surrounding each molecular group is developed. The gradient-like distribution of the apparent temperature offers a plausible molecular-level explanation for photoinduced diffusion of azobenzenes and helps understanding why photoisomerization renders these materials malleable at the temperatures far below their glass transition.

14:05 **ATR-IR Spectroscopic Observations of Water Structure in Zwitter-Ionic Polymers**  
TU508

Shigeaki Morita  
Water structure in antithrombogenic biomaterials having zwitter-ionic groups was investigated using ATR-IR spectroscopy. An effect of NaCl addition to the water contacting with the material surface was discussed. Water in the zwitter-ionic polymers hardly dehydrated by the salt addition, while that in neutral polymer easily dehydrated. However, spectral shape variation of the OH stretching band induced by the salt addition was clearly observed. Detailed structure change of water in the polymer matrix will be discussed from the spectral shape variation.

14:20 **Chemical Structural Analysis of an Antifreeze Solution by Using Infrared Spectroscopy with an Aid of Chemometrics**  
TU509

Takafumi Shimoaka, Takeshi Hasegawa

To reveal the anti-freezing protection mechanism of an aqueous solution of ethylene glycol (EG) at a molecular level, concentration-dependent infrared spectra are analyzed with an aid of chemometrics. The result indicates that the spectral variation is explained by the quantity changes of three constituents, two of which are the 'bulk water' and the 'bulk EG', and the rest is assigned to a 'complex' of water and EG molecules.

14:35 **Variable Temperature ATR-IR Spectroscopy as a Valuable Tool for the In Situ Spin State Detection of Iron(II) Spin Crossover Complexes**  
TU510

Christian Knoll, Marco Seifried, Danny Müller, Peter Weinberger

Variable temperature vibrational spectroscopy has proved a valuable tool for structural characterization of iron(II) coordination compounds undergoing a high-spin (HS) low-spin (LS) transition. MIR- and FIR-spectroscopy of iron(II) compounds allows not only for the observation of the first order structural phase transition, but also concomitant for an in-situ detection of the spin state.

## Variable Temperature ATR-IR spectroscopy as a valuable tool for the *in situ* spin state detection of Iron(II) Spin Crossover complexes

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Keywords: tetrazoles, iron(II) spin crossover, ATR, variable temperature.

Variable temperature vibrational spectroscopy has proved a valuable tool for structural characterization of iron(II) coordination compounds undergoing a high-spin (HS)  $\leftrightarrow$  low-spin (LS) transition. MIR- and FIR-spectroscopy of iron(II) compounds allows not only for the observation of the first order structural phase transition, but also concomitant for an *in-situ* detection of the spin state [1]. The reason for this is the drastic bond strength change of the Fe-N bonds due to the spin transition.

Especially, temperature-dependent FIR-spectroscopy is an often neglected technique, mainly due to the obstacle of sensitivity and sample preparation. It has been shown that in the FIR region there is a vibrational mode of the iron(II) coordination center towards the centroids of the coordination octahedron formed by the six coordinating nitrogen atoms of the tetrazole ligands [2]. The calculations reveal that this N3-Fe-N3' vibrational mode is almost totally decoupled from any other atomic motions of the rest of the molecule. Therefore, this absorption feature can be

used for the quantification of the high spin and low spin species, respectively, thus allowing for a very sensitive *in-situ* determination of the ratio between the high spin and low spin compounds. The molecular spin transition properties derived by variable vibrational spectroscopy is compared to complementary physico-chemical characterizations by UV-VIS-NIR spectroscopy, SQUID/VSM and <sup>57</sup>Fe-Mössbauer spectroscopy [3].

Herein we present an innovative custom-made setup for both temperature-dependent MIR and FIR-spectroscopy based on a PIKE Technologies ATR-Unit with a Perkin Elmer Spectrum 400 FT-MIR/FIR combination (see Fig. 1).

The resulting spectra during the observation of a phase transition using the novel ATR-setup are compared to calculated spectra for detailed assignments using DFT. The DFT calculations implemented in the Gaussian 09 software package [4] used for the free ligands the basis set 6-311G++ (2d,3p) and SDD for the complexes for the B3LYP functionals.

Acknowledg

We gratefull  
(FWF), proje  
short time s  
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computatio  
and VSC-3.

<sup>1</sup>Weinberger  
<sup>2</sup>Valtiner M  
Mathematic  
<sup>3</sup>Reissner N  
Hyperfine  
<sup>4</sup>Gaussian 0



Figure 1. Variable temperature MIR/FIR-ATR unit

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<sup>1</sup>Weinberger P., Matthias G., (2004) *Vibrational Spectroscopy* 34(1), 175-186.

<sup>2</sup>Valtiner M., Paulsen H., Weinberger P. and Linert W., (2007) *MATCH Communications in Mathematical and in Computer Chemistry*, 57, 749-761.

<sup>3</sup>Reissner M., Weinberger P., Wiesinger G., Hilscher G., Mereiter K., Linert W., (2009) *Hyperfine Interactions*, 191, 81-86.

<sup>4</sup>Gaussian 09, Revision C.01, M. J. Frisch et al. Gaussian, Inc., Wallingford CT, (2010)

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