35th European Congress on Molecular Spectroscopy

Jyväskylä, Finland
14.-17.8.2023
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35th EUROPEAN CONGRESS ON MOLECULAR SPECTROSCOPY

JYVÄSKYLÄ, FINLAND

14.-17.8.2023

ABSTRACT BOOK

JYVÄSKYLÄN YLIOPISTO
UNIVERSITY OF JYVÄSKYLÄ

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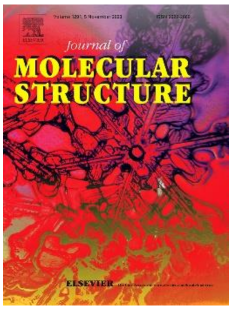

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The 35th European Congress on Molecular Spectroscopy (EUCMOS2023)

Scientific program:

Sunday 13.8.2023

Arrival to Jyväskylä

17:00-20:00 Conference office open at Hotel Alba (Mattilanniemi, Ahlmanninkatu 4, 40100 Jyväskylä)

18:00–20:00 Welcome Buffet to conference participants at Hotel Alba

Monday 14.8.2023

(Agora Ag102 (Martti Ahtisaari Auditorium))

09:00-09:30 Opening session of EUCMOS2023

Session: Applied spectroscopy 1 (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Jan Lundell (Jyväskylä, Finland)

09:30-10:15 KN1: Malgorzata Baranska (Cracow, Poland) “Clinical Raman Spectroscopy - can it support the diagnosis and pharmacology of civilization diseases? “

10:15-10:45 IT1: Saara Kaski (Jyväskylä, Finland) “LIBS, Raman and LIF analysis of apatite-bearing rocks“

10:45-11:15 *Coffee break* (Agora Aula)

Session: Spectroscopy of materials (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Jacek Waluk (Warsaw, Poland)

11:15-11:45 IT2: Kari Rissanen (Jyväskylä, Finland) ”Probing halogen bonding with 15N NMR in solution and in the solid state”

11:45-12:15 IT3: Ermelinda Macoas (Lisbon, Portugal) “Optical properties of 0D nanocarbons: Is there a trend from amorphous carbon dots to well-defined nanographenes?“

12:15-12:35 OC1: Maciej Ptak (Wrocław, Poland) “Molecular dynamics of 2D methylhydrazinium lead bromide”

12:35-12:55 OC2: Eva Kočišová (Prague, Czech Republic) “Vanadium pentoxide nanoparticle films as a new platform for plasmon-free surface-enhanced Raman spectroscopy”

13:00-14:30 *Lunch* (Restaurant Piato, Agora)

Session: Molecular spectroscopy 1 (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Maurizio Ferrari (Trieste, Italy)

14:30-15:00 IT4: Kazimierz Orzechowski (Wroclaw, Poland) “What can be learn from dielectric methods, IR spectroscopy and theoretical calculations about mixtures of alcohols and hydrocarbons?”

15:00-15:30 IT5: Benjamin Frandsen (Helsinki, Finland) “Probing amphiphiles at the air-water interface using external reflection-absorption spectroscopy”

15:30-15:50 OC3: Szymon Smołka (Wrocław, Poland) “Temperature- and pressure-dependent vibrational studies of lead bromide perovskite compound”

15:50-16:20 *Coffee break* (Agora Aula)

Session: Molecular spectroscopy 2 (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Kari Rissanen (Jyväskylä, Finland)

16:20-16:50 IT6: Sebastian Riedel (Berlin, Germany) “From matrix-isolation spectroscopy to preparative chemistry: The world of halogenated species”

16:50-17:20 IT7: Nanna Myllys (Helsinki, Finland) “Structures and stabilities of atmospheric molecular clusters“

17:20-17:40 OC4: Justyna Krupa (Wrocław, Poland) “Molecular interactions of weak complexes of atmospheric relevance“

17:40-18:00 OC5: Navdeep Kajal (Jyväskylä, Finland) “Synthesis of novel metallogel and metal complexes using hexa-pyridine ligands”

Tuesday 15.8.2023

Session: Novel chemistry (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Jouko Korppi-Tommola (Jyväskylä, Finland)

09:00-09:45 KN2: Gary Schrobilgen (Hamilton, Canada) “Current topics in noble-gas chemistry; from xenon(II) and xenon(IV) oxo-species to the coordination chemistry of NgF_2 (Ng=Kr, Xe), XeF_6, and XeO_3 “

09:45-10:15 IT8: Rui Fausto (Coimbra, Portugal) “Non-covalent interactions relevance to tunneling-driven and vibrationally-induced chemistry under matrix isolation conditions“

10:15-10:35 OC6: Rakesh Puttreddy (Jyväskylä, Finland) “Halogen bonding modules for use in supramolecular materials”

10:45-11:15 *Coffee break* (Agora Aula)

Session: Molecular spectroscopy 3 (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Sylvia Turrell (Lille, France)

11:15-11:45 IT9: Michael Schmitt (Duesseldorf, Germany) ”Determination of exact excited state dipole moments for complex systems - Stepping from the gas into the condensed phase”

11:45-12:15 IT10: Janusz Cukras (Warsaw, Poland) “Modelling the magneto-chiral spectra of amino acids and some other molecules“

12:15-12:35 OC7: Irina Osadchuk (Tallinn, Estonia) ”ECD spectra of porphyrin complexes using TD-DFT”

12:35-12:55 OC8: Śtěpán Jílek (Prague, Czech Republic) “Shedding light on the structural polymorphism of G-Quadruplexes using Raman optical activity”

13:00-14:30 *Lunch* (Restaurant Piato, Agora)

14:30-16:30 Poster session 1 (Agora Aula)

19:00-20:30 Jyväskylä City Reception (City Hall, Vapaudenkatu 32, 40100 Jyväskylä)

Wednesday 16.8.2023

Session: Photonics (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Bernhard Lendl (Vienna, Austria)

09:00-09:45 KN3: Maurizio Ferrari (Trieste, Italy) “Glass photonics: From nanoceramics to flexible photonics“

09:45-10:15 IT11: Jouko Korppi-Tommola (Jyväskylä, Finland) “Light induced addition reactions, charge transfer and chemical exchange of Ru and Os bipyridyl complexes in solution and on nanocrystalline semiconductor surfaces“

10:15-10:35 OC9: Ivan Nemec (Prague, Czech Republic) “Molecular crystals for nonlinear optics – Vibrational spectroscopic characterization and study of phase transformations”

10:45-11:15 *Coffee break* (Agora Aula)

Session: Spectroscopy of biological systems 1 (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: Malgorzata Baranska (Cracow, Poland)

11:15-11:45 OC10: H. Michael Heise (Iserlohn, Germany) “Improvements of a noninvasive Blood Glucose Assay using diffuse reflection NIR-spectroscopy”

11:45-12:05 OC11: Anna Pieczara (Cracow, Poland) “Modified glucose as a sensor to track the metabolism in single endothelial cells – observation of the “Raman spectroscopic signature of life” band”

12:05-12:25 OC12: Kristina Serec (Zagreb, Croatia) “Effects of sodium, magnesium and manganese ions on the structure of short-chain DNA”

12:25-12:45 OC13: Alžbeta Kuižová (Prague, Czech Republic) “Thermotropic phase transition of dehydrated glycerophospholipids monitored by drop coating deposition Raman spectroscopy (DCDRS)”

13:00-14:30 *Lunch* (Restaurant Piato, Agora)

Session: Spectroscopy of biological systems 2 (Agora Ag102 (Martti Ahtisaari Auditorium))

Chair: H. Michael Heise (Iserlohn, Germany)

14:30-15:00 OC14: Gülce Öğruç Ildiz (Istanbul, Turkey) “IR and Raman spectroscopies for the complementary diagnosis of psychiatric and neurodevelopmental disorders“

15:00-15:20 OC15: Karolina Socha (Lodz, Poland) “The degradation progression studies of human knee cartilage tissues with Raman spectroscopy measurements”

15:20-15:40 OC16: Patrycja Dawiec (Cracow, Poland) “Tracking metabolic changes in cancer cells using Raman imaging”

15:45-16:15 *Coffee break* (Agora Aula)

16:00-17:45 Poster session 2 (Agora Aula)

18:00-19:00 Boat cruise on Lake Jyväsjärvi

(departure at pier by Hotel Alba, arrival at Jyväskylä harbour in the city center)

Thursday 17.8.2023

Session: Molecular spectroscopy 4 (Agora Ag105 (Agora 2))

Chair: Rui Fausto (Coimbra, Portugal)

09:00-09:45 KN4: Jacek Waluk (Warsaw, Poland) “Single molecule spectroscopy and tautomerism“

09:45-10:15 IT12: Bernhard Lendl (Vienna, Austria) “Novel laser-based mid-IR sensing schemes“

10:15-10:35 OC17: Ewa Machalska (Warsaw, Poland) Resonance Raman optical activity spectra of chiral and light-absorbing molecules: atropisomeric naphthalenediimides case”

10:45-11:15 *Coffee break* (Agora Aula)

Session: Applied spectroscopy 2 (Agora Ag105 (Agora 2))

Chair: Jan Lundell (Jyväskylä, Finland)

11:15-11:45 IT13: Assimo Maris (Bologna, Italy) ”Paleo-spectroscopy: How to retrieve past data for new purposes”

11:45-12:05 OC18: Alexandra Wesełucha-Birczynska (Cracow, Poland) “2D-COS in a Neolithic graphite bead analysis”

12:05-12:35 IT14: Sylvia Turrell (Lille, France) ”From Alzheimer’s disease to functional nanomaterials: 60 years of advances in vibrational spectroscopy”

12:35-12:45 *Break*

12:45-13:30 Closing of EUCMOS2023

13:30-14:30 Lunch (Restaurant Piato, Agora)

19:00 Conference dinner, Restaurant Harald (Kauppakatu 33, 40100 Jyväskylä)

Keynote lectures

KN1: Clinical Raman Spectroscopy - can it support the diagnosis and pharmacology of civilization diseases?

Malgorzata Baranska[1], Anna Piezara[2], Aleksandra Borek-Dorosz[1], and Krzysztof Brzozowski[1]

[1]Jagiellonian University, Faculty of Chemistry, Krakow, Poland

[2]Jagiellonian University, Doctoral School of Exact and Natural Sciences, Krakow, Poland

Raman spectroscopy is considered as a promising tool for detection of subtle chemical alterations in various cells due to low signal from water, non-destructive approach, good spatial resolution, photostability, and the possibility of obtaining full chemical information at once. However, spontaneous scattering is rather weak and requires long time for spectra acquisition. The alternative is Stimulated Raman Spectroscopy (SRS) or Coherent Anti-stokes Raman Spectroscopy (CARS) using non-linear effects to enhance intensity of scattered light.

Raman microscopy can be successfully used for living systems to analyse below the micron scale, at the level of single organelles and molecules (metabolites), but sometimes it lacks sensitivity or specificity or speed. Hence, the main goal of this study is to overcome methodological and technical limits of Raman imaging in detecting small organelles and specific molecules within cells by harnessing physics, chemistry, medicine, pharmacology, biology, engineering, and data analysis, to use these advanced technologies in life sciences.

The combination of specificity and sensitivity of the Raman probes with information obtained from spontaneous Raman spectroscopy and SRS/CARS on living cells gives diagnostic potential to these methods. They can support classic approaches in tracking cellular processes, studying chemoresistance, and characterizing drug-cell interactions.

KN2: Chemistry at the Edge of the Periodic Table; from Xe(II) Oxo-Species to the Coordination Chemistries of NgF_2 (Ng = Kr, Xe), XeF_6, and XeO_3

Gary J. Schrobilgen

Department of Chemistry

McMaster University, Hamilton, ON L8S 4M1, Canada

The first example of a Xe(II) oxide species and a noble-gas dication, $[XeOXeOXe]^{2+}$, was synthesized as its $[\mu\text{-}F(ReO_2F_3)_2]^-$ salt by reaction of ReO_3F with XeF_2 in anhydrous hydrogen fluoride (aHF) at –30 °C (**1**). A LT single-crystal X-ray structure (SCXRS) revealed that $[XeOXeOXe]^{2+}$ is a planar, zigzag-shaped $[XeOXeOXe]^{2+}$ cation (C_{2h}) that is fluorine bridged through its terminal Xe atoms to two $[\mu\text{-}F(ReO_2F_3)_2]^-$ anions. The $[XeOXe]^{2+}$ dication was also synthesized as its adduct-cation, $[CH_3CNXeOXeNCCH_3]^{2+}$, by reaction of [FXeOXe---FXeF]$[AsF_6]$ with CH_3CN in aHF and characterized by a LT SCXRS (**2**).

The oxidative fluorinator, XeF_6, and CH_3CN react at −40 °C in Freon-114 to form the highly endothermic and shock-sensitive $F_6XeNCCH_3$ and $F_6Xe(NCCH_3)_2{\cdot}CH_3CN$ adducts, and first Xe^{VI}–N bonds (**3**). Their low-temperature (LT) crystal structures show the XeF_6 moieties have local C_{3v} and C_{2v} symmetries, respectively, with a stereo-active Xe valence electron lone pair.

Numerous examples of XeF_2 complexes with s- and d-block cations are known, but coordination complexes of the potent oxidative fluorinator, KrF_2, have only recently been synthesized. Among the F-coordinated KrF_2 complexes that have been synthesized and structurally characterized are $[Mg(KrF_2)_4(AsF_6)_2]$ (**4**), a series of Hg^{2+} salts in which as many as eight KrF_2 molecules are homoleptically coordinated to Hg^{2+}, e.g., $[Hg(KrF_2)_8][AsF_6]_2$ (**5**), $[F_2OBr(KrF_2)_2(AsF_6)]$ (**6**), $F_4OMFKrF$ (M = Cr, Mo, or W), and $F_4OCrFKrFCrOF_4$ (**7**).

The LT reaction of KrF_2 with $[XeF][AsF_6]$ in aHF has yielded $[FXeFKrF][AsF_6]$ (**8**). The $[FXeFKrF]^+$ cation is isovalent with the known and structurally characterized $[F(XeF)_2]^+$ and $[F(KrF)_2]^+$ cations. The reactions of $[XeF_5][AsF_6]$ with KrF_2 yielded $[F_5Xe(FKrF)AsF_6]$ and $[F_5Xe(FKrF)_2\ AsF_6]$. The $[FXeFKrF]^+$ cation and coordination complexes $[F_5Xe(FKrF)AsF_6]$ and $[F_5Xe(FKrF)_2AsF_6]$ are presently the only examples of isolable mixed Kr^{II}/Xe^{II} and Kr^{II}/Xe^{VI} noble-gas species.

Xenon trioxide is a potent shock-sensitive detonator that exhibits Lewis acid properties towards halide ions. The crystal structures of $[N(C_2H_5)_4]_3[X_3(XeO_3)_3]{\cdot}2CH_3CN$ and $[N(CH_3)_4]_4[X_4(XeO_3)_4]$ (X = Cl, Br) have been obtained (**9**). The anions of these room-temperature stable and shock-insensitive salts are the only examples of isolable species with stable Xe–Br bonds. Adduct formation between XeO_3 and a variety of nitrogen and oxygen donors will also be briefly described. A notable example is the stable 15-crown-5 complex, $(CH_2CH_2O)_5XeO_3$ (**10**), in which XeO_3 is coordinated to the five O atoms of the crown ether.

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KN3: Glass photonics: From nanoceramics to flexible photonics

M. Ferrari[1], T.N.L. Tran[1], A. Carlotto[1], G. Zanetti[1], A. Szczurek[2], K. Startek[3], S. Varas[1],
F. Scotognella[4], G.C. Righini[5], J. Krzak[2], A. Lukowiak[6], A. Chiasera[1]

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[2] DMMBE, University of Science and Technology Smoluchowskiego St 25, 50-370 Wroclaw, Poland;
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[4] Department of Physics, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy;
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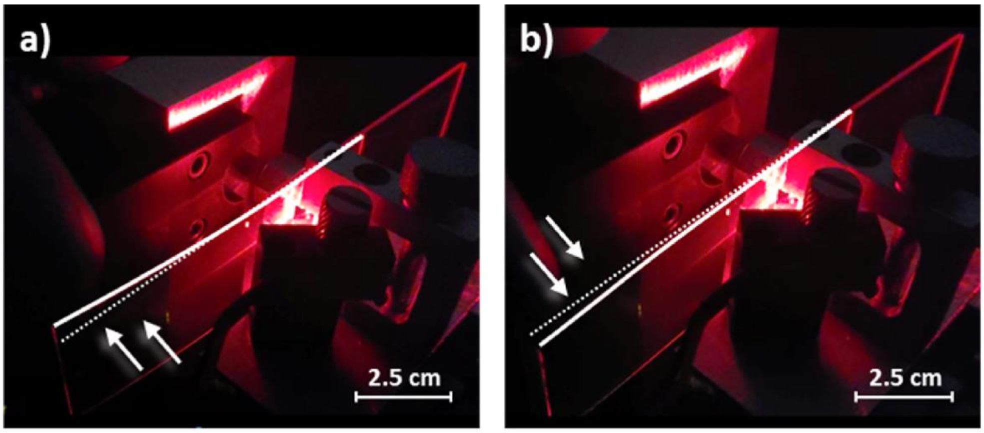
[6]Institute of Low Temperature and Structure Research, PAS, Okolna 2, 50-422, Wroclaw, Poland;

Glasses constitute a fantastic material for photonics applications thanks to their unique properties in terms of transparency on a broad wavelength spectrum and reduced constraints for the chemical composition, allowing tailoring of the refractive index as well as of the luminescence activation. Among the more exciting glass-derived structures and applications we have optical fibers, high power lasers, sensors for bio species detection and structural monitoring of civil buildings, lighting, integrated optics devices, metastructures, solar glasses, automotive glasses [1]. In the last years the applied and fundamental research in glass photonics is vigorously driven by glass-ceramics and ultra-thin glasses [1,2]. Transparent glass ceramics are constituted by nanoceramics imbedded in a glass matrix and, when activated by rare earth ions, are a perfect tools for photon management. Ultra-thin glasses are intensely developed by glass producer for foldable, wafer and flexible photonics applications.

In this lecture, after a short summary about the state of art in glass photonics we will focus on the more impressive results obtained in luminescent glass ceramics and on the appealing behavior of the mechanically flexible glasses.



Planar waveguide, deposited on flexible glass substrate, operating under bending condition.

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[2] T.N.L. Tran et al. *Opt. Mater*. 124, (2022), 111978 - 1/7

KN4: Single molecule spectroscopy and tautomerism

Jacek Waluk[1,2]

[1] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland; [2] Faculty of Mathematics and Science, Cardinal Stefan Wyszyński University, Dewajtis 5, 01-815 Warsaw, Poland

Removal of ensemble averaging, achieved in single molecule studies, allows a deeper insight into structure and reactivity. Moreover, analysis of data obtained for a large population of single molecules makes it possible to determine the proper distribution function from a great (in some cases, infinite!) number of possibilities.

Our investigations of single molecules focus on tautomerism in porphyrin isomers, porphycene and hemiporphycene (Figure 1). Three complementary techniques are used: (1) confocal fluorescence[1] and (2) Raman spectroscopy,[2] and (3) scanning probe microscopy.[3] Taken together, these approaches provide a complex picture of a reaction governed by tunneling (vibrational mode specific), with an important role of environment, regarding both the tautomerization rate and mechanism, and the structure of the most stable tautomeric form.

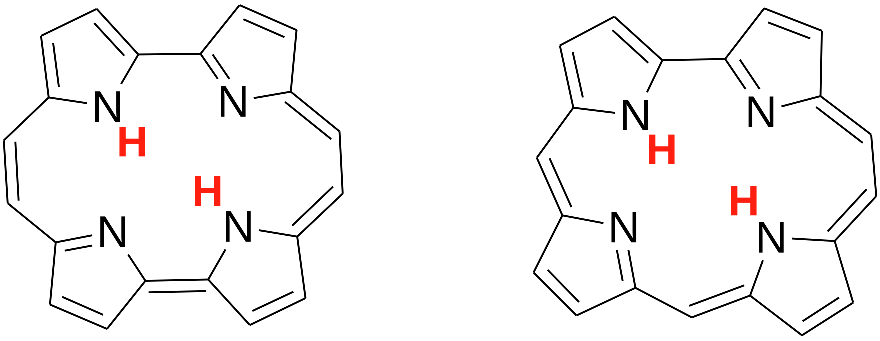

Figure 1: Left, porphycene, right, hemiporphycene.

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Invited talks

IT1: LIBS, Raman and LIF analysis of apatite-bearing rocks

Saara Kaski[1], Sari Romppanen[2], and Heikki Häkkänen[1]

[1]University of Jyväskylä, P.O. Box 35 FI-40014 Jyväskylä, Finland

[2]Geological Survey of Finland, P.O. Box 96 FI-02151 Espoo, Finland

In analysis of solid samples like rocks, time-resolved laser spectroscopic techniques are advantageous, as the sample preparation is minimal and rich spectral information reveals the location of the minerals, the size and the shape of the mineral grains and their chemical variations (Fig 1.). In laser-induced breakdown spectroscopy (LIBS) the spectra detected from plasma emission presents the elemental composition on the surface of the rock. Raman spectroscopy recognizes the specific minerals based on the molecular vibration peaks. Laser-induced fluorescence shows the signal originating from luminescence activators in the mineral structure, e.g., the occurrence of rare earth elements (REE). In this study the main features of these time-resolved methods will be demonstrated in analysis of apatite rocks.

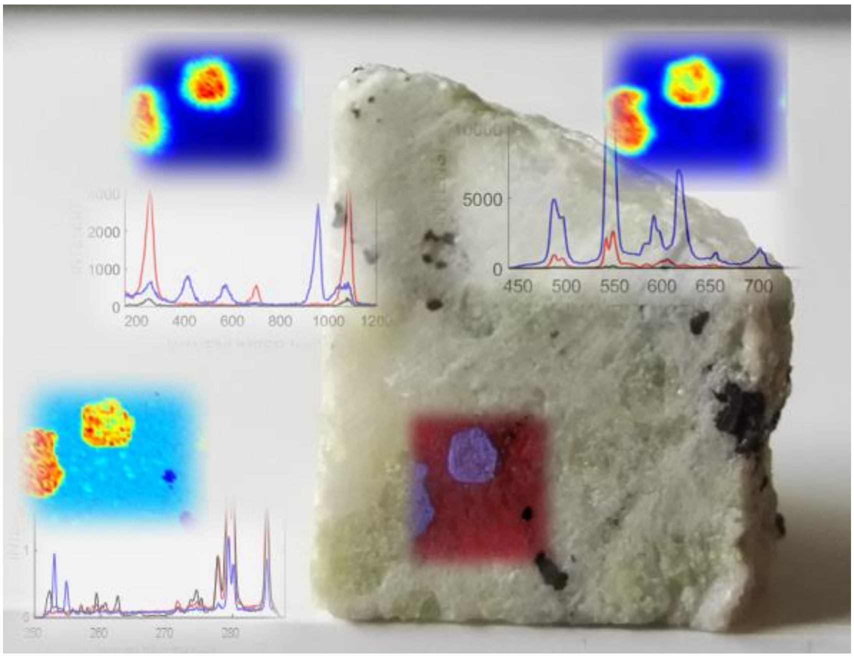

Figure 1: Spectral data reveals the location of minerals and rare-earth elements.

IT2: Probing halogen bonding with ^{15}N NMR in solution and in the solid state

Jas S. Ward, Elina Sievänen and Kari Rissanen

Department of Chemistry, University of Jyväskylä, Survontie 9 B, 40014 Jyväskylä, Finland

Over the last twenty years halogen bonding (XB) has matured as one of the most studied non-covalent interactions, experiencing an amazing boom since 2007. Halogen(I) complexes[1] are predominantly studied in the solid state due to their inherent reactivity, hence their ubiquitous nature as halogenation reagents (*cf.* [I(pyridine)$_2$]BF$_4$, *Barluenga's Reagent*). As the halogen bonding will affect the electron density of the nitrogen atom of the XB acceptor (typically a pyridine derivative) the 15N NMR through the ^{1}H–^{15}N HMBC (Heteronuclear Multiple Bond Correlation) measurement is a good measure to probe halogen bonding in these complexes. In addition to the solution NMR, the solid-state ^{15}N NMR spectroscopy can be applied to stydy the halogen bonding on similar or even same systems. The ss-NMR results confirm equivalent chemical shifts as those previously reported from solution studies, thus offering a directly comparable synergy between the NMR spectroscopic data and the single crystal structures of the same halogen-bonded complexes. The lecture summarises some recent results obtained on Barluenga-type complexes as well as carbonyl hypoiodites, a new family of neutral halogen-bonded complexes.

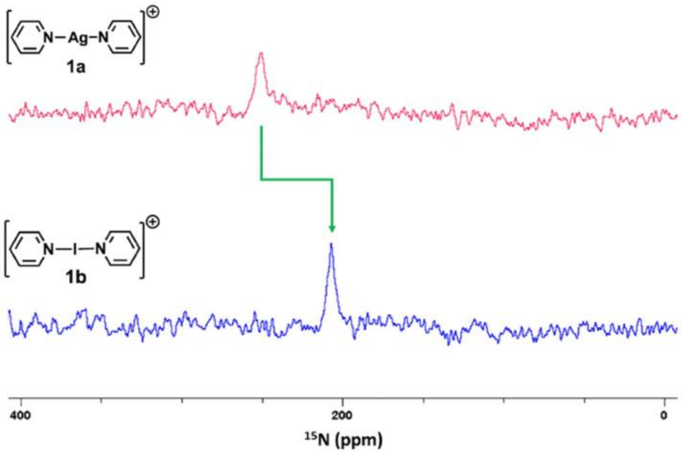

Figure 1: The solid-state ^{15}N NMR spectra of **1a** and **1b** (referenced to zwitterionic form of glycine, $C_2H_5{}^{15}NO_2$), with the characteristic δ_N coordination shift to upfield resulting from the Ag^+ to I^+ cation exchange annotated with a green arrow.[2]

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IT3: Optical properties of 0D nanocarbons: is there a trend from amorphous carbon dots to well-defined nanographenes?

Ermelinda M. S. Maçôas[1]

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The nonlinear optical properties of 0D nanocarbons have been explored in optoelectronic and photonic devices and in biomedical applications. However, the limited number of studies that focus on nonlinear absorption, the large dispersion of quantitative data reported in literature, and the poor structural characterization of the materials, prevent translation of research results into truly impactful solutions. Systematic studies are needed for unambiguous definition of the design guidelines to produce materials with high nonlinear response in a reproducible and scalable way. This presentation focus on recent work on the nonlinear optical properties of 0D nanocarbons produced by three different approaches: bottom-up amorphous carbon dots (Cdots), top-down graphene quantum dots (GQD) and step-by-step controlled organic synthesis of distorted nanographenes (NG), illustrated in Figure 1.[1-3] The low emission yields of oxidized 0D nanocarbons produced by top-down or bottom-up methods is discussed, it is shown that the two-photon cross-section of the carbon core is not as high as initially anticipated and that, to some extent, distortion of the sp^2 network can improve the nonlinear optical properties.

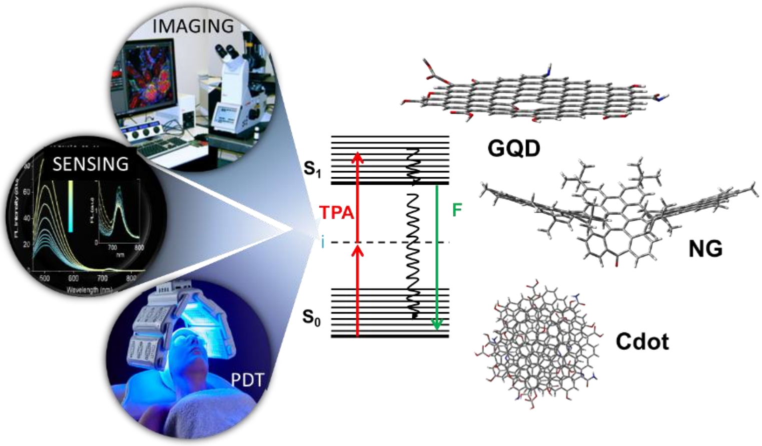

Figure 1: Illustration of the 0D nanocarbons studied, the two-photon absorption (TPA) process and its potential applications.

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IT4: What can be learned from dielectric methods, IR spectroscopy and theoretical calculations about mixtures of alcohols and hydrocarbons?

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The non-linear dielectric effect (NDE) involves comparing of the electric permittivity measured at strong and weak dielectric fields. For liquids composed of dipolar molecules, the NDE should be negative and proportional to the square of the electric field. This effect at first was theoretically predicted and later it was experimentally confirmed. The experiment conducted in diethyl ether was challenging, and qualitatively consistent with the theoretical predictions. This positive confirmation of the theory diminished interest in further application of this technique. Why bother with complex and sometimes dangerous experiments (involving electric voltages up to 10 kV) when the same results one can achieve through the calculations? Fortunately, some of the results deviate from the theoretical predictions showing a positive NDE effect. This inconsistency motivated researchers to investigate the NDE effect more precisely. It was found that the discrepancy between the "calculated" and "experimental" effects is a source of valuable information on fluctuations, molecular conformation, and association phenomena.

In my presentation, I would like to demonstrate the results of combined IR, dielectric, and theoretical studies on association phenomena in alcohol-hydrocarbon mixtures. An application of different, yet complementary methods allows to obtain independent experimental data, and enables to investigate the association phenomena throughout the entire concentration range of alcohol + hydrocarbon. Figure 1 illustrates the variations in concentrations of cyclic associates of hexanol as a function of alcohol mole fraction in hexane [1].

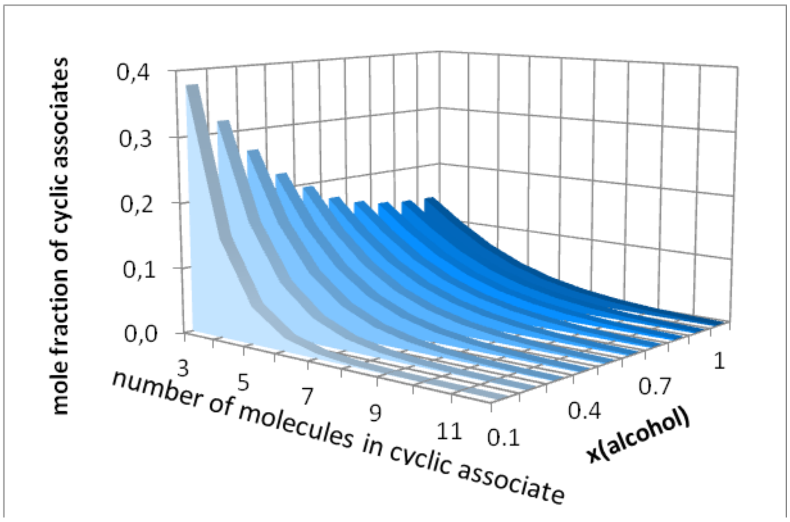

Figure 1: Concentration of cyclic associates of hexanol in hexanol-hexane mixture.

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IT5: Probing Amphiphiles at the Air-Water Interface using External Reflection-Absorption Spectroscopy

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The air-water interface is a ubiquitous environment on Earth which exists both at the surface of bodies of water and to an even greater degree on water-based aerosols like cloud condensation nuclei. The air-water interface is a unique reaction environment where accumulation of organic material can influence chemical processing and properties. Amphiphiles are organic molecules with both polar and non-polar groups that have a high propensity towards placing themselves at the air-water interface. Spectroscopy of molecules at the air-water interface can provide information about molecular structure, orientation and properties which can be useful for investigating how molecules may have altered reactivity and how they modify the refractive index of water, which, for example, can be important for aerosol scattering properties.

In this presentation the experimental setups for spectroscopy are discussed; the infrared reflection absorption spectroscopy (IR-RAS) and the UV-Vis-RAS instruments, the latter of which was constructed as part of this work. These instruments were used to record both IR and UV-Vis spectra of monolayer all-*trans*-retinoic acid (ATRA) at the air-water interface. Angled incidence of light and polarization of light relative to the water surface was used to aid assignments and provide information about molecular orientation. ATRA is also known as vitamin A acid, which is produced biologically and exists in aqueous environments but with low aqueous solubility, and it is thus a highly relevant research target for the air-water interface sensitive spectroscopy methods we employed.

The work demonstrates how the air-water interface can significantly alter the spectroscopy of amphiphiles such as ATRA, both in the UV-Vis range and the IR range. This implies that photochemistry at the air-water interface differs from that of bulk water or gas phase. Secondly, the changes in molecular geometry, orientation, packing of molecules and surface concentration (surface excess) at the air-water interface can be inferred from spectroscopy and surface tension measurements. This implies that chemical reactivity can be significantly changed as compared to bulk water or gas phase – and the surface can cause both speedups or a slowing of chemical processes depending on the surface environment. It was additionally shown that pure monolayers of ATRA was lost over a timescale of a few hours due to ATRA clustering, but mixed monolayers of ATRA and stearic acid could stabilize the monolayers.

IT6: From Matrix-Isolation Spectroscopy to Preparative Chemistry: The world of Halogenated Species

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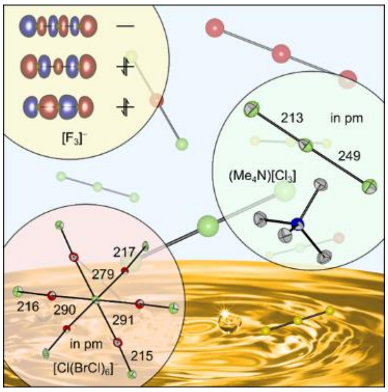
In the recent years several polyhalogen- and polyinterhalogen- anions have been investigated under cryogenic conditions using matrix-isolation spectroscopy. A very powerful method to prepare such ionic species is the pulsed salt laser-ablation technique combined with matrix-isolation spectroscopy. In this context the formation of several free polyhalides like $[F_3]^-$, $[Cl_3]^-$ could be spectroscopically characterized under cryogenic conditions in rare-gas matrices. Thereby the matrix environment is a crucial factor as shown by theoretical modeling of the interaction between rare-gas matrices and a trifluoride guest anions. Beyond these free ions, new techniques have been developed to prepare ion-paired complexes like $M[AuF_4]$ under such matrix-isolation conditions. Based on these previous investigations novel synthetic strategies have been developed to prepare such species also in bulk quantities which can now be used as chlorine storage materials and afterwards applied in industrial processes like the phosgene production.



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IT7 “Structures and stabilities of atmospheric molecular clusters”

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Acid–base chemistry plays a key role in atmospheric cluster formation. Atmosphere contains a plethora of acid and base compounds which have different abilities to form clusters and further grow into aerosol particles. Additionally, the role of water in atmospheric aerosol particle formation is not fully understood as it can stabilize or destabilize cluster structures, which has non-linear effects on the cluster formation dynamics. Direct measurements of water-containing clusters are limited because water is likely to evaporate before detection, and therefore, theoretical and spectroscopic tools are needed to understand the role of water in aerosol particle formation (Frederiks *et al.,* 2023).

Structures and stabilities of acid–base clusters with and without water are studied using state-of-the-art quantum chemical calculations together with cluster dynamics simulations. Using combinations of three representative acid molecules with nine representative base molecules, molecular properties affecting cluster stabilities and aerosol formation efficiency are investigated. The best predictor of forming stable acid–base heterodimers, and thus particles, was found to be gas-phase acid and base strength.

The hydration ability of a base follows in the order of gas-phase base strength whereas the proton transfer ability of a base in a water cluster is related to the aqueous-phase basicity (Myllys *et al.*, 2021). Hydration ability of acid–base clusters seem to be related to the number of hydrogen binding sites (Yang *et al.*, 2018). Increased relative humidity can enhance the aerosol particle formation several orders of magnitude when the smallest clusters are stabilized by water molecules, but it can also slightly reduce the particle formation in the case of strongly bound acid–base systems (Myllys, 2023).

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IT8: Non-covalent interactions relevance to tunneling-driven and vibrationally-induced chemistry under matrix isolation conditions

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In the last decades, we have assisted to rapid progress on the use of vibrationally-induced chemistry as a powerful tool to manipulate molecular structures in a highly selective way, and on the application of quantum mechanical tunneling as a tool to explore the reactivity of organic molecules in an unprecedented way. This progress has revealed new paradigms in organic chemistry reactivity, which are being now made accessible to organic chemistry synthesis practitioners. Our own contribution to this topic has been recently reviewed [1], and the intertwining between the two research strategies has been highlighted.

This talk will address the relevance of non-covalent interactions to tunneling-driven and vibrationally-induced chemistry. After a brief introduction to the general subject, some representative examples will be provided.

Acknowledgments

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IT9: Determination of Exact Excited State Dipole Moments for Complex Systems - Stepping from the Gas into the Condensed Phase

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Rotationally resolved electronic Stark spectroscopy is a versatile tool for the accurate determination of (i) rotational constants (i.e. the geometries) of molecules in both electronic states, connected by the electronic transition, (ii) centrifugal distortion constants (i.e. the force field of the molecule), (iii) barriers to hindered internal motions, (iv) transition dipole moments (i.e. the electronic nature of the excited state), and (v) the permanent dipole moments of both states connected by the electronic transition. The latter provide an easy access to the electronic nature of the state under investigation because they differ in size and in direction for different electronic states.

Historically, excited-state dipole moments (or more precisely their changes upon electronic excitation) have been determined from electrooptical absorption measurements or from solvatochromic shifts in solvents of different static dielectric constants. This method of using solvent shifts, engender criticism by Lombardi, who compared so determined excited state dipole moment changes with those from high resolution gas phase Stark effect measurements.

In some cases, the condensed phase values exceeded the more precise gas phase values by an order of magnitude. The reason for this strong discrepancy is the approximate nature of the field induced perturbations in case of the strong fields, exerted by the solvents. This strong field couples especially energetically close-lying electronically excited states, leading to an effective dipole moment, which is a combination of the excited-state dipole moments of the coupled states as well as the transition moment between these two states. This effect can be viewed as a field induced dipole moment borrowing from the state with the larger dipole moment. Especially for substituted indoles, for which the energetic distance between the lowest electronically excited singlet states is small, this perturbation plays a large role. The most reliable values for dipole moments of ground and electronically excited states are obtained from gas phase electronic Stark experiments since the dependence of the frequency shift of individual rovibronic lines from the electric field strength yields immediately the dipole moment in ground and excited state. Moreover, not only the absolute value of the total dipole moment can be determined, but also the unsigned Cartesian components of the dipole moment in both electronic states.

The use of genetic algorithms (GA) and evolutionary strategies (ES), which we advanced in the last years, greatly improved the possibility to fit and simulate also very congested and overlapping spectra. We extended the existing experiment in order to measure electronic Stark spectra using different geometrical set-ups with different selection rules. The resulting spectra with parallel and perpendicular selection rules at different electric field strengths are fitted at the same time using evolutionary strategies, improving the accuracy by about one order of magnitude. In this presentation we will critically discuss the limits for the method, as well as the future aspects, which keep alive this fascinating facet of molecular spectroscopy.

A variation of the thermochromic effect will be presented, which is able to yield dipole moment changes that are largely independent of the solvent used to close the gap between gas phase dipole moment changes and those obtained in solutions.

IT10: Modelling the magneto-chiral spectra of amino acids

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Magneto-chiral dichroism (MChD) is the difference of the absorption of unpolarized light by a chiral molecule in the presence of external magnetic field which is parelell and antiparallel to the direction of the propagation of light. The phenomenon was predicted in 1984 by Barron and Vrbancich (1) and confirmed experimentally only in 1997 by Rikken and Raupach (2).

Hypothetically, it is connected to homochirality of life, it is relevant for astrochemistry of molecular clouds and interesting *per se* as a potentially new type of spectroscopy allowing for the study of chirality and chiral species. It has also been shown that it can be used for enantioselective photochemistry (3).

Some advancements took place since the experimental verification of MChD but no successful measurement for closed-shell, simple and biologically relevant species which are interesting from the perspective of life sciences were reported.

Since the implementation of a computational method in the framework of the complex response theory (4) we have been screening for molecules exhibiting large MChD signal. Here, the results of modelling of the dichroic spectra for a series of aminoacids and other molecules, from the small fluorocyclopropanone to the whopping 6-helicene, are presented.

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IT11: Photochemistry of Ruthenium and Osmium Carbonyl Complexes in Solution and on Mesoscopic Semiconductor Films

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Metal carbonyl complexes are potential light harvesting compounds that can be used in solar catalytic processes and solar cells. In here we discuss light induced reactions of ruthenium carbonyl compounds *trans-, cis*-$Ru(dcbpy)X_2(CO)_2$ (X=Cl,I) in solution and light induced charge transfer dynamics of osmium carbonyl compound $Os(dcbpy)I_2(CO)_2$ on nanocrystalline TiO_2 films.

In ruthenium complexes the initial step of the reaction, breaking the ruthenium-carbon bond was over in 62fs. Coherent transient absorption signals revealed *trans to cis* reorganization of the halogens during the transition state, in 500fs. Subsequent solvent complex formation and product cooling occured in the picosecond time domain. In contrast, the osmium complex in solution remained intact under light excitation. When bound to nanocrystalline TiO_2, light excitation resulted in an ultrafast sub 100 fs charge transfer, followed by slower non-exponential picosecond transfer.

To study the underlying reasons for the slower charge transfer, 2DIR studies were undertaken. In the dry films binding of the osmium complexes was highly heterogeneous. When the films were brought in contact with a solvent, reorganization took place. Two separate species were identified with strongly coupled carbonyl vibrations. IR excitation of one of the species was transformed into the other species, and in time, finally a *chemical exchange* took place. The interconversion occurred in the same time domain as the previously observed picosecond charge transfer. The observations clearly infer that sensitizer molecules on nanocrystalline metal oxide cavities are subject to solvent induced dynamics. Such motions have substantial impact on efficiencies of light induced charge transfer reactions, in catalytic processes and in dye sensitized solar cells.

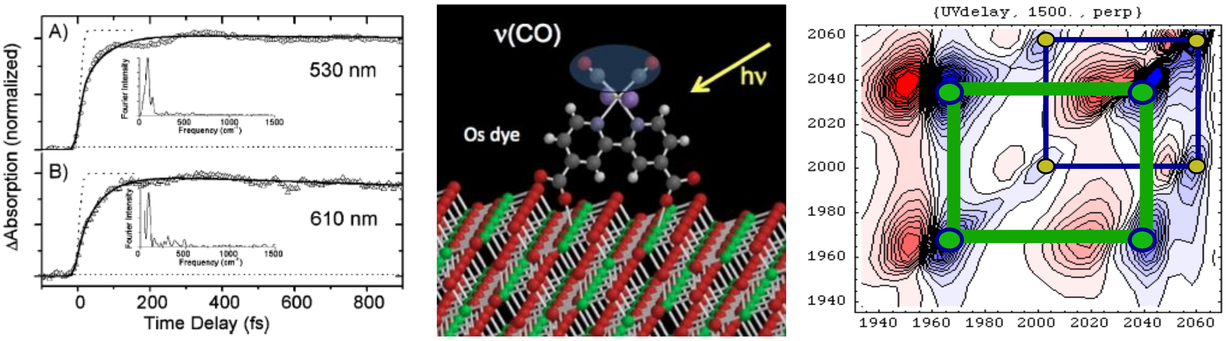

Figure 1: On the left: Transient absorption signal reveals 62 fs carbonyl dissociation of *trans*-(dcbpy)$RuI_2(CO)_2$ in ACN. In the middle: Os(dcbpy)$I_2(CO)_2$ sensitized TiO_2 surface. On the right: the two binding configurations of the Os-dye on TiO_2 under ACN seen in a 2DIR spectrum.

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IT12: Novel Laser-Based mid-IR Sensing Schemes for Liquids

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Advances in Instrumental Analytical Chemistry are often linked to technological developments in neighboring disciplines. This is the case with respect to recent advances in mid-IR quantum cascade lasers (QCLs) which are increasingly used as light sources in mid-IR spectroscopy. Recently also quantum cascade detectors have been developed (QCDs). QCLs offer high spectral power densities, fast amplitude and frequency modulation possibilities, polarized and coherent radiation. Based on these properties a range of new sensing schemes, often clearly outperforming established FTIR spectrometers, can be developed.

This presentation will introduce balanced detection EC-QCL absorption spectroscopy for sensitive protein analysis in aqueous solutions [1] and a fully immersible lab-on-a-chip system comprising the laser, a plasmonic waveguide and the detector (QCD) for in-line sensing applications [2]. Furthermore, dispersion spectroscopy implemented in a free space optics Mach Zehnder Interferometer will be introduced for measuring the real part of the complex refractive index of liquid samples [3]. The proposed design is made possible by the coherent nature of the light provided by the EC-QCL. Dispersion spectroscopy has several advantages over absorbance spectroscopy: It is a baseline free technique, the reading is independent of power fluctuations of the laser source and the recorded signal is direct proportional to the analyte concentration hence providing constant sensitivity over a large concentration range. Finally, an outlook on photothermal spectroscopy will be given. The most remarkable feature of photothermal spectroscopy is that the recorded signal is directly proportional to the analyte concentration, a feature particularly interesting in laser-based sensing schemes [4].

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IT13: Paleo-spectroscopy: How to retrieve past data for new purposes

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Rotational spectroscopy is a well-established technique suitable for identifying and quantifying molecules in the gas phase. It is worth noting that since its origin laboratory measurements coupled with radioastronomy observations have been used to explore the composition of the universe. Obviously, the number of molecules studied in the laboratory is largely greater than that of the ones observed in space. Nowadays, advanced techniques open to the use of rotational spectroscopy for new applications such as analytical purposes.

However, the spectra of smaller and more volatile species, which are expected to be the most abundant in interstellar space and the most suitable for analytical detection, were recorded several decades ago and their modelling, aimed at the prediction of accurate spectral features, can be improved by both complementing the data with new measurements and using updated Hamiltonians. In this process, the two main critical points are: (i) retrieving the past original data, since sometimes information was not published but only available from the authors; (ii) managing the presence of misprinted or badly assigned values.

Once all difficulties have been overcome, to prevent the same kind of issue, both the data and the working model should be released. It is worth noting that the availability of this information will be useful not only in astronomy but also in the new emerging applications of rotational spectroscopy.

Some examples and applications related both to astronomical detection and chemical analysis will be discussed, focusing on the challenges derived from the presence of internal motions.

IT14: From Alzheimer's Disease to Functional Nanomaterials: 60 Years of Advances in Vibrational Spectroscopy

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The present-day panoply of tools used for vibrational spectroscopic studies seems all-powerful and infinitely adaptable. So simple have the techniques become, that it is very easy to forget that less than 200 hundred years ago, none of these things were even imaginable, much less in existence. And in the case of Raman spectroscopy, the conception dates to less than a hundred years ago.

The aim of this talk is to remind us of some of the genius researchers who led to the conceptions of vibrational spectroscopies, as well as to bring to mind some of the instrumentation and works which served as little thresholds obtained during the development of these fields.

From the initial instrumentation, we will watch techniques develop which will make possible the evolution of exploration into the domains of the very small and of very short-timed events. From small, isolated molecules, studies gradually extended to those of complex inorganic systems and then to the numerous biological and medical systems. The technological evolutions allowed the possibilities of going out of the laboratory and to undertake "in-field" studies.

The experimental examples presented here will be both from work performed in my laboratories, as well as from numerous literature results from research laboratories around the world. Though not an exhaustive presentation, this review should highlight the scope and the extent of developments in vibrational spectroscopies over the past 60 years.

a) b)

Figure 1 a) Dispersive IR spectrometer, 1958. b) In-field Raman apparatus, 2010

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Oral contributions

OC1: Molecular dynamics of 2D methylhydrazinium lead bromide

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Two-dimensional (2D) lead halide hybrid perovskites are potential photovoltaic, light-emitting, nonlinear optical, and ferroelectric materials. The dynamic adaptability of the crystal structure has a significant impact on the main optoelectronic features and polar arrangement of organic cations. In this study, we present polarized Raman spectra and infrared spectroscopy studies of MHy_2PbBr_4 exhibiting ferroelectricity, photoluminescence, and multiple nonlinear optical phenomena [1].

In this study, we estimated the wavenumbers and symmetries of longitudinal (LO) and transverse (TO) optical modes. The results showed that vibrations of the inorganic sublattice dominate the dielectric properties of MHy_2PbBr_4. We also investigated the influence of temperature on dynamics and the effect of structural phase transitions on phonon modes using temperature-dependent Raman spectroscopy. These data revealed very narrow bands at 80 K, indicating a well-ordered structure. The increase in temperature leads to a strong widening of bands, indicating a significant rise in the anharmonicity caused by the unlocked motional freedom of organic cations. Our X-ray diffraction investigation showed that MHy_2PbBr_4 experiences an order-disorder phase transition at 351 K, which leads to weak band shifts and broadening. We observed no evident Raman abnormalities at the second phase transition at 371 K, indicating the occurrence of another disordered phase. In contrast to many reported 2D lead halide perovskites, our findings show that the dynamics in MHy_2PbBr_4 do not exhibit sudden freezing at the order-disorder phase transition temperature but decrease gradually over a broad range of temperatures [2].

High-pressure XRD and Raman studies showed that the MHy_2PbBr_4 crystal experiences an uncommon phase transition at about 4 GPa, which is connected with the partial extrusion of organic cations from the interlayer space into voids situated inside the inorganic sheets. Raman observations indicated that this phase transformation is accompanied by substantial structural deformation and reorganization of the hydrogen bonds [3].

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OC2: Vanadium pentoxide nanoparticle films as a new platform for plasmon-free surface-enhanced Raman spectroscopy

Eva Kočišová[1], Anna Kuzminova[2], Alžbeta Kuižová[1], Adéla Hanková[2], Marek Procházka[1] and Ondřej Kylián[2]

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Metal-oxide (MeO) nanomaterials represent a promising and cheap alternative to plasmonic metallic nanostructures currently used for surface-enhanced Raman scattering (SERS) spectroscopy. In contrast to plasmon metallic SERS-active platforms, MeO nanomaterials provide good signal uniformity, spectral reproducibility, and reduced local heating upon laser irradiation (Han et al., 2017). However, the limiting factor of MeO-based SERS is its lower signal enhancement as compared to plasmonic-based metallic SERS. Therefore, new concepts are still to be developed to improve the performance of MeO-based SERS-active materials, such as vanadium pentoxide (V_2O_5) nanoparticles (NPs) (Pan et al., 2015).

We present a newly developed approach for the synthesis of V_2O_5 NPs that employs magnetron-based gas aggregation sources of vanadium NPs and thermally induced transformation of deposited vanadium nanoparticle films into V_2O_5 ones (Hanková et al., 2023). The SERS spectra were measured using a confocal Raman system and 623.8 nm excitation. The SERS performance of V_2O_5 nanoparticle films was found to be strongly linked with the appropriate crystalline structure and porosity. Raman spectrum of characteristic V_2O_5 crystalline structure has been observed only for samples annealed at temperatures equal to or higher than 300^o C. These V_2O_5 nanoparticle films allow for sensitive and reproducible SERS detection of organic dyes (methylene blue, rhodamine 6G and crystal violet). Spectral detection limits were determined as 5×10^{-8} M, 1×10^{-6} M, and 3×10^{-6} M for methylene blue, crystal violet, and rhodamine 6G, respectively. Spectral mapping over the surface proved excellent spectral reproducibility (relative standard deviation of signal less than 10%). In conclusion, our results represent an important step in designing novel plasmon-free SERS-active platforms with better stability and spectral reproducibility than plasmonic ones.

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OC3: Temperature- and Pressure-dependent Vibrational Studies of Lead Bromide Perovskite Compound

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We present a comprehensive study on the temperature- and pressure-dependent vibrational characteristics, phase transitions, and crystallographic structures of the lead bromide perovskite compound, IM_3PbBr_5. This compound exhibits a unique crystal structure comprising $PbBr_6$ octahedra arranged in 1D single-chains and imidazolium cations (Im) situated within the cavities between the octahedral chains[1,2].

Through vibrational measurements using Raman and infrared (IR) spectroscopy, we observed pronounced shifts in vibrational modes during the phase transitions associated with the ordering of the imidazolium cation. These transitions were accompanied by notable changes in peak positions, intensities, and bandwidths, revealing the coupling between the ordering of Im cations and the inorganic sublattice.

In addition to the vibrational measurements, crystallographic structures were determined for each phase, shedding light on the structural changes accompanying the phase transitions. The solved crystallographic structures provided detailed insights into the rearrangement and ordering of the imidazolium cations within the IM_3PbBr_5 crystal structure.

Furthermore, we investigated the influence of pressure on the phase transitions and vibrational properties of IM_3PbBr_5. By applying controlled pressure, we observed transitions and explored their effects on the crystal structure and vibrational modes. The interplay between external stimuli and structural dynamics in IM_3PbBr_5 was revealed, enhancing our understanding of its behavior under varying environmental conditions.

Overall, this comprehensive study provides valuable insights into the temperature and phonon properties, mechanisms of phase transitions, and crystallographic structures of IM_3PbBr_5. The findings highlight the importance of the ordering of imidazolium cations and their impact on the material's vibrational properties. These results contribute to the development and optimization of lead bromide perovskite-based devices, unlocking their potential applications in advanced optoelectronics, photovoltaics, and related fields.

In summary, our study elucidates the temperature- and pressure-dependent vibrational characteristics, phase transitions, and crystallographic structures of IM_3PbBr_5. The observed coupling between the ordering of imidazolium cations and lattice dynamics provides valuable insights for the development of lead bromide perovskite-based devices.

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OC4: Molecular interactions of weak complexes of atmospheric relevance

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Non-covalent interactions are considered to have a significant influence on properties of chemical and biological systems. They also have an impact on atmospheric chemistry, affecting existing reactions and contributing to new reaction channels. Molecular complexes formed in dense environments at low temperature can affect the chemistry of interstellar media and some planetary atmospheres. Isothiocyanic acid (HNCS) and isocyanic acid (HNCO) are well known as interstellar molecules and were detected in the rich molecular cloud Sagittarius B2 (Sgr B2).

We will present results of theoretical and experimental studies of aggregates and complexes formed by HNCS and HNCO with small acceptors (SO_2 and N_2). As the main experimental method, matrix isolation (MI) combined with the infrared spectroscopy (FTIR) was used. MI-FTIR is an established technique for studying weak molecular complexes providing valuable spectroscopic and structural information. In the gas phase the concentration of complexes formed is often too low to allow detection. Matrix isolation technique is considered to be a good approximation to the gas phase. Moreover, for the majority of the molecular complexes studied, their structure in low temperature matrices is the same as in the gas phase. However, there are examples of weak complexes for which matrix environment can affect structure of species under consideration. Here, we will show examples of both situations.

The experimental studies were supported by theoretical calculations at the MP2 and B3LYPD3 levels with the 6-311++G(3df,3pd) basis set.

Acknowledgements

The research was supported by the National Science Centre Project No. 2013/11/B/ST4/00500, as well as the Academy of Finland, grant number 332023, for the work performed at the University of Jyväskylä. Allocation of computer time from the Wrocław Centre for Networking and Supercomputing (Wrocław, Poland) is gratefully acknowledged. The support of the COST Action CA21101 (COSY) is highly appreciated.

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OC5: Synthesis of novel metallogel and metal complexes using hexa-pyridine ligands

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Coordination Polymer Gels (CPGs) constitute a subset of solid-like metal ion and bridging organic ligand structures (like MOFs) that form multi-dimensional networks through a trapped solvent because of non-covalent interactions. The pyridine qualifies as a ligand for transition metals and can form metal complexes with all the metals in the periodic table due to its Lewis basic nature, which is rooted in its nitrogen lone pair. It is typically a weak monodentate ligand that can bind metal in a variety of ratios to form a variety of metal complexes.

In this work, we have synthesized the hexa-pyridine triphenylene ligands by Suzuki coupling reaction, where nitrogen is at meta (Figure 1, I) and para (Figure 1, II) position respectively. The synthesis of ligands is confirmed by both NMR and single crystal X-ray measurements respectively. Thereafter, these ligands were used in the gelation and metal complex formation. From (I) we got a gel with $CuCl_2$ in DMSO. The optimized ratio of ligand to metal is 1:2. We tried with other metal-chlorides also but there was no gelation except $CuCl_2$. The minimum gelation concentration (MGC) is 0.6 % (w/v). We also got some metal complexes from (I) with mercury and silver. On the other hand, with (II), we got copper, cadmium and silver metal complexes.

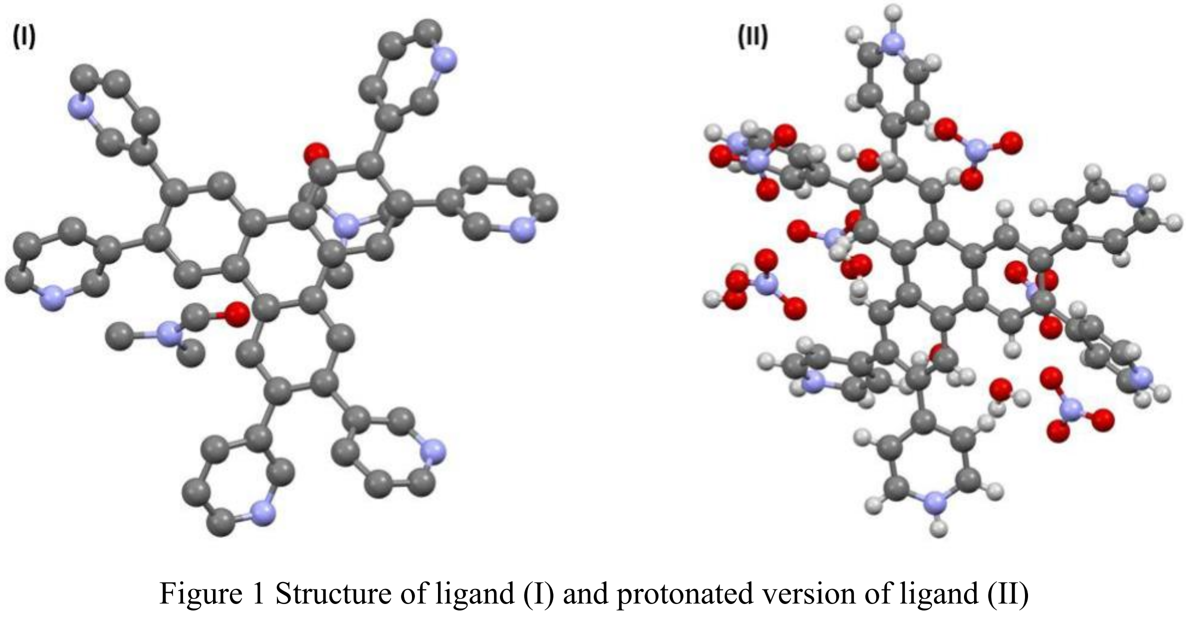

Figure 1 Structure of ligand (I) and protonated version of ligand (II)

OC6: Halogen bonding modules for use in supramolecular materials

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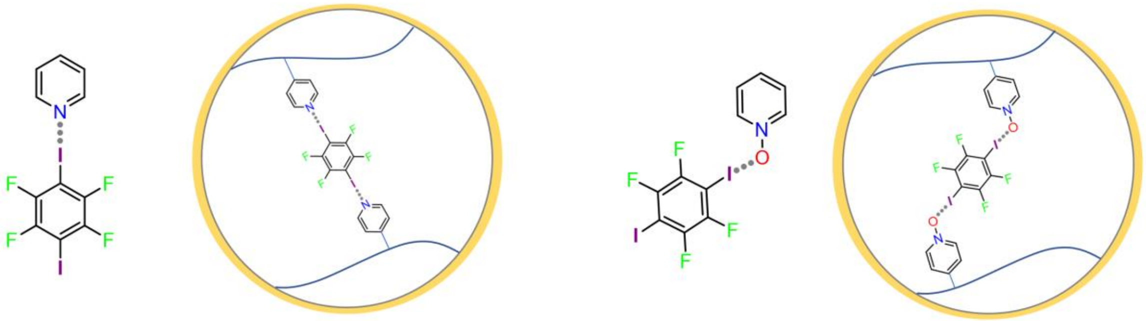
Identifying robust non-covalent interaction modules is crucial for many applications including drug discovery and materials. Examples of such modules include hydrogen bonds, spanning from one to sextuple hydrogen-bonded motifs, which are frequently utilized for assembling simple molecular systems into more sophisticated and complex structures. The benefits of hydrogen bonding motifs include synthetic accessibility, directionality, and responsiveness to external stimuli. Similarly, halogen bonding, "a long-lost brother of hydrogen bonding", involving a polarized electron deficient halogen atom interacting with an electron rich counterpart, typically a nitrogen atom, has manifested itself in applications in a variety of fields. The halogen bonding to an oxygen atom, instead of a nitrogen atom, has attracted much less interest. The talk covers recent findings that demonstrate how a previous understanding of pyridine halogen bonding motifs has been used to generate new functional materials. It also summarizes aromatic N-oxide halogen bonding modules that can be useful to develop a range of supramolecular polymers.



Pyridine halogen bonding module

Supramolecular functional polymer

Pyridine N-oxide halogen bonding module

Supramolecular functional polymer?

Figure 1: Pyridine and pyridine N-oxide halogen bonding motifs and their use in supramolecular functional polymers

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OC7: ECD spectra of porphyrin complexes using TD- DFT

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The determination of molecular stereochemistry and absolute configuration is an important part of modern chemistry, pharmacology, and biology.[1] Chirooptical spectroscopy, based on the different response of a substance to light with left and right circular polarization, makes it possible to distinguish between enantiomers and determine absolute configuration of diastereomers. Among the methods of chirooptic spectroscopy, electronic circular dichroism (ECD) is one of the most used methods for determining the absolute configuration.[2] However, the main requirement for measuring of an ECD spectrum is the presence of chromophores in the molecule under study. The effect of chirality transfer, when a chiral guest forms a chiral supramolecule with achiral porphyrins (strong chromophores), makes it possible to overcome this limitation (Figure 1). Moreover, with the development of theoretical and computational chemistry (in particular, the time dependent density functional theory (DT-DFT) approach), both interpretation and rationalization of induced ECD spectra in porphyrin-based supramolecules became possible.

Here, based on the DFT and TD-DFT approaches, factors affecting the induced ECD spectra of mono-porphyrin complexes (conformers, presence of another chromophore, distortion of the porphyrin plane) will be considered.

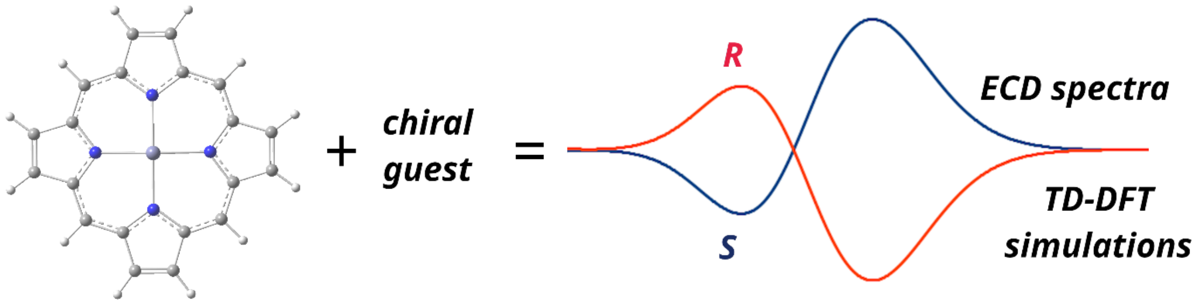

Figure 1: Effect of chirality transfer.

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OC8: Shedding Light on the Structural Polymorphism of G-Quadruplexes using Raman Optical Activity

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Molecular self-assembly of nucleotides and their oligo- and poly- forms is a prevalent phenomenon that establishes the structural and functional framework within living cells. Among mononucleotides, Guanosine 5’-monophosphate (5’-GMP) and its derivates exhibit a remarkable ability to form distinct structures at higher concentrations. Initially, 5’-GMP molecules associate to form G-quartets[1] through hydrogen bonding which subsequently stack to generate ordered structures known as G-quadruplexes (G4). The stability of G4 structures arises from various factors, including Hoogsteen base pairing, stacking, hydrophobic interactions, cation coordination, and hydrogen bonds between adjacent mononucleotide phosphate and hydroxyl groups.

In this study, we employed Raman spectroscopy and its chirally sensitive variant, Raman optical activity, to investigate the process of 5’-GMP agglomeration. Our findings demonstrate the exceptional sensitivity of ROA to GMP self-association. The formation of G4 structures was accompanied by enhanced intensity and sharpening of ROA bands, particularly in the terahertz region, which enabled the examination of their secondary structures, stability, and dynamics. Additionally, we observed structural transitions between different types of G4 secondary structures when stabilized by Li ions. Moreover, we discovered that the stability of the agglomerates was significantly reduced (with a drop in melting point of ~ 30°C) upon the replacement of ribose with 2’-deoxyribose. Other vibrational techniques, such as infrared spectroscopy (IR) and vibrational circular dichroism (VCD), were also employed in this study. Furthermore, Raman microspectrometry and X-ray diffraction were utilized to investigate the solid-phase agglomerates.

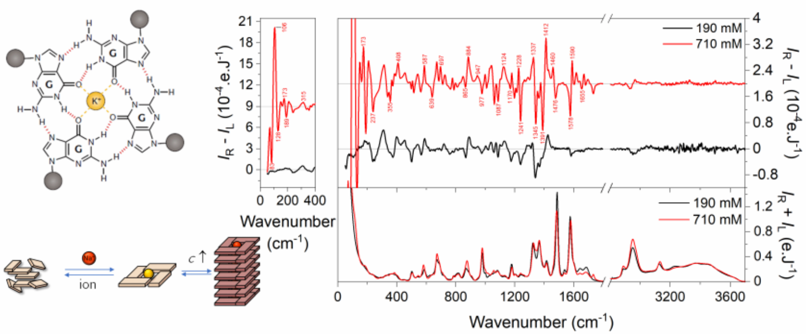

Figure 1: Structure of G-quartet and scheme of formation G4 (left). The concentration dependency of 5’-GMP with Na^+ ions at pH ~ 8.5 indicates the formation of G4 (right).

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OC9: Molecular Crystals for Nonlinear Optics – Vibrational Spectroscopic Characterization and Study of Phase Transformations

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Hybrid crystalline materials based on polarizable organic molecules, which act as carriers of nonlinear optical (NLO) properties, are still very attractive field of material science. The variety of selected promising molecules provides great potential for crystal engineering of novel molecular crystals with advantageous physical and chemical properties. The obtained materials benefit from the existence of hydrogen bonds as a key interaction in the molecular self-assembly process leading to crystal formation. The energy of formed hydrogen bonds counteracts the natural tendencies of the organic molecules to form centrosymmetric pairs. The resulting NLO properties – based on $\chi^{(2)}$ and $\chi^{(3)}$ processes – could provide several technical applications ranging from harmonic generations to stimulated light scattering.

This contribution deals with the characterization of selected hydrogen-bonded molecular materials – i.e. salts and co-crystals of guanidine and pyrimidine derivatives with inorganic and organic anions – by the combination of experimental (e.g. FTIR spectroscopy, Raman spectroscopy, X-ray diffraction and calorimetry) and theoretical (solid state quantum-chemical calculations) methods. Particular attention will be focused on the vibrational spectroscopic characterization of the studied phases and the explanation of the observed phase transformations (see Figure 1). Moreover, linear and nonlinear optical properties of the promising materials will be discussed.

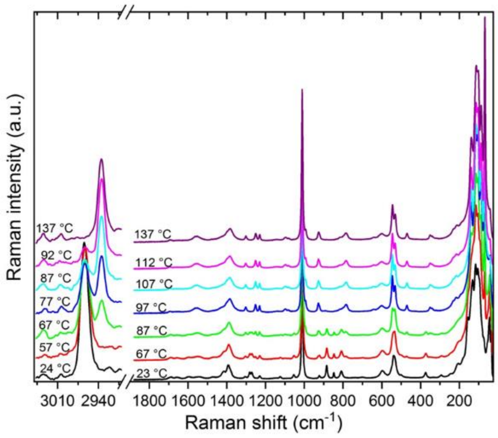

Figure 1: Temperature-dependent Raman spectra of guanidinium L-tartrate

Acknowledgements: Financial support from the CUCAM project (project No. CZ.02.1.01/0.0/0.0/15_ 003/0000417) is gratefully acknowledged

OC10: Improvements of a noninvasive Blood Glucose Assay using diffuse Reflection NIR-Spectroscopy

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Noninvasive blood glucose measurement technology is an important field of medical research. Diffuse reflection NIR spectroscopy of skin is a promising approach to realize such a noninvasive assay.[1] The performance of a custom-built noninvasive NIR spectrometric measurement system based on a rotational ellipsoidal mirror[2,3] to focus backscattered photons, was investigated by various skin phantoms. Lean muscle tissue or phantoms from gel-building gelatin as matrix scaffold with defined water and glucose content were chosen with scatter either with particles of TiO_2 or glass fiber paper. The accessory allowed us to study tissue spectra within 10000 to 4000 cm^{-1} with different photon penetration depths by varying the aperture in front of the InGaAs photo-detector. By this, the solid angle for the accumulated backscattered photons is changed discriminating photons escaping the same skin area at high angles, allowing calculating difference spectra, which are representative for deep-lying dermis layers by eliminating surface variations.

For the simulation of scattering by the *stratum corneum*, an NIR-transparent porous Teflon film was implemented as superficial layer. Further investigations were carried out on the effect of optical clearing by application of a perfluorinated polyether liquid, which reduces scatter from the horny skin layer and allows refractive index matching to the immersion lens of the reflection accessory used for reproducible skin presentation. Remarkably. the phantoms developed bear considerable potential for optimizing the noninvasive NIR spectrometric skin measurement technique and quantitative multivariate determination of glucose, whereby the composition complexity can be enlarged to approximate the relevant *in-vivo* conditions for skin measurements.

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OC11: Modified glucose as a sensor to track the metabolism in single endothelial cells - observation of the "Raman spectroscopic signature of life" band

Anna Pieczara[1,2], Aleksandra Borek-Dorosz[3], Szymon Buda[3], William Tipping[4], Duncan Graham[4], Robert Pawlowski[5], Jacek Mlynarski[5], Malgorzata Baranska[1,3]

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Endothelial cells (ECs) play a significant role in a healthy and dysfunctional state, the latter is correlated with a range of lifestyle diseases. Therefore, knowledge of the dysfunctional state, cellular metabolism, and especially glucose metabolism, is important from the point of view of studying disease mechanisms. The metabolism and glucose uptake may reflect the physiopathological conditions and cell activity correlated with energy metabolism. In this research labeled Raman microscopy was used to investigate the metabolism and tracking of glucose uptake in healthy and dysfunctional endothelial cells. The alkyne-labeled glucose, 3-OPG, was used as a tool to track its accumulation and then metabolism in live and fixed ECs by employing two spectroscopic techniques, i.e. spontaneous Raman and stimulated Raman scattering microscopies. The results showed that 3-OPG is suitable sensor for monitoring glucose metabolism in both normal and inflammatory conditions, by analyzing the Raman band of 1602 cm^{-1} attributed to the glucose metabolites, and the 2124 cm^{-1} Raman band of glucose accumulation. The study also revealed that glucose metabolism and uptake are slowed down in inflammation. Gaining further knowledge about metabolic patterns in the endothelium, and especially in the various pathologies affecting ECs, should open up valuable opportunities for entirely new medical treatments.

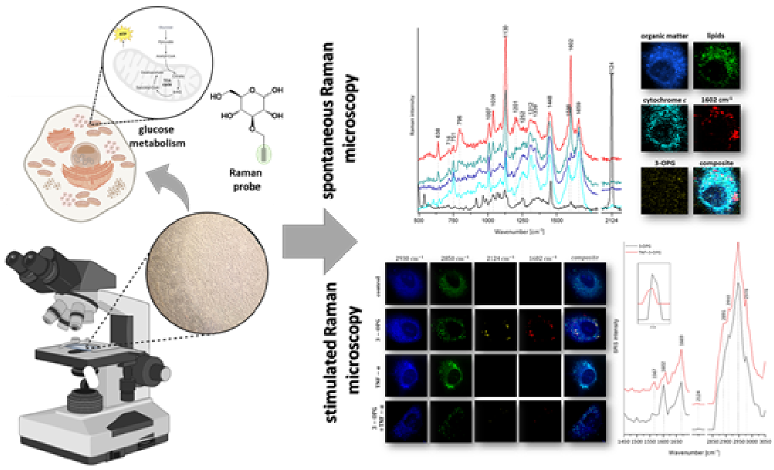

Figure 1: Schematic representation of the experimental with the microscopic techniques used in the study.

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OC12: Effects of sodium, magnesium and manganese ions on the structure of short-chain DNA

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The double-stranded DNA exhibits complex polyelectrolyte behavior modulated by the type, valence and concentration of the positive counterions that surround it, as well as the polyion length and concentration. Two distinct regimes should be noted when considering the length and concentration of DNA: semidilute and dilute. In the semidilute regime, DNA concentration is high, and the chains are long enough to become entangled, whereas in the dilute regime, each segment is well-separated from the others. Over the last years, we have conducted extensive dielectric spectroscopy measurements on polydisperse 2-20 kbp DNA chains with an average length of 4 µm (long-chain DNA) and monodisperse 146 bp DNA fragments of 50 nm (short-fragment DNA) which surveyed the electrostatic repulsion regime in semidilute and dilute limits, respectively [1-3]. In more recent years, our research has focused on the vibrational dynamics of long-chain DNA in the single and mixed ion atmospheres under semidilute DNA conditions [4-6].

In this study, we employ FTIR spectroscopy to investigate the dynamic and structural aspects of short-chain DNA thin films with the estimated DNA fragment length of 5-17 nm (15-50 bp) in the presence of sodium, magnesium and manganese counterions, while also providing a comparative overview of previously obtained results on long-chain DNA. Ion atmosphere has been controlled by the counterion to phosphate molar concentration ratio *r*, which varied between 0.1 and 2. In order to potentially differentiate between the semidilute and dilute solution regimes, three distinct short-fragment DNA concentrations were prepared; 5 g/L, 1 g/L and 0.1 g/L. By comparing the short-chain DNA studied in this research with the long-chain DNA analyzed in our previous studies, we observe that Mg^{2+} counterions have similar effect on vibrational signatures, regardless of chain length, at DNA concentrations of 5 g/L and 1 g/L. In contrast, Mn^{2+} counterions exhibit distinct changes, particularly at DNA concentrations $\leq$ 1 g/L, indicating a modified screening effect of Mn^{2+} counterions in the case of dilute regime.

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OC13: Thermotropic phase transition of dehydrated glycerophospholipids monitored by drop coating deposition Raman spectroscopy (DCDRS)

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Glycerophospholipids as one of the main components in the cell membrane are extensively studied to understand their properties and behavior. To explore the properties of lipids in biological membranes, liposomes composed of one type of lipids are commonly used. Liposomes undergo physical changes over temperature range denoted as the thermotropic phase transitions. The most studied transition is from a gel phase to a liquid crystalline phase known as a main transition attributed to the "chain-melting" of the hydrocarbon tails. It is characterized by a temperature T_m specific for each lipid. Many techniques are available to study phase transitions including differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), fluorescence spectroscopy, or vibrational spectroscopy [1]. Raman spectroscopy is a rapid and non-invasive analytical tool providing unique information about the vibrational motion of molecules. The method requires minimal sample preparation and is sensitive to structural changes present during the phase transition of lipids. Raman spectra obtained from the gel and liquid crystalline state of lipids can reveal relevant changes related to the structural alternations during the transition.

Here we focused on the thermotropic phase transition of lipids in a dry state studied by drop coating deposition Raman spectroscopy (DCDRS). The method is based on the evaporation of a solvent from a small droplet of a studied solution or suspension deposited on a hydrophobic substrate. The evaporation of a droplet leads to the preconcentration of the analyte into a dried pattern ("coffee-ring" for lipids) from which the Raman spectra are acquired [2]. DCDRS technique enables to obtain Raman spectra from small sample volumes at very low initial concentrations in comparison with the conventional Raman measurements. Raman spectra from dried deposits of different glycerophospholipids (differing in acyl chain length and type of the head group) were acquired in the temperature range covering the phase transition. Changes in spectral bands (intensity ratio, wavenumber shift) related to the phase transition were observed mainly in spectral regions for C-H stretching vibration (2800–3100 cm^{-1}) or C-C stretching vibration (1050–1150 cm^{-1}) of alkyl chains [3].

Acknowledgement: Financial support from the Charles University Research Centre SVV260716 is gratefully acknowledged.

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OC14: IR and Raman spectroscopies for the complementary diagnosis of psychiatric and neurodevelopmental disorders

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Psychiatric and neurodevelopmental disorders, like autism, schizophrenia and bipolar diseases, with the lack of proper treatment, have negative impacts on the individuals and society, and can result in unnecessary disability, unemployment, substance abuse, homelessness, inappropriate incarceration, suicide, and poor quality of life. Psychiatric diagnoses are complex and based on subjective interviews and questionnaires. Due to the heterogeneity of their symptoms, the initial clinical diagnosis can end up with 30-70 % errors. The reliability of psychiatric diagnosis can be enhanced by using complementary molecular based strategies, which may successfully help the clinicians to improve the accuracy of their medical diagnosis. Vibrational spectroscopic methods can be used to achieve this goal, by identifying the spectroscopic features (biomarkers) through analysis of body fluids. These techniques have already been used for biomarker detection for many other diseases, such as cancer, Alzheimer's and Parkinson's diseases.

In this study both IR and Raman Spectroscopies, together with chemometric methods, have been used as sensitive, fast and cheap analytical techniques for complementary diagnosis of schizophrenia and bipolar diseases, and other neurodevelopmental disorders, specifically autism spectrum disorder (ASD) and attention deficit and hyperactivity disorder (ADHD). The analytical statistic models are based on the spectra of patients' blood serum samples, and were applied for ASD, ADHD, schizophrenia and bipolar diseases (including subgroups: bipolar depressive episode, manic episode and otimic), and allow the discrimination of the diseases with good sensitivity and sensibility.

Acknowledgements

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OC15: The degradation progression studies of human knee cartilage tissues with Raman spectroscopy measurements

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The loss of synovial fluid and changes in cartilage structure can lead to changes in the mechanism of joint function and in tribological properties. Such disruptions lead to degeneration of joint surfaces and the formation of arthritis. This degenerative joint disease (osteoarthrosis) is one of the leading causes of disability in the world population. Degradation assessment of cartilage tissue in joints is essential for diagnosing the progression of osteoarthritis. No effective test methods for enabling such assessment are yet available on the market.

Raman spectroscopy is proving to be one of the techniques that allow tissue surface analysis. Quantitative and qualitative analysis, as well as the study of intermolecular interactions, enable the determination of the relationship between the structure of articular cartilage and the degree of degeneration. The technique's adaptability may allow its application in a clinical study. With the use of a probe, it may be possible to perform in vivo studies. Such an approach would allow the degree of cartilage degradation in a joint assessment during an arthroscopy procedure.

Raman spectroscopy allows the analysis of joint tissue providing information on molecular changes caused by the progression of degradation (Pavlou 2018). The scope of the study included the analysis of human knee cartilage with varying degrees of degradation taken from different patients during endoprosthesis implantation. Research to date has shown that measurements using Raman spectroscopy can identify damaged tissues.

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OC16: Tracking metabolic changes in cancer cells using Raman imaging

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Cancer cells are able to continuously adapt to changing conditions by actively reprogramming their metabolism. This leads to the uncontrolled proliferation of malfunctioning cells and a subsequent increase in the number of malignant cells and tumour mass. This impacts significantly difficulties in leukaemia diagnosis and treatment. To better understand what alterations, control the metabolism of haematological malignancies comprehensive spectroscopic research focused on biochemical profiling using label-free Raman imaging to monitor metabolic changes in leukaemia cells was proposed.

Using Raman confocal microscopy molecular and morphological evaluation of representing *in vitro* models of leukaemia and lymphoma was obtained. Chemometrics methods were applied to identify differences in the spectral profile of normal and malignant cells and to develop classification algorithms enable to distinguish subtypes of leukaemia and lymphoma cells.

Obtained results revealed spectral, and therefore chemical, differences between normal and leukaemia cells were identified. The highest differences were observed in the intensities of Raman bands originating from proteins (mostly hemoproteins), nucleic acids, lipids, and carotenoids. These biomolecules have been identified as diagnostic markers in Raman-based classifications of cells. Alterations in their content and contribution are crucial in understanding molecular alterations in cancer metabolism and oncogenesis processes. The presented approach of Raman-based diagnostic leukaemia screening is also a novel approach offering the possibility of developing faster diagnostics and testing of new treatment methods.

The „Label-free and rapid optical imaging, detection and sorting of leukemia cells" project is carried out within the Team-Net programme of the Foundation for Polish Science co-financed by the EU. POIR.04.04.00-00-16ED/18-00

OC17: Resonance Raman optical activity spectra of chiral and light-absorbing molecules: atropisomeric naphthalenediimides case

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Chiral phenomena based on different absorption or scattering of left and right circularly polarized (CP) light attract attention because they deliver rich structural information about molecules, usually in the form of spectral bands differing in sign. They sensitively reflect molecular conformation most greatly in solutions. Commonly utilized chiroptical techniques are electronic circular dichroism (ECD) and vibrational circular dichroism (VCD), measuring the difference in absorption of the left and right CP light, circularly polarized luminescence (CPL) registering the difference in luminescence and Raman optical activity (ROA) which measures the intensity difference in Raman scattering of right and left CP light. More specialized techniques use the resonance effect (resonance Raman optical activity, RROA) or magneto-optical effects (magnetic circular dichroism, MCD, and magnetic Raman Optical activity, MROA).

However, using a resonance effect is not straightforward for ROA spectroscopy. We have reported that true RROA spectra of color and resonating compounds may be masked by other effects, such as ECD in combination with (CP)Raman (i.e., ECD-Raman effect). The ECD-Raman effect has probably been ignored in many previously conducted RROA measurements that could result in incorrect interpretation of experimental data. In resonance conditions, the sample absorbs the incident light, which gives rise to the imbalance of left and right CP components of incident light when the samples exhibit ECD. Typically, the scattered light is also absorbed under resonance terms, which can cause the imbalance of the scattered light's left and right CP components. These effects of ECD produce vibrational bands different from the ROA signal and contaminate the ROA spectrum. An example of the ECD-Raman effect is recording a strong signal of achiral solvents (e.g., DMSO, $CHCl_3$) in the presence of chiral solutes (e.g., cobalamin derivatives).[1] Moreover, this effect is observed not only for solvent signals but also on those from chiral, light-absorbing solutes. Our study shows that the ECD-Raman effect is the dominant factor over the natural ROA in a series of atropisomeric naphthalenediimides and can be extracted from the recorded ROA spectra using a newly developed experimental and computational strategy.[2]

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OC18: 2D-COS in a Neolithic graphite bead analysis

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Graphite was widely used in ancient cultures, which is confirmed by archaeological excavations. An example of such an object was a bead from a Neolithic site close to Kraków. The origin of the material of the object is made is always intriguing. Knowledge of the structure of the material can be useful and helpful in deciphering it. Therefore, the aim of the research was to characterize the material used for the production of the graphite bead at the molecular level, to check its homogeneity and the presence of any admixtures.

Raman microspectroscopy has been used as the method of choice for the study of carbon materials, additionally a non-invasive test method not interfering with the tested object. Two laser lines were used as excitation sources: 514.5 nm and 785 nm, because each of them strengthens other moieties in the carbon material. The location of the bands, their intensity and half width, and finally the ratios of the respective band intensities indicate the degree of order in the graphite material [1].

Two-dimensional correlation spectroscopy was used to obtain additional information about graphite that is not directly visible in dynamic Raman spectra [2]. In this calculations as an external perturbation the spatial position in which the spectrum was measured was considered. The analysis points towards different graphite/carbon structural phases that correlates synchronously or asynchronously.

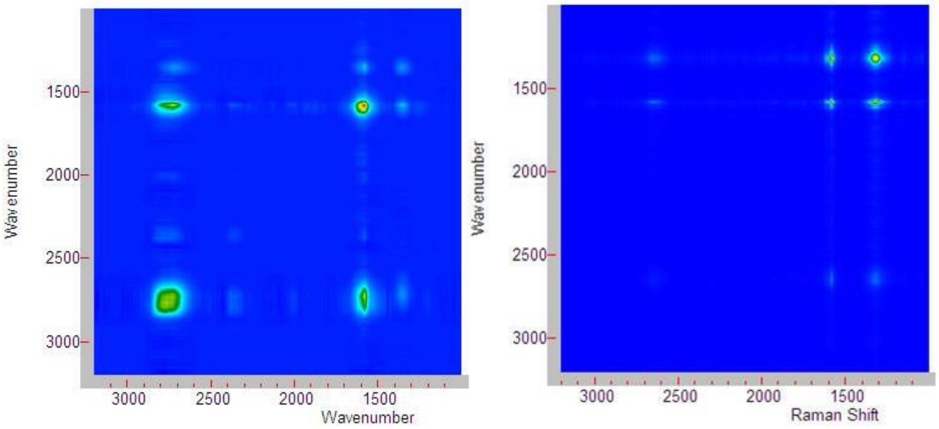

Figure 1: 2D Synchronous spectra, 514.5 nm (left) and 785 nm (right) excitation laser line.

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Posters

P1: Mechanisms of phase transitions in 2-bromoethylammonium bismuth bromide

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The bismuth-based halide hybrids composed of halogenobismuthate anionic subnetworks intercalated by organic cations form a very large group of compounds. Because of the many structural motifs of the anionic subnetwork, compounds of this class can form a wide range of crystal structures with varying dimensionality. Organic-inorganic halide hybrids based on bismuth ions have generated ongoing attention due to their potential ferroelectric, thermochromic, luminescent, optoelectronic, semiconducting, and dielectric properties [1,2].

The crystals of 2-bromoethylammonium bismuth bromide experience three phase transitions at about 256, 342, and 371 K. At lower temperatures, two of them are second-order, while the other is first-order and isostructural. The high-temperature phase I is dynamically disordered, according to temperature-dependent XRD, IR, and Raman measurements. Organic cation disorder is partially suppressed in phases II and III and eventually disappears in low-temperature phase IV.

Our research is primarily concerned with describing the mechanisms of crystal transformations that occur in terms of changes in molecular dynamics, hydrogen bond rearrangement, and structural deformations of inorganic sub-lattice. Furthermore, we aimed to understand how changes in the halide ligand and bromination of organic cations affect the key structural, phonon, thermal, dielectric, and optical characteristics. A better knowledge of the structural characteristics is especially important for future applications.

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P2: Assurance of insulin quality by infrared ATR spectroscopy of dry-film preparations and HPLC measurements

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For the analysis of human and analog insulin formulations as well as their quality monitoring, reliable analytical methods are required after recent publication of alarming studies on insulin formulations as available from pharmacies. Human insulins and their analogs can undergo different degradation processes on a molecular level, when exposed to stress conditions such as temperatures or shear strain, deviating from recommended manufacturer's storage recommendations. These molecular processes lead to conformational reorganization of the insulin molecules, followed by irreversible agglomeration and fibrillation, accompanied by biological potency decrease.

For the quality assessment of human and analog insulin formulations, reliable analytical methods are required. Infrared spectroscopy offers a reliable approach for quantitative and qualitative insulin monitoring without the application of sophisticated HPLC reference methods, as requested from international pharmacopoeias.[1,2] Different from such standard methods, measurements for total insulin quantification and formed aggregates were done by using an efficient reversed-phase HPLC method. Changes in the molecular structure of short- and long-acting insulins were observed after several weeks when stored at 37 °C. When kept at ambient temperatures or just above 0 °C, no significant changes were found for formulated insulins, in contrast to samples purified by ultrafiltration. An analysis of the insulin`s secondary structure reveals early molecular conformational changes as identified by IR-spectroscopy of dry-film samples. Agglomerates were detected by using our novel HPLC protocol and comparative IR and SDS PAGE measurements confirming extensive misfolding. Consequently, infrared spectroscopy offers a reliable method for quality assurance and quantification of commercial insulins for replacing current pharmacopoeial methods.

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P3: Immobilization of proteins on silver halide fibers by 12-mercapto-dodecanoic acid NHS ester for signal enhanced infrared spectroscopic biosensing

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Evanescent wave spectroscopy based on silver halide fiber elements is frequently used for chemical and biochemical analysis.[1,2] By surface modification of the wave-guide materials the selectivity for special analytes can be warranted. Surface-modified sensors of different geometries for signal enhancement were prepared from an N-hydroxysuccinimide (NHS) ester derivative containing a long-chain alkane with a reactive thiol group for forming self-assembled monolayers (SAM) on silver halide as substrate as a first step. Hereinafter, these NHS ester compounds function as coupling agent to covalently bind amine-containing biomolecules (e.g., enzymes, antibodies or peptides) for the fabrication of bioanalytical sensors of high selectivity, aiming at the immobilization of special proteins for specific antigen-antibody interaction. The kinetics of the two-step preparations, i.e. SAM formation and protein binding, operating expenses and efforts have been studied in particular. After antibody immobilization, the disposable sensor elements could be used for a follow-up step of selective binding of special peptides or proteins, extracted from complex bodyfluids such as plasma or cerebrospinal fluid (CSF) and representing specific health indicators. The latter process can be seen as an enrichment step for quantification or a further secondary structure analysis as illustrated for Alzheimer screening. Such disposable infrared immuno-sensors will play a significant role in future medical diagnostics.

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P4: NIR-Spectroscopy of Grass Forage – Sampling Aspects for dried Powders and Consequences for multivariate Calibrations

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For decades now, NIR spectroscopy has been used for rapid and non-destructive quantitative analyses of forages. A powerful measurement technique is diffuse reflection spectroscopy, which can be applied to powders, requiring little preparation. Important for routine work are multivariate PLS calibrations, which require a population of samples representative for the forage to be analyzed. For reference analysis often laborious analytical methods are applied that can handle larger forage specimens for assuring representative analytical results.

Whole grass samples were dried and milled to powders with the fibrous part of sub-millimeter size. Sieving of the milled samples was also carried out for analysis of particle size fractionated grass. From the powderous samples, diffuse reflection spectra were recorded by using an ellipsoidal mirror-based accessory attached to a Bruker Vector FT-NIR spectrometer[1, 2]. Samples were repeatedly cup-loaded, leading to a five-fold spectral data set for each forage sample. Such spectra were averaged providing another calibration data set leading to a smaller cardinality of the calibration population, but being more representative for the studied samples. Besides the use of raw spectra, pretreatment such as derivation was applied for the spectral range of 7600 – 4000 cm^{-1}. For calibration optimization, different numbers of PLS factors were obtained by either using all spectra or mean spectra of the five-fold measurements for several parameters such as sugar, hemi-cellulose, raw protein and others, also based on different validation schemes. Interesting results are obtained for the milled grass after sieving, which show significant variations in composition for the different size fractions.

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P5: Vibrational spectroscopic markers of high and low molecular hyaluronic acids for detection of colorectal carcinogenesis

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Vibrational spectra exploit the capability of intrinsic markers and provide biochemical information without additional fluorescent or radioactive labeling. Hyaluronic acid (HA), a polysaccharide of the extracellular matrix, is one of such intrinsic biomarker capable of cancer detection. It can regulate cell migration, proliferation, and differentiation during homeostatic and pathological processes, including carcinogenesis. HA contributes to cellular recognition dependently on its molecular mass and other structural parameters. Spectroscopic tracking of changes in HA during carcinogenesis supports the recognition of cancer lesions.

This work focuses on specific HA vibrational bands sensitive to colorectal carcinogenesis. FTIR and Raman (λ_{ex} 785 nm) spectra of colon tissues and benign and malignant colon polyps were compared to the corresponding spectra of hyaluronic acids of various molecular masses and model oligosaccharides. HA samples differ in their vibrational spectra depending on their molecular masses (Fig. 1), and specific molecular size-depending bands and regions were described using multivariate analysis. These sensitive bands were attributed to the specific vibrations based on the calculations of vibrational spectra of HA building blocks both in vacuum and water. The corresponding spectral regions, obtained for colon tissues and colon polyps, were examined for the contribution of HA vibrations.

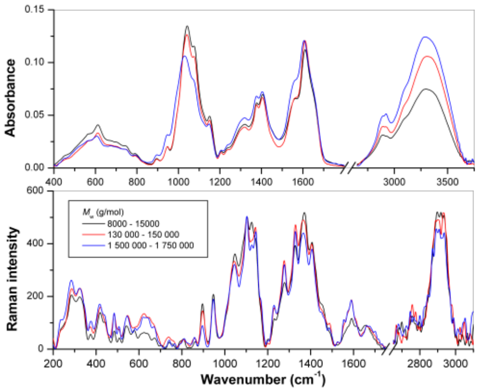

Figure 1: FTIR (top) and Raman (bottom) spectra of HA of various molecular masses.

Acknowledgment: This research was funded by the Ministry of Health of the Czech Republic grant No NU20-09-00229.

P6: Vibrational spectra of polysaccharides isolated from medicinal mushrooms of genera *Pleurotus*, *Ganoderma* and *Hericium*

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Vibrational spectroscopic methods are effective in the structural analysis of natural polysaccharides, including glucans, which are polymers of glucose units linked at various configurations. Mushrooms are the source of immune active cell wall polysaccharides, which include structurally diverse glucans (1), chitin (2), and heteropolysaccharides like mannogalactans (3). Composition, molecular mass, and structure influence their physical properties and biological activities, a prerequisite for food and medicinal applications.

This work focuses on vibration spectroscopic analysis of purified polysaccharide fractions isolated from fruiting bodies (basidiocarps) of medicinal mushrooms (genera *Pleurotus*, *Ganoderma*, and *Hericium*) by successive extractions with cold water, hot water, and alkaline solution. Small molecules were washed out by acidified ethanol, and proteins were removed by the treatment with proteolytic enzymes (pepsin, pronase). FTIR and FT Raman spectra obtained from purified polysaccharides were analyzed compared to those of commercial polysaccharides yielding specific bands sensitive to the configuration of glycosidic bonds and monosaccharide units. The results obtained from the spectra were consistent with the GC-FID monosaccharide composition analysis. Vibrational spectra can assist in identifying and distinguishing fungal polysaccharides and determine their presence in basidiocarps and thus assess the quality and potential of mushroom raw materials for the preparation of dietary supplements.

Acknowledgment: This research was supported by the Ministry of Agriculture of the Czech Republic, project No QK1910209, and by the grant of Specific University Research, grant No A1_FPBT_2023_006.

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P7: Structure, spectra and photochemistry of 2-amino-4-methylthiazole: FTIR matrix isolation and theoretical studies

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Thiazoles are basic heterocyclic compounds with five-membered ring including one nitrogen and one sulfur atom. Many compounds containing the thiazole system in the molecule exhibit a broad spectrum of pharmacological activity. Sulfathiazole, Ritonavir, Abafungin, Tiazofurin or Bleomycin are often used antimicrobial, antiretroviral, antifungal, antineoplastic or antitumor drugs with the thiazole ring in the structure, respectively. [1,2]

The structure, tautomerization pathways, vibrational spectra and photochemistry of 2-amino-4-methylthiazole (AMT) molecule were studied by matrix isolation FTIR spectroscopy and DFT calculations undertaken at the B3LYP/6-311++G(3df,3pd) level of theory. Out of eight optimized isomers of this molecule located on the singlet potential energy surface the most stable one, the amine tautomer with the five-membered ring stabilized by two double C=C and C=N bonds, was detected experimentally in argon matrices after deposition.

When the AMT/Ar matrices were exposed to 265 nm irradiation emitted by a tunable laser beam, three main photoproducts, N-(1-sulfanylprop-1-en-2-yl)carbodiimide (fp1), N-(1-thioxopropan-2-yl)carbodiimide (fp2) and N-(2-methylthiiran-2-yl)carbodiimide (fp3), were produced by a cleavage of the CS-CN bond with hydrogen atom migration.

The minor photoreaction caused by the cleavage of the CS–CC bond and followed by hydrogen migration formed 2-methyl-1H-azirene-1-carbimidothioic acid (fp15) molecule. We have also found that cleavage of the CS–CN bond followed by disruption of the N–C bond produced cyanamide (fp11) and the $^{\bullet}$C(CH3)=CH-S$^{\bullet}$ biradical that transformed into 2-methylthiirene (fp12) and further photoreactions produced 1-propyne-1-thiole (fp13) or methylthioketene (fp14). Cleavage of the CS–CC bond followed by disruption of the N–C bond produced propyne (fp22) and the $^{\bullet}$S-C(NH$_2$)=N$^{\bullet}$ biradical that transformed into 3-aminethiazirene (fp23); further photoreactions produced N-sulfanylcarbodiimide (fp25).

As a result of these transformations several molecular complexes were identified as photoproducts besides new molecules in the AMT photolysis process. [3] The molecular complexes presented in this paper may have potential significance for astrophysics, astrochemistry or astrobiology.

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P8: FTIR spectroscopic studies of matrix-isolated 3-thio-1,2,4-triazole complexes with dinitrogen. First experimental evidence for the UV-induced formation of thiol$\cdots N_2$ complexes

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Weakly bound molecular complexes are involved in many biological and chemical processes, including those occurring in the Earth's atmosphere. Dinitrogen, being its most abundant component, was found to interact strongly with various molecules, considerably changing their spectroscopic properties [1,2]. Heterocyclic compounds are often characterized by the presence of a rigid structure containing acidic A-H moieties as well as electron pair donors. They are widely used e.g. as building blocks for the formation of various metal–organic frameworks (MOFs) designed for many purposes, including gas storage and separation [3].

In this work, complexes of 3-thio-1,2,4-triazole (ST) with N_2 were studied theoretically by the DFT/B3LYP-D3 method and experimentally by FTIR spectroscopy combined with the matrix isolation technique and UV laser irradiation. The computational results show that ST interacts specifically with dinitrogen in several different ways. For the 1:1 complexes of the most abundant ST thione tautomer, three stable minima were located on the potential energy surface. The two most stable structures, containing both N-H$\cdots$N hydrogen bond and S$\cdots$N van der Waals contact, were detected experimentally in the argon matrix after deposition. Interestingly, it was found that laser irradiation at $\lambda = 270$ nm, besides generating the thiol tautomer of ST, also leads to the formation of its corresponding complexes, characterized by N-H$\cdots$N hydrogen bonds. What is more, it appeared that the efficiency of hydrogen atom transfer in ST complexed with N_2 is lower than in the monomeric form. Based on the kinetic profiles, it could be also concluded that even a small admixture of N_2 (0.1 %) in the matrix environment noticeably slows down the process.

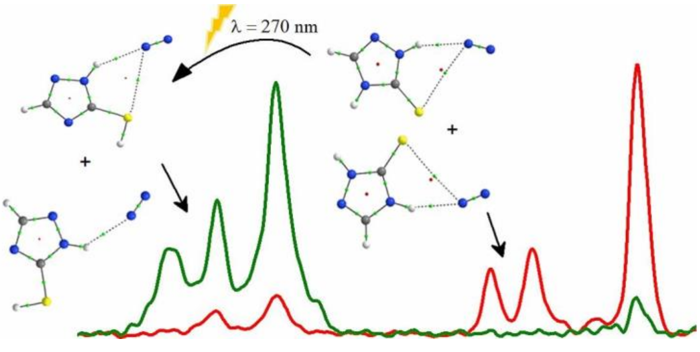

Figure 1. *Summary of the thione-thiol tautomerization process for 1,2,4-triazole-3-thiol complexes in a nitrogen-doped argon matrix.*

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P9: Photochemistry of 2-(tetrazol-5-yl)benzoic acid isolated in cryogenic matrices

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The most spectacular are applications of tetrazoles in medicine and pharmacy. Many of the medicinal applications of tetrazole derivatives originate from the properties of the tetrazolic acid fragment CN_4H. It has similar acidity to the carboxylic group, is almost allosteric with it, but is metabolically more stable. Hence, the COOH groups are often replaced by the CN_4H fragments in biologically active molecules and the tetrazole ring is found in drugs or potent medicines with diverse pharmacological activity. The title compound 2-(tetrazol-5-yl)benzoic acid (TAC) is an interesting molecule that contains both a carboxylic group and its isostere tetrazolyl group.

From the fundamental point of view, tetrazole derivatives have been found to be challenging molecules due to their interesting structures (tautomers/conformers) and usually rich photochemistry that strongly depend on the specific substituents attached to the ring. [1-3]

In this contribution, the molecular structure and photochemistry of TAC were studied in argon and nitrogen matrices by infrared spectroscopy and B3LYP/6-311++G(2d,2p) calculations.

TAC exists in two tautomeric forms: 1*H* and 2*H*. The infrared spectra of TAC/Ar and TAC/N_2 show that only 1*H*-tautomer is present in low temperature matrices. A global minimum is the *cis*-TAC-1*H*-1 isomer stabilized by the N-H···O intramolecular hydrogen bond.

Phototransformations of the monomeric TAC isolated in solid nitrogen were induced by narrow-band UV radiation from the OPO laser system. The monochromatic radiation of the 305 nm wavelength led to the *cis*-TAC-1*H*-1→*cis*-TAC-1*H*-2 transformation. Irradiation at 240 nm promotes the back reaction.

Photochemical decomposition of the studied compound was also observed. The obtained results indicate that the tetrazole ring cleavage and nitrogen elimination take place in the matrices leading to the carbodiimidyl benzoic acid formation.

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P10: Transient absorption oscillations during singlet fission in thin films of diketopyrrolopyrrole derivative

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Initial stages of the singlet fission (SF) process in bis(thienyl)- diketopyrrolopyrrole (Bu-TDPP) thin films, which provided triplet yield 160 % in a long-time asymptote [1], were studied using a transient absorption (TA) spectroscopy. Ultrafast oscillatory modulation in the ground state bleach recovery was observed persisting up to several picoseconds. The antiphase oscillations in the TA signal at 505 and 581 nm (Fig.1, left) with a period of 1.6 ps can be explained by the population exchange of singlet and triplet states controlled by low frequency vibrational modes. The excited state delocalization over two adjacent molecules at the centrosymmetric configuration enabled an efficient coupling of the SF process to the low-frequency intermolecular vibrational modes at ca 10 cm^{-1} (0.00125 eV). This coupling was explained by a very broad distribution of these low frequency modes ($\hbar\omega = 0.00125$ eV $\ll k_B T$), which promoted the population exchange between singlet and triplet states near crossing of their potential energy surfaces at the wing of the broad vibrational distribution (Fig.1, right).

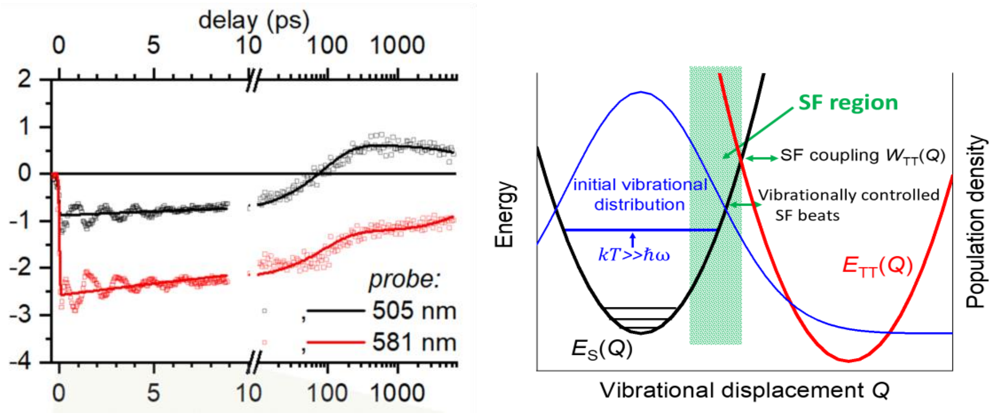

Figure 1: Left, transient absorption characteristics of Bu-TDPP thin films after photoexcitation by laser pulses with central wavelength 450 nm: the kinetics traces at various probe wavelengths shown in legends. Symbols denote the experimental data, and full lines show the best fits. Right, the process of the singlet fission.

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P11: DNA under different light: infrared spectroscopy, circular dichroism spectroscopy and UV-visible spectrophotometry study

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Fourier transform infrared spectroscopy (FTIR), circular dichroism (CD), and UV-visible spectrophotometry have been utilized to study influence of sodium, magnesium and manganese ions on the structure and dynamics of double-stranded deoxyribonucleic acid (dsDNA).

FTIR spectroscopy is a powerful tool for studying the interactions between metal ions and DNA [1-3]. CD, on the other hand, is a sensitive absorption spectroscopy technique that utilizes left- and right-circularly polarized UV light to examine the conformation of biomolecules [4,5]. UV-visible spectrophotometry is widely employed to study biomolecular conformation as well. Each of these techniques has its own advantages, but they also come with specific limitations when it comes to DNA concentrations. For CD and UV experiments, the DNA concentrations are typically limited to 10-100 μM for 1mm and 10 mm pathlength cuvettes. In the case of FTIR spectroscopy, the concentrations need to be in the mM range, which makes the analysis more challenging since DNA structural features must be analyzed under diverse environments.

In this work, we prepared and analyzed samples with a wide range of DNA concentrations and varying salt concentrations. Our aim was to test the screening ability of divalent cations under different conditions and interpret the charge neutralization that occurs with the addition of salt. To achieve this, we applied the approximate two-variable Manning condensation theory, which considers a mixture of two types of cations in our DNA systems. We use the counterion condensation theory for divalent cations as a convenient limiting result that can describe some features of the experiments in different ionic conditions and thus illuminate observed spectral signatures and differences observed across FTIR, CD and UV tehnicques.

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P12: Position dependent study on 2-, 3-, 4- and 5-Cyanoindole via high resolution laser induced Stark spectroscopy

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For indole and its derivatives exist two close lowest electronically excited singlet states, labeled L_a and L_b in the nomenclature of Platt [1,2]. The transition dipole moment orientation, the angle of the reorientation of the inertial axis system upon excitation, the leading contributions to the excitation to the lowest excited singlet state and geometry changes upon excitation are used for identification of these states. The parameters were accessible via rotationally resolved Stark spectroscopy, obtained from fit using an evolutionary strategy, for the lowest excited state in combination with *ab initio* calculations. It is commonly believed that L_a-states of substituted indoles tend to have larger dipole moments than the respective L_b-states, but the investigation of 2-cyanoindole (2-CI) concludes that the change of the permanent dipole moment upon excitation of the singlet state can not be used as a sensitive indicator anymore [3-5]. In this contribution investigations of the electronic nature of 2-, 3-, 4- and 5-cyanoindole (CI) are presented. The studies showed L_b character for the lowest excited state of 2- and 3-CI while for 4- and 5-CI the lowest excited state was determined to be an L_a-state [6-8]. A confirmation of the conclusion that substitution in the pyrrole ring leads to the L_b-state as lowest excited singlet state is possible, when the missing 6- and 7-CI will be investigated.

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P13: Franck-Condon analysis of the vibronic structure and excited state geometry changes in 3-Tolunitrile dimers

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Laser induced and dispersed fluorescence spectra measured under jet-cooled conditions can be utilized to optimize the calculated geometry changes upon electronic excitation postulated by ab initio methods. The ground state structure can be approximated with high precision but excited states pose a challenge for typical computational methods that need further modification. The calculation of Franck-Condon factors in combination with the simulation of emission spectra allows the analysis of the vibronic structure through the program FCFit by the assignment and targeted distortion of vibrational modes to modify the spectra and obtain a more accurate molecular geometry [1]. This method has successfully been applied in the past to determine the changes in bond lengths in 2-Tolunitrile (2TN) and 3-Tolunitrile (3TN), leading to similar results [2]. The process also allowed to examine the dimer and water clusters of 2TN [3]. In contrast 3TN possesses a wider range of possible dimers depending on the orientation of the methyl substituent permitting an *out* or *in* facing alignment which influences the vibronic structure. This work aims to determine the geometric changes of these dimers and to demonstrate the method of the program FCFit.

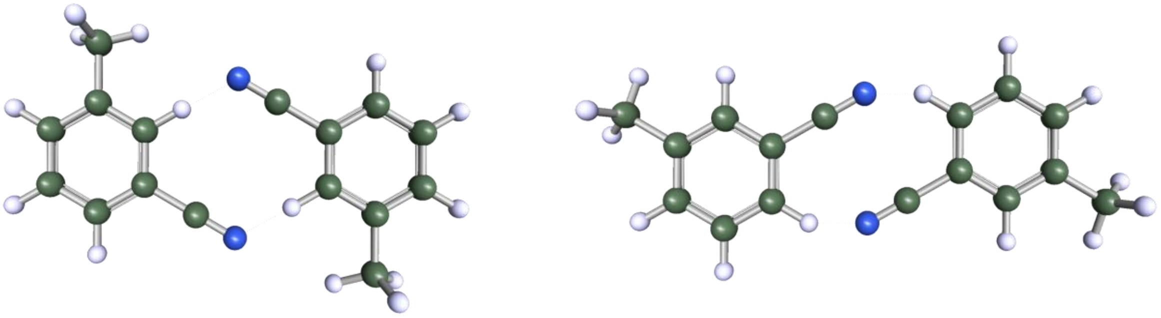

Figure 1: Two of the possible isomeric configurations of the 3TN Dimer with in (left) and out (right) facing methyl substituents.

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P14: Raman spectroscopy and 2T2D correlation study of lymphocytes in infectious mononucleosis

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The use of vibration spectroscopy in the study of biological macromolecules important to living organisms, tissues and cell components is already well proven, for example, tracking the activation of human lymphocytes after contact with a virus [1,2]. The analyzed blood samples were taken from patients diagnosed with infectious mononucleosis treated at the University Hospital in Krakow. The 520 cm^{-1} band indicating the formation of immunoglobulins, a biomarker of cell activation [2,3]. In addition, the mean spectra calculated for both healthy and EBV infected, as well as 2T2D correlation also indicate other differences (Fig. 1). In the range of CH stretching vibrations for blood cells infected with the EBV virus the intensity ratio of the I_{2930}/I_{2850} bands is 4.07, while for healthy blood cells it is 1.53. Changes in the aliphatic chains of lipids and proteins were also observed, as for blood cells infected with EBV the intensity ratio I_{2890}/I_{2850} is 1.53, and for healthy blood cells it is 2.46. The I_{1460}/I_{1445} intensity ratio for infected blood cells is 0.85 and for healthy cells 0.89, indicating conformational changes in protein binding that Proline seems to be involved in. Another feature for infected lymphocytes is the I_{903}/I_{896} intensity ratio equal to 1.09, and for healthy ones 0.94. The bands observed in the Raman spectra of infected leukocytes indicate an ongoing response of the body's immune system.

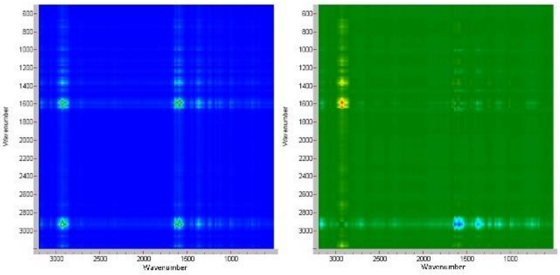

Figure 1: 2T2D synchronous and asynchronous map of healthy vs EBV infected lymphocytes.

Acknowledgment

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P15: A new class of tunable plasmonic nanostructures for detection of anthropogenic water pollutants by SERS spectroscopy

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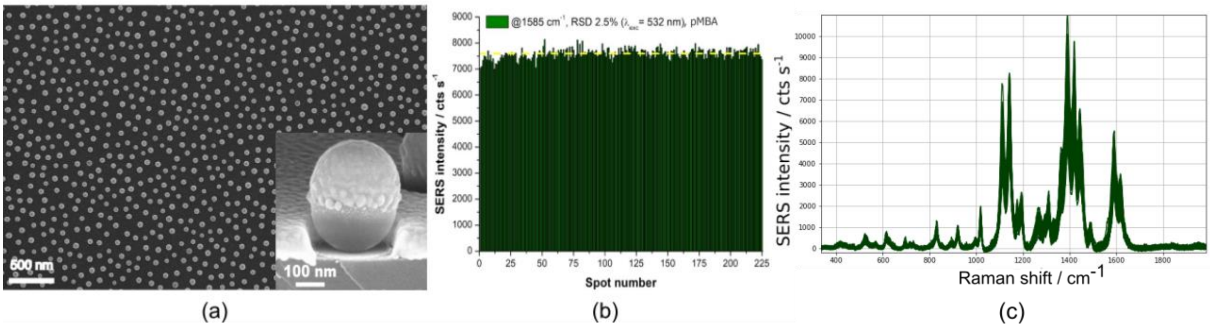
Nanostructures containing sub-10-nm wide gaps allow for extreme light trapping and enhancement at the nanometric scale due to the excitation of localized surface plasmon resonance. This makes them a perfect platform to amplify otherwise very weak Raman signal by exploiting the surface-enhanced Raman scattering (SERS) effect. However, SERS performance is strictly related to the quality of plasmonic substrate. Therefore, successful and reliable SERS measurements require numerous demands imposed on plasmonic nanostructures.

In this work, we propose a simple method of fabricating comprehensive plasmonic substrates in a novel geometry, providing a core-shell-like response. A modified nanosphere lithography method was used to create non-periodic arrays of nanoholes filled with metal-capped dielectric spheres (Fig 1a). This approach is quick, cost-effective, and allows for the simultaneous nanostructurization of multiple substrates. The resonance can be easily tuned from 300 nm to 1100 nm by controlling the synthesis conditions. This allowed for improved SERS performance due to matching plasmon resonance with the excitation wavelength or the analyte's absorption/Raman peak.

We first tested the substrates using p-mercaptobenzoic acid and obtained an extraordinarily low RSD of SERS signal: 2.5% for nearly 700 points a few mm apart (Fig 1b). After such benchmarking, we proceeded to detection of anthropogenic water pollutants (methyl red and methyl orange), and successfully identified low concentrations of these dyes without additional host-guest interactions (Fig 1c). This shows the potential of the new substrates to develop a universal methodological approach, adaptable to SERS detection of any analyte. The demonstrated uniform surface enhancement ensures high repeatability of SERS studies.



(a) (b) (c)

Figure 1: (a) SEM images of core-shell-like nanostructures, (b) SERS intensity distribution of p-mercaptobenzoic acid band at 1585 cm^{-1} across 225 spots, (c) 225 SERS spectra of 10^{-5} M methyl orange.