

Description of the main research directions investigated by the institute

The research directions of the institute during the period 2015 to 2019 covered several areas from theory, via molecular dynamics, gas phase ion chemistry, astronomically relevant spectroscopy, low dimensional systems (graphene etc.), biophysical chemistry, electrochemistry to catalysis. The main research directions correspond to the flat structure of the departments represented by the individual evaluated teams. Detailed description of the team focuses and results achieved during the evaluated period are given in the appropriate Reports on the research activities (Parts 3-4) thus only the main directions are overviewed here. The results are typically published in peer reviewed scientific journals, Web of Science database includes 924 articles, 43 reviews and 50 proceedings paper for the period 2015-2019.

Theoretical and computational Chemistry

Research in the directions of theoretical and computational chemistry covered several areas during the period 2015-2019:

1. Development of electronic structure methods
2. Theory of collisions of electrons with molecules
3. Theoretical study of (bio)catalytic processes
4. Molecular dynamics simulations biophysical and photochemical processes

The first two areas are traditional and they have been explored here for several decades, the latter two areas are relatively new. They are devoted to the development of theories for the description of various physico-chemical phenomena observed in chemistry and biology. The main areas of interest included:

- (i) reaction mechanisms of redox-active metalloenzymes (mononuclear non-heme iron enzymes) and electronic structure contributions to selectivity,
- (ii) computational electrochemistry applied to understanding redox and acidobasic contributions to asynchronicity in proton-coupled electron transfers,
- (iii) computational biophysics for biological interfaces supported by experiments,
- (iv) large- scale QM/MM MD investigation of behavior of enzymes in organic solvents, dynamical aspects in enzyme catalysis, and
- (v) computational study of the effects of AI organization in silicon-rich zeolites.

Spectroscopy

The Spectroscopy research direction covers applied and fundamental research into spectroscopic techniques used for basic science and in the engineering and security industries. This includes the development of sensitive gas-phase sensors and their arrays, the exploration of new high-tech solid-state materials for use in high-power light sources, the characterization of new materials, the generation of reactive species (such as singlet oxygen) and the development of new analytical techniques in forensics. An important area of spectroscopy research is also oriented towards primordial Earth's chemical evolution, and identifying and quantifying the prebiotic processes needed to support the emergence of life, both here and on other terrestrial planets such as Mars, or even exoplanets. Also, fundamental processes of plasma generated by laser sparks or combustion flames are studied by new laser-

spectroscopic diagnostic tools for monitoring combustion intermediates and minor products of the pyrolysis of oxygenated fuels and nitrogen oxide precursors. In the field of fundamental spectroscopy, new high-energy Rydberg transitions of metals relevant to stellar spectroscopy are studied, and infrared spectroscopy relevant to observations of hot exoplanets is explored.

The selected areas of interest during 2015-2019 were:

- (i) Chemical processes initiated by hypervelocity impacts during the early evolution of terrestrial planets and their consequences to early planetary chemistry and prebiotic evolution,
- (ii) Spectroscopy of exoplanets, stellar atmospheres and meteors applied to the characterization of their chemical composition,
- (iii) Development and characterization of light-converting materials for high-performance solid-state light sources,
- (iv) Exploration of the photophysical and photochemical properties of materials that generate singlet oxygen,
- (v) Research into metal oxide materials and their role in processes related to planetary chemistry
- (vi) Technical development of advanced laser and photoacoustic spectrometers for gas-phase sensing

State-of-the-art instrumentation, data analysis, and supporting theoretical work are combined to study these topics. Most experiments are done at the institute on a series of laboratory laser sources (ArF, XeCl, CO₂, Nd:YAG, dye laser), three high-resolution Fourier-transform spectrometers (Bruker 125, 120 and Vertex) used for absorption and time resolved emission studies, two echelle emission spectrometers, laser and photoacoustic spectrometers, a GC-MS mass spectrometer and laboratories for chemical, vacuum, technical and R&D operations.

Selected demanding experiments are carried out at the terawatt-class research infrastructure PALS (in close neighbourhood at the Institute of Plasma Physics, CAS).

Molecular and Cluster Dynamics

Research direction of molecular and cluster dynamics involves processes induced by the interaction of free electrons or photons with molecules. There are two main areas of interest:

- (i) processes in isolated molecules, where the aim is to get as much information as possible using complementary experimental techniques, and
- (ii) environmental effects on these, which are mimicked by experiments with clusters.

This experimental research is performed mainly by using a bespoke instrumental infrastructure – a number of interrelated experimental setups designed and made for probing the specific interaction channels using particle beams: CLUB (Cluster beam apparatus), AIM (Apparatus for imaging), EELS (Electron energy loss spectrometer), DEA (dissociative electron attachment) spectrometer, DEA VMI (velocity map imaging). The experiments use electron beams from various types of electron guns. The photoionization and photodissociation experiments are performed by using various laser systems. Additionally an IR Overtone Spectrometer is used for ro-vibrational spectroscopy of molecules, ions, radicals and clusters.

Apart from providing fundamental information or reaction dynamics, the results have implications in the fields of radiation damage, atmospheric chemistry, astrochemistry or in emerging technologies such as nanofabrication technologies or novel dielectric gases.

Chemistry of Ions in Gaseous Phase

The research direction of Chemistry of Ions in Gaseous Phase is in the experimental research into the properties and reactivity of gas phase ions present in natural environments (atmosphere of the Earth, other planets and their moons, space in stellar systems and interstellar gas clouds) and of ions created by artificial ionisation for various scientific and technological purposes. The experimental research is chiefly carried out using mass spectrometry methods and is supported by theoretical physical chemistry approaches to explain and substantiate the findings.

The main areas of interest during the period 2015-2019 were the following:

- (i) Kinetics of gas phase ion-molecule reactions.
- (ii) Ion chemistry of the Titan and Enceladus (moons of Saturn) atmospheres and of the ionosphere of Mars.
- (iii) Research of advanced new analytical methods for trace gas analysis.
- (iv) Interdisciplinary research of volatile metabolites in physiology, medicine and biology.
- (v) Mass spectrometry methods for environmental research, food science and for synthesis of organometallic catalysts. mass spectrometry or mass spectrometric

In this research fundamental questions are identified that relate to the behaviour of ions at the molecular level which are highly relevant either to understanding of yet unknown natural phenomena or to answering practical societal needs. These fundamental questions are then answered by state-of-the art experimental research, often using original approaches or newly developed experimental techniques, the results of which are interpreted using molecular physical chemistry, quantum chemistry, reaction kinetics and thermodynamics. In order to assess the value of the potentially practically important research, interdisciplinary studies are carried out in collaboration with experts in biology, medicine and other areas.

The key experimental methods and instruments used in this direction are: Selected ion flow tube mass spectrometry (SIFT-MS), gas chromatography / mass spectrometry (GC/MS), electrospray ionisation and atmospheric pressure chemical ionisation mass spectrometry (APCI-ESI-MS), secondary electrospray ionisation mass spectrometry (SESI-MS), selected ion flow drift tube mass spectrometry (SIFDT-MS) and also the traditional electron ionisation mass spectrometry (sector EI/MS).

Biophysical Chemistry

The direction of Biophysical Chemistry aims at understanding biologically relevant processes at the molecular level. The primary interest is in the processes taking place on plasma or mitochondrial membranes and model systems derived from them, including vesicles and supported phospholipid bilayers. Fluorescence spectroscopy and microscopy are the key methods that are further developed and combined with

complementary theoretical and molecular dynamics- based approaches. An additional area is Biomimetic Electrochemistry.

The main areas of interest during the period 2015-2019 were:

- (i) understanding membrane biophysics at an atomistic level,
- (ii) elucidating dynamic/hydration-function relationships in proteins,
- (iii) relation between structure, membrane nanoscale organisation and protein function in cells,
- (iv) fluorescence probes and sensors,
- (v) ultrafast photophysics and photoinduced electron transfer,
- (vi) biomimetic electrochemistry at the polarized liquid/liquid interfaces.

The research topics in this direction are identified as those with broad impact and high physiological relevance.

The key experimental methods and instruments used in this direction are: Time-resolved fluorescence spectroscopy and Fluorescence Lifetime Imaging (FLIM), single molecule Fluorescence Correlation and Cross-Correlation Spectroscopy (FCS and FCCS), imaging FCS and single molecule imaging using TIRF, 3D nanoscope with photoactivated localization microscopy (PALM) and Stochastic Reconstruction Microscopy (STORM), fast transient electrochemical techniques for the polarization of both macroscopic and microscopic liquid/liquid interfaces, dynamic interfacial tension measurements using a video-image pendant-drop method. These state-of-the-art techniques facilitate cutting-edge research in the field of biophysical chemistry.

Molecular electrochemistry and catalysis

This research direction involves design and synthesis of new molecules and elucidation of their structure-reactivity relationship using electrochemical approach on molecular level. Motivation comes from applications in catalysis, photovoltaics, medicine, light emitting devices, organic semiconductors or specific receptors. One of the main aims is to reveal thermodynamic and kinetic properties of novel organic and organometallic molecules, to define their intramolecular electron interactions and to elucidate (multi)electron reaction mechanism and its role in expected application in order to design and synthesize improved generations of catalytic compounds.

The main areas of scientific interest during the period 2015-2019 were the following:

- (i) new multicomponent catalytic systems based on transition metal complexes, electrophilic boranes, silanes or Fischer aminocarbenes,
- (ii) new metallocene complexes for medical use with cytostatic and migrastatic properties,
- (iii) intramolecular activation of ligands and molecules upon thermal, photolytic, or reduction-induced metal activation in coordination compounds,
- (iv) spectro-electrochemical investigation of new molecules suitable for transformation of solar energy via Singlet Fission principle: characterization, stability, mechanism,
- (v) spectro-electrochemical investigation of new nitro-substituted calix[4]arenes and their thia-derivatives as specific receptors and electrochemically generated ligands,
- (vi) structure-properties relationship of carboranes and their radicals as extremely strong oxidation agents in liquid SO₂,

- (vii) new luminescent transition metal complexes (ligand-to-metal charge transfer).

This research direction has a vertical structure, the synthetic work is instantly followed by an electrochemical and spectroscopic characterization, and probing the hypothetical function of the prepared compounds. This multidisciplinary approach offers precious feedback for the design of new generation of molecules or materials customized for a given application. Results emerging from the fundamental research performed at the molecular level are also continuously correlated with quantum-chemical calculations.

The key experimental methods and instruments are: Experimental facilities and equipment comprising synthetic laboratories capable of handling highly air- and moisture-sensitive materials, glovebox, solvent purification, Büchi autoclaves and reactor for polymerization and high-pressure reactions, magnetic resonance spectroscopies (NMR, EPR) / combined with electrochemistry, UV-vis/IR spectrometers / *in-situ* combined with electrochemistry, broad spectrum of advanced (spectro)electrochemical equipment for steady-state and transient techniques for studies of radical intermediates, sonoelectrochemistry, and 3D-printers for design and manufacturing of special spectroelectrochemical cells.

Electrochemistry at the nanoscale

This direction involves fundamental research of electroactive systems down to a single molecule level with the aim of understanding charge transport and transfer mechanisms and the structure-property relationship in newly synthesized organic, organometallic, bioactive or industrially significant compounds. This knowledge finds applications in molecular electronics, catalysis, pharmaceutical industry and in the development of novel electrode materials and biosensors.

Main research areas were:

- (i) Molecules with multiple redox centres.
- (ii) Molecular conductors and molecular switches for molecular electronics.
- (iii) Organometallic electroactive systems for molecular catalysis.
- (iv) Biologically important molecules at electrified interfaces.
- (v) New molecular sensors and 2D architectures at electrified interfaces.

In this research, fundamental understanding is gained of charge transfer and transport processes and related phenomena at the interface of newly designed and tailored molecular systems and novel electrode materials down to the nanoscale level. Applications extend broadly to multidisciplinary areas bridging physics, chemistry, biology and medicine with clear emphasis on delivering socially relevant results. The design and characterization of molecular systems aims at seeking structure-property-function relationships with the ultimate goal of developing building blocks for future molecular electronic devices (molecular conductors and switches) as well as electrocatalysts to tackle challenges of the anthropogenic climate change (production of hydrogen as a sustainable fuel, mitigation of global warming by the reduction of atmospheric carbon dioxide). Physico-chemical processes induced by the interfacial charge transfer are further employed to provide valuable insights into biological functions of pharmacologically and industrially relevant compounds (antioxidants and

dyes). Charge transfer phenomena are additionally utilized in electrochemical sensing of environmentally relevant substances (pollution markers, genotoxic compounds).

Instrumentation and methodology used for this research direction includes: Advanced electrochemical instrumentation relying on commercial and proprietary lab-assembled potentiostats involving diverse techniques (harmonic and pulse perturbation, ultrafast voltammetry, bulk and thin-layer electrolysis, current measurements down to a femtoampere range), in-situ spectroscopic techniques (ultraviolet, visible and infrared range as well as fluorescence) enabling the scrutiny of short-living reaction intermediates leading to elucidation of reaction mechanisms, analytical separation/detection platforms for the identification/quantification of reaction products, atomic force and scanning tunnelling microscopy for the nanoscale characterization of surfaces, break-junction techniques to explore charge transport and thermoelectric properties of nanoscale constrictions involving single molecule electronic components, density functional theory based computational approaches to predict electronic structure, spectral and charge transfer/transport characteristics, continuum-based numerical simulations of charge transfer and mass transport phenomena, 3D printing and computer assisted design to manufacture customized electrochemical devices.

Electrochemical materials

The research direction of Electrochemical materials involves the synthesis and characterization of advanced electrochemically active materials and electrode materials, with special focus to nanomaterials based on elemental carbon, oxide semiconductors and inorganic 2-D solids. This research is dedicated to functional mesoscopic materials, relevant to electrochemistry, photocatalysis, spectro- and photoelectrochemistry. The scientific activities are balanced between fundamental studies of these materials and their practical applications, which are focused to outputs in energy conversion and storage and in remediation of environment pollutants. The main areas of interest during the period 2015-2019 were:

- (i) Carbonaceous materials: graphene and nanodiamond.
- (ii) Oxidic semiconductors: Ti(IV) and Sn(IV) oxides.
- (iii) 2-D materials based on transition-metal dichalcogenides.
- (iv) Electrochemical and nanobubble-assisted nanostructuring; gaseous nanodomains on solid/liquid interfaces.
- (v) Dye-sensitized and perovskite photovoltaics.
- (vi) Li-ion and Na-ion batteries.
- (vii) Photocatalysis for environment protection.

The first four areas comprise mainly fundamental research, the remaining three areas are oriented towards practical applications and to industrial collaborations. Yet, all these themes are mutually interconnected into a complex network of scientific and technological problems. For instance, the basic knowledge acquired in the field of nanocarbons finds unique use in our developed solar cells. Oxidic semiconductors turn out to be applicable in all the practical tasks investigated.

The key experimental methods and instruments used in this direction are: Instruments for advanced syntheses (glove boxes, vacuum lines, ALD set up.), electrochemistry equipment (impedance spectroscopy and battery testing), Raman spectroscopy and

spectroelectrochemistry, scanning probe microscopes for imaging at ambient atmosphere, in liquids and electrochemical environment, atomic force microscopy with quantitative nanomechanical mapping, coupled AFM – Raman (TERS, photocurrent mapping), ellipsometry with micrometre resolution, photoelectrochemistry, including solar simulator, IPCE/QE/IV and photocatalytic reactors interfaced with TOC and HPLC analyses.

Low dimensional materials

This research direction involves advanced studies of low dimensional materials and surfaces. In particular the research is focused on studies of nanostructures synthesis, characterization and optimization by means of chemical composition and electronic structure to yield interfaces and thin layers of novel properties Two distinct areas of interest are:

- (i) Low dimensional systems (LDS) covering the development and study of 2DM-derived hybrids with multi-way control of their band structure via external stimuli and control of reactivity via physical fields applicable in quantum technologies, nanoelectronics, and bio-interfacing. The strategic pillars of this research are represented by three research lines: Tailored chemical and electrochemical modifications of 2DMs, adaptation of functionalization of 2DMs for the UHV condition and studies of new functional properties of 2DMs by advanced microscopies and spectroscopies.
- (ii) Electrocatalysis (EC) focused on investigation of surface confined charge transfer processes for reversible storage of the renewable electricity. In particular two topics were pursued: design of catalysts for oxygen electrochemistry including the active site identification and identification of parasitic processes in chlorate production. So-called “rational catalyst design approach” is used when novel (electro)catalysts are synthesized to replicate active sites identified by X-ray absorption spectroscopy and confirmed by DFT.

The key experimental methods and instruments used in this research direction are: Clean room for optical lithography, XPS/spin resolved ARPES/LEED/STM, in-situ Raman spectroscopy (electrochemistry, magnetic field, low temperature, pressure), microscopy techniques (HRTEM, SEM, AFM), wet-chemical and low temperature solution based synthesis, solvothermal, microwave assisted, spray freeze drying, Operando X-ray absorption spectroscopy and differential electrochemical mass spectroscopy (DEMS)

Structure and dynamics in catalysis

This research direction involves experimental studies in the field of heterogeneous redox and acid-base catalysis, photocatalysis, and gas sorption. The research encompasses the whole route of the catalytic process from synthesis and modification of catalysts, their characterization and performance, to reaction kinetic studies. The development of the catalyst's preparation methods from the laboratory scale to the pilot plant level is covered. The research is carried out by using a combination of methods

including a multi-spectroscopic approach up to the operando conditions mode supported by DFT calculation.

The main areas of interest during the period 2015-2019 were the following:

- (i) Structure and activity of distant binuclear TM ion sites in zeolite matrices for methane utilization.
- (ii) Synthesis of porous matrices (zeolites by ADOR, carbon replicas of zeolites).
- (iii) Organization of Al atoms in zeolite matrices (analysis and tuning).
- (iv) Redox catalysis over zeolites (NO_x and N₂O abatement).
- (v) Hydrocarbon transformations over acid zeolite catalysts.
- (vi) Photocatalytic processes for abatement of NO_x and organic pollutants.

The focus is on the design and preparation of catalytic sites on the atomic level, comprehension of the relationship between their structure and activity, and on the understanding of the mechanism of materials synthesis and their sorption properties. The research covers both understanding of yet unknown natural phenomena or structures (and their design), and application of the obtained knowledge to answer current practical societal needs. This is achieved by state-of-the-art experimental research, often using original approaches or newly developed characterization techniques in the fields of molecular physical chemistry, quantum chemistry, and reaction kinetics. In order to assess the value of the potentially applicable research, collaboration with industrial partners is established.

The key experimental methods and instruments used are: high-pressure autoclaves, adsorption apparatuses, ss-NMR, UV-Vis-NIR, FTIR, high and low pressure IR reactor, computerized catalytic reactors with GC/MS, high-pressure Microactivity-Reference catalytic reactors with GC, Computerized catalytic reactors for N₂O/NO/NO₂ abatement reactions with N₂O and chemiluminescence analyzers and a MultiGas FTIR Continuous Gas Analyzer.

Nanocatalysis

At the beginning of 2019 a new research direction of Nanocatalysis was introduced and the new Department of Nanocatalysis was established with primary focus on the fundamental studies of model catalysts designed with atomic precision down to the subnanometer scale in heterogeneous reactions under realistic reaction conditions of pressure and temperature, aiming to establish relations between the size and composition of the nanocatalysts and their performance, including support effects, in reactions of various complexity - from model reactions to industrially relevant ones.

For this purpose, new laboratories have been allocated and set-up with size-selected cluster deposition equipment (high vacuum), dedicated catalyst testing equipment (mass-spectrometry, gas-chromatography). Synchrotron-based characterization (absorption, scattering, diffraction) is also used for specialised experiments.

Note that the year 2019 was devoted to setting up brand new laboratories and installing equipment that no specific results are reported for this department. Introduction of this research direction of Nanocatalysis was facilitated by the Heyrovský Chair ERA Chair project (H2020-EU.4.c. - Establishing 'ERA Chairs').

Research activity and characterisation of the main scientific results

The fundamental and applied scientific, and technical R&D activities of our department have produced a wide range of varied results. A common denominator is the clever and careful usage of established fundamental spectroscopic techniques and commercial instruments, along with experimental technologies that are in the stage of laboratory development. Another core strategy has been to develop synergic and open co-operation with outside research teams in an exchange of our expertise and instrumental capabilities with the skills and facilities of our partner's where these are unavailable within our own department. Therefore, our department has been able to apply itself to research dealing with the exploration of gas- and solid -phase chemical breakdown products with the terawatt-class PALS laser, observation of meteor events, space-based projects such as the developing ARIEL telescope, complex problems in planetary chemistry, and in the preparation of cubesat missions. In-house research has involved the development of laser spectrometers, materials research, the characterization and fundamental spectroscopy of excited Rydberg transitions, targeted measurement of molecular spectra as references for space-based astronomical observatories, and experimental work on the roles of plasma chemistry, thermal synthesis and catalysis in prebiotic chemistry.

Main scientific results

In order to structure and optimise research within the department, it is divided into several working groups and laboratories. Published references are listed in the section “The relevant publications authored by the team members.” The main results achieved either in mutual cooperation or independently can be summarized as follows:

In the **Laboratory of High Resolution Spectroscopy**, during the monitored period, 2015 to 2019, our systematic research of **high-energy prebiotic processes** resulted in a series of papers, with several of them appearing in high-impact multidisciplinary journals. This research line has been in progress since 2004 and addresses an important hypothesis surrounding the origin of life, i.e. the scenario where extra-terrestrial impacts are a source of delivered and also *de novo* synthesized biogenic molecules. In 2015 and 2017, systematic exploration of high-energy formamide chemistry resulted in two publications (Ferus et al. 2017), (Ferus et al. 2015) in the prestigious Proceedings of the National Academy of Sciences of the United States of America. A wide response to both papers is recorded on web pages of this journal (see notes ¹ and ² on this page).

The first paper (Ferus et al. 2015) finds evidence that the heavy bombardment of Earth prior to 4 billion years ago could result in the *de novo* high-energy synthesis of basic prebiotic molecules: all the canonical nucleobases and glycine. As noted above, this research is built on know-how in development since 2004 but with the present research we have performed the most comprehensive and complex study into impact-plasma and shock chemistry as experimentally simulated with the unique high-power

¹ PNAS, 20, 2015, 112, (3), 657-662, <<<https://pnas.altmetric.com/details/3013712/news>>>

² PNAS, 20, 2015, 112, (3), 657-662, <<<https://pnas.altmetric.com/details/18706037/news>>>

terawatt-class PALS laser and in combination with a series of other analytical techniques; quantum chemical calculations performed by our partners; targeted supporting laboratory experiments; and kinetic chemistry calculations. This combination was needed in order to completely describe a new and so far unexamined scenario for a network of high-energy reactions leading from a prebiotic substance of established importance, formamide, to all canonical nucleobases. This exploration is followed by further systematic research focused on the important role of formamide as a starting molecule for other variants of high-energy synthesis. In 2017, we have published our results again in PNAS (Ferus et al. 2017). We have shown that plasma generated by hypervelocity impacts can initiate chemical transformations also in reducing mixtures containing ammonia, carbon monoxide and water. Under such conditions, formamide is synthesized *de novo* and continues on to undergo the subsequent chemical reactions isolated in the previous study.

Publication of these papers does not represent the end of this story, but is another important step in this topic within our laboratory, ongoing for almost two decades. The ongoing research into high energy chemistry induced by hypervelocity impacts has been recently split in several directions, discussed in what follows.

First of all, we have **continued in the exploration of *de novo* synthesis of prebiotic molecules initiated in high-energy impact plasma**, expanded to include solid surfaces in contact with the gas-phase-induced plasma in a simulation of planetary surfaces, and liquid phase precursors simulating ponds containing accumulated feedstock molecules such as formamide. These experiments utilise the terawatt-class laser PALS and are supported by in-house laboratory experiments with laboratory laser-induced breakdown and electric discharges. This investigation of high-energy chemistry has shown that hypervelocity plasma plays an important role in synthesising prebiotic molecules (canonical nucleobases, sugars, aminoacids) starting from far more ubiquitous compounds such as formaldehyde (Civis et al. 2016), (Ferus et al. 2019), methane mixed with water and nitrogen (Civiš et al. 2017) etc. In the case of formaldehyde (Civis et al. 2016) or Miller-type mixtures (Ferus et al. 2017), formamide still plays a role as the central molecule at the center of ongoing plasma chemistry. However, it has also now known that in atmospheres containing methane, hydrogen cyanide is a different central molecule for promoting impact-initiated high-energy prebiotic synthesis (Ferus et al. 2017a), (Civiš et al. 2017). Based on our results, it is clear that plasma induced by hypervelocity impacts during an era of heavy bombardment of terrestrial planets triggers *de novo* prebiotic synthesis starting with simple mixtures as well as when including rather more complex feedstock molecules. In planned future research, it will be challenging but worthwhile to show if similar chemistry can occur in neutral chemical environments and hypothesise the relevant scenario of reactions. The initial kick-off of such studies is embodied in two works (Civiš et al. 2017), (Civis et al. 2019) that offer an alternative explanation for the origin of methane on Mars, but also consider this planet as a general prototype of neutrally-composed, thin, and CO₂-rich terrestrial atmospheres. This research has identified a feasible scenario for synthesising a reducing gas (methane) from a neutral atmosphere over acidic photoactive surfaces. It is natural that this new result leads to many additional and worthwhile questions concerning the availability of these surfaces in early planetary environments, their production efficiency, the depletion of generated methane and so on.

A second direction of study is the **investigation of subsequent post-impact processes** taking place in the hot hydrothermal environment of craters, similar to what

is expected for instance in the Gale Crater on Mars. We have explored (Pastorek et al. 2019) catalytic properties of iron-rich smectites formed by the reprocessing of basalts due to residual post-impact heat that could catalyse the synthesis and accumulation of important prebiotic building blocks such as nucleobases, amino acids and urea. The research following this has demonstrated striking evidence for the variability of impact-related synthesis of prebiotic molecules: This process can be triggered by radical chemistry that directly takes place during an extraterrestrial impact even, as well as by simple thermal chemistry in the presence of impact-altered rocks.

A third direction is closely connected to future exoplanet exploration missions like Ariel and JWST. Our investigations in this area are focused on **target experiments and the transformation of early planetary atmospheres by impacts** and the characteristic products of impact chemistry. This is in order to investigate further roles of impacts in the chemical and physical evolution of exoplanetary environment, the possibility and consequences of prebiotic synthesis, deposition of molecules onto surfaces, influence on warming or cooling of the planet and their possible role as markers of heavy bombardment for detection with space telescopes. It should be noted that our recent involvement in the Ariel consortium (Tinetti et al. 2018) is a crucial driver and practical recipient of the results about to be published.

The fourth direction is related to the others but oriented towards the fundamental investigation of **physical processes taking place during meteoroid or asteroid descent**. Meteor plasma is again simulated by terawatt-class laser dielectric breakdown, however, it is now used to ablate real meteorite specimens in order to investigate spectra of impact-ablated material, plasma-induced alteration of meteoroid surfaces, the production of dust etc. This laboratory work is a comparative baseline for examining spectra of real meteors as recorded by our own network of meteor spectroscopic cameras built in cooperation with domestic observatories. Results on the simulation and understanding of meteor spectra and behaviour of plasma under laboratory conditions have been published in several papers regarding the main meteoritic spectral features simulated by high power laser ablation (Ferus et al. 2019a) and the spectral analysis of meteoroid body composition (Ferus et al. 2018).

Another topic in fundamental atomic spectroscopy involves the **exploration of high-resolution spectral transitions of atomic Rydberg states**. One important result, among others, relates to an investigation of oxygen. This element is the third most abundant in the Universe and plays a major role in multiple astrophysical processes. Observation of oxygen's spectral lines is used by astronomers to investigate, for instance, the chemical history of the Galaxy. Atomic oxygen also contributes significantly to processes and diagnosis of the Sun's interior. High-precision reference data are needed to correctly interpret such astronomical observations. We have measured, analyzed, and reported such spectroscopic data for 135 O I lines (including many refinements and 51 lines not previously measured in the laboratory). We have also re-optimized many O I level energies and calculated oscillator strengths for the investigated transitions (Civis et al., 2018). Neon and argon are other elements of considerable astrophysical significance. Besides this fact, the precise knowledge of their physical (radiative and structural) properties is also essential from the experimental point of view because of their frequent application in numerous physical and chemical experimental studies (for example, as the buffer gas in discharges). High-precision spectroscopic data of these two elements provide a reliable wavelength reference applicable in both the interpretation of astronomical observations and calibration of laboratory measurements (Kubelik et al., 2016, 2015).

Finally, we have finished the investigation of **isotope exchange between CO₂ and solid phases of metal oxides** and other materials (Civiš et al. 2015), (Civiš et al. 2016). Our laboratory experiments supported a theoretically-proposed mechanism whereby isotopic exchange is associated with a kind of “rotation” of CO₂ molecules trapped in surface vacancies.

The **laboratory of photophysics** collaborated with several domestic and international teams in the synthesis of new photoactive materials, by sharing our expertise in transient absorption, time-resolved luminescence spectroscopy, and steady-state infrared spectroscopy. Several types of photoactive materials based on singlet-oxygen generation were formulated, fabricated, and tested for photobiological and environmental applications:

Electrospun polymeric nanofibers with encapsulated or externally-bound photosensitizers (Dolansky et al., ACS Appl. Mater. Interfaces, 2015) are capable of performing multiple tasks, e.g., photodisinfection, decontamination, and separation, using the same material. It was shown that nanoparticles prepared from these materials have enhanced photophysical and antimicrobial properties and can be easily separated by filtering with pristine electrospun materials (Kubat et al., ACS Appl. Mater. Interfaces, 2017) (Henke et al., ACS Appl. Mater. Interfaces, 2016) (Dolansky et al., Nanoscale, 2018).

Hexanuclear molybdenum (Kirakci et al., Inorg. Chem., 2016) and **rhenium clusters** (Solovieva et al., Inorg. Chem., 2017) photogenerated singlet oxygen can be activated by X-ray radiation, even in the solid state. Layers fabricated from these clusters strongly absorb harmful UV light, converting it to red light, and the quenching of this luminescence provides a way of measuring oxygen concentrations. **Borane clusters** were found to be extremely photostable (Londesborough et al., Inorg. Chem., 2019).

Polymeric layers with carbon quantum dots were shown to be time-effective and financially-undemanding antibacterial materials suitable for coating, e.g., the surfaces of textiles (Kováčová et al., ACS Biomater. Sci. Eng., 2018).

The **photophysical properties of (aza)phthalocyanines** (Machacek et al., J. Med. Chem., 2016) and **metal organic frameworks** containing porphyrins (Buzek et al., J. Mater. Chem. B, 2017) were evaluated in a search of prospective species for application to the photodynamic therapy of tumors.

The **laboratory of Laser-Diode and Photoacoustic Spectroscopy** achieved several results in the development of advanced laser spectrometers and detectors for gas sensing. Selected results are divided between focus areas of this laboratory as follows:

Research on **micro-levers for laser photoacoustic detection** involved multilayer graphene and mica cantilevers (Tarabkova et al., Physical Chemistry Chemical Physics, 2018) as part of an optical microphone (Suchanek et al., Measurement, 2017; Dostal et al., Energy & Fuels, 2018) in combination with lasers (Zelinger et al., Journal of Sensors and Sensor Systems, 2015) were employed in a multicomponent analysis of a mixture of acetone, acetic acid and methanol by photoacoustic spectroscopy (Suchanek et al., Microchemical Journal, 2019). This method enable us to detect acetic acid in a high background of acetone, and could be beneficial in the medical analysis of breath.

Environmental influence of photochemical processes were investigated in the urban canyon environment of Legerova Street. This forms part of the north-south trunk road that passes through the centre of Prague and remains an unresolved

environmental issue for the capital of the Czech Republic. As many as one hundred thousand cars move through this region per day, and mortality has increased as a result of dust, NO_x and other exhaust pollutants. The spatial distribution of pollutants (i.e., NO₂, NO, and O₃) during the course of a day was measured by combined DIAL/SODAR techniques and spot analyzers appropriately located near the bottom of the street canyon. The use of a photochemical reactor to describe chemical processes in a street canyon atmosphere was developed and verified as a useful tool for prediction purposes (Strizik et al., *Journal of Atmospheric and Solar-Terrestrial Physics*, 2016).

Spectroscopic studies in gaseous flows were applied to the applicability of **Tunable Laser Diode Absorption Spectroscopy** to non-invasive diagnostics in a harsh combustion environment (Nevrly et al., *Fuel*, 2020). Several aims were achieved: (i) to explore the combustion regime and structure of preheated ultralean Dimethyl ether/air atmospheric pressure laminar premixed flames both experimentally and employing chemical kinetic modelling, (ii) to characterise appropriately targeted spectral absorption features useful for characterising these flames using Wavelength Modulation Spectroscopy measurements (Nevrly et al., *Meas. Sci. Rev.*, 2018)

Societal relevance

Is there life beyond Earth? How did it evolve? Which processes in planetary evolution led to the Earth and other Solar System bodies being as they are? These fundamental questions have been asked many times; and scientists, thinkers, and curious people still raise them with respect to not only our own existence or the possibility of other life-giving worlds, but even other civilizations. The societal relevance of seeking answers on this topic is extremely high and can have positive, as well as negative, consequences for the structure and hierarchy in society, economics, religion etc. Our research contributes a careful investigation of the chemistry expected on young exoplanets. In a wider context, systematic statistically-significant spectroscopic observations in a survey of exoplanets will help us understand the evolution of the Solar System and our own planet. For this, it is necessary to prepare reference materials for spectroscopic telescope observations and explore in the laboratory the basic processes driving the evolution of physical and chemical environments similar to the early Earth. In this way, we also open a rare window on our own Hadean eon, a critical period for life's origins, but generally obscured by information from this time being long erased from the planet's geological record. Our research performed over almost two decades, and described above, focuses on specific topics relating to impact events, in order to secure a place for another piece of the puzzle surrounding planetary and organic origins. In a more practical direction, the fight against infectious microorganisms is becoming a worldwide priority due to serious concerns about the rising numbers of drug-resistant pathogenic bacteria. Photoactive materials based on singlet-oxygen generation are useful predominantly for medical applications where they effectively combat resistant biofilms and antibacterial and antiviral treatment resistant infections. The new materials investigated in our department may contribute to preventing and slowing down the transmission of harmful bacteria and viruses. Since most of our results achieved so far probe the relevant character and fundamental physical properties of atomic and simple molecular systems, these are also usable in various fields of research and have applications including plasma physics, plasma

chemistry, plasma processing, astrophysics, remote sensing, analytical spectrometry, and other research areas dealing with laboratory or natural plasmas.

The research projects investigated in the team in the period 2015 – 2019:

2019 - 2019 Exploration of exoplanets and their atmospheres and the origin of life in the Universe – era of TESS, PLATO and ARIEL

Program Strategy AV21 - VP16, Academy of Sciences of the Czech Republic

Responsible investigator: prof. RNDr. CIVIŠ Svatopluk CSc.

2018 - 2019 Powerful light sources

Technological Agency of the Czech Republic

Responsible investigator: prof. RNDr. CIVIŠ Svatopluk CSc.

2018 - 2023 Center of advanced applied natural sciences

Ministry of Education, Youth and Sports of the Czech Republic

Responsible investigator: prof. RNDr. CIVIŠ Svatopluk CSc.

Responsible investigator: RNDr. FERUS Martin, PhD.

2016 - 2017 Formamide and chemical evolution of life

Ministry of Education, Youth and Sports of the Czech Republic

Responsible investigator: prof. RNDr. CIVIŠ Svatopluk CSc.

2014 - 2016 Metal oxide nanoparticles and their reactivity studied by high resolution FT infrared spectroscopy

Ministry of Education, Youth and Sports of the Czech Republic

Responsible investigator: prof. RNDr. CIVIŠ Svatopluk CSc.

2014 - 2017 Advanced phosphor for high power LEDs and laser diodes

Technological Agency of the Czech Republic

Responsible investigator: prof. RNDr. CIVIŠ Svatopluk CSc.

2018 - 2020 SeLOS – Common laboratory for observation spectroscopy

Academy of Sciences of the Czech Republic

Responsible investigator: RNDr. FERUS Martin Ph.D.

2019 - 2021 Plasma and UV/XUV/X-Ray Reprocessing of planetary atmospheres: What can we expect on young exoplanets?

19-03314S Grant Agency of the Czech Republic

Responsible investigator: RNDr. FERUS Martin Ph.D.

2018 - 2020 Simulation of Meteor Plasma using Terawatt Laser: Experiments, Theory and Real Observations

18-27653S Grant Agency of the Czech Republic

Responsible investigator: RNDr. FERUS Martin Ph.D.

2017 - 2017 Development of meteor observation and spectroscopy

Academy of Sciences of the Czech Republic

Responsible investigator: RNDr. FERUS Martin Ph.D.

2017 - 2019 Origin of life on Earth and in the space - experiment and theory

17-05076S Grant Agency of the Czech Republic

Responsible co-investigator: RNDr. FERUS Martin Ph.D.

2014 - 2016 Theoretical and experimental studies on the origin of life

14-12010S Grant Agency of the Czech Republic

Responsible co-investigator: RNDr. FERUS Martin Ph.D.

2017-2019 Decomposition pathways of intelligent carriers of energy studied by infrared spectroscopy

LTC17071, COST Ministry of Education, Youth and Sports of the Czech Republic

Responsible investigator: prof. Ing. ZELINGER Zdeněk CSc.

2014-2016 Micromechanical sensor and laser photoacoustic detection for trace gas sensing technologies

LD14022, COST Ministry of Education, Youth and Sports of the Czech Republic

Responsible investigator: prof. Ing. ZELINGER Zdeněk CSc.

2014-2016 Versatile micromechanical sensor and laser photoacoustics for combined gas/liquid diagnostics

14-14696S Grant Agency of the Czech Republic

Responsible investigator: prof. Ing. ZELINGER Zdeněk CSc.

2011 – 2015 Fabrication of thin films of UV-Vis-NIR transparent dielectrics by repetitive, capillary-discharge XUV laser ablation

P108/11/1312 Grant Agency of the Czech Republic

Responsible investigator: prof. Ing. ZELINGER Zdeněk CSc.

2013 – 2015 Multifunctional photoactive nanofiber materials

13-12496S Grant Agency of the Czech Republic

Responsible investigator: prof. Ing. ZELINGER Zdeněk CSc.

2017 - 2019 Micro/nano-spring enhanced photoacoustics: devices, methods and applications

17-05167S Grant Agency of the Czech Republic

Responsible investigator: prof. Ing. ZELINGER Zdeněk CSc.

2019 - 2021 Light-Responsive Nanofiber Materials and Nanoparticles for Inactivation of Pathogens

19-09721S Grant Agency of the Czech Republic

Responsible investigator: RNDr. KUBÁT Pavel, CSc.

2017 - 2019 Exploration of ionospheric plasma using Sudden ionospheric disturbance monitoring (SID)

R200401721 Academy of Sciences of the Czech Republic

Responsible investigator: Mgr. KUBELÍK Petr Ph.D.

2013 – 2015 Hexanuclear molybdenum clusters with tunable photophysical properties

13-05114S Grant Agency of the Czech Republic

Responsible investigator: RNDr. KUBÁT Pavel, CSc.

The relevant publications authored by the team members³

Buzek, D., Zelenka, J., Ulbrich, P., Ruml, T., Krizova, I., Lang, J., **Kubat, P.**, Demel, J., Kirakci, K., & Lang, K. (2017). Nanoscaled porphyrinic metal-organic frameworks: photosensitizer delivery systems for photodynamic therapy. *J. Mater. Chem. B*, 5(9), 1815-1821.

Civiš S, Kubelík P, Ferus M et al (2018) FTIR Laboratory Measurement of OI Spectra in the 0.77–12.5 μ m Spectral Range: Rydberg States and Oscillator Strengths *Astrophysical Journal Supplement Series* 239:11, 1-19.

³ We note that due to page limit of this report, we have shortened the full lists of authors.

- Civiš S, Ferus M, Zúkalová M, et al** (2015) Oxygen Atom Exchange between Gaseous CO₂ and TiO₂ Nanoclusters. *J Phys Chem C* 119:3605–3612. doi: 10.1021/jp512059b
- Civiš S, Knížek A, Ivanek O, et al** (2017) The origin of methane and biomolecules from a CO₂ cycle on terrestrial planets. *Nat Astron* 1:721
- Civiš S, Knížek A, Kubelík P, et al** (2016) Spontaneous Oxygen Isotope Exchange between Carbon Dioxide and Oxygen-Containing Minerals: Do the Minerals Breathe CO₂? *J Phys Chem C* 120:508–516. doi: 10.1021/acs.jpcc.5b11306
- Civis S, Knizek A, Rimmer PBPB, et al** (2019) Formation of Methane and (Per)Chlorates on Mars. *ACS Earth Sp Chem* 3:221–232. doi: 10.1021/acsearthspacechem.8b00104
- Civis S, Szabla R, Szyja B, et al** (2016) TiO₂-catalyzed synthesis of sugars from formaldehyde in extraterrestrial impacts on the early Earth. *Sci Rep* DOI: 10.10:1–7
- Civiš S, Ferus M, Zúkalová M, et al** (2015) Oxygen Atom Exchange between Gaseous CO₂ and TiO₂ Nanoclusters. *J Phys Chem C* 119:3605–3612. doi: 10.1021/jp512059b
- Civiš S, Knížek A, Ivanek O, et al** (2017) The origin of methane and biomolecules from a CO₂ cycle on terrestrial planets. *Nat Astron* 1:721
- Civiš S, Knížek A, Kubelík P, et al** (2016) Spontaneous Oxygen Isotope Exchange between Carbon Dioxide and Oxygen-Containing Minerals: Do the Minerals Breathe CO₂? *J Phys Chem C* 120:508–516. doi: 10.1021/acs.jpcc.5b11306
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- Civis S, Szabla R, Szyja B, et al** (2016) TiO₂-catalyzed synthesis of sugars from formaldehyde in extraterrestrial impacts on the early Earth. *Sci Rep* DOI: 10.10:1–7
- Dolansky, J., Henke, P., **Kubat, P.**, Fraix, A., Sortino, S., & Mosinger, J. (2015). Polystyrene Nanofiber Materials for Visible-Light-Driven Dual Antibacterial Action via Simultaneous Photogeneration of NO and O₂(¹Δ(g)). *ACS Appl. Mater. Interfaces*, 7(41), 22980-22989.
- Dolansky, J., Henke, P., Mala, Z., Zarska, L., **Kubat, P.**, & Mosinger, J. (2018). Antibacterial nitric oxide- and singlet oxygen-releasing polystyrene nanoparticles responsive to light and temperature triggers. *Nanoscale*, 10(5), 2639-2648.
- Dostal, M., Suchanek, J., Valek, V., Blatonova, Z., Nevrlý, V., Bitala, P., Kubat, P., & Zelinger, Z. (2018). Cantilever-Enhanced Photoacoustic Detection and Infrared Spectroscopy of Trace Species Produced by Biomass Burning. *Energy & Fuels*, 32(10), 10163-10168.
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Research activity and characterisation of the main scientific results

Selected scientific results presented here are organized according to our primary research areas (outlined in section 1.1) and pursued by five theoretical groups in our department

Development of electronic structure methods

In the period 2015-2019 we continued our effort on the development of multireference coupled clusters (CC) methods. In particular, we developed an iterative form of the USS correction by means of correcting effective Hamiltonian matrix elements and via the left Bloch equations. Various forms of the USS and simplified diagonal USS corrections at the singles and doubles and perturbative triple levels were numerically assessed on several model systems and on the ozone and tetramethyleneethane molecules. We have shown that the iterative USS correction can successfully replace the previously developed a posteriori Brillouin-Wigner coupled cluster size-extensivity correction, while it is not sensitive to intruder states and performs well also in other cases when the a posteriori one fails, like, e.g., for the asymmetric vibration mode of ozone (Banik et al. 2015).

We further introduced a perturbative variant of the USS(2) approach (USS(pt)), which substantially reduces the numerical overhead of the full USS(2) correction while preserving its accuracy. On the example of several benchmark systems, we demonstrated accuracies of USS(pt) and USS(2) approaches and their efficiency in describing quasi-degenerate electronic states (Brabec et al. 2016).

We developed a local variant of Mukherjee's state-specific multireference coupled cluster method based on the pair natural orbital approach (LPNO-MkCC) at SD level. The assessment has shown that 99.7-99.8% of correlation energy was recovered with respect to the MkCC method based on canonical orbitals (Demel et al. 2015). Next, we transitioned to the computationally more efficient domain-based LPNO approach, developing a local variant of Mukherjee's state-specific multireference coupled cluster method based on the domain-based pair natural orbital approach (DLPNO-MkCC) at the singles and doubles level. To demonstrate the applicability of the method to large systems, singlet-triplet gaps of triangulene and bis(1-(2,6-diisopropylphen-yl)-3,3,5,5-tetramethylpyrrolidine-2-ylidene)beryllium complex were studied. For the last system (105 atoms), we were able to perform a calculation in cc-pVTZ with 2158 basis functions on a single CPU in less than 9 days (Brabec et al. 2018).

Finally, we implemented also the noniterative triples correction to the DLPNO-MkCC method, which together with the DLPNO-MkCCSD part accounts for about 99.70-99.85% of the corresponding canonical correlation energy. The applicability of the method was demonstrated on calculations of singlet-triplet gaps for several large systems: triangulene, dynemicin A, and beryllium complex (Lang et al. 2019).

As an alternative to "genuine" multireference CC methods, we investigated externally corrected CC methods, employing DMRG as the source of active space amplitudes describing static correlation. In the past decade, the quantum chemical version of the density matrix renormalization group (DMRG) method has established itself as the method of choice for calculations of strongly correlated molecular systems. We illustrated the potential of this method on prominent multireference systems, in particular, N₂ and Cr₂ molecules and also oxo-Mn(Salen), for which we have performed the first post-DMRG computations in order to shed light on the energy ordering of the lowest spin states (Veis et al. 2016).

We investigated the intricate case of tetramethyleneethane molecule, where we have performed a quantum Monte Carlo FCI-quality benchmark and employed it for the assessment of the accuracy of Mukherjee's coupled clusters with up to triple excitations (MkCCSDT) and CCSD tailored by the density matrix renormalization group method (DMRG) (Veis et al. 2018).

To improve the efficiency of the DMRG-tailored CC method, we introduced a new implementation which employs the local pair natural orbital (LPNO) approach. By exploiting locality in the coupled cluster stage of the calculation, we were able to remove some of the limitations that hindered the application of the canonical version of the method to larger systems and/or with larger basis sets. We assessed the accuracy of the approximation using two systems: tetramethyleneethane (TME) and oxo-Mn(Salen). We examined dependence of the ground state of oxo-Mn(Salen) on the CAS composition (Antalík et al. 2019).

Theory of collisions of electrons with molecules

The main focus in this area was in the development of methods and tools for a theoretical description of the electron-induced decomposition of the neutral and cationic molecular systems, i.e. the dissociative electron attachment (DEA) and the dissociative recombination (DR) processes.

In the DR project the team closely collaborated with a theoretical partner prof. Chris. H. Greene from Purdue University and with the experimental group from MPIK at Heidelberg led by prof. Andreas Wolf. The computed inelastic cross sections for electrons scattered by HeH^+ cations (Čurík and Greene 2017) were used by experimental group in Heidelberg for determination of the rotational population of cations in the storage ring. The multichannel quantum defect theory (MQDT) used in this study (and some of our previous studies) employed several ansatzs that needed to be checked rigorously. For this a two-dimensional model for the electron – $\text{H}^{\frac{1}{2}}$ recombination was developed (Hvizdoš et al. 2018).

A theory for the dissociative electron attachment (DEA) typically involves a description of nuclear dynamics on the resonant (temporary) surfaces of negative ions. In order to determine these surfaces and their corresponding life times, the team collaborated with prof. Jiří Horáček from Charles University on the development of a method to determine the electronic resonances (Horáček et al. 2015). The method applies a simple one-electron perturbation potential to the molecular Hamiltonian. This potential transforms the resonant state into a truly bound state, making it amenable for the common quantum chemistry software.

The expertise in the field of electron-molecule collisions naturally led to its application in the ultracold molecular physics. The team developed a new two-electron approach for long-range Rydberg molecules (Tarana and Čurík 2016) that allowed more accurate determination of the molecular energy surfaces and their behavior in the electro-magnetic fields (Schmid et al. 2018). The two-electron method separates the long-range molecule to two spatial parts. The first part forms a sphere around the neutral atom, while the second, remaining outer part consists of an electron moving in the screened Coulomb field. The wave function inside the sphere, computed by the two-electron R-matrix method (Tarana and Čurík 2019) is connected to the outer solution by use of the Green-function approach. The results provided by this method offer a better understanding about validity of the previously used models based on the contact (δ) potentials. In contrast to the methods of contact potentials, the two-electron approach takes into account also the effects of the polarization of the neutral atom by the other ionic core and interaction of the Rydberg electron with the neutral

atom in higher partial waves.

Theoretical study of (bio)catalytic processes

Concerning redox properties of biological non-heme iron active sites and their effects on H-atom abstraction reactivity, we used (in collaboration with Prof. E. I. Solomon from Stanford University) the low temperature magnetic circular dichroism (LT MCD) spectroscopy in combination with quantum-chemical calculations to define the electronic structure associated with the geometric structure of the Fe(IV)=O intermediate in the halogenase SyrB2 (Srnc et al. 2016). As a follow-up of this study we studied redox-related electronic contributions to chlorination vs. hydroxylation selectivity in SyrB2. Namely, we show that hydroxylation is thermodynamically favored, but chlorination is intrinsically more reactive. A higher intrinsic chlorination reactivity derives from the energy splitting between two key redox-active $d\pi^*$ frontier molecular orbitals (FMOs): the lower is the FMO energy for chlorination relative to that for hydroxylation, the higher is the intrinsic reactivity for chlorination. The orbital splitting arises from the differential ligand-field effect of Cl^- versus OH^- on the Fe $d\pi^*$ orbitals. This factor makes chlorination effectively competitive with hydroxylation (Srnc et al. 2017). Both publications on SyrB2 thus provide a complete and comprehensive picture on the reaction mechanism of SyrB2 and reveals key physico-chemical factors that controls halogenation over thermodynamically favored hydroxylation.

We developed the theoretical protocol for accurate calculation of reduction potentials of mononuclear nonheme iron species, which can serve as a highly useful tool for: (i) the interpretation of electrochemical data, including the assignment of redox couples and characterization of their geometric/electronic properties, (ii) the description of redox and catalytic properties of otherwise experimentally elusive N_HFe species, and (iii) correlations of their electron transfer, proton-coupled electron-transfer, and H-atom-abstraction reactivities (Bím et al. 2016 and Bím et al. 2018a). In addition, we developed a concept of the asynchronicity in hydrogen atom abstraction reactivity, which loosely arose from our methodological studies on reduction potentials/acidity constants. Beyond the classical thermodynamic effect on reactivity, we discovered a significant contribution arising from a factor reflecting propensity for (a)synchronicity in concerted H^+/e^- transfers, which stems directly from the reduction potentials and acidity constants of reactants and products (Bím et al. 2018b). To further strengthen the concept, we investigated the effect of asynchronicity on the temperature dependence of the reaction rate and we showed that this factor contributes to a counter-intuitive slowdown of hydrogen-atom abstraction reaction between the iron(II)-tris[2,2'-bi(tetrahydropyrimidine)] complex and the organic TEMPO radical (Bím et al. 2019). Furthermore, we linked the kinetic energy distribution within a reactive mode with the asynchronicity in C–H bond activation, as they both evolve in a series of coupled proton–electron transfer reactions between FeO oxidants and 1,4-cyclohexadiene - the proposed analysis thus yields an intuitive link between the atomic motion in the chemical step and the thermodynamic contributions to reactivity in CPET (Maldonado-Domínguez et al. 2019).

In the area of zeolite catalysis a new method based on a combination of Li–Li correlation MAS NMR spectroscopy and periodic DFT calculations including molecular dynamics was developed to determine the siting of Li^+ and the local structure of Li^+ sites in crystalline aluminosilicate matrixes. The developed approach (Klein et al. 2015) can be in general applied to Li^+ cations in other zeolites and various crystalline matrixes with large unit cells and low concentrations of Li^+ and

also to other NMR- active cations without a significant limitation of their concentration. Moreover, this method is complementary to ^{27}Al MAS NMR spectroscopy in determining the Al organization in the corresponding zeolite. The catalytic properties of zeolite-based catalysts strongly depend on the Al organization of the corresponding material. The new method was applied on SSZ-13 which is a catalytically very important zeolite. The results (Mlekodaj et al. 2019) show that most of the framework Al atoms in SSZ-13 form close unpaired Al atoms.

Molecular dynamics simulations biophysical and photochemical processes

Several subtopics were investigated regarding biophysics of biological interfaces. As a basis, we continued the development of a molecular-level model of Tear Film Lipid Layer, combining computational and experimental approaches. Here, based on our ongoing research, we published a key review paper explaining molecular foundations of the processes occurring in human tear film (Cwiklik 2016). We further developed the model based on our experimental work, introducing a minimalistic representation of the Tear Film Lipid Layer that can be further used by community for in vitro investigations of biophysical and pharmaceutical phenomena pertinent to physiological tear film. We used our models to address a specific role of cholesteryl esters for tear film stability and specific interactions of tear film with proteins (Wizert et al. 2017).

As the second subtopic, we investigated interfacial phenomena occurring at the pulmonary surfactant under oxidative stress. We developed a molecular models mimicking the surfactant and tested them both experimentally (Olzyska et al. 2016) and computationally (Javanainen et al. 2018). Then we successfully employed them to study interactions of lung surfactant with oxidants, air pollutants and the consequences of the elevated oxidative stress (Stachowicz-Kusnierz et al. 2017).

In 2015, we started a successful scientific collaboration regarding properties of implant surfaces, with strong medical application impact. We applied computational methods for deciphering molecular-level properties of plasma-modified polymeric implant surfaces (Golda-Cepa et al. 2017). As a support for the abovementioned topics, we took part in collaborative efforts to unravel various physiologically relevant properties of lipid-based interfaces, mostly lipid membranes. Such aspects as interactions with cytosolic ions, role of charged lipids and lipid nanodomains were addressed in this context (e.g., in Bilkova et al. 2017).

We also followed our long-term interest in molecular dynamics methods for description of photochemical processes, aiming now at the description of intersystem crossings. We developed an approach for surface hopping dynamics on potential energy surfaces resulting from the spin-orbit splitting, i.e., surfaces corresponding to the eigenstates of the total electronic Hamiltonian including the spin-orbit coupling. As a test case, we applied our methodology to deactivation of thiophene and selenophene in the gas phase, ethanol solution, and bulk liquid phase. We have shown that for both thiophene and selenophene molecules, the deactivation of the S_2 state proceeds via the ring opening pathway. The total population of triplet states reached around 15% and 40% after 80 fs for thiophene and selenophene, respectively (Pederzoli et al. 2017). We applied the developed method to a study of the photophysics of BODIPY. Halogenated BODIPY derivatives are emerging as important candidates for photodynamic therapy of cancer cells due to their high triplet quantum yield. We probed fundamental photophysical properties and interactions with biological environments of such photosensitizers. To this end, we employed static TD-DFT quantum chemical

calculations as well as TD-DFT surface hopping molecular dynamics on potential energy surfaces resulting from the eigenstates of the total electronic Hamiltonian including the spin-orbit (SO) coupling (Pederzoli et al. 2019)

Societal relevance

The wide range of the theoretical projects studied in the department covers fundamental areas of an understanding basic molecular reactions, the early Universe chemistry but also areas with the industrial, biological and medicine applications. The interdisciplinary theoretical and experimental research line related to biophysics of biological interfaces aims at bringing new, fundamental knowledge in the fields related to biomedical and pharmaceutical fields. In particular, our studies of tear film are strongly related to the issue of dry eye disease and development of ophthalmologic eye drop formulation that would stabilize the film - this research is performed in direct collaboration with pharmaceutical companies. Investigations of pulmonary surfactant and its properties under elevated oxidative stress would bring new insights into degradation of pulmonary surfactant under pathological conditions in lungs. The implants-related research addresses a very current of designing and engineering of a novel class of hybrid polymeric materials with functionalized surfaces for biomedical applications.

The research projects investigated by the team in the period 2015 – 2019:

The team is carrying out fundamental scientific research, mostly structured by 3-5 years research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), the Academy of Sciences of the Czech Republic (ASCR), and by the European Commission (EC). The findings and results of this research are published primarily as original articles in impacted peer-reviewed international scientific journals. The research projects listed below cover most of the research activity of the teams in the five-year period.

Modelling of electron collisions with molecules adsorbed on surfaces (GACR 2011 – 2015), grant no. P208/11/0452.

The Principal Investigator: R. Čurík

Explicitly correlated multireference coupled cluster methods (GACR 2011 – 2015), grant no. P208/11/2222

The Principal Investigator: J. Pittner

Ab initio molecular dynamics with non-adiabatic and spin-orbit effects applied to time-dependent fluorescence (GACR 2012 – 2016), grant no. P208/12/0559

The Principal Investigator: J. Pittner

Parallel Implementation of Hilbert-space Multireference Coupled Cluster Methods and Application on Excited States (MEYS 2013 – 2015), grant no. LH13117

The Principal Investigator: J. Pittner

Multireference coupled-clusters methods with local pair natural orbital approach (ASCR2014–2015)

The Principal Investigator: J. Pittner

Theory and calculations of electron scattering for needs of nanolithography (MEYS2014–2017), grant no. LD14088.

The Principal Investigator: R. Čurík

Interactions of electrons with neutral polyatomic molecules and positive molecular ions (GACR 2014 – 2016), grant no. P208/14-15989P.

The Principal Investigator: M. Tarana

Investigation of the tear film lipid layer at the molecular level - molecular dynamics simulations and experiments employing model lipid films (GACR 2015

– 2016), grant no. 15-14292S

The Principal Investigator: L. Cwiklik

Local multireference coupled cluster methods (GACR 2015 – 2017), grant no. 15-00058Y

The Principal Investigator: O. Demel

Redox properties and reactivities of nonheme iron active sites (GACR 2015 – 2017), grant no. 15-10279Y.

The Principal Investigator: M. Srnec

Advanced methods for treatment of systems with static and dynamic correlation based on the density matrix renormalization group technique and their applications (ASCR 2016 – 2018)

The Principal Investigator: J. Pittner

New coupled-clusters methods corrected with the DMRG: An implementation for the new generation of supercomputers and applications to the transition-metal complexes (MEYS 2017-2020), grant no. LTAUSA17033

The Principal Investigator: J. Pittner

Lung surfactant under oxidative stress: molecular dynamics simulations and Langmuir film experiments (GACR 2017 – 2019), grant no. 17-06792S

The Principal Investigator: L. Cwiklik

Towards better Synchronisation of Priority Settings and Evaluation Mechanisms for Research Infrastructures Beyond National Relevance (EC 2017 – 2018), grant no. 730928

The Principal Investigator: J. Hrušák

Solvent effects in non-aqueous biocatalysis (GACR 2017 – 2019), grant no. 17-01982Y

The Principal Investigator: E. Pluhařová

Theoretical Research of Long-range Rydberg Molecules (GACR 2017 – 2019), grant no. 17-26751Y

The Principal Investigator: M. Tarana

Penetration, accumulation and interactions of selected drug-model molecules with mimics of human Tear Film Lipid Layer (GACR 2018 – 2020), grant no. 18-26751S

The Principal Investigator: L. Cwiklik

Theory of Electron-Induced Decomposition of Molecules in Plasma and Nano- technology (GACR 2018 – 2020), grant no. 18-02098S

The Principal Investigator: R. Čurík

Relativistic DMRG-based externally corrected coupled cluster methods (GACR 2018 – 2020), grant no. 18-24563S

The Principal Investigator: J. Pittner

Radical catalysis of enzymatic and biomimetic polynuclear transition-metal active sites (GACR 2018 – 2020), grant no. 18-13093S

The Principal Investigator: M. Srnec

Massively parallel tensor network methods for strongly correlated quantum chemistry (GACR 2018 – 2020), grant no. 18-18940Y

The Principal Investigator: L. Veis

Deep learning for strongly correlated systems in quantum chemistry (GACR 2019 – 2021), grant no. 19-13126Y

The Principal Investigator: J. Brabec

Domain based local pair natural coupled cluster method for symmetric and periodic systems (GACR 2019 – 2021), grant no. 19-01897S

The Principal Investigator: O. Demel

Time evolution of conjugated systems in excited states by surface hopping nonadiabatic molecular dynamics (GACR 2019 – 2021), grant no. 19-06860S

The Principal Investigator: J. Pittner

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Research activity and characterisation of the main scientific results

The achieved results of the department can be divided into 6 main categories according to their focus.

Research Direction 1: Understanding Membrane Biophysics at an Atomistic Level

A) Protein oligomerization at the membrane

Oligomers of amyloid A β , originated in the early stages of amyloid aggregation, are thought to be the entities that spark neuronal dysfunction, cell death and Alzheimer's disease onset. Using advanced single-molecule fluorescence techniques, we found that oligomerization of A β monomers is induced by sphingomyelin and inhibited by monosialoganglioside GM1 organized in nanodomains. These new findings support the idea of GM1 as a protective factor rather than GM1 as an enhancer of the A β toxic oligomerization (as suggested in the literature using non-physiologically high A β and GM1 concentrations). (**Amaro et al Angew. Chem 2016**) Positive results of this paper followed up by a perspective article (**Cebecauer et al Biophys. J. 2017**) resulted in formulation of a new grant proposal entitled 'The role of gangliosides in the development of neurodegenerative amyloidogenic diseases:(...)' which was funded for the time period 2017-2019 by GACR.

B) Membrane permeabilization

Membrane permeabilization is often a consequence of protein-membrane or peptide-membrane interactions. In (**Steringer et al eLife 2017**) we developed a new fluorescence correlation spectroscopy assay that enables to correlate membrane permeability to the oligomeric size of FGF2, a transmembrane protein opening membrane pores. This assay can be used on single vesicles to relate in-membrane oligomerization, specifically, the numbers of proteins per oligomer to their function. In a follow up paper, we introduced a new statistical approach that can be used to study membrane permeabilization on a large ensemble of vesicles varying in size. A significant difference between nano- and microscale systems is revealed and needs to be taken into account when conclusions about microscale objects, such as cells, are drawn from nanoscale models (**Braun et al ACS Nano 2018**). We further used our expertise in fluorescence to investigate the role of oxidative stress in permeabilization of mitochondrial membranes by a proapoptotic protein, Bax. The oxidative stress was clearly shown to emulate the activity of Bax, thereby underlying the important role of oxidative stress in apoptotic processes (**Dingeldein Biophys. J. 2017**), (**Lidman, M et al BBA 2016**). Based on these results, a project entitled 'Oxidative stress as an

essential modulator of Bax apoptotic activity: (...)’ was formulated and received funding for 2018-2020 by GACR.

C) Membrane fusion

Fusion of cellular membranes has recently attracted considerable scientific attention, not only for being ubiquitous and vital in living organisms, but also for its potential to be used for in vivo applications. In eukaryotic cells, membrane fusion is mediated by so-called SNARE proteins. In **(Koukalová et al Nanoscale 2018)** we use a model system for membrane fusion inspired by SNARE proteins and based on two complementary lipopeptides. Our data provide crucial insights as to how fusion is initiated and highlight the importance of both peptides in this process. In a parallel paper **(Allolio, C et al PNAS 2018)** we investigated the entrance of arginine rich peptides into cells through induction of membrane multilamellarity and fusion. We proposed a hitherto unrecognized mechanism of passive cell entry involving fusion of multilamellar structures generated by the cell-penetrating peptides.

D) In-membrane nanoscopic segregation of lipids

As documented by **(Cebeauer et al Chem. Rev. 2018)**, nanoscopic segregation of lipids into nanodomains has been a hot topic of the last decade. Since the postulation of rafts as sphingomyelin- and cholesterol-enriched platforms in cellular plasma membranes, scientist have tried to detect these nanoheterogeneities both in plasma membranes of living cells and in model lipid bilayers. Although the existence of model membranes showing the coexistence of liquid-ordered and -disordered phases is well established, there was so far only indirect evidence on the existence of nanodomains in model membranes. In the 4 selected publications we continued developing new approaches that would enable detecting and characterizing these nanodomains. Our findings show that purely lipid driven nanodomains exist and form symmetrically in both bilayer leaflets. More specifically, in **(Šachl et al BBA-Mol.Cell Res. 2015)** we detected nanodomains of GM1 of 6 nm in vesicles containing high number of DOPC and cholesterol molecules. In **(Šachl et al J Phys D – Appl. Phys. 2016)** we questioned the so called ‘diffusion law’ analysis of sv-FCS routinely used by fluorescence spectroscopists. We simulated how lipid domain movement (up to now neglected) influences the diffusion time/spot-size dependence observed in FCS experiments and showed that domain movement substantially changes conclusions on ‘anomalous’ diffusion of nanodomains, even when having super resolution available. In **(Koukalová et al Sci. Rep. 2017)** we found and characterized nanodomains in binary and ternary bilayers of compositions that should result in homogeneous bilayers according to published phase diagrams. And in **(Vinklársek et al J. Phys. Chem. Lett. 2019)** we provided the first experimental evidence that nanodomains of variable sizes between 10 and 160 nm are interleaflet coupled (i.e. penetrating both bilayer leaflets).

E) Specific effects in lipid bilayers – ions and beyond

Specific weak interactions of lipids with small solutes like ions, oxidized lipids including oxysterols and transmembrane domains of various proteins may have significant consequences for membrane organization and structure. In **(Melcrová et al Sci. Rep. 2016)** we characterized the adsorption of calcium ions to lipid bilayers and have shown that calcium binds simultaneously several groups of many lipid molecules in a fashion related to calcium concentration and lipid composition. Moreover, we showed that the

adsorption of Ca^{2+} is modulated and enhanced by the curvature of the lipid bilayer (**Magarkar et al J. Phys. Chem Lett. 2017**). When compared with other ions present at biological membranes calcium not only adsorbs the strongest to various model membranes, but also the mechanism of this binding is qualitatively different from that of monovalent ions like sodium (**Javanainen et al Chem. Comm. 2017**).

Furthermore, in (**Kulig et al J. Phys. Chem. Lett. 2018**) we investigated the role of oxysterols in lipid bilayers. We showed that these interesting molecules preserve to large extent the structural integrity of lipid membranes, but despite their resemblance to cholesterol they change the flip-flop dynamics of the bilayer. Finally, in (**Olšínová et al iScience 2018**) we showed that the presence of a single transmembrane domain can significantly slow down lipid dynamics and influence local lipid composition. Our postulate that it is the roughness of the surface of a typical transmembrane domain that generates these effects implicates the universality of the mechanism, and therefore, its importance for lipid membranes.

Research Direction 2: Elucidating Dynamics/Hydration-Function Relationships in Proteins

Understanding the molecular basis of enzyme-substrate interactions that effectively contribute to their function is important for understanding these molecular machines and constructing superior enzymes by protein engineering. Under this umbrella we have studied two different types of proteins: ATPases and Haloalkane dehalogenases (Dh). In both cases we investigated the implications of hydration and dynamics of the active site and of protein movement, i.e. conformational changes, in enzyme function. In our joint efforts with our collaborators (Jiri Damborsky - MU Brno, Czech Rep. and Karim Fahmy - TU Dresden, Germany) we have successfully investigated these enzymes in a site-specific manner. In the 3 selected articles it is shown how we developed a new fluorescence method based on Unnatural Amino Acid (UAA) to monitor hydration in the tunnel mouths of Dhs (**Amaro et al, JACS 2015**), applied our unique time-dependent fluorescence shift (TDFS) method to monitor hydration and dipole dynamics around the conserved ion-binding motif of the copper-transporting P1B-type ATPase (Fischermeier et al Angew. Chem. 2017), and used the advanced single molecule fluorescence photoinduced electron-transfer-fluorescence correlation spectroscopy (PET-FCS) to monitor in real time the nanosecond conformational changes that constitute a molecular gate to the active site of Dhs on a single molecule level (**Kokkonen et al JACS 2018**). These parameters are connected with other observations to determine their role in enzyme function. Fluorescence labeling as well as all fluorescence experiments were performed in the Department of Biophysical Chemistry. Molecular modeling, construction of the mutants, and CD spectroscopy were performed by the partner labs.

Research Direction 3: Relation between structure, membrane nanoscale organisation and protein function in cells

We continued to investigate the impact of protein structure on cell membrane organisation and protein function. Carefully predicted motifs within the structure of cell surface receptors were mutated and the nanoscale localisation and protein function investigated in cells using cutting edge (super-resolution) fluorescent techniques. The

idea and concepts of the projects were formulated by our team and our collaborators T. Lasser (Switzerland), E. Luescher (Switzerland) and M. Dejneka (Czech Rep.). Most of the work comprising measurements and data analysis has been performed at the Department of Biophysical Chemistry. More specifically, in **(Lukeš et al Nat. Comm. 2017)** we have developed a robust, model-free, quantitative clustering analysis to determine the distribution of membrane molecules that excels in densely labelled areas and is tolerant to various experimental conditions, i.e. multiple-blinking or high blinking rates. The method is based on a TIRF microscope followed by a super-resolution optical fluctuation imaging (SOFI) analysis and is trying to circumvent the limitation of single molecule localization techniques to identify and localize molecules in densely populated areas.

In agreement with our long-term plan, we successfully established fluorescence imaging of live cells at the Department of Biophysical Chemistry. This is documented by the following interdisciplinary publications **(Vogl et al BBA – Mol. Cell. Biol. Lip. 2016)**, where fluorescence microscopy was used to show a direct interaction of oxidised lipids (products of disease and aging) with the PKC δ protein. The paper is an important contribution to the understanding of the detailed mechanism of oxidised lipid-induced cell death. In **(Chum et al J. Cell. Sci. 2016)** the role of palmitoylation of proteins in the sorting of TRAP proteins was addressed. It was concluded that, in addition to the trans membrane domain length, secondary sorting determinants such as palmitoylation or flanking sequences have evolved for the localization of membrane proteins. In **(Lunova et al Sci. Rep. 2017)** we used functionalized nanoparticles, which hold great promise for biomedical applications to demonstrate complex cellular responses to these nanoparticles, suggesting that they can be used for modulation of mTOR signalling in hepatic cells. And finally in **(Liu et al J. Mol. Biol. 2019)**, we showed that CD8 binding to pMHC in cis involves a different docking mode than binding in trans orientation. Differential binding of CD8 to pMHC in cis or trans is a means to regulate CD8 β T-cell responses and provides new translational opportunities.

Research Direction 4: Fluorescence probes and sensors

Understanding the photophysical behavior of fluorescent probes is essential not only for the correct interpretation of their fluorescence parameters and translation into observed phenomena but also for the development of new fluorescent sensors. In the past 5 years we have explained the fluorescence behavior of nitrobenzoxadiazole (NBD)- lipid probes at an atomistic level thus resolving some standing issues **(Amaro et al PCCP 2016, Filipe et al PCCP 2019)**. More specifically, we demonstrated that lipids labelled at the headgroup with NBD do not report on lipid mobility as previously thought but that NBD has a high sensitivity to water molecules in its microenvironment. This translates into NBD sensing the location depth of the probe within the lipid bilayers instead of the lipid mobility. Related to this topic, we studied in detail the applicability of recent membrane probe Di-4-ANEPPDHQ **(Amaro et al J Phys. D.-App. Phys. 2017)**. We showed that the probe has a complex relaxation kinetics involving multiple processes and that these do not correlate with lipid packing. Our findings caution the use of the probe and its common application in cell biology.

In our joint efforts with our collaborators (the group of Michal Hocek, UOCHB) new fluorescence probes with improved sensing capabilities were developed for analysis of DNA-associated processes, DNA-protein or DNA-lipid interactions, cellular structures, DNA-based nanomaterials and for information on DNA hydration and dynamics (**Dziuba et al Chem. Sci. 2016, Dziuba et al Angew. Chem 2016**). The idea and the concepts of the projects were formulated in collaborations with L. Loura (Coimbra, PT), E. Sezgin (Oxford, UK) and M. Hocek (UOCHB, C.R.). Fluorescence experiments were performed in the Department of Biophysical Chemistry. Molecular modeling and synthesis of new probes were performed by the partner labs.

Research Direction 5: Ultrafast photophysics and photoinduced electron transfer

Investigations of characters and dynamics of electronically excited transition-metal containing complexes were geared toward unravelling new photophysical phenomena and developing photosensitizers of electron-transfer reactions, biomimetic photocatalysts for light-energy conversion and phosphorescent probes with long emission lifetimes (related to Research Direction 4 above). The research was based on combining spectroscopic experiments with broad time (fs– μ s) and spectral (IR-vis-UV) resolution with advanced quantum chemical calculations: (TD)DFT, explicit spin-orbit, anharmonic vibrational analysis. We have concentrated on photophysics of di-platinum (and di-iridium) complexes that exhibit both fluorescence and phosphorescence, act as strong photooxidants, photochemically abstract hydrogen atoms from suitable substrates, and possess several electrochemically accessible oxidation states (**Darnton et al JACS 2016, Hofbeck et al Inorg. Chem. 2016**, critically summarized and discussed in **Gray et al Coord. Chem. Rev. 2017**). Unique photophysics and photochemistry of these complexes arises from the presence of two interacting metal atoms in a square planar configuration and a d^8 electron configuration. Discovery of a transfer of vibrational coherence between singlet and triplet excited state on a fs – early fs timescale (**Monni et al PNAS 2018**) is the most interesting result that could have implications for singlet and triplet electron-transfer reactivity.

In a parallel research line, we have investigated photoinduced electron transfer (ET) involving electronically excited Re(I) carbonyl-polypyridyl complexes (critically summarized in (**Viček et al Acc. Chem. Res. 2015**)). We have found that Cu(I) photooxidation in a blue copper protein by covalently appended Re(I) photosensitizer is strongly accelerated by hole hopping through tryptophan residues inserted into the ET pathway, and, namely, that two tryptophans in a series have a much larger accelerating effect than a single one (ca. 10,000- vs. 300- fold vs. long-range electron tunneling) (**Takematsu et al ACS Centr. Sci. 2019**). In the same system, we have also described photoinduced pico-nanosecond interfacial charge separation mediated by a tryptophan quadruplex occurring at a protein-protein interface.

Research Direction 6: Biomimetic electrochemistry at the polarized liquid/liquid interfaces

Research in this direction was focused on the instability phenomena at the liquid-liquid interfaces including thermal fluctuations, interfacial turbulence, dynamics of co-extraction of water, and the collisions of the emulsion droplets with the liquid/liquid

interface. In **(Josypčuk et al Electrochem. Comm. 2015)** the fluctuation analysis was shown to be a reliable method for the determination of the kinetic parameters of ion transfer across a polarized liquid-liquid interface. The source of fluctuations is the real component of the impedance of the cell. Fluctuation analysis was utilized to determine the rate constant of the tetraethylammonium ion transfer across the water/1,2-dichloroethane interface. The obtained data were compared with those derived from the electrochemical impedance spectroscopy experiments using the same electrolytic cell. The used experimental approach exhibits a very small effect of the stray capacitance, proving that this system is suitable for the evaluation of the fast ion transfer kinetics.

In **(Trojánek et al Electrochem. Comm. 2017)** the interfacial turbulence was demonstrated to arise at the polarized water/1,2-dichloroethane interface in the form of the rotating surface structures. The turbulence lead to a remarkable amplification of the faradaic current (polarographic maximum) associated with the transfer of the Na^+ ion from 1,2-dichloroethane to water. Interfacial turbulence was visualized at the surface of the sessile electrolyte drop using suspended graphite microparticles as a fluid flow tracer. We have shown that the magnitude of the faradaic current increases as the circular surface structures rotate more rapidly. Self-amplifying permanent small perturbations, which result in the interfacial turbulence observed, are likely to play a role in the largely unexplored emulsification of a polarized liquid/liquid interface, or the fusion of the nano-emulsion particles with the interface.

In **(Mareček et al Electrochem. Comm 2018)** an electrochemical approach based on the open circuit potential (OCP) measurements has been developed with an aim to analyze the dynamics of co-extraction of water with hydrated ions (chloride) from the aqueous phase to 1,2-dichloroethane. The interfacial potential was controlled by the distribution of a common tetralkylammonium (TAA^+) ion. Transfer of hydrated chloride ions was accompanied by the transfer of TAA^+ , decreasing its concentration on the aqueous side of the interface, thereby resulting in a change of the OCP with time. The proposed mechanism of TAACl extraction involves a follow-up reaction with the co-extracted water molecules, leading to the formation of clusters of water containing TAACl in the organic solvent phase. This may finally result in the formation of a water-in-oil emulsion. Finally, in **(Trojánek et al Electrochem. Comm. 2018)** measurements of the open circuit potential (OCP) transients at a sessile aqueous electrolyte drop in contact with a 1,2-dichloroethane (DCE) electrolyte solution were used to detect the collisions of the single DCE-in-water emulsion droplets carrying 0.35 M tetradodecylammonium chloride with the interface between two immiscible electrolyte solutions (ITIES). Analysis of the CP transients yielded the droplet size distribution, which is comparable with distributions obtained from the current transient measurements at a constant applied potential. These results were supported by dynamic light scattering measurements and microscope droplet image processing. From the molecular point of view, an analysis of the emulsion droplet collisions can improve understanding of the important biological transport mechanism known as the exocytosis.

Societal relevance

Whereas all the main research results are in the form of articles and reviews in

international peer reviewed journals, all topics of research of the team are motivated by clear needs of our society. Specifically:

- The investigations on protein's dynamics/hydration and on how protein's structure/dynamics and its impact on membrane biophysics are connected to the protein's function in cells (topics 1 through 3) are motivated by current challenges in increasing enzyme efficiency and the biology of disease. The former addresses the needs in protein engineering and the findings can serve as a basis for further development of enzymes that will find application in biomedicine in the effective preparation of drugs, and thus can be used in the biotechnology and pharmaceutical industries. The latter addresses a need for information on the nanoscale organisation and dynamics of biomedically relevant events in cell biology, e.g., immune cell communication or protein aggregation and misfolding in neurodegenerative diseases, etc. Understanding such processes not only improves our knowledge of the physical world and of bioactivity, but it can have a direct impact on biotechnical developments and medical applications.

- Electrochemically polarizable liquid/liquid interfaces provide a versatile environment to study the effects of the electrical field and solvation on the accumulation of biomolecules (lipids, polypeptides, proteins, carbohydrates, DNA) at the interface, as well as the interfacial ion or electron transfer eventually induced by light irradiation. A biomimetic process, which is currently in our focus, is the fusion of the emulsion particles with the liquid/liquid interface, in a way resembling exocytosis, and its inverse: the emulsification of the interface. Practical aspects of these studies are represented by electro-separation and bioanalytical applications.

- Our research on photophysics and photoinduced electron transfer in constructs combining organometallic photosensitizers and metalloproteins is relevant to photocatalysis and solar energy harvesting. In a long term, we aim at developing bioinspired systems ("photoenzymes") that would perform energy-saving transformations upon solar irradiation, for example water splitting to hydrogen, reducing CO₂ to CO or simple organic compounds, or reducing N₂ to NH₃. We participate in the EU SUNERGY initiative, preparing a large-scale research program ("partnership") for HORIZON EUROPE in the field of direct solar-energy conversion and generation of "solar fuels".

- The societal impact of the research is also represented by results that are judged highly by our peers in terms of scientific excellence, i.e. contribution to knowledge, and by the building of high-level skills in early stage researchers. The group actively welcomes national and international researchers, from early stage to advanced researchers. This has a societal value in advanced training and in acceleration of introduction of new methods in practice.

The research projects investigated in the team in the period 2015 – 2019:

The team is carrying out fundamental scientific research, mostly structured by three-year research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), and by the European Commission (EC). The findings and results of this research are thus published primarily as original articles in impacted peer-reviewed international scientific journals. The

interim results are also presented at scientific meetings and published in their proceedings. Wider consequences of the work are presented to the scientific community in the form of review articles, book chapters and keynote lectures at conferences.

The research projects listed below cover most of the research activity of the team in the five-year period.

- Praemium Academiae of the Czech Academy of Sciences (end 2017, PI M.Hof).
- Concert of lipids, ions, and proteins in cell membrane dynamics and function (GACR 2019 – 2023, PI M. Hof).
- Proton transport and proton-coupled transport (EC 2019 – 2023, PI M. Hof). PI M. Hof.
- Exploring the structure function relationship of membrane-pore-forming FGF2 oligomers - a single molecule approach (GACR 2014 – 2016, PI M. Hof).
- Membrane interactions of proteins associated with alzheimer's disease and parkinson's disease implications for diseases' pathologies and therapeutic avenues (MEYS, 2013 – 2015, PI M. Hof).
- Essential chemical databases - reaction, structure, bibliographic and patent databases (MEYS, 2013 – 2017, PCo-I M. Hof).
- The role of hydrophobic plasma membrane interior in DOR regulation of trimeric G protein activity (GACR 2014 – 2016, PCo-I M. Hof.).
- Controlling Structure and Function of Biomolecules at the Molecular Scale: Theory Meets Experiments (GACR 2012 – 2018, PCo-I M. Hof.).
- Biomimetic electrochemistry of emulsion micro-droplets at the polarised interface between two immiscible electrolyte solutions (GACR 2017 – 2019, PI V. Mareček).
- Novel Methodology for the Determination of the Rate of Ion-Transfer Across Liquid/Liquid Interfaces (ITIES) (GACR 2013 – 2016, PI V. Mareček).
- Elucidating the role of dynamic tunnels in enzyme catalysis: simulations and fluorescence experiments (GACR 2016 – 2018, PCo-I J. Sýkora).
- Alterations of δ -opioid receptor mobility and function by acute and chronic depletion of plasma membrane cholesterol content of live cells (GACR 2017 – 2019, PCo-I J. Sýkora).
- Acceleration and control of photoinduced electron transfer (GACR 2017-2019, PI A.Vlček).
- Photochemical Activation of Redox Centers in Proteins (MEYS 2019-2022, PI A.Vlček).
- Structure and dynamics of excited and redox states of photocatalytic complexes (MEYS 2014-16, PI A.Vlček).
- Electron transfer dynamics in complex molecular systems (MEYS 2017-2019, PI S. Zálíš).
- Solar Energy for a Circular Economy (European Commission, 2018-2019). PI A.Vlček
- Participation of Czech research institutions in EERA – EUPRO II (MEYS 2016-2017, PI A.Vlček).
- Participation of Czech research institutions in EERA – EUPRO II (MEYS 2019-2021, PI A.Vlček).
- Microscopic insight into collapse thermodynamics of thermoresponsive polymers (GACR 2016-2018, J. Heyda).
- New electrophoretic approaches in studies of obesity and diabetes (GACR

2015-2017, PI Z.Samec).

- Tological regulation of CD4 and CD8 in T cells (GACR 2019-2021, PI M.Cebecauer).
- Organisation and function of CD4 co-receptor on the surface of T cells at nanoscale (GACR 2015-2017, PI M.Cebecauer).
- Oxidative stress as an essential modulator of Bax apoptotic activity: molecular insights by single-molecule fluorescence (GACR 2018-2020, PI R.Šachl).
- The role of gangliosides in the development of neurodegenerative amyloidogenic diseases: Molecular insights by advanced fluorescence microscopy (GACR 2017-19, PI M.Amaro).

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Research activity and characterisation of the main scientific results

The scientific work of the team has led to several results that are worth noting due to their importance for the fields of catalysis and zeolite science, and some of them with practical impact on industrial technology. Selected results in the focus areas of the team are as follows:

1. Structure and activity of distant binuclear TM ion sites in zeolite matrices for methane utilization. This is a new area of research that started in the period 2015 – 2019, in which a new type of active sites stabilized in the zeolite matrix was studied – distant binuclear transition metal ion sites. A pair of divalent TM ions located in opposite zeolite rings so far that the formation of bridging structure with dioxygen (analogous to oxidized metalloenzyme active sites) is not permitted. However, these ions are close enough to cooperate on the interaction with dioxygen and able to activate it by a new mechanism – splitting of dioxygen and formation of a pair of so-called α -oxygens ($M^{4+}=O_2$)²⁺, even at room temperature. The α -oxygens are so active that they can oxidize methane (to methanol) or other liquid products at room temperature, without the need for an effluent. (Tabor et. al., *Sci. Advances*). Besides dioxygen, binuclear TM ion sites are promising in the activation of other molecules, as it was shown for N₂O (Tabor et. al., *Commun. Chem.*). Due to the significant economic potential of the selective oxidation of methane, measures to protect intellectual property have been implemented (*Dedecek et al., WO 2020 200336*). Research in this area, e.g. selective oxidation of other industrially important molecules and activation of other selected molecules over binuclear sites is supposed to be the key area of the team research in the near future.

2. Synthesis of porous matrices (zeolites by ADOR, carbon replicas of zeolites). This wide area of research covers several independent (both by methodology, nature of materials and their application) subtopics concerning the synthesis of materials with unique properties:

2.1. Synthesis of zeolites with novel topologies. Up to now, more than two hundred zeolite materials with different topologies were prepared. However, there are plenty of possible zeolite structures, some of them with interesting properties (e.g. with seven- or nine-member ring channels, which are extremely rare), but thermodynamically unfeasible to prepare. The ADOR (assembly–disassembly–organization–reassembly) strategy of zeolite preparation developed by the team allows us to overcome these limitations and prepare zeolite structures with new topologies. The main novelty of this strategy lays in the chemical attack of Ge atoms in the germanosilicate framework, which results in the formation of zeolite lamellar material. These lamellar precursors are then reorganized to form zeolites with thermodynamically unfavorable topologies. This study represents a continuation of the successful research from the period 2010 – 2014. Several new topologies were prepared (*Kasneryk et al., Angew. Chem. Int. Ed.*) and extensive team experience was concluded in the reviewed papers (*Eliasova et al., Chem. Soc. Rev., Mazur et al., Nature Chem.*).

2.2. Zeolites with a hierarchical porosity and 2D zeolite materials. The lamellar precursors prepared by the ADOR approach can be reorganized not only to form new zeolites but also to form mesopores and thus materials with hierarchical micro-

mesoporosity or pillared 2D zeolite materials (Prech et al., Chem. Soc. Rev., Opanasenko et al., Catal. Sci. & Technol.). Combination of zeolite local arrangement with mesopores prepared by ADOR (or other ways) enabling access of large molecules is essential for the transformation of bulky molecules (Kim et al., ACS Catal.).

2.3. 3D graphene. Graphene is a unique material but rather inconvenienced for application in heterogeneous catalysis due to the low accessibility of the active sites stabilized on this material. 3D carbon replicas of zeolites, the preparation of which was mastered by the team, eliminates this disadvantage while maintaining promising properties of graphene-based materials (Sazama et al., ACS Catal.). Highly promising appears application of 3D graphene in CO₂ capture (Vorokhta et al., J. of CO₂ Util.). This area of research is to be continued as one of the main themes of the team.

2.4. Solvent-free synthesis of zeolites. Minimization of waste is a critical issue of sustainable chemical technology. Recently started research (2017) of the solvent-free synthesis of zeolite matrices represents an emerging innovation in zeolite synthesis. A significant step ahead in our approach is based on the application of well-controlled mechanical grinding (planetary mill) beside applied till now hand milling (mortar) (Pashkova et al., Chem. – Eur. J. and CZ 308130).

2.5. Synthesis of Al-rich beta zeolites. Beta zeolite is the only large-pore Si-rich zeolite with a 3D channel system. This results in its significant industrial importance. An increase in the concentration of Al atoms in the framework of this material enables to overcome a barrier of low activity for its application in numerous reactions. The team acknowledged the synthesis of Al-rich beta zeolites in the previous period 2010 – 2014. Attention is now focused on the catalytic applications of these materials (see later) and mainly on the commercialization of the knowledge previously obtained (Sazama et al., WO 2015 197036).

3. Organization of Al atoms in zeolite matrices (analysis and tuning).

Organization of Al atoms in the zeolite framework is together with the framework topology a key parameter controlling the performance of zeolite catalyst. Distribution of Al atoms in zeolites was introduced to zeolite science by the team and this issue represents the “family silver” of the team and its advantage to other zeolite/catalytic research groups.

3.1. Analysis of Al distribution. The methodology of the analysis of Al distribution in the zeolite framework and cation siting in the zeolites was significantly improved (Martineau-Corcos et al., Solid. State Nucl. Magn. Reson., Klein et al., Chem. Commun.) including DFT calculations and extended to other than pentasil-ring zeolite matrices, which was concluded in the review (Dedecek et al., Chem. Sus. Chem.). The obtained knowledge allowed to analyze Al organization and cationic sites e.g. in one of the most complex zeolite structure – TNU-9 (Karcz et al., Jchem. – Eur. J.) and Al-rich beta zeolite (Sazama et al., J. Catal.).

3.2. Tuning of Al distribution in zeolites. Research in the area of synthesis of zeolites with desired Al distribution tuned for individual reactions continued. Attention was focussed, besides ZSM-5, to one of the currently most studied zeolites – SSZ-13

(Mlekodaj et al., J. Phys. Chem. C and CZ 2017 00832).

4. Redox catalysis over zeolites (NO_x and N₂O abatement). Redox catalysis is a core area of the catalytic studies of the team in which fundamental research of the structure-activity relationship on an atomic level, is extended to the attempts at the commercialization of the obtained knowledge. The experience of the team in the area of Al organization in zeolites is fruitful. A highly promising material appeared to be TMI-containing Al-rich beta zeolite, which shows synergy of the high concentration of active cationic sites (Sazama et al., J. Catal. and WO 2015 197036). Another direction is the development of catalysts for N₂O abatement at high temperatures, in which substantial improvement was reached for ferrierite-base catalysts (Sadovska et al., Catal. Commun., Tabor et al., Appl. Catal. B) and perovskite-based catalysts (Sadovska et al., CZ 2017 00050). In the case of ferrierite catalysts, a key role played an understanding of the local perturbation/stability of Al atoms in the ferrierite framework studied on the atomic level (Brus et al., Angew. Chem. Int. Ed.).

5. Hydrocarbon transformations over acid zeolite catalysts. Hydrocarbon transformations/acid catalysis is both a key area of the heterogeneous catalysis and the catalytic research of the team. Also, in this field was fructified unique knowledge of the team covering synthesis of unique (by the topology, hierarchical porosity and Al organization) zeolite materials.

5.1. Control of acid catalysed reaction by tuning of Al organization. Research in this area represents basic science and was focused on the role of Al distribution (proton distances) in catalysts for hydrocarbon transformations. After years of discussion, it was shown by the team that Al atoms in ZSM-5 are located exclusively at the channel intersection (Pashkova et al., Chem. – Europ. J.). Al distribution in the framework plays the key role in the number of reactions, and affects not only the reaction pathway (selectivity) (Li et al., ACS Catal.) but also activity of catalyst through release of the product from the active site (Bernauer et al., J. Catal.).

5.2. (Hydro)isomerization of hydrocarbons. This topic is focused on application research, often carried with industrial partners. Attention was paid on the utilization of Al rich beta zeolites, which on one side preserve advantages of large pore beta zeolite but posses dramatic increase of activity due dramatic increase of active sites in stable (on contrary to systems derived from faujasite) catalyst (Sazama et al., Applied Catal. A, Belecky et al., CZ201500605).

5.3. Catalysis over catalysts with hierarchical porosity. Other important parameter resulting in high catalytic activity of catalyst is the improvement of accessibility of active sites by tuning of micro- and meso-porosity of catalysts, especially in the case of bulkier substrate molecules. Also this area is rather oriented to the applied research. Various approaches for the preparation of porous materials with hierarchical porosity were successfully employed. Significant improvement was obtained e.g. for mordenite catalyst by post-synthetic modification (Pastvova et al., ACS Catal., Kaucky et al., CZ201700006), direct synthesis of zeolite nano-sponges (Kim et al., ACS Catal.). Other possible improvement in this field is an application of ordered 2D materials (Opanasenko et al., Catal. Sci. & Technol., Prech et al., Catal. Sci. & Technol., Heard. et al., Adv. Mater.)

5.4. Catalysis over MOF catalysts. Metal organic framework materials enable to prepare well-defined active sites in well-defined environment for basic research. It was successfully employed for deeper understanding of a number of reactions e.g. aldol condensations ([Kikhtyanin et al., Catal. Today](#)).

6. Photocatalytic processes for abatement of NO_x and organic pollutants.

The research in the field represents continuation of the work in the period 2010 – 2014 which was focused on the preparation of nanomaterials. Nevertheless, a substantial extension has been made in the period 2015 - 2019 to cover application of nanomaterials in photocatalysis.

6.1. Novel porous nanocomposites for the application in

photoelectrochemistry. Nanostructured transparent conducting oxide layers gain increasing importance as high surface area electrodes enabling incorporation of functional redox species with high loading. The novel antimony-doped tin oxide films were fabricated using the self-assembly of preformed antimony-doped tin oxide nanocrystals with poly(ethylene oxide-*b*-hexyl acrylate) block copolymer, the pore size being tunable in the range from mesopores to macropores ([Peters et al., Adv. Funct. Mater.](#)). The combination of tunable porosity with a large conducting interface makes the obtained layers versatile current collectors with adjustable performance. Nanocrystalline cellulose is an abundant biogenic nanomaterial with unique properties that enables the efficient synthesis of mesoporous crystalline titania ([Ivanova et al., Chem. Mater.](#)). We significantly enhanced the photocatalytic activity of titania thin films by introducing solvothermally synthesized preformed anatase nanoparticles into a sol–gel based biotemplated titania scaffold.

6.2. Photocatalytic purification of water. Novel photocatalytic layers were prepared by quantitative electrophoretic deposition of nanoparticles of TiO₂ doped with carbonaceous additive species without sintering and without the use of any dispersive additive. The obtained immobilized reduced graphene oxide/TiO₂ composites exhibited high purity and mechanical resistance, showing markedly increased photocatalytic degradation rate in the mineralization of important aqueous pollutants, such as chlorophenols and antibiotics ([Guerin et al., Appl. Catal. B](#)).

6.3. Photocatalytic purification of the air. The extensive experimental research showed that porous layers containing TiO₂ nanocrystals and inorganic binder deposited on a range of building materials exhibit high photocatalytic performance with regard to NO and NO₂ abatement ([Zouzelka et al., Appl. Catal. B](#)). The effect of all the important process parameters (character of flow, temperature, relative humidity, irradiation intensity, pollutant concentration) was determined, which enabled to extrapolate the laboratory data to real world conditions and to calculate the realistic rate of pollutant removal.

Societal relevance

Catalysis is an important human activity with a grand impact on our daily life. More than 20 % of gross world product results from catalytic processes. Zeolites represent the widest and the most important group of heterogeneous catalysts. Moreover, the application of zeolites in gas separation is also essential (nitrogen production). It is expected that the role of heterogeneous catalysis will further increase as the

transformation of chemical production towards sustainability (environmentally friendly, low to zero carbon) represents one of the biggest tasks for today's society. Therefore, catalysis on zeolites and/or zeolite science is in a unique position. Specific properties of zeolites make zeolite matrices very suitable materials for the fundamental research in catalysis – understanding of the structure-activity relationship of active sites on the atomic level. On the other hand, a number of promising applications of zeolites emerged in the important areas for the development of sustainable chemical production such as the utilization of small molecules (carbon dioxide and methane), renewables and biomass, as well as the capture of CO₂ and abatement of a wide variety of pollutants. Moreover, there is an enormously fast transfer of knowledge from zeolite basic research to industrial application.

Thus, whilst all the main research results are in the form of articles, all issues studied by the team concerns hot topics from the point of societal relevance, as shown below for main areas of interest of the team during the period 2015-2019.

Structure and activity of distant binuclear TM ion sites in zeolite matrices for methane utilization. Methane utilization by transformation to valuable liquids is one of the biggest challenges in catalysis. Activation and utilization of small molecules, such as CO₂ and methane, is regarded as crucial for the transformation of the chemical industry towards its sustainability. Selective oxidation of methane to methanol as an energy carrier and chemical platform is thus of extremely high societal relevance.

Synthesis of porous matrices. Porous matrices can play a significant role in the capture of CO₂. Solvent-free synthesis of zeolites enables the environmentally friendly synthesis of zeolite catalysts. Preparation of zeolite matrices is a starting point for the development of highly active (minimization of energy consumption) and selective (minimization of waste) catalyst for hydrocarbon transformations, and utilization of renewables/biomass (hierarchical porous materials) also required for the transformation of the chemical industry towards its sustainability.

Organization of Al atoms in zeolite matrices. Al organization is a key parameter controlling the performance of zeolite catalysts. Tuning of Al distribution allows the preparation of optimized zeolite matrices functioning as highly active (minimization of energy consumption) and selective (minimization of waste) catalyst for hydrocarbon transformations, methane utilization, N₂O abatement, and deNO_x processes.

Redox catalysis over zeolites. End of pipe solution for N₂O abatement and deNO_x processes for automotive and process gases is of high importance for clean air protection.

Hydrocarbon transformations over acid zeolite catalysts. Development of highly active (minimization of energy consumption) and selective (minimization of waste) catalyst for hydrocarbon transformations is essential for new processes required for the transformation of chemical products to sustainable ones (change of substrates).

Photocatalytic processes for abatement of NO_x and organic pollutants. The development of materials and processes for cleaning of exterior and interior atmosphere and water is an issue with enormous societal relevance. With the

application of nanotechnologies is connected important question of their safe use, solved in newly started research on the toxicity of nanomaterials

The societal impact of the research is also represented by a strategic partnership with industrial partners. The team continues in deep cooperation with two partners, UNICRE a.s. (research body of Chemopetrol a.s., the main Czech oil and petrochemical company) and Euro Support Manufacturing Czechia, s.r.o. (main Czech catalysts producer). This strategic partnership is demonstrated in several joint projects in the frame of the Technological Agency of the Czech Republic. The high societal relevance of the teamwork is also reflected in the short-term cooperation with two important oil European companies (BP Chemicals Inc. and Shell).

The research projects investigated by the team in the period 2015 – 2019:

Although the team is carrying out predominantly fundamental scientific research, also applied scientific research (scale-up) and direct cooperation with an industrial partner is covered. The research is mostly structured by three-year research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), Ministry of Industry and Trade of the Czech Republic (MIT) Ministry of Culture (MC) and by longer projects funded by the Technology Agency of the Czech Republic (TACR) and European Commission (EC) and by Academy of Sciences of the Czech Republic (ASCR) in the frame of the program framework Strategy AV21. The findings and results of this research are thus published primarily as original articles in high-impact peer-reviewed international scientific journals. The interim results are also presented at scientific meetings, wider consequences of the work are presented to the scientific community in the form of review articles and invited, plenary and keynote lectures. The results of applied research cover a wide variety of forms from patent/patent applications to unpublished know-how co-owned with industrial partners.

The research projects listed below cover most of the research activity of the team in the five-year period.

Innovative approaches for methane utilization – enzyme inspired zeolite catalysts (GACR 2019 - 2021) GA19-02901S

Principal Investigator: J. Dedecek.

Selective oxidation of methane to methanol and other valuable products (MEYS 2019 - 2021) 8JPL19046

Principal Investigator: J. Dedecek.

Progressive materials for protection from serious damage of environment (TACR 2018 - 2021) TH03010207

Co-investigator: J. Dedecek.

Molecules and Materials for Life (AV21, 2018 - 2024)

Co-investigator: J. Dedecek.

Concept for creation of zeolite based catalysts with enhanced functionality for industrially relevant acid- and redox-catalysed reactions (GACR 2018 - 2020)

GA18-20303S

Principal Investigator: P. Sazama.

Development of high-performance alkylation and isomerization catalysts (TACR 2018 - 2020) TH03020184

Co-investigator: P. Sazama.

Innovative approaches for zeolite synthesis (GACR 2017 - 2019) GJ17-09188Y

Principal Investigator: V. Pashkova.

Binuclear metal ion structures in zeolites (GACR 2017 - 2019) GA17-00742S

Principal Investigator: J. Dedecek.

Creating and mastering structure of hierarchical zeolites to design advanced hydroisomerization catalyst (GACR 2015 - 2017) GA15-12113S

Principal Investigator: P. Sazama.

Zeolites with (semi)monomodal aluminum distribution in the framework (GACR 2015 - 2017) GA15-13876S

Principal Investigator: J. Dedecek.

Catalytic process for complete elimination of nitrogen oxides emissions for the production of nitric acid (TACR 2015 - 2017) TH01021259

Principal Investigator: P. Sazama.

Catalysts for eliminating N₂O in the high temperature regime in the production technology of nitric acid (GACR 2014 - 2016) GA14-10251S

Principal Investigator: Z. Sobalik

Nanomaterials and Nanotechnologies for Environment Protection and Sustainable Future (MEYS 2016 – 2023) LM2015073

Co-investigators: Z. Sobalik, P. Sazama, J. Rathousky

Photocatalytic NO_x removal from polluted air. Mechanism and overall impact on the environment (ASCR 2019 - 2020) L200401902

Principal Investigator: R. Zouzelka

Photocatalytic technology for air purification in interiors and exteriors of buildings: overall environmental impact (GACR 2019 – 2021) GA19-12109S

Principal Investigator: L. Brabec

Graphene / semiconductor heterojunction for efficient photocatalytic degradation of resistant water pollutants (GACR 2019 – 2021) GA19-21801S

Principal Investigator: J. Rathousky

Utilization of Optimized Photocatalytic Nanocomposites for Depollution of Air from Harmful Contaminants (MIT 2019 – 2022) FV40209

Principal Investigator: J. Rathousky

Smart materials for the complex protection of the surfaces of historical buildings (GACR 2017 – 2019) GA17-18972S

Principal Investigator: J. Rathousky

New materials and technologies for the conservation of the materials of historical monuments and the preventive care (MC 2011 – 2015)

DF11P01OVV012

Principal Investigator: J. Rathousky

Engineering of advanced catalysts from modular parts (GACR 2015 – 2017) GA17-01440S

Principal Investigator: J. Cejka

Next generation personal protection garments against warfare agents (European Defence Agency 2015 – 2017) PRO-SAFE (A-1152-RT-GP)

Investigator: Jiri Cejka

Maximizing the EU shale gas potential by minimizing its environmental footprint (EC, 2015 - 2018), H2020-LCE-2014-1, 640979.

Investigator: Jiri Cejka

Combined Experimental and Theoretical Investigation of Catalytic Properties of Metal Organic Frameworks (GACR 2014 – 2016) GA14-07101S

Principal Investigator: J. Cejka

Catalytic oxidation of alkenes (TACR 2013 – 2016) TA03011148

Principal Investigator: J. Cejka

CAScade deoxygenation process using tailored nanoCATalysts for the production of BiofuELs from lignocellulosic biomass (EC, 2013 - 2017), FP7-NMP-2013-LARGE-7, 604307

Investigator: Jiri Cejka

Two-dimensional zeolites with modifiable architecture (GACR 2012 – 2016) GAP106/12/0189

Principal Investigator: J. Cejka

Intelligent Design of Nanoporous Adsorbents and Catalysts (GACR 2012 – 2018) GBP106/12/G015

Principal Investigator: J. Cejka

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Research activity and characterisation of the main scientific results

First of all, it should be mentioned that the Department of Molecular Electrochemistry and Catalysis was established only two years ago (2018) from the team of Molecular Electrochemistry and the team of Molecular Catalysis. Although both teams keep their original experiences, skills and interests, it emerged that many themes are complementary. The common topic is the **fundamental research of new metalloorganic and transition metal coordination compounds with various expected applications**. Such newly designed molecules are very attractive from the electrochemical, spectroscopic and mechanistic point of view, e.g., molecules with multiple redox centres, with various geometry in solution, with various extent of delocalization and therefore often with a new and unexpected (photo)reactivity initiated by electron transfer.

During the last two years it appeared that this thematic interconnection enabled very efficient scientific cooperation and sharing of knowledge and instrumentation in a "vertical" way, as mentioned above. Nevertheless, the majority of the below presented results come still from the time before the constitution of the new Department, although currently several mutual projects are already running.

New Fischer aminocarbene complexes as prospective catalysts

Several series of iron, chromium and tungsten aminocarbene complexes were prepared with various substituents on the carbene carbon (substituted aromates and heterocycles) and various structure (chelating ligands, dinuclear complexes). Besides the fundamental redox characterization, the relationship between the structure (substitution site) and electron delocalization, hence reducibility and stability of radical intermediates, was followed and summarized in the article published within the series *Current Opinion in Electrochemistry* [1]. During biphasic (acetonitrile-hexane) preparative electrolysis of heterocyclic Fischer aminocarbene complexes stereoisomeric products were found. For identification of products, EC-MS tandem was developed [2]. This project was performed in the cooperation with Inorg. Chem. Dept. of UCT Prague (VŠCHT), where the compounds were prepared. All electrochemical part including the EC-MS measurements was done in our team.

[1] Hoskovcová, I., Ludvík, J. (2019). Electrochemical approach to Fischer carbene complexes. *Current Opinion in Electrochemistry*, 15, 165–174.

[2] Metelková, R., Hoskovcová, I., Polášek, M., Urban, J., David, T., Ludvík, J. (2015). Stereoisomeric products of electrochemical reduction of heterocyclic Fischer aminocarbene Cr(0) complexes. Development of the EC-MS tandem approach using biphasic (acetonitrile-hexane) preparative electrolysis. *Electrochim. Acta*, 162, 17-23.

Electrochemistry and structure-properties relationship of carboranes and dicarboranes

Substituted carboranes bearing negative charge are able to form at highly positive potentials relatively stable radicals under extreme electrochemical conditions (liquid SO₂, low temperature, vacuum line, special fluorinated supporting electrolyte, special (spectro)electrochemical cell) [3]. These species are very strong oxidizing agents which undergo dimerization under formation of Borenium and Iodonium ylides [4]. An unexpectedly large shift of the reduction potential to negative values as a result of strong prolongation of the C-C bond (closo-structure

was changed nearly to nido-) was found in 1,2-dicarba-closo-dodecaborane cage as a result of the electron capture [5]. This project was performed in the cooperation with IOCB Prague (ÚOCHB) and University of Colorado at Boulder, where the compounds were prepared and theoretical calculations performed. All electrochemical experiments, kinetic measurements and evaluation of experimental data were done in our team where A. Wahab worked as a post-doc.

[3] Wahab, A., Douvris, Ch., Klíma, J., Šembera, F., Ugolotti, J., Kaleta, J., Ludvík, J., Michl,

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Phthalaldehyde (OPA) – biologically significant mechanism of reactions with N-, S- and O- nucleophiles and amino acids

Phthalaldehyde is an aromatic dialdehyde with a strong disinfection ability, which is also used in analysis of amino acids by their derivatization. The reaction mechanism is extremely complicated due to the series of acidobasic, hydration/dehydration and cyclization/decyclization equilibria and its understanding is important for efficiency of the mentioned applications. Using the electrochemical monitoring of the reaction of OPA with primary amines [6], diamines [7] and amino acids [8], the role of the substitution on the α -carbon was discovered and the effect of OPA hydration on the course of the reaction was also described. In contrary to the published information, the dialdehydic unhydrated form is not the primary reactive species and for the successful reaction of OPA with amines, the presence of water is necessary. All this research was performed only in our team (Joel Donkeng was our PhD student).

[6] Donkeng Dazie, J., Liška, A., Ludvík, J. (2016). Electrochemical and Quantum Chemical Study of Reactivity of Orthophthalaldehyde with Aliphatic Primary Amines. *J. Electrochem. Soc.*, 163, G127-G132.

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Singlet fission – testing of newly synthesized derivatives and dimers of diphenylisobenzofuran

Electrochemical examination of four series of new molecules – materials that are promising to perform efficient singlet fission – have been performed. Dimeric 1,3- diphenylisobenzofurans linked covalently by various bridging units revealed

changing level of intramolecular electronic communication [9], fluorinated 1,3-diphenyliso-benzofurans exhibit discontinuities of electron distribution and geometry depending of number and site of substituents [10]. Substituted diketopyrazines appeared to be

unsuitable due to their instability. Recently, derivatives of cibalackrot (related to indigo) are the most promising. All measured data are always correlated with DFT calculations.

This project is performed in the cooperation with IOCB Prague (ÚOCHB) and University of Colorado at Boulder, where the compounds were prepared and theoretical calculations performed. All electrochemical experiments, kinetic measurements and evaluation of experimental data were done in our team.

[9] Akdag, A., Wahab, A., Beran, P., Rulíšek, L., Dron, P., Ludvík, J., Michl, J. (2015). Covalent Dimers of 1,3-Diphenylisobenzofuran for Singlet Fission: Synthesis and Electrochemistry. *J. Org. Chem.*, 80, 80-89.

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Nitro-Calix[4]arenes – molecules with multiple redox centers, receptors, stereoelectrochemistry, electrochemically generated ligand.

The intramolecular communication of a very extended series of mono-, di-, tri- and tetranitro substituted Calix[4]arenes was elucidated using spectro-electrochemical approach. Elucidation of the structure-redox activity relationship enables to design new anionic receptors. Nitro-substituents attached of the calixarene skeleton were used as "redox probes" which reflect the extent of intramolecular electron delocalization.

The electrochemical data revealed, that the shape of the calixarenes has not the symmetry C₄, but C₂ and the inner cavities are not circular, but strongly pinched and undergoing a dynamic pinched-pinched interconversion. This finding opened a new electrochemical discipline, Stereoelectrochemistry, where electrochemical data can decipher the real geometry of the dissolved molecule and its dynamic behaviour in the solution. The examples and generalized rules of this phenomenon are summarized in the article published within the series Current Opinion in Electrochemistry [11].

Besides that, surface modification and specific recognition was tested using various types of calixarenes [12,13, 14]. The following investigation of thiacalixarenes revealed, that the thia bridges in combination with meta-substitution open partial electron communication between the nitro groups [15]. The compounds were prepared in the UCT Prague, or in University of Guj'arat, India, all mentioned research was performed in our team, with Dr. Krunal Modi as a post-doc.

The most important finding in this project is the **first observation of electrochemically generated ligand**. Due to the total absence of intramolecular communication in calixarenes bearing methylene bridges, all nitro groups are reduced independently. As a result, a stable tetranitro tetraanion tetraradical is generated which forms stable complexes with heavier alkali metal cations (K⁺, Rb⁺, Cs⁺). This finding offers various applications as an electrochemically triggered sensor or receptor [16]. [11] Liška, A., Ludvík, J. (2018). Stereoelectrochemistry of calixarenes – Molecules with

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Oxidative degradation of nucleic acids in mutagenesis and carcinogenesis

New project with Masaryk University Brno is dealing with the detailed investigation of the role of oxidation of nucleic acids in genetic changes. The study starts with guanine (G), guanosine, deoxyguanosine, guanosine monophosphate and deoxyguanosine monophosphate, and the experimental results were compared with the theoretical ones. Significant difference (more than 200 mV) between the oxidation potentials of guanine nucleobase and its nucleosides and nucleotides is discussed [17].

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Electrochemical investigation of remediation mechanism in water cleaning using "zero-valent iron"

Project of (up to now informal) cooperation with University of Ngaoundere, Cameroon aimed to actual problem (not only) in Africa with water cleaning. Our common research is focused to the use of "zero-valent iron" for removal of Zn^{2+} , Cd^{2+} and Pb^{2+} from water, where the efficiency of remediation is correlated with the iron "aging" [18]. All this work was performed in our laboratory with the J. Donkeng Dazie as post-doc.

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Aluminum free catalytic system utilizing hydrosilane-B(C6F5)3

The basic concept of this topic [19], which comprised activation of zirconocene dihalide complexes toward ethylene polymerization, presented a novel aluminum-free activator based on combination of hydrosilane and tris(pentafluorophenyl)borane (HSiB), which replaced a well-known methylaluminoxane (MAO). The activator was successfully used for activation of transition metal complexes to obtain a system

catalytically active for olefin polymerization as well as, see below, for other catalytic processes (hydrodehalogenation). The versatility of this system was demonstrated on activation of titanocene dihalides and titanium halfsandwich ketimide complexes in ethylene polymerization or ethylene and 1-hexene (co)polymerization, respectively [20]. We obtained evidence for the formation of active catalysts for ethylene polymerization in chlorinated solvents with heterometallic binuclear titanocene chloride – cyclopentadienylchromium dichloride complexes. The polymerization activity in the above systems is prevailingly due to the catalysis of the titanium species, while the contribution of the chromium species is marginal. Nevertheless, selected binuclear catalysts were able to produce HDPE with preferred bimodal molar weight distribution [21]. Currently we are investigating the HSiB activator for activation of titanocene derivatives. We see a high potential of the system for basic knowledge (silylene generation) as well as possible application

In addition, catalytic chlorination of tertiary, secondary and primary hydrosilanes by Ph_3CCl with $\text{B}(\text{C}_6\text{F}_5)_3$ as the catalyst was evaluated. The reaction was substantially faster than its noncatalyzed version. In the case of secondary silanes and PhSiH_3 , an

effect of different Ph_3CCl /silane ratio on the formation of chlorohydrosilanes and dichlorosilanes was explored [22]. Activation of the metal catalyst by a combination of hydrosilane Et_3SiH and catalytic amount of $\text{B}(\text{C}_6\text{F}_5)_3$ described previously was used also for hydrodehalogenation of aliphatic organohalides. In comparison to dehalogenation procedures reported in literature, we were able to perform defluorination of trifluorotoluene as a model substrate with 5 mol % of readily available and bench stable Cp_2TiCl_2 and related complexes in combination with $\text{B}(\text{C}_6\text{F}_5)_3$ under mild conditions and with a high degree of selectivity (i.e., suppression of Friedel-Crafts by-products)[23]. Moreover, the hydride transfer from hydrosilane to $\text{B}(\text{C}_6\text{F}_5)_3$ and finally to a transition metal was recently found to be efficient for other transition metals (Ni) halide complexes where the formation of a metal–hydride bond is a prerequisite for their catalytic performance.

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Intramolecular activation of ligands in early transition metal complexes

This topic is aimed at basic research of organometallic compounds of electron-deficient transition elements and relates to the applied research of catalysts for C-C bond-forming reactions. The research consisted of preparation, characterization, and application studies of titanium and zirconium derivatives carrying auxiliary highly substituted cyclopentadienyl ligands. The ability of these compounds to activate electrons on these ligands, as well as simple molecules such as hydrogen, hydrogen sulfide, and unsaturated hydrocarbons under thermal, photolytic, or reduction-induced activation has been studied. Two review articles summarizing transformations of functional groups attached to cyclopentadienyl or related ligands in group 4 metal complexes[24] and the development and current progress in the field of titanocene sulfide chemistry[25] were published by the team members.

We have demonstrated the use of decamethyltitanocene hydride complex for catalytic hydrogenation of alkynes and dienes leading to relevant olefins and saturated hydrocarbons at low hydrogen pressure and laboratory temperature[26]. A methodology has been developed for the preparation of new metallocene titanium and zirconium complexes with a tethered ketimide moiety attached to the cyclopentadienyl ring and intramolecular ligand transformations were studied[27]. A follow-up investigation of previously studied titanocene complexes leading to the preparation of new titanium species using thermal and photolytic activations of substituted cyclopentadienyl ligands, displacement of ethylene with alkynes was studied[28].

The previously reported study about “aluminum free catalytic system” gives evidence for the formation of active catalysts for ethylene polymerization in chlorinated solvents where the higher observed polymerization activity in the above systems is prevailing due to the better stability of the titanium active species. Novel hydride species based on titanocene and zirconocene compounds were prepared, characterized, and their reactivity towards different substrates was investigated[29]. The results show that the knowledge obtained from these studies can help to understand the formation of catalytically active transition-metal hydride cationic species, which are present in many catalytic processes such as discussed above.

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Organometallic complexes with cytostatic and migrastatic properties

In collaboration with Masaryk Memorial Cancer Institute and Institute of Chemical Processes Fundamentals we have continued in the development of organometallic complexes (Fe, Ru, Ti) as potential active pharmaceutical species in cancer treatment. As spreading metastases from primary tumour and their progression is responsible for the vast majority of cancer-associated deaths, we synthesized new compounds suppressing metastasis such as cyclopentadienyl-arene ruthenium complexes connected to glucose moieties via coordination of the glucose O-benzyl protecting group to a ruthenium centre. The complexes were found essentially non-toxic, while they showed strong anti-migration and anti-invasion properties.[30]

In addition, we extended our electrochemical approach concerning determination of ferrocene derivatives uptake into various cancer cell lines [31]. The synthesis of a series of about 20 derivatives [32] allowed us to determine ferrocene derivatives bearing N-heterocycles on their periphery as a highly potent cytostatics against ovarian cancer cell lines, having activity several times higher in comparison to cisplatin. These compounds were studied to determine their mode of cellular internalization and mechanism of anticancer activity. Results showed, that strong anticancer efficacy of these compounds is due to their intracellular accumulation caused by transferrin receptor-mediated endocytosis. The ferrocene moiety then becomes redox active in the biological milieu and generates reactive entities such as free radicals, which led to mitochondrial stress and induction of apoptosis [33].

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Societal relevance

Majority of research topics of our Department are motivated by the needs to search and design new molecules containing new chemical motifs and exhibiting new properties in order to improve their abilities, to find new phenomena, to formulate new rules, to introduce new approaches, to reveal (re)action mechanisms (e.g., of biological/medicinal relevance) in order to understand (and model) the respective processes. The general aim is to contribute to a pool of fundamental knowledge of molecules selected according to the clear international global needs.

An important societal impact of all the pursued research topics is also represented by enabling students to participate at actual and real fundamental research in the frame of their Bc., Ms and PhD theses. During the last five years about twenty students (local as well as foreign) were implemented into our research teams to work, present results and professionally grow on scientific tasks under the supervision of experienced colleagues. A part of them were still high-school students in the project organized by the Czech Academy which is called "Otevřená věda" (Open(ed) science).

- Aluminum free catalytic system utilizing hydrosilane-B(C₆F₅)₃

This catalytic system brings about at least two benefits. The first benefit arises from connecting of fine control over the polymer properties that molecular single site catalytic system entails with a reduced system cost. Taking into account that even a modest improvement in process efficiency is likely to result into huge profits due to gigantic polyolefin production scale, research is crucial to maintain competitiveness at global scale. The reduced amount of aluminum in the resulting polymer will be an important benefit. We would like to stress out that the proposed system can be applied to a majority of known group 4 precatalysts including half-sandwich complexes, constrained geometry complexes (CGC), post-metallocene complexes and various catalytic processes. Moreover, its applicability towards late transition metal complexes can be anticipated as well. The second benefit arises from possible fine control over the polymer properties that this system entails due to the introduction of terminal silane group. Incorporation of functionality (silane group for post modification, polar group or unsaturated group for copolymerization) into these polymers would bring new and valuable properties, which are not typical for polyolefins.

- Intramolecular activation of ligands in transition metal complexes

The topic is aimed at basic research on organometallic compounds of early transition metals that has some relationship to applied research of catalysts for polymerization and oligomerization of olefins. A substantial part is either devoted or related to catalysis of C–C bond forming reactions with emphasis on understanding elementary steps of the reaction cycle. The ligand transformation at low-valent metals has been proved to be a powerful synthetic tool allowing obtaining structurally new products that cannot be obtained by conventional synthetic methods.

- Organometallic complexes with cytostatic and migrastatic properties

Approved platinum drugs are among the most effective chemotherapeutics known, displaying activity against a wide range of human tumours. However, their utilization is limited by two main drawbacks: a toxic side effect and development

of resistance to platinum-based drugs. In this topic we have been trying to address both these drawbacks. First, increase in the drug transport preferentially to cancer cell by GLUT will minimize unwanted side effects often observed as a consequence of anticancer treatment. And second, using of compounds structurally different (Fe, Ru, Ti) from platinum drugs may induce different molecular mechanisms of action compared to recently used platinum-based drugs providing new treatment options for platinum-resistant tumours.

- Singlet fission – a new approach to photovoltaics

Currently, photovoltaics has the efficiency around 20% working on the principle "one photon – one electron". Recently, special molecules were designed and synthesized, where their triplet energy is lower or equal as the half of their first excited singlet energy. These molecules are able to form biradicaloids, which could transform one photon via excited state into two triplet states, hence "one photon – two electrons" principle which enhances the efficiency of solar batteries.

- Calix[4]arenes – promising sensors, and first electrochemically generated ligands as specific receptors

Suitable substitution of Calixarenes enables their various use in sensors, specific ligands and receptors. Our most important result in this field is the electrochemical formation of a stable tetraanion tetraradical based on tetranitrocalixarene which was successfully characterized and tested as the first known electrochemically generated ligand for K^+ , Rb^+ and Cs^+ in organic media. Its application in potential-controlled extraction of alkali metal ions from non-aqueous solutions by immobilization and reduction of calixarenes on the electrode surface is envisaged.

Investigation of biologically significant mechanisms of action – reactivity of phthalaldehyde and oxidative degradation of nucleic acids

Both current projects are aimed to understanding of important reaction mechanisms in biology – the guanine project is focused on its role in mutagenesis, carcinogenesis and aging, the phthalaldehyde theme is important for disinfection and "cold sterilization" of plastic surgery instruments (tubes, probes, catheters, ...) in hospitals which cannot be treated thermally.

Electrochemical investigation of remediation mechanism in water cleaning using "zero-valent iron"

Project of (up to now informal) cooperation with University of Ngaoundere, Cameroon aimed to actual problem (not only) in Africa with water cleaning. Our common research is focused to understanding of mechanism and enhancement of remediation efficiency using "zero-valent iron" for removal of Zn^{2+} , Cd^{2+} and Pb^{2+} from natural/waste waters.

The research projects investigated in the team in the period 2015 – 2019:

The team is carrying out aimed fundamental scientific research, mostly structured by three-year research projects funded by the Czech Science Foundation (GACR). The findings and results of this research are thus published primarily as original articles in impacted peer-reviewed international scientific journals. The research projects listed below cover most of the research activity of both (electrochemical and catalytic) teams in the five-year period.

Singlet Fission: Redox and Photophysics of Captodative Biradicaloids (GACR 2019 - 2021). Project number: 19-22806S. The principal investigator: J. Ludvík

Singlet fission is a process in which a singlet excited chromophore and its ground state neighbour share energy to produce a pair of triplet excited species. Recent intense interest in singlet fission is motivated by its potential utility in solar cell applications. The phenomenon has not been used outside of the laboratory so far, because of the instability of the tested compounds. The current project is focused to three novel types of compounds selected as the most promising ones.

Complexes of electron-deficient transition metals with luminescent properties (GACR 2019 - 2021). Project number: 19-00204S. The Principal Investigator: M. Lamač.

The aim of this project is to prepare new luminescent materials based on electron-deficient transition metal complexes and to reveal the relationship between structural features of the compounds and their resultant luminescent properties both in the solid state and in solutions.

Synthesis and characterization of semiconducting supramolecules of novel type and their use in preparation of organic transistors (OFETs). (GACR 2018 - 2021). Project number: 18-12150S. The principal investigator in JHI: J. Ludvík

6 structural types of new, purely organic semiconducting substances as alternative materials for molecular electronics were designed, synthesized and electrochemically investigated. They are composed from tetrasubstituted double bond (core) and two pyrene units (photo- and redox active centres). Stability of their radicalic forms, redox reactivity and mechanisms, intramolecular communication and electron distribution were elucidated.

Aluminum free catalytic system utilizing hydrosilane-B(C₆F₅)₃ adducts as activators in transition metal catalyzed ethylene polymerization (GACR 2017 - 2019). Project number: 17-13778S. The Principal Investigator: M. Horáček.

Aim of the project was the development and optimization of novel aluminum-free ternary catalytic system and its utilization for the coordination polymerization or oligomerization of olefins.

Ruthenium-carbohydrate conjugates as cytostatic drugs with an enhanced selectivity to cancer cells (GACR 2017 - 2019). Project number: 17-05838S. The Principal Investigator: J. Pinkas.

The project goal was to develop cytotoxic species profiting from Warburg effect and displaying enhanced efficacy for cancer cell lines. The series of ruthenium-carbohydrate conjugates were prepared and the effect of the carbohydrate on cytotoxicity, transport, and selectivity was investigated.

Novel electrochemically active thiacalix[4]arenes and their oxidized analogues as ligands and receptors (GACR 2017 - 2019). Project number: 17-18108S. The principal investigator: J. Ludvík

The project is focused on synthesis of novel electrochemically active thiacalix[4]arenes as potential specific ligands and receptors for electroanalysis. The thia-bridges introduced in the molecule instead of the methylene groups, changed their properties substantially because the non-bonding electrons on sulphur atom enabled partial mutual interactions among multiple redox centres.

Organometallic frustrated Lewis pairs for stoichiometric and catalytic bond activations (GACR 2014 - 2016). Project number: 14-08531S. The Principal Investigator: M. Lamač.

The aim of this project was to prepare novel types of organometallic frustrated Lewis pairs based on complexes of group 3 and 4 elements and study their properties and reactivity particularly with respect to their ability to activate bonds in small molecules.

Group 4 metallocenes: activation of ligands for synthetic and catalytic applications (GACR 2012 - 2016). Project number: P207/12/2368. The Principal Investigator: M. Horáček.

The aim of the project was to investigate metallocene (Ti, Zr, or Hf) derivatives bearing auxiliary highly substituted cyclopentadienyl ligands for their ability to react with bonding electrons in the auxiliary ligands as well as in simple molecules and unsaturated hydrocarbons upon thermal, photolytical, or reduction-induced metal activation.

Electrochemically active calix[4]arenes and their use for preparation of new receptors and (bio)sensors (GACR 2013 - 2015). Project number: 13-21704S. The principal investigator: J. Ludvík

The project was focused on synthesis, fundamental electrochemical investigations and possible applications of electrochemically active calix[4]arenes as specific receptors and (bio)sensors in electroanalysis. These molecules with four redox active centres were electrochemically characterized and the nitro groups were used as redox probes for understanding of the structure-redox properties relationship of the newly synthesized molecules. Their abilities as polydentate ligands to form complexes were found.

Electrochemical study of complex formation and host-guest interaction of reduced oligo-nitro calixarenes and their analogues. (Grant Agency of the Charles University GAUK, No.: 798214; 2014-2016). Principal investigator A. Liška.

The project was focused on the experimental and theoretical investigations of stereo- electrochemistry, conformation, shape and space-orientation of (thia)calixarenes.

Research activity and characterisation of the main scientific results

Carbonaceous materials: graphene and nanodiamond.

The mutual influence of graphene and polymer were investigated. Substantial advances have been achieved on the field of controlling the structure and surface of graphene through permanent deformation/shaping of its substrate [1,2]. These results have significant implications for the production of affordable composites [2]. The impact of the interlayer distance between two misoriented graphene layers on the optoelectronic properties of the stack was explained by experimental and theoretical studies [3]. The possibility of improving the stress transfer in graphene-polymer composites was documented for thicker graphene flakes by topographic corrugation (e.g. wrinkles), which cause an increased friction between the layers. For the first time, we described the behavior of the Raman second-order 2D' mode in monolayer graphene under uniaxial strain. These results expand the possibilities of Raman spectroscopy to determine and disentangle strain from charge-transfer doping in graphene [4]. Simultaneous biaxial stretching of graphene/polymer and its functionalization by diazonium salt was studied by Raman spectroscopy to determine the level of functionalization [5]. Long-range ordering of oriented topographic corrugations (wrinkles) in graphene was explored in a field of nano-scale pillars. The work highlights the importance of linear defects to create the ordering, as opposed to a random short-range wrinkling in the absence of such defects. Furthermore, a novel methodology is described for discriminating grain boundaries from thin wrinkles by AFM [6]. Easy routes were identified for quantifying shear and hydrostatic strain or uniaxial and biaxial strain. This work expanded the methodology of determining the level of doping and strain in graphene through Raman spectroscopy [7]. All the cited works on graphene were mostly hosted by the team. Some studies were supported by collaborations with FORTH/ICE-HT Patras, IPHT Jena, Institute of Physics, CAS, Faculty of Mathematics and Physics Charles University, Faculty of Mechanical Engineering CTU in Prague.

In collaboration with Institute of Physics, CAS, boron-doped nanodiamond was prepared by novel protocols including the use of optically transparent substrates and templating by silica nanofibers [8]. This result was also patented (CZ-Pat-307885, 2019; 50% share of our Institute). Diamond was characterized by Raman spectroscopy and electrochemistry [9]. In collaboration with Uni Hasselt, the first electrochemical study of n-doped diamond was presented, too [10]. The sensitization of nanodiamond to visible light was systematically explored in collaboration with Inst. of Organic Chemistry, CAS [11] and crowned with a demonstration of champion performance under solar light [12]. Covalent anchoring of sensitizing dye to the H-terminated diamond provided enhanced photoelectrochemical performance considerably outperforming that of non-covalently derivatized diamond with the same dye. These efforts represent proof-of-concept towards the p-type dye sensitized solar cell based on diamond. Yet, some photochemical instability of P1-sensibilization of diamond was also found during these studies and its mechanism was disclosed [13,14]. The team hosted electrochemical, spectroelectrochemical, photoelectrochemical and imaging

studies. External colleagues contributed by fabrication of diamond layers and by surface modification with dyes.

Oxidic semiconductors: Ti(IV) and Sn(IV) oxides.

In collaboration Uni Bremen, fundamental studies of TiO₂ (anatase/rutile) resolved the long-term controversy about the conduction band position and water splitting [15,16]. The team hosted electrochemical studies; external colleagues contributed by theoretical calculations. In collaboration with Uni Milano, we disclosed a metal-like electrochemical behavior of Ta-doped TiO₂, for the first time [17]. The team hosted electrochemical studies; external colleagues contributed by fabrication of samples using laser ablation. Novel synthesis was developed to get highly compact TiO₂ (rutile) thin films with the conduction-band minimum and valence band maximum downshifted by 0.2 eV against those in a macroscopic single-crystal rutile [18]. In collaboration with EPF-Lausanne, we disclosed that ALD-grown SnO₂ thin-films exhibited excellent electrochemical rectifying, which was not perturbed by thermal annealing (crystallization), and showed unexpectedly large downshift of the conduction band edge (by ca. 0.5 eV) [19]. The team hosted the electrochemical, AFM and XPS studies. External colleagues contributed by sample syntheses, Hall-effect and TEM studies.

2-D materials based on transition-metal dichalcogenides.

Phase transition in monolayer MoS₂ were induced by a unique pressure method/anvil cell without a pressure-transmitting medium. Much lower pressures are needed to achieve similar results compared to the standard anvil cell imposing hydrostatic pressure [20]. Our tip-enhanced photoluminescence study of monolayer MoS₂ highlighted the importance of utilizing spatially resolved (<60 nm) photoluminescence in determining the optoelectronic properties of two-dimensional materials [21]. We elucidated theoretically the influence of uniaxial out-of-plane compression on transition metal dichalcogenides, as a function of their composition (Mo/W, S/Se) and number of layers. The effects of pressure on band-gap character and energy were interrelated with the changes in the lattice and bond parameters [22].

Electrochemical and nanobubble-assisted nanostructuring; gaseous nanodomains on solid/liquid interfaces.

Large-area parallel nanostructuring was disclosed in polystyrene/water interface through ambient gaseous nanobubbles, densely populating the surface. Both positive (nanoprotrusions) and negative (nanopinholes) structures were obtained, and plausible explanation of the mechanism was given [23]. In the area of electrochemical nanostructuring, we demonstrated, for the first time, a reversible coiling/uncoiling of carbon (sp²) nanoscroll controlled by the applied electrochemical potential in aqueous electrolyte solution. This achievement represents an advance in the development of biocompatible nanoelectromechanical actuators with a prospective use in biomedical applications [24]. The studies of electrochemical nanostructuring were extended also to sp³-carbon (diamond). They disclosed that non-diamond impurities acted as the primary perturbation sites of at which gaseous nanobubbles can evolve, causing local detachment of surface layers. Furthermore, the effect surface termination (H or O) was identified for the electrochemical corrosion of diamond [25]. These findings are relevant to application of diamond electrodes at extreme conditions, such as in oxidative removal of environmental pollutants in water. All these works were almost fully hosted by the team; external colleagues contributed by fabrication of diamond and by

cantilever response modeling.

Dye-sensitized and perovskite photovoltaics.

Some activities of the team in the field of electrochemistry of dye-sensitized solar cells were reviewed in [26] (quoting 10 references to own works during 2015-17). Similar reviews on perovskite solar cells were presented too [27,28]. Of particular interest is the experimental work rationalizing the literature conflicts about facet-engineered TiO₂ anatase (001/101) and electron traps in anatase nanosheets or nanoparticles [29]. Besides the major work focused at semiconductor materials for photoanode (electron collection electrode), we also presented the first electrochemical study of CuSCN/graphene and related systems for applications as hole-conductor in perovskite photovoltaics. This work discovered unique effect of anodic Raman enhancement and novel redox probe for blocking tests. Promising performance of this hole conductor in perovskite solar cell (achieving 19.6 % solar conversion efficiency) is caused by enhanced driving force for the hole injection from CuSCN into reduced graphene oxide [30]. Novel Pt/graphene composite catalyst [31] was developed for the state-of-art Cu-mediated dye-sensitized solar cells. It is outperforming all the earlier catalyst particularly at low light intensity. All the mentioned experimental works were carried out in collaboration with EPF-Lausanne. The Department hosted the electrochemical, XPS, Raman and SPM imaging studies, optimization of graphene catalysts and hole conductors. The Swiss colleagues contributed by syntheses of Cu-mediators and by solar tests. Industrial collaboration with G24 Power, Ltd, UK was formalized within the Graphene Flagship project (see Part 4).

Li-ion and Na-ion batteries.

In collaboration with industrial partner (HE3DA, Czech Republic) we worked on a project of 48 V Li-ion accumulator with energy storage capacity of 1.2 kWh consisting of 4 V modules with energy of 80-100 Wh enabling economic production. Our home-made nanocrystalline Li₄Ti₅O₁₂ spinel offered excellent performance in both Li-ion and Na-ion batteries [32]. Electrochemical and Raman studies determined the charge capacity for Li and Na insertion/extraction, elucidated the mechanism of Na-ion storage and influence of anatase or rutile impurities on the cycling stability. The optimized Li₄Ti₅O₁₂ spinel provided four times larger charge capacities compared to those of the commercial microcrystalline material. We also disclosed a novel low-temperature and energy saving pathway to anode materials for fast and stable Li-ion batteries. Our Li₄Ti₅O₁₂ spinel with bimodal morphology exhibited high capacity, nearly 100% coulombic efficiency and excellent long-time cycling stability. This work also addressed environmental impacts of syntheses of materials for battery applications [33]. The studies of battery materials were almost fully hosted by the team; external colleagues contributed by TEM imaging and by preparation of some samples.

Photocatalysis for environment protection.

In collaboration with Vietnam National University, highly efficient and durable floating photocatalysts based on the SiO₂/TiO₂ composite materials were developed and characterized for water treatment [34]. One of the central motivations for this study was detoxification of water in areas contaminated during the Vietnam War with dioxin. This work was almost fully hosted by the team; external colleagues contributed by some outdoor tests. In collaboration with Clermont University, CNRS and Institute of

Chemical Technology, Prague, we developed photocatalysts for water treatment based on ZnCr–CO₃ layered double hydroxides [35]. The materials, which were obtained after calcination above 600°C, exhibited the highest photocatalytic activity. It was attributed to the formation of well crystallized ZnO and ZnCr₂O₄ spinel. Another type of material, lanthanum-modified TiO₂ nanosheets prepared via green freeze-casting method, were synthesized and characterized in cooperation with Institute of Chemical Technology, Institute of Chemical Processes and Fundamentals, Nuclear Research Center-Negev (Israel) and the University of Edinburgh. La³⁺ cation acted as a structural promoter supporting the controlled crystallite size of TiO₂, and the electronic promoter reducing the band gap of 2D TiO₂ nanosheets [36]. The team hosted photocatalytic studies, focused on the ability of the materials to remove selected model pollutants and on the monitoring of total organic carbon decrease, while the external colleagues contributed by syntheses, TEM, FTIR, UV-Vis and XRD characterizations. In collaboration with National Institute of Biology, Slovenia, we explored the photodegradation of ketoprofen, 2-(3-benzoylphenyl)-propionic acid. This substance is a widely used non-steroidal anti-inflammatory drug, and an important water pollutant at the same time. Kinetics and mechanism of photolytic degradation was studied experimentally and modelled by quantum chemistry calculations [37]. The practical studies of photocatalysis included industrial collaborations, which were formalized by several joint projects with the following main industrial partners: Advanced Materials, JTJ, s.r.o., Advanced Technology Group, s.r.o., Barvy a Laky Teluria, s.r.o., Betosan, s.r.o., Denas Color, a.s. For photocatalytic water splitting, the photoelectrochemical behavior of (101)- and (100)-oriented anatase single crystals was compared in water oxidation in acidic and alkaline solutions. This work reflected the role of surface orientation in control of selectivity towards oxygen and ozone generation [38]. Besides these key activities, we also supported the Department of spectroscopy in their own studies of photocatalytic transformation of CO₂ producing six joint publications (including Nature Astronomy); our contribution consisted in preparation of photocatalysts, isotopic labeling of photocatalysts (Ti¹⁸O₂) and characterization by their gas-adsorption properties.

Societal relevance

The societal relevance of our work is naturally expressed by solving variety of practically significant themes of solar cells, batteries and environment protection, including also vital collaboration with industrial partners mentioned above. More formally, these activities are codified by our participation in the CAS action Strategy AV21 “Basic Research in Public Interest”. Since 2018, our team is integrated within the action “Efficient conversion and storage of energy” (Strategy AV21, program No. 3). L. Kavan is a member of the coordination board and principal investigator of the theme “Nanostructured materials for conversion and storage of energy” addressing specifically the following subjects: (i) Li and Na batteries, (ii) organic and perovskite solar cells, (iii) new concepts of silicon photovoltaics. This program is still running. During 2015-18, our team has been incorporated within the action “Molecules and materials for life” (Strategy AV21, program No.10). Here, L. Kavan was the principal investigator of the theme Nanostructured materials for environment protection. During the evaluating period (2015-19), our team was involved into the research infrastructure NanoEnviCZ (coordinated by our Institute) putting together six Czech research institutions in the field of nanomaterials for environment. Specifically, L.

Kavan has been the topic manager of WP6-Effective photocatalytic technologies. This program was oriented at mastering nanomaterials for photocatalysis, effective photocatalytic processes, photovoltaic paints, functional surfaces for environmental protection, hybrid materials and thin photocatalytic films for direct solar splitting of water. During the evaluation period (2015-19) we have carried out 7 individual projects within WP6 for external users. This program is still running.

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The research projects investigated in the team in the period 2015 – 2019:

The team is carrying out fundamental scientific research, mostly structured by three-year research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), Ministry of Industry and Trade of the Czech Republic (MIT), Technology Agency of the Czech Republic (TACR) and by the European Commission (EC). The findings and results of this research are thus published primarily as original articles in impacted peer-reviewed international scientific journals. The interim results are also presented at scientific meetings and published in their proceedings.

The research projects listed below cover most of the research activity of the team in the five-year period.

Photoactive nanocomposite system for improving of environment (TA CR 2019- 2021) TH04030090 The Principal Investigator: J. Jirkovský.

Multi-probe in-situ characterization of the environmental responses of two-dimensional materials (MEYS 2018 – 2019) 8J18AT005. The Principal Investigator: O.Frank.

Electron-Selective Interfaces Applicable for Perovskite Solar Cells (GA CR 2018-2020) 18-08959S The Principal Investigator: L. Kavan

Floating photocatalyst with synergic adsorption function (MEYS 2017 – 2018)
8X17016. The Principal Investigator: J. Jirkovský.

Heterostructures of 2D and 3D materials for solar energy conversion (GA CR 2017-2019) 17-18702S The Principal Investigator: O. Frank

Development and application of an innovative floating photocatalyst with synergic adsorption function for solar detoxification of water in areas contaminated during the Vietnam War with dioxin (TA CR 2017-2019)
TF05000045, The Principal Investigator: J. Jirkovský

Pb-free Perovskite solar cells with Long-term stability (MEYS 2017 – 2020)
8F17001, The Principal Investigator: L. Kavan

Research and Construction Design of 48V Lithium Accumulators for New Generation of Automobiles (MIT 2017-2020) FV20471 The Principal Investigator:
M. Zúkalová

Innovative photocatalytic materials and concrete additives (MIT 2017-2020)
FV20234, The Principal Investigator: J. Jirkovský

Graphene-based disruptive technologies (EC 2016-2018) No. 604391, The Principal Investigator: L. Kavan

Study and optimization of inorganic nanomaterials for capacitive and insertion alkali metals storage (GA CR 2015-2017) 15-06511S, The Principal Investigator: M. Zúkalová

Structure-function relationship of advanced nanooxides for energy storage devices (MEYS 2015 – 2017) 8F15003, The Principal Investigator: L. Kavan

Strain engineering of electronic structure in graphene (GA CR 2014-2016) 14-15357S, The Principal Investigator: O. Frank

Graphene-Based Revolutions in ICT and Beyond (EC 2014-2016) No. 604391, The Principal Investigator: L. Kavan

Fourth generation photocatalysts: nano-engineered composites for water decontamination in low-cost paintable photoreactors (EC 2013-2015) No. NMP- SL-309636, The Principal Investigator: J. Jirkovský

Research for the production of multifunctional photoactive nanocomposites for use in the construction industry and for paints (TA CR 2013-2016)
TA03010994, The Principal Investigator: J. Jirkovský

The use of photoactive nanosurfaces to solve current problems of air and water cleaning (TA CR 2013-2016) TA 03020948, The Principal Investigator: J. Jirkovský

Electron Injection into Ti(IV) Oxide Materials: Applications in Li-ion Batteries and Solar Cells (MEYS 2013 – 2016) LD13060, The Principal Investigator: L. Kavan

Materials engineering towards Innovative Graetzel solar cells (GA CR 2013-2017) 13-07724S, The Principal Investigator: L. Kavan

Study of interfacial charge transfer process on boron and phosphorus doped diamond in contact with electrolyte solution (GA CR 2013-2017) 13-31783S, The Principal Investigator: L. Kavan

Research activity and characterisation of the main scientific results

The main theme of our research activities during the evaluation period 2015-2019 was the fundamental electrochemical research of the **structure–redox activity–reactivity relationship** of new molecules with targeted properties. New organic molecules were studied from the viewpoint of electron transfer and transport mechanisms, electronic communication in the individual molecules and in the organized systems. We aimed at understanding the electron transfer–initiated processes at molecular level with focus on the systems important in catalysis, electrosynthesis, molecular electronics and biology. Research strategies included the development of advanced instrumentation and in–situ spectro-electrochemical and scanning probe microscopy techniques. We have mastered methodology for the insulation of STM probe tips that enabled experimentation in solvent environments of different polarity focusing on charge transport in metal-molecule-metal junctions down to a single molecule level (**Kolivoška et al. ChemElectroChem 2019**). During the evaluation period Department of Electrochemistry at the Nanoscale published **155 papers** in impacted scientific journals, **2 papers** in other refereed journals, **2 book chapters** and received **2 patents** from the Industrial Property Office. Research activities were in line with the research plan of our team submitted for 2015-2019 during the past evaluation. Main scientific results in the focus areas of our team interest are given below.

Topic 1: Molecules with multiple redox centres.

Several systems with interesting redox properties were investigated. Compounds serving as models for “redox antenna” were synthesized in collaboration with French partners and their performance initiated by an intramolecular electron transfer was demonstrated (**Lachmanová et al. Journal of the American Chemical Society 2015**). Our work showed the unprecedented versatility of expanded pyridinium electrophores towards multielectron transfer by manipulating the intramolecular steric hindrance. The validity of Marcus theory for multi-electron transfer was clearly demonstrated for molecules with different skeletal rigidity. Measured electron transfer (ET) rate constants consistently reflected the main reorganization step having further implications for the design of molecular switches. We have demonstrated that adsorption of expanded pyridinium electrophores at electrode-electrolyte interface efficiently manipulates the multielectron transfer by blocking the desired intramolecular structural changes associated with transfer of electrons. Such blocking of *N*-pyramidalization of the pyridinium redox centre leads to a change of the mechanism from a single two-electron transfer process to a stepwise transfer of two electrons (**Nováková Lachmanová et al. Langmuir 2018**).

Extended viologens represent a promising group of molecules serving as building blocks (conducting wires) in future molecular electronic devices. For this type of molecules, the electrochemical formation of a triplet state in the pi-dimer configuration was confirmed both experimentally and theoretically. This result may have further implications in the field of future spintronic devices (**Tarábek et al. Journal of Physical Chemistry C 2015**). The complex electron transfer mechanism leading to current oscillations and dimer switching properties was demonstrated in our subsequent work (**Plutnar et al. Journal of Physical Chemistry C 2017**).

Our group has a unique aptitude (knowledge and instrumentation) to address the relationship between charge transfer properties and charge transport characteristics of the same “redox active molecule”. This can contribute tremendously to understanding of fundamental principles of charge transport phenomena being mainly in the focus of physicists. This comparison was given in several works (**Nováková Lachmanová et al.**

Electrochimica Acta 2018, Kolivoška et al. ChemElectroChem 2019, Šebera et al. Electrochimica Acta 2019). Since the evaluation of critical parameters like charge transfer rate constants and single molecule conductance values is essential in this type of studies, we proposed a simple evaluation of the ET rate constants from convolution voltammetry and Faradaic phase angle data, which was demonstrated for kinetics of radical dimerization (**Pospíšil et al. Electrochimica Acta 2019**).

Our team was involved in the design of target organic molecules. We conducted electrochemical and spectro-electrochemical studies complemented by the theoretical characterisation of compounds. The organic synthesis was done primarily by our partner institutions.

Topic 2: Molecular conductors and molecular switches for molecular electronics.

Computers relying on individual molecules as circuit elements (molecular wires and switches) are viewed as an alternative to currently used silicon technologies. Members of our team utilize break junction techniques to investigate electric junctions based on single molecules with functional backbones and anchoring groups and employ diverse physical and chemical stimuli to trigger the conductance switching in these structures.

Within the evaluated period, a multicomponent experimental platform has been completed and allowed the inspection of charge transport phenomena with an unprecedented level of detail and accuracy. Besides scanning tunnelling microscopy-based approaches, mechanically controllable break junction apparatus was put into operation and offered significantly broadened range of accessible single molecule conductance values. Achieved results substantially contributed to the understanding of charge phenomena in a broad range of investigated systems (**Moreno-García et al. Journal of the American Chemical Society 2015, Šebera et al. Journal of Physical Chemistry C 2017, Kolivoška et al. ChemElectroChem 2019, Šebera et al. Electrochimica Acta 2019**). Electrochemical characterization of single molecule electronic elements organized in monolayers adsorbed at monocrystalline electrodes provided valuable insights into the adsorption geometry and bonding of anchoring groups (**Lindner et al. Chemistry - A European Journal 2016, Šebera et al. Journal of Physical Chemistry C 2017, Sebechlebská et al. Electrochim. Acta 2017, Nováková Lachmanová et al. Langmuir 2018**). Members of our team further rely on density functional theory based computational concepts predicting the charge transmission in particular configurations of electric junctions. This approach is crucial for exploring structure-property-function relationships in future single molecule electronic devices.

The conductance of molecular wires terminated by fullerene anchoring groups was found to scale with the pressure exerted on the junction paving the way towards reversible mechanically-controlled molecular switches (**Moreno-García et al. Journal of the American Chemical Society 2015**). Switching of the electronic circular dichroism signal by voltage pulses that was demonstrated for spiral-shaped aromatic azoniahelicenes might underpin a read-out method in the storage of the binary information (**Rončević et al. ChemElectroChem 2019**). Experimental charge transport properties of photochemically switchable expanded bipyridinium derivatives were found to match characteristics derived from theoretical concepts indicating that these moieties can serve as well-predictable switches in real molecular electronic devices (**Šebera et al. Electrochimica Acta 2019**). Solvent as a surrounding environment alters electronic properties of molecules in electric junctions. Members of our team employed helquats as potential units of future spintronic devices to demonstrate that the single molecule value may be augmented by two orders of magnitude when increasing the solvent polarity (**Kolivoška et al. ChemElectroChem 2019**). The team further contributed to the

fundamental understanding of relationships between charge transfer and charge transport at the single molecule level employing expanded bipyridinium cations (**Nováková Lachmanová et al. *Electrochimica Acta* 2018**).

Stable, highly conductive and well-defined coupling between molecular electronic elements and metallic electrodes as charge reservoirs is critical for the realization of functional molecular electronic devices. Novel tripodal anchoring groups based on 9,9'-spirobifluorene and tetraphenylmethane have been implemented into structures of molecular wires and their charge transport properties were investigated in single molecule junctions both experimentally and theoretically (**Lindner et al. *Chemistry - A European Journal* 2016**, **Šebera et al. *Journal of Physical Chemistry C* 2017**, **Sebechlebská et al. *Electrochimica Acta* 2017**, **Kolivoška et al. *Chemical Communications* 2019**, **Šebera et al. *Nanoscale* 2019**). Obtained results not only confirm high robustness and directionality of thus formed molecule-electrode contacts, but additionally demonstrate their control by molecular design. Above-cited works further constitute a comprehensive methodological platform to investigate single molecule junctions with complex multipodal architectures. These structures are currently utilized as anchoring groups in electrochemically addressable single molecule switches with transition metal complexes employed as their electroactive cores.

Our team was involved in the design of target organic molecules. Our team members conducted electrochemical and single molecule conductance studies complemented by the theoretical charge transport characterisation of single molecule devices. A unique instrumentation was developed jointly with our Hungarian colleagues. The organic synthesis of new molecules was done primarily by our partner institutions.

Topic 3: Organometallic electroactive systems for molecular catalysis.

Members of our team studied several organometallic redox systems in the context of mechanistic investigation of electrochemical hydrogen evolution and carbon dioxide reduction. Several potential catalysts were investigated in cooperation with German and Italian partners. Our expertise is in the electrochemical and spectro-electrochemical evaluation of the charge transfer mechanisms of such catalytic processes.

*The development of electrocatalysts based on Group VI transition metals became attractive because of their low costs. New tetracarbonyl complexes of low-valent Mo or W, with modified bipyridine or dipyridylamine ligands exhibit significant catalytic activity in acetonitrile towards electrochemical reduction of CO₂. In contrast to the two-electron activation mechanism of bipyridine complexes, the complexes with dipyridylamine ligand showed an uncommon one-electron activation and higher catalytic efficiency (**Franco et al. *ChemElectroChem* 2015**). Newly synthesized potential electrocatalysts for CO₂ reduction HMn(CO)₃(dRpf), where dRpf = diphenylphosphino- or diisopropylphosphino-ferrocen exhibited rapid H₂ evolution from H⁺. The vacant coordination site after the hydride ligand was removed allowing the formation of an intramolecular Fe-Mn dative bond. Reduction chemistry of thus formed cationic complexes revealed their change from distorted octahedral coordination to square-pyramidal ones (**Schäfer et al. *Inorganic Chemistry* 2017**). Two complexes bearing OH groups as a local proton source have been designed and synthesized. A significant enhancement of their catalytic activity towards the electrochemical reduction of CO₂ in acetonitrile has been demonstrated. Investigation by means of spectro-electrochemistry, catalytic activity and density functional theory calculations revealed atypical reduction mechanism in comparison with that reported for Mn(bpy)(CO)₃Br. Furthermore, we have shown that a small structural change (position of OH) substantially influences the reduction pathway (**Franco et al. *Chemistry - A European Journal* 2017**). In another work (**Chatterjee et al. *Chemistry****

An Asian Journal. 2018) structural versatility of new binuclear complexes with $Ru(acac)_2$ fragments bridged by doubly deprotonated indigo in both trans and cis configuration was demonstrated. Although trans N,O; N',O' coordination with two equivalent six-membered ring chelates is common, the cis N,N'; O,O' arrangement leading to one five-membered ring chelate and one seven-membered ring chelate was observed for the first time. Different structures of the isomers resulted in different electrochemical and spectral properties.

Our team also investigated several systems from the viewpoint of electronic communication between redox centres. Dinuclear systems allowed for the observation of ligand/ligand and metal/metal site differentiation within the multistep redox series (**Ansari et al. Inorganic Chemistry 2016**).

Intensively coloured coordination compounds of formazanate ligands have a high importance in the development of industrial dyes and colorimetric applications. Newly synthesized ruthenium complexes revealed "bidirectional" noninnocent behavior of the formazanate ligand, i.e. ability to share the charge with the metal both in reduction and oxidation pathway. We have proved that the six-membered chelate ring of the complexes acts as the redox site in the reduction and oxidation processes (**Mandal et al. Inorganic Chemistry 2015**).

Catalytic hydrogen transfer ability is important in the development of new artificial metalloenzymes. Spectro-electrochemical investigation of hydrogenase-enzyme model 1,1'-dithiolatoferrrocene-hexacarbonyldiiron revealed a reduction-induced isomerization, where the thiolate ligand changed from bridging to terminal one and one CO ligand moved to a quasi-bridging position. Electrocatalytic activity of the complex in hydrogen-evolving reaction was verified and the catalytic scheme incorporating a newly revealed structure was proposed (**Häßner et al. Inorganic Chemistry 2019**).

Our team was involved in the design and synthesis of organometallic molecules. Team members conducted electrochemical and spectro-electrochemical experiments. Colleagues from partner institutions were also involved in the design and synthesis of the compounds and provided additional characterization. The papers were written in close collaboration of all co-authors.

Topic 4: Biologically important molecules at electrified interfaces.

Structural analysis of reaction intermediates and products generated in electrochemical processes represents an immensely powerful tool in providing insights into mechanistic aspects of charge transfer processes and related phenomena. Equipped with diverse spectro-electrochemical and analytical separation/detection tools as well as quantum chemical calculations, members of our team scrutinized reaction mechanisms of a broad range of biologically and pharmacologically important compounds. The combination of electrochemical and in-vitro liver cell studies complemented by density functional theory calculations was applied to elucidate structure-electron donor-antioxidant-hepatoprotective activity relationships for an important group of natural silymarin flavonolignans (**Pyszková et al. Free Radical Biology & Medicine 2016**). The oxidation of flavonolignan silybin was investigated further in detail by electrochemical methods combined with in-situ electron paramagnetic resonance spectroscopy. The presence of electrochemically generated silybin radical was unequivocally verified by the spin trapping method. The structure of such formed product was found to be consistent with the generally accepted position of the active site in flavonolignan antioxidants in the radical scavenging and the inhibition of lipid peroxidation (**Sokolová et al. Electrochimica Acta 2016**). The difference in oxidation mechanism of flavonone taxifolin and flavonol quercetin was rationalized employing spectro-electrochemical techniques

*complemented by the analysis of products based on mass spectrometry. Electroactive sites in these pharmacologically relevant compounds were identified enabling the clarification of long-standing controversy concerning the oxidation pathways of natural flavonoids (Kocábová et al. **Electrochimica Acta 2016**). The oxidation mechanism of natural antioxidant fisetin, chosen as a reference system for structurally similar pharmacologically important quercetin, was investigated by spectro-electrochemical techniques and density functional theory calculations. We have elucidated the role of ambient oxygen on the compound stability and delineated the methodology for future studies of electrochemical and physico-chemical properties of natural antioxidants under strictly controlled conditions (Ramešová et al. **Electrochimica Acta 2015**). In-situ spectro-electrochemical detection of reaction intermediates was utilized as a pivotal method for untangling a rather complex redox behavior of a model azoquinoline dye. The obtained oxidation mechanism agrees with that reported for reactions occurring in biosystems such as tyrosinase enzyme. The understanding of addressed effects is critical for explaining the bio-efficiency of hydroxyquinolines in living organisms (Sokolová et al. **Electrochimica Acta 2018**).*

Our team was involved in the design of target organic molecules. Team members conducted spectro-electrochemical characterization of compounds and the analysis of reaction products complemented by the theoretical characterization of molecules. The organic synthesis was done primarily by our partner institutions.

Topic 5: New molecular sensors and 2D architectures at electrified interfaces.

The team pursues venues of designing new electrode materials for different areas of applications. Molecular electronic applications profit from the design of sturdy contacts between electrodes and molecules. Formation of self-assembled monolayers by treatment of metal with alkanethiols has its drawbacks, since the attachment of alkyls to gold via a sulfur-metal bond is sensitive to oxidation and results in poor electrical conductivity. We described an alternative access to alkyl-covered gold surface via direct formation of Au-C bond employing alkylstannanes (Kaletová et al. **Journal of the American Chemical Society 2015**). Monolayers were characterized by different techniques including local electrochemical impedance spectroscopy. Obtained results benefit from the cooperation between our Institute and Institute of Organic Chemistry and Biochemistry, where our team designed and performed electrochemical characterization of monolayers involving local impedance measurements.

Electrochemical methods have been utilized in our team also for the development of new sensing applications. We focused in particular on the implementation of novel electrode materials (boron doped diamond electrodes, carbon screen printed electrodes, carbon and metal based conductive composites processable by 3D printing) and tailored (mostly miniaturized) electrochemical cells. Such measurement platforms were combined with advanced electrochemical techniques including square-wave voltammetry, ion transfer voltammetry and multipulse amperometric detection realized in the flow injection analysis regime. This electrochemical methodology has been successfully employed in the sensing of broad range of biologically and environmentally important substances including genotoxic derivatives (Hájková et al. **Sensors and Actuators B: Chemical 2016**), antimuscarinic agents (Langmaier et al. **Electrochimica Acta 2019**) and tumor markers (Němečková-Makrlíková et al. **Analytica Chimica Acta 2019**). Particular attention has been paid to investigate phytochelatin/metallothioneins considered as potential environmental pollution markers and transporters of heavy metals across cell membranes (Křivská et al. **Ecological Indicators 2019**). Limitations of specific analytical methods may be eliminated by their hyphenation. Team members designed,

constructed and verified the applicability of a new patented device (**Jaklová Dytrtová et al. CZ Patent 305266, 2015**) based on the coupling of an electrochemical ion generator with a mass spectrometer equipped with an electrospray (**Jaklová Dytrtová et al. Electrochimica Acta 2016**). An increased productivity of realized electrochemical experiments and increased amount of information gained within one measurement may be reached by applying an automatic device constructed according to our invention developed in the framework of the project supported before the evaluation period by the Czech Ministry of Industry and Trade (**Navrátil et al. CZ Patent 305433, 2015**).

Team members further demonstrated that biomarkers examined in blood, urine and exhaled breath condensate may be used to assess the extent of oxidative stress/inflammation caused by ultraviolet radiation (**Pelclová et al Nanomaterials 2019**). An investigation of lipid peroxidation markers revealed that the process of the lipid peroxidation plays a significant role in the mechanisms of acute methanol poisoning. Neuronal membrane lipid peroxidation seems to activate leukotriene-mediated inflammation as a part of the neuroprotective mechanisms (**Hlušička et al. Clinical Toxicology 2018**). Many biomarkers and other body parameters and factors (blood pH, serum ethanol, methanol, bicarbonate, lactate levels, anion gap, osmolal gap, pCO₂, color vision, visual fields, contrast sensitivity, etc.) have been investigated in patients intoxicated by methanol during the “methanol outbreak” in the Czech Republic between 2012 and 2014 (**Zakharov et al. Annals of Emergency Medicine 2016**). The study concludes that the pH of arterial blood evaluated on admission is the strongest predictor of chronic retinal nerve fibre layer thickness decrease and chronic retinal neurodegeneration associated with the progressive loss of visual functions and necrotic brain lesions (**Nurieva et al. American Journal of Ophthalmology 2018**). Last three papers resulted from our collaboration with the First Faculty of Medicine of Charles University. We contributed by statistical data analysis and prediction of methanol outbreak scenarios (see Societal Relevance Section for details).

Research projects investigated by the team in the period 2015-2019.

Scientific activities summarized above were supported by **12 national** and **6 international** research grants focused on the fundamental research. The financial support was typically granted for a three-year period and included personnel expenditures. Projects were granted by the **Czech Science Foundation** (GAČR, junior and standard projects), **Ministry of Education, Youth and Sports** (MEYS) of the Czech Republic and **Czech Academy of Sciences** (CAS) either in the framework of bilateral projects with their partner counterparts (Hungarian Academy of Sciences, CNRS France and CNR Italy) or in the form of the **European Union subsidy** (programme supporting perspective human resources at CAS). We were further successful in obtaining funding for two doctoral student projects from **Grant Agency of Charles University in Prague** (GAUK).

The following projects were granted and investigated:

- **Electron Transport in Nanoscale Assemblies. From Redox Mechanism to Molecular Conductance (GAČR 2014-2016)**. The main goal of this project was the fundamental understanding of charge transfer in single molecules, with the emphasis being placed on correlating their redox properties and conductance values. (Hromadová)
- **Electrochemical and Corrosion Properties of Fe₂ZrSi Heusler Alloy (GAČR 2016-2018)**. The aim of this project was the investigation of electrochemical and corrosion properties of intermetallic Fe₂ZrSi Heusler alloys and their comparison with properties of standard nuclear fuel cladding materials. The project involved the collaboration with

Institute of Physics CAS and University of Chemistry and Technology Prague.
(Hromadová)

- **Electron Transport in Single Molecule Junctions. Direct measurement of electrical and thermoelectric currents using break junction techniques (bilateral CAS 2016-2018).** Aim of this project was to investigate electrical properties of well-defined redox states of a single molecule and to probe simultaneously electric and thermoelectric currents enabling direct probing of the molecular energy level alignment with the electrode's Fermi level. Project involved collaboration with Hungarian Academy of Sciences. (Hromadová)
- **Multi-electron transfer within oligopyridinium assemblies: structure-reactivity relationship (MEYS 2015-2016).** Aim of the project was focused on the structure-reactivity relationship within the pyridinium-based molecules containing multiple redox centres with particular focus on the effect of structural and conformational changes on the reactivity of such molecules. The project involved collaboration with Université de Paris. (Hromadová)
- **Probing Electron Transport Mechanism in Single Molecule Junctions by Conductance and Thermoelectricity Measurements (GAČR 2018-2020).** Project is focused on experimental studies of different aspects of the electron transport mechanism (tunnelling, hopping and quantum interference effects) in a series of molecules containing increasing number of repeating units connected in series or in parallel. (Hromadová)
- **Electrochemical characterization of synthetic metalloenzymes (MEYS 2018-2019).** Aim of this project was focused on establishing the relationship between electron transfer properties and catalytic activities of selected artificial metalloenzymes. The project involved collaboration with Sorbonne University. (Hromadová)
- **Electron Transfer at Nanoscale. The effect of steric switching on the conductance of expanded pyridinium compounds. (bilateral CAS 2012-2015).** Project was focused on international cooperation with CNRS (ITODYS) laboratory in Paris aiming at electron transfer studies in a series of model pyridinium-type of redox active compounds in their branched and fused form. (Hromadová)
- **Transfer of Charge in Single Molecules. From Redox Mechanism to Molecular Conductance (bilateral CAS 2013 – 2015).** Aim of this project was the methodological development of single molecule conductance measurements by mechanically controllable break junction methods. The project included the collaboration with Hungarian Academy of Sciences. (Hromadová)
- **Synthesis of helical cyanines, their chirality, self-assembly, and redox switching (GAČR 2013-2015).** Project aimed at the design of new functional molecules with chiroptical switching properties. New synthetic methodology was complemented by electrochemical and spectro-electrochemical studies. This was a collaborative project with Institute of Organic Chemistry and Biochemistry CAS. (Pospíšil)
- **Study of electron transport in circuits composed of molecular electronic components (perspective human resources at CAS 2015 – 2016).** This postdoctoral project aimed at fundamental studies of charge transport phenomena in single molecule electric junctions as building blocks of devices based on molecular electronics. (Kolivoška)
- **Study of electron transport in electrochemically controlled molecular switches (GAČR 2016- 2018).** This junior project focused on the investigation of electron transport in electrochemically addressable single molecule switches attached to

electrodes by novel tripodal anchors. The research involved the collaboration with Karlsruhe Institute of Technology. (Kolivoška)

- **Photoelectrochemical reduction of carbon dioxide on copper foam electrodes modified by copper oxides (GAČR 2018-2020).** Running project aims at exploring fundamental properties of catalysts for the (photo)electrochemical reduction of carbon dioxide. The project utilizes 3D printing for the manufacture of catalysts and involves the collaboration with University of Bern. (Kolivoška)
- **Electrochemistry of bioflavonoids and the drug interface interaction (bilateral CAS, 2012-2015).** Project investigated redox mechanisms and stability of bioactive compounds (flavonoids, flavonolignans, derivatives of salicylic and quinolone acids) and the procedure of formation of well-defined supported phospholipid bilayer was developed. Further aim of this project was the development of cooperation with University of Pisa. (Sokolová)
- **Electrochemical study on new artificial enzymes and their role in sensing of neurotransmitters (GAČR 2019-2021).** Running project aims at detailed electrochemical and spectroscopic characterization of new artificial enzymes (complexes with tyrosinase redox centre motif) and studies of structure-deposition kinetics of catalytic substrate transformation leading to analytical determination of neurotransmitters. The project is solved in the collaboration with University of Pardubice. (Sokolová)
- **New Approaches for Monitoring of Transport of Selected Xenobiotics across Biomimetic Membranes (GAČR 2017-2019).** Project aimed at the development and application of new approaches for monitoring of transport of selected xenobiotics and other biologically important compounds across biomimetic membranes and at elucidation of transporting processes across these membranes. The project was solved in the cooperation with Palacký University Olomouc. (Langmaier)
- **New approaches to monitoring of agrochemicals, food additives and contaminants and their transformation processes in environmental and food matrices (GAČR 2017-2019).** Aim of this project was focused on the development of new electrochemical sensors, biosensors, detectors and measuring protocols for monitoring of biologically active compounds (chemical carcinogens, pesticides, growth stimulators and drugs) for environmental and human health protection. This project was solved in the cooperation with Charles University in Prague and University of Pardubice. (Navrátil)
- **Novel electrochemical sensors and sensing techniques for the analysis of nucleic acids structure and interactions (GAČR 2011-2015).** Aim of this project was focused on behavioural study of natural and chemically modified nucleic acids at surfaces of different amalgam and carbon-based electrode materials. The development of new techniques for the detection of DNA damage, its chemical modification and interactions within the project was solved in the cooperation with Institute of Biophysics. (Josypčuk)
- **Aspects of hazardous metals transfer across biomembranes (GAČR 2012-2015).** The project aimed at elucidation and modelling of transport processes of hazardous (heavy) metals and their complexes with cysteine-rich peptides, phytochelatins and low molecular weight organic acids across biomembranes. Detailed elucidation of transport processes contributed to their possible control (e.g. for phytoremediation). This project was solved in cooperation with the Czech University of Life Sciences Prague. (Navrátil)

Societal relevance

Societal impact of our research activities can be demonstrated by the following examples:
(i) Limits of currently employed silicon semiconductor technologies have stimulated the development of alternative approaches including molecular electronics. Successful implementation of these technologies requires minimizing high conformational variability of contacts between metallic electrodes and anchoring groups of molecular electronic elements. Members of our team developed molecular conductors terminated with novel tripodal anchoring groups showing significantly reduced conformational freedom. These structures were further incorporated into single molecule switches, which are currently being scrutinized by team members.

(ii) Atmospheric CO₂ is the most significant contributor to the greenhouse effect and diverse strategies have been devised to suppress the anthropogenic production of CO₂ and to intensify its removal from the air. Present endeavours in electrocatalysis involve the development of affordable technologies for the production of hydrogen as a sustainable fuel and the electrochemical reduction of CO₂ to value-added products. Members of the team contributed to the development of inexpensive transition metal-based organometallic electrocatalysts for these processes by *spectro-electrochemical evaluation of their charge transfer mechanisms*.

(iii) Chronic liver disease is a serious condition that potentially leads to life-threatening complications. Natural *silymarin flavonolignans* are considered as effective remedies for treating its various stages. We have been engaged in the study combining electrochemical, quantum chemical and medicinal approaches to elucidate relationship between the structure of silymarin flavonolignans and their antioxidant and hepatoprotective activity.

(iv) In the period of 2012 to 2014, the Czech Republic has faced “methanol outbreak” leading to intoxication cases resulting in death and varied degrees of the visual impairment. Members of our team have been engaged in investigating biomarkers of intoxicated patients demonstrating that pH of arterial blood is the strongest predictor of chronic nerve fibre and retinal degeneration associated with the progressive vision loss.

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Research activity and characterisation of the main scientific results

The scientific work by the team has led to several results that are worthy of note due to their importance for the fields of fundamental gas phase ion chemistry and practical analytical mass spectrometry. Selected results in the focus areas of the team are as follows:

Kinetics of gas phase ion-molecule reactions

The reactions of H_3O^+ , NO^+ and O_2^+ ions with an homologous series of six aliphatic

ketones, acetone through 2-octanone, have been investigated in a helium-buffered selected ion flow-drift tube, SIFDT, in order to reveal their dependence on ion-molecule interaction energies, E_r , and to gain insight into their mechanisms. Whilst the primary motivation was to allow analysis and absolute quantification of trace amounts of these ketones, and ultimately other volatile organic compounds, in air using selected ion flow-drift tube mass spectrometry, SIFDT-MS, a fundamentally interesting discovery was made concerning the rate coefficients for charge transfer reactions. The reactions of H_3O^+ with the ketone molecules, M, proceeded *via* exothermic proton transfer producing MH^+ ions and their rate coefficients, k , were seen to reduce by about one third over the E_r range from 0.05 eV to 0.5 eV. The NO^+ /ketone reactions were found to initially proceed *via* the formation of NO^+M adduct ions that partially fragment, and thus the k reduces with E_r by as much as four times for the acetone reactions but remains close to their respective collisional rate coefficients, k_c , for the higher-order ketones. This indicates long lifetimes of the NO^+M ions with respect to the stabilising collision times with He atoms. The k for the O_2^+ /ketones dissociative charge transfer

reactions were observed, surprisingly, to be greater than their calculated k_c , implying that long distance electron transfer occurs in these interactions ([Spesyvyi et al., Phys. Chem. Chem. Phys., 2017](#)). This finding stimulated a follow-up study where the same effect of long-distance charge transfer was observed for the reaction of O_2^+ with isoprene molecules ([Spesyvyi et al., J. Phys. Chemistry A, 2018](#)).

Ion chemistry of the atmospheres of Titan, Enceladus (moons of Saturn) and of Mars.

Three space missions investigating atmospheres of several bodies in the Solar system were recently completed. The Cassini probe started its research around Saturn in 2005 and operated until September 2017, the MAVEN probe sent its first data from Mars in 2015, and Juno entered the Jovian orbit in 2016. Data from these missions indicate that complex physical and chemical processes occur in the investigated ionised parts of the atmospheres, the ionospheres (formation of complex nitrogen-containing hydrocarbon anions in Titan's atmosphere, unexpected concentration of HNO^+ , HO_2^+ , H_2O^+ , H_3O^+ in the Martian atmosphere, observations of organic compounds in the Jovian atmosphere). The Huygens probe significantly expanded knowledge of Titan's atmosphere which is like the prebiotic terrestrial atmosphere and represents a frozen model of it. Theoretical models of the Titan ionosphere were not able to explain the observations, especially the abundances of larger polyatomic negative ions. This was due to a lack of knowledge of the rate constants of ion-molecule reactions as the

previous kinetics data were obtained at room temperature and extrapolation to the temperature of Titan ionosphere ($\sim 80\text{K}$) was required, which is an inaccurate procedure. There were no kinetics data for the important anions. Thus, the relevant atmospheric ion chemistry was experimentally studied at temperatures 80-300K using the variable temperature selected ion flow tube, VT-SIFT-MS, instrument constructed by the team, in combination with a tandem quadrupole mass spectrometer. Data were obtained on the reactions of negative ions (CN^- , C_3N^- , C_5N^- , C_7N^-) with neutral molecules (HC_3N , C_2H_2 , C_2H_4 , C_3H_4), including their rate constants and product branching ratios, and their dependence on the interaction energy. Experimental and theoretical work was carried out in collaboration with laboratories abroad (Physical Laboratoire Chimie, Universite Paris XI - Orsay, Dept. of Physics, University of Trento, Dept. of Physics, University of Stockholm and the Synchrotron SOLEIL, Saint Aubin). Comparative studies of the rate constants of anions were conducted using SIFT-MS and FTICR-MS, and the energy thresholds for formation of products were investigated at the SOLEIL beamline. Of special astrophysical interest is the reaction $\text{C}_5\text{N}^- + \text{C}_2\text{H}_2$, since it represents a possible growth mechanism of large anions that have been detected in Titan's upper atmosphere by the Cassini plasma spectrometer. Experimental studies have been performed in the team's laboratory using a tandem quadrupole mass spectrometer that allows identification of the different reaction channels and their reaction thresholds. Results of these investigations were compared with the predictions of *ab initio* calculations, which identified possible pathways leading to the observed products and the associated thermodynamics. The chain elongation reaction of $\text{C}_5\text{N}^- + \text{C}_2\text{H}_2$ leading to C_7N^- , was found to be slightly exoergic, but with an energy barrier of 1.91 eV. Therefore, it is unlikely to be responsible for the formation of large anions in cold environments such as the interstellar medium and planetary ionospheres. ([Linden et al., Phys. Chem. Chem. Phys., 2018](#)). A similar conclusion was reached for the analogous reaction of C_3N^- ([Linden et al., J. Phys. Chem. A, 2016](#)). The data obtained for the kinetics and dynamics of ion-molecule reactions are relevant to modelling of the ionospheric chemistry at Titan and other cosmic objects ([Španěl et al., Rapid Commun. Mass Spectrom., 2017](#); [Romanzin et al., Icarus, 2016](#); [Polasek et al., J. Phys. Chem. A, 2016](#); [Linden et al., J. Phys. Chem. A, 2016](#); [de Miranda et al., J. Phys. Chem. A, 2015](#)). These data will be included in numerical models for the ion chemistry occurring in these ionospheres and atmospheres. They include kinetics data for the reactions of CN^- and C_3N^- anions with cyanoacetylene (HC_3N) molecules and those for C_5N^- with reacting with acetylene molecules considered to be intermediate steps in the production of large anions in Titan's ionosphere. ([de Miranda et al., J. Phys. Chem. A, 2015](#); [Polasek et al., J. Phys. Chem. A, 2016](#); [Romanzin et al., Icarus, 2016](#); [Cernuto et al., J. Chem. Phys., 2017](#); [Linden et al., Phys. Chem. Chem. Phys., 2018](#)). Reactions were also described that may occur in the ionospheres of Jupiter and Titan and the influence of internal energy in the CH_3^+ cation on its reactivity with hydrocarbon molecules (synchrotron SOLEIL) ([Cernuto et al., J. Chem. Phys., 2017](#)).

Some ionic processes were studied because of their potential importance in the ionosphere of Mars, including the reaction of CO_2^- with methane ([Ascenzi et al., Frontiers in Chemistry](#)) and its dependence on the vibrational state of the reactant ion. The effect of temperature on the reactivity of the negative ions NO_2^- ([Zymak et al., Icarus, 2020](#)) and O^- was also investigated and the data on the reaction of NO_2^- ions

with CO₂ molecules showed that this reaction proceeds relatively slowly to form CO₃.

Research of advanced new analytical methods for trace gas analyses.

An experimental apparatus was constructed that allowed establishment of electric drift fields (E) along the axis of a SIFT-MS flow tube. Thus, new **selected ion flow drift tube mass spectrometry SIFDT-MS** analytical method ([Spesyvyi et al., Anal. Chem., 2015](#)) was developed and validated, and its utility explored for the analysis of volatile organic compounds, VOCs, present in the earth atmosphere ([Spesyvyi et al., Rapid Commun. Mass Spectrom., 2016](#)), in exhaled breath, and in the headspace of food products and bacterial cultures. SIFDT-MS extends the utility of the established selected ion flow tube mass spectrometry, SIFT-MS, by varying the axial E-field in the reaction zone, which allows investigations of the influence of interaction energy on ion-molecules reaction kinetics. The ion axial speed is increased in proportion to the reduced field strength E/N (N is the carrier gas number density), and the residence/reaction time, t, which is measured by Hadamard transform multiplexing ([Spesyvyi et al., Anal. Chem., 2015](#)), is correspondingly reduced. The analytical performance of SIFDT-MS is demonstrated to be superior to SIFT-MS, and a much lower speed of the flow-drive pump is required. This facilitates the development of smaller cost-effective analytical instruments for real time analyses of trace (parts per billion range) amounts of VOCs in air. The mobility in helium of the product ions of the reactions of H₃O⁺, O₂⁺ and NO⁺ with different trace compounds, together with their

hydrates, were studied as a function of E-field strength. Collisional dissociation of the hydrated ions was also studied. During the last five years this SIFDT-MS technique has been significantly enhanced and studies have been carried out of in-tube collision-induced dissociation for the selective analyses of isomers ([Spesyvyi et al., Rapid Commun. Mass Spectrom., 2016](#)) and by the addition of electrostatic switching and selection of H₃O⁺, NO⁺, and O₂⁺ reagent ions (ERIS) ([Španěl et al., Anal. Chem., 2019](#)).

The **secondary electrospray ionization mass spectrometry (SESI-MS)** technique is a promising highly sensitive technique for the analyses of complex mixtures of trace gaseous analytes in air and exhaled breath, achieving limits of detection in the pmol/mol range. However, a major weakness of SESI-MS is the difficulty to accurately quantify gaseous analytes in complex matrices, which is important in the biological, environmental and medical areas, and where using standards is difficult. Thus, a robust absolute quantification method for calculation of gas phase concentrations from the ratios of SESI-MS ion signals is needed that is based on kinetics of sequences of ion molecule reactions and mathematic descriptions of the ion transport processes. To this end, a new SESI ion source was constructed and ion chemistry experiments are presently being carried out, and it is anticipated that a numeric model will be formulated that will lead to a practical method of absolute trace vapour concentration calculations. Meanwhile, SESI-MS is being qualitatively validated by case studies in the medical, environmental and food science areas ([Dryahina et al., Rapid Commun. Mass Spectrom., 2018](#); [Michalcikova et al., Rapid Commun. Mass Spectrom., 2020](#); [Dryahina et al., Flavour and Fragrance Journal, 2020](#)).

Interdisciplinary research of volatile metabolites in medicine and biology

The notable results in this area are the data obtained on volatile metabolites released by bacteria associated with infections in cystic fibrosis ([Dryahina et al., J. Breath Res.](#); [Shestivska et al., J. Breath Res.](#)), which indicate their potential for non-invasive screening of such infections by breath analysis ([Španěl et al., J. Breath Res., 2016](#)). Also important are the discoveries of the relation of breath pentane concentration to the activity of inflammatory bowel disease ([Dryahina et al., J. Breath Res., 2018](#)) and the change of breath acetic acid, formed from the plasma acetate, in response to airways acidification in gastric reflux disease and in cystic fibrosis ([Španěl et al., Journal of Cystic Fibrosis](#); [Smith et al., J. Breath Res.](#)).

In the area of development of new methods for analyses of volatile metabolites present in breath, a **thermal desorption, TD**, device for off-line SIFT-MS analysis, and a nasal probe for breath analysis based on infrared absorption spectroscopic sensing of exhaled CO₂ and a fast flow capillary were constructed. As a case study, concentrations of methanol were analysed in oral and nasal exhalations and the effect of aspartame ingestion ([Španěl et al., J. Breath Res., 2015](#)) was found to be significant even for an acceptable daily dose of this sweetening compound. Further to this, clinically relevant pathogens were studied in collaboration with LBG-NIPH, where phenotypic and genotypic characterization was achieved of the bacterial taxa most relevant to respiratory infections in CF patients, i.e. *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Stenotrophomonas maltophilia* and the *Burkholderia cepacia* complex. Volatile metabolites produced by cultures of these bacteria were analysed by GC/MS and by SIFT-MS ([Dryahina et al., J. Breath Res., 2016](#); [Shestivska et al., J. Breath Res., 2015](#)). The results indicated which compounds can act as markers of infection in CF patients. A study was then carried out at CFC of volatile metabolites present in exhaled breath and sputum samples of 62 CF patients. Concentrations of 45 VOCs, including some common breath metabolites, and 12 volatile biomarkers selected in a previous *in vitro* study were quantified in the exhaled breath of CF patients. None of these compounds taken individually differentiate the two groups to a clinically useful degree. However, the concentrations of VOC can be used in a linear

combination obtained using a linear logistic model maximising the area under the receiver operator characteristics, ROC, curve, to discriminate between infected and uninfected patients (Španěl et al., *J. Breath Res.*, 2016). An important observation (mentioned above) is that the acetic acid vapour concentration measured by SIFT-MS is significantly elevated in the exhaled breath of CF patients, independent of the *P. aeruginosa* infection status, presumably because the acetic acid is dominated by the decreased *pH* of the mucus lining the CF airways. Thus, non-invasive measurement of breath acetic acid concentration could serve as an indicator of the acidity of the CF airways mucosa (Španěl et al., *Journal of Cystic Fibrosis*, 2017; [Smith et al., *J. Breath Res.*, 2016](#)).

An original method was also developed for the direct SIFT-MS quantification of malondialdehyde (as a cell peroxidation stress biomarker) in cancer cell culture headspace ([Shestivska et al., *Rapid Commun. Mass Spectrom.*, 2015](#); [Shestivska et al., *Rapid Commun. Mass Spectrom.*, 2017](#)).

A new analytical approach has been researched involving the combination of **SIFT-MS with electrochemical (EC) methods** for the study of the mechanisms of production of volatile organic compounds (VOCs) by damaged bacterial and mammalian cell cultures *in vitro*. The EC method was used to produce reactive oxygen species (ROS) and real time analyses and quantification of the VOCs was achieved by SIFT-MS. A cell for electrochemically controlled peroxidation stress of cells was constructed. This new method has been successfully tested on model membranes ([Shestivska et al., *Rapid Commun. Mass Spectrom.*, 2018](#)) and on living cancer cell cultures and it was found that concentration of volatile aldehydes strongly depend on the representation of unsaturated fatty acids in the liposomes and a protective effect of cholesterol was observed.

Mass spectrometry methods for environmental research, food science and for the synthesis of organometallic catalysts

In the area of **environmental research**, instrumental monitoring of biogenic volatile organic compounds (BVOCs) by mass spectrometric methods is the focus of the team. Presently utilized techniques allow off-line analysis of air samples (e.g. TD-GC/MS), whilst the currently-exploited on-line techniques (e.g. proton transfer reaction mass spectrometry, PTR-MS) can quantify only the total concentration of several isomers of important non-methane BVOCs as represented by mono- and sesqui-terpenes. The initial focus was on immediate selective quantification of isomers of monoterpenes. These are present in the atmosphere as biogenic volatile organic compounds and are reactive with the OH[•] radicals, which ultimately forms oxides of nitrogen, ozone and particulates, all of which are harmful to human health. The new methods developed by the team, viz. the time integrated thermal desorption ([Sovova et al., *Anal. Bioanal. Chem.*, 2019](#)) and fast GC extension to SIFT-MS ([Lacko et al., *Atmos. Meas. Tech.*, 2019](#)) will allow selective monitoring of individual isomers of mono- and sesqui-terpenes in real time. The potential of the unconventional styrene radical cations as reagent ions for SIF(D)T-MS has also been explored ([Spesvyi et al., *Rapid Commun. Mass Spectrom.*, 2019](#)).

Societal relevance

Whilst all the main research results are in the form of articles and reviews in international peer-reviewed journals, all topics of research by the team are motivated by clear international global needs. Specifically:

- **Planetary ion chemistry**. The space research to which this area belongs is not only

answering fundamental questions about the Universe, but also drives and accelerates technological advances in satellite communication and monitoring and in new technologies in general. Participation in this research resulted in the scientist of the team being respected members of the international community, now involved in the preparation of state-of-the art space research programmes.

- **Analytical methods for trace gas analyses** are motivated by current needs in analyses of volatiles in the following areas:

(i) food production, postharvest handling, storage, freshness monitoring and safety control.

(ii) air quality monitoring for health-and-safety of workers potentially exposed to fumigants and other harmful compounds and for quality assurance in for example semiconductor manufacturing ultimately leading to wide availability of digital technologies

(iii) environmental research related to BVOC will ultimately lead to decreased population exposure to harmful atmospheric immissions

(iv) research in new methods of non-invasive screening and monitoring based on breath sampling will result in widely adopted methods for prevention of chronic or terminal illness.

The societal impact of the research is also represented by building local centres of excellence in specific areas that facilitate international networking, building of high level of skills in early stage researchers and generating potential for innovative small and medium enterprise stemming from the specific mass spectrometry knowledge and technology. Also mentoring of researches who need to gain experience in the novel MS methods on the international level has societal value in advanced training and in acceleration of introduction of new methods in practice.

The research projects investigated by the team in the period 2015 – 2019:

The team is carrying out fundamental scientific research, mostly structured by three-year research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), and by the European Commission (EC). The findings and results of this research are thus published primarily as original articles in impacted peer-reviewed international scientific journals. The interim results are also presented at scientific meetings and published in their proceedings. Wider consequences of the work are presented to the scientific community in the form of review articles, book chapters and keynote lectures at conferences.

The research projects listed below cover most of the research activity of the team in the five-year period.

Excitation, separation and fragmentation of ions by drift fields in SIFT-MS for immediate selective trace gas quantification (GACR 2013 – 2016). 13-28882S. The Principal Investigator: P. Španěl.

The aim was to reveal new physical principles applicable to immediate, simultaneous and separate quantification of the individual components of mixtures of volatile compounds in air and exhaled breath by selected ion flow tube mass spectrometry, SIFT-MS.

Chemical processes in the atmosphere of Titan - experimental study (GACR 2014 – 2016). 14-19693S. The Principal Investigator: J. Žabka.

The aim was to characterise temperature and energy dependencies of the ion- molecule reactions taking place in the Titan atmosphere.

Mass spectrometric quantification of volatile metabolites in breath for noninvasive diagnosis and monitoring of bacterial infection in cystic fibrosis. (GACR 2014-2016). 14-14534S. The Principal Investigator: K. Dryahina.

The research was carried out in collaboration between the team and the Cystic Fibrosis centre (CFC) at Motol University Hospital and the Laboratory of Bacterial Genetics (LBG) at National Institute of Public Health (NIPH). The aim of this project was to develop and test new analytical method for discovery of breath biomarkers for diagnostic and monitoring of bacterial infections in cystic fibrosis (CF).

Combination of SIFT-MS with electrochemical methods for real-time quantification of volatiles released by damaged bacterial and cell cultures (GACR 2014 – 2016). 14-15771P. The Principal Investigator: V. Shestivská.

The aim of the project was the development and assessment of a new analytical technique for the study of the mechanisms of production of volatile organic compounds (VOCs) by damaged bacterial and mammalian cell cultures in vitro using a combination of electrochemical (EC) methods to produce reactive oxygen species (ROS) and real time analyses and quantification of the VOCs.

High-energy ion-induced ionization and dissociation for mass spectrometry analysis. (GACR 2014 – 2016). 14-20915S. The Principal Investigator: M. Polášek.

The aim of this project was to explore the possibilities of a new type of tandem mass spectrometry experiment for analytical purposes in which the ions trapped in a linear ion trap (LIT) are exposed to a beam of high (keV) kinetic energy ions. An instrument setup was constructed combining a sector type mass spectrometer (MS) with a quadrupole. MS serves as a source of high-energy ions interacting with molecules in a collision cell and the product ions are analysed by a quadrupole.

High-energy collisions of ions with complex organic molecules. (MEYS 2014 – 2017) LD14024. The Principal Investigator: M. Polášek.

The goal of the project was to build a specially designed experimental apparatus for studies focused on high-energy ion-induced excitation, ionization and dissociation of complex organic and bioorganic molecules, and to use this new instrument to perform series of experiments with selected ions and molecules aiming at understanding elementary processes connected with ultrafast high-energy interactions of ions with molecules in the gas phase, namely the energy transfer and its deposition in both collision partners and their subsequent chemical reactions.

New ion chemistry methods for rapid mass spectrometric monitoring of atmospheric biogenic volatile organic compounds responsible for air pollution (GACR 2017 – 2019). 17-13157Y. The Principal Investigators: K. Sovová.

The aim of this junior project was to research new methods for selective monitoring of biogenic volatile organic compounds in the Earth atmosphere.

Experimental and theoretical study of the chemical processes in the planetary atmospheres (GACR 2017 – 2019). 14-20915S. The Principal Investigators: M.

Polášek and J. Žabka.

The aim was to characterise temperature and energy dependencies of the ion- molecule reactions taking place in the atmospheres of Mars, Titan and Enceladus (moons of Saturn).

Secondary electrospray ionization mass spectrometry (SESI-MS) for quantification of gaseous analytes in air, headspace and breath (GACR 2018 – 2020). The Principal Investigator: K. Dryahina.

The aim is to develop a robust absolute quantification method for calculation of gas phase concentrations from the ratios of SESI-MS ion signals based on kinetics of sequences of ion molecule reactions and mathematic description of ion transport processes.

The relevant publications authored by the team members

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Cernuto, A., Lopes, A., Romanzin, C., de Miranda, B. C., Ascenzi, D., Tosi, P., Tonachini, G., Maranzana, A., Polasek, M., Zabka, J., & Alcaraz, C. (2017). Effects of collision energy and vibrational excitation of CH₃⁺ cations on its reactivity with hydrocarbons: But-2-yne CH₃CCCH₃ as reagent partner. *J. Chem. Phys.*, 147(15), 14.

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Dryahina, K., Som, S., Smith, D., & Španěl, P. (2020). Characterization of spoilage-related volatile organic compounds in packaged leaf salads. *Flavour and Fragrance Journal*, 35(1), 24-33.

Dryahina, K., Sovova, K., Nemeč, A., & Španěl, P. (2016). Differentiation of pulmonary bacterial pathogens in cystic fibrosis by volatile metabolites emitted by their in vitro cultures: *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Stenotrophomonas maltophilia* and the *Burkholderia cepacia* complex. *J. Breath Res.*, 10(3), 037102.

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Linden, C. F., Zabka, J., Polasek, M., Zymak, I., & Geppert, W. D. (2018). The reaction of C₅N⁻ with acetylene as a possible intermediate step to produce large anions in Titan's ionosphere. *Phys. Chem. Chem. Phys.*, 20(8), 5377-5388.

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with C₂H₂ a Possible Process for Chain Elongation in Titan's Ionosphere? *J. Phys. Chem. A*, 120(27), 5337-5347.

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Španěl, P., Spesyvyi, A., & Smith, D. (2019). Electrostatic Switching and Selection of H₃O⁺, NO⁺, and O₂⁺ Reagent Ions for Selected Ion Flow-Drift Tube Mass

Spectrometric Analyses of Air and Breath. *Anal. Chem.*

Španěl, P., Zabka, J., Zymak, I., & Smith, D. (2017). Selected ion flow tube study of the reactions of H_3O^+ and NO^+ with a series of primary alcohols in the presence of water vapour in support of selected ion flow tube mass spectrometry. *Rapid Commun. Mass Spectrom.*, 31(5), 437-446.

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Research activity and characterisation of the main scientific results

Main scientific results

The institute covers only personal costs of key scientist and the base rough working space, hence the main research directions and results are closely related to the previously and recently funded projects. The work of the team resulted in 135 publications in impacted journals between 2015-2019. In section 1.2.1 there is complete list of all projects, in which were/are members of department involved as PIs or co-PIs.

The scientific work of the team has led to several results, which should be singled out due to their impact to the field. Here are the representatives of those results together with references to relevant publications:

Tuning the properties of 2D materials by external stimuli

The properties graphene and other 2D materials can be modulated by different approaches. The most straightforward way is based on external stimuli, like doping [121], strain [130], [127], temperature [126] and interaction with the substrate. In some cases the external stimuli are unintentional as they can be introduced by treatment or manipulation with the sample. In any case it is required to understand how these external stimuli act on graphene, how they can be monitored, tuned and potentially exploited. Using isotope labelling and in situ spectroscopy techniques we have been able to uncover and assign these effects, and ultimately gain rational control over them.

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126) Costa, S., Weis, J. E., Frank, O., & Kalbac, M. (2015). Temperature and Face Dependent Copper -Graphene Interactions. *Carbon*, 93, 793-799.

130) Verhagen, T. G. A., Drogowska, K., Kalbac, M., & Vejpravova J. (2015). Temperature induced strain and doping in mono- and bilayer isotopically labeled graphene. *Phys. Rev. B*, 92, 125437.

127) Álvarez, M. P., Corro, E. D., Morales-García, Á., Kavan, L., Kalbac, M., & Frank, O. (2015). Single Layer Molybdenum Disulfide under Direct Out-of-Plane Compression: Low-Stress Band-Gap Engineering. *Nanoletters*, 15(5), 3139-3146.

Structural corrugation problem or a practical tool?

Wrinkles are important for real graphene samples as they significantly affect the properties of the samples. They can compromise the performance of graphene-based devices but they can also serve as a knob to control the graphene properties. In this result we provide a tool to control the occurrence of the wrinkles as well as their quantification and characterization [1]. In this result we also show that the wrinkles change as a function of temperature. [2] The so-called peapods can be prepared by filling fullerenes into carbon nanotubes. We prepared and characterized two-dimensional analogy of this material by trapping fullerenes between two graphene layers. Thanks to isotope labelling we have been able to distinguish and address these

effects separately for the top and the bottom graphene layers. [3] We also demonstrated that the wrinkles can be used to exercise precise spatial control over graphene functionalization with nanometre resolution. [4]

1) Pacakova, B., Vejpravova, J.*, Repko, A., Mantlikova, A., & Kalbac, M. (2015). Formation of wrinkles on graphene induced by nanoparticles: atomic force microscopy study. *Carbon*, 95, 573-579.

2) Verhagen, T., Vales, V., Frank, O., Kalbac, M., & Vejpravova, J. (2017). Temperature-induced strain release via rugae on the nanometer and micrometer scale in graphene monolayer. *Carbon*, 119, 483-491.

3) Vales, V., Verhagen, T., Vejpravova, J., Frank, O., & Kalbac, M. (2016). Addressing asymmetry of the charge and strain in a two-dimensional fullerene peapod. *Nanoscale*, 8, 735.

4) Drogowska-Horna¹, K., Valeš¹, V., Plšek¹, J., Michlová¹, M., Vejpravová², J.*, & Kalbáč, M. (2020). Large scale chemical functionalization of locally curved graphene with nanometer resolution. *Carbon*, 164, 207-214.

Rational pathways for tailored functionalization of graphene

The functionalization of graphene is studied quite widely. However, the control (in terms of both quality, quantity and spatial resolution) and versatility of this process is still very limited. In this result, we at first have chosen fluorination of graphene as a model reaction. The product - fluorinated graphene was easily detectable by Raman spectroscopy. We discovered a new approach based on laser assisted decomposition of SF₆. The method enables to control the density of fluorine atoms by adjusting the laser power and number of pulses [5]. This model reaction enable us to study also stability of the products [6] as well as master and control the functionalization process also for other methods of graphene functionalization. We achieved spatially controlled functionalization using UV light. The reaction network was designed in a way that irradiated and non-irradiated parts of the surface underwent opposite transformations due to the limited diffusion in close proximity to the surface and share photosensitive reactant [7]. Furthermore, we have been able to exploit mastering the functionalization process for advanced applications like formation of tailored composites [8], forming heterostructures with perovskites [9], control reactions at the surface [10] and pH gradient directed movement of ultrafine nanoparticles on graphene surface [11].

5) Plšek, J., Drogowska, K. A., Fridrichova, M., Vejpravova J., & Kalbac, M. (2019). Laser-ablation-assisted SF₆ decomposition for extensive and controlled fluorination of graphene. *Carbon*, 145, 419-425.

6) Costa, S. D., Weis, J. Ek, Frank, O., Bastl, Z., & Kalbac, M. (2015). Thermal treatment of fluorinated graphene: an in-situ Raman spectroscopy study. *Carbon*, 84, 347-354.

7) Valenta, L., Kovaricek, P., Vales, V., Bastl Z., Drogowska, K. A., Verhagen, T. A, Cibulka, R., & Kalbac, M. (2019). Spatially Resolved Covalent

Functionalization Patterns on Graphene. *Angew. Chem. Int. Ed.*, 58, 1324-1328.

8) Kovaříček, P., Drogowska, K., Melníková Komínková, Z., Blechta, V, Bastl, Z., Gromadzki, D., Fridrichová, M., & Kalbáč, M. (2017). EDOT polymerization at photolithographically patterned functionalized graphene. *Carbon*, 113, 33-39.

9). Guerra, V. L. P, Kovaříček, P., Valeš, V., Drogowska, K., Verhagen T., Vejpravova, J., Horák, L., Listorti, A., Colella, S., & Kalbáč*, M. (2018). Selective self-assembly and light emission tuning of layered hybrid perovskites on patterned graphene. *Nanoscale*, 10, 3198-3211.

10). Fu, Ch, Mikšátko, J., Assies, L., Vrkoslav, V., Orlandi, S., Kalbáč, M., Kovaříček, P., Zeng, X., Zhou, B., Muccioli, L., Perepichka, D. F., & Orgiu E.(2020). Surface-Confined Macrocyclization via Dynamic Covalent Chemistry. *ACS Nano*, 14, 2956-2965.

11) Kovaříček, P., Cebecauer, M., Neburková, J., Bartoň, J., Fridrichová M., Drogowska, K. A., Cigler, P., Lehn, J. M., & Kalbac, M. (2018). Proton-Gradient-Driven Oriented Motion of Nanodiamonds Grafted to Graphene by Dynamic Covalent Bonds. *ACS Nano*, 12, 7141-7147.

Game changer: Identification of functional groups in 2D materials

Fast direct identification of functional groups at 2D materials is crucial for both fundamental research and application of graphene in devices. However, this problem still represents a formidable challenge. Though surface enhanced Raman spectroscopy enables to detect extremely small number of Raman active molecules, this obvious potential of the method it was previously not applied to identify functional groups on graphene. In this result we successfully implemented this method and demonstrate that it is indeed possible to identify to graphene covalently attached functional groups [12]. Infrared spectroscopy is complementary to Raman spectroscopy; however due the very weak IR absorption from monolayer thin materials this method was used only rarely and so far did not provide conclusive results. In our study [13] we discovered that roughened copper can serve as active substrate for enhanced IR spectroscopy. Using this approach, we monitored transformation of fluorinated graphene (phenyl sulfanyl modified graphene). Furthermore, we showed that functionalized graphene can be also used as substrate for the enhancement of the spectra. Also, we demonstrated that the enhancement can be further tuned by specific functional groups [14].

12) Kovaříček, P., Vrkoslav, V., Plšek, J., Bastl Z., Fridrichová, M., Drogowska, K., & Kalbáč, M. (2017). Extended characterization methods for covalent functionalization of graphene on copper. *Carbon*, 118, 200–207.

13) Matulková, I., Kovaříček, P., Šlouf, M., Němec, I., & Kalbáč, M. (2017). Surface enhanced infrared absorption spectroscopy for graphene functionalization on copper. *Carbon*, 124, 250-255.

14) Valeš, V., Kovaříček, P., Fridrichová, M., Ji, X., Ling, X., Kong, J., Dresselhaus, M. S., & Kalbáč, M. (2017). Enhanced Raman scattering on functionalized graphene substrates. *2D Materials*, 4, 025087.

Breaking the scaling relations in electrocatalytic oxygen evolution

The theoretical aspects of electrocatalytic oxygen evolution were investigated by DFT for most of conceivable oxide based catalysts. The unfavourable behaviour of catalysts in OER was ascribed to the interdependence of the adsorption energy of the *-OH and

*-OOH intermediates which restricts optimization. The scaling relationship restriction may be avoided by careful design of a multifunctional surface, either forming a metastable surface or exploiting the phase boundary between a catalysts and substrate [15-16]. This concept was extended into a model joining oxygen evolution and oxygen reduction processes and outlining the conceptual approach towards reversible oxygen electrocatalysis [17].

15) Frydental, R., Busch, M., Halsck, N. B., et al., & Paoli, E. A. (2015). Enhancing activity for the oxygen evolution reaction: the beneficial interaction of gold with manganese and cobalt oxides. *ChemCatChem*, 7(1),149-154.

16) Macounová, K, Simic, N., Ahlberg, E., & Krtil, P. (2015). Electrochemical water-splitting based on hypochlorite oxidation. *Journal of the American Chemical Society*, 137(23)7262-7265.

17) Busch, M., Halck, N. B., Kramm, U. I., et al., & Siahrostami, S. (2016). Beyond the top of the volcano? - A unified approach to electrocatalytic oxygen reduction and oxygen evolution. *Nano Energy*, 29, 126-135.

Identification of catalytic sites in cobalt-nitrogen-carbon hybrid materials for the oxygen reduction reaction

The oxygen reduction reaction is the bottle-neck reaction of the fuel cell technologies which are an important instrument in renewable sources based electricity generation and distribution. Replacement of Pt in the fuel cells with affordable more abundant metals is crucial for successful deployment of fuel cells. In this study, we have identified the active sites of the Co-N-C catalysts in oxygen reduction in acid media. The results were obtained by combining the conventional electrochemistry with in-operando X-ray absorption spectroscopy [18].

18) Zitolo, A., Ranjbar-Sahraie, N., Mineva, T., et al. & Li, J. (2017). Identification of catalytic sites in cobalt-nitrogen-carbon materials for the oxygen reduction reaction. *Nature Communications*, 8 (1) 1-11.

In its first year, the activities of the new Department of Nanocatalysis were focused on the hiring of team members and preparation of laboratory spaces for the new effort. In December of 2019, seven custom apparatuses for the synthesis of (sub)nanometer size catalysts with atomically precise size and composition and catalytic testing were transferred from the US. The year 2019 publications by the members of the Department of Nanocatalysis were based on results collected at their former affiliations before joining the Institute in 2019: (Halder et al., *Nanoscale*, 2019); (Lee et al., *Nature Communications*, 2019); (Mammen et al., *Journal of Physics: Condensed Matter*, 2019); (Yang et al., *ACS Sustainable Chemistry & Engineering*, 2019); (Liu et al., *The Journal of Chemical Physics*, 2019).

The research projects investigated by the team in the period 2015 – 2019:

During the period 2015-2019 the members of the team were involved in 24 research projects. Doc. Kalbac was a PI or co-PI of 15 projects, doc. Krtil was a PI of four projects, prof. Vajda, Dr. Jirka, Dr. Kovaricek Dr. Vales, Dr. Shiozawa were each PI or co-PI of one project.

The team carried out fundamental scientific research, mostly structured by three-year research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), and by the European Commission (EC). The findings and results of this research are thus published primarily as original articles in impacted peer-reviewed international scientific journals. The interim results were also presented at scientific meetings and published in their proceedings. Two applied research projects were funded by Technology Agency of the Czech Republic (TACR). Wider consequences of the work were presented to the scientific community in the form of review articles, book chapters and keynote lectures at conferences.

The research projects listed below cover most of the research activities of the team in this five-year evaluation period. The largest fundamental research projects were: ERC-CZ: From Graphene Hybrid Nanostructures to Green Electronics (39 mil. CZK for the team), ERC -Starting grant: Trans-Spin NanoArchitectures: from birth to functionalities in magnetic field (15 mil. CZK for the team). If not stated otherwise the the research is carried out by the team of the J. Heyrovský Institute of Physical Chemistry of the CAS.

1) Nanocapsules for targeted delivery of radioactivity (Raddel) was funded by European commission under ITN Program, doc. Kalbac was the PI in this project representing the team. This large project connected 9 partners from EU.

2) Spectroscopy and spectroelectrochemistry of graphene and graphene multilayers. (GACR 2012-2016). GAP208/12/1062. The Principal Investigator: M. Kalbáč.

The project resulted in a discovery of a new class of nanomaterials made of encapsulated molecules and nanocrystals in between two layers of graphene, so called graphene sandwiches. We studied the interaction between graphene shell and encapsulated species. Graphene sandwiches were also ideal systems to study charge transfer through the graphene sheet. The project results have a potential in new applications of graphene and its modifications in targeted drug delivery, energy storage or as “cans” to preserve unstable substances.

3) Isotopically labelled graphene layers. (MYES 2013-2015). LH13022. The Principal Investigator: M. Kalbáč.

The aim of the project was to prepare and characterise isotopically labelled graphene layers, to functionalize them and to study them using in situ spectroelectrochemical methods.

4) Carbon nanostructures for sensor applications. (TACR 2013-2016) The Principal Investigator: M. Kalbáč.

The research is carried out in collaboration between the team and the TESLA BLATNÁ a.s., COC s.r.o, and University of West Bohemia. The project deals with new technology of carbon nanostructure sensing film deposition for smart microsystems

applied for environmental protection and to provide rescue teams safety. Project goals comprise new materials, technology of their preparation, purification and processing, film depositions and their integration with other functional blocks, integration of nano- and microtechnologies, procedures of testing and measurements as part of ammonia, methane, nitrogen and carbon oxides sensor development.

5) From Graphene Hybrid Nanostructures to Green Electronics. (MYES 2013-2018). LL1301. The Principal Investigator: M. Kalbáč.

The aim of the project was a study of novel principles for the development of new electronic devices with low energy consumption. The ultimate challenge of the project is the construction of a bilayer pseudospin field effect transistor (BISFET) based on hybrid graphene nanostructures.

6) The effect of inorganic additives on the efficiency of the anodic processes in chlorate electrolysis (Akzo Nobel Pulp and Fine Chemicals S.A. 2015 – 2017). Principal Investigator: P. Krtil. The aim was to gain the fundamental understanding of the effect of oxide additives on the performance of industrial anodes in chlorate production.

7) Nanocomposite systems of plasmonic/magnetic nanoparticles-graphene-aromatic molecules for enhanced Raman scattering processes. (GACR 2015-2017). GA15-01953S. The Principal Investigator: M. Kalbáč.

The research is carried out in collaboration between the team and the Institute of Physics of the CAS and Charles University – Faculty of Science.

In this project we designed, fabricated and tested novel nanocomposite systems based on graphene, plasmonic (and/or magnetic) nanoparticles (NPs) and aromatic molecules, in which the electromagnetic mechanism (EM) of surface-enhanced Raman scattering (SERS) was effectively coupled with the charge transfer (CT) mechanism of graphene-enhanced Raman scattering. The Raman resonances was further tuned by adjusting the energies of surface plasmon resonances in nanoparticles, the exciting light, or the Fermi level of graphene.

8) Nanomaterials and Nanotechnologies for Environment Protection and Sustainable Future. (MYES 2016-2019). LM2015073. The Principal Investigator and coordinator: M. Kalbáč.

The research was carried out in collaboration between the team and the Technical University of Liberec (TUL), University J. E. Purkyně in Ústí nad Labem (UJEP), the Institute of Experimental Medicine of the CAS (IEM), Palacký University Olomouc – Faculty of Science (UPOL), the Institute of Inorganic Chemistry of the CAS (UACH). The project integrates the capacities of several research organisations in the Czech Republic in the field into multi-disciplinary research over a wide range of nanomaterials and nanotechnologies. The portfolio of NanoEnviCz equipment and expertise provided by NanoEnviCz covers various research areas of nanomaterials and nanocomposites such as materials for environmental protection and related applications. NanoEnviCz services include the controlled synthesis of nanostructured materials, their complex chemical, structural, morphological and surface characterization, optimization of their functional properties, monitoring of their potential toxicity and environmental hazards and development of their applications for advanced technologies.

NanoEnviCz creates an effective multipurpose platform for partner research organisations involved in the structure as well as for external users from the academic community and from the industrial sphere, as well as the state administrative bodies of the Czech Republic. NanoEnviCz provides open, centralized access to all capacities of this distributed research infrastructure for both domestic and international users.

9) Silikalitové nanofilmy s laditelnými vlastnostmi jako perspektivní biokompatibilní materiál. (GACR 2016-2020). GA16-02681S. The Principal Investigator: I. Jirka.

The aim is to prepare silicalite films, with tunable properties of their outer surfaces, supported on Ti-6Al-4V alloy coupons is proposed to get highly osteoconductive and biocompatible material suitable for fabrication of prostheses.

10) Advance photocatalytic materials for water splitting and their rational design (GACR 2017 – 2019). 17-12800S. Principal Investigator: P. Krtil.

The aim was to implement rational design approach to develop novel nanoparticulate materials for photoelectrochemically driven water splitting.

11) Trans-Spin NanoArchitectures: from birth to functionalities in magnetic field (TSuNami). (H2020-EU 2017-2020). ID: 716265. The co-investigator: M. Kalbáč. The research is carried out by the team of the J. Heyrovský Institute of Physical Chemistry of the CAS and Charles University.

The main objective of the project is a control over electrons in molecules and periodic solids can be reached via manipulation of their internal quantum degrees of freedom. The most prominent and exploited case is the electronic spin accommodated in standalone spin units composed of $1 - 10^5$ of spins. A challenging alternative to the spin is the binary quantum degree of freedom, termed pseudospin existing e.g. in two-dimensional semiconductors. The aim of the proposed research is to build prototypes of trans-spin nano-architectures composed of at least two divergent spin entities, the TSuNAMles.

12) Completing and upgrade RI Nanomaterials and nanotechnologies for environment protection and sustainable future. (MYES 2017-2020). EF16_013/0001821. The Principal Investigator and coordinator: M. Kalbáč.

The research was carried out in collaboration between the team and the Technical University of Liberec (TUL), University J. E. Purkyně in Ústí nad Labem (UJEP) and the Institute of Experimental Medicine of the CAS (IEM).

The project is directly linked to the program of the current infrastructure RI NanoEnviCz and complements it in the area of critically missing instrumental techniques and expertise. The key scientific activities are focused on the synthesis, complex characterization, tuning the functional properties and exploring the application potential of nanomaterials and nanocomposites for environmental applications as well as the determination of their potential hazard.

13) Capacity Development of ÚFCH JH, v.v.i. for Research and Development. (MSMT 2017-2022). EF16_028/0006251. The Principal Investigator: M. Kalbáč.

The purpose of the project is to achieve the basic conditions for the creation of a coherent system of human resources development of the HIPC i.e. research,

managerial and technical staff through the HRS4R (Human Resources Strategy for Researchers) tool. The main objective of the HIPC is to obtain and maintain the "HR Award", which will prove the development of the capacities, knowledge and skills of all the staff of the HIPC.

14) Kombinatoriálně vtištěné substráty pro hmotnostní, spektroskopickou a elektrochemickou detekci. (GAČR 2018 -2020). GJ18-09055Y. The Principal Investigator: P. Kovaříček. The research was carried out by the team of the J. Heyrovský Institute of Physical Chemistry. The aim of the project is to develop new universal concept of trainable 2D monolayer functionalization for selective binding and detection of analytes using dynamic combinatorial imprinting of a selected molecule to the 2D material, e.g. graphene, by the implementation of covalent grafting and supramolecular recognition, which in turn delivers binding selectivity for the given analyte.

15) Chemically functionalized carbon nanostructures for application in composite materials. (MYES 2018-2020). LTC18039. The Principal Investigator: M. Kalbáč.

The aim of the project is the design, realization and probing of the optimized functional interfaces of carbon nanostructures and polymers.

16) Atomically thin membranes with smart pores engineered in two-dimensional crystals. (GACR 2018-2020). GA18-20357S. The Principal Investigator: M. Kalbáč. The research is carried out in collaboration between the team and Charles University – Faculty of Mathematics and Physics.

In this project we created atomically thin membranes from single- and double/layered graphene with smart functionalized nanopores, which will be further externally tuned by light, temperature and magnetic field (MF). The controlled perforation was realized using oxygen plasma, fast electrical pulses and by Ar ion bombardment. Modification of the nanopores was done recently by hydrogenation or fluorination in gas phase and by functionalization with active molecules.

17) Electrochemical conversion of renewable energy into fuels and chemicals (MSCA Actions, H2020, EC 2018 – 2021). 722614. Principal Investigator: P. Krtíl. The scientific focus is on fundamental understanding of the electrocatalysis of oxygen evolution and CO₂ reduction. Training of 14 new PhDs is an integral part of the project.

18) Carbon allotropes with rationalized nanointerfaces and nanolinks for environmental and biomedical applications. (MYES 2018-2022). EF16_026/0008382. The Principal Investigator and coordinator: M. Kalbáč.

The research is carried out in collaboration between the team and the Institute of Physics of the CAS, OZM Research s.r.o., TESLA BLATNÁ a.s., the Institute of Organic Chemistry and Biochemistry of the CAS (IOCB), Charles University – Faculty of Science, University of West Bohemia – Faculty of Electrical Engineering.

The main objective of the project is to establish and implement intensive long-term cooperation between academic and commercial partners for the purpose of high-level research with a significant impact on areas determining the quality of

human life: saving energy, the environment and human health. The proposed research strategy aims to rationalize communication channels (interfaces and nanolinks) in hybrid and sensor structures based on optimized carbon allotropes for enviro and bio applications. This synergy is motivated by a number of critical scientific questions about the implementation of carbon nanomaterials in specific applications.

19) Implementation of the state-of-the-art physico-chemical methods for studies of innovative materials and bio/chemical processes. (MYES 2018-2022). EF16_027/0008355. The Principal Investigator: M. Kalbáč.

The aim of the project is significant improvement of analytical methods for monitoring changes in the environment and diagnostics of diverse biomedical samples, which are currently studied and developed at the Heyrovsky institute. More specifically, we will focus on improvements of sensitivity and accuracy of physico-chemical methods used in monitoring and diagnostics.

20) ERA Chair at J. Heyrovský Institute of Physical Chemistry CAS - The institutional approach towards ERA. (H2020-EU 2018-2023). ID: 810310. The Principal Investigator: J. Hrusak, co-PI: S. Vajda and M. Kalbáč.

The project makes part of concerted actions of management of the J. Heyrovský Institute of Physical Chemistry to induce structural changes, which will help develop Institute's most promising potential in long-term perspective, and turn into recognized, widely known research body. It is envisaged that this project will result in meeting the following main objectives: Increase of scientific excellence, Support of structural changes within the Institute, Enhancement of international visibility and attractiveness, Improvement of human resources and capacities, Maintenance of sustainability of introduced changes.

21) Energy-X – transformative chemistry for a sustainable energy future (EC 2019-2020). 820444 Energy-X. Principal Investigator: P. Krtil.

The project was Coordination and Support Action aimed at preparation of large scale funding scheme supporting scientifically the transition of European economy to energy concept based on renewable energy sources.

22) Organokovové sítě pro přeměnu a ukládání energie. (GACR 2019-2021). GA19-15217S. The Principal Investigator: H. Shiozawa.

This project aims to explore new conductive MOFs, understand the relation between their chemical composition, crystal structure and electronic properties, determine the type of electronic interactions responsible for the electrical conduction, exploit quantum confinement effects, and realize patterned synthesis of optimally conductive MOF thin films as active electrodes suited for optoelectronics and energy harvesting and storage.

23) Metal-organic frameworks on 2D materials. (MSMT 2019 – 2021). 8J19AT026. PI: V. Valeš. The research was carried out in collaboration between the team and the University of Vienna. The aim of the project is to better understand the electrical properties of 2D MOFs, with the emphasis on the role of the substrate. 2D MOFs with different (transition and heavy) metals and structures will be synthesized and optimized towards advanced physical properties and chemical functionalities required as active electrodes in electrochemical devices.

24) SEPIOT – Gas sensors based on hybride nanostructures for IoT applications. (TACR 2019-2022) TH04010211 The Principal Investigator: M. Kalbáč.

The research is carried out in collaboration between the team and the TESLA BLATNÁ a.s., COC s.r.o, and University of West Bohemia.

The project is focused on the realization and subsequent mass production of sensors for the detection of carbon monoxide, ammonia and gaseous hydrocarbons. These sensors will use sensitive layers based on hybrid nanostructures that allow the realization of planar sensor structures, thereby increasing their integration. It will also include design and implementation of electronic circuits to analyze and evaluate signals from these sensors. The integrated communication system allows connection to IoT applications using LoRa, SigFox or IQRN networks. The main target group is households or plants where these sensors can continuously and over extended time monitor the level of concentration of these gases, where the exceedance of the levels can cause damage of health or property.

Societal relevance

Whilst all the main research results are in the form of articles and reviews in international peer reviewed journals, all topics of research of the team are motivated by clear international global needs. As a prime example, the team members also participate in applied research projects: **‘Carbon nanostructures for sensor applications’** and **‘SEPIOT – Gas sensors based on hybride nanostructures for IoT applications’** (for project description please refer to section 1.2.1) The results of these projects are expected to have both direct and in direct socioeconomic impact. The direct impact is production of new sensors, which will increase the employment in the South Bohemia region where the company Tesla Blatna is situated. The indirect impact is expected to be in the area of environment protection and public health.

The decarbonization of the energetic concept

The activities towards the field of electrocatalysis underscore one of the main challenges of the science and technology in 21st – the response to the climate change. Specifically they support current public initiatives aiming at curbing the antropogenic carbon dioxide production by replacing the current fossil energy based technologies with renewable alternatives. Since the temporal and geographic distribution of renewable energy sources does not match the needs of today’s society there is urgent need to store and transport renewable energy using a new energy vector, e.g. hydrogen. The hydrogen, however, needs to be produced and water electrolysis is the only process capable of the necessary scale up. The water electrolysis despite relative maturity is still not feasible namely because of kinetically difficult oxygen evolution. The development of novel oxygen evolving catalysts is therefore of the highest priority in the context of the Green deal and similar initiatives.

Size- and composition based subnanometer clusters, will allow to identify new classes catalysts for green chemistry as well as in industrially relevant processes, with high activity and selectivity, and with atom-efficient use of the catalytic metals, both precious and their affordable alternatives.

Research activity and characterisation of the main scientific results

The scientific work of the team has led to several results that are worth noting due to their importance for the fields of catalysis and zeolite science, and some of them with practical impact on industrial technology. Selected results in the focus areas of the team are as follows:

1. Structure and activity of distant binuclear TM ion sites in zeolite matrices for methane utilization. This is a new area of research that started in the period 2015 – 2019, in which a new type of active sites stabilized in the zeolite matrix was studied – distant binuclear transition metal ion sites. A pair of divalent TM ions located in opposite zeolite rings so far that the formation of bridging structure with dioxygen (analogous to oxidized metalloenzyme active sites) is not permitted. However, these ions are close enough to cooperate on the interaction with dioxygen and able to activate it by a new mechanism – splitting of dioxygen and formation of a pair of so-called α -oxygens ($M^{4+}=O^{2-})^{2+}$, even at room temperature. The α -oxygens are so active that they can oxidize methane (to methanol) or other liquid products at room temperature, without the need for an effluent. (Tabor et al., Sci. Advances). Besides dioxygen, binuclear TM ion sites are promising in the activation of other molecules, as it was shown for N_2O (Tabor et al., Commun. Chem.). Due to the significant economic potential of the selective oxidation of methane, measures to protect intellectual property have been implemented (Dedecek et al., WO 2020 200336). Research in this area, e.g. selective oxidation of other industrially important molecules and activation of other selected molecules over binuclear sites is supposed to be the key area of the team research in the near future.

2. Synthesis of porous matrices (zeolites by ADOR, carbon replicas of zeolites). This wide area of research covers several independent (both by methodology, nature of materials and their application) subtopics concerning the synthesis of materials with unique properties:

2.1. Synthesis of zeolites with novel topologies. Up to now, more than two hundred zeolite materials with different topologies were prepared. However, there are plenty of possible zeolite structures, some of them with interesting properties (e.g. with seven- or nine-member ring channels, which are extremely rare), but thermodynamically unfeasible to prepare. The ADOR (assembly–disassembly–organization–reassembly) strategy of zeolite preparation developed by the team allows us to overcome these limitations and prepare zeolite structures with new topologies. The main novelty of this strategy lays in the chemical attack of Ge atoms in the germanosilicate framework, which results in the formation of zeolite lamellar material. These lamellar precursors are then reorganized to form zeolites with thermodynamically unfavorable topologies. This study represents a continuation of the successful research from the period 2010 – 2014. Several new topologies were prepared (Kasneryk et al., Angew. Chem. Int. Ed.) and extensive team experience was concluded in the reviewed papers (Eliasova et al., Chem. Soc. Rev., Mazur et al., Nature Chem.).

2.2. Zeolites with a hierarchical porosity and 2D zeolite materials. The lamellar precursors prepared by the ADOR approach can be reorganized not only to form new zeolites but also to form mesopores and thus materials with hierarchical micro-

mesoporosity or pillared 2D zeolite materials (Prech et al., Chem. Soc. Rev., Opanasenko et al., Catal. Sci. & Technol.). Combination of zeolite local arrangement with mesopores prepared by ADOR (or other ways) enabling access of large molecules is essential for the transformation of bulky molecules (Kim et al., ACS Catal.).

2.3. 3D graphene. Graphene is a unique material but rather inconvenienced for application in heterogeneous catalysis due to the low accessibility of the active sites stabilized on this material. 3D carbon replicas of zeolites, the preparation of which was mastered by the team, eliminates this disadvantage while maintaining promising properties of graphene-based materials (Sazama et al., ACS Catal.). Highly promising appears application of 3D graphene in CO₂ capture (Vorokhta et al., J. of CO₂ Util.). This area of research is to be continued as one of the main themes of the team.

2.4. Solvent-free synthesis of zeolites. Minimization of waste is a critical issue of sustainable chemical technology. Recently started research (2017) of the solvent-free synthesis of zeolite matrices represents an emerging innovation in zeolite synthesis. A significant step ahead in our approach is based on the application of well-controlled mechanical grinding (planetary mill) beside applied till now hand milling (mortar) (Pashkova et al., Chem. – Eur. J. and CZ 308130).

2.5. Synthesis of Al-rich beta zeolites. Beta zeolite is the only large-pore Si-rich zeolite with a 3D channel system. This results in its significant industrial importance. An increase in the concentration of Al atoms in the framework of this material enables to overcome a barrier of low activity for its application in numerous reactions. The team acknowledged the synthesis of Al-rich beta zeolites in the previous period 2010 – 2014. Attention is now focused on the catalytic applications of these materials (see later) and mainly on the commercialization of the knowledge previously obtained (Sazama et al., WO 2015 197036).

3. Organization of Al atoms in zeolite matrices (analysis and tuning). Organization of Al atoms in the zeolite framework is together with the framework topology a key parameter controlling the performance of zeolite catalyst. Distribution of Al atoms in zeolites was introduced to zeolite science by the team and this issue represents the “family silver” of the team and its advantage to other zeolite/catalytic research groups.

3.1. Analysis of Al distribution. The methodology of the analysis of Al distribution in the zeolite framework and cation siting in the zeolites was significantly improved (Martineau-Corcos et al., Solid. State Nucl. Magn. Reson., Klein et al., Chem. Commun.) including DFT calculations and extended to other than pentasil-ring zeolite matrices, which was concluded in the review (Dedecek et al., Chem. Sus. Chem.). The obtained knowledge allowed to analyze Al organization and cationic sites e.g. in one of the most complex zeolite structure – TNU-9 (Karcz et al., Jchem. – Eur. J.) and Al-rich beta zeolite (Sazama et al., J. Catal.).

3.2. Tuning of Al distribution in zeolites. Research in the area of synthesis of zeolites with desired Al distribution tuned for individual reactions continued. Attention was focussed, besides ZSM-5, to one of the currently most studied zeolites – SSZ-13 (Mlekodaj et al., J. Phys. Chem. C and CZ 2017 00832).

4. Redox catalysis over zeolites (NO_x and N₂O abatement). Redox catalysis is a core area of the catalytic studies of the team in which fundamental research of the structure-activity relationship on an atomic level, is extended to the attempts at the commercialization of the obtained knowledge. The experience of the team in the area of Al organization in zeolites is fruitful. A highly promising material appeared to be TMI-containing Al-rich beta zeolite, which shows synergy of the high concentration of active cationic sites (Sazama et al., J. Catal. and WO 2015 197036). Another direction is the development of catalysts for N₂O abatement at high temperatures, in which substantial improvement was reached for ferrierite-base catalysts (Sadovska et al., Catal. Commun., Tabor et al., Appl. Catal. B) and perovskite-based catalysts (Sadovska et al., CZ 2017 00050). In the case of ferrierite catalysts, a key role played an understanding of the local perturbation/stability of Al atoms in the ferrierite framework studied on the atomic level (Brus et al., Angew. Chem. Int. Ed.).

5. Hydrocarbon transformations over acid zeolite catalysts. Hydrocarbon transformations/acid catalysis is both a key area of the heterogeneous catalysis and the catalytic research of the team. Also, in this field was fructified unique knowledge of the team covering synthesis of unique (by the topology, hierarchical porosity and Al organization) zeolite materials.

5.1. Control of acid catalysed reaction by tuning of Al organization. Research in this area represents basic science and was focused on the role of Al distribution (proton distances) in catalysts for hydrocarbon transformations. After years of discussion, it was shown by the team that Al atoms in ZSM-5 are located exclusively at the channel intersection (Pashkova et al., Chem. – Europ. J.). Al distribution in the framework plays the key role in the number of reactions, and affects not only the reaction pathway (selectivity) (Li et al., ACS Catal.) but also activity of catalyst through release of the product from the active site (Bernauer et al., J. Catal.).

5.2. (Hydro)isomerization of hydrocarbons. This topic is focused on application research, often carried with industrial partners. Attention was paid on the utilization of Al rich beta zeolites, which on one side preserve advantages of large pore beta zeolite but posses dramatic increase of activity due dramatic increase of active sites in stable (on contrary to systems derived from faujasite) catalyst (Sazama et al., Applied Catal. A, Belecky et al., CZ201500605).

5.3. Catalysis over catalysts with hierarchical porosity. Other important parameter resulting in high catalytic activity of catalyst is the improvement of accessibility of active sites by tuning of micro- and meso-porosity of catalysts, especially in the case of bulkier substrate molecules. Also this area is rather oriented to the applied research. Various approaches for the preparation of porous materials with hierarchical porosity were successfully employed. Significant improvement was obtained e.g. for mordenite catalyst by post-synthetic modification (Pastvova et al., ACS Catal., Kaucky et al., CZ201700006), direct synthesis of zeolite nano-sponges (Kim et al., ACS Catal.). Other possible improvement in this field is an application of ordered 2D materials (Opanasenko et al., Catal. Sci. & Technol., Prech et al., Catal. Sci. & Technol., Heard. et al., Adv. Mater.)

5.4. Catalysis over MOF catalysts. Metal organic framework materials enable to

prepare well-defined active sites in well-defined environment for basic research. It was successfully employed for deeper understanding of a number of reactions e.g. aldol condensations ([Kikhtyanin et al., Catal. Today](#)).

6. Photocatalytic processes for abatement of NO_x and organic pollutants.

The research in the field represents continuation of the work in the period 2010 – 2014 which was focused on the preparation of nanomaterials. Nevertheless, a substantial extension has been made in the period 2015 - 2019 to cover application of nanomaterials in photocatalysis.

6.1. Novel porous nanocomposites for the application in photoelectrochemistry.

Nanostructured transparent conducting oxide layers gain increasing importance as high surface area electrodes enabling incorporation of functional redox species with high loading. The novel antimony-doped tin oxide films were fabricated using the self-assembly of preformed antimony-doped tin oxide nanocrystals with poly(ethylene oxide-*b*-hexyl acrylate) block copolymer, the pore size being tunable in the range from mesopores to macropores ([Peters et al., Adv. Funct. Mater.](#)). The combination of tunable porosity with a large conducting interface makes the obtained layers versatile current collectors with adjustable performance. Nanocrystalline cellulose is an abundant biogenic nanomaterial with unique properties that enables the efficient synthesis of mesoporous crystalline titania ([Ivanova et al., Chem. Mater.](#)). We significantly enhanced the photocatalytic activity of titania thin films by introducing solvothermally synthesized preformed anatase nanoparticles into a sol-gel based biotemplated titania scaffold.

6.2. Photocatalytic purification of water. Novel photocatalytic layers were prepared by quantitative electrophoretic deposition of nanoparticles of TiO₂ doped with carbonaceous additive species without sintering and without the use of any dispersive additive. The obtained immobilized reduced graphene oxide/TiO₂ composites exhibited high purity and mechanical resistance, showing markedly increased photocatalytic degradation rate in the mineralization of important aqueous pollutants, such as chlorophenols and antibiotics ([Guerin et al., Appl. Catal. B](#)).

6.3. Photocatalytic purification of the air. The extensive experimental research showed that porous layers containing TiO₂ nanocrystals and inorganic binder deposited on a range of building materials exhibit high photocatalytic performance with regard to NO and NO₂ abatement ([Zouzelka et al., Appl. Catal. B](#)). The effect of all the important process parameters (character of flow, temperature, relative humidity, irradiation intensity, pollutant concentration) was determined, which enabled to extrapolate the laboratory data to real world conditions and to calculate the realistic rate of pollutant removal.

Societal relevance

Catalysis is an important human activity with a grand impact on our daily life. More than 20 % of gross world product results from catalytic processes. Zeolites represent the widest and the most important group of heterogeneous catalysts. Moreover, the application of zeolites in gas separation is also essential (nitrogen production). It is expected that the role of heterogeneous catalysis will further increase as the

transformation of chemical production towards sustainability (environmentally friendly, low to zero carbon) represents one of the biggest tasks for today's society. Therefore, catalysis on zeolites and/or zeolite science is in a unique position. Specific properties of zeolites make zeolite matrices very suitable materials for the fundamental research in catalysis – understanding of the structure-activity relationship of active sites on the atomic level. On the other hand, a number of promising applications of zeolites emerged in the important areas for the development of sustainable chemical production such as the utilization of small molecules (carbon dioxide and methane), renewables and biomass, as well as the capture of CO₂ and abatement of a wide variety of pollutants. Moreover, there is an enormously fast transfer of knowledge from zeolite basic research to industrial application.

Thus, whilst all the main research results are in the form of articles, all issues studied by the team concerns hot topics from the point of societal relevance, as shown below for main areas of interest of the team during the period 2015-2019.

Structure and activity of distant binuclear TM ion sites in zeolite matrices for methane utilization. Methane utilization by transformation to valuable liquids is one of the biggest challenges in catalysis. Activation and utilization of small molecules, such as CO₂ and methane, is regarded as crucial for the transformation of the chemical industry towards its sustainability. Selective oxidation of methane to methanol as an energy carrier and chemical platform is thus of extremely high societal relevance.

Synthesis of porous matrices. Porous matrices can play a significant role in the capture of CO₂. Solvent-free synthesis of zeolites enables the environmentally friendly synthesis of zeolite catalysts. Preparation of zeolite matrices is a starting point for the development of highly active (minimization of energy consumption) and selective (minimization of waste) catalyst for hydrocarbon transformations, and utilization of renewables/biomass (hierarchical porous materials) also required for the transformation of the chemical industry towards its sustainability.

Organization of Al atoms in zeolite matrices. Al organization is a key parameter controlling the performance of zeolite catalysts. Tuning of Al distribution allows the preparation of optimized zeolite matrices functioning as highly active (minimization of energy consumption) and selective (minimization of waste) catalyst for hydrocarbon transformations, methane utilization, N₂O abatement, and deNO_x processes.

Redox catalysis over zeolites. End of pipe solution for N₂O abatement and deNO_x processes for automotive and process gases is of high importance for clean air protection.

Hydrocarbon transformations over acid zeolite catalysts. Development of highly active (minimization of energy consumption) and selective (minimization of waste) catalyst for hydrocarbon transformations is essential for new processes required for the transformation of chemical products to sustainable ones (change of substrates).

Photocatalytic processes for abatement of NO_x and organic pollutants. The development of materials and processes for cleaning of exterior and interior atmosphere and water is an issue with enormous societal relevance. With the application of nanotechnologies is connected important question of their safe use,

solved in newly started research on the toxicity of nanomaterials

The societal impact of the research is also represented by a strategic partnership with industrial partners. The team continues in deep cooperation with two partners, UNICRE a.s. (research body of Chemopetrol a.s., the main Czech oil and petrochemical company) and Euro Support Manufacturing Czechia, s.r.o. (main Czech catalysts producer). This strategic partnership is demonstrated in several joint projects in the frame of the Technological Agency of the Czech Republic. The high societal relevance of the teamwork is also reflected in the short-term cooperation with two important oil European companies (BP Chemicals Inc. and Shell).

The research projects investigated by the team in the period 2015 – 2019:

Although the team is carrying out predominantly fundamental scientific research, also applied scientific research (scale-up) and direct cooperation with an industrial partner is covered. The research is mostly structured by three-year research projects funded by the Czech Science Foundation (GACR), Ministry of Education, Youth and Sports of the Czech Republic (MEYS), Ministry of Industry and Trade of the Czech Republic (MIT) Ministry of Culture (MC) and by longer projects funded by the Technology Agency of the Czech Republic (TACR) and European Commission (EC) and by Academy of Sciences of the Czech Republic (ASCR) in the frame of the program framework Strategy AV21. The findings and results of this research are thus published primarily as original articles in high-impact peer-reviewed international scientific journals. The interim results are also presented at scientific meetings, wider consequences of the work are presented to the scientific community in the form of review articles and invited, plenary and keynote lectures. The results of applied research cover a wide variety of forms from patent/patent applications to unpublished know-how co-owned with industrial partners.

The research projects listed below cover most of the research activity of the team in the five-year period.

Innovative approaches for methane utilization – enzyme inspired zeolite catalysts (GACR 2019 - 2021) GA19-02901S

Principal Investigator: J. Dedecek.

Selective oxidation of methane to methanol and other valuable products (MEYS 2019 - 2021) 8JPL19046

Principal Investigator: J. Dedecek.

Progressive materials for protection from serious damage of environment (TACR 2018 - 2021) TH03010207

Co-investigator: J. Dedecek.

Molecules and Materials for Life (AV21, 2018 - 2024)

Co-investigator: J. Dedecek.

Concept for creation of zeolite based catalysts with enhanced functionality for

industrially relevant acid- and redox-catalysed reactions (GACR 2018 - 2020)

GA18-20303S

Principal Investigator: P. Sazama.

Development of high-performance alkylation and isomerization catalysts (TACR 2018 - 2020) TH03020184

Co-investigator: P. Sazama.

Innovative approaches for zeolite synthesis (GACR 2017 - 2019) GJ17-09188Y

Principal Investigator: V. Pashkova.

Binuclear metal ion structures in zeolites (GACR 2017 - 2019) GA17-00742S

Principal Investigator: J. Dedecek.

Creating and mastering structure of hierarchical zeolites to design advanced hydroisomerization catalyst (GACR 2015 - 2017) GA15-12113S

Principal Investigator: P. Sazama.

Zeolites with (semi)monomodal aluminum distribution in the framework (GACR 2015 - 2017) GA15-13876S

Principal Investigator: J. Dedecek.

Catalytic process for complete elimination of nitrogen oxides emissions for the production of nitric acid (TACR 2015 - 2017) TH01021259

Principal Investigator: P. Sazama.

Catalysts for eliminating N₂O in the high temperature regime in the production technology of nitric acid (GACR 2014 - 2016) GA14-10251S

Principal Investigator: Z. Sobalik

Nanomaterials and Nanotechnologies for Environment Protection and Sustainable Future (MEYS 2016 – 2023) LM2015073

Co-investigators: Z. Sobalik, P. Sazama, J. Rathousky

Photocatalytic NO_x removal from polluted air. Mechanism and overall impact on the environment (ASCR 2019 - 2020) L200401902

Principal Investigator: R. Zouzelka

Photocatalytic technology for air purification in interiors and exteriors of buildings: overall environmental impact (GACR 2019 – 2021) GA19-12109S

Principal Investigator: L. Brabec

Graphene / semiconductor heterojunction for efficient photocatalytic degradation of resistant water pollutants (GACR 2019 – 2021) GA19-21801S

Principal Investigator: J. Rathousky

Utilization of Optimized Photocatalytic Nanocomposites for Depollution of Air from Harmful Contaminants (MIT 2019 – 2022) FV40209

Principal Investigator: J. Rathousky

Smart materials for the complex protection of the surfaces of historical buildings (GACR 2017 – 2019) GA17-18972S

Principal Investigator: J. Rathousky

New materials and technologies for the conservation of the materials of historical monuments and the preventive care (MC 2011 – 2015) DF11P01OVV012

Principal Investigator: J. Rathousky

Engineering of advanced catalysts from modular parts (GACR 2015 – 2017) GA17-01440S

Principal Investigator: J. Cejka

Next generation personal protection garments against warfare agents (European Defence Agency 2015 – 2017) PRO-SAFE (A-1152-RT-GP)

Investigator: Jiri Cejka

Maximizing the EU shale gas potential by minimizing its environmental footprint (EC, 2015 - 2018), H2020-LCE-2014-1, 640979.

Investigator: Jiri Cejka

Combined Experimental and Theoretical Investigation of Catalytic Properties of Metal Organic Frameworks (GACR 2014 – 2016) GA14-07101S

Principal Investigator: J. Cejka

Catalytic oxidation of alkenes (TACR 2013 – 2016) TA03011148

Principal Investigator: J. Cejka

CAScade deoxygenation process using tailored nanoCATalysts for the production of BiofuELs from lignocellulosic biomass (EC, 2013 - 2017), FP7-NMP-2013-LARGE-7, 604307

Investigator: Jiri Cejka

Two-dimensional zeolites with modifiable architecture (GACR 2012 – 2016) GAP106/12/0189

Principal Investigator: J. Cejka

Intelligent Design of Nanoporous Adsorbents and Catalysts (GACR 2012 – 2018) GBP106/12/G015

Principal Investigator: J. Cejka

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