

Characteristics of main research directions investigated at the institute and the achievements 2010–2014

Institute	J. Heyrovský Institute of Physical Chemistry of the CAS, v. v. i.
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A. Novel fluorescence techniques and their applications in biophysics (Department of Biophysical Chemistry)

The development of novel “*fluorescence*” (F-)techniques has been for the last 15 years a main activity of the head of department Prof. Hof. Methods like time-dependent fluorescence shift approach (TDFS), z-scan Fluorescence Correlation Spectroscopy (FCS), or F lifetime CS (FLCS) were developed and are the reason for the international recognition. Within the last 5 years two novel single molecule techniques (Fluorescence Spectral Correlation Spectroscopy (FSCS) (Benda *Optics Express* 2014) and Dynamic Saturation Optical Microscopy (DSOM) were presented. Moreover, the department succeeded in putting forward fluorescence lifetime imaging and energy transfer (FLIM/ET) for quantitative size determination of nanodomains (Sachl *Biophys. J.* 2011), fluorescence antibunching for membrane-associated aggregation phenomena (Sachl *BBA-Mol. Cell Res.* 2015) and 2-foci FCS (Stefl *Optics Express* 2014). Naturally, the unique techniques developed attract biologists to collaborate with that department (e.g. Huranová *J. Cell Biol.* 2010 or Pembouong *J. Controlled Release* 2011).

“*Biophysics*” stands for the usage of such F-techniques in membrane and protein sciences. Specifically, the combination of TDFS, z-scan FCS, FLIM/ET, and antibunching with Molecular and Monte Carlo Simulations was used to investigate specific ion effects on a molecular level (e.g. Jurkiewicz *BBA-Biomembranes* 2012) and the effect of oxidised lipids (e.g. Volinsky *Biophys. J.* 2011) and sterols (e.g. Kulig *Free Radical Biology and Medicine* 2015) on lipid bilayers. Moreover, those techniques were used to characterise size and dynamics of lipid nanodomains beyond the phase separation (e.g. Sachl *BBA-Mol. Cell Res.* 2015) and the impact of transmembrane domains (Machan *Langmuir* 2014). In ongoing research the department is increasing the physiological relevance of those biophysical studies by addressing the molecular mechanisms of neurodegenerative diseases (Amaro submitted) and the molecular organisation of the plasma membrane and its impact on function in human cells (Chum submitted).

Concerning protein science TDFS was used to unravel the role of hydration and dynamics in enzymatic catalysis (Sykora *Nature Chem. Biol.* 2014). Recently, unnatural amino acid fluorescence (UAA-F) as a new tool for a site-specific analysis of protein hydration was presented (Amaro *J. Am. Chem. Soc.* 2015). Based on UAA-F the department presently develops in collaboration with protein scientists a tool for distinguishing active and blind enzyme tunnels.

In summary, although the department will further put forward cutting edge “*fluorescence*” methods, the present and future research emphasizes the physiological and medical relevance of the biomembrane studies as well as aims for unravelling generic phenomena in enzyme catalysis.

Amaro et al Site-specific analysis of protein hydration based on unnatural amino acid fluorescence; ; **J. Am. Chem. Soc.**, 2015 137, 4988-4992; **Amaro** et al. Oligomerization of β -amyloid monomers is induced by sphingomyelin and inhibited by monosialoganglioside GM1 organized in nanodomains; submitted; **Benda** et al Fluorescence spectral correlation spectroscopy (FSCS) for probes with highly overlapping emission spectra. **Optics Express**. 22, 3 (2014), 2973-2988; **Chum** et al The role of palmitoylation and transmembrane domain in sorting of transmembrane adaptor proteins, submitted; **Huranová** et al.. The differential interaction of snRNPs with pre-mRNA reveals splicing kinetics in living cells. **Journal of Cell Biology**. 191, 1 (2010), 75-86. **Jurkiewicz** et al.. Structure, dynamics, and hydration of POPC/POPS bilayers suspended in NaCl, KCl, and CsCl solutions. **Biochimica Et Biophysica Acta-Biomembranes**. 1818, 3 (2012), 609-616.; **Kulig** et al. Cholesterol under oxidative stress—How lipid membranes sense oxidation as cholesterol is being replaced by oxysterols. **Free Radical Biology and Medicine** 84, (2015) 30-41. **Macháň** et al.. Peripheral and Integral Membrane Binding of Peptides

Characterized by Time-Dependent Fluorescence Shifts: Focus on Antimicrobial Peptide LAH4. *Langmuir*. 30, 21 (2014), 6171-6179.; **Pembouong** et al. A comprehensive study in triblock copolymer membrane interaction. *J. Controlled Release*. 151, 1 (2011), 57-64. **Šachl** et al.. Limitations of Electronic Energy Transfer in the Determination of Lipid Nanodomain Sizes. *Biophysical Journal*. 101, 11 (2011), L60-L62.; **Šachl** et al.. On multivalent receptor activity of GM1 in cholesterol containing membranes. *Biochimica Et Biophysica Acta-Molecular Cell Research*. 1853, 4 (2015), 850-857; **Štefl** et al.. The fast polarization modulation based dualfocus fluorescence correlation spectroscopy. *Optics Express*. 22, 1 (2014), 885-899.; **Sýkora** et al.. Dynamics and hydration explain failed functional transformation in dehalogenase design. *Nature Chemical Biology*. 10, 6 (2014), 428-430.; **Volinsky** et al.. Oxidized Phosphatidylcholines Facilitate Phospholipid Flip-Flop in Liposomes. *Biophysical Journal*. 101, 6 (2011), 1376-1384.

B. Biomimetic properties of interfaces and metal complex systems (Department of Biomimetic Electrochemistry)

Research in this direction was focused on the charge transfer processes at the polarized interfaces between two immiscible electrolyte solutions (ITIES) or the supported phospholipid bilayer (SPLB) membranes, on the development of biosensors based on the solid amalgam electrodes (SAE), and (d) on the photo-induced processes in the biomimetic metal complexes.

Synthetic metal-free porphyrins were shown to catalyze the oxygen reduction at ITIES and in an organic solvent. Kinetic studies revealed a fine tuning of the homogeneous catalysis by the acid-to-catalyst molar ratio (Trojánek et al, Chem. Commun. 2011), and a strong inhibition of the catalysts by water and the acid counter-anion (Trojánek et al, Chem. Commun. 2012). To simulate numerically the observed behavior, a mechanistic model was proposed (Trojánek et al, Electrochim. Acta 2013).

A progress was made in fundamental electrochemistry at ITIES including (a) novel methodology to produce glass micro- and nano-capillaries for a more reliable determination of the rate of ion transfer across ITIES (Silver et al, J. Electroanal. Chem. 2014), and (b) synthesis of new hydrophobic room-temperature ionic liquids (RTILs) that were used to investigate the charge transfer across the water/RTIL interface, e.g. electron transfer (Langmaier et al, Electrochem. Commun. 2010).

SPLB membranes were designed to study the membrane transport of environmentally abundant heavy metal ions, with the phospholipid bilayers supported on (a) a microporous polycarbonate membrane (Navrátil et al, Electroanalysis 2010), (b) a gel-type electrode (Navrátil et al, Int. J. Electrochem. Soc. 2011), and (c) ITIES (Jaklová-Dytrtová et al, Collect. Czech. Chem. Commun. 2011).

New electroanalytical applications of SAEs were introduced such as (a) tubular silver amalgam detector for flow cells (Yosypchuk O. et al, Electroanalysis 2012), (b) the procedure for a modification of SAEs with liquid mercury film (e.g., Yosypchuk B. et al, Electroanalysis 2010), and (c) amperometric biosensors based on SAE (e.g., Josypčuk B. et al, Anal. Chim. Acta 2013).

Using *Pseudomonas aeruginosa* azurin as a platform, a remarkable acceleration of electron transfer was observed in the presence of a tryptophan residue between the redox centers. Acceleration mechanism was clarified and design rules for efficient photoactivated redox proteins were improved (e.g., Blanco-Rodriguez et al, Inorg. Chem. 2011). Solvent correction was found to be essential for a realistic quantum chemical description of IR and UV-visible spectro-electrochemical data of organometallic species (Záliš et al, Coord. Chem. Rev. 2010).

Blanco-Rodríguez et al. Photoinduced Intramolecular Tryptophan Oxidation and Excited-State Behavior of [Re(L-AA)(CO)₃(*alpha*-diimine)]⁺. *Inorganic Chemistry*. 50 (2011) 6122-6134. **Jaklová-Dytrtová** et al. Phospholipid layer stabilization via Yb(III) on ITIES and facilitated K(I) transport. *Collection of Czechoslovak Chemical Communications*. 76 (2011) 1917-1930. **Josypčuk** et al. Flow electrochemical biosensors based on enzymatic porous reactor and tubular detector of silver solid amalgam. *Analytica Chimica Acta*. 778 (2013) 24-30. **Langmaier** et al. Electron transfer across the polarized interface between water and a hydrophobic redox-active ionic liquid. *Electrochemistry Communications*. 12 (2010) 1333-1335. **Navrátil** et al. Electrochemical Measurements on Supported Phospholipid Bilayers: Preparation, Properties and Ion Transport Using Incorporated Ionophores. *Electroanalysis*. 22 (2010) 2043-2050. **Navrátil** et al. Supported Phospholipid Membranes Formation at a Gel Electrode and Transport of Divalent Cations across them. *International Journal of Electrochemical Science*. 6 (2011) 6032-6046. **Silver** et al. Ion transfer kinetics at the micro-interface between

two immiscible electrolyte solutions investigated by electrochemical impedance spectroscopy and steady-state voltammetry. *Journal of Electroanalytical Chemistry*. 731 (2014) 107-111. **Trojánek** et al. Mechanistic model of the oxygen reduction catalyzed by a metal-free porphyrin in one- and two-phase liquid systems. *Electrochimica acta*. 110 (2013) 816-821. **Trojánek** et al. Fine tuning of the catalytic effect of a metal-free porphyrin on the homogeneous oxygen reduction. *Chemical Communications*. 47 (2011) 5446-5448. **Trojánek** et al. Competitive inhibition of a metal-free porphyrin oxygen-reduction catalyst by water. *Chemical Communications*. 48 (2012) 4094-4096. **Yosypchuk O.** Tubular Detector of Silver Solid Amalgam for Electrochemical Measurements in Flow Systems. *Electroanalysis* 24 (2012) 2230-2234. **Yosypchuk B.** et al. Preparation and Properties of Mercury Film Electrodes on Solid Amalgam Surface. *Electroanalysis* 22 (2010) 1967-1973. **Záliš** et al. Quantum chemical interpretation of redox properties of ruthenium complexes with vinyl and TCNX type non-innocent ligands. *Coordination Chemistry Reviews*. 254, (2010) 1383-1396.

C. Novel materials for interfacial charge transfer processes in solar energy conversion and charge storage (Department of Electrochemical Materials)

The research activity accents synthesis, characterization and applications of advanced electrode materials, particularly nanomaterials based on carbon [Kavan et al. *Top.Curr.Chem.* 2014] and oxide semiconductors [Kavan et al. *Chem.Rec.* 2012] with optimized charge transfer processes. In the field of solar cells the first optically transparent graphene nanoplatelet cathode was developed for I-mediated DSSCs [Kavan et al. *ACS Nano* 2011]. Alternative represents the metal (W/PEN) grids [Kavan et al. *ACS Appl.Mater.Interfaces* 2014]. Electrospun TiO₂ exhibited reversible conversion to titanium nitride/oxyntiride fibers [Zukalova et al. *Chem.Mater.* 2010]. For electron-collector in perovskite solar cell, a novel sol-gel synthetic protocol [Kavan et al. *Chemphyschem* 2014] and electrochemical blocking test [Kavan et al. *J.Phys.Chem.C* 2014] were developed. The electrochemical doping stability of our compact layers approached that of single crystal anatase [Zukalova et al. *J.Phys.Chem.C* 2014]. Research on materials for Li-ion batteries highlighted the lithium insertion into TiO₂ (anatase) with ^{16/18}O and ^{6/7}Li isotope labeling [Laskova et al. *Chem.Mater.* 2013] and the distinction of capacitive and insertion Li-storage in monoclinic TiO₂(B) and anatase [Laskova et al. *J.Power Sourc.* 2014]. In the scope of nanocarbons the details of 2D band splitting in graphene were elucidated [Frank et al. *Nano Lett.* 2012]. The mechanical deformation of graphene monitored by Raman spectroscopy led to design of universal stress sensor [Frank et al. *Nature Comm.* 2011]. For B-doped nanodiamond, considerable simplification of the surface modification was achieved by sensitizing with non-covalently anchored dye [Krysova et al. *Phys.Chem.Chem.Phys.* 2015]. In photocatalysis, an array of specific photocatalysts has been developed, such as TiO₂ immobilized on layered double hydroxides and TiO₂-SiO₂ composites. The high-purity isotopically labeled TiO₂, Frank et al. *Phys.Chem. Chem.Phys.* 2012] was developed for photo/catalytic transformations of CO₂ [Civis et al. *J.Phys.Chem.C* 2011] and other model molecules. The novel field of gaseous nanodomains was addressed [Janda et al. *Nanotechnology* 2010] with the discovery of specific surface interactions of gaseous nanobubbles [Tarabkova et al. *Langmuir* 2014].

Kavan Exploiting Nanocarbons in Dye-Sensitized Solar Cells; *Top.Curr.Chem.* 348, (2014), 53-94.; **Kavan** Electrochemistry of Titanium Dioxide: Some Aspects and Highlights; *Chem.Rec.* 12, (2012), 131-142.; **Kavan** et al. Optically Transparent Cathode for Dye-sensitized Solar Cells Based on Graphene Nanoplatelets; *ACS Nano* 5, (2011), 165-172.; **Kavan** et al. Optically Transparent FTO-Free Cathode for Dye-Sensitized Solar Cells; *ACS Appl.Mater.Interfaces.* 6, (2014), 22343-22350.; **Zukalova** et al. Facile Conversion of Electrospun TiO₂ into Titanium Nitride/Oxyntiride Fibers; *Chem.Mater.* 22, (2010), 4045-4055.; **Kavan** et al. Sol-Gel Titanium Dioxide Blocking Layers for Dye-Sensitized Solar Cells: Electrochemical Characterization; *Chem.Phys.Chem.* 15, (2014), 1056-1061.; **Kavan** et al. Electrochemical Characterization of TiO₂ Blocking Layers for Dye Sensitized Solar Cells; *J.Phys.Chem.C*, 118, (2014), 16408-16418.; **Zukalova** et al. Electrochemical Doping of Compact TiO₂ Thin Layers; *J.Phys.Chem.C*, 118, (2014), 25970-25977.; **Laskova** et al. Lithium Insertion into Titanium Dioxide (Anatase): A Raman Study with ^{16/18}O and ^{6/7}Li Labeling; *Chem.Mater.* 25, (2013), 3710-3717.; **Laskova** et al. Capacitive contribution to Li-storage in TiO₂ (B) and TiO₂ (anatase); *J.Power Sourc.* 246, (2014), 103-109.; **Frank** et al. Phonon and structural changes in deformed Bernal stacked bilayer graphene; *Nano Lett.* 12, (2012), 687- 693.; **Frank** et al. Development of a universal stress sensor for graphene and carbon fibres; *Nature Comm.* 2, (2011), DOI: 10.1038/ncomms1247.; **Krysova** et al. Visible-Light Sensitization of Boron-Doped Nanocrystalline Diamond

through Non-covalent Surface Modification; **Phys.Chem.Chem.Phys.** 17, (2015), 1165-1172.; **Frank et al.** Raman spectra of titanium dioxide (anatase, rutile) with identified oxygen isotopes (16, 17, 18): **Phys.Chem.Chem.Phys.** 14, (2012), 14567-14572.; **Civis et al.** Oxygen Isotope Exchange between CO₂ and Solid Ti₁₈O₂; **J.Phys.Chem.C**, 115, (2011), 11156-11162.; **Janda et al.** Nanobubble-assisted Formation of Carbon Nanostructures on Basal plane Highly Ordered Pyrolytic Graphite Exposed to Aqueous Media; **Nanotechnology**. 21, (2010), 095707-0957077.; **Tarabkova et al.** Surface Rearrangement of Water-Immersed Hydrophobic Solids by Gaseous Nanobubbles; **Langmuir**. 30, (2014), 14522-14531.

D. Reactivity of transient species in the gas phase (Department of Chemistry of Ions and Clusters)

The accent of experimental research of **reactivity of transient species in the gas phase**, including ions, molecular clusters, radicals and molecules of gases and vapours of volatile compounds is placed on filling the current gaps in knowledge identified in highly relevant areas of science ranging from understanding of planetary atmospheres via environmental issues to clinical diagnoses. Whilst the motivation for the research is provided by practical needs and interdisciplinary scientific interactions, the core research is focussed on innovative experimental work providing solid fundamental understanding of the chemistry and physics of the processes occurring at the molecular level.

This department consists of two distinct groups, each working in a specific area of reactivity of transient species in the gas phase: "Chemistry of Ions in Gaseous Phase" and "Molecular and Cluster Dynamics"

1. Chemistry of Ions in Gaseous Phase.

The general research direction of this group are studies of reactions of ions (both positive and negative) with molecules in gases. These studies include an extensive programme of research of ion molecule reactions for trace gas analysis related to the Selected Ion Flow Tube Mass Spectrometry, SIFT-MS, methods that was previously initiated by P. Španěl, the current head of department, and his colleagues and that was continuously developed and enhanced at our institute since 1997. Of great interest to medical research is breath analysis for clinical diagnostics and therapeutic monitoring. The knowledge obtained in ion chemistry studies (Španěl & Smith *Mass Spectrom. Rev.* 2011) is being used in interdisciplinary studies to discover biomarkers in breath of various diseases (Dryahina *Rapid Commun. Mass Spectrom.* 2013) and infections (Shestivska *Rapid Commun. Mass Spectrom.* 2011). Other interdisciplinary areas of SIFT-MS research are microbiology, food science and environmental and atmospheric sciences. The second major research direction of this group are the reactions of ions with molecules occurring in planetary atmospheres. Current interest is in the Titan's atmosphere and the rate constants and their temperature dependencies resulting from this work have been widely adopted internationally in modelling and understanding of the origin of organic compounds observed by the Cassini-Huygens mission (Zabka *Icarus* 2012).

2. Molecular and Cluster Dynamics

The main research direction of this group is in the studies of chemistry of clusters, representing transition between gaseous and condensed phases of matter and also characterising behaviour of isolated nanoparticles. A major programme of studies of fundamental properties of clusters containing tens or hundreds of atoms is carried out using a unique Cluster Beam experimental apparatus combining mass spectrometry (Kocisek *J. Chem. Phys.* 2013) optical spectroscopy (Farnik *Mol. Phys.* 2012) and a novel approach to imaging of reaction products (Fedor *J. Chem. Phys.* 2011). Reactivity of ice nanoparticles (Lengyel *Physical Review Letters* 2014) is studied because of the need to understand their key role in stratospheric ozone depletion. An emerging research direction is the chemistry of clusters related to radiative damage of biological molecules (Poterya *Phys. Chem. Chem. Phys.* 2012).

Dryahina et al. Quantification of pentane in exhaled breath, a potential biomarker of bowel disease, using selected ion flow tube mass spectrometry. **Rapid Commun. Mass Spectrom.** 27, 17 (2013), 1983-1992; **Farnik et al.** Short review on the acetylene photochemistry in clusters: photofragment caging and reactivity. **Mol. Phys.** 110, 21-22 (2012), 2817-2828.; **Fedor et al.** Velocity map imaging of HBr photodissociation in large rare gas clusters. **J. Chem. Phys.** 134, 15 (2011), 154303.; **Kocisek et al.** Energy and charge transfer in ionized argon coated

water clusters. *J. Chem. Phys.* 139, 21 (2013), 214308.; **Lengyel** et al. Irregular Shapes of Water Clusters Generated in Supersonic Expansions. *Physical Review Letters* 112, 11 (2014), 113401.; **Poterya** et al. Hydrogen bond dynamics in the excited states: Photodissociation of phenol in clusters. *Phys. Chem. Chem. Phys.* 14, 25 (2012), 8936-8944.; **Shestivska** et al. Quantification of methyl thiocyanate in the headspace of *Pseudomonas aeruginosa* cultures and in the breath of cystic fibrosis patients by selected ion flow tube mass spectrometry. *Rapid Commun. Mass Spectrom.* 25, 17 (2011), 2459-2467.; **Španěl** & Smith Progress in SIFT-MS: Breath analysis and other applications. *Mass Spectrom. Rev.* 30, 2 (2011), 236-267. **Zabka** et al. Anion chemistry on Titan: A possible route to large N-bearing hydrocarbons. *Icarus* 219, 1 (2012), 161-167.

E. Structure-reactivity relationship in electroactive molecules, electron transfer kinetics and mechanisms (Department of Molecular Electrochemistry)

The **fundamental research of electron transfer processes and knowledge of reaction mechanisms of electrochemically initiated transformations** of newly synthesized organic and organometallic molecules with specific redox abilities is inevitable for understanding and further development of various applications including energy harvesting, photovoltaics (Ludvík *Inorg. Chem.* 2012), molecular catalysis (Fiedler *Chem. Commun.* 2012 and *Angewandte Chemie-Int. Ed.* 2013), non-linear optics (Ludvík *Dyes and Pigments* 2010) and molecular electronics (Hromadová *Phys. Chem. Chem. Phys.* 2011 and *J. Phys Chem. Lett.* 2013). Additionally, this knowledge is being applied in the development of sensors (Hromadová *Langmuir* 2013) and novel energetic materials (Šimková *Curr. Org. Chem.* 2011).

Further research is focussed on elucidation of the **structure-reactivity relationship on a single molecule level** including in-situ characterization of (radical) intermediates and determination of redox reaction mechanisms. For this purpose a continuous advancement of the electrochemical and in-situ spectroelectrochemical techniques and methodology is necessary to achieve these goals (Ludvík *Electrochim. Acta* 2014). Currently the experimental setup permits measurements of single molecule conductance values down to $10^{-8.5} G_0$ (G_0 stands for quantum conductance) using break junction techniques developed recently. Stereoelectrochemistry is a newly introduced research field, exploring electrochemical data for 3D-characterization of dissolved molecules in solution.

The results concerning the above mentioned research direction published in the period 2010-2014 involve the following themes: description, understanding and tuning of redox properties of new organic molecules; organometallic electroactive systems for molecular catalysis; molecules with multiple redox centres and push-pull systems; new molecular sensors and 2D architectures at electrified interfaces; antioxidant properties of flavonoids, their oxidative degradation and redox mechanisms (Sokolová *Chem. Commun.* 2012); single molecule conductance for molecular electronics (Hromadová *J. Phys Chem. Lett.* 2013); understanding molecular switching and oscillatory phenomena (Hromadová *J. Am. Chem. Soc.* 2012, Kolivoška *Chem. Commun.* 2014, Pospíšil *J. Phys. Chem. C* 2014, Pospíšil *J. Am. Chem. Soc.* 2014) etc.

Fiedler et al. Donor-acceptor systems of Pt(II) and redox-induced reactivity towards small molecules. *Chem. Commun.* 48, 18 (2012), 2388-2390; **Fiedler** et al. Identifying Intermediates of Sequential Electron and Hydrogen Loss from a Dicarboxylcobalt Hydride Complex. *Angewandte Chemie – Int. Ed.* 52, 26 (2013), 6781-6784; **Hromadová** et al. Electron dopable molecular wires based on the extended viologens. *Phys. Chem. Chem. Phys.* 13, 23 (2011), 11422-11429; **Hromadová** et al. Single-Step versus Stepwise Two-Electron Reduction of Polyarylpyridiniums: Insights from the Steric Switching of Redox Potential Compression. *J. Am. Chem. Soc.* 134, 5 (2012), 2691-2705; **Hromadová** et al. Single-Molecule Conductance in a Series of Extended Viologen Molecules. *J. Phys. Chem. Lett.* 4, 4 (2013), 589-595; **Hromadová** et al. Atrazine-Based Self-Assembled Monolayers and Their Interaction with Anti-Atrazine Antibody: Building of an Immunosensor. *Langmuir* 29, 52 (2013), 16084-16092; **Kolivoška** et al. Electrochemical control of a non-covalent binding between ferrocene and beta-cyclodextrin. *Chem. Commun.* 50, 79 (2014), 11757-11759; **Ludvík** et al. Push-pull molecules with a systematically extended pi-conjugated system featuring 4,5-dicyanoimidazole. *Dyes and Pigments* 85, 1-2 (2010), 57-65; **Ludvík** et al. Measured and Calculated Oxidation Potentials of 1-X-12-Y-CB11Me10- Anions. *Inorg. Chem.* 51, 9 (2012), 5128-5137.; **Ludvík** et al. Stereoisomeric products of electrochemical reduction of heterocyclic Fischer aminocarbene

Cr(0) complexes. Development of the electrochemistry mass spectrometry tandem approach using biphasic (acetonitrile-hexane) preparative electrolysis. **Electrochim. Acta** (2014) <http://dx.doi.org/10.1016/j.electacta.2014.10.110>, available online 27 October 2014; **Pospíšil et al.** Stochastic Resonance in Electron Transfer Oscillations of Extended Viologen. **J. Phys. Chem. C** 118, 17 (2014), 9066-9072; **Pospíšil et al.** Intense Chiroptical Switching in a Dicationic Helicene-Like Derivative: Exploration of a Viologen-Type Redox Manifold of a Non-Racemic Helquat. **J. Am. Chem. Soc.** 136, 31 (2014), 10826-10829; **Sokolová et al.** The oxidation of natural flavonoid quercetin. **Chem. Commun.** 48, 28 (2012), 3433-3435.; **Šimková et al.** 2,2-Dinitroethene-1,1-Diamine. **Curr. Org. Chem.** 15, 17 (2011), 2983-2995.

F. Carbon nanostructures and surfaces. (Department of Low-dimensional Systems)

The research direction **Carbon nanostructures** is the main activity of the Department of low dimensional systems (DLDS) and it is supervised by Dr. Kalbac. In the period 2009-2014 was this research direction supported by 8 projects, including large ERC –CZ project (since 2014), which allowed to hire new members of the group and to establish necessary instrumental base. The major achievements include establishing a new method of the graphene synthesis, which led to improved quality of the graphene samples (Kalbac Carbon 2012) and demonstrating the effects of the copper facets on the strain and the doping of the graphene prepared by CVD. (Frank Carbon 2014). We contributed significantly to uncover the mechanism of defect formation in graphene (Kalbac Adv. Mat. 2013) and the understanding of the changes in electronic structure in single walled carbon nanotubes induced by defects (Kalbac Nano Letters 2010.). The results obtained on doping of double walled carbon nanotubes (DWCNT) allowed to disentangle the role of electronic properties of specific tubes on the charge distribution between the inner and outer tube in DWCNT. (Kalbac Chemistry - A Eur. J. 2011). The in situ spectroelectrochemical study of graphene enabled the first experimental demonstration of a quantum interference effect in graphene (Kalbac ACS Nano 2010). The isotope labelling method was established for the application in the studies of graphene multilayers (Kalbac J. Phys. Chem. C 2012) and led to uncovering of the behaviour of graphene (Ek Weis J. Phys. Chem. Lett. 2014) and fluorinated graphene (Costa Carbon 2015) during the heating process, demonstration of the charge distribution between graphene layers in doped turbostratic and AB stacked graphene bilayers (Frank Acc. chem. res. 2015) and addressing the reactivity of AB stacked and turbostratic graphene bilayers (Ek Weis Chem. Eur. J 2015). The research direction **Electrocatalysis on solid surfaces** (supervised by Dr. Krtíl) focuses on fundamental understanding of electrocatalytic processes with aim to develop new classes of catalytic materials for fuel cell and electrolytic applications. The used rational design of catalysts combines understanding the catalyst's reactivity (He J. Am. Chem. Soc. 2012) and stability (Hoffmannova Langmuir 2013) with theoretical predictive tools to synthesize novel catalysts for fuel cells, water electrolysis (Petrykin Angew. Chem. Int. Ed. 2010) and organic synthesis (Jirkovsky et al et al. J. Am. Chem. Soc. 2011).

References: Ek Weis et al.: Heating Isotopically Labeled Bernal Stacked Graphene: a Raman Spectroscopy Study. **J. Phys. Chem. Lett.** 5 (3), (2014) 549–554. Ek Weis et al.: Fluorination of Isotopically Labeled Turbostratic and Bernal Stacked Bilayer Graphene. **Chem. Eur. J.**, 21, (2015) 1081-1087. Costa et al. Thermal treatment of fluorinated graphene: An in situ Raman spectroscopy study. **Carbon.** 84, 1 (2015), 347-354 Frank et al.: Interaction between graphene and copper substrate: The role of lattice orientation. **Carbon**, 68, (2014), 440-451, Frank et al.: Raman spectroscopy and In-situ Raman spectroelectrochemistry of isotopically engineered graphene systems. **Acc. chem. res.**, 48, (2015), 111-118, He et al. "Dramatically enhanced cleavage of the C-C bond using an electrocatalytically coupled reaction" J. Am. Chem. Soc. 2012; Hoffmannova et al. „Surface stability of Pt3Ni nanoparticulate alloy electrocatalysts in hydrogen adsorption" Langmuir 2013, Jirkovsky et al et al. , "Switching on the electrocatalytic ethene epoxidation on nanocrystalline RuO₂" **J. Am. Chem. Soc.** 2011, Kalbáč, et al.: The Influence of Strong Electron and Hole Doping on the Raman Intensity of CVD Graphene. **ACS Nano**, 4 (10), (2010) 6055-6063. Kalbáč et al.: Defects in Individual Semiconducting Single Wall Carbon Nanotubes: Raman Spectroscopic and in Situ Raman Spectroelectrochemical Study. **Nano Letters**, 10, 11 (2010), 4619-4626, Kalbáč et al.: Probing charge transfer between shells of double-walled carbon nanotubes sorted by outer-wall electronic type. **Chemistry - A Eur. J.**, 17, 9806-9815 (2011) 9806-9815, Kalbáč et al.: The control of graphene double-layer

formation in copper-catalyzed chemical vapor deposition. **Carbon**, 50, (2012) 3682-3687, **Kalbáč** et al.: Raman Spectroscopy as a Tool to Address Individual Graphene Layers in Few Layer Graphene **J. Phys. Chem. C**, 116, 35 (2012) 19046–19050. **Kalbáč**, et al.: Ion-irradiation-induced defects in isotopically-labeled two layered graphene: enhanced in-situ annealing of the damage: **Adv. Mat**, 25, 7, (2013) 1004-1009. **Petrykin** et. al. "Tailoring Selectivity for Electrocatalytic Oxygen Evolution on Ruthenium Oxides by Zn Substitution" **Angew. Chem. Int. Ed.** (2010).

G. Novel techniques of UV/Vis, infrared and microwave spectroscopy and their applications (Department of Spectroscopy).

Theoretical and experimental study related to the prebiotic chemistry has been for more than 15 years a main activity of the head of department Prof. Civiš. The question related to prebiotic chemistry is to answer what were the sources of the larger organic molecules that made up the first self-replicating systems. One of the best approaches to solving this problem is simulation of the environment in which life is presumed to emerge. A typical method is to use an external source to excite gas mixtures that simulate the primitive planetary atmosphere and then analyze the products. Examples of external energy sources for excitation are electrical discharges, high-energy particle or photon beams, and strong laser irradiation, which simulate cosmic rays in outer space, and sunlight as well as lightning discharge in the air (Ferus *J. Am. Chem. Soc.* 2012, Ferus *PNAS* 2015). The techniques of high resolution FTIR spectroscopy have been applied for isotopic labelling to study processes on titanium dioxide photoactive surface (Civiš *J. Phys. Chem. C* 2011, Civiš *Chem. Commun.* 2014).

New technique for sensitive detection of singlet oxygen in solid samples based on singlet oxygen-sensitized delayed fluorescence (Mosinger *Langmuir*, 2010) has been developed. The spectroscopic techniques have been used to study photoactive materials, to investigate elementary processes occurring after excitation especially formation of $O_2(^1\Delta_g)$ and correlate the data with the nature of the photosensitizer environment (Demel *Inorg. Chem.* 2013, Makhseed *Chem. Commun.* 2013).

A new technique of laser ablation of metal targets has been developed for a precision laboratory measurements of time resolved spectra of a broad series of atoms in the infrared range using high resolution FTIR spectroscopy (Civiš *Astronomy & Astrophysics* 2012, Civiš *Astronomy & Astrophysics* 2013). Time-resolved spectroscopy is a wide-spectrum technique used for studying the dynamics of chemical reactions, or the dynamic properties of molecules, radicals and ions in liquid, gas and solid states (Civiš *J. Phys. Chem. A* 2012). In the emission study of laser spark formamide decomposition, we have identified the fragmentation of formamide into small radicals such CN, NH, CH and highly excited molecules (CO) (Ferus *J. Phys. Chem. A* 2011). One of the major experimental problems of high resolution spectroscopy is an achievement of high sensitivity over reasonable large spectral range. In the frame of common international project together with École polytechnique fédérale de Lausanne (Prof. Eli Capon), Switzerland, new type of laser sources has been developed in wavelength range of 1200-2000 nm (InAlGaAs/InP-AlGaAs/GaAs wafer-fused VCSELs) (Civiš *J. Quant. Spectrosc. Rad. Trans.* 2014). Together with several business companies, the development of new optical materials for laser light conversion will be applied in an automotive car industry (project of TACR).

Civiš et al. Infrared transitions and oscillator strengths of Ca and Mg*. **Astronomy & Astrophysics**. 554, (2013), A24; **Civiš** et al. Li I spectra in the 4.65–8.33 micron range: high-L states and oscillator strengths. **Astronomy & Astrophysics**. 545, (2012), A61.; **Civiš** et al. Room temperature spontaneous conversion of OCS to CO₂ on the anatase TiO₂ surface. **Chem. Commun.** 50, 57 (2014), 7712-7715.; **Civiš** et al. Near-infrared wafer-fused vertical-cavity surface-emitting lasers for HF detection. **J. Quant. Spectrosc. Rad. Trans.** 147, (2014), 53-59.; **Civiš** et al. Time-Resolved Fourier Transform Emission Spectroscopy of He/CH₄ in a Positive Column Discharge. **J. Phys. Chem. A**. 116, 12 (2012), 3137-3147.; **Civiš** et al. Oxygen-Isotope Exchange between CO₂ and Solid Ti₁₈O₂. **J. Phys. Chem. C**. 115, 22 (2011), 11156-11162.; **Demel** et al. Lanthanide-Porphyrin Hybrids: from Layered Structures to Metal-Organic Frameworks with Photophysical Properties. **Inorg. Chem.** 52, 5 (2013), 2779-2786.; **Ferus** et al. High-energy chemistry of formamide: A unified mechanism of nucleobase formation. **PNAS** 112, 3 (2015), 657-662.; **Ferus** et al. High-Energy Chemistry of Formamide: A Simpler Way for Nucleobase Formation, **J.**

Phys. Chem. A 118, 4 (2014), 719-736.; **Ferus et al.** HNC/HCN Ratio in Acetonitrile, Formamide, and BrCN Discharge. **J. Phys. Chem. A**. 115, 10 (2011), 1885-1899.; **Makhseed et al.**: Water-soluble non-aggregating zinc phthalocyanine for photodynamic therapy. **Chem. Commun.** 49, 95 (2011), 1149-11151.; **Mosinger et al.** Fluorescent polyurethane nanofabrics: A source of singlet oxygen and oxygen sensing. **Langmuir** 26, 12 (2010), 10050-10056

H. Nanostructures in oxidic matrices and their dynamic behaviour (Department of Structure and Dynamics in Catalysis)

Main attention is focused on the (photo) catalytic application of (sub)nano 3D structures in/of oxidic materials. Analysis of subnanostructures on an atomic level and stabilized in oxidic matrices of zeolites and their dynamic behaviour in industrially relevant catalytic reactions has been in the centre of the research in last 20 years. A multi-spectroscopic approach combining FTIR, UV-Vis-NIR, MAS NMR, EPR (some of them applied up to in situ conditions) including new developed methods and methodologies (UV-Vis-NIR, MAS NMR) supported by quantum chemical calculations (cooperation with the Department of Theoretical Chemistry) (Brus, *Angew. Chem. Int. Ed.* 2015,) enabled in last 5 years elucidation of the structure relevant for catalysis in various redox- and acid- catalysed processes. Al organization in Si-rich zeolites including first complex analysis of Al in Si-rich zeolite was recognized as a key parameter controlling activity, selectivity and stability of zeolite catalysts and was introduced to zeolite science (Dedecek, *Catal. Rev.-Sci.Eng.* 2012). Moreover, we developed methods for the control of Al distribution in zeolites (Dedecek, *Chem. Mater.* 2012) also applicable up to the industrial scale (Bortnovsky, WP 2011). The extension of the topics from structure/activity/selectivity studies by mastering of the synthesis of zeolites, moreover with unique properties (defined Al distribution/organization) significantly spread up the capability of the department in the catalytic research, e.g. the synthesis of Al-rich beta zeolite with specific Al organisation serve as a base for development of extraordinary catalysts (Sazama, *J. Catal.* 2014). The department thus now uniquely covers the whole field of catalysis research from the preparation of catalysts, complex analysis of its structure, control and description of transport phenomena (Sazama, *Angew. Chem. Int. Ed.* 2013) to (long time) catalytic testing. The design, study and development of catalysts can be provided scaling from the laboratory measure up to the industrial scale (Sazama, patent application 2014).

In the field of photocatalysis over oxidic materials, the attention was in last 15 years focused to the preparation of nano-structured assemblies of a great variety of oxidic (Ni, Sn, Zn, Ti, In) nanoparticles. In cooperation with groups from abroad (e.g. prof. Bein, Munich) photovoltaic, electrochemical and sensing applications of these materials are also studied. The main achievement in this field was gained in last 5 years in the preparation of ultrasmall oxidic nanoparticles (Müller, *Small* 2010, Szeifert, *JACS* 2010) and in the tailored assembling of nanoparticles to films with unique properties (Liu, *ACS Nano* 2010).

Bortnovsky et al. Process for preparing zeolites of pentasil structure with controlled distribution of aluminium ions within skeleton. **WO2011095140-A1** (2011); **Brus et al.** Structure of framework aluminum Lewis sites and perturbed aluminum atoms in zeolites as determined by $^{27}\text{Al}\{1\text{H}\}$ REDOR (3Q) MAS NMR spectroscopy and DFT/molecular mechanics. **Angew. Chem. – Int. Ed.** 54 (2015) 541-545; **Dedecek et al.** Siting and Distribution of Framework Aluminium Atoms in Silicon-Rich Zeolites and Impact on Catalysis. **Catal. Rev.-Sci. Eng.** 54 (2012) 135-223; **Dedecek et al.** Synthesis of ZSM-5 Zeolites with Defined Distribution of Al Atoms in the Framework and Multinuclear MAS NMR Analysis of the Control of Al Distribution. **Chem. Mater.** 24 (2012) 3231-3239; **Liu et al.** Niobium doped titania nanoparticles: synthesis, assembly into mesoporous films and electrical conductivity. **ACS Nano.** 4 (2010) 5373-5381; **Müller et al.** Transparent conducting films of antimony-doped tin oxide with uniform mesostructure assembled from pre-formed nanocrystals. **Small** 6 (2010) 633; **Sazama et al.** Enhancement of Activity and Selectivity in Acid-Catalyzed Reactions by Dealuminated Hierarchical Zeolites. **Angew. Chem. – Int. Ed.** 52 (2013) 2038-2041; **Sazama et al.** Acid and redox activity of template-free Al-rich H-BEA* and Fe-BEA* zeolites. **J. Catal.** 318 (2014) 22-3; **Sazama et al.** Cobalt-containing beta zeolite, method of its preparation, and use thereof in catalyzed reduction of nitrogen oxides, **Patent application PV2014-448** (2014); **Szeifert et al.**

Ultrasmall titania nanocrystals and their direct assembly into mesoporous structures showing fast lithium insertion. *J. Am. Chem. Soc.* 132 (2010) 12605-12611.

I. Molecular sieve & organometallic chemistry and catalysis (Department of Synthesis and Catalysis)

Main research focus has been centred on mastering of the synthesis of “zeolites”, covering synthesis of new templates, novel zeolitic structures, and understanding of the mechanisms of their synthesis. We have developed a totally new synthetic mechanism, so-called *Top-down* synthesis (Roth et al. *J. Am. Chem. Soc.* 2011), which enormously contributed to the general understanding of zeolite synthesis. New synthetic protocol of controlled chemical selective hydrolysis of germanosilicate zeolites to two-dimensional layers with preserved zeolitic structure was established (Elišová et al. *Chem. Mater.* 2013). Preparation of two-dimensional zeolitic layers by *top-down* approach enabled to layer condensations providing two new zeolites, IPC-4 (code **PCR**) and IPC-2 (**OKO**), Roth et al. *Nat. Chem.* 2013. It allowed the preparation of other two new zeolites IPC-6 and IPC-7 with adjustable zeolite micropore volumes (Wheatley et al. *Angew. Chem. Int. Ed.* 2014). The zeolitic layers were treated with organic or inorganic linkers to form pillared hybrid materials organic or inorganic pillars (Opanasenko et al. *J. Am. Chem. Soc.* 2014). These studies exploit a weakness in a material when challenged by chemical stimuli to synthesize new materials (Morris & Čejka, *Nat. Chem. PERSPECTIVE*). Synthesis of novel zeolitic materials allowed us to investigate the relationship: texture/acidity-activity/selectivity for organic transformations to targeted fine chemicals. Nanosheet zeolites were investigated in alkylations and disproportionations of aromatic hydrocarbons (Jo et al. *Catal. Sci. Technol.* 2013), acylation reactions (Serrano et al. *J. Catal.* 2011), and hydroxyalkylations (Perez-Mayoral et al. *ChemSusChem* 2013) utilizing different zeolitic and MOF catalysts.

The direction of “organometallic” chemistry is aimed at basic research on organometallic compounds of early transition metals closely related to catalysts for polymerization and oligomerization of olefins. A substantial part of the direction is either devoted to catalysis of C–C bond forming reactions with emphasis on understanding elementary reaction steps (Pinkas *Organometallics* 2014). The development of new type of ligands or their transformation has been proved to be a powerful synthetic tool allowing obtaining structurally new products that cannot be obtained by conventional synthetic methods (Pinkas *Coord. Chem. Rev.* 2015). The investigation of the metallocene chemistry focused on activation of small molecules is a further challenge that will aid understanding of some elementary reactions at the early transition metals and exploitation of their complexes in organometallic and organic synthesis (Pinkas *Organometallics* 2011).

Elišová, et al. 3D to 2D Routes to Ultrathin and Expanded Zeolitic Materials, *Chem. Mater.* 25 (2013), 542-547. Jo, et al. The effect of MFI zeolite lamellar and related mesostructures on toluene disproportionation and alkylation. *Catal. Sci. Technol.* 3 (2013), 2119-2129. Morris & Čejka, Exploring chemically selective weakness in solids as a route to new porous materials, *Nat. Chem.* (2015) DOI:10.1038/NCHEM.2222, **PERSPECTIVE**. Opanasenko, et al. Hierarchical Hybrid Organic–Inorganic Materials with Tunable Textural Properties Obtained Using Zeolitic-Layered Precursor. *J. Am. Chem. Soc.* 136 (2014), 2511-2519. Pérez-Mayoral, et al. Intramolecular Hydroalkoxylation of Non-Activated C=C Bonds Catalysed by Zeolites: An Experimental and Theoretical Study. *ChemSusChem* 6 (2013), 1021-1030. Pinkas et al. Steric Effects in Reactions of Decamethyltitanocene Hydride with Internal Alkynes, Conjugated Diynes, and Conjugated Dienes. *Organometallics* 33 (2014), 3399-3413. Pinkas et al. Transformations of Functional Groups Attached to Cyclopentadienyl or Related Ligands in Group 4 Metal Complexes, *Coord. Chem. Rev.*, 10.1016/j.ccr.2015.03.007. Pinkas et al. Reactions of Hydrogen Sulfide with Singly and Doubly Tucked-in Titanocenes. *Organometallics* 30 (2011), 1034-1045. Roth et al. Postsynthesis Transformation of Three-Dimensional Framework into a Lamellar Zeolite with Modifiable Architecture. *J. Am. Chem. Soc.* 133 (2011) 6130-6133. Roth, et al. A family of zeolites with controlled pore size prepared using a top-down method. *Nat. Chem.* 5 (2013) 628-633. Wheatley, et al. Zeolites with Continuously Tuneable Porosity. *Angew. Chem. Int. Ed.* 53 (2014) 13210-13214. Serrano, et al. Acidic and catalytic properties of hierarchical zeolites and hybrid ordered mesoporous materials assembled from MFI protozeolitic units. *J. Catal.* 279 (2011), 366-380.

J. Development and applications of theoretical methods in chemistry (Department of Theoretical Chemistry)

Several directions of research in theoretical and computational chemistry have been followed: Development of electronic structure methods (Pittner), Theory of collisions of electrons with molecules (Čurík and Čársky), Theoretical study of (bio)catalytic processes (Sklenák and Srnec), and Molecular dynamics simulations of biophysical and photo-chemical processes (Cwiklik and Pittner).

1. Development of methods for strongly correlated systems – The main topic in the last decade was development of multireference coupled cluster methods, aimed at description of strongly correlated molecular systems, where well-established single-reference computational methods do not perform well or completely fail. We have developed multireference CC method with triexcitations (Bhaskaran-Nair *J. Chem. Phys.* 2011), explicitly correlated versions of MRCC methods, which accelerate basis set convergence (Demel *Phys.Chem.Chem.Phys.* 2012). as well as massively parallel versions of the algorithms, which allow to compute large molecules (Brabec *J. Chem. Phys.* 2012).

2. Theory of collisions of electrons with molecules - several topics relevant for the theoretical description of inelastic electron-molecule scattering have been investigated. An important achievement was the development of density fitting for evaluation of integrals in a mixed Gaussian and plane-wave basis (Čársky *J. Phys. B* 2010), which are needed in the scattering calculations, as well as a new GPU algorithm for the integrals based on Fourier transform of the $1/r$ term (Čársky *Theor. Chem. Acc.* 2014) with a speedup of 3 orders of magnitude.

3. Understanding Properties of Zeolites and Catalysis over Zeolites at an Atomistic Level – studies of the nature, structure, and properties of active sites of transition metal exchanged forms of silicon-rich zeolites, which are well known as exceptional redox catalysts, have been performed. Several important results have been achieved, for example detailed description of N₂O decomposition over Fe exchanged zeolites (Sklenak *J. Catal.* 2010), determination of the effect of the Al siting on the structure of Co(II) and Cu(II) active sites of ferrierite (Sklenak *J. Phys. Chem. C* 2013), or the Determination of the Al siting in the framework of ferrierites by an interplay between theoretical and experimental techniques Dedecek *J. Phys. Chem. C* 2011).

4. Molecular dynamics simulations of biophysical and photochemical processes - molecular dynamics simulations mainly focused on biologically relevant systems, have been performed. For example, the molecular-level details of lipid membrane hydration were studied in collaboration with experimental group of Prof. Martin Hof (Jurkiewicz *Biochimie* 2012), and a mixed Monte-Carlo-MD study of lateral arrangement of lipids in lipid membranes has been performed (Lis *J. Chem. Theory Comput.* 2012). The work included also computational study of lipid monolayers (Griffith *J. Phys. Chem. B* 2015) and study of fluorescent probes in a biological environment (Pederzoli *Chem. Phys. Lett.* 2014).

Bhaskaran-Nair, K. et al., Multireference state-specific Mukherjee's coupled cluster method with noniterative triexcitations using uncoupled approximation. *J. Chem. Phys.* 134, (2011), 154106; **Brabec**, J. et al., Universal state-selective corrections to multi-reference coupled-cluster theories with single and double excitations. *J. Chem. Phys.* 136, (2012), 124102; **Čársky**, P. Towards efficient ab initio calculations of electron scattering by polyatomic molecules. II. Efficient evaluation of exchange integrals. *J. Phys. B* 43, (2010), 175204; **Čársky**, P. et al., Efficient evaluation of the exchange integrals by means of Fourier transform of the $1/r$ operator and its numerical quadrature. *Theor. Chem. Acc.* 133, (2014), 1466; **Dedecek**, J. et al., Complex Analysis of the Aluminum Siting in the Framework of Silicon-Rich Zeolites. A Case Study on Ferrierites. *J. Phys. Chem. C* 115, (2011), 11056-11064; **Demel**, O. et al., An explicitly correlated Mukherjee's state specific coupled cluster method: development and pilot applications. *Phys. Chem. Chem. Phys.* 14, (2012), 4753-4762; **Griffith**, E. Et al., Interaction of L-phenylalanine with a Phospholipid Monolayer at the Water-Air Interface. *J. Phys. Chem. B* (2015) (in press); **Jurkiewicz**, P. Et al., Lipid hydration and mobility: An interplay between fluorescence solvent relaxation experiments and molecular dynamics simulations. *Biochimie* 94 (2012), 26-32; **Lis**, M. Et al, GPU-Based Massive Parallel Kawasaki Kinetics in the Dynamic Monte Carlo Simulations of Lipid Nanodomains. *J. Chem. Theory and Comput.* 8 (2012), 4758-4765; **Pederzoli**, M. Et al., Fluorescence of PRODAN in Water: a Computational QM/MM MD Study. *Chem. Phys. Lett.* 597 (2014), 57-62; **Sklenak**, S. - et al., N₂O decomposition over Fe-zeolites: Structure of the active sites and the origin of the distinct reactivity of Fe-ferrierite, Fe-ZSM-5, and Fe-beta. A combined periodic DFT and multispectral study. *J. Catal.* 272, (2010) 262-274; **Sklenak**, S. et al., Effect of the Al Siting on

the Structure of Co(II) and Cu(II) Cationic Sites in Ferrierite. A Periodic DFT Molecular Dynamics and FTIR Study.
J. Phys. Chem. C **117**, (2013) 3958-3968.

Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Biophysical Chemistry
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A. Personal Structure at 12/2014

In 12/2014 the department of biophysical chemistry consisted of 9 scientists, one research assistant, 7 PhD students and one Master student. Additionally, one PhD student was on maternity leave. Out of those 9 scientists, 6 scientists (Prof. Hof (52 years old), Drs. Amaro (32 years old), Humpolickova (36 years old; 0.8 full time equivalent (FTE)), Jurkiewicz (37 years old), Sykora (37 years old) and “Purkyne Fellow” Cebecauer (44 years old)) can be considered as key personal (although all of them were fully or partially financed by grant money). Further 3 scientists (Drs. Sachl, Olzynska, and Kral (only 0.3 FTE) as well as a research assistant taking care about the instrumentation (Dr. Kapusta; 0.8 FTE)) were exclusively paid by grant money. Moreover, there are presently 8 students working in the department. Two facts might be worth to mention: 1) In comparison with other scientific units within the Czech Republic, this department has a very international character. 2) The work of several members of the department have gained recognition by Czech awards (2010-2014: Premium Academiae, Purkyne Fellowship, Otto Wichterle Award, Award of the Learned Society, L’Oréal For Women in Science, The Josef Hlávka Award) as well as by several invitations to the major international conferences on biophysics and fluorescence (most prestigious: Plenary lecture given by Prof. Hof to 800 participants at the 9th EBSA European Biophysics Congress 2013).

B. Research Activities at a Glance

The main activities of the Department of Biophysical Chemistry can be summarised as „**development of novel fluorescence techniques and their applications in biophysics and cell biology**“.

Specifically, in the years 2010-2014 the department developed two **novel single molecule techniques** (Fluorescence Spectral Correlation Spectroscopy (FSCS) (**Benda et al. Optics Express 2014**) and Dynamic Saturation Optical Microscopy (DSOM) (**Humpolickova et al. PCCP 2010**)). Moreover, the department succeeded in **significant improvement of the following techniques**: a) Fluorescence lifetime imaging and energy transfer (FLIM/ET) for quantitative size determination of nanodomains (**Sachl et al. Biophysical Journal 2011; Amaro et al. Biophysical Journal 2014**). b) Fluorescence antibunching for membrane-associated aggregation phenomena (**Sachl et al. BBA-Molecular Cell Research 2015**). c) 2-foci FCS (**Stefl et al. Optics Express 2014**). Beside our initiatives in the development of fluorescence techniques, the department has implemented cutting edge fluorescence techniques like raster image correlation spectroscopy (RICS) (**Norris et al. Acta Biomaterialia 2011**), the super-resolution imaging technique „photoactivation localization microscopy“ (PALM), and cross correlation Number & Brightness analysis to investigate the organisation of cellular membranes and associated processes. These activities were supported by several grants from Ministry of Education, Youth and Sports of the Czech Republic („Fluorescence microscopy in biological and medicinal research“ ended 2011), Grant Agency of the Academy of Sciences of the Czech Republic („Development of modular spectral confocal fluorescence microscope with enhanced spatial resolution, using combined EM-CCD and SPAD detection, and offering special FCS-based point measurement modes“ ended 2011), and Czech Science Foundation („Development of New Fluorescence Methods for the

Characterization of Pores Formed by Antimicrobial Peptides“ ended 2012). Moreover, the Praemium Academiae awarded to Prof. Hof for the years 2012-2017 has given excellent conditions for a stepwise improvement of the experimental possibilities in that department.

The applications of those and earlier developed fluorescence techniques are mainly connected with running/recent grants: „Controlling Structure and Function of Biomolecules at the Molecular Scale: Theory Meets Experiments“ (ends 2018), „The role of hydrophobic plasma membrane interior in DOR regulation of trimeric G protein activity“ (ends 2016), „Exploring the structure function relationship of membrane-pore-forming FGF2 oligomers - a single molecule approach“ (ends 2016), „Membrane interactions of proteins associated with Alzheimer's disease and Parkinson's disease implications for diseases' pathologies and therapeutic avenue“ (ended 2/2015), „The effect of transmembrane domains of integral proteins on dynamic organisation of the plasma membrane of T lymphocytes“ (ended 2014), „Molecular level physiology and pathology of oxidized phospholipids“ (ended 2012); „Specific ion effects for proteins in solution and related biologically relevant systems“ (ended 2012), „Interaction of antibacterial peptides with the model membranes and possibility of the prediction of their biological activity“ (ended 2012) „Fluorescence microscopy in biological and medicinal research“ (ended 2011), and „DNA condensation: Monte-Carlo simulations, light scattering, fluorescence correlation spectroscopy in vitro and in vivo“ (ended 2010). The key publications on the ***applications of fluorescence techniques in biophysics and cell biology*** appeared in Journals like **Nature Chemical Biology, Journal of Cell Biology, Journal of the American Chemical Society, Small, Journal of Controlled Release, Biophysical Journal, Faraday Discussions, Langmuir, Soft Matter, Journal of Physical Chemistry, Biochimica Et Biophysica Acta, Physical Chemistry Chemical Physics, and Journal of Chemical Physics** and are summarised in the following chapter.

C. Detailed description of our results in 2010-2014:

The activities of the department might be divided in **4 main research directions**:

- 1) “Understanding Membrane Biophysics at an Atomistic Level”,
- 2) “Advanced Fluorescence Microscopy in Cell Biology”
- 3) “Elucidating the Dynamic/Hydration-Function Relationships in Hydrolytic Enzymes”
- 4) “The impact of transmembrane domain on the membrane organisation of proteins”

Within those 5 years the department published 78 papers in impacted journals (including papers which were already published on line in 2014, but appeared in printed version in 2015). **This report focuses on the highlights** connected with defined projects:

Research Direction 1: Understanding Membrane Biophysics at an Atomistic Level

1) Specific ion effects in lipid bilayers

*Interactions of ions with the lipid headgroups are known to be important for maintaining the structure and function of biological membranes. Our combined time-dependent fluorescence shift (TDFS; method developed by us: see recent review: Jurkiewicz et al. **Biochimie 2012**; Highly cited paper; Amaro et al. **Biophysical Journal 2014**), z-scan Fluorescence Correlation Spectroscopy (FCS based method developed by us; see recent review: Machan, Hof **BBA-Biomembranes 2010**; Highly cited paper) and computational studies revealed the molecular origin of the apparent “Hofmeister” ordering of ions for the interaction with biomembranes. The entire project was supported by a related grant of the Czech Science Foundation, in which Prof. Hof was together with Prof. Jungwirth (IOCB AS CR) principal investigator. However, all the experiments and the majority of the writing of those **4 selected papers** were done by members of the Department of Biophysical Chemistry. Moreover the close collaboration with Dr. Lukasz Cwiklik (Theoretical Chemistry JH-inst) in 3 of those papers should be highlighted.*

a) **Interaction of monovalent anions and cations with neutral bilayer**

Time-dependent fluorescence shifts and MD simulations characterise the interaction of Cl⁻, Br⁻, I⁻, ClO₄⁻, SCN⁻ with zwitterionic lipid bilayers using K⁺ and Na⁺ as counterions. Interactions increase with anion size and polarizability, polarizable anions penetrating to the lipid carbonyl. We identify mechanisms of ion-membrane interaction (ion pairing within the membrane, presence of the water/hydrophobic interface, and counterion effects) explaining anion/lipid Hofmeister series. (Vácha et al. *J. Phys. Chem. B* 2010). Highly cited paper.

b) **Interaction of monovalent cations with negatively charged bilayers**

We present a comprehensive picture on the interaction of monovalent cations and anions with negatively and positively charged bilayers, respectively. Cs⁺, K⁺, Na⁺ penetrate unexpectedly deep into the carbonyl region of negatively charged bilayers. The cations cluster up to 4 lipid molecules via the carbonyls leading to a rigidification and dehydration of the headgroup region. The amount of this effect is highly ion specific (Cs⁺<K⁺<Na⁺). We give a novel molecular explanation for the „Hofmeister“ series for cation/lipid interactions. (Jurkiewicz, Cwiklik et al. *BBA-Biomembranes* 2012). Highly cited paper.

c) **Interaction of monovalent anions with positively charged bilayers**

Interactions of anions with positively charged membranes are again highly ion-specific, but reversing the „Hofmeister“ series: Bromide strongly rigidifies the membrane while fluoride enhances its fluidity. Here the soft large bromide anion is penetrating deeply into the bilayer and bridges the headgroups. Fluoride on the other hand breaks the hydrogen bonds between the lipid headgroups. (Pokorná et al. *Faraday discussions* 2013, *J. Chem. Phys.* 2014).

2) **Effect of oxidised phospholipids and cholesterol derivatives on lipid bilayers**

*Oxidized phospholipids (OxPL) have been shown to increase their occurrence significantly in apoptosis, as well as in inflammation. Besides, they are involved in several pathological conditions, such as atherosclerosis, cancer, Alzheimer's and Parkinson's disease and type 2 diabetes. However, a coherent overall view of the causalities and mechanisms behind these conditions is lacking, mainly because of insufficient understanding of the occurring processes on a cellular as well as a molecular level. Within the project „OxPL: Molecular level physiology and pathology of oxidized phospholipids“ supported by the European Science Foundation „EUROMEBRANES“ network (network coordinator Prof. Kinnunen; Helsinki) Prof. Hof coordinated the objective „Understanding the biophysics of OxPL in model biomembranes“. In order to unravel the impact of OxPL on the biophysical properties of model membranes we combined our fluorescence experiments mainly with computational studies (performed by Dr. Lukasz Cwiklik (Theoretical Chemistry JH-inst) and to a lesser extent by Prof. Pavel Jungwirth (IOCB AS CR)) aiming for a comprehensive picture of the impact of those OxPL on the biophysics of model membranes. Two of those contributions were done in close collaboration with the network coordinator Prof. Kinnunen. However, except the NBD-quenching experiments in Volinsky et al *Biophysical Journal* 2011, all experiments as well as the majority of the writing of those 6 selected papers were carried out by members of the Department of Biophysical Chemistry.*

a) Using TDFS, z-scan FCS and MD simulations the impact of aldehyde- and carboxy-truncated OxPL (acting differently *in vivo*) on biophysics of membranes was characterised. Experiments and simulations demonstrate different action on bilayers indicating: carboxy-group orients towards water phase, aldehyde-group aligns parallel to the bilayer. (Beranova et al. *Langmuir* 2010). Highly cited paper.

b) NBD-quenching and time-dependent fluorescence shift experiments as well as MD simulations of model membranes reveal, for the first time, that the loss of lipid asymmetry

can be solely caused by altered biophysical properties of the lipid bilayer imparted by oxidized phospholipids. Oxidative attack could represent a causative factor that induces the loss of phospholipid asymmetry in apoptosis and cancer, resulting in the exposure of phosphatidylserine on the outer surface of the affected cells. (Volinsky et al **Biophysical Journal** 2011). Highly cited paper.

- c) We elucidate the influence of truncated oxidised phospholipids (OxPL) on the biophysics of complex lipid mixtures. Those studies were performed in different kind of model membranes, like monolayers on air/water interface, large and giant unilamellar vesicles. Specifically, we find that OxPL have the tendency to associate with cholesterol and we give a molecular explanation for this phenomenon. (Stefl et al. **BBA-Biomembranes** 2014, Khandelia et al. **Soft Matter** 2014). **Applying a novel combination of FCS with Langmuir-Blodgett monolayers we show that OxPL stabilize ordered domains containing sphingomyelin and cholesterol (Parkilla et al. BBA-Biomembranes 2015).**
- d) In Jurkiewicz et al. **BBA-Biomembranes** 2012 we reviewed the knowledge on „biophysics of lipid bilayers containing oxidatively modified phospholipids“ gained from „fluorescence and EPR experiments and from MD simulations“.

3) Size and dynamics of lipid nanodomains - beyond the phase separation

The existence and possible role of nanodomains (sometimes called „lipid rafts“) in the plasma membrane is a controversially discussed issue. However, these nanometer sized, highly dynamic platforms have not been up to now unambiguously detected in the plasma membrane of living cells. 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 beyond the optically or EPR resolvable phase separation boundary. In the selected 3 contributions using fluorescence techniques developed by us we were able to characterise the size and dynamics of such nanodomains. Our findings show that purely lipid driven nanodomains exist, but those domains have a liquid disordered character. All experiments, data analysis and the interpretation as well as the entire writing of those 3 selected publications were done by members of the Department of Biophysical Chemistry

- a) We calculate the limitations for determining lipid nanodomain sizes and occupied fraction of bilayer area by a novel „Monte-Carlo simulations/Fluorescence-Lifetime Imaging“ approach based on resonance energy transfer (ET). It considers ET across phase separation boundaries as well as the intra- and inter-leaflet ET (Sachl et al. **Biophysical Journal** 2011; Amaro et al. **al Biophysical Journal** 2014). In the papers listed under b) and c) we experimentally demonstrate the spatial resolution of this approach by characterising domains of sizes between 5 and 24 nm.
- b) For the first time, size and dynamics of nanodomains in model membranes of (quaternary) lipid compositions beyond the optically resolvable phase separation boundary are characterised. By two-color z-scan FCS, Monte Carlo simulation of lifetime imaging data (both approaches developed by us), and Phasor plot analysis we characterise transitions of 5 to 8 to 24 nm sized domains depending on sphingomyelin and cholera toxin subunit B (CT) content. Diffusion law analysis distinguishes between lipid and CT driven domains (Stefl et al. **Biophysical Journal** 2012).
- c) In a follow-up study the same methodologies were used to determine size and dynamic of monoganglioside GM1 nanoclusters in free-standing bilayers. Surprisingly, 6 nm clusters contain high number of DOPC and cholesterol molecules, and have liquid-disordered

character. Moreover, we developed a new binding assay for cholera toxin subunit B (CT) based on fluorescence antibunching and give a complex portrait of GM1 clustering and cholesterol involvement on CT/GM1 interaction (**Sachl et al. BBA-Molecular Cell Research 2015**).

Research Direction 2: Advanced Fluorescence Microscopy in Cell Biology:

New fluorescence approaches were developed and further cutting-edge fluorescence techniques were implemented. We continued our collaborations with several institutes within the Czech Republic and shared our expertise in single molecule fluorescence spectroscopy and microscopy with those partners. Here selected examples for such collaborations will be described. The idea, concept, theory, and experimental realization of those novel single molecule fluorescence approaches were done solely by members of the Department of Biophysical Chemistry. In the here described applications of our fluorescence techniques the actual scientific topic was formulated by our partners and we contributed by fluorescence measurements, which were essential for those projects.

a) Development of novel single molecule fluorescence approaches

We developed two novel single molecule fluorescence approaches: 1) Lately, various approaches of super-resolution fluorescence microscopy have been introduced, two of them being recently awarded by the Nobel Prize for Chemistry. In 2010 we presented dynamic saturation optical microscopy (DSOM), a new technique that overcomes the diffraction limit by monitoring the temporal decay of the excited singlet state due to a dark state formation. By mapping the intensity dependent decay kinetics, images with enhanced resolution up to a factor 4 were recorded. The advantage of DSOM over the other techniques is its simplicity for the implementation and inexpensiveness (**Humpolickova et al. PCCP 2010**). 2) We introduced the Fluorescence spectral correlation spectroscopy (FSCS). FSCS is analogous to Fluorescence Lifetime CS (also developed by us) but instead of the time-resolved detection the spectrally resolved data are utilized. By FSCS clean auto- and cross-correlation curves (i.e. free of cross-talk) can be obtained even for dyes with highly overlapping emission and excitation spectra. FSCS allows simultaneous monitoring of diffusion in regions of different order using environmentally sensitive membrane dyes, making FSCS an attractive novel tool for living cell studies (**Benda et al Optics Express 2014**).

b) Application of single molecule fluorescence approaches in the cell nuclei (collaboration with D. Stanek (IMG CAS))

1) Spliceosome formation has been mostly studied in vitro. We apply fluorescence lifetime correlation spectroscopy (FLCS; *method developed by us; see recent review: Machan et al. Anal. Bioanal. Chem. 2014*) and fluorescence recovery after photobleaching (FRAP) to monitor dynamic interaction of splicing factors with pre-mRNA to understand spliceosome assembly in living cells. We show that splicing factors differ in their interaction time with pre-mRNA, supporting a step-wise assembly model of the spliceosome and helping to solve a controversy in the field. The application of FLCS (instead of classical FCS) provides one of the first estimates of human pre-mRNA splicing rates in vivo, which is essential for this study and actually presents the first example of FLCS in living cells published in the impacted journal (**Huranová et al. J.Cell Biol. 2010**; Highly cited paper.) 2) RICS was applied for the *in vivo* characterization of protein diffusion together with binding to chromatin. Specifically, we mapped the average binding time of a member of the bromodomain extra terminal (BET) protein family to chromatin and quantified the contributions of individual proteins. This novel application of RICS (**Hnilicová et al. Molecular Biology of the Cell 2013**) opens new imaging possibilities in chromatin research.

c) The effect of plasma membrane organization on the G-protein coupled receptor (GPCR) functioning studied by fluorescence techniques (collaboration with P. Svoboda (FGU AS CR))

The capability of GPCR to activate the G-proteins was tested on plasma membrane (PM) fragments isolated from control and cholesterol-depleted HEK293 cells stably expressing δ -

opioid receptor (DOR-Gi1 α). The data obtained with the environment sensitive fluorescence dyes showed that the depletion intruded the optimum PM organization. Functional coupling between DOR-Gi1 α and corresponding G-protein deteriorated, while the receptor – ligand site remained unchanged. The biophysical state of hydrophobic plasma membrane should be therefore regarded as a regulatory factor of DOR-signaling cascade (**Brejchova et al. BBA-Biomembranes 2011**). As a follow-up, we investigated the effect of disruption of plasma membrane integrity by cholesterol depletion on the mobility of thyrotropin-releasing hormone receptor (TRH-R fused with eGFP) stably expressed in HEK293 cells. The receptor mobility was monitored by FRAP and RICS approach. The decrease in cholesterol content resulted in weakening of the TRH-R/G-protein coupling, but was accompanied by a minor change in the lateral receptor mobility (**Brejchova et al. BBA-Biomembranes 2015**).

d) Applications aiming for a rational design of new gene delivery agents (collaboration with N. Mignet; Paris)

Copolymer triblock L64 enhances gene transfer in muscle. By Single Photon Counting-FCS (TCSPC-FCS), NMR, and DSC in dilutions close to conditions of muscle transfection, we show that L64 does not interact with DNA, but with membranes. Since the behavior could be predictive of muscle transfection, the study is crucial for rational design of transfection agents. TCSPC-FCS (originally introduced to DNA research by us) is sensitive to structural DNA changes on nm to μm scale and is essential for this work. This paper (**Pembouong et al. Journal of Controlled Release 2011**) is selected as an example out of 5 papers contributing to the rational design of new gene delivery agents.

e) Applications of our fluorescence techniques in different fields: Collaborations with J. Valenta (Charles University, Prague) and with A. Vlček (Department of Biomimetic Electrochemistry)

Naturally our expertise in fluorescence spectroscopy and microscopy is also attractive for scientists in other than biological fields. For this report we selected two directions, namely the characterization of the emission of quantum dots and transition metal complexes. In collaboration with Prof. J. Valenta (**Dohnalová et al. Small 2012**), a comprehensive study of the fast blue-green luminescence of chemically synthesized non-oxidized silicon quantum dots (Si-QDs) of 2–3 nm size is reported. Comparison of the results obtained on the ensemble and those on the single nano-object level provides conclusive evidence that efficient and tunable emission arises due to radiative recombination of electron–hole pairs confined in the Si-QDs. This understanding paves the way towards the development of Si-QDs with tunable sizes and bandgaps. Our group contributed by the determination of the photoluminescence lifetime of single quantum dots, which was essential for this study. Additionally, in cooperation with Prof. Vlček and Prof. Gray (Caltech, USA) the nature of the photoinduced electron transfer between the tryptophan residue and Badan fluorophore within the cytochrome protein was characterized (**Pospíšil et al. J. Phys. Chem. B 2014**). Furthermore, the measurements of the platinum complexes revealed that functionalization with BF₂ leads to the dramatic slow-down of the intersystem crossing rate yielding unusually long fluorescence lifetime (**Durrell et al. J. Am. Chem. Soc. 2012**). We also participated in the characterization of low-lying singlet and triplet excited states within a set of Rhenium complexes (**Blanco-Rodríguez et al. J. Am. Chem. Soc. 2014**).

Research Direction 3: Elucidating the Dynamic/Hydration-Function Relationships in Hydrolytic Enzymes:

Understanding the molecular basis of enzyme-substrate interactions that contribute to enantioselectivity is important for constructing selective enzymes by protein engineering. Haloalkane dehalogenases (Dh) can convert halogenated aliphatic substrates to their corresponding alcohols, and because of the simplicity of the reaction represent a good model system to study structural basis of reactivity and enantioselectivity. In our joint efforts with the group of Jiri Damborsky (MU Brno,) we have developed a new fluorescence (“TDFS”) method to monitor dynamics and hydration in such

proteins in a site-specific manner (Jesenska et al., *J. Am. Chem. Soc.* 2009). Together with MD simulations (performed in Brno) we try to unravel the role of these parameters in the enzyme enantioselectivity. The idea and concept of the project were formulated by Hof (JH-Inst) and Damborsky (MU, Brno). 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 partner labs in Brno. Crystal structures were determined in Ceske Budejovice.

- a) We addressed an issue which is fundamental for the broader use of the TDFS method in protein sciences: Is the TDFS response affected by probe's chemical nature? We designed compounds with different probe and linker lengths to label different dehalogenase mutants at different positions in the enzyme tunnel. The quantitative TDFS response depends on the chromophore, but the qualitative comparison between different mutants is valid. The narrower the tunnel and the deeper the location, the stronger the influence of the chemical nature of the probe on the quantitative TDFS appears to be. (Amaro et al. *J. Phys. Chem. B* 2013).
- b) We used that TDFS technique to unravel the role of hydration and dynamics in enzymatic catalysis: Natural enzymes have superior catalytic rates and selectivity to the enzymes created by *de novo* protein design. We addressed this problem by transplanting the active site from a Dh with high enantioselectivity to nonselective one. TDFS and simulations showed that dynamics and hydration at the tunnel mouth differ between the redesigned and target Dh. Our results emphasize the importance of dynamics and hydration for enzymatic catalysis and rational protein design (Sykora et al. *Nature Chem. Biol.* 2014).

Research Direction 4: The impact of transmembrane domain on the membrane organisation of proteins

In 11/2010, biologist Marek Cebecauer has joined the department to establish a group studying molecular organisation of the plasma membrane and, especially, its impact on function in human cells. The focus was on the impact of transmembrane domains (TMD) of proteins on the organisation of membranes employing the combination of molecular dynamics simulations with experiments performed using model membrane system and fluorescence imaging of live/fixed cells. Our observations underline a unique character of each TMD and its importance the localisation of proteins in cells. Molecular genetics and flow cytometry was performed in the lab of Dr. Brdicka (IMG, Prague) but project definition, all imaging experiments and data processing as well as writing was performed by us.

- a) We have designed and synthesized fluorescent probes for the analysis of membrane environment and performed detailed characterisation in model membranes (Olsinova et al. *PCCP* 2014). The probes were synthesized in the group of Prof. J. Svoboda (ICT, Prague). All the rest was done by us.
- b) We presented the first systematic study of the effect of 4 TMDs on mobility and polarity at the glycerol level of lipid bilayers. Interestingly, all TMDs rigidify the bilayer but increase the probed polarity. The effect indicates direct interaction between the peptide and lipid acyl groups. The amount correlates with the flexibility of the TMDs. We demonstrated that time-dependent fluorescence shifts can be new approach for characterising the membrane action of peptides (Machan et al. *Langmuir* 2014).
- c) Using model membranes and synthesized TMD-derived peptides we confirm the rigidifying effect of hydrophobic TMD-like peptide (KK-LW21) on the surrounding lipids in the absence and presence of cholesterol. Co-operative effect of peptides and cholesterol was observed (Olsinova et al. **submitted**). MD simulations uncover proline kink within the helical structure

of LAT peptide (23 residues long) reducing its capacity to incorporate into thick and rigid membranes, in contrast to a shorter LW21 peptide (21 residues). In cells, we confirm limited capacity of LAT to incorporate into thick and rigid membranes (e.g. plasma membrane).

- d) In living cells, we have investigated the plasma membrane (PM) sorting of membrane adaptor proteins and artificial proteins based on model TMD. We confirm the importance of TMD length for sorting but provide novel data for proteins with suboptimal TMD – help is provided by the glycosylated extracellular domain and post-translational palmitoylation (Chum et al. submitted).

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Biomimetic Electrochemistry
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A. Personal Structure in December 2014

In 12/2014, the department of biomimetic electrochemistry consisted of 3 senior scientists, 9 scientists and 3 graduate students. 8 of those 12 scientists (Prof. Z. Samec, Prof. V. Mareček, Prof. A. Vlček, jr., Dr. S. Záliš, Dr. A. Trojánek, Dr. J. Langmaier, Assoc. Professor T. Navrátil, and Dr. B. Josypčuk (Yosypchuk)) can be considered as key members of the department. The total work load was 9.1 FTE (full time equivalent), including 5.8 FTE paid from the institute budget and 3.3 FTE paid from project grants. Some of the members had a part-time appointment due to other commitments (Prof. Mareček/0.6 FTE, vice-president of the Czech Academy of Sciences; Prof. Vlček/0.075 FTE, Professor of Inorganic Chemistry at Queen Mary, University of London), or due to their emeritus status (Dr. K. Holub/0.3 FTE, Dr. I. Šestáková/0.55 FTE, Dr. M. Heyrovský/0.25 FTE, all with 0.05 FTE paid from the institute budget and the remainder FTE paid from project grants). One member in the position of a postdoctoral fellow (O. Josypčuk/1.0 FTE) was paid exclusively from a project grant.

B. Research Activities at a Glance

The main activities of the department in 2010-2014 included the investigations of the biomimetic properties of the polarized interface between two immiscible electrolyte solutions (ITIES), the supported phospholipid bilayer (SPLB) membranes, and metal complex systems. An attention was also paid to the development of biosensors.

In particular, the members of the department (a) elucidated the mechanism of catalysis of the oxygen reduction in one- and two-phase liquid systems by a metal-free porphyrin (**Trojánek et al, *Electrochim. Acta* 2012 and 2013**), and by the corresponding cobalt porphyrin (**Trojánek et al, *J. Phys. Chem. A* 2014**), (b) revealed new charge transfer processes at the interface between a room-temperature ionic liquid (RTIL) and an aqueous electrolyte solution (**Langmaier et al, *Electrochem. Commun.* 2010 and 2012**), (c) introduced an original methodology to produce glass capillaries of nano- and micro-scale dimension for kinetic studies at ITIES (**Silver et al, *Electrochim. Acta* 2013**), (d) developed a model of the ion transport across biomembranes (**Navrátil et al, *Electroanalysis* 2010**), (e) presented new applications of the solid amalgam electrodes in electroanalysis (**Josypčuk B. et al, *Anal. Chim. Acta* 2013**), (f) discovered a new mechanism of electron transfer acceleration through Re(I) modified Azurins (**Blanco-Rodriguez et al, *Chem.-Eur. J.* 2011**).

These activities were supported by 5 grants from Czech Science Foundation (CSF), 7 grants from Ministry of Education, Youth and Sports of the Czech Republic (MEYS, international programs COST or KONTAKT), and 1 grant from Grant Agency of the Academy of Sciences (GAAS) for the 13 projects in total. Specifically, 3 projects were focused on the catalytic O₂ reduction ("Molecular catalysis at liquid-liquid interfaces: Towards chemical fuel cells, 2007-2010, MEYS; "Molecular catalysis of the oxygen reduction at a polarized liquid-liquid interface", 2007-2010, CSF; and "Catalysis of the oxygen reduction by metal-free porphyrins at the electrochemically polarized liquid-liquid interfaces", 2011-2013, CSF), 2 projects were focused on the charge transfer across the water/RTIL interface ("Study of the mechanism of complexation at the hydrophobic ionic liquid-water interface", 2008-2010, MEYS; and "Voltammetric assessment of new ionic liquids for their applications in capillary electrophoresis", 2011-2013, CSF), 1 project was focused on the ion transfer kinetics at ITIES ("Novel methodology for the determination of the rate of ion transfer across liquid/liquid interfaces", 2013-2016, CSF), 3 projects were focused on the ion transport across the SPLB membranes and biosensors ("Transport of Charged and Uncharged Species across Models of Biological Membranes", 2008-2012, GAAS; "Aspects of hazardous metals transfer across biomembranes", 2012-2015, CSF; and "Novel electrochemical sensors and sensing techniques for the analysis of nucleic acids structure and interactions", 2011-2015, CSF), and 5 projects were focused on the photoinduced processes in the biomimetic metal complex systems ("Properties and dynamics of electronic states of transition metal complexes, 2009-2010, MEYS; "Photoinduced Charge Separation in Metalloprotein-Based Systems: Theory and Experiment", 2010-2012, MEYS; and

“Quantum chemical interpretation and prediction of spectral characteristics of heavy transition metal complexes”, 2011-2014, MEYS; “Metalloprotein photoactivation: Structural dynamics and electron transfer, 2013-2015, MEYS; and „Structure and dynamics of excited and redox states of photocatalytic complexes”, 2014-2016, MEYS).

C. Detailed description of the results achieved in 2010-2014

The research in the department was conducted in **4 main directions**:

- 1) Biomimetic properties of ITIES
- 2) Use of the SPLB membranes in mimicking the membrane ion transport
- 3) Biosensors based on the solid amalgam electrodes
- 4) Photo-induced processes in biomimetic metal complex systems

In those 5 years the department published 141 papers in the impacted journals. This report highlights the most important results achieved in these 4 research directions.

Research Direction 1: Biomimetic properties of ITIES

1) Catalysis of the oxygen reduction in one- and two-phase liquid systems

Biotransformations of molecular oxygen are mediated by enzymes that contain metallic active sites, e.g., bimetallic heme/Cu active site in cytochrome c oxidase. The synthetic analogues of metalloporphyrins have been commonly used to activate the molecular oxygen for the O₂ reduction in solutions, or at solid electrodes. The catalysis of the O₂ reduction by a metal-free-porphyrin had not been reported until our first paper providing evidence of catalysis of the O₂ reduction by tetraphenylporphyrin free base (H₂TPP) at ITIES was published in 2009 (**Trojánek et al, Electrochem. Commun. 2009**), shortly before the evaluated period started. This voltammetric study demonstrated that rather slow interfacial reduction of O₂ in water with an electron donor (decamethylferrocene) in 1,2-dichloroethane (DCE) proceeds remarkably faster when tetraphenylporphyrin monoacid (H₃TPP⁺) and diacid (H₄TPP²⁺) are formed in DCE by the successive transfer of two protons from the acidified aqueous phase. Our activity in 2010-2014 led to 10 publications in the impacted journals, of which the most important ones are referred to below, and to one contribution to a monograph (**Samec et al, Handbook of Porphyrin Science 2014**).

a) Homogeneous catalysis of the O₂ reduction by metal-free and metallo-porphyrins

The homogeneous catalysis of the O₂ reduction in the DCE solutions was investigated at the defined concentrations of the acid and water in DCE using absorption spectroscopy, stopped-flow kinetic measurements and DFT calculations. Results of these investigations allowed us to propose the detailed mechanism of the catalytic O₂ reduction in one- and two-phase liquid systems. An important aspect of the experimental approach was the proper choice and synthesis of the strong acid, i.e., tetrakis(pentafluorophenyl)boric acid (HTB), as a source of proton.

We have shown that the catalytic effect of H₂TPP on the reduction of the molecular oxygen by ferrocene can be finely tuned by the acid-to-catalyst molar ratio (Trojánek et al, Chem. Commun. 2011). All experiments and DFT calculations were performed by the members of the department of the biomimetic electrochemistry, the role of the acid was consulted with prof. H. Girault from EPFL; the catalyst was synthesized by Dr. J.-M. Barbe from University of Burgundy. The catalytic mechanism was proposed, which involves the binding of O₂ to the tetraphenylporphyrin diacid (H₄TPP²⁺), in competition with the acid anion TB⁻. This competition appears to be responsible for the fine tuning of the catalytic effect. Mechanistic considerations were supported by the DFT calculations.

Kinetic measurements, which were performed at various water concentrations in DCE, provided convincing evidence for the inhibition of the catalyst by water (**Trojánek et al, Chem. Commun. 2012**). The DFT calculations indicated that the inhibitory effect might be linked to the free energy of extraction of the ligand L = O₂, water, and TB⁻ from the complex {(H₄TPP²⁺)(TB⁻)L}, which allows estimating the equilibrium constant for the competitive inhibition reaction following the sequence TB⁻ ≈ H₂O > (H₂O)₄ >> H₂O₂. In contrast to the inhibitory effects of water and TB⁻, the auto-inhibition of the catalyst by H₂O₂ and HO₂[•] radical is probably weak. All experiments and the DFT calculations in this study were carried out by the members of the department of biomimetic electrochemistry.

A mechanistic model was presented (**Trojánek et al, Electrochim. Acta 2013**), which made it possible to simulate numerically the effect of the acid-to-catalyst molar ratio, as well as the effects of the TB⁻ anion or water concentrations. Model calculations were based on the assumption that the electron

transfer between the complex $\{(H_4TPP^{2+})\cdot(TB^-)\cdot O_2\}$ and ferrocene is the rate determining step (r.d.s.). The model calculations were performed using the reported acid dissociation constants for mono- and diprotonated H_2TPP forms, and the equilibrium constants of the extraction of the ligands $L = O_2$, water, or TB^- from the porphyrin complex $\{(H_4TPP^{2+})\cdot(TB^-)\cdot L\}$ calculated by the DFT methods.

The role of the metal in metalloporphyrines was addressed in the study of the inhibitory effect of water on the O_2 reduction with ferrocene in DCE catalyzed by cobalt(II) tetraphenylporphyrin (Trojánek et al, *J. Phys. Chem. A* 2014). Kinetic data point to the competitive coordination of water to the metal center leading to a strong inhibition of the catalytic reaction. In agreement with this finding, DFT calculations indicated that water is bound to the metal center much more strongly than triplet O_2 . A similar effect was demonstrated in the O_2 reduction catalyzed by metal-free porphyrin (H_2TPP), though in this case the catalytic rate was found to be lower by 2 orders of magnitude under comparable experimental conditions. All experiments and the DFT calculations in this study were carried out by the members of the department of biomimetic electrochemistry.

b) A comparison of the catalytic effects in one- and two-phase liquid systems

Investigations of the homogeneous catalysis of the O_2 reduction could be relevant to analogous studies at the polarized ITIES. Therefore, the catalytic effect of tetraphenylporphyrin free base (H_2TPP) was examined at both the polarized water/DCE interface and in the homogeneous DCE solution by using the voltammetric and stopped-flow technique, respectively (Trojánek et al, *Electrochim. Acta* 2012). The study involved also the analysis of the thermodynamic driving force effect, which was examined using a series of electron donors represented by the methyl (Me)-substituted ferrocenes Me_nFc ($n = 0, 2, 4, 6, 8, 10$) enabling to vary the driving force over the range of ca. 0.5 V. Kinetic analysis suggested that the reduction of the activated O_2 with Me_nFc is the rate-determining step in both electrochemical and chemical catalytic cycles, with the Tafel (or Brønsted) plots that are characteristic for reactions with the symmetric activation barrier. Observed differences between the catalytic rates of the homogeneous and heterogeneous oxygen reduction were ascribed to much higher water and TB^- anion concentrations in DCE in the latter case being responsible for the inhibition of the process (see C.1a above).

c) Effects of substitution on the porphyrin ring

Experimental kinetic and DFT studies of the effect of the substitution on the porphyrin ring were aimed to boost the catalytic effect through a modification of the basicity of the tetrapyrrole ring, or through introducing an amphiphilic moiety that increases the affinity of the catalyst to the ITIES. In the former case, a perfluorinated free base porphyrin 5-(p-amino-phenyl)-10,15,20-tris(pentafluorophenyl)porphyrin (H_2FAP) was synthesized and used as a metal-free catalyst of the O_2 reduction with ferrocene (Hatay et al, *J. Am. Chem. Soc.* 2010). The catalyst combines the lipophilicity suitable to be investigated by voltammetry at the ITIES, and fluorination of three phenyl rings to ensure a strong electron-withdrawing effect to provide a weak basicity of the tetrapyrrole ring to favor oxygen reduction. Indeed, in the presence of H_2FAP in DCE, a significance enhancement of the reduction at the polarized water/DCE interface was observed, while such effect was not seen in the presence of H_2TPP . The publication was co-authored by two members of the department of biomimetic electrochemistry, who contributed by the preliminary DFT calculations (S. Zálíš), discussion of the results (Z. Samec), and preparation of the manuscript.

In the latter case, a metalloporphyrin (2,8,13,17-tetraethyl-3,7,12,18-tetramethyl-5-p-amino-phenylporphyrin cobalt (II) (CoAP) was synthesized and used as a catalyst in a similar way as H_2FAP (B. Su et al *J. Am. Chem. Soc.* 2010). CoAP exhibited a strong potential dependent adsorption at the polarized water/DCE interface, and a catalytic activity over other Co porphyrins that do not adsorb at ITIES. The publication was also co-authored by two members of the department of biomimetic electrochemistry, who contributed by the interfacial tension measurements of the adsorption of CoAP at ITIES (A. Trojánek), discussion of the results, and preparation of the manuscript (Z. Samec).

2) Charge transfer processes at the water/RTIL interface

Hydrophobic ionic room-temperature liquids (RTILs) have been proposed as suitable substitutes for organic electrolyte solutions to form an alternative ITIES. Around 40 RTILs were synthesized in the department of biomimetic electrochemistry, which were used as thin supported liquid membranes in electrochemical studies of the membrane electron and ion transfer.

The preliminary study (Langmaier et al, *Electrochem. Commun.* 2010) reported the synthesis of a new highly hydrophobic redox-active RTIL, and evidence of the interfacial electron transfer between RTIL and an aqueous redox couple. The approach was extended to include a series of the aqueous

redox couples to clarify the thermodynamic aspects of this new type of charge transfer processes at the water/RTIL interface (**Langmaier and Samec, *Electrochim. Acta* 2011**).

Another RTIL (tridodecylmethylammonium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate was shown to be useful for development of a sensor for anticoagulant heparin polyion (**Langmaier et al, *Electrochem. Commun.* 2012**). The study is an example of the application of the mixed-potential concept, which allowed us to explain the curious tuning effect of the trace concentrations of tetraalkylammonium ions on the interfacial polyion transfer. Voltammetric and capillary electrophoresis (CE) measurements were used to demonstrate the remarkable unity-slope correlation between the Gibbs energies of ion transfer from water to RTIL and an organic solvent (**Langmaier et al, *J. Electroanal. Chem.* 2014**). These two studies were carried out jointly with our project partners from 3rd Faculty of Medicine, Charles University in Prague, who contributed by CE measurements, while the contribution of the members of the department of biomimetic electrochemistry consisted in the synthesis of the RTILs, electrochemical measurements and their interpretation.

A combined DFT, voltammetry and dielectric relaxation spectroscopy (DRS) study of the ion transfer across the water/RTIL interface (**Langmaier et al, *Electrochim. Acta* 2013**) has led to an important conclusion that the correlation established between the Gibbs energies of ion transfer from water to RTIL has the origin in similar solvophobic contributions rather than in comparable polarity of the RTILs studied, as characterized by static dielectric constant inferred from DRS measurements. DFT calculations, voltammetric measurements and their interpretation, as well as the analysis of the DRS data preparation of the manuscript were performed by the members of the department of biomimetic electrochemistry; DRS experiments were conducted by our colleagues from the Institute of Physics.

3) Ion transfer kinetics at ITIES

In the last several decades, ion transfer kinetics at ITIES has been a controversial issue, e.g., the reported ion transfer rate constants for the tetraethylammonium (TEA⁺) ion transfer spread over a wide range of values ($10^{-3} \text{ cm s}^{-1}$ - 110 cm s^{-1}). Extremely high values, which were claimed to be the most reliable ones, were obtained using the steady-state voltammetry (SSV) at the micro- and nano-ITIES supported on the orifice of a glass capillary with diameter of 1-150 nm. However, our recent polarization measurements using thick-wall microcapillaries have indicated that the role of the glass-wall based electrokinetic effects should not be ignored (**Silver et al, *Electrochim. Acta* 2013**). Consequently, we re-measured the TEA⁺ ion transfer at the microITIES using both the electrochemical impedance spectroscopy (EIS) at the equilibrium cell potential and SSV (**Silver et al, *J. Electroanal. Chem.* 2014**). Both methods yielded about the same value of the ion transfer rate constant (ca. 0.2 cm s^{-1}), which is much lower than the upper limit above. Important aspect of the experimental approach was the development of facile methodology to produce novel, robust and reusable thick-wall glass capillaries of nano- and micro-scale dimension.

We have also re-measured the TEA⁺ ion transfer at the macroscopic ITIES (diameter of 5 mm) using the equilibrium EIS to analyze both the effects of the parasitic couplings between the electrodes and ion transfer kinetics (**Trojánek et al, *Electrochim. Acta* 2014**). The analysis provided the ion transfer rate constant of about 0.1 cm s^{-1} , which corroborated our kinetic studies at microITIES. The four-terminal electric equivalent circuit including the impedances of the organic reference and counter electrodes, as well as the impedances of the parasitic coupling between the counter and reference electrodes, allowed simulating the experimental impedance behaviour over the whole range of frequencies of the applied ac voltage (1 Hz-100 kHz),

Research Direction 2: Use of the SPLB membranes in mimicking the membrane ion transport

Our activities in this research direction were focused on mimicking the transfer of heavy metal ions across biomembranes using the supported phospholipid bilayers (SPLB) as a model. Some of the heavy metal ions, e.g., Zn²⁺, Cu²⁺ and Fe²⁺, are components of essential micronutrients, but may become toxic when present in excess. Others, like Cd²⁺ and Pb²⁺, have no apparent natural role in organisms and are toxic almost at all concentrations. They represent prevalent environmental pollutants in industrial countries. Apart from the acute exposure in the working environment, their uptake by plants seems to be main entry pathway into human, as well as into animal food chain.

We developed three types of the SPLB membranes, namely the phospholipid bilayers supported on (a) a microporous polycarbonate membrane filters, (b) the gel-type electrodes, and (c) ITIES. The model membranes eventually incorporated an ionophore facilitating the interfacial ion transfer. Ion transfer processes were studied using electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Electro spray ionization mass spectrometry (EIS-MS) provided an insight into structure of metal ion complexes.

In the introductory study (**Navrátil et al, Electroanalysis 2010**), the SPLB was formed by self-assembling of phospholipids in the holes of a microporous polycarbonate membrane filter. The solution of phospholipids used for the preparation of the SPLB contained valinomycin or calcimycin as an ionophore. EIS allowed monitoring the formation of the phospholipid bilayer, as well as the enhanced transport of the Cd^{2+} ions in the presence of the Ca^{2+} ions. The effect of the applied DC voltage was also examined, and reversible changes were observed. This study was extended to examine the effect of low-molecular weight organic acids (malic acid, oxalic acid or citric acid) on the membrane transport of the Cd^{2+} and Cu^{2+} ions (**Parisova et al. Int. J. Electrochem. Soc. 2013**). The transport is also influenced by the presence/absence of ionophore calcimycin, and by pH of the aqueous phase. The stoichiometry of the oxalate complexes of Cu^{2+} was elucidated by ESI-MS. In a related study (**Navrátil et al, Int. J. Electrochem. Soc. 2011**), the formation of the phospholipid bilayer on the hydrophilic surface of the gel-type (agar or agarose) electrode was monitored by EIS and CV, and the transport of Cd^{2+} and Pb^{2+} across the SPLBs was examined.

The addition of Yb^{3+} to the aqueous phase was shown to lead to a stabilization of the lecithin layers at ITIES (**Jaklová-Dytrtová et al, Collect. Czech. Chem. Commun. 2011**). The effect was evaluated as a function of time and the potential applied across ITIES. The ability of the phospholipid layer to inhibit the transfer of bulky ions was demonstrated by CV measurements of the K^{+} ion transfer facilitated by dibenzo-18-crown-6 as an ionophore. The stoichiometry of the Yb^{3+} /anion/lecithin complexes was assessed by ESI-MS.

We have shown that Cu^{2+} forms complexes with dipalmitoylphosphatidyl choline (lecithin), which are detectable using ESI-MS (**Jaklová-Dytrtová et al, Monatsh Chem, 2014**). Lecithin (L) as a relatively bulky ligand prevents Cu^{2+} reduction during the electrospray process. The detected complexes include dication $[\text{Cu}(\text{L})_n]^{2+}$ and monocations $[\text{CuCl}(\text{L})_k]^+$, which are stable enough to utilize Cu^{2+} for the stabilization of the phospholipid bilayer. The impermeability of an artificial phospholipid membrane for oxalic acid and its complexes with copper ions at pH 5-6 was confirmed voltammetrically.

Three of five studies referred to above where co-authored by our colleagues from the Institute of Organic Chemistry and Biochemistry (J. Jaklová-Dytrtová, V. Šádek) and Czech University of Life Sciences Prague (M. Jaki). They were responsible for the ESI-MS measurements and their evaluation (J. Jaklová-Dytrtová, M. Jaki), and for the DFT calculations (V. Šádek)

Research Direction 3: Biosensors based on solid amalgam electrodes (SAEs)

1) SAEs in classical and flow cells

Mercury and solid amalgam electrodes (SAEs) offer unique possibilities for performing electrochemical reductions at high negative potentials. Introduction of SAEs in 2000 (**Novotný and Yosypchuk, Chem. Listy 2000**) has made it possible to replace the metallic mercury. The advantage of SAEs over mercury electrodes is their mechanical stability, and the possibility of preparing electrodes of required size and shape. Beside conventional pen-type SAEs, mini-electrodes were constructed and incorporated in a chromatographic capillary, or a joint. Introduction of tubular AgSA-detector substantially simplified the design of flow electrochemical cells and increased the reliability and reproducibility of the measured signals (**Yosypchuk et al, Electroanalysis 2012**).

Polishing of the surfaces of SAEs is a convenient pre-treatment facilitating chemical modification of the surfaces with different modifiers. One possible way of the chemical modification of SAEs is their covering with the liquid mercury film (MF). A simple, reliable and environmentally friendly procedure for preparation of stable and exactly defined MFs at the silver solid amalgam support was developed (**Yosypchuk et al, Electroanalysis 2010**). Such mercury films were used to obtain ideally smooth, stable, and easily renewable surface suitable for preparation of monolayer or multilayer films of biologically important substances, e.g., DNA.

The reference electrodes, where the metallic mercury was replaced with silver paste amalgam, were designed, prepared and tested (**Yosypchuk et al, Electroanalysis 2011**). Calomel, mercury-mercurous sulfate and mercury-mercuric oxide electrodes based on silver paste amalgam have proved to be very stable in both long- and short-term measurements. The calomel electrode with paste amalgam is most resistant to polarization, but all three tested electrodes are suitable for voltammetric measurements. Another benefit of the paste amalgam is that it is not liquid and, unlike metallic mercury, it cannot be spilled.

All experiments in these three studies were carried out by the members of the department of biomimetic electrochemistry. Co-authors J. Barek and M. Fojta participated in discussions of the measurement results.

2) Solid amalgams as a support for the thiol monolayers

Formation and properties of the thiol monolayers at the silver, copper, bismuth and cadmium SAEs covered with the mercury meniscus or the mercury film were investigated (**Yosypchuk et al, J. Electroanal. Chem. 2011**). The monolayer was deposited from a thiol solution at the optimum accumulation potential. By choosing an appropriate amalgam forming metal, a thiol monolayer can be prepared, which is stable in the given potential range. In the related study (**Josypčuk et al, J. Electroanal. Chem. 2013**), the parameters of the adsorption isotherm (surface coverage, adsorption energy) of 11-mercaptoundecanoic acid (MUA) at various amalgam electrodes were determined. A good reproducibility of the preparation of the thiol monolayer, and its subsequent desorption, indicated that this approach is suitable for the development of biosensors. The realization of the biosensor for the determination of biotin based on the strong and selective interactions between biotin and (strept)avidin covalently bonded to the MUA monolayer on the silver SAE has been demonstrated. All experiments in these two studies were carried out by the members of the department of biomimetic electrochemistry. Co-author M. Fojta participated in discussions of the measurement results.

3) Biosensors based on the solid amalgams in flow systems

Two important results are worth mentioning. First, the flow amperometric enzymatic biosensor for the determination of glucose was constructed (**Josypčuk et al, Anal. Chim. Acta. 2013**). Biosensor consists of a flow reactor based on the MUA modified porous silver solid amalgam and a flow tubular detector based on solid silver amalgam electrode. Enzyme glucose oxidase was covalently immobilized at the MUA layer. Biosensor was tested for the determination of glucose in the samples of honey. Second, an enzyme reactor based on the silver amalgam powder was developed as the main part of the amperometric biosensors in flow systems (**Josypčuk et al, Electroanalysis 2014**). Biosensors were tested with the following enzymes: ascorbate oxidase, glucose oxidase, catalase, tyrosinase and laccase. Biosensor with the ascorbate oxidase reactor was used for the determination of the ascorbic acid in the vitamin C tablets. All experiments in these two studies were carried out by the members of the department of biomimetic electrochemistry. Co-author J. Barek participated in discussions of the measurement results.

Research Direction 4: Photo-induced processes in biomimetic metal complex systems

1) Electron transfer acceleration through Re(I)-modified Azurins

Electron transfer (ET) processes play important roles in bioenergetics, namely natural and artificial photosynthesis and respiration. In biological systems, ET often occurs surprisingly fast over long distances and is strongly influenced by structural modifications. Using *Pseudomonas aeruginosa* azurin as a platform, we have shown that the presence of a tryptophan residue between the redox centers dramatically accelerates ET. By comparing photophysics of small-molecule Re-tryptophan complexes and tryptophan-containing Re-labelled azurins, we have revealed the acceleration mechanism and have contributed to formulating design rules for efficient photoactivated redox proteins. We have provided evidence that tryptophan acceleration of long-distance (2 nm) $\text{Cu}^{\text{I}} \rightarrow \text{Re}^{\text{II}}$ ET is due to splitting the ET pathway into two steps, as well as a strong π - π interaction between the the Re chromophore and tryptophan indole. The following studies should be highlighted:

a) Photoinduced intramolecular oxidation of tryptophan in $[\text{Re}(\text{L-AA})(\text{CO})_3(\text{diimine})]^+$ (L = pyridine or imidazole, AA = tryptophan (trp), tyrosine (tyr), phenylalanine (phe)) was examined by a combined experimental and theoretical study (**Blanco-Rodriguez et al, Inorg. Chem. 2011**). Near-UV optical excitation populates a $^3\text{MLCT}$ excited state $^*[\text{Re}^{\text{II}}(\text{L-AA})(\text{CO})_3(\text{N,N}^-)]^+$ that decays to the ground state on a hundreds-of-nanosecond timescale for AA = tyr, phe, whereas its lifetime shortens to 10-30 ns in the case of trp due to a $\text{Trp}(\text{indole}) \rightarrow \text{Re}^{\text{II}}$ ET producing a charge-separated (CS) state $[\text{Re}^{\text{I}}(\text{L-Trp}^+)(\text{CO})_3(\text{N,N}^-)]^+$ that was characterized by time-resolved spectroscopy. It was found that $\text{Re}^{\text{I}}(\text{CO})_3(4,7\text{-dimethyl-1,10-phenanthroline})(\text{histidine-124})(\text{tryptophan-122})\text{Azurin}$, denoted $\text{Re}^{\text{I}}(\text{dmp})(\text{W122})$, undergoes a series of fast photoinduced ET steps, whereby the Re chromophore is reduced and Trp oxidized (**Blanco-Rodriguez et al., Chem. Eur. J. 2011**). Time-resolved IR spectra together with excited-state DFT/TDDFT calculations revealed the character, energetics and dynamics of the relevant electronic and redox states, and a cascade of photoinduced ET and relaxation steps. Namely, we found evidence for a partial electron delocalization between $\text{Re}^{\text{I}}(\text{CO})_3(\text{dmp})$ and indole in the reactive $^3\text{MLCT}$ state before the ET proper. These results demonstrate a consequence of the protein environment that places the redox active units into the right orientation and distance. Investigations of a related azurin mutant $\text{Re}^{\text{I}}(\text{dmp})(\text{W126})$, indicated that the ultrafast electron transfer $\text{Trp} \rightarrow \text{Re}^{\text{II}}$ occurs intermolecularly, across a hydrophobic protein-protein interface. (**Takematsu et al, J. Am. Chem Soc. 2013**) Investigated azurins were synthesized and structurally characterized at California Institute of

Technology. Members of the department of biomimetic electrochemistry performed and interpreted TRIR experiments and carried out DFT/TDDFT calculations revealing the electron delocalization, while Dr. Sýkora from the department of biophysical chemistry contributed by measuring static and time resolved luminescence.

b) The influence of relativistic effects on photophysics of $[\text{Re}(\text{imidazole})(\text{CO})_3(\text{phen})]^+$, a model photosensitizer of biomolecular ET, was examined by spin-orbit (SO) calculations at TDDFT and CAS/CASPT2 levels at ground- and excited- state geometries (**Baková et al, Coord. Chem. Rev. 2011**). The relativistic excited-state model accounts well for electronic absorption and emission spectra of Re^I carbonyl diimines, provides a comprehensive view of the $[\text{Re}(\text{imH})(\text{CO})_3(\text{phen})]^+$ photophysical behavior and accounts well for the principal experimental observations on this system and analogous Re^I complexes. All calculations and relevant spectroscopic experiments were performed by the members of the department of biomimetic electrochemistry. C. Daniel (University of Strasbourg) contributed by discussing SO calculations, part of time resolved measurements to characterize the excited states were done by M. Chergui (Ecole Polytechnique Fédérale de Lausanne, EPFL). Advanced TDDFT and SO calculations on related halide-containing photosensitizers interpreted UV-Vis spectra of their excited- and reduced states as well as state-of-the-art picosecond time-resolved X-ray absorption spectra obtained jointly with M. Chergui, EPFL. The latter study amounts to the first direct observation of delocalized CT excitation from a metal-halide moiety to a diamine ligand. (**Záliš et al, Inorg. Chim. Acta 2011, Záliš et al, Inorg. Chem. 2013, El Nahhas et al, J. Phys. Chem. A. 2013**)

c) Photoreactivity of Re-based sensitizers which relies on ultrafast intersystem crossing (ISC) from optically excited $^1\text{MLCT}$ states to the corresponding triplets was determined jointly with M. Chergui (EPFL) (**El Nahhas et al, Inorg. Chem. 2011**). Recently, we have found that the ISC rate slows down when the lowest excited state changes from MLCT to intraligand (IL) by a judicious choice of the ligand. This is the case of $[\text{ReCl}(\text{CO})_3(3\text{-R-1-(2-pyridyl)-imidazo}[1,5\text{-}\alpha\text{]pyridine)]$ complexes ($\text{R} = \text{CH}_3, \text{Ph}, \text{PhBu}^t, \text{PhCF}_3, \text{PhNO}_2, \text{PhNMe}_2$). TRIR together with quantum chemical calculations identified the two spectroscopically observable singlet and triplet states localized predominantly at the organic ligand and determined the ISC rates (**Blanco-Rodríguez et al, J. Am. Chem. Soc. 2014**). Members of the Dept. of Biomimetic Electrochemistry performed and interpreted time resolved spectroscopic experiments and DFT/TDDFT calculations, and proposed the mechanism. Luminescence experiments were performed by J. Sýkora (department of biophysical chemistry). Complexes were synthesized at the University of Torino.

2) Quantum chemical interpretation of redox properties of transition metal complexes.

We have shown that solvent correction is needed for correct DFT and TDDFT description of IR and UV-visible spectroelectrochemical data of organometallic species (**Záliš et al, Coord. Chem. Rev. 2010; Grupp et al, J. Organomet. Chem. 2014**). A computational methodology including solvent and counterion effects was successfully used to calculate redox potentials of the Fischer-type chromium aminocarbene complexes (**Kvapilová et al, Organometallics 2014**). All calculations were performed by members of the department of biomimetic electrochemistry. Electrochemical and spectroelectrochemical measurements were done by W. Kaim (University of Stuttgart), R. Winter (University of Konstanz); redox potentials of the carbene complexes were measured in the Institute of Chemical Technology, Prague.

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Electrochemical Materials
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A. Personal Structure at 12/2014

In 12/2014 the Department of electrochemical materials consisted of one senior scientist, Prof. Kavan, 1.0 of full time equivalent (FTE), 6 scientists (Dr. Frank, Dr. Janda, Dr. Jirkovsky, Dr. Mocek, Dr. Weber and Dr. Zupalova; 1.0, 1.0, 1.0, 0.8, 0.05 and 1.0 of FTE), 3 associate scientists (Dr. Del Corro, Dr. Krysova and Dr. Vlckova; 0.65, 1.0 and 0.8 FTE), two postdoctoral fellows (Dr. Hykrdova and Dr. Tarabkova, 1.0 and 0.7 FTE), 3 graduate student (MSc. Bibova, MSc. Klusackova and MSc. Zlamalova; 1.0, 0.55 and 0.1 FTE), 6 research assistants (MSc. Bousa, MSc. Elias, MSc. Laskova, MSc. Mansfeldova, MSc. Vik and Dr. Svata; 1.0, 1.0, 1.0, 1.0, 0.3 and 0.15 FTE) and one master student (Bc. Rahova). Dr. Weber and Dr. Svata are advisors. In 2013, one staff scientist (Dr. M. Kalbac) left the Department together with his student, MSc. Kominkova. The reason was the formation of new Department of low-dimensional systems which is now directed by Dr. Kalbac. The current key scientific members of our Department are: Prof. Kavan, Dr. Frank, Dr. Janda, Dr. Jirkovsky and Dr. Zupalova. These five colleagues take over the individual responsibility for specific research tasks, which are, to a great deal, defined by the corresponding grant projects. Furthermore, all these key-scientists are responsible for supervising of six PhD students: MSc. Bibova, MSc. Bousa, MSc. Klusackova, MSc. Laskova, MSc. Mansfeldova, MSc. Vik and MSc. Zlamalova. The contemporary personal structure is well stabilized, and is sufficient to guarantee the solution of all scientific tasks of the Department at high level. The age and gender composition are also very favorable at the moment: the Department has 12 females (55%) and 10 males (45%) with the average age of 43. We have one foreign co-worker (Dr. del Corro).

B. Research Activities at a Glance

The main activities of the Department of electrochemical materials can be summarised as: synthesis, characterization and applications of advanced electrode materials, with special focus to nanomaterials based on elemental carbon [Kavan et al. **Top.Curr.Chem.** **2014**] and oxide semiconductors, such as titanium dioxide [Kavan et al. **Chem.Rec.** **2012**]. The available synthetic infrastructure consists of several high-vacuum lines, autoclaves, preparative centrifuge, spin-coating system, vibration-free dip coating apparatus, glove boxes etc. The prepared materials are characterized by a palette of standard experimental methods (XRD, SEM, AFM/STM, UV-Vis spectroscopy, HPLC, TOC-analyser, IR/Raman, thermal analysis with DSC) and - in collaboration - by various other methods (XPS, TEM, EPR, adsorption isotherms, etc.) as well as by theoretical modelling. The dominating experimental approach is based on various electrochemical methods. They include, besides the standard potentiostatic and galvanostatic techniques, also electrochemical impedance spectroscopy, EQCM, UV-Vis photoelectrochemistry, in-situ electrochemical AFM, solar simulator etc. Considerable expertise exists in spectroelectrochemistry, particularly in-situ optical and Raman spectroelectrochemistry, where several pioneering studies were presented in the past [Frank et al. **Nanoscale** **2014**, Frank et al. **Acc.Chem.Res.** **2015**, Kavan et al. **Chemphyschem** **2011**].

The scientific activities of the Department are balanced between fundamental studies on nanocarbons, oxide semiconductors, and reactions mechanisms in photocatalysis on one side, and on more applied research on the other side. The applications are focused to outputs in solar cells, Li-ion

batteries and remediation of environment pollution. These studies are supported by industrial contracts, both direct and indirect (via grant projects) with several partners in the Czech Republic and in Europe. In summary, the scientific works were financed - in the evaluated period - by 16 large projects, viz.: 5 European (FP7) grants, 2 grants from Technological Agency of the CR, 5 grants from Czech Science Foundation, 2 grants from ASCR and 2 Research centre-grants from Czech Ministry of Education; in addition to various smaller projects. The currently running large projects cover all areas of our research as follows: (1) perovskite-graphene solar cells and modules; (2) materials engineering towards innovative Graetzel solar cells; (3) electron injection into Ti(IV) oxide materials: applications in Li-ion batteries and solar cells; (4) strain engineering of electronic structure in graphene; (5) nanobubbles on electrode surfaces: properties, interactions and surface restructuring; (6) study of interfacial charge transfer process on boron and phosphorus doped diamond in contact with electrolyte solution; (7) fourth generation photocatalysts: nano-engineered composites for water decontamination in low-cost paintable photoreactors; (8) research for the production of multifunctional photoactive nanocomposites for use in the construction industry and for paints; (9) the use of photoactive nanosurfaces to solve current problems of air and water cleaning,

The scientific outputs are detailed below. Specifically, in the years 2010-2014 the department produced valuable results in the field of innovative cathodes for dye sensitized solar cells, which avoided problematic (expensive) materials like platinum and transparent conductive oxides without compromising on the electrocatalytic activity and stability of the cathode. Another novel and promising approach was based on the application of isotope labeling of electrode materials (graphene, TiO₂, Li_xTiO₂) with multifaceted inputs to refined assignment in Raman spectroelectrochemistry, phase analysis during Li-insertion [Kavan et al. **J.Solid State Electrochem. 2014**] and detailed kinetic and mechanistic studies in titania catalysis/photocatalysis. The latter theme was developed jointly with the Department of spectroscopy (S. Civiš) who contributed by their expertise in HR-FTIR spectroscopy of gas phase surrounding the (photo)catalyst. Valuable studies were presented in the area of graphene, particularly those addressing mechanical and Raman spectroelectrochemical properties of graphene. The research on nanodiamond, which has been developed only since 2013, produced already interesting data about possible spectral sensitization of B-doped diamond to visible light. These initial studies provide viable perspective of future development of photocathode of dye-sensitized solar cell, i.e. a mirror device to the traditional solar cell with titania photoanode, which would achieve similar or better parameters compared to the known photocathode materials, such as p-NiO.

C. Detailed description of our results in 2010-2014:

The activities of the department might be divided in **4 main research directions** which are, however, synergically interconnected by many links at various levels:

- 1) "Electrode materials for dye-sensitized and perovskite solar cells"
- 2) "Electrode materials for advanced Li-ion batteries"
- 3) "Nanocarbons: nanotubes, graphene, nanodiamond"
- 4) "Photocatalysis for environment protection"

Within those 5 years, the Department published 104 papers in impacted journals (counting solely papers which appeared in printed versions). Various high-profile journals like *Acc.Chem.Res.* (IF=24), *Energy Environ. Sci* (IF=15), *Nano Letters* (IF=13), *ACS-Nano* (IF=12) and *Nature Comm.* (IF=11) are among the target media. **This report focuses on the highlights** connected with defined projects:

Research Direction 1: Electrode materials for dye-sensitized and perovskite solar cells.

The research on solar cells was carried out in broad international collaboration, and was recently supported by three European grant projects, in which L. Kavan acted as the Czech-team representative

and sometimes as a work-package leader: *FP7-Large*: ORION (2009-13), *FP7-NMP*: SANS (2011-13), *FP7-Energy*: MOLESOL (2010-13). In 2014, the project ORION has been evaluated by the European Commission as the **Success Story** entitled „Nanomaterials for better batteries and solar cells“. Furthermore, B. Laskova was awarded in 2013 by a Swiss SciEx-NMS project of student exchange to collaborate with EPF-Lausanne (prof. Graetzel). In 2014, L. Kavan was awarded by a *FP7* project PERHENE (will expire in 2016), which is a part of the largest European activity in graphene (*FLAGSHIP* – the L. Kavan’s team is, actually, the only Czech participant in Flagship). The latter project is specifically focused to graphene application in perovskite cells. Czech Science Foundation finances furthermore one active grant project on innovative Graetzel solar cells (L. Kavan, 2013-2017) and one past projects was financed aiming at hierarchical metal oxide architecture for solar cells (M. Zikalova, 2012-14).

a) Cathode in dye-sensitized solar cell

A principal breakthrough in the field was the development of the first optically transparent cathode based on graphene nanoplatelets for I-mediated DSSCs [Kavan et al. **ACS Nano** 2011]. This paper accumulated high number of citations (220 citations by March 2015, i.e. 55 cits/yr) The initial work was subsequently upgraded towards even more promising application of graphene in Co-mediated DSSCs, while certain materials were even outperforming the electrocatalytic activity of Pt [Kavan et al. **ACS Nano** 2011, Kavan et al. **Nano Lett.** 2011] (240 citations). From practical points of view (stability, activity, ease of fabrication) the best material was identified as reduced graphene oxide [Kavan et al. **ACS Appl.Mater.Interfaces** 2012] (39 citations). The subject of graphene cathodes for DSSC was reviewed in [Ahmad et al. **Energy Environ.Sci.** 2013, Kavan et al. **Electrochim.Acta** 2014] (49 citations). A general review of nanocarbons for solar cells was presented too [Kavan et al. **Top.Curr.Chem.** 2014]. Recently, novel pathways towards alternative cathode materials were explored by replacing the traditional materials for cathodes by metal (W/PEN) grids [Kavan et al. **ACS Appl.Mater.Interfaces** 2014]. All electrodes fabrication, electrochemical experiments, data analysis and the interpretation, as well the full writing of the relevant publications (except for review articles) was done by the Department of Electrochemical Materials. External co-authors contributed by solar tests, discussions and critical reading of the manuscripts.

b) Photoanode in dye-sensitized solar cell

Systematic studies towards optimization of nanocrystalline titania photoanode highlighted the organized mesoporous TiO₂ films stabilized by phosphorus [Zikalova et al. **J.Electrochem.Soc.** 2010] and electrospun nanofibers [Krysova et al. **Catal.Today** 2014]. Among principal achievements of the period 2010-14 belongs an improvement of solar conversion efficiency of mesoporous TiO₂ photoanode in DSSC by incorporation of nanofibrous TiO₂ as a bottom layer directly on a conducting glass support. A parallel investigation of electrospun TiO₂ revealed its facile and reversible conversion into titanium nitride/oxyntiride fibers [Zikalova et al. **Chem.Mater.** 2010] (39 citations). Our experimental [Laskova et al. **J.Solid State Electrochem.** 2012] (24 citations) and theoretical [De Angelis et al. **J.Phys.Chem.C** 2012] works of (001)-oriented anatase TiO₂ nanosheets revealed an interesting voltage enhancement in dye-sensitized solar cell as compared to the usual (101)-oriented nanoparticles. The anatase (001) face adsorbs a smaller amount of the used dye sensitizer (C101) per unit area than the (101) face which was tested as a reference. Details of electron kinetics in dye sensitized solar cells, employing anatase with (101) and (001) facets, were elucidated by electrochemical impedance and transient photovoltage spectroscopy [Laskova et al. **Electrochim.Acta** 2015]. This study shows that a larger number of electron traps in the anatase (001) nanosheets decreases the diffusion coefficient of electrons in this material due to multiple electron-trapping. On the other hand, it results in larger electron lifetime in the (001) nanosheets, which can contribute to their previously reported better photocatalytic activity. The works on titania electrochemistry were reviewed [Kavan et al. **Chem.Rec.** 2012] (53 citations). All synthetic works, electrodes fabrication, electrochemical experiments, data analysis and the interpretation, as well the writing of the relevant

parts of publications was done by the Department of Electrochemical Materials. External co-authors contributed by theoretical simulations, solar tests, XRD, XPS, TEM, time-resolved spectroscopy studies, transient photovoltage spectroscopy, as well as with discussions and critical reading of the manuscripts.

c) Electron-collection electrode in perovskite solar cell

The subject of perovskite solar cell is young, but rapidly developing. We have concentrated our efforts to the investigation of titania blocking layers, which are useful both for perovskite as well as classical solid-state dye-sensitized solar cells. To this purpose, we developed a novel sol-gel synthetic protocol to grow these buffer layers in a simple way [Prochazka et al. **J.Mater.Res.** **2013**, Kavan et al. **Chemphyschem** **2014**]. Furthermore, we developed facile electrochemical methods to test the quality of blocking [Kavan et al. **J.Phys.Chem.C** **2014**] (10 citations in 7 months). Our sol-gel-made compact buffer layers exhibited unique stability of their electrochemical n-doping which approached that of single crystal anatase [Zukalova et al. **J.Phys.Chem.C** **2014**]. Doping manifests itself by characteristic morphological differences of the surface. A complete structural, optical, morphological and electrochemical analysis proved excellent blocking function and single crystal-like properties during electrochemical doping, which is stable for at least weeks of electrode storage in air at room temperature. All synthetic works, electrodes fabrication, electrochemical experiments, data analysis and the interpretation, as well the writing of the relevant parts of publications was done by the Department of Electrochemical Materials. External co-authors contributed by special non-electrochemical measurements, as well as with discussions and critical reading of the manuscripts.

Research Direction 2: Electrode materials for advanced Li-ion batteries

The work on Li-ion batteries represented an integral part of the project FP7-Large: ORION (2009-13) mentioned above (European Commission **Success Story** „Nanomaterials for better batteries and solar cells“). Furthermore, the research was also supported by a grant from the Czech Ministry of Education through the COST Action CM1104, Reducible oxide chemistry (2012+) in which L. Kavan is acting as the Czech representative in the Management Committee. Significant financing for R&D on Li-ion batteries (specifically for high-power 3D batteries) comes also from industrial contracts with the company HE3DA.

a) Cathode materials

A systematic study of the composites of electrode active materials with multiwalled carbon nanotubes was carried out, while both cathode and anode materials were optimized. Considerable activation was achieved for phosphate olivine-based (LiMnPO_4 , LiFePO_4) cathodes [Kavan et al. **J.Power Sourc.** **2010**] (45 citations). A spontaneous activation of LiFePO_4 was found for reduced graphene oxide [Bousa et al. **Electroanalysis** **2014**] All electrodes fabrication, electrochemical experiments, data analysis and the interpretation, as well the writing of the publications was done by the Department of Electrochemical Materials. External co-authors contributed by modification of MWNT, as well as with discussions and critical reading of the manuscripts.

b) Anode materials

In the study of anode materials for Li-ion batteries, we have found that TiO_2 anatase with a large proportion of crystal facets (001) exhibited considerably improved lithium insertion electrochemistry [Bousa et al. **J.Electrochem.Soc.** **2010**]. Detailed study of lithium insertion into titanium dioxide (anatase) was made by using Raman spectroelectrochemistry with $^{16/18}\text{O}$ and $^6/7\text{Li}$ isotope labeling [Laskova et al. **Chem.Mater.** **2013**]. The distinction of capacitive and insertion Li-storage was compared in monoclinic $\text{TiO}_2(\text{B})$ and TiO_2 (anatase) [Laskova et al. **J.Power Sourc.** **2014**]. An electrochemical study

of charge storage mechanism in two TiO₂ polymorphs with similar band gap energy proved the enhancement of 30% in capacitive contributions (normalized to the total stored charges) in TiO₂ (B) compared to that in anatase, in spite of ca. three times smaller surface area of the former. The subject of isotope labeling in Li-ion insertion was reviewed [Kavan et al. **J.Solid State Electrochem.** 2014]. All synthetic works, electrodes fabrication, electrochemical experiments, data analysis and the interpretation, as well the writing of the publications was done by the Department of Electrochemical Materials. External co-authors contributed by DFT simulation of Raman spectra, by TEM measurements, as well as with discussions and critical reading of the manuscripts.

Research Direction 3: Nanocarbons: nanotubes, graphene, nanodiamond

Various forms of nanocarbons are studied in the department, particularly with recent accent on graphene. The research is carried out in broad international collaboration, including joint works with Nobel laureates, Geim and Novoselov. The works on nanocarbons have been financed by several grants from Czech Science Foundation, which support specific tasks, such as strain engineering in graphene (O. Frank, 2014-16), nanobubbles on electrode surfaces (P. Janda, 2012-16) and nanodiamond (L. Kavan, 2013-17). The latter grant was awarded jointly with Institute of Physics AVCR (V. Mortet, principal investigator). Past projects on nanocarbons were also financed by ASCR, they included a large project on biocompatible surfaces - BOKOM (L. Kavan, 2008-2012) and a project on supramolecular assemblies with carbon nanotubes (L. Kavan, 2008-12). Another large project was Research center for nanotechnologies and materials for nanoelectronics (L. Kavan 2005-2011) which was financed by Czech Ministry of Education.

a) Carbon nanotubes

In addition to the practically-oriented studies of carbon nanotubes in Li-ion batteries (see above) we have also carried out fundamental spectro/electrochemical works on carbon nanotubes, which were focused to the influence of doping on the Raman intensity of the D band [Kalbac et al. **Carbon** 2010] spectroelectrochemical charging of double-walled carbon nanotubes [Kalbac et al. **ACS Nano** 2010] and individual nanotubes [Kalbac et al. **Nano Lett.** 2010]. More complex (peapod-like) systems, viz. C₆₀ (fullerene) [Kalbac et al. **J.Phys.Chem.C** 2010] and sexithiophene [Kalbac et al. **Chemistry Eur.J.** 2010] embedded in single-walled carbon nanotubes followed similar research strategy. Spectroelectrochemistry of carbon nanotubes was reviewed in [Kavan et al. **Chemphyschem** 2011]. Electrodes fabrication, spectro/electrochemical experiments, data analysis and the interpretation as well the writing of the publications was done by the Department of Electrochemical Materials. Some work was carried out in collaboration with IFW Dresden. External co-authors contributed by ultracentrifugal sorting of nanotubes, as well as with discussions and critical reading of the manuscripts.

b) Graphene

In addition to the practically-oriented studies of graphene and graphene oxide in DSSC cathode and Li-ion batteries (see above) we have also carried out various fundamental studies on graphene, in which research was focused at spectroelectrochemical charging of single-layer graphene [Kalbac et al. **ACS Nano** 2010] (76 citations) and bilayer ¹²C/¹³C labeled graphene [Kalbac et al. **Nano Lett.** 2011] (36 citations). The subject of isotope labeling in graphene spectroelectrochemistry was reviewed in [Frank et al. **Nanoscale** 2014, Frank et al. **Acc.Chem.Res.** 2015]. Details of 2D band splitting in graphene were elucidated by theoretical/experimental Raman spectra [Frank et al. **ACS Nano** 2011] (73 citations) and by subsequent focused study of Bernal stacked bilayer graphene [Frank et al. **Nano Lett.** 2012]. The mechanical deformation of graphene has been monitored by Raman spectroscopy, which further lead to the design of an universal stress sensor for graphene and carbon fibers [Frank et al. **Nature Comm.**

2011]. The role of substrate and/or pressure transmitting medium has been studied under hydrostatic compression of graphene [Filintoglou et al. *Phys.Rev.B* **2013**], and the buckling of graphene embedded between polymer layers has been examined under uniaxial compression [Androulidakis et al. *Sci.Rep.* **2014**]. The defects found on basal plane highly ordered pyrolytic graphite after interaction with gaseous nanobubbles in aqueous media [Janda et al. *Nanotechnology* **2010**] became basis for further thorough exploration of nanobubble ternary interface behavior on other hydrophobic surfaces, which led to discovery of nanobubble-assisted nanopatterning and nanoporation [Tarabkova et al. *J.Phys.Cond.Mat.* **2013**, Tarabkova et al. *Langmuir* **2014**]. *Some work has been done in collaboration with external partners from ICE-HT Patras, Greece, University of Manchester and TU Berlin, however, the majority of experimental and analytical work has been done by members of the Department.*

c) Nanodiamond

In the area of boron-doped diamond electrodes a systematic study was presented aiming at electrochemistry and in situ Raman spectroelectrochemistry of low- and high-quality boron doped diamond [Vlckova-Zivcova et al. *Electrochim.Acta* **2013**]. A new field was explored in the area of spectral sensitization of B-doped diamonds towards visible light [Yeap et al. *RCS Adv.* **2014**]. We have succeeded in considerable simplification of the surface modification by sensitizing dyes by using a strategy of non-covalent modification of B-doped diamond via polymeric (PEI) linker [Krysova et al. *Phys.Chem.Chem.Phys.* **2015**]. *For these works, all diamond synthesis was carried out by external collaborators, either in Inst. of Physics ASCR or in Uni-Hasselt. Surface modification was made in Hasselt and IOCHB, ASCR, Prague. All remaining spectro/photo/electrochemical studies, as well the writing of the relevant part of publications, were done by the Department. External co-authors contributed also by discussions and critical reading of the manuscripts.*

Research Direction 4: Photocatalysis for environment protection

Research on photocatalysis is carried in broad international and domestic collaborations with academia and industry. They include both European and Asian (Singapore, Malaysian and Vietnam) partners. Among the practical goals is detoxification of water from persistent organic pollutants which represent a serious health issue in remote rural areas of Vietnam and other countries. Recent research tasks aim at design, construction and testing of solar photoreactors for decontamination of drinking and surface water, for standard ISO tests of photoactivity of suspended or immobilized photocatalysts and for explanation of reaction mechanism of oxidative degradation of model organic pollutants. The research on photo-degradation of model pollutants has been further upgraded in collaboration with the Department of Spectroscopy (S. Civiš) who contributed by their unique HR-FTIR method to follow the reaction mechanisms. In this collaborative research, our Department developed the corresponding photocatalysts, particularly the isotope labeled and tailored nanomaterials. Research in photocatalysis for water purification is currently supported by one European NMP grant 4G-PHOTO CAT (J. Jirkovsky, 2013-2015) and by two project from Technological Agency of the Czech Republic (J. Jirkovsky, 2013-2016) from which one grant is oriented to construction industry and paints and the other grant is focused at air/water cleaning. Past projects include large research center for nano-surface engineering (NANOPIN) financed by Czech Ministry of Education (L. Kavan and J. Jirkovsky, 2005-2011).

a) Photocatalysts for water/air purification

Research and development of photocatalysts has been focused at practical tasks of water and air purification from environmental pollutants. An array of specific photocatalysts has been developed, such as TiO₂ immobilized on layered double hydroxides [Pausova et al. *Environ.Sci.Pollution Res.* **2012**], TiO₂-SiO₂ composite photocatalysts [Pausova et al. *J.Chem.Technol.Biotech.* **2014**], S-doped TiO₂ [Szatmary et al. *Catalysis Today* **2011**] and several other materials. *For these works, some syntheses and analytical characterizations were carried out by external collaborators. All photocatalytic studies, as well the writing of the relevant parts of publications, were done by the*

Department. External co-authors contributed also by discussions and critical reading of the manuscripts.

b) Mechanism of (photo)catalytic reactions

The development of high-purity isotopically labeled TiO₂ [Kavan et al. **Phys.Chem.Chem.Phys.** **2011**, Frank et al. **Phys.Chem.Chem.Phys.** **2012**] (43 citations) opened new pathways to elucidation of mechanisms of catalytic and photocatalytic reactions. They were focused at transformations of CO₂ [Civis et al. **J.Phys.Chem.C** **2011**], formic acid [Civis et al. **J.Phys.Chem.C** **2012**] and OCS [Civis et al. **Chem.Comm.** **2014**]. The study on the surface reactivity of partially reduced isotopically labelled nanocrystalline TiO₂ with OCS was combined with quantum chemical calculations. Analysis of the isotopic composition of the product gases has revealed that the reaction involves solely OCS molecules from the gas-phase. The experiments indicate that the reaction does not involve lattice oxygen atoms. The details of transformation of CO₂ at (001)-titania nanosheets [Ferus et al. **J.Phys.Chem.C** **2014**] and nanoclusters [Civis et al. **J.Phys.Chem.C** **2015**] were studied including theoretical simulations. These works revealed not only oxidative degradation of model molecules, but also an opposite reaction was traced in certain systems: examples are the transformation of CO₂ and H₂O into methane and acetylene [Civis et al. **J.Phys.Chem.C** **2011**], the so-called solar fuels. During the study of kinetics of oxygen mobility an additional phase (TiOF₂) in as made anatase with dominating (001) facets was detected and identified for the first time. This impurity is responsible for low exchange activity of oxygen, but can be removed by annealing at temperatures above 500°C. For these works, all syntheses of (photo) catalysts and their analytical characterizations were carried out by the members of Departments, who also wrote the relevant parts of publications. External co-authors contributed by theoretical modeling. The studies of HR-FTIR were made by colleagues from the Department of spectroscopy.

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
Scientific team	Department of Chemistry of Ions and Clusters

A. Personal Structure at 12/2014

As of 31. December 2014 the department of Chemistry of Ions and Clusters consisted of sixteen scientists, one technician, four PhD students and one Master student. Amongst the scientists there were two senior scientists: Patrik Španěl leading the Chemistry of Ions in Gaseous Phase Group and Michal Fárník leading the Molecular and Cluster Dynamics Group. The key permanent staff members in these groups were represented by three scientists (J. Kubišta, J. Žabka, and O. Votava) together with three associate scientists (M. Polášek, K. Dryahina and A. Pysanenko). Five postdoctoral fellows were employed on the fixed term basis and funded from research projects (V. Shestivska, I. Zymak, P. Rubovič, V. Zelenková and J. Rakovsky) as was the technician (P. Pasztor). Four PhD students were also on the staff (V. Křížová, A. Spesyvyi, J. Lengyel and P. Svrčková), some of them as part time employees. Three emeriti were also employed part time in various roles (Z. Herman as a senior scientist, Z. Dolejšek as a scientist and L. Hládek as a research assistant). Whilst not formally employed on the last day of the year, two other colleagues were integral part of the department: a scientist V. Poterya on the maternity leave and a postdoctoral fellow K. Sovová on a yearlong research stay in London. Seven Master students and one PhD student (combined form with other employment) participated in the research work without a contract of employment in accordance with the current institute's policy.

B. Research Activities at a Glance

The research carried out in the Department of Chemistry of Ions and Clusters has been aimed at experimental studies of reactivity of transient species in the gas phase, including ions, molecular clusters, radicals and molecules of gases and vapours of volatile compounds. The accent was placed on obtaining results that are highly relevant and fill the current gaps in knowledge ranging from understanding of planetary atmospheres via environmental issues to clinical diagnoses. However, whilst the motivation for the work has been provided by practical needs and various interdisciplinary scientific interactions, the core research was based on innovative experimental work providing solid fundamental understanding of the chemistry and physics of the processes occurring at the molecular level.

During the years 2010-2014 multiple research projects that brought important and original results were carried out in the following areas:

1. Ion molecule reactions for trace gas analysis.

The method for trace gas analysis of air called Selected Ion Flow Tube Mass Spectrometry, SIFT-MS was enhanced by multiple studies of kinetics of ion molecule reactions including (**K. Sovová et al. Anal. Chem. 2012**) supported by grants from Czech Science Foundation GACR "Pulse mode and microwave plasma sources-research and application" and Grant Agency of the Charles University GAUK "Study of volatile compounds released by plants during phytoremediation of contaminated soil using SIFT-MS".

2. Breath analysis for clinical diagnostics and therapeutic monitoring.

The knowledge obtained in ion chemistry studies (**Španěl & Smith Mass Spectrom. Rev. 2011; Smith & Španěl TrAC 2011**) was used in interdisciplinary studies to discover biomarkers in breath of various diseases (**Dryahina et al. Rapid Commun. Mass Spectrom. 2013**) and infections (**Shestivska et al.**

Rapid Commun. Mass Spectrom. 2011) supported by grants from Czech Science Foundation GACR „Identification of trace gases in human breath using SIFT-MS“, “Selected ion flow tube mass spectrometry studies of volatile compounds emitted by bacterial cultures” and „Mass spectrometric quantification of volatile metabolites in breath for non-invasive diagnosis and monitoring of bacterial infection in cystic fibrosis“.

3. Molecular characterisation of organometallic catalysts.

Mass spectrometry methods have been implemented for analyses of organometallic catalysts in collaboration with the Department of Synthesis and Catalysis (**Pinkas et al. Organometallics 2013**) and for characterisation of their reactivity (**Pinkas et al. Organometallics 2011**). This work has been complemented by a newly initiated programme in the field of nuclear quadrupole resonance (**Kubišta et al. Analyst 2012**) funded by Czech Science Foundation “NQR spectroscopy of explosives and titanocene complexes”.

4. Ionic reactions in the Titan atmosphere.

Reactions of ions with molecules occurring in the Titan’s atmosphere have been studied. The rate constants and their temperature dependencies resulting from this work have been widely adopted internationally in modelling and understanding of the origin of organic compounds observed previously by the Cassini-Huygens mission (**Žabka et al. Icarus 2012**).

5. Studies of fundamental phenomena in clusters

A major programme of studies of properties of clusters containing tens or hundreds of atoms was carried out using a unique Cluster Beam experimental apparatus combining mass spectrometry (**Kocisek et al. J. Chem. Phys. 2013b**) optical spectroscopy (**Fárník et al. Mol. Phys. 2012**) and novel approach to imaging of reaction products (**Fedor et al. J. Chem. Phys. 2011a**). This work was funded by European Commission FP7 projects “Imaging Photochemistry in Nanoparticles” and “Imaging and Control in Chemistry”.

6. Clusters and nanoparticles important in atmospheric chemistry

The original laboratory investigations of photochemical reactions occurring on ice nanoparticles enhanced the understanding of the chemistry and physics underlying the processes relevant to ozone depletion in the stratosphere (**Lengyel et al. J. Phys. Chem. Lett. 2012; Fárník et al. Mol. Phys. 2012; Poterya et al. J. Phys. Chem. A 2014**). Important was also the discovery of large cross sections of these ice clusters (**Lengyel et al. J. Phys. Chem. Lett. 2012**). This work was supported by Czech Science Foundation grant “Atmospheric Clusters and Aerosols: Molecular Beam Experiments and Theory”.

7. Clusters with biological relevance

Chemistry of clusters was also investigated in order to understand radiative damage of biological molecules using both reaction product imaging (**Poterya et al. Phys. Chem. Chem. Phys. 2012**) and mass spectrometry (**Lengyel et al. J. Phys. Chem. A 2013**) approaches. This was funded by Czech Science Foundation projects “Study of photochemical processes in free nanoparticles of atmospheric and biophysical relevance” and “Dynamics of Solvated Electrons in Molecular Clusters: Experimental and Theoretical Approach”.

8. IR spectroscopy of molecular, radical and ionic species of atmospheric relevance.

An original and improved experimental procedure has been developed for accurate determination of lower state rotational quantum numbers from molecular absorption spectra using a unique planar supersonic jet experimental apparatus (**Votava et al. J. Quant. Spectrosc. Radiat. Transf. 2014; Masat et al. J. Mol. Spectr. 2013**). Results of interpretation of the methane spectra are relevant to the spectroscopy of atmospheres of the giant outer planets and their moons and are internationally widely adopted and included in the key line lists and spectral databases. This was funded by Ministry of Education, Youth and Sports of the Czech Republic project “Role of peroxy radicals in atmosphere and combustion chemistry”.

C. Detailed description of our results in 2010-2014:

During this 5 year period the scientists from the department of Chemistry of Ions and Clusters published 141 papers in impacted journals. This report highlights the results obtained within the following research directions introduced in the previous section:

1. Ion molecule reactions for trace gas analysis.
2. Breath analysis for clinical diagnostics and therapeutic monitoring.
3. Molecular characterisation of organometallic catalysts.
4. Ionic reactions in the Titan atmosphere.
5. Studies of fundamental phenomena in clusters
6. Clusters and nanoparticles important in atmospheric chemistry
7. Clusters with biological relevance
8. IR spectroscopy of molecular, radical and ionic species of atmospheric relevance.

1. Ion molecule reactions for trace gas analysis.

This area represented one of the main research interests of P. Španěl, the head of department. He has carried out a series of experimental studies together with associate scientist K. Dryahina, foreign collaborators that visited the department for periods of several weeks or months (D. Smith from England, A. Olivares from Spain, P. Heynderickx from Belgium) and PhD students (K. Sovová, R. Bruhová-Michalčíková and A. Spesyvyi). Studies of the kinetics of ion-molecule reactions were motivated by the growing interest in the use of Selected Ion Flow Tube Mass Spectrometry, SIFT-MS that was developed previously by Španěl and Smith (**Španěl & Smith Mass Spectrom. Rev. 2011; Smith & Španěl Analyst 2011, TrAC 2011**) for trace gas analysis of air. Most significant results were on reactivity of the H_3O^+ , NO^+ and O_2^+ ions that selectively ionise vapours and gases present in air whilst being unreactive with major air components. Rate constants and ion product branching ratios were determined for the reactions of these three ions with selected classes of compounds, including phytogetic esters (**K. Sovová et al. Int. J. Mass Spectrom. 2011**), organoselenium molecules (**K. Sovová et al. Anal. Chem. 2012**), isomers of hexanol (**Smith et al. Int. J. Mass Spectrom. 2012**) and carboxylic acids (**Michalčíková & Španěl Int. J. Mass Spectrom. 2014**). Several studies in the area of ion-molecule chemistry were related to aroma and freshness markers in food science (**Flores et al. Curr. Anal. Chem. 2013; Olivares et al. Food Chem. 2012; Olivares et al. Journal of Agricultural and Food Chemistry 2011**), aldehydes in models of laundry washing (**Heynderickx et al. Fluid Phase Equilibria 2014**). All these studies were carried out entirely within the team, including visiting foreign scientists. Additionally, in collaboration with the department of Spectroscopy, SIFT-MS studies were carried out of the decomposition products of various explosives (**K Sovová et al. Analyst 2010; Civiš et al. Anal. Chem. 2011**). P. Španěl also participated in several studies of reactions of the H_3O^+ , NO^+ and O_2^+ ions with aldehydes and organosulphur compounds that were carried out abroad (**Smith et al. Rapid Commun. Mass Spectrom. 2014; Mochalski et al. Rapid Commun. Mass Spectrom. 2014, Int. J. Mass Spectrom. 2014**).

2. Breath analysis for clinical diagnostics and therapeutic monitoring.

A specific interdisciplinary area where SIFT-MS was exploited is analysis of trace amounts of volatile compounds in breath for diagnostics of infections and other diseases and for monitoring of the treatment effects. The research in this area within the team was largely responsibility of K. Dryahina with direct involvement of P. Španěl and a biologist postdoctoral fellow V. Shestivska. PhD, Mgr. and Bc. students (K. Sovová, V. Pospíšilová, P. Beránková) were directly involved and defended their theses within this subject area.

A foundation for breath diagnostics is the discovery of volatile compounds that can be used as biomarkers of bacterial infection. Two well cited papers were published by the team, in collaboration with the colleagues from the Institute of Public Health (**Shestivska et al. J. Appl. Microbiol. 2012; Shestivska et al. Rapid Commun. Mass Spectrom. 2011**) in which several compounds including hydrogen cyanide, methyl thiocyanate, 2-butanone, 2-pentanone, isoprene, aminoacetophenone, dimethyl sulphide, dimethyl disulphide, dimethyl trisulphide, 3-methyl-butanone, acetophenone, methylthioacetate and methyl thiobutanoate were quantified for 36 genetically characterised strains

of *Pseudomonas aeruginosa* that cause life threatening infections to patients with cystic fibrosis. These studies were carried out at the department using cultures prepared by microbiologists at the Institute of Public Health and were supported by the Czech Science Foundation “Selected ion flow tube mass spectrometry studies of volatile compounds emitted by bacterial cultures” and „Mass spectrometric quantification of volatile metabolites in breath for non-invasive diagnosis and monitoring of bacterial infection in cystic fibrosis“.. An interesting study of population dynamics of bacterial cultures was carried out in collaboration with the Department of Philosophy of the Charles University Science Faculty (**Sovova et al. Analyst 2013**). Whilst the strains included in this study are not dangerous pathogens, the observations are important for diagnostics of simultaneous infections by several bacterial species. P. Španěl also collaborated at several SIFT-MS studies of bacterial cultures abroad (**Chippendale et al. Rapid Commun. Mass Spectrom. 2011; Chippendale et al. Analytical Methods 2014b; Smith et al. J. Breath Res. 2013; Chippendale et al. Analytical Methods 2014a; Gilchrist et al. Journal of Clinical Microbiology 2013; Gilchrist et al. Analytical Methods 2012; Gilchrist et al. European Respiratory Journal 2011**).

The knowledge obtained in ion chemistry studies was used in interdisciplinary studies to discover breath biomarkers of oxidative stress in inflammatory bowel disease diseases (**Dryahina et al. Rapid Commun. Mass Spectrom. 2013**) and to find a breath biomarker of gastric reflux disease (**Dryahina et al. J. Breath Res. 2014**). In this work the members of the team carried out the ion chemistry part of the study and also used their SIFT-MS instrument in the clinic. The clinical co-authors were responsible for the selection of patients, ethics and contributed to writing of the papers. The initial phases of the work were supported by a grant from Czech Science Foundation GACR „Identification of trace gases in human breath using SIFT-MS“. As background work to clinical breath analysis, influence of inhaled compounds on their concentrations in exhaled breath was studied by the team and published in a well cited paper (**Španěl et al. J. Breath Res. 2013**). P. Španěl is also actively involved in “International Association for Breath Research” IABR and in the editorial board of Journal of Breath Research.

3. Molecular characterisation of organometallic catalysts.

Development and implementation of mass spectrometry methods for analyses of organometallic catalysts titanocenes and zirconocenes represented the main are of J. Kubišta’s research. This work was carried out in collaboration with the department of Department of Synthesis and Catalysis where the compounds were synthesised. J. Kubišta contributed by their analysis using doubly focusing magnetic sector mass spectrometer and by interpretation of their mass spectra (**Horacek et al. Journal of Organometallic Chemistry 2014; Pinkas et al. Organometallics 2013**) and for characterisation of their reactivity (**Strasak et al. Organometallics 2013; Pinkas et al. Organometallics 2014; Pinkas et al. Organometallics 2011**). This work has been complemented by a newly initiated programme in the field of nuclear quadrupole resonance (**Kubišta et al. Analyst 2012**) funded by Czech Science Foundation “NQR spectroscopy of explosives and titanocene complexes”.

4. Ionic reactions in the Titan atmosphere.

The reactions of ions with molecules occurring in the Titan’s atmosphere were researched by J. Žabka and his colleagues (associate scientist M. Polášek, postdoctoral fellow I. Zymak and several Mgr. and PhD. students). Data were obtained for the kinetics of the reactions of the N^+ ions with C_3 hydrocarbons (**Dryahina et al. J. Phys. Chem. A 2011**) that have been adopted internationally in modelling and understanding of the origin of organic compounds observed previously by the Cassini-Huygens mission. A complete range of production processes and reactions of N , N^+ , N_2^+ , N^{++} , and N_2^{++} ions important to Titan’s atmosphere has been reviewed including neutral, ion–molecule, and recombination reactions. The data on reactions of ions with molecules include those obtained by original experiments in our team. Values for the rate constants and their temperature dependencies resulting from this work have been widely adopted internationally in modelling and understanding of planetary atmospheres. Two members of the team (Z. Herman and J. Žabka) contributed to this major work especially in the area of reactions of positive ions with molecules. Their contribution was based

on their previously published original research articles based on experimental work in our institute and also on their expertise in critically reviewing the literature. (**Dutuit et al. *Astrophys. J. Suppl. Ser.* 2013**). Recently, the research was extended to the area of negative ions (**Žabka et al. *Icarus* 2012**; **Žabka et al. *Int. J. Mass Spectrom.* 2014**) in collaboration with the French colleague C. Alcaraz who together with his students visited the department in order to participate in experiments elucidating the origin of larger hydrocarbon molecules detected in Titan atmosphere. This work is funded by the Czech Science Foundation GACR in projects “Experimental and theoretical study of chemical reactions occurring in the Titan's ionosphere” and “Chemical processes in the atmosphere of Titan - experimental study”. J. Žabka is also an actively involved in the work of international consortia focused on planetary atmospheric research including EuroPlanet.

5. Studies of fundamental phenomena in clusters

A major programme of studies of properties of clusters containing tens or hundreds of atoms was carried out by M. Fárník and his colleagues (scientist V. Poterya, associate scientist A. Pysananko and several PhD. and Mgr. students) using a dedicated Cluster Beam experimental apparatus, that was constructed by this team. In one experimental study performed on this apparatus using mass spectrometry detection it was discovered that mixed Ar-water clusters have a structure of water clusters fully covered with the Ar solvation shell (**Kocisek et al. *J. Chem. Phys.* 2013b**). Similar studies of clusters generated in acetylene-Ar expansions have led to discovery of polymerisation leading to covalently bound $C_6H_6^+$ ions upon the acetylene cluster electron ionization (**Kocisek et al. *J. Chem. Phys.* 2013a**). A programme of fundamental studies of the solvent effects on acetylene photodissociation in clusters of different sizes and compositions ranging from pure acetylene clusters $(C_2H_2)_{(10-200)}$ to mixed $(C_2H_2)_{(10-200)}Ar_nXe_m$ species was completed (**Fárník et al. *Mol. Phys.* 2012**). It was found, for example, that a single acetylene molecule or a small acetylene cluster can be either adsorbed on the surface or embedded inside the rare gas cluster. Photodissociation dynamics were studied by the H-fragment time-of-flight (TOF) technique and an unusual manifestation of the cage effect leading to a formation of fast hydrogen fragments was observed. Also, in xenon clusters with acetylene molecules adsorbed on the surface, evidence was found for generation of organo-xenon molecules $HXeCCH$ from excited acetylene molecules.

The experimental possibilities were greatly extended by construction of a novel velocity map imaging set up allowing imaging of reaction products. This technique was used to study clusters of hydrogen bromide with helium, argon, and xenon and fragment caging by the cluster was observed and it was concluded that single HBr molecule is encompassed within a rare gas "snowball" (**Fedor et al. *J. Chem. Phys.* 2011a**). This imaging technique was also used to investigate the photochemistry of iodine monochloride (ICl) clustered with He and Xe and to establish that ICl photodissociation occurs inside larger xenon clusters and on surface of smaller Xe species. (**Glodic et al. *J. Chem. Phys.* 2012**). This work was funded by European Commission FP7 projects “Imaging Photochemistry in Nanoparticles” and “Imaging and Control in Chemistry”.

The experimental research of fundamental cluster chemistry was carried out entirely by the team with involvement of foreign researchers that visited Prague in order to participate in these experiments (M.L. Lipciuc and T.N. Kitsopoulos).

6. Clusters and nanoparticles important in atmospheric chemistry

The same team (M. Fárník, V. Poterya and A. Pysanenko) with a notable contribution of a PhD student J. Lengyel used the knowledge and techniques developed for the studies of cluster chemistry to investigate photochemical reactions occurring on ice nanoparticles that contribute to ozone depletion in the Terrestrial stratosphere.

Notable examples of such studies are an investigation of nucleation of mixed nitric acid-water ice nanoparticles that starts with a HNO_3 molecule (**Lengyel et al. *J. Phys. Chem. Lett.* 2012**), a series of

studies of important process of molecular pickup and accurate measurements of its cross sections (Fedor et al. *J. Chem. Phys.* **2011b**; Lengyel et al. *J. Chem. Phys.* **2012**), and detailed experimental characterisation of cluster photochemistry of CF₂Cl₂ (Poterya et al. *Phys. Chem. Chem. Phys.* **2014**; Poterya et al. *J. Phys. Chem. A* **2014**). Important was also the discovery of large cross sections of these ice clusters (Lengyel et al. *J. Phys. Chem. Lett.* **2012**), irregular shape of these ice clusters (Lengyel et al. *Physical Review Letters* **2014**) and description of extensive water cluster fragmentation after low energy electron ionization (Lengyel et al. *Chem. Phys. Lett.* **2014**).

This work was carried out entirely by the team and was supported by Czech Science Foundation grant "Atmospheric Clusters and Aerosols: Molecular Beam Experiments and Theory".

7. Clusters with biological relevance

Chemistry of clusters was also investigated by M. Fárník and colleagues in order to understand radiative damage of biological molecules. Rigorous studies of photochemistry of five-membered nitrogen containing heterocycles in clusters have led to explanation of photostability of biologically active heterocyclic molecules and complexes. Combination of critical interpretation of literature with original experiments and quantum chemical theory provided a unified view on photoinduced processes and a finding that reconstruction of the ground state occurs in preference to energetically possible destructive channels (Slavicek & Fárník *Phys. Chem. Chem. Phys.* **2011**). Reaction product imaging was used to describe photodynamics of phenol molecules in clusters after excitation with ultra violet laser radiation (Poterya et al. *Phys. Chem. Chem. Phys.* **2012**). Mass spectrometry was used in similar reaction system to study the processes occurring after ionising of phenol clusters leading to proton and hydrogen transfer processes (Lengyel et al. *J. Phys. Chem. A* **2013**). This research was funded by Czech Science Foundation projects "Study of photochemical processes in free nanoparticles of atmospheric and biophysical relevance" and "Dynamics of Solvated Electrons in Molecular Clusters: Experimental and Theoretical Approach".

8. IR spectroscopy of molecular, radical and ionic species of atmospheric relevance.

This area represents major research interest of O. Votava who carries out experimental research of atmospherically important molecules together with postdoctoral fellows V. Zelenková and J. Rakovsky. An original and improved experimental procedure has been developed for accurate determination of lower state rotational quantum numbers from molecular absorption spectra using a unique planar supersonic jet experimental apparatus (Votava et al. *J. Quant. Spectrosc. Radiat. Transf.* **2014**; Masat et al. *J. Mol. Spectr.* **2013**). As a result of this work, the low energy levels of CH₄ were determined that correspond to spectral lines in the highly congested near infrared spectrum by rigorous studies of absorption spectra at low temperatures and from the temperature variation of the transition intensities between 296 and 81 K. Results of interpretation of the methane spectra are relevant to the spectroscopy of atmospheres of the giant outer planets and their moons and are internationally widely adopted, included in the key line lists and spectral databases and often cited in literature.

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Molecular Electrochemistry
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A. Personal Structure (December 2014)

In December 2014 the Department of Molecular Electrochemistry consisted of 16 members, including 8 scientists, 1 research assistant, 1 technician (Kantnerová – undergraduate student) and 6 graduate students. Five scientists (Fiedler, Hromadová, Kolivoška, Ludvík, Sokolová) can be considered as key personnel (they are partially financed by institutional and partially by grant support). Additional three scientists (Pospíšil, Klíma, Urban) reached their retirement age and are paid mainly or exclusively by grant support. One research assistant (Gasior, also retired) and two graduate students (Lachmanová, Ramešová) are paid exclusively by grant support. The personal structure of Department at the end of 2014 did not take into account another scientist, who is presently on maternity leave (Bulíčková-Kocábová) and should be considered among the key personnel. The average age of the Department is 44.

B. Research Activities at a Glance

Main activity of the Department of Molecular Electrochemistry can be formulated as fundamental studies of newly synthesized organic and organometallic molecules with specific redox properties designed for various applications. The stress is given on intramolecular electron interactions in molecules with multiple redox centers. Our research involves elucidation of the structure-reactivity relationship on a single molecule level, determination of redox reaction mechanisms, interception and characterization of (radical) intermediates and application of this knowledge in different fields of everyday life including bioanalysis, sensors, catalysis, energy harvesting, non-linear optics, molecular electronics, energetic materials, art preservation etc.

During the evaluation period the Department published **115 papers in impacted journals** (including two papers, which were published online in 2014, but appeared in print in 2015), **4 papers** in refereed journals without impact factor and **4 monograph chapters**. One utility model was granted by the Industrial Property Office in 2011.

Research activities of the Department in 2010-2014 were focused on:

- (1) **Understanding and tuning of the electronic properties of new organic molecules** (29 papers)
- (2) **Organometallic electroactive systems for molecular catalysis** (38 papers)
- (3) **Molecules with multiple redox centers, push-pull systems** (14 papers)
- (4) **New molecular sensors and 2D architectures at electrified interfaces** (11 papers)
- (5) **Antioxidant properties of flavonoids, their oxidative degradation and redox mechanisms** (9 papers)
- (6) **Single molecule conductance for molecular electronics** (5 papers)
- (7) **Understanding molecular switching and oscillatory phenomena** (7 papers)
- (8) **Advances in electrochemical techniques and methodology** (5 papers)

These activities were supported by **12 national research grants**

- from **Grant Agency of the Academy of Sciences of the Czech Republic** („Investigation of long-distance intramolecular electronic interactions and reactivity of mono- and binuclear aminocarbene complexes using electrochemical methods.“, ended in 2011; „Cationic redox catalysis and its role in the observation of electrochemical oscillatory phenomena.“, ended 2012; „Electrochemistry of bioflavonoids and their interaction at the interface.“, ends in 2015),
- from **Grant Agency of the Czech Republic** („Tailoring the lock and key motifs in novel low-dimensional structures at electrified interface.“, ended 2011; „Electrochemistry of natural pigments and their host-guest complexes.“, ended 2012; „Transfer of charge in single and assembled molecules.“ and "New type of connection between electrochemistry and mass spectrometry - mechanistic studies of redox reactions of organic compounds" ended 2013; „Synthesis of helical cyanines, their chirality, self-assembly and redox switching.“, ends in 2015; „Electron Transport in Nanoscale Assemblies. From Redox Mechanism to Molecular Conductance“, ends in 2016; „Electrochemically active calix[4]arenes and their use for preparation of new receptors and (bio)sensors.“, ends in 2016)
- from the **Ministry of Education, Youth and Sports of the Czech Republic** („Redox activity of host-guest, organometallic and molecular structures at electrode interfaces.“, ended 2010; „Chemical and Electrochemical Properties of Aromatic Dialdehydes and their Derivatives, Chemical Principles of Sensors for Aminoacids and New Disinfection Processes.“, ended 2012).

Our research was further supported by 4 grants for international cooperation (program KONTAKT, „Electron transfer in new materials for molecular electronics.“, ended in 2011; program SCIEX, „Electron transport in nanoscale host-guest assemblies (ETNA).“, ended 2013; priority project with Hungarian Academy of Sciences „Transfer of Charge in Single Molecules. From Redox Mechanism to Molecular Conductance.“, ends in 2015 and international cooperation program of ASCR with French partners „Electron transfer in nanoscale. The effect of steric switching on the conductance of expanded pyridinium compounds.“, ends in 2015.

C. Detailed description of our results in 2010-2014:

Research Direction 1: Understanding and tuning of the electronic properties of new organic molecules.

Several redox systems with interesting electronic properties were investigated in our laboratories (**Gál et al. Bioelectrochemistry 2010** – highly cited paper; **Metelková et al. Electrochimica Acta 2012**; **Sokolová et al. Electrochimica Acta 2010**; **Pospíšil et al. Physical Chemistry Chemical Physics 2010** – highly cited paper). Molecules serving as solar cell sensitizer models and molecular dyads were investigated in collaboration with French and German partners.

Pospíšil et al. Carbon 2010 reported the determination of formal redox potentials of a series of fullerene-containing compounds designed for applications in protic media. Pristine fullerene is practically insoluble in water, whereas these compounds retain redox activity (multi-electron transfer) of fullerene moieties in aqueous media. Compounds were characterized by electrochemical admittance technique, which offers advantage of separating faradaic and capacitive properties. Forms of fullerene in aqueous medium were discussed. Our team designed and performed all experiments as well as wrote the entire paper. French partners synthesized fullerene derivatives.

Development of new redox shuttles for photovoltaic cells requires full reversibility of oxidation-reduction process involved. Our team (**Wahab et al. Inorganic Chemistry 2012**) investigated redox properties of a series of 31 icosahedral carborane anions and showed among them prospective candidates for such applications. Experimentally obtained redox potential values were correlated with HOMO energies obtained by various quantum mechanical methods and reasons for preventing the radical dimerization after electron transfer were given. Department members conducted all electrochemical measurements and

interpretation and wrote the paper. Synthesis and theoretical calculations were performed by our partners.

Boron heterocycles are tested for the use in optoelectronics, some of them (diazaborines) exhibited antibacterial and anticancer activity. Newly synthesized triazaborines and oxazaborines were electrochemically characterized in our laboratory (**Josefik et al. Organometallics 2014**).

Research Direction 2: Organometallic electroactive systems for molecular catalysis.

Newly synthesized dicarbonylhydridocobalt complex with diphosphinoferrrocene ligand proved to be important in the context of mechanistic investigations of hydrogen production and conversion reactions (**Krafft et al. Angewandte Chemie-International Edition 2013**). Spectroelectrochemical measurements revealed a redox sequence including cobalt-centered oxidation of the neutral complex and subsequent homolytic cleavage of the Co-H bond leading to hydrogen and an electron-deficient cationic complex which was structurally characterized. This new result differs from the previously observed heterolytic cleavage of the metal-ligand bond in the structurally similar complexes (**Sixt et al. Organometallics 2010**). Our team contributed to the paper particularly by performing the spectroelectrochemical measurements (Dr. Fiedler) and their interpretation supported by DFT calculation (Dr. Zálíš). The paper was compiled in close collaboration of the Czech and German teams.

Donor-acceptor systems based on Pt(II) and non-innocent ligands belong to a prominent class of complexes because of their intriguing electronic properties and applicability in catalysis and solar energy harnessing. The novel isomeric Pt(II) complex with a substituted iminobenzoquinone ligand revealed an enhanced reactivity on the central metal after a redox transition primarily localized on the ligand. The capability to coordinate and activate small molecules has been proved (**Deibel et al. Chemical Communications 2012**). Contribution of the members of the Department consists of performing the spectroelectrochemical measurements, their interpretation and finding the factors which influence the behavior of electro-generated states. The paper was written in collaboration with the German team.

The investigation of the catalytically important effect of redox-induced labilization of the metal-ligand bond was extended to the complexes with potentially hemilabile ligands. In the case of iminoquinone ligands (N,O donors) involving a third (S or O) donor function on a thioether or ether substituent the redox change and a fractional charge transfer to the metal plays the crucial role for the coordination bond labilization and the coupled structural change (**Bubrin et al. Organometallics 2014**). Hemilability of some oxo-pteridine-type bioactive ligands can be induced by a ligand-based redox change too (**Jana et al. Organometallics 2014**). Fischer type Cr-aminocarbene complexes are widely used in organic synthesis and in redox catalysis. A systematic electrochemical research of these mono- and dinuclear compounds with various ligands and metals has been performed in our laboratory. Extent and position of electron delocalization was determined and correlated with structure and properties. Electroreduction mechanism was formulated and products identified by MS. J. Ludvík served as a corresponding author in all papers (**Hoskovcová et al. Electrochimica Acta 2010; Hoskovcová et al. Electrochimica Acta 2011, Metelková et al. Electrochimica Acta 2012; Kvapilová et al. Organometallics 2014**).

A series of substituted alloxazinium perchlorates has been prepared and tested as catalysts for the oxidation of sulfides to sulfoxides with hydrogen peroxide. The logarithms of the observed rate constants of thioanisole oxidation correlate with the Hammett ρ constants of the substituents on the alloxazinium catalysts, as well as with their reduction potentials. All electrochemical part was done in our laboratory (**Ménová et al. Advanced Synthesis Catalysis 2013**).

Several potential catalysts based on the redox active transition metal complexes were investigated in cooperation with German and Italian partners. This work is highly cited and was

published in **Angewandte Chemie-International Edition; Catalysis Today; Chemistry – A European Journal; Dalton Transactions; Inorganic Chemistry and Organometallics** among the others. The spectroelectrochemical measurements were done by the members of the Department of Molecular Electrochemistry (**Das D. et al. Chemistry - A European Journal 2011; Das H. S. et al. Chemistry - A European Journal 2010; Kundu et al. Inorganic Chemistry 2010** – highly cited papers).

Research Direction 3: Molecules with multiple redox centers, push-pull systems.

Tetranitrocallyx[4]arenes are not only promising framework for sensors due to their ability to host-guest interactions, but also molecules with four reduction centers. The electrochemical investigation revealed that the nitro groups are not equivalent. They form two different couples of non-interacting centers. The molecule has therefore symmetry C_{2v} (pinched, not circular). The four-electron reduction results in tetraanion tetraradical proved by EPR spectroelectrochemistry and confirmed by DFT calculations (**Liška et al. Journal of Organic Chemistry 2013, Liška et al. Electrochimica Acta 2014**).

When an electron withdrawing group (reduction center) and electron donating group (oxidation center) are interconnected by a conjugated - delocalized system, the resulting molecule is strongly polarized (push-pull electron system) and can exhibit non-linear optical properties. Six series of such molecules were electrochemically characterized in order to reveal the structural rules for the most NLO-active derivatives (**Kulhánek et al. Dyes and Pigments 2010 and 2011** – highly cited papers; **Bureš et al. Tetrahedron Letters 2010; Kulhánek et al. Chemistry-An Asian Journal 2011**). Syntheses were performed in the cooperating team from University of Pardubice, all electrochemical treatment and interpretations were done in our team.

The strong polarization of the push-pull molecule can result in intramolecular electron transfers leading to total degradation (principle of explosives). Recently synthesized energetic material 2,2-dinitroethene-1,1-diamine (FOX-7) was electrochemically reduced and spectrometrically studied in our team. It was found that low number of consumed electrons together with gaseous products resembles the process during explosion which is slowed down by low concentration and cooled by the solution. The starting structure as well as the radical intermediates were intercepted and characterized by EPR/UV-vis/EC spectroelectrochemistry (**Šimková et al. Current Organic Chemistry 2011**).

Research Direction 4: New molecular sensors and 2D architectures at electrified interfaces.

Lock and key motif was utilized for the design of functional immunosensor for detection of pesticide atrazine and performance of the sensor was demonstrated. (**Hromadová et al. Langmuir 2013**) Several techniques were used for characterization of the immunosensing layer including scanning tunneling microscopy, time-resolved ellipsometry, polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS), XPS and quartz crystal microbalance. Kinetic aspects of self-assembly were discussed. The members of the Department designed and performed experiments as well as wrote the paper. French partners synthesized atrazine-containing disulfide dimers for preparation of self-assembled monolayers. PM-IRRAS measurements were performed in collaboration with French colleagues.

Several works have been devoted to preparation of well-defined 2D architectures. For example, bovine serum albumin served as a template for controlled nanopancake and nanobubble formation (**Kolivoška et al. Colloids and Surfaces B-Biointerfaces 2012**). In-situ and ex-situ scanning tunneling and atomic force microscopy imaging techniques were utilized.

Research Direction 5: Antioxidant properties of flavonoids and their oxidative degradation mechanisms.

A long-standing controversy concerning the oxidation pathways of natural flavonoid quercetin has been clarified in a series of highly cited papers (**Sokolová et al. *Electrochimica Acta* 2011**; **Sokolová et al. *Chemical Communications* 2012**; **Ramešová et al. *Analytical and Bioanalytical Chemistry* 2012**). Strong antioxidant properties affect quercetin stability under aerobic conditions and this has to be taken into account. Electrochemical oxidation mechanism under strictly anaerobic conditions has been proposed and the number of electrons involved in the oxidation of quercetin established. Results can help understand properties of similar pharmacologically important compounds. Our team designed the research project, performed electrochemical and most of the product characterization experiments and wrote the papers. M. Valasek synthesized selected reaction intermediates for support of the suggested redox mechanism. I. Degano measured LC-MS of the oxidized samples (international cooperation program of ASCR with Italian partners). Oxidation mechanism of bioflavonoids luteolin, hematoxylin and flavonol rhamnazin has been proposed in other works (**Ramešová et al. *Electrochimica Acta* 2013**).

Research Direction 6: Single molecule conductance for molecular electronics.

Molecular electronic devices require robust elements (molecules) sufficiently stable upon repeated electron transfer and able to conduct charge over long distances. Electrochemical properties of a series of rigid pyridinium-based molecules, which are intended to function as molecular wires, have been characterized (**Kolivoška et al. *Physical Chemistry Chemical Physics* 2011**). Molecules can accept reversibly up to ten electrons and their stability upon electron transfer was confirmed by in-situ spectroelectrochemistry. The electron transfer mechanism was proposed and adsorption properties of these rigid molecules at electrified interfaces were studied using time-resolved capacitance measuring techniques (**Hromadová et al. *Langmuir* 2010**). We showed that these compounds form compact monolayers at the electrode/electrolyte interface around potential of zero charge and the adsorption process is diffusion-controlled. Molecules are oriented parallel to the surface. Their reduction at more negative potentials is accompanied by reorientation. Our team conceived and designed the experiments and wrote the paper. Synthesis of the compounds was done by M. Valasek.

Our team further demonstrated (**Kolivoška et al. *Journal of Physical Chemistry Letters* 2013**) that molecular wires containing extended viologen motifs show unprecedented conductance. The longest molecule (11 nm long) has a conductance of 2.9 nanosiemens which is nearly three orders of magnitude higher than that of the carbon-based wires of a comparable length. The wires withstand repeated cycling between oxidized and reduced states. Paper was highlighted in February 2013 issue of C&EN of ACS. Our team designed and performed the research as well as wrote the paper. Extended viologen molecules were synthesized by M. Valasek, whereas G. Meszaros collaborated on the development of the single molecule conductance measuring technique and instrumentation (program KONTAKT).

Oligophenyleneethynylene (OPE) molecules have been studied as potential building blocks for molecular electronics (**Lipnická et al. *Chemistry-A European Journal* 2013**). Here we describe electrochemical properties of a series of OPEs bearing laterally-attached tetrathiofulvalene (TTF) following the concept of zipper-type multiple donor-acceptor interactions. We demonstrated that for such molecules only one half of TTF units is electrochemically active leading to the formation of persistent mixed-valence dyads of unusual stability towards oxidation. Two research teams were equally involved in the conceptual design of presented research. Our team studied and explained electrochemical properties of the compounds that were synthesized by team of Dr. Stary. Text dealing with electrochemical and spectroelectrochemical properties of these molecules as well as the explanation of redox mechanism was written by Dr. Pospisil.

Research Direction 7: Understanding molecular switching and oscillatory phenomena.

Development of molecular switches

An electrochemically-addressable molecular switch based on the host-guest interaction between ferrocene and beta-cyclodextrin has been designed, constructed and characterized. Non-covalent interaction was controlled by the redox state of ferrocene at single molecule level. Combination of single molecule force spectroscopy with the concept of electrochemical gating enabled determination of nanomechanical properties of individual complexes of cyclodextrin with guest moiety in its different redox states. (**Kolivoška et al. Chemical Communications 2014**). Our team conceived the research project, designed the experiments and wrote the paper. Experimental work was divided between Bern and Prague group (program Sciex). M. Valasek synthesized thiol-terminated compounds and G. Meszaros collaborated on the development of the single molecule conductance measuring technique and instrumentation (program KONTAKT).

Pospíšil et al. Journal of the American Chemical Society 2014 demonstrated intense modulation of chiroptical properties of the viologen-type electroactive unit, embedded in the helical scaffold, by changing a redox state of the molecule. UV-Vis, EPR and electronic circular dichroism spectroelectrochemistry was used for this demonstration. Selected helically-chiral system features the most intense chiroptical switching response documented in the field of helicenes. Paper was selected for the cover of August 6 issue of JACS. Our team performed the electrochemical and spectroelectrochemical characterization of the compounds and developed in-situ measurements of the electronic circular dichroism of electrochemically generated reduced forms. We wrote the paper jointly with external partners, who designed the compounds. Expertise in electronic circular dichroism was provided by L. Bednarova.

Fast monomer/dimer switching was demonstrated in a series of pyridinium and quinolinium cations by **Teplý et al. Journal of Physical Chemistry C 2014**. In this paper we showed the advantage of using combination of electrochemical impedance data with simulation of cyclic voltammograms for determination of kinetic parameters of the heterogeneous electron transfer rates and coupled chemical reactions. Our team designed and performed the experiments, performed theoretical calculations and simulations and wrote the paper. Redox active compounds were synthesized by the team of Dr Teplý, Dr. Tarabek performed EPR experiment.

Manipulating several electrons at the same time is a challenging task. Main factors contributing to reversible transfer of two electrons in a single step as opposed to two single-electron (stepwise) transfers in a series of polyarylpiperidiniums were identified leading to the steric switching of the redox potential compression (**Fortrage et al. Journal of the American Chemical Society 2012**). We proved (by combined spectroelectrochemical and time-dependent DFT study) that two-electron transfer is achieved by enabling hybridization of the *N*-pyridinio atom, whereas possible dimerization is blocked by a judicious substitution. Three teams contributed equally to this work. Our team performed the electrochemical and spectroelectrochemical characterization of the compounds, whereas synthetic work and theoretical computations were done by French partners (international cooperation program of ASCR with French research institutions). We wrote parts of the paper dedicated to the explanation of electrochemical properties.

Oscillatory phenomena

We reported the first example of selective generation of odd harmonics for electrochemical oscillator. (**Hromadová et al. Journal of Physical Chemistry C 2014**) Such systems were known before only in physics and biology. Here small perturbation of the applied voltage by a sine wave signal with amplitude of few millivolts results in current oscillations, which selectively enhance only the odd harmonic frequencies during the reduction process. The effect is explained in terms of the theory of stochastic resonance occurring in driven oscillating reactions. Our team conceived and designed the experiments and wrote the paper. Synthesis

of the compounds was done by M. Valasek. General procedure for synthesis and characterization of newly prepared molecules is reported elsewhere.

Several electrochemical oscillators have been studied during period 2010-2014. Phenomenon of cationic catalysis was studied in the electrochemical systems containing organic molecules undergoing two consecutive electron transfers. Possibility to modify the reactivity of the electrochemically generated organic radicals and/or ion radicals is extremely important in the newly emerging field of molecular electronics and this consideration was taken into account in the selection of model systems. (**Pospíšil et al. Physical Chemistry Chemical Physics 2011**).

Research Direction 8: Advances in electrochemical techniques and methodology.

In order to investigate single molecule conductances, special techniques were developed in the years 2010-2014. Commercially available scanning tunneling microscope was modified electronically to access a wide current range from several units of quantum conductance G_0 to $10^{-6.5} G_0$. (**Kolivoška et al. Journal of Physical Chemistry Letters 2013**). Another methodology using a so-called mechanically controllable break junction was developed with our Hungarian partners. In this arrangement a significant improvement of the noise level has been achieved ($10^{-8.5} G_0$).

Our researchers contributed to the development of hyphenated spectroelectrochemical techniques (UV-Vis-IR, EPR, tandem MS, HPLC-MS, ECD) that enable proper characterization of short-lived reaction intermediates (**Krafft et al. Angewandte Chemie-International Edition 2013; Liška et al. Electrochimica acta 2014, Metelková et al. Electrochimica Acta 2014;**) and characterization of molecular switches (**Kolivoška et al. Chemical Communications 2014; Pospíšil et al. Journal of the American Chemical Society 2014**). Dr. Klíma continued in the development and application of the ultrasound in electrochemistry (**Klíma Ultrasonics 2011**). An effective contribution to the methodology of characterization of the carbon paste electrodes was introduced, tested and applied to various carbon materials (**Mikysek et al. RSC Advances 2012**). The idea, experimental work and interpretation came from our team, the papers and related two book chapters were written by J. Ludvík.

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Low-dimensional Systems
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A. Personal Structure at 12/2014

The group of Dr. Kalbac was previously part of the Department of electrochemical materials. In 2013 Dr. Kalbac was appointed to lead the ESCA group. The Department of Low Dimensional Systems was established in 2014 by joining the group of Dr. Kalbac and group of Dr. Krtil, which was formerly part of the Department of Biomimetic Electrochemistry. In 2013 ERC-CZ project was awarded to Dr. Kalbac, which enabled to hire 3 new postdoc and 1 new PhD. student. In 12/2014 the Department of Low Dimensional Systems consisted of 3 senior scientists (Dr. M. Kalbac –head of the department, Dr. Bastl –vice head of the department, Dr. Krtil), 3 scientists (Dr. I. Jirka, Dr. J. Plsek, Dr. K. Minhova-Macounova), 1 associate scientist (Dr. H. Hoffmannova), 5 postdocs (Dr. S. Costa, Dr. J. Ek Weis, Dr. K. Drogowska, Dr. H. Hajova, Dr. M. Lehtimaki), 3 graduate students (Mgr. V. Vales, Mgr. Z. Kominkova, Mgr. V. Blechta), 4 research assistants (Mgr. L. Kucera, Mgr. A. Santidrian, T. Hiratoko, Ing. I. Spirovova), 3 undergraduate students (Bc. K. Jurkova, R. Nebel, M. Mergl) and one technician (M. Werner 0.5 FTE). Currently 6 members of the Department of Low Dimensional Systems are foreigners (3 Spain, 1 Portugal, 1 Swedish, 1 Poland). The involvement of all postdoc and students is exclusively covered by project funds including European Commission projects, Czech Ministry of education youth and sports and Czech science foundation.

B. Research Activities at a Glance

The main activities of the Department of Low Dimensional Systems can be summarized as advanced studies of low dimensional materials and surfaces. In particular the research is focused on studies of carbon nanostructures (fullerenes, carbon nanotubes and graphene), characterization of chemical composition and electronic structure of surfaces, interfaces and thin layers by photoelectron spectroscopy methods and integration of theoretical, synthetic and electrochemical approaches in the so called rational design of the electrocatalytically active surfaces with tailored activity and selectivity. Establishing the Department of Low Dimensional Systems was an excellent opportunity to combine expertise and collaboration between formerly separated groups. The positive effect of this organizational changes is demonstrated already by two publications which resulted from joint activities of the members of previously different groups (**Costa et al. Carbon 2015, Ek Weis et al. Chem. Eur. J. 2015**).

The Department of Low Dimensional Systems was established in 2014, hence we review the activities of the Department during the year 2014 and also the previous activities of the group of Dr. Kalbac, Dr. Bastl and Dr. Krtil for the period 2010-2013. Since these activities are relatively broad this report focuses on the most important research directions, which are related to the previously or recently funded research projects.

In the period 2010-2014 the members of the Department of Low Dimensional Systems published as authors or co-authors in total **112** papers in impacted journals

C. Detailed description of our results in 2010-2014:

The institute can cover only personal costs of key scientist and the working space, hence the main research directions are closely related to the previously and recently funded projects. During the period 2010-2014 the members of the Department of Low Dimensional Systems were in charge of 13 projects, where the senior team members acted as principal investigators. (Dr. Kalbac 8 projects, Dr. Krtil 3 projects, Dr. Jirka 1 project and Dr. Plsek 1 project. Although the projects and research activities are getting interconnected, it is possible to define three main research directions:

- A) Spectroscopy and spectroelectrochemistry of carbon nanostructures
- B) Characterization of chemical composition and electronic structure of surfaces, interfaces and thin layers by photoelectron spectroscopy methods
- C) Rational design of the electrocatalytically active surfaces

Ad A)

1) The project entitled: **Spectroscopic and spectroelectrochemical study of chemically doped carbon nanostructures** was realized in the period **2009-2012** and it was funded by Grant agency of the Academy of sciences. The principal investigators of the project was Dr. Kalbac. Our research work compared a charge transfer processes in different nanocarbon systems including fullerene peapods, double walled carbon nanotubes and graphene bilayers. In fullerene peapods the changes in the most important $A_g(2)$ mode induced by doping were found to be dependent on laser excitation energy, which indicate resonant character of the Raman signal enhancement for the nanotube embedded fullerenes (Kalbac et al. *J. Phys. Chem C* **2010**). The charge transfer between outer and inner wall carbon nanotubes was found to be a function of electronic type of these tubes. We discovered that to observe a charge transfer between the nanotube walls, the first van Hove singularity of the outer tube must be filled (Kalbac et al. *ACS Nano* **2010**, Kalbac et al. *Chemistry - A European Journal* **2011**). For graphene bilayers we developed a new approach based on isotope labelling, which allows to address the doping of individual layers by Raman spectroscopy (Kalbac et al. *Nanoletters* **2011**). Furthermore, in graphene bilayers we experimentally observed formation of distinct electronic states which lead to the resonantly enhanced Raman signal depending on rotational angle between the graphene layers (Kalbac et al. *J. Phys. Chem. Lett* **2012**). The experimental work on this project was mostly realized by Dr. Kalbac, the interpretation of the results was done jointly with other co-authors of the papers. The results of the project were peer reviewed by the panel of the grant agency and it obtained the highest evaluation remark –finished with excellent results.

2) The bilateral project: **Electrochemical doping of single walled carbon nanotubes –individual and in bundles** funded by Czech Ministry of youth and education was realized between **2009-2012**. The PI of the project was Dr. Kalbac, the partner institution was MIT, Cambridge (the group of prof. Mildred Dresselhaus and group of prof. Jing Kong). We succeed to prepare individual single walled carbon nanotubes and to study their behaviour during doping using in situ Raman spectroscopy (Hsieh et al. *Applied Physics Letters* **2010**). We discovered that defects in nanotubes broaden the Raman resonance window (Kalbac et al. *Nanoletters* **2010**). Also we contributed to the discovery of electronic Raman scattering in metallic carbon nanotubes (Farhat et al. *Phys. Rev. Lett* **2011**). Our studies were extended to graphene where we succeed to experimentally demonstrate a quantum interference effect in graphene (Kalbac, Reina -Cecco et al. *ACS Nano* **2010**). (The experiments on graphene were performed mostly by Dr. Kalbac, the spectroscopy study of carbon nanotubes were realized jointly with co-authors from MIT. The interpretation of the results was performed jointly by all co-authors.) The results of the project were peer reviewed by an independent committee and obtained the highest evaluation remark –finished with excellent results.

3) Project funded by Czech Science Foundation: **Magnetic properties of carbon nanostructures in neutral and doped state (2010-2014)**. Dr. Kalbac was the coordinator and principal investigator of the project. The project was solved jointly with Institute of Physics, Prague. A novel methodology for determination of content of remnant magnetic catalyst was introduced (Bittova et al. *J. Phys. Chem C*

2011, Pacakova -Bittova et al. Physical Chemistry Chemical Physics 2013). Furthermore, our work led to development of new methods for purification of double walled carbon nanotubes (**Kominkova et al. Carbon 2014**). We also described the role of Li doping in C₇₀ fullerene peapods (**Kalbac et al. Nanotechnology 2014**). The tasks of the group of Dr. Kalbac included mainly to synthesize the samples, their characterization and purification and the performing the doping experiments. The measurements of magnetic properties were performed at the partner institution (Institute of Physics, Prague).

4) The project entitled **Spectroscopy and spectroelectrochemistry of graphene and graphene multilayers**, duration **2012-2016** is funded by Czech Science Foundation. The principal investigator of the project is Dr. Kalbac. We succeed to control formation of add layers during the graphene growth process by CVD (**Kalbac et al. Carbon 2012**). We extended our isotopic labelling approach, which enabled us now to address individual graphene layers in general graphene multilayer samples (**Kalbac et al. J. Phys. Chem. C. 2012**). Using heating experiments performed on isotopically labelled graphene we could monitor the process of stress transfer in graphene multilayers (**Kalbac et al. Chemistry - A European Journal 2012**) and also in fluorinated graphene layers (**Costa et al. Carbon 2015**). The isotope labelling together with theoretical modelling (performed by the group of prof. Krasheninikov, University of Helsinki) also helped to understand the defect creation in graphene multilayers by ion bombardment (**Kalbac et al. Adv Mat., 2013**). A specific modification of graphene layers by polyelectrolytes also enabled us to achieve extreme doping levels of graphene by electrochemistry. (**Kominkova et al. RSC Advances 2014**).

5) In 6/2013 we started a large ERC-CZ project funded by Czech Ministry of youth and education: **From Graphene Hybrid Nanostructures to Green Electronics (6/2013-6/2018)**. The aim of the project is to develop new approaches to study novel electronic devices based on low dimensional materials. Recently a revolutionary transistor architecture called BISFET (Bilayer pseudospin field effect transistor) has been suggested. The fundamental principle of this architecture is based on two layers with slightly different doping that could form the Bose- Einstein condensate. These layers can be formed from graphene. Our group demonstrated that using isotope labelling, it is possible to monitor the charge on the graphene layers in the graphene bilayers (**Frank et al. Nanoscale 2014**), which is crucial for the BISFET development. In order to prepare high quality graphene samples, which are required for electronic devices and to improve the graphene transfer process, we studied growth on different faces of copper single crystal and we succeed to identify the face specific interaction between graphene and Cu (**Frank et al. Carbon 2014**). The transfer process of graphene includes heating of the sample to remove the sacrificial polymer layer, hence we also analysed the behaviour of the AB stacked two layered graphene during heating procedure and we identified the changes in the doping and strain in these samples (**Ek Weis et al. J. Phys. Chem. Lett. 2014**). To modify the electronic properties of graphene samples we employed fluorination, which we unambiguously confirmed by XPS. We discovered that fluorination is fastest for single-layer graphene, slower for turbostratic and the slowest for AB stacked bilayer (**Ek Weis et al. Chem. Eur. J. 2015**). The experimental work on this project was performed by members of the Department of Low Dimensional Systems, the interpretation of the results was done jointly with Dr. Frank from Department of electrochemical materials.

6) The bilateral project **Isotopically labelled graphene layers (2013-2015)** funded by Czech Ministry of youth and education, is a follow-up project dedicated to support collaboration and scientific exchange between group of Dr. Kalbac, the group of prof. M. Dresselhaus and prof. J.Kong (both MIT, Cambridge). Dr. Kalbac is the principal investigator of the project. We contributed to the identification method of the AB stacked isotopically labelled bilayer graphene by Raman spectroscopy (**Fang et al. Nano Lett 2013**) and discovered specific charge distribution between graphene layers in doped AB stacked bilayer (**Araujo et al. Scientific reports 2013**). Our joint activities were also recently reviewed in (**Frank et al. Accounts of chemical research, 2015**). The doping experiments were performed mostly by Dr. Kalbac, while the interpretation of the data was done jointly with collaborating groups.

7) The applied research project: **Carbon nanostructures for applications in sensors**, duration **2013-2016** is funded by Czech technological agency. Dr. Kalbac is the principal investigator of the project. The other partners of the project are The University of West Bohemia, Centre of organic chemistry (private company) and Tesla Blatna (private company), which is also a coordinator of the project. The project is aimed to develop, test and commercialize new gas sensors based on carbon nanostructures. The main task of the group of Dr. Kalbac is preparation and testing of carbon nanotube based sensors. During the two years of the project realization we succeed to prepare and tested new composites based on carbon nanostructures with promising properties for sensing of NO_x and NH₃.

8) The project entitled: **Nanocapsules for targeted delivery of radioactivity** is funded by European commission under Initial Training Networks Program, the duration of the project is 2012-2015. Dr. Kalbac is the principal investigator in this project representing JH IPC. This large project connects 9 partners from EU and the main task is to train young scientist in the progressive field of science. The group of Dr. Kalbac organized one network meeting, one training and one hands on school on spectroelectrochemistry. A student Ana Santidrian is supported from the project, she joined the group in 1/2013. The main scientific task of the Department of Low Dimensional Systems is to perform thermogravimetric, spectroscopic and spectroelectrochemical studies of functionalized/filled samples of carbon nanotubes.

ad B)

1) Project supported by Czech Science Foundation: **Preparation characterization and chemical properties of gold nano -alloys on a support (2008-2010)**. The PI of the project was Dr. Plšek. Model catalysts consisting of bimetallic Au–Pt nanoparticles on cerium oxide supports were prepared by Nd-YAG pulsed laser ablation and deposition and investigated using X-ray photoelectron spectroscopy and temperature-programmed desorption of isotopically labelled carbon monoxide ¹³C¹⁸O. The experimental results proved that the majority of the sites from which desorption occurred were likely present on the bimetallic phase. All experiments were carried out exclusively by members of the group (**Plšek et al. Journal of Catalysis 2013**). The effect of deposition method on gold growth on clean and oxidized tungsten was examined and the influence of high-kinetic energy particles produced by pulsed laser deposition in vacuum on the morphology of deposits was investigated. In contrast to conventional vacuum evaporation the pulsed laser deposition suppressed gold superstructure formation and caused reduction of the oxide interlayer. Displaying of the field emission images in logarithmic scale was introduced and it was demonstrated that it can provide new information about metal nanoparticles deposited on thin oxide layers (**Plšek et al. Applied Surface Science 2014**).

2) The project: **Nanostructured materials for catalytic, electrocatalytic and sorption applications (2007-2011)** was supported by Academy of Sciences of the Czech Republic. The principal investigator of the project was prof. Z. Samec (Department of Biomimetic Electrochemistry), Dr. Bastl was a member of the research team. Gold surface attachment of altitudinal molecular rotors provided with ten -HgSCH(2)CH(2)SCH(3) "tentacles" has been monitored with X-ray photoelectron spectroscopy (XPS), ellipsometry and scanning tunnelling microscopy. The rotors appear to adsorb on the gold surface in the intended orientation, with rotor axle parallel to the surface, without any inclination for multilayer growth. According to XPS data, the sulfur-containing tentacles start to be detectably oxidized within hours of exposure to air and can be removed by washing. The rotor molecules nevertheless remain firmly attached in the desired orientation. Compounds were synthesized at Dept. of Chem. and Biochem., Univ. of Colorado, Boulder, preparation of samples and their characterization by XPS important for determination of the mode of bonding of these complex molecules to surface by Dr. Bastl. (**Mulcahy et al. Journal of Physical Chemistry C 2010**) Dicarba-closo-dodecaboranedithiols 1,2-(HS)(2)-1,2-C₂B₁₀H₁₀ (1) and 9,12-(HS)2-1,2-C₂B₁₀H₁₀ (2), have been investigated as cage building blocks for self-assembled monolayers (SAMs). Using photoelectron and Auger electron spectroscopy we found that each positional isomer requires completely different conditions for the preparation of self-assembled monolayer on copper surfaces. The samples were prepared in Dr. Baše's laboratory

(Inst. Inorg. Chem. ASCR), characterization of surface composition and bonding of carborane thiol positional isomers to metal surface by Dr. Bastl (**Baše et al. Langmuir 2012**).

Ad C)

1) The project **Nanocrystalline oxides for selective anodic electrocatalysis** funded by Grant Agency of the Academy of Sciences of the Czech Republic was realized between **2009-2012**. The principal investigator of the project was Dr. Krtil. Following the DFT based single descriptor models of oxygen and chlorine evolution processes, treating both reactions as a sequence of single electron charge transport events, we have develop low temperature synthetic approaches to modify the local structure of the anticipated active site and characterized the resulting materials by means of the X-ray absorption spectroscopy (**Petrykin et al. Chem. Mat. 2011, Macounova et al. Catal Today 2013, Abbott et al. J. Electrochem Soc. 2015**). The active site modification effects were assessed in terms of the actual reaction mechanism and catalysts selectivity. The targeted breaking of the cus site stacking results in effective suppression of chlorine evolution during sea water electrolysis (**Petrykin et al. Angew. Chem. Int. Ed. 2010**). The stacking of the binding and non-binding sites introduced by Ni and Co doping of the surface of a RuO₂ based oxide catalyst surface was also explored in effective steering the selectivity of the direct epoxidation of ethane to ethylene oxide which is selectively promoted by Co doping (**Jirkovsky et al. J. Am Chem. Soc. 2011**). A similar approach exploring the in-situ formation of a Pb(IV) oxo moieties at the surface of polycrystalline Pt was explored in selective oxidation of ethanol in alkaline fuel cells (**He et al. J. Am Chem. Soc. 2012**). The application of Pb(IV) based acetate leads to a formation of Pb based surface moieties which direct the adsorption of the target ethanol molecule via μ bridge affecting considerably the effectiveness of the ethanol oxidation process.

2) A project **Surface Electrochemical Reactivity in Electrocatalysis, A combined Theoretical and Experimental Approach (2009-2012)** was supported European Commission. The principal investigator of the project was Dr. Krtil. The research was done in a close collaboration with prof. T. Jacob (University Ulm). The collaborating institution was responsible for the development of the DFT models while our group was solely responsible for all synthetic and spectroscopic experiments. A combined theoretical and experimental approach was elaborated to characterize the behaviour of the alloy at conditions relevant to electrocatalytic reaction conditions. Density functional theory (DFT) was used to develop systematic tools rationalizing driving forces potentially affecting the surface stability of the binary alloy based catalysts relevant to the polymer electrolyte membrane fuel cells (PEMFC). The theoretical predictions were experimentally verified by means of the in-situ electrochemical X-ray absorption spectroscopy (XAS) working in extended absorption X-ray fine structure (EXAFS) mode. The combined theoretical and experimental approach was employed to outline intrinsic stability restrictions of the Pt-Ni binary system (**Hoffmannova et al. Langmuir 2013**) as well as topological sensitivity of the surface segregations in Au-Pd binary system (**Okube et al. ChemElectroChem 2014**). The experimental data were explored in formulation of a conceptual framework clearly showing that the actual active sites are present at the catalysts surface only under reaction conditions hence the synthetic approaches may generate merely precursors of the active sites (**Mueller et al. PhysChemChemPhys 2014**). This concept summarizes the restrictions of the rational design approach commonly used in alloy catalyst design which disregards the reaction conditions triggered surface structure changes.

Facility and instrumentation development

In the year 2014 we finished construction of the clean room. This dust-free environment (ISO 6) will elevate our studies of low dimensional materials as it enables to implement photolithography in nanodevice fabrication and processing of these materials under well-defined conditions. During the 2010-2014 period we also reconstructed and upgraded our labspace (4 laboratories).

We also built two chemical vapour deposition reactors for synthesis of isotopically labelled graphene and new apparatus for graphene fluorination at low pressure. For advanced Raman measurement we purchased new Witec Raman spectrometer with ultra-fast and high-sensitivity back illuminated CCD

detector. In co-operation with Institute of physics and Charles University we installed combined confocal magneto-Raman system, which serves for fast Raman mapping in temperatures down to 1.8 K and magnetic fields up to 14T.

Collaboration

The scientific cooperation is distinguished as important aspect of the research activities in the Department of Low Dimensional Systems. The group of Dr. Kalbac was formerly part of the Department of electrochemical materials, hence a close cooperation between these two departments is kept active. Since 2013 we published jointly 13 publications. A close collaboration was established with Institute of Physics for realization of advanced measurements of the Raman spectroscopy in magnetic field. These activities are supported by Grant Agency of Czech republic project (Magnetic properties of carbon nanostructures in neutral and doped state), which resulted in 7 joint publications. In the field of applied research we cooperated with The University of West Bohemia, Center of organic chemistry (private company) and Tesla Blatna (private company) on the development of the carbon nanostructure based gas sensor. The cooperation is supported by Czech technological agency. The important international cooperation included former group of prof. Dunsch (IFW Dresden) and groups of prof. Dresselhaus and prof. Kong (MIT, Cambridge). The corporation with MIT Cambridge was supported by two projects (Electrochemical doping of single walled carbon nanotubes –individual and in bundles, Isotopically labelled graphene layers) and resulted in total in 12 joint publications in the period between 2010-2014. The European commission funded project under Initial Training Networks Program (The nanocapsules for targeted delivery of radioactivity) was also vital source of collaboration activities and exchange of students between partner laboratories.

Due to wide applicability of the XPS methods in many areas of chemistry, physics and technology the group of Dr. Bastl had numerous collaborations within the J. Heyrovsky Institute as well as with other academic and university laboratories of basic research in Czech Republic and abroad (USA, Japan, India, France, Slovakia) and contract based cooperation with institutions of applied research (e.g. Teva Czech Industries s.r.o., Surface Treat Trutnov s.r.o., UniCRE Záluží, 40-30 Grenoble, France). In addition to photoelectron spectroscopy temperature programmed desorption and field electron emission techniques are used to investigate adsorption/desorption processes on solid surfaces.

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Spectroscopy
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A. Personal Structure at 12/2014

In 12/2014 the department of spectroscopy consisted of 5 full time equivalent (FTE) scientists, 1 technical, 4 PhD students and Master and Bachelor students. Out of those employees, 5 scientists (Profs. Civiš, Zelinger, Drs. Kubát, Kubelík and Ferus can be considered as key personal (although all of them are partially financed by grant money). Dr. Kaprálová (only 0.2 FTE) as well as the technician Ing. Ivánek (0.5 FTE) were exclusively paid by grant money. Moreover, there are presently 8 students working in the department.

B. Research Activities at a Glance

The main activities of the Department of spectroscopy can be summarised as „development of novel techniques of UV/Vis, infrared and microwave spectroscopy and their applications in astrophysics, material sciences and biology.“ The applications are mainly connected with running/recent grants.

First of all, for more than 15 years, our department has been focusing on theoretical and experimental studies related to the prebiotic chemistry. Several works have been published in high impacted journals (e.g. Proceedings National Academy of Sciences, IF = 9.8; Journal of the American Chemical Society, IF = 11.44). The formamide-based synthesis of nucleic acids is considered as a nonaqueous scenario for the emergence of biomolecules from inorganic matter. These experiments aimed to capture all the steps of those chemical transformations lead to the formation of all canonical nucleobases during the impact of an extraterrestrial body on an early Earths' surface. (**Ferus et al. J. Am. Chem. Soc. 2012**). The department cooperated on development of a comprehensive mechanistic model, which accounts for all the steps of formamide-based in plasma chemistry. The work concerning an origin of basic molecules of the genetic code was identified by the Editorial Board of P.N.A.S. journal as a part of a series reporting findings of exceptional significance (**Ferus et al PNAS 2015**).

Beside our initiatives in research field Origin of Life our department has applied the techniques of high resolution FTIR spectroscopy and isotopic labelling to study processes on titanium dioxide photoactive surface. In this research we used our long-lived experience in high resolution infrared spectroscopy (see research direction 3) and know-how of Department of Electrochemical Materials in synthesis of titanium dioxide to obtain unique information on titania surface (**Civiš et al. J. Phys. Chem. C 2014**).

Our department has also developed a novel technique for sensitive detection of singlet oxygen in solid samples based on singlet oxygen-sensitized delayed fluorescence (**Mosinger et al. Langmuir, 2010**). We used this and other spectroscopic techniques to study photoactive materials and systems to investigate elementary processes occurring after excitation especially formation of $O_2(^1\Delta_g)$ and correlate the data with the nature of the photosensitizer environment. Our results contribute to formulation of novel more efficient materials with application in biology and environmental science.

In the years 2010-2014 we have applied a laser ablation of metal targets method for a precision laboratory measurements of time resolved spectra of alkali and alkali earths metals in the infrared range using time-resolved Fourier transform infrared spectroscopy. The 6g, 6h, and 7h levels have been observed for the first time and compared with ACE solar spectra, in addition to updated energy values of the other new levels and the f-values for the transitions involving these levels (**Civiš et al. Journal of the Optical Society of America. B 2012; Civiš et al. Astronomy & Astrophysics. September 2012; Civiš et al. Astronomy & Astrophysics. May 2012; Civiš et al. Astronomy & Astrophysics. June 2012), Civiš et al. Astronomy & Astrophysics. 2013**). In addition to these data we also calculate transition probabilities and line and oscillator strengths for a number of metal transitions (**Civiš et al. Phys. Review. 2010; Civiš et al. Physical Review 2010**).

Detailed description of our results in 2010-2014:

The activities of the department might be divided in **4 main research directions**:

- 1) "Origin of Life",
- 2) "UV/Vis and IR spectroscopy of photoactive molecules and materials"
- 3) "Time-resolved spectroscopy of radicals and molecular ions"
- 4) "Development of new types of lasers a applications in industry"

Within those 5 years, the department published 71 papers in impacted journals with 515 citations (according to WOS, March 11, 2015). This report focuses on the highlights connected with defined projects and supported by selected papers:

Research Direction 1: Origin of life

Theoretical and experimental studies related to the prebiotic chemistry are a central goal of our research. The question related to prebiotic chemistry is to answer what were the sources of the larger organic molecules that made up the first self-replicating systems. One of the best approaches to solving this problem is simulation of the environment in which life is presumed to emerge. A typical method is to use an external source to excite gas mixtures that simulate the primitive planetary atmosphere and then analyze the products. Examples of external energy sources for excitation of small inorganic molecules are electrical discharges, high-energy particle or photon beams, and strong laser irradiation, which simulate cosmic rays in outer space, and sunlight as well as lightning discharge in the air.

- a) The formamide-based synthesis of nucleic acids is considered as a nonaqueous scenario for the emergence of biomolecules from inorganic matter. We scrutinized the chemical composition of formamide ices mixed with FeNi meteorite material treated with laser-induced dielectric breakdown plasma created in nitrogen buffer gas. These experiments aimed to capture the first steps of those chemical transformations that may lead to the formation of nucleobases during the impact of an extraterrestrial icy body containing formamide on an early Earth atmosphere. High-resolution FT-IR spectroscopy combined with quantum chemical calculations was used to analyze the volatile fraction of the products formed during such an event (**Ferus et al. J. Am. Chem. Soc. 2012**).
- b) The coincidence of the Late Heavy Bombardment (LHB) period and the emergence of terrestrial life about 4 billion years ago suggest that extraterrestrial impacts could contribute to the synthesis of the building blocks of the first life-giving molecules. We simulated the high-energy synthesis of nucleobases from formamide during the impact of an extraterrestrial body. A high-power laser has been used to induce the dielectric breakdown of the plasma produced by the impact. The results

demonstrate that the initial dissociation of the formamide molecule react with formamide to produce adenine, guanine, cytosine, and uracil. The two papers (**Ferus et al J. Phys. Chem. A 2014**; **Ferus et al PNAS 2015**) addresses one of the central problems of the origin of life research, i.e., the scenario suggesting extraterrestrial impact as the source of biogenic molecules. Likewise, the results might be relevant in the search of biogenic molecules in the universe. This work has been cited by international and Czech media:

<http://www.rsc.org/chemistryworld/2014/12/asteroid-bombardment-may-have-made-building-blocks-life-early-earth-dna-formamide>
<http://www.popularmechanics.com/science/space/deep/how-comets-asteroids-could-have-started-life-on-earth>
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<http://www.livescience.com/49049-beginning-of-life-experiment.html>
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http://www.huffingtonpost.com/2014/12/10/spark-of-life-earth-simulate_n_6295796.html?1418223723
<http://www.examiner.com/article/nucleic-acids-created-asteroid-like-conditions-for-the-first-time>
<http://www.sciencemag.org/content/346/6215/1279.full.pdf?sid=09154312-148a-4977-8502-87d19579f181>

Research Direction 2: UV/Vis and IR spectroscopy of photoactive molecules and materials

We continued our collaborations with several institutes within the Czech Republic especially with Faculty of Natural Sciences of Charles University and Institute of Inorganic Chemistry CAS, and shared our expertise in transient absorption, time-resolved luminescence spectroscopies and steady-state infrared spectroscopy with those partners. We participated in formulation of the photoactive molecules and materials, and contributed by development of appropriate techniques of spectroscopy measurements and evaluation of the data, which were essential for those projects. The syntheses of the materials and their basic characterization were performed in cooperating teams. Here, several examples of such collaborations are described.

1. Development and application of novel technique of singlet oxygen detection

Singlet oxygen, $O_2(^1\Delta_g)$, plays a key role in many important photochemical and photobiological processes e.g. in photodynamic therapy of tumors.

- a) We developed novel technique of $O_2(^1\Delta_g)$ detection based on singlet oxygen-sensitized delayed fluorescence (SODF). Strong SODF was observed for the first time for porphyrin photosensitizers encapsulated in polyurethane nanofibers and occurs only by the reaction of triplet photosensitizers with $O_2(^1\Delta_g)$. Other mechanisms, which is typical for solution was excluded. A simple model allows calculation of lifetimes of formation and decay and estimation of quantum yield of $O_2(^1\Delta_g)$ (**Mosinger et al. Langmuir, 2010**). Highly cited paper. The SODF technique was used for the imaging of $O_2(^1\Delta_g)$ inside of the nanofibers. The limitation of this method is in the small intensity of SODF, which strongly depends on the environment and/or diffraction-limited resolution of a several hundreds of nm. Cooperation with Department of Biophysical Chemistry (**Mosinger et al. J. Phys. Chem. B 2010**).
- b) This technique is limited to materials with immobilized photosensitizer triplets that are localized at specific sites within the polymer/solid material and cannot diffuse to a close contact. It was applied to evaluate formation and decay of $O_2(^1\Delta_g)$ in some types of photoactive nanofiber material, where the measurement using conventional phosphorescence method failed due to low intensity. The examples of such materials include polymeric nanofiber materials with low oxygen permeability (**Jesenská et al. J. Biomed. Materials Res. 2011**), with low concentration of photosensitizers (**Henke et al., ACS Appl. Mater. Interfaces 2013**), with high concentration of $O_2(^1\Delta_g)$ quenchers due to post-processing surface modifications (**Henke**

et al. *ACS Appl. Mater. Interfaces*, 2014), and in measurements at low temperatures (Suchánek et al. *J. Phys. Chem. B* 2014).

2. Optimization of photosensitizers and materials for photobiological and environmental processes

We carried out measurements and evaluation of photophysical properties of photosensitizers and materials by steady-state and time-resolved absorption and luminescence spectroscopy for application in photobiology and medicine. Elementary processes occurring after excitation especially formation of $O_2(^1\Delta_g)$ were investigated and correlated with the nature of the sensitizer environment. The photophysical measurements are essential for applications as the environment may influence the behavior of $O_2(^1\Delta_g)$ and other reactive species significantly.

- a) Newly synthesized zinc phthalocyanine photosensitizer for photodynamic therapy of tumor (PDT) was selected on the basis of our photophysical measurements. The high photodynamic activity was confirmed on prototypic malignant HeLa cells. The unique spatial arrangement of imidazolyl substituents that covers the hydrophobic macrocycle completely precludes aggregation. The bulky substituents on the periphery slightly decrease high singlet oxygen quantum yield typical for phthalocyanines due to limited diffusion of oxygen to the phthalocyanine core. Cooperation with Faculty of Pharmacy, Charles University, Hradec Králové and University of Kuwait (**Makhseed et al. Chem. Commun. 2013**). Highly cited paper.
- b) We formulated and fabricated several types of polymeric nanofiber materials, which was tested for photobiological and environmental applications. An example of such material is based on sulfonated polystyrene nanofibers with externally bound porphyrin molecules. It consists of a polystyrene core and a shell that is capable of performing multiple tasks, e.g., photodisinfection, decontamination, and separation using the same material. Our measurements allow estimation of diffusion length of $O_2(^1\Delta_g)$, which limits efficient antibacterial action to close proximity to nanofiber surfaces. Cooperation with Faculty of Sciences, Charles University (**Henke et al. ACS Appl. Mater. Interfaces, 2013**). Highly cited paper.
- c) We optimized the photophysical properties of medical grade polymeric nanofiber materials with significant antiviral properties due to $O_2(^1\Delta_g)$ formation (**Lhotáková et al. PLoS ONE 2012**). Similar type of the material was successfully used for the antibacterial treatment of infected wounds in patients, which is usually time-consuming and costly. This method is an alternative of conventional antibiotics treatment, which may failed due to increased resistance of bacteria. Cooperation with and Faculty of Sciences, Charles University (**Arenbergerová et al. Exp. Dermatol. 2012**).
- d) We found that water-soluble sulfonatocalixarenes are not suitable transportation vehicles for porphyrin based drugs in PDT due to strong interactions between individual components. Our measurements showed partial intramolecular charge transfer that proceeds predominantly from the ionized groups of calixarene to the methylpyridinium peripheral substituents of porphyrin. The redistribution of electron density within complexes can be linked to the increase of quenching efficiency of the excited singlet states resulting in low concentration of $O_2(^1\Delta_g)$. Cooperation inside Institute of Physical Chemistry and with Institute of Inorganic Chemistry and University of South Bohemia. (**Kubát et al. Phys. Chem. Chem. Phys. 2011**).
- e) We measured photophysical properties of a series of photoactive compounds formed by coordination of ligands to the $\{Mo_6I_8\}$ cluster core *via* carboxylic functions. These clusters are excellent producers of $O_2(^1\Delta_g)$, however, their photostability is lower than porphyrins and other

common photosensitizers. Cooperation with Institute of Inorganic Chemistry CAS (**Kirakci, Inorg. Chem. 2014**).

- f) Intercalation of photosensitizers into layered double hydroxides (LDHs) affects photophysical and photochemical properties; however, such important features as formation of $O_2(^1\Delta_g)$ may remain preserved. This finding opens application of LDHs for antibacterial treatment e.g. in water disinfection. Cooperation with Institute of Inorganic Chemistry CAS (**Káfuňková et al. Chem. Mater. 2010**). Highly cited paper.
- g) Europium and terbium layered hydroxides with intercalated porphyrin were also prepared. A slight variation of the synthetic procedure led to the metal-organic framework (MOF). The ability of the MOF to produce $O_2(^1\Delta_g)$ with a relatively long lifetime of 23 μs motivates us to design novel metal organic framework with tuned photoresponses and porosity (see research plans in 2015-2019). Cooperation with Institute of Inorganic Chemistry CAS and Université de Versailles, France (**Demel et al. Inorg. Chem. 2013**). Highly cited paper.

3. Application of FTIR spectroscopy and isotopic labelling to study processes on photoactive surface of titanium dioxide

In this research we used our long-lived experience in high resolution infrared spectroscopy (see research direction 3) and know-how of Department of Electrochemical Materials in synthesis of titanium dioxide to obtain unique information on titania surface.

- a) The spontaneous and UV light-induced oxygen-isotope exchange took place between the vacuum-calcined solid $Ti^{18}O_2$ and CO_2 . The rate of oxygen-isotope exchange is highly sensitive to the conditions of the titania pretreatment, vacuum-annealed $Ti^{18}O_2$ at 450 °C exhibited a very high spontaneous oxygen exchange activity. The photocatalytic formation of methane, acetylene, and $C^{16}O$ released from the $Ti^{18}O_2$ surface was observed after irradiation by an excimer laser (**Civiš et al. J. Phys. Chem. C. 2011**).
- b) Formic acid underwent photocatalytic decomposition over $Ti^{18}O_2$, and CO_2 , CO , and H_2O isotopologues containing ^{18}O atoms were formed. Formic acid does not exchange oxygen atoms with the lattice oxygen atoms of $Ti^{18}O_2$ spontaneously and/or during photocatalytic decomposition; moreover, it blocks the active sites on the lattice (**Civiš et al. J. Phys. Chem. C. 2012**).
- c) High-resolution FT-IR spectroscopy combined with quantum chemical calculations was used to study the chemistry of OCS-disproportionation over the reduced surface of isotopically labelled, nanocrystalline TiO_2 . Using quantum chemical calculations we proposed a plausible mechanistic scenario, in which two reduced Ti^{3+} centres mediate the reaction of the adsorbed OCS molecules forming CS_2 and CO_2 (**Civiš et al. Chem. Commun. 2014**).
- d) Isotopic exchange of oxygen atoms between gaseous $C^{18}O_2$ and $Ti^{16}O_2$ nanoparticles has been studied using high-resolution Fourier transform infrared absorption spectroscopy and density functional theory calculations. The unprecedented faster kinetics on high-surface-area titania made from Ti(IV) isopropoxide points at fundamental differences between this material and the usual nanocrystalline TiO_2 (anatase). The experimental observations are rationalized by calculations of the activation barriers for oxygen exchange on a $(TiO_2)_{10}$ cluster. The calculations confirmed that titanium nanoclusters have much lower barriers for O atom exchange than previously found for the oxygen defect sites on the single crystal (101) anatase surface (**Civiš et al. J. Phys. Chem. C 2014**).

Research Direction 3: Time Resolved Spectroscopy of Radicals and Molecular Ions

1. Time-Resolved Fourier Transform Emission Spectroscopy.

- a) Time-resolved spectroscopy (TRS) is a wide-spectrum technique used for studying the dynamics of chemical reactions, or the dynamic properties of molecules, radicals and ions in liquid, gas and solid states. The presented part of our research is focused on the development and application of a time resolved system based on commercially available continuously scanning high resolution interferometer and its modification for time resolved Fourier transform spectroscopy (TR-FTS). Our TR-FTS was used for emission measurement of He/CH₄ in a positive column discharge (**Civiš et al. J. Phys. Chem. A 2012**). The laboratory discharge study of HNC/HCN ratio in different type of the discharged precursors has great value to theoretical modelling of the interstellar chemistry of HNC and HCN molecules.
- b) Formamide is one from very important astrophysical molecules which stays behind of building blocks of large organic molecules (bases of nucleic acids) in the early stage of our planet. In the emission study of laser spark formamide decomposition we have identified the fragmentation of formamide into small radicals such CN, NH, CH and highly excited molecules (CO) (**Ferus et al, J. Phys. Chem. A 2011**).
- c) The environmentally important decomposition of halogenated species CF₃Br and CF₃CHFCF₃ in helium discharge plasma was investigated by time-resolved high-resolution Fourier transform infrared emission spectroscopy. Contrary to classical pyrolysis, a deeper fragmentation of precursors up to atoms and lower molecular species was observed in agreement with a kinetic model based on radical chemistry (**Ferus et al. Plasma Chemistry and Plasma Processing 2011**).
- d) Excitation of helium Rydberg states and doubly excited resonances in strong extreme ultraviolet fields were studied using Full-dimensional quantum dynamics and exponentially tempered Gaussian basis sets (**Kapralova et al. J. Chem. Phys. 2013**).

2. The laser ablation of metal targets

- a) Precision laboratory measurements are presented for Li, Na, K, Cs atoms in the infrared (including many new lines not measured previously in the laboratory) range using time-resolved Fourier transform infrared spectroscopy. The 6g, 6h, and 7h levels of alkali metals I are observed for the first time and compared with ACE solar spectra, in addition to updated energy values of the other new levels and the f-values for the transitions involving these levels (**Civiš et al. Journal of the Optical Society of America. B 2012; Civiš et al. Astronomy & Astrophysics. September 2012; Civiš et al. Astronomy & Astrophysics. May 2012; Civiš et al. Astronomy & Astrophysics. June 2012**).
- b) Although solar spectra contain a lot of Ca I and Mg I infrared (IR) lines, no laboratory-measured spectra of these atoms have been reported for wavenumbers below 2000 cm⁻¹. In our study (**Civiš et al. Astronomy & Astrophysics. 2013**), the Ca I spectra in the 1300-4500 cm⁻¹ range and Mg I spectra in the 1300-4500 cm⁻¹ range. We performed a time-resolved Fourier transform infrared spectroscopy study of a plasma created by the laser ablation of MgF₂ and CaF₂ targets in a vacuum. The oscillator strengths (f-values) were calculated using quantum defect theory (QDT).
- c) The time-resolved infrared emission spectrum of Ag and Au was recorded in the 1300-3600 cm⁻¹ spectral region using the time resolved Fourier transform infrared spectroscopy. The line classification was performed using relative line strengths expressed in terms of transition dipole matrix elements calculated with the help of the Fues model potential; these calculations

show agreement with the large experimental and calculated data sets available in the literature. In addition to these data we also calculate transition probabilities and line and oscillator strengths for a number of transitions in the 1300- to 5000 cm^{-1} range between $(4d(10))nl(j)$ states of Ag and Au (Civiš et al. *Phys. Review.* 2010; Civiš et al. *Physical Review* 2010).

d) The infrared emission spectra additional metals have been analysed and theoretically assigned using Quantum defect theory (Zn, Cu, Sr, In and Rb). Due to a large number of published papers we have excluded these citations from this report.

3. Laser induced breakdown spectroscopy (LIBS) and selected ion flow tube mass spectrometry (SIFT-MS) of explosives

- a) A novel high-energy explosive material, FOX-7 (1,1-diamino-2, 2-dinitroethylene), was studied using a combination of laser-induced breakdown spectroscopy (LIBS) and selected ion flow tube mass spectrometry (SIFT-MS). The LIBS technique uses short laser pulses (ArF excimer laser) to convert small quantities of a sample into plasma and to induce the emission of its molecular fragments or atoms. SIFT-MS was used to determine concentrations of trace gases and vapors of the products in real time (Civiš M. et al. *Anal. Chem.* 2011).
- b) Four additional types of explosives were studied using a combination of LIBS and SIFT-MS. This study represents the first employment of SIFT-MS to study the release of NO, NO(2), HCN, HNO(3), HONO, HCHO and C(2)H(2) after a laser-induced breakdown of pure explosive compounds HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane), RDX (1,3,5-trinitro-2-oxo-1,3,5-triazacyclo-hexane), PETN (pentaerithryl-tetranitrate) and TNT (2,4,6-trinitrotoluene). Electronic bands of the CN, C₂, NH and OH radicals together with atomic lines of oxygen, nitrogen and hydrogen were identified using emission spectroscopy. Additionally, scheme of chemical reactions responsible for the formation of the observed species was proposed (Sovová et al. *Analyst* 2010).

Research Direction 4: Development of new type of lasers and detection techniques and their application in industry

- a) One of the major experimental problems of high resolution spectroscopy is an achievement of high sensitivity over reasonable large spectral range. The solution concerns many fields, such as fundamental physics, metrology, trace gas detection, atmospheric optics, molecular dynamics, reaction kinetics, biology, etc. In the frame of common international project together with Prof. Eli Capon, École polytechnique fédérale de Lausanne (EPFL), Switzerland, we have used new laser sources in wavelength range of 1200-2000 nm (InAlGaAs/InP-AlGaAs/GaAs wafer-fused VCSELs). Their combination of laser design and fabrication expertise and high resolution spectroscopy of J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, resulted in a consortium that has concerned with the development of wafer fused long wavelength VCSELs emitting in 1200-2000 nm wavelength range and evaluation of different spectroscopy techniques based on these laser sources (Civiš, et al. *J. Quant. Spectrosc. Rad. Trans.* 2014).
- b) Vertical-Cavity Surface-Emitting Laser (VCSEL) diodes are among the youngest members of the semiconductor laser diode family. The main aim of our work was focused on the measurement of the basic properties (the spectral range of the laser emission, temperature and current tunability) of experimental VCSEL diode lasers based on GaSb operating in the infrared region around 4250 cm^{-1} . A high-resolution spectrometer was used in the emission setup for the laser diagnostic research. The absorption spectra of atmospheric pollutants like methane, carbon monoxide and

ammonia have been measured using these VCSELs for the first time (**Civiš et al. Opto-Electronics Review 2010; Matulková et al. Appl. Phys. B 2010**).

- c) In frame of international collaboration with Prof. Pavel Cheben from NRC Canada a spatial heterodyne Fourier-transform spectrometer was implemented with an array of optical fiber interferometers. This configuration generates a wavelength-dependent stationary interferogram from which the input spectrum is retrieved in a single shot without scanning elements. The spectral resolution of such developed system can be readily scaled up by incorporating longer optical fiber delays, providing a pathway toward surpassing current spectroscopy resolution limits (**Velasco, A. V. et al. Opt. Letters 2013**).
- d) New methods based on micromechanical sensing elements, including functional materials were investigated for gas sensing. The responses of various sensing systems, including graphene sensors, cantilever systems and microphones were compared. The first experimental results of analytical testing of MLGsheet-based sensing elements as well as results obtained for AFM-based silicon cantilever systems were presented (**Zelinger et al. Journal of Sensors and Sensor Systems 2015**).

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
Scientific team	Department of Structure and Dynamics in Catalysis

A. Personal Structure at 12/2014

In 12/2014 the Department of structure and dynamic in catalysis consisted of 13 scientists, 5 postdocs, 3 research assistants, one technician and 6 PhD students. The department has undergone a successful generational change within the last 5 years. Nevertheless, the long-time development of the department is reflected in the rather **high number of the members on emeritus positions** (ca. 0.05 full time equivalent (FTE) per person, given by Czech law regulations) - 4 scientists, one research assistant and one technician. The **high number of non-scientists** personnel (three research assistants and one technician) results from the specific requirements of catalytic research (complex catalytic apparatuses including pilot unit for deNO_x) and operation of MAS NMR spectrometer. The complexity of the approach required in the field of research covered by the department (from atomic level up to industrial applications) requires cooperation of a high number of co-workers reflected in rather high number of scientists. Out of the **9 non-emeritus scientists**, 6 scientists (Drs. Dedecek, Sobalik, Rathousky, Sazama, Tabor, Pashkova) can be considered as key personal although all of them are partially financed by grant money (due to regulations of the Czech grant agencies). Also other members of the department were in last five 5 years financed partially or exclusively (two postdoc and one research assistant, in 2014) by grant money. Nevertheless, due to the regulations of Czech grant agencies allowing maximum three years projects, number of researchers financed by grant agencies varies each year. The linkage of the department to the international scientific community is reflected in the fact that four young members of the department (two key scientists and two postdocs) are from abroad (EC). Beside standard members of the department, there are presently two high school students working in the department.

B. Research Activities at a Glance

The main activities of the Department of structure and dynamic in catalysis represent in general design of oxide-based materials structured up to nano or atomic level exhibiting unique properties, and application of these material in a wide area covering e.g. (photo)catalysis, high-tech applications (photovoltaic, electrochromic, and chemical sensing).

The experience of the members of the department and its equipment allows uniquely (in the Czech republic) cover the whole range of material research beginning from analysis, design and synthesis of materials at the atomic level through the sophisticated preparation of materials with unique properties, control of their texture, investigation/characterization of their properties and performance covering transport phenomena, understanding their properties at atomic level and ending large scale preparation of materials and their industrial applications (patents and development of technological processes). Two main groups of prepared and investigated materials represent zeolite based materials and organized mesoporous crystalline layers of metal oxides. For the characterization of developed materials and analysis of the structure/performance relationship of these materials a wide set of analytic methods based on a multi-spectroscopic approach covering MAS NMR, (diffuse reflectance)

UV-Vis-FTIR absorption/emission, FTIR, Mossbauer, and EPR spectroscopies (majority of them up to in situ/operando conditions) interpreted using quantum chemical calculations (in the cooperation with the Department of theoretical chemistry, group of Dr. Sklenak) is employed. Some of these methods were developed in the department. The multi-spectroscopic approach is further complemented by other methods as XRD, SEM, temperature programmed techniques, surface characterization by gas adsorption etc. The testing of (photo)catalytic properties and analysis of the structure/activity/selectivity relationship of designed materials represents finalization of the activity of the department. Thus, the department now uniquely covers the whole field of catalysis research from the preparation of catalysts, complex analysis of its structure, control and description of transport phenomena to (long time) catalytic testing. Moreover, the design, study and development of catalysts can be provided scaling from the laboratory measure up to the pilot plant scale. This is reflected in the fact that the department serves as scientific base for several Czech chemical industrial companies (e.g. Unipetrol a.s., Chemoprojekt a.s., Euro Support Manufacturing Czechia, s.r.o./Euro Support BV Nederland) and cooperates also with chemical companies from abroad (e.g. BP Chemicals).

Specifically, in the years 2010-2014 in the field of zeolite science were reached following breakthrough results:

a) The unique methodology for the analysis of Al siting in the framework T sites of Si-rich zeolites was developed (**Dedecek et al. J. Phys. Chem. C 2011**). This approach is complementary to the method for characterization of Al distribution between single Al and Al pairs in the zeolite (**Dedecek et al. Chem. Commun. 2001**) and allows thus complex analysis of the organization of Al atoms in the zeolite framework. The first conclusive presentation of the issue of Al organization in the zeolite framework and its relevance to catalysis was then concluded in a review (**Dedecek et al. Catal. Rev.-Sci. Eng. 2012**). The effort spent in this area has been completed by the first description of methods enabling tuning of Al distribution in Si-rich zeolites (**Dedecek et al. Chem. Mater. 2012**) and by description of procedures allowing control of Al distribution in large scale synthesis (**Bortnovsky et al. WO2011095140-A1**). b) Significant enhancement of activity and selectivity of high-silica zeolite catalysts in acid catalyzed reactions was reached by the controlled preparation of hierarchical zeolites (**Sazama et al. Angew. Chem. Int. Ed. 2013**). c) Successful mastery of Al-rich beta zeolite enabled to demonstrate the unique potential for application of the Al-rich beta zeolite in numerous acid- and redox-catalyzed processes (**Sazama et al. J. Catal. 2014**) and in a patent application on selective catalytic reduction of NO_x by hydrocarbon over Al-rich beta (**Sazama et al. PV2014-448 2014**). d) Implementation of a new method for characterization of local structures in zeolites by multinuclear MAS NMR allowed the description of the structure of framework Al-Lewis sites in zeolites (**Brus et al. Angew. Chem. Int. Ed. 2015**). e) Understanding of the relationship between local structure of metallozeolite catalysts and its activity (**Sazama et al. J. Catal. 2014**) resulted in the design of prototypes of catalysts for selective catalytic reduction of NO_x by ammonia (**Sazama et al. ID 62582640 and ID 25417681**). In the field of nanostructured oxidic materials were achieved following breakthroughs a) A completely new general approach to the design of nanocrystalline architectures of metal oxides at very mild conditions ("brick and mortar") was developed (**Szeifert et al. JACS 2010, Szeifert et al. Chem. Mater. 2012**). b) Mesoporous thin films for dye-sensitized solar cells were prepared (**Liu et al. ACS Nano 2010, Ivanova et al. JACS 2014**). c) Unique photocatalytic activity in the degradation of environmental pollutants (**Ivanova et al. JACS 2014**) and electrochemical oxygen generation (**Fominykh et al. Adv. Funct. Mater. 2014**) of developed nanostructured oxidic materials was demonstrated.

These above research activities were supported by several grants of **a)** Grant Agency of the Czech Republic: New category of zeolites with pentasil ring structure: Catalytic processes on zeolites with controlled distribution of aluminum atoms in the Framework (2011-2013), Catalysts for eliminating N₂O in the high temperature regime in the production technology of nitric acid (2014-2016), **b)** Grant Agency of the Academy of Sciences of the Czech Republic: NMR crystallography of extra framework sites in silicon rich zeolites (2009-2013), **c)** Technological Agency of the Czech Republic: Development of a process for the abatement of nitrogen oxides for industrial applications for especially demanding conditions (2011-2013), **d)** Academy of Sciences of the Czech Republic: Nanostructured materials for catalytic, electrocatalytic and sorption applications (2007-2011), **e)** Ministry of Industry and Trade of the Czech Republic: The upgrading of the Fischer-Tropsch synthesis products into alternative motor fuels and other refinery products and the research of their properties (2008-2010), Research and development of highly active catalyst based on ZrO₂ and its application for isomerization of C₅-C₆ hydrocarbons (2011-2014), **f)** Ministry of Culture: New materials and technologies for the conservation of the materials of historical monuments and the preventive care (2011-2015), **g)** European Commission: Innovative catalytic technologies & materials for next gas to liquid processes (2009-2013 7th FP), Center for innovations in the field of nanomaterials and nanotechnologies (2008-2010 European Regional Development Fund) and **h)** project granted by British Petrol (data in specific regime, 2013-2014).

C. Detailed description of our results in 2010-2014:

The activities of the department are represented in **two main research directions:**

1. Preparation of sophisticated oxidic materials with properties controlled on atomic or nanoscale level,
2. (Photo)catalytic application of oxidic materials with properties controlled on atomic or nanoscale level,

and in **two secondary research directions:**

1. Nanotechnologies for the preservation of historic artefacts,
2. Microporous and composite materials for sorption and membrane separation.

It has to be stressed that both main research directions are significantly interconnected. Materials prepared in the frame of Direction 1 are investigated as catalysts in under the Direction 2. The knowledge on the structure/activity relationship and description of the active site on atomic level represents the starting point for the development of optimized catalyst with properties tuned on atomic level. This approach requires deep cooperation of scientists of the department in individual research directions and high number of scientists involved in the research in the frame of both main research directions.

Within last 5 years the department published 65 papers in impacted journals (including papers which were already published on line in 2014, but appeared in printed version in 2015) and obtained 7 patents. **This report focuses on the highlights** connected with defined projects:

Research direction 1: Preparation of sophisticated oxidic materials with properties controlled on atomic or nanoscale level

1) Si-rich zeolites with controlled Al organization in the framework

Zeolites – crystalline microporous aluminosilicates represents today the widest and most important group of heterogeneous catalysts applied in industry. There are two complementary types of Al organization in the zeolite framework of Si-rich zeolites – siting of Al atoms in the crystallographically distinguishable framework T sites and distribution of Al atoms in Al pairs of Al-

O-(Si-O)₂-Al sequences as isolated Al atoms. Both parameters can dramatically affect activity and selectivity of zeolite catalysts due to the fact that extra-framework cationic species balancing negative charge of framework AlO₄⁻ tetrahedron represents active sites in zeolite catalysts. Thus, Al distribution controls the nature of cationic species while Al siting their location in the zeolite channel system, which controls shape selective (product, substrate, transition state) properties of zeolite catalysts.

a) Analysis of Al siting in the zeolite framework

In the case of Al siting there was only known (from our previous papers) that it is not random. First successful analysis of Al siting in the framework crystallographic sites in Si-rich zeolites was performed by us. Al atoms can occupy different sites in the framework and can represent quite different catalysts (ferrierite is one of most applied zeolites in catalysis) despite the same topology and chemical composition of the zeolite. This enables understanding of catalytic properties of zeolites on an atomic level. The problem was solved in deep coordination with Department of theoretical chemistry. (**Dedecek et al. J. Phys. Chem. C 2011**).

b) Analysis of Al distribution in the zeolite framework, its control and relevance for catalysis

This issue was introduced to the zeolite science by us. In the review we represent the first conclusive presentation of the issue of Al distribution and siting in the framework of Si-rich zeolites including definitions and methodology of analysis. Based on our results the Al distribution is shown as a key parameter for zeolite catalysts. This approach opens a way for rational control of zeolite properties and development of a new generation of catalysts. (**Dedecek et al. Catal. Rev.-Sci. Eng. 2012**).

The decisive role of Al distribution on the performance of zeolite catalysts was demonstrated on deNO_x reactions over metallozeolites. Al distribution controls the speciation of Fe, Cu and Co ions and thus, maximum possible concentration of sites balancing single Al atoms and active in C₃H₈-SCR-NO_x/H₂O, NH₃-SCR-NO_x and NO-NO₂, or balancing Al pairs and active in N₂O decomposition, and C₁₀H₂₂-SCR-NO_x/H₂O over zeolite catalysts (**Sobalik et al. Micropor. Mesopor. Mater. 2011, Sazama et al. J. Catal 2013, Sobalik et al. Appl. Catal. A-General 2014, Sazama et al. J. Catal 2014**). Significant effort was spent on the critical issue of the development of a new generation of catalysts with properties controlled by tuning of Al distribution – control of Al distribution in the zeolite. We focused on ZSM-5 zeolite as the most applied Si-rich zeolite catalyst. We gave the first description of methods enabling tuning of Al distribution in Si-rich zeolites. Further, the parameters controlling incorporation of Al to the zeolite framework were first time elucidated. Al distribution in the zeolite is a result of the interplay between the composition and structure of the zeolite building blocks originating from the synthesis gel, nature of structure directing agent(s) and physical parameters affecting this interplay. Polarization of the SDA by anions present in the gel, presence/absence of inorganic co-cation and reactivity of Si and Al source controlling their speciations were identified as key parameters. (**Dedecek et al. Chem. Mater. 2012, Pashkova et al. Micropor. Mesopor. Mater. 2015**). The results reported in the above papers represent a knowledge base for the control of Al distribution in large scale synthesis (**Bortnovsky et al. WO2011095140-A1**). The knowledge obtained opens a possibility for rational design of a new generation of zeolite based catalysts with high activity, selectivity, and durability as it was proved in the frame of industrial project granted by British Petrol (**data in specific regime**).

c) Local arrangement of active sites in the framework

Beside the bridging Bronsted acid sites of tetrahedral Al framework atoms, framework Al-Lewis sites were reported for zeolites. The presence of these sites can significantly affect selectivity of zeolite catalyst. By the implementation of a new method for characterization of local structures in zeolites by multinuclear MAS NMR the description of the structure of framework Al-Lewis sites in zeolites as well the nature of their precursor were identified. Framework Al-Lewis sites represent planar trigonal Al atoms three-coordinated to the zeolite framework and perturbed framework terminal Al atoms was suggested as their precursor. (**Brus et al. Angew. Chem. Int. Ed. 2015**).

The local arrangement of cationic sites in extra-framework positions of zeolite is essential for the understanding to catalytic processes over metallozeolites. We extended our previous work and identified in the detail Co, Fe and Cu siting and local geometry in ferrierite, ZSM-5 and beta zeolites

by the combination of Mossbauer and UV-Vis-FTIR and FTIR spectroscopies interpreted employing QCH calculations (Dept. of theoretical chemistry). (Sklenak et al. *J. Catal* 2010, Sklenak et al. *J. Phys. Chem. C* 2013)

2) Al-rich pentasil ring zeolites

Zeolite beta is the only one large pore highly stable zeolite with three dimensional channel structures and from these reasons one of four most important zeolite catalysts. The synthesis of Al-rich template-free BEA* zeolite (Si/Al 4.6) was mastered in a large laboratory scale. The concentration of active acid centers in the beta zeolite can be multiplied by the incorporation of high concentration of Al atoms in the framework without significant change of their properties. This provides potential for application of the Al-rich beta zeolite in acid-catalyzed processes which was successfully demonstrated. (Sazama et al., *J. Catal.* 2014). We reported also significant potential for the improvement of metallozeolite catalysts for deNOx processes. (Sazama et al. **patent application PV2014-448**)

3) Zeolites with hierarchically organized porous system

Our studies demonstrate high potential of hierarchical zeolites with acid sites predominantly located in the confined reaction space for acid catalyzed shape-selective reactions. The studies provided further insights into improving catalysts performance including a highly desirable enhancement of catalysts life-time, selectivity and activity for the process of catalytic cracking of paraffins, acylation reactions and transformation of methanol to hydrocarbons. (P. Sazama et al. *Angew. Chem.-Int. Ed.* 2013, P. Sazama et al. *Micropor. Mesopor. Mater.* 2011)

4) Novel nanostructured oxidic materials for advanced technologies

The crystallinity of a metal oxide scaffold in combination with a high interfacial surface area of mesoporous crystalline layers and a periodic ordering on the nanoscale is of special interest in applications involving interfacial charge transfer and bulk charge transport processes such as in solar cells, sensors, energy storage devices and photocatalysis. The basic approach to manufacturing such layers is the self-assembly of metal oxide building units assisted by a suitable structure-directing agent. The critical point here is the amorphous character of the common metal oxide precursors, which usually emanate from sol-gel synthesis and require crystallization at elevated temperatures, often resulting in the collapse of the mesostructure. This limitation motivates the search for largely crystalline building units that could convert to the final crystalline periodic scaffolds under mild conditions and low temperatures. To make such an approach successful, the building blocks need to be extremely small in order to be compatible with the size of the structure-directing agents, and they should be dispersible in the required solvents without agglomeration. We have developed a general "bricks and mortar" procedure, which is based on the fusion of preformed nanocrystals with surfactant templated sol-gel metal oxides, which act as a structure-directing matrix and as a chemical glue. The oxidic materials addressed include titanium dioxide, zinc and nickel oxides and range of transparent conduction oxides (especially ITO, ATO, NTO). Major breakthroughs achieved include:

a) Preparation of ultrasmall nanoparticles

Novel method for the fast preparation of ultrasmall nanoparticles of metal oxides with excellent dispersibility in various solvents, which enables to prepare mesoporous films with outstanding electrochemical properties, such as the high lithium insertion capacities and remarkably fast charging rates. (Szeifert et al. *JACS* 2010).

b) Multilayer mesoporous titanium dioxide films

These films exhibit exceptional morphological properties, which set a new record for surfactant-derived mesoporous titanium dioxide films. Applied in dye-sensitized solar cells, the multilayered "brick and mortar" films feature a remarkably high performance level (Szeifert et al. *Chem. Mater* 2012, Nemeč et al. *Appl. Phys. Lett.* 2010).

c) Nanocrystalline cellulose as a novel biotemplating agent

This approach enabled the straightforward synthesis of mesoporous titania thin films, which show very high activity as anodes in dye-sensitized solar cells, outperforming the conventional ones. (Ivanova et al. *JACS* 2014).

d) Ultrasmall, crystalline, and dispersible NiO nanoparticles

Such NiO nanoparticles were prepared for the first time. Their unique features provide great potential for the preparation of novel composite materials with applications in (photo)electrochemical water splitting and for the preparation of uniform hole-conducting layers for organic solar cells. (Fominykh et al. *Adv. Funct. Mater.* 2014).

e) Transparent mesoporous films of niobium-doped titanium dioxide

A novel method for the preparation of transparent mesoporous films of niobium-doped titanium dioxide with well-defined porosity and excellent electrical conductivity with application in photovoltaics, electrochromic devices, and chemical sensing. (Liu et al. *ACS Nano* 2010)

f) Highly dispersible nanoparticles of indium tin hydroxide

A novel strategy for the preparation of nanosized, nearly spherical and highly dispersible nanoparticles of indium tin hydroxide ("nano-hydroxides"), which can be assembled into regular mesoporous architectures. We believe that the nano-hydroxides can become universal building blocks for the fabrication of crystalline ITO materials with arbitrary nanomorphologies (Liu et al. *Chem. Sci.* 2012).

g) Transparent mesoporous doped tin oxide

The transparent mesoporous frameworks of doped tin oxide, which are owing to the open and accessible character of their porosity, the high surface area, and the uniform pore size promising host materials for the accommodation of functional redox moieties. The high potential of the obtained mesoporous layers as nanostructured transparent electrodes with high surface areas was demonstrated for ferrocene molecules and redox proteins, which were covalently immobilized in the conducting matrix, showing the significantly enhanced electrochemical response proportional to the electrode surface area (Liu et al. *ACS Nano* 2010, Muller et al. *Small* 2010, Mater. Chem. and Phys. 2012, *Electrochimica Acta* 2014, Fried et al. *Nanoscale* 2011, Liu et al. *Electrochimica Acta* 2014).

h) Deposition of mesoporous films of TiO₂

A low-cost procedure for the deposition of mesoporous films of TiO₂, was developed, which is easy to use and applicable for objects of various shape and size. (Rathousky et al. *J. Photochem. Photobiol. A Chem.* 2010).

Research direction 2: (Photo)catalytic application of oxidic materials with properties controlled on atomic or nanoscale level

5) Redox structures in zeolite based materials for N₂O and NO/NO₂ abatement

The relationships between structural properties and catalytic activity of zeolite and metal/metal-oxo catalysts for transformation of hydrocarbons and N₂O and NO/NO₂ abatement was elucidated on a molecular level using nano-scale directed synthesis and spectroscopic (UV-Vis-NIR, FTIR, Mossbauer, and MAS NMR supported by quantum chemical calculations in the cooperation with the Department of theoretical chemistry) and diffraction techniques. Study on the heterogeneity of Fe-ions in Fe-ZSM-5 and provides an explanation for the formation of distinct Fe-cationic species. Manipulation with structure of Fe-cationic species by aluminum distribution in the framework and selection of optimum topology of the zeolite together with kinetic analysis enabled identification of the most active sites for N₂O decomposition and NH₃-SCR-NO_x. It sets a milestone in understanding the formation and activity of different Fe species in Fe-ZSM-5 for abatement of emissions of nitrogen oxides and represents a complex description and explanation of N₂O and NO/NO₂ abatement catalysts. (Sklenak et al. *J. Catal.* 2010, Sobalik et al. *Micropor. Mesopor. Mater.* 2011, Sobalik et al. *J. Catal.* 2012, Ruggeri et al. *Catal. Today* 2012, Sazama et al. *J. Catal.* 2014, Sobalik et al. *Appl. Catal. A-General* 2014) The fundamental understanding of Fe-oxo structures in zeolite based materials was exploited in development of novel synthesis and large scale production of catalysts for N₂O and NO/NO₂ abatement described in two industrial prototypes. (Sazama et al. ID 62582640 and ID 25417681)

6) Enhancement of activity and selectivity for sustainable chemical processes

a) Selective catalytic oxidation of propane to propene over Fe zeolites

The quantitative analysis of the structure of the counter ion Fe species and their reorganization after the steaming, and a picture on the function of the individual Fe species and acid sites enabled fundamental understanding of relationship between structure of catalyst and activity and selectivity in selective oxidation of propane to propene. The study identified critical parameters for selectivity and durability of the catalyst. It represents a fine contribution to the investigation of the fundamental issues of utilization of propane for selective production of propene. (**P. Sazama et al. J. Catal. 2013**)

b) Enhancement of activity and selectivity in acid-catalyzed reactions by hierarchical zeolites

See Research direction 1-3) for highly desirable enhancement of catalysts life-time, selectivity and activity for the process of catalytic cracking of paraffins, acylation reactions and transformation of methanol to hydrocarbons. hydrocarbons (**Sazama et al. Angew. Chem.-Int. Ed. 2013, Sazama et al. Micropor. Mesopor. Mater. 2011**)

c) Ultra-active Al-rich pentasil ring zeolites

Al-rich template-free BEA* zeolite described in Research direction 1-2) exhibits dramatically enhanced activity in alkylation of aromatics, hydroamination of aromatics and cracking of paraffins, and in specific cases, also higher selectivity compared to conventional Si-rich zeolites. This provides potential for application of the Al-rich beta zeolite in acid-catalyzed processes. (**Sazama et al. J. Catal. 2014**)

7) Photocatalytic elimination of highly relevant organic environmental pollutants

Mesoporous titania thin films prepared employing cellulose as a templating agent show very high activity in the photocatalytic degradation of environmental pollutants. (**Ivanova et al. JACS 2014**). A major attention was devoted to the field of scientific aspects of photocatalytic processes and basic understanding of photocatalysis in a set of publications in solving the environmental issues, namely the photocatalytic elimination of highly relevant organic environmental pollutants. For the first time the mechanism of the self-cleaning process was explained by combining the experimental and theoretical DFT studies. Additionally the data obtained are essential for the correct standard testing of the photocatalyst performance. (**Rathousky et al. J. Photochem. Photobiol. A Chem. 2010, Ismail et al. J. Mater. Chem. 2011, Rathousky et al. Catal. Today 2011, Mills et al. J. Hazard. Mater. 2012, Guerin et al. ACS Applied Materials and Interfaces 2010, Hynek et al. Langmuir 2014**)

8) Electrochemical water oxidation

Ultrasmall, crystalline, and dispersible NiO nanoparticles were prepared for the first time. They are promising candidates as catalysts for electrochemical water oxidation. The unique features of these NiO nanocrystals provide great potential for the preparation of novel composite materials with applications in (photo)electrochemical water splitting and for the preparation of uniform hole-conducting layers for organic solar cells (**Fominykh et al. Adv. Funct. Mater. 2014**).

Secondary research direction 3: Nanotechnologies for the preservation of historic artefacts

The cleaning of an artefact is one of the most delicate and potentially dangerous operations in the cultural heritage conservation. We have developed a general procedure for the preparation of cleaning mixtures based on the combination of two functions which are realized by two components: a) the "standard" micellar solution or microemulsion of nonionic surfactants with co-surfactants added, which is practically the same for various target substances (such as the polymers to be removed from the surface), and b) the specific solvents selected according to the respective substance to be removed.

There are several advantages of this approach, namely the substantially facilitated formulation of the cleaning mixtures, easier preparation and better understanding of the mechanism of their action. Prospective production in larger amounts would be easier and economically more favorable (**Rathousky, patent applications PV2013-508, 509, 510, 804, 805**).

Secondary research direction 4: Microporous and composite materials for sorption and membrane separation

The experience of the department both in the synthesis of zeolites and in analysis of transport phenomena served as a knowledge base in the attempt to develop zeolite membrane. Although some parameters essential for synthesis of membrane were elucidated (**Brabec et al. J. Phys. Chem. C 2010**, **Jirka et al. Micropor. Mesopor. Mater. 2011**, **Prokopova et al. J. Phys. Chem. C 2013**) and substantial step ahead in the synthesis of oriented microporous crystalline layers were made (**Hrabanek et al. Micropor. Mesopor. Mater. 2013**), the breakthrough in this field was not reached, similarly to other laboratories working in this area. Nevertheless, promising results were obtained in the field of microporous hybrid material thin films based on metal-organic Framework ZIF-8. (**Cookney et al. Chem. Commun. 2014**)

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
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Scientific team	Department of Synthesis and Catalysis
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A. Personal Structure at 12/2014

In 12/2014 the **Department of Synthesis and Catalysis** consisted of 10 scientists, 4 Research assistants, 7 PhD students and 3 Senior researchers. Out of those 10 Senior and Associate scientists, 7 of them (Prof. Čejka, Drs. Horáček, Pinkas, Lamač, Eliášová, Opanasenko, Shamzhy) can be considered as key personal (although all of them were fully or mostly financed by grant money). 3 Senior scientists (Drs. Balcar, Mach, Zuka) as well as the Research assistants (Drs. Varga, Lupíková, Ochoa, Žilková) were exclusively or partly paid by grant money. Dr. Gyepes (0.2 FTE) is our computer expert with main job at the Faculty of Science, Charles University. Dr. Roth (founder of mesoporous materials, originally ExxonMobil) was contracted for 3-4 months/year. Moreover, there were presently 7 students working in the department. Decisive strength of this Department is in young and very talented researchers between 30-35 years (Drs. Lamač, Eliášová, Opanasenko, Shamzhy, Kubů). Dr. Eliášová was awarded by the Jean Marie Lehn Award in Chemistry 2013 and in particular by the Czech Intellect 2014 for the best PhD student in the Czech Republic. Currently Dr. Eliášová is as Research associate at KAIST (Daejeon, Korea) in the group of prof. R. Ryoo (till 11/2015).

B. Research Activities at a Glance

The main activities of the **Department of Synthesis and Catalysis** can be summarised as „development of novel microporous materials and organometallic complexes and their applications in adsorption and catalysis“.

The most important achievements of the Department were related to the development of new synthetic methodology for the manipulation with zeolites, resulting in the first transformation of parent three-dimensional zeolite into the individual two-dimensional layers with preservation of their structure (**Roth et al. Journal of the American Chemical Society 2011**). This key discovery opened a new pathway not only to the design and synthesis of novel materials possessing zeolitic layers but to novel zeolites (**Roth et al. Nature Chemistry 2013**). These important studies, highly cited by zeolite community, were supported by the Czech Science Foundation by grant (Two-dimensional zeolites with modifiable architecture, 2012-2016) and in particular Centre of Excellence (Intelligent Design of Nanoporous Adsorbents and Catalysts, 2012-2018). Currently, this topic is also partially developed in EU project (Framework 7 – CasCatBel – 2013-2017 CAScade deoxygenation process using tailored nanoCATalysts for the production of BiofuELs from lignocellulosic biomass). Another important area deals with non-zeolitic microporous materials, namely metal-organic-frameworks. We focused particularly on exploring their catalytic activity in various condensation reactions leading to important fine chemicals (**Dhakshinamoorthy et al. Advanced Synthesis & Catalysis 2013**, **Opanasenko et al. ChemSusChem 2013**). These studies were supported by EU project (MACADEMIA - MOFs As Catalysts and Adsorbents: Discovery and Engineering of Materials for Industrial Applications, 2009-2013) and currently have been developed under the Czech Science Foundation project (Combined Experimental and Theoretical Investigation of Catalytic Properties of Metal Organic Frameworks, 2014-2016). Adsorption and catalytic experiments were designed in our laboratory and the results were

corroborated with quantum chemical calculations carried out in the group of Prof. Nachtigall (Faculty of Natural Science, Prague).

Organometallic derivatives based on group 4 metallocene complexes bearing auxiliary highly substituted cyclopentadienyl ligands were investigated 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. New metallocene-derived skeletons were synthesized, and a number of C-C bond forming reactions were effected with new catalytically active complexes. These studies were supported by several grants from Czech Science Foundation ("The electron deficient transition metal complexes containing bifunctional beta-diketimate and cyclopentadienyl ligands – design of new catalysts" ended 2014; "Complexes of Group 4 Elements Containing Cyclopentadienyl Ligands with Pendant Unsaturated Bonds: Synthesis and Reactivity" ended 2013) Ministry of Education, Youth and Sports of the Czech Republic ("Transition metal complexes - structure and synthetic application" ended 2011), and Grant Agency of the Academy of Sciences of the Czech Republic ("Activation of small molecules by titanocene(II) and zirconocene(II) complexes" ended 2011).

Important research issues have been pursued by young and talented coworkers in the field of novel zeolite synthesis and research and exploring the fundamental reactivity of organometallic compounds of early transition metals. All the young researchers have been investigating their own projects supported by the Czech Science Foundation (Kubů, Opanasenko, Preparation of Novel Structure-Directing Agents for the Synthesis of Zeolites 2013-2015, **Kubů et al. Chemistry - A European Journal 2013**; Shamzhy - Understanding of catalytic activity of novel isomorphously substituted microporous germanosilicates 2014-2016, **Shamzhy et al. Chemistry of Materials 2014**; Lamač - Organometallic frustrated Lewis pairs for stoichiometric and catalytic bond activations 2014-2016, **Pinkas and Lamač, Coordination Chemistry Reviews, in press**). This clearly evidence continuous support of young talented researchers by the **Department**.

Successful approvals of number of projects supported by the Czech Science Foundation, EU – Framework 7, Technological Grant Agency (Catalytic oxidation of alkenes), and Ministry of Industry and Trade (Research and development of deoxygenation catalysts for production of automotive fuels and feedstocks for petrochemical industry from renewable feedstock) have provided excellent conditions for developing of the infrastructure for experimental research of the Department. In addition, Micromeritics company awarded Prof. Čejka by a research grant, consisting of free instrument – high resolution adsorption apparatus ASAP 2020.

C. Detailed description of our results in 2010-2014:

The activities of the **Department of Synthesis and Catalysis** might be divided in **4 main research directions**:

- 1) Synthesis, characterization, modification and application of zeolites
- 2) Rational design of ordered organic-inorganic materials and their utilization
- 3) Early transition metals in homogenous catalysis: from understanding of the fundamental steps to new catalytic systems
- 4) Heterogenization of transition metal complexes on solid supports

Within those 5 years the **Department** published more than 160 papers in impacted journals (including papers which were already published on line in 2014, but appeared in printed version in 2015). In particular, recent papers in **Nature Chemistry, Angewandte Chemie, Chemical Reviews, Journal of the American Chemical Society** are of the highest importance, which is evident by excellent citing records. **This report focuses on the highlights** connected with defined research projects (not grant projects):

Research Direction 1: Synthesis, characterization, modification and application of zeolites

Mastering of the synthesis of zeolites in all their aspects, covering synthesis of new templates, novel zeolitic structures, and understanding of the mechanisms of their synthesis, was the primary goal of our research in 2010-2014 period. Hand in hand with these studies, detailed

textural and structural characterization and application of zeolites in adsorption and catalysis have continued. Within this period, we have developed a new synthetic mechanism, so-called Top-down synthesis (Roth et al. Journal of the American Chemical Society 2011, highly cited paper), which substantially moved our orientation in this research area and influenced also other synthetic activities worldwide. All syntheses, modifications, and manipulations with zeolitic layers were designed and performed in our laboratory while Prof. Nachtigall (Faculty of Natural Science, Prague) was very helpful with theoretical calculations and Prof. Morris (Department of Chemistry, St. Andrews University) with structural determinations using synchrotron XRD and high-resolution TEM.

a) **Top-down formation of two-dimensional zeolites**

New synthetic protocol has been not only proposed but also proven dealing with controlled chemically selective hydrolysis of germanosilicate zeolites to provide two-dimensional layers of original zeolitic structure, which can be further manipulated with to prepare different zeolitic materials or new zeolites (Elišková et al. Chemistry of Materials 2013). Optimization of the conditions of selective hydrolysis allowed us to understand in more detail the mechanism of hydrolysis and to control at some extent the individual steps of this process (Smith et al. Chemistry - A European Journal 2013).

b) **Development of the strategies for fabrication of new zeolite structures – ADOR process**

Successful preparation of two-dimensional zeolitic layers by top-down approach continued in their further manipulation with respect to the synthesis of new zeolites with different bridges connecting the individual layers or in reconstruction of the original structure of the parent zeolite. We have optimized the conditions of layer condensations providing two new zeolites, IPC-4 (international code PCR) and IPC-2 (OKO), which was published in Roth et al. Nature Chemistry 2013 and is highly cited paper. Further investigation of the control of hydrolysis conditions resulted in the preparation of other two new zeolites IPC-6 and IPC-7 enabling precise control adjustment of zeolite micropore volume (Wheatley et al. Angewandte Chemie - International Edition 2014, HOT PAPER). It was also observed that some conditions of hydrolysis treatment favored “memory effect”, as a result of which, the original structure of zeolite IWW was reconstructed (Elišková et al. Angewandte Chemie - International Edition 2014).

c) **Hierarchical, lamellar and extra-large pore zeolites**

Synthesis of extra-large pore zeolites (e.g. UTL) represents a real challenge in the area of microporous materials. Our synthetic effort has been focused on the synthesis of UTL to understand the effect of organic templates controlling the synthesis of this zeolite and to investigate the isomorphous substitution of Si for Al, Ga, Fe, and B, to induce some catalytic activity (Shvets et al. Chemistry of Materials 2010). In the follow-up paper we have shown the limits of this isomorphous substitution for individual three-valent elements (Shvets et al. Chemistry of Materials 2011). These studies started our particular focus on hydrolysis of germanosilicates to provide two-dimensional zeolites.

d) **Investigation of the relationship : treatment conditions vs. texture/acid properties**

Structure – activity – selectivity relationship is another key topic in our Department. Number of different reactions was investigated over zeolites and related catalysts including alkylations and disproportionations of aromatic hydrocarbons (Jo et al. Catalysis Science & Technology 2013), acylation reactions (Serrano et al. Journal of Catalysis 2011), and hydroxyalkylations (Perez-Mayoral et al. ChemSusChem 2013). All these papers are based on our synthetic achievements of new zeolitic materials and their application in catalysis.

Research Direction 2: Rational design of ordered organic-inorganic materials and their utilization in acid-base catalyzed reactions

The multifunctional structured porous hybrid materials being of considerable interest for many applications have been comprehensively investigated and found as prospective catalysts for

reactions proceeding under mild conditions. Metal-organic frameworks possessing high concentration of Lewis acid sites and layered zeolitic organic-inorganic materials prepared by top-down approach from zeolite UTL were two groups of materials under investigation in 2010–2014. Main efforts have been directed to the synthesis and characterization of novel hybrid porous solids, evaluation of their catalytic activity in liquid-phase acid-base catalyzed reaction and understanding of the mechanisms of these catalytic processes proceeding on the active sites of metal-organic frameworks.

a) Fabrication of novel organic-inorganic materials derived from two-dimensional zeolites

Porous pillared materials containing organic linkers or polyhedral oligomeric silsesquioxane covalently bonded to zeolitic layers of IPC-1P were synthesised (Opanasenko et al. *Journal of the American Chemical Society* 2014). Obtained solids exhibited a hierarchical micro/mesoporous system with excellent textural characteristics overcoming existing analogues ($S_{\text{BET}} > 1000 \text{ m}^2/\text{g}$, $V_{\text{micro}} > 0.3 \text{ cm}^3/\text{g}$, $V_{\text{total}} > 1 \text{ cm}^3/\text{g}$). Catalytic properties of such hybrid materials have been tuned by varying the nature of organic component, which was exemplified using Knoevenagel condensation as model reaction.

b) Investigation of sorption properties and catalytic behaviour of metal organic frameworks vs. conventional microporous solids

To examine the features of metal-organic frameworks as adsorbents, sorption experiments and related calculations have been performed using diverse probe molecules (argon, nitrogen, *n*-, *i*-, and cyclopentane isomers). It was shown that in some types of metal-organic frameworks (e.g. $\text{Cu}_3(\text{BTC})_2$) the energy of lateral interactions between adsorbed molecules dominates the gas–solid energy heterogeneity. In other cases (like $\text{Fe}(\text{BTC})$) almost constant isosteric adsorption heats show that the variations of the gas–solid interaction energy are compensated by the energy of lateral interactions (Zukal et al. *Catalysis Today* 2015). The catalytic performance of selected MOFs have been evaluated in such acid-catalyzed reactions as Pechmann, Friedländer and Knoevenagel condensations, Friedel-Crafts acylation, Beckmann rearrangement, Prins and annulation reactions (e.g. Dhakshinamoorthy et al. *Advanced Synthesis & Catalysis* 2013) and compared with conventional zeolites. Characteristics determining the activity and selectivity of the catalysts (particularly their relation to the type and concentration of acid sites, the size of the channels, and structure of the active centres) were investigated in details.

c) Understanding of reaction mechanisms of catalytic reactions over metal-organic frameworks

To explain high catalytic activity and selectivity of the particular metal-organic frameworks observed experimentally, computational investigations have been performed at the density functional theory level employing cluster and periodic models (Polozij et al. *ChemCatChem* 2014). A particular emphasis was put on the mechanism of Friedländer and Knoevenagel reactions catalysed by Lewis acid Cu^{2+} sites in $\text{Cu}_3(\text{BTC})_2$. Simultaneous involvement of two adjacent coordinatively unsaturated sites (concerted effect) of metal-organic framework in activation process was shown to be responsible for the facilitation of studied transformations.

Research Direction 3: Early transition metals in homogenous catalysis: from understanding of the fundamental steps to new catalytic systems

This research direction have been focused on basic research in organometallic chemistry of early transition metals, understanding of some elementary reactions at the titanium and zirconium and exploitation of their complexes in organometallic and organic synthesis. 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 and activation of small molecules. The ligand transformation of low-valent metals evidenced an excellent synthetic

way for preparation of structurally new products that cannot be obtained by conventional synthetic methods. All synthesis procedures were designed and carried out in our laboratory followed by detailed characterization. Dr. Císařová (Faculty of Natural Science, Prague) contributed to the structural characterization of prepared complexes.

a) Activation of small molecules by titanocene complexes

We have investigated preparation of titanocene-ethene complexes, products of their thermolysis, formation of monomeric titanocenes thereof, and their reactivity to internal alkynes, conjugated diynes, and butenyne (Pinkas et al. *Organometallics* 2012). As impurity occurring during thermolysis of ethene complexes we have identified so far unknown extremely sterically crowded titanocene oxide and have found the synthetic access to it (Pinkas et al. *Organometallics* 2013). Our research on properties and chemical reactivity of decamethyltitanocene-ethene complex in 2012 led among other achievements to synthesis of pure decamethyltitanocene and to establishing of its disproportionation in solution into titanocene hydride. The latter complex was known before, however, not used as a chemical reagent. A clean synthetic preparation of this hydride was explored for an extensive study of its reactivity to $C\equiv C$ and $C=C$ bonds (Pinkas et al. *Organometallics* 2014). Along with simple insertion of Ti-H bond into unsaturated $C\equiv C$ and $C=C$ bonds it is the first well-characterized titanium-based hydrogenation catalyst.

b) Titanocene sulfide complexes

In 2011 a zero-waste synthetic access has been used to prepare decamethyltitanocene dihydrosulphide and monohydrosulphide from the doubly tucked-in titanocene and the singly tucked-in titanocene, respectively, by reacting them with H_2S (Pinkas et al. *Organometallics* 2011). Both sulphur compounds appeared to be sensitive to sunlight in toluene solution liberating the cyclopentadiene and H_2S in comparable amount. Subsequent investigation of solid products of photolysis of dihydrosulfide in solution revealed that new cage clusters were isolated from the sunlight photolysis (Gyepes et al. *Eur. J. Inorg. Chem.* 2013).

c) Titanocenes with cytostatic properties

An overexpression of the carbohydrate transporters (GLUT) is a known phenomenon (called Warburg effect) of cancer cells. Therefore, we have investigated carbohydrate-metalocene conjugates as potential cytostatics, which will be preferentially transported into malignant cells. We have prepared a series of titanocene dihalides (chlorides and fluorides) and ferrocenes bearing pendant xylofuranosyl and ribofuranosyl moieties. The most active titanocene-ribofuranose difluoride were found to be ca 2 times stronger cytostatic towards A2780cis cell line (ovarian cancer) than cisplatin (a conventional drug). The work is a joint project, where our group designed and prepared active substances, Dr. R. Hrstka (Masaryk Memorial Cancer Institute, MMCI) performed biological experiments, and Dr. J. Karban (Institute of Chemical Process Fundamentals, ICPF) synthesized cyclopentadienyl ligands (Hodík et al. *Organometallics* 2014).

d) Metallocenes with pendant functional group

Novel examples of group 4 metal complexes bearing cyclopentadienyl ligands modified with a pendant Si-H or nitrile group were shown to have a great potential for further synthetic modifications. By various methods we were able to perform transformations of the pendant functional moieties at the group 4 bent metallocene framework. The Si-H group on the metallocene periphery can subsequently be modified via either catalytic hydrosilylation or intramolecular dehydrocoupling reactions. The pendant nitrile group has been successively converted to an intramolecularly bound ketimide moiety (Pinkas et al. *Dalton Trans* 2013). Generally, the metallocene complexes with pendant functional groups give space for the study of their reactivity in oligomerization and polymerization reactions as well as for anchoring such catalysts on solid support.

Research Direction 4: Heterogenization of the catalysts based on transition metal complexes

Two main research areas were of the primary focus on heterogenization of transition metal complexes, although both of them bring similar challenges and goals. Heterogenization of organometallic complexes has been targeted from different angles, i) preservation of the catalytic activity of these complexes after immobilization to the solid surface, and ii) attachment of the complex to prevent leaching during the catalytic reaction (**Balcar et al. Coordination Chemistry Review 2013**). Heterogenization chemistry and catalytic studies were completely performed in our laboratory, these investigations were supported by several groups providing special complexes for immobilizations or characterization, e.g. by MAS NMR.

a) Immobilization of Ru-complexes for metathesis reactions.

Grubbs and Hoveyda-Grubbs metathesis catalysts were immobilized on mesoporous molecular sieves of different architecture and pore size. The attachment of Ru complexes to the support surface was accomplished either by covalent bonds (by means of carboxylate and phosphine linker molecules) or by non-covalent interactions. New heterogeneous catalysts, highly active and selective in all types of olefin metathesis reaction, were obtained (**Bek et al. ACS Catalysis 2011**). The catalyst activity was found to increase with increasing pore size of supports. The catalysts were reusable, low Ru leaching allowed preparation of products free of catalyst residues. Particularly, Hoveyda-Grubbs type catalysts immobilized by non-covalent interactions on mesoporous molecular sieve SBA-15 appeared to be very perspective from the practical point of view since the simplicity of their preparation and their very high efficiency (**Pastva et al. ACS Catalysis 2014**).

b) Immobilization of Zr-complexes for polymerizations.

In this topic we have investigated catalytic performance of zirconocene silanolates in dehydrogenative polymerization of phenylsilane. The workflow started from synthesis of homogeneous zirconocene silanolate molecular species, followed by preparation of zirconocene-silsesquioxane complexes and finally zirconocene-silica heterogeneous species were constructed. In this concept, we use silica as a macroscopic silanol ligand rather than inert support. The heterogeneous species were found as recyclable catalysts in poly(phenylsilane) production, whereas the prepared polymer showed an identical properties in each repeated cycle. (**Varga et al. Catalysis Today 2012**) In this work, our group have designed catalytic experiments and wrote the article and co-authors performed some analytical measurements.

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Research Report of the team in the period 2010–2014

Institute	J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i.
Scientific team	Department of Theoretical Chemistry

A. Personal Structure at 12/2014

In 12/2014 the department of theoretical chemistry consisted of 12 scientists, of whom 3 are retired and have only a partial position (financed by grants) and one (Slavicek) is an externist with 20% partial position. The 7 full-time researchers (Čurík, Cwiklik, Demel, Hrušák, Pittner, Sklenák, Srnec) forming the core of the department for the near future have an age average slightly over 40 years. Moreover, there are presently four postdocs/scientific assistants, 3 PhD students and one undergraduate, one more PhD student and one undergraduate should join during 2015.

B. Research activities overview

The department of theoretical chemistry is not focused on a single research area, but is formed by several independent groups led by senior researchers, which work on different topics from theoretical and computational chemistry: Development of electronic structure methods (Pittner), Theory of collisions of electrons with molecules (Čurík and Čársky), Theoretical study of (bio)catalytic processes (Sklenák and Srnec), and Molecular dynamics simulations of biophysical and photo-chemical processes (Cwiklik and Pittner).

C. Detailed description of results in 2010-2014

Research direction 1: Development of electronic structure methods

1. Development of methods for strongly correlated systems

The main topic in last five years was development of multireference coupled cluster methods. This research was supported by two grants of Czech Science Foundation, where J. Pittner and O. Demel acted as principal investigators. Another support was obtained from a grant of Czech Ministry of Education, Youth and Sports, in which J. Pittner was the principal investigator. All the presented publications are dominantly results of the work of our PhD students and postdocs with an exception of collaborations with groups of K. Kowalski and J. Noga, where the contribution of the two groups was about equal.

a) Development of Mukherjee's multireference CC with tri-excitations

The tri-excitations are based on the uncoupled approach and they have been included perturbatively (Bhaskaran-Nair et al. *J. Chem. Phys.* 2011) or within an iterative scheme (Demel et al *J. Chem. Phys.* 2010). With triexcitations, the method is able to describe systems with a multiconfigurational character (like e.g. diradicals) at a comparable level of accuracy as CCSD(T) or CCSDT does for molecules with a single-reference character.

b) Development of explicitly correlated versions of the state-specific MRCC methods

In collaboration with the group of J. Noga (Bratislava), we have developed explicitly correlated versions of the state-specific MRCC methods, which have the advantage of accelerated basis set convergence. This convergence improvement achieved in multireference case was analogous to

explicitly correlated single reference CCSD and CCSD(T) methods. (**Kedžuch et al. Chem. Phys. Lett. 2011, Demel et al. Phys. Chem. Chem. Phys. 2012, Demel et. al Mol. Phys. 2013**)

c) Massively parallelized implementation of MRCC methods

In order to compute large molecules and exploit modern supercomputer architectures, in collaboration with K. Kowalski (PNNL) we have developed massively parallelized implementations of our MRCC methods. Our best algorithm for the MRCC method with perturbative triexcitations achieved an excellent scaling up to tens of thousands of computer cores. (**Brabec et al. J. Chem. Phys. Lett. 2011, Bhaskaran-Nair et al. J. Chem. Phys. 2012, Brabec et al. J. Chem. Phys. Lett. 2012, Brabec et al. J. Chem. Phys. 2012**).

d) Quantum computing applied to quantum chemistry

We have made some endeavour on the field of quantum computing applied to quantum chemistry, where we have tested this novel approach on computation of the ground and excited state energies of methylene biradical (**L. Veis and J. Pittner J. Chem. Phys. 2010**). In collaboration with the Dirac program developers, we have also generalized this approach to four component relativistic regime and applied it to the problem of spin-orbit splitting in the SbH molecule (**Veis et al. Phys. Rev. A 2012**). We have not restricted ourselves solely to the quantum circuit model, but examined also the possibilities of quantum chemical ground state preparations on an adiabatic quantum computer, which appears to be more accessible for an experimental realization (**Veis and Pittner J. Chem. Phys. 2014**).

2. Negative ions – electron attachments

The research in the past years was determined by the aim to develop a methodology (computational tool) for describing unstable (resonant) electronic states of the atomic and molecular systems. This research was funded by the GACR project Molecular resonances and their dynamics (principal investigator J. Horáček, MFF UK, Praha, co-investigator I. Páidarová). The methods based on the analytical continuation in the complex plane, whose principal advantage is the use of standard (real) quantum chemistry programs for obtaining complex energies of the unstable states, were developed and successfully applied on the model as well as actual systems. The research was done in close collaboration with MFF UK (**Papp et al. Chem. Phys. 2013**) and IRSAMC, University Paul Sabatier, Toulouse, France (**Páidarová and Durand Adv. Quant. Chem. 2010, Durand and Páidarová J. Phys. B 2013**) and at the application stage with R.Čurik (**Horáček et al. J. Phys. Chem. A 2014**).

3. Reaction dynamics

In the field of reaction dynamics we contributed, in collaboration with the group of R. Kalus (Technical University Ostrava) and F.X. Gadea University Paul Sabatier, Toulouse, to the study of the properties including spin-orbit interactions and dynamics of the ionic rare-gas clusters by providing high quality ab initio input data for semi-empirical methods developed and used in Ostrava (**Svrčková et al. J. Chem. Phys. 2011**). These studies led to a standing collaboration that will be fortified in the next future in projects related to the Huygens-Cassini mission to Titan. As a first step towards this direction, in collaboration with the group of J. Žabka (grant GAČR Experimental and theoretical study of chemical reactions occurring in the Titan's ionosphere), we started a series of calculations on the reaction of several excited states of O⁺ (2P, 2D, 4S) with methane. The envisaged reactions under study are simple charge transfer or dissociative charge transfer reactions, and/or complicated molecular rearrangements that lead to stable species like H₂O, H₂CO, CH₃OH etc. For these important reactions, we began with the development of a computational multilevel strategy that allows through proper atomic manipulations, to approach in a chemically reasonable manner, the description of elementary processes of this rather complex system. We succeeded to rationalize the reaction pathway for the CH₄ + O⁺ (2P, 2D) → CH₃⁺ + OH reaction on the multiple potential energy and property surfaces – a reaction that is pertinent for the stability and dynamics of Titan atmosphere (**Hrušák and Páidarová Int. J. Mass. Spec. 2013**). This area is not fully explored yet and it will form the basis for our future research direction.

Research direction 2: Theory of collisions of electrons with molecules

1. Development of a computational method describing collisions of electrons with molecules adsorbed on surfaces and clusters

The approach is based on the Discrete Momentum Representation (DMR) method developed in our group for computational modeling of inelastic electron-molecule collisions (see Čársky J. Phys. B 2010a, Čársky J. Phys. B 2010b, Čurík and Šulc J. Phys. B 2010). This project was (and still is) supported by a grant of Czech Science Foundation, in which R. Čurík acts as the principal investigator. All the work on the following three publications was done by members of our group. Š. Varga's consultations with regards of a numerical implementation of Cholesky decomposition is acknowledged.

a) Development of density fitting method for electron-molecule interaction

Ab initio treatment of electron scattering by polyatomic molecules requires an evaluation of Coulomb integrals in a mixed Gaussian and plane-wave basis. Although the formulas of this type of integrals have been available in literature for decades, their application to somewhat larger molecules becomes too demanding computationally. This problem was overcome in quantum chemistry by using the density fitting technique and its use contributed greatly to applicability of quantum ab initio calculations to larger molecules. We show that density fitting can also be beneficial for evaluation of integrals in a mixed Gaussian and plane-wave basis (Čársky et al. J. Phys. B 2012).

b) Fourier transform decomposition of the exchange interaction

Lengthy evaluation of two-electron integrals in a mixed Gaussian and plane-wave basis has been a bottleneck in the scattering theory, and it hampers ab initio applications to larger polyatomic molecules up to these days. Hence, the stimulus for undertaking this study arose from our urgent need to calculate these integrals efficiently in order to extend the applicability of the DMR method for larger scattering targets. The developed method is based on the Fourier transform of the $1/r$ term and it is very naturally amenable to computation on Graphics Processing Unit (GPU) devices (Čársky and Čurík Theor. Chem. Acc. 2014).

2. Resonances in vibrational excitation of polyatomic molecules

As a natural outcome of the above described enhancements of the DMR method we found ourselves in a position that we could calculate vibrationally inelastic collisions of electrons with molecules of the size no one else could. All the ab initio calculations published in the following three papers were done by member of the Department of Theoretical Chemistry. Collaboration with our experimental partner from University of Fribourg is deeply appreciated.

a) Vibrational excitation of cyclopropane

In this study we computed absolute cross section for excitation of cyclopropane by electron impact. Beyond that we also performed a symmetry analysis of the dominant resonance process and in one particular case we found that this process does not conform to symmetry selection rules formulated by Wong and Schulz 1975. An exception from these symmetry selection rules was not reported in literature yet. The computational details can be found in Čurík et al. Phys. Rev. A 2012.

b) Vibrational excitation of diacetylene

We extended the approach for determination of the resonant symmetry components and applied it to a molecule of higher symmetry, the diacetylene. Diacetylene is a very important case because of a long lasting argument in literature about a mechanism behind the molecular dissociation after the electron impact. Also for this molecule we documented several resonant processes not described by the symmetry selection rules (Čurík et al. 2014 J. Phys. Chem. A 2014).

3. Electron-induced astrochemistry

Collision processes of astrochemical interest happen at very low collision energies, typically up to a few hundreds of meV. Our work in this field may be separated to two main domains of interests: electron-

induced chemistry in upper levels of atmosphere and early universe chemistry. The project was supported by a grant of Czech Ministry of Education. All the ab-initio calculations and preparation of the resulting two papers was carried out by members of the Department of Theoretical Chemistry. While the ab initio calculations for the second publication were done by R. Čurík, his contribution to preparation of the paper is minor.

a) Early universe LiHe chemistry

We computed the evolution of LiHe⁺ ions as a function of redshift in the early universe. One of the last unknown reactions in the full chemical network of the lithium and helium atoms in the early universe was the recombination rate of the LiHe⁺ ions. This rate is hard to determine experimentally because the respective neutral molecule LiHe does not form a bound state. Therefore, the energy and temperature dependence of the recombination rate was determined computationally in our group (Čurík and Gianturco *Phys. Rev. A* **2013**) and applied in the following macroscopic simulation carried out in group of Prof. Gianturco in Rome (Bovino et al. *ApJ* **2012**).

Research direction 3: Theoretical study of (bio)catalytic processes

1. Understanding Properties of Zeolites and Catalysis over Zeolites at an Atomistic Level

Transition metal exchanged zeolites

We studied the nature, structure, and properties of active sites of transition metal exchanged forms of silicon-rich zeolites since they are well known as exceptional redox catalysts. Furthermore, we investigated the N₂O decomposition over Fe(II) exchanged zeolites. The idea and concept of the projects were formulated at JH-Inst. The projects were supported by corresponding grants. Dr. Sklenak was the principal investigator of some of them. All the DFT calculations were done by Dr. Sklenak and members of his group. All the creations of models of the studied species and all the writing of the papers were done by Dr. Sklenak and the experimental collaborators. The collaborators from the University of Vienna (Prof. Hafner, Drs. Benco and Bucko) contributed to the studies a) and d) with their advice regarding the periodic DFT calculations. Moreover, the close collaboration with Dr. Zdenek Sobalik and Dr. Petr Sazama who carried out the experimental part (Department of Structure and Dynamics in Catalysis JH-Inst) should be highlighted.

a) N₂O decomposition over Fe exchanged zeolites

We provide a detail description of (1) plausible active sites of Fe-ferrierite and their structures, (2) the origin of the distinct reactivity of Fe-ferrierite, Fe-ZSM-5, and Fe-beta, (3) first steps of the N₂O decomposition (Sklenak et al. *J. Catal.* **2010**; Highly cited paper). We show that two Fe(II) cations accommodated in two adjacent six-membered rings in the eight-membered ring channel of Fe-ferrierite form the active site responsible for the superior activity of this catalyst in the N₂O decomposition in the absence of NO.

b) Identification of the nature of Fe species in Fe exchanged zeolites active in the N₂O decomposition and SCR NO_x

Various Fe species responsible for the N₂O decomposition and SCR NO_x over Fe exchanged zeolites were investigated and described (Sathu et al. *J. Catal.* **2013**, Sazama et al. *J. Catal.* **2014**). Our results show that the manipulation of the structure of Fe-cationic species can be achieved by the synthesis of zeolites with different distributions of Al atoms between Al pairs and single Al atoms in the framework.

c) Oxygen exchange in Fe-zeolites

We developed the first complete atomistic model of an oxygen exchange in the Fe(II) exchanged ferrierite (Andrikopoulos et al. *ChemPhysChem* **2013**). This model describes all the steps which are proposed to occur during the exchange of ¹⁸O (from N₂¹⁸O) and ¹⁶O (from the Fe(II) active site of the Fe(II)-zeolite).

d) Effect of the Al siting on the structure of Me(II) cationic sites in zeolites

We investigated the effect of the Al siting on the structure of Co(II) and Cu(II) active sites of ferrierite (Sklenak et al. *J. Phys. Chem. C* 2013). Our results reveal that upon binding Me(II) both the local structure of the zeolite framework as well as the binding energies of Me(II) strongly depend on the Al siting in the rings forming the cationic sites

Al siting in important silicon-rich zeolites

Zeolites are widely used as catalysts in industrial chemical processes. The species assumed to be the active sites in the mentioned processes, i.e. protons, metal ions, and metal-oxo species, are positively charged and compensate the negatively charged aluminosilicate framework. Therefore the Al siting in zeolite frameworks governs the location of the active sites as well as their properties. We developed a multispectroscopic approach coupled with DFT calculations that allows for the complex analysis of the Al siting in silicon-rich zeolites independent of the presence of Al-O-(Si-O)_n-Al (n = 1, 2) sequences in the zeolite framework. The idea and concept of the project were formulated at JH-Inst. The entire project was supported by corresponding grants. Dr. Sklenak was the principal investigator of some of them. All the DFT calculations were done by Dr. Sklenak and members of his group. All the creations of models of the studied species and all the writing of the paper were done by Dr. Sklenak and the experimental collaborators. Moreover, the close collaboration with Dr. Jiri Dedecek who carried out the experimental part (Department of Structure and Dynamics in Catalysis JH-inst) should be highlighted.

a) Determination of the Al siting in the framework of ferrierites

We developed a new method employing multiple spectroscopies and DFT calculations and applied it on several ferrierite samples to determine the complete Al siting (Dedecek et al. *J. Phys. Chem. C* 2011). Our new method can be used without limitations even on zeolite samples with a significant concentration of Al-O-(Si-O)_n-Al (n = 1, 2) sequences

Properties of Al-rich beta zeolites

Beta zeolites (BEA*) are industrially very important catalysts. The structure of BEA* possesses 12-membered ring openings. The successful synthesis of the template-free and Al-rich beta zeolites with a low Si/Al ratio provided a promising material for preparing new catalysts. Our goal was to compare such a material with conventional Si-rich beta zeolites. The idea and concept of the project were formulated at JH-Inst. All the DFT calculations were done by Dr. Sklenak. All the creations of models of the studied species and all the writing of the paper were done by Dr. Sklenak and the experimental collaborators. Moreover, the close collaboration with Dr. Petr Sazama who carried out the majority of the experiments (Department of Structure and Dynamics in Catalysis JH-inst) should be highlighted. Some catalytic experiments were performed by the Rumanian collaborators.

a) Acid and redox activity of Al-rich H-beta and Fe-beta zeolites

Acid and redox properties of Al-rich BEA* zeolite samples were compared with those of Si-rich BEA* (Sazama et al. *J. Catal.* 2014). Our study shows that a high concentration of Al-related active sites and the highly regular structure of Al-rich beta zeolite are directly manifested in enhanced activity compared with conventional Si-rich beta zeolite

Catalytically relevant defects in zeolites

We studied employing multiple spectroscopies and DFT the nature, structure, and properties of defects relevant to catalysis in silicon rich zeolites. The idea and concept of the project were formulated at JH-Inst. All the DFT calculations were done by Dr. Sklenak and a member of his group. All the creations of models of the studied species and all the writing of the paper were done by Dr. Sklenak and the experimental collaborators. Moreover, the close collaboration with Dr. Jiri Dedecek who carried out a significant part of experiments (Department of Structure and Dynamics in Catalysis JH-inst) should be

highlighted. The collaborators from the joint NMR laboratory at the Institute of Macromolecular Chemistry and the Austrian collaborator were responsible for the highly special NMR experiments.

a) Structure of Framework Aluminum Lewis Sites and their precursors

We determined the nature and structure of catalytically very important framework Lewis sites and also of perturbed Al atoms which are their precursors employing multiple spectroscopies and DFT calculations (**Brus et al. Angew. Chem., Int. Ed. 2015**). Our study revealed that framework aluminum Lewis sites correspond to Al tricoordinated to the zeolite framework while their precursors relate to $(\text{SiO})_3\text{AlOH}$ groups

2. Metalloenzymatic catalysis: understanding geometric and electronic structures of non-heme iron enzymes and their contributions to reactivity/selectivity

a) Difference in reactivity of mononuclear ferryl complexes with different ground spin state

Ferryl intermediates are known to play the essential role in reactivity of many enzymes including the important family of α -ketoglutarate dependent dioxygenases. While these biological systems use the high spin ($S=2$) state for various reactions, most of their synthetic mimics have the intermediate ground spin state ($S=1$). Our approach is to use density functional theory and advanced (multireference) quantum-chemical methods in combination with various spectroscopies (in collaboration with Prof. E. I. Solomon, Stanford, USA) to understand geometric and electronic structure properties that tune reactivity of these ferryl species. The work was aimed at the formulation of a general picture of how mono-nuclear iron enzymes control reaction selectivity (**Srnc, et al. Dalton Transactions 2014**). Major of calculations were done by Dr. Srnc, member of the Department of theoretical chemistry at IPCH. The spectroscopic data were collected by members of the Solomon group at Stanford University (some of these experiments were also conducted by Dr. Srnc while working with Prof. E. I. Solomon as a postdoctoral fellow in 2011-2013).

b) Reactivity of binuclear non-heme iron desaturase and other related enzymes

Binuclear non-heme iron enzymes are of great importance in chemistry and biology due to their ability to perform very "difficult" reactions with high selectivity. These systems are challenging from several perspectives: (i) complexity of the protein structure; (ii) complexity of the binuclear active site comprising two highly open-shell iron centers (iii) fine-tuned effects that control various reactivities in structurally related enzymes. We use large-scale, multireference (DMRG-based) methods developed in the group of Dr. T. Yanai (Japan) in combination with hybrid QM/MM calculations to elucidate the reaction mechanism of the early stage of catalytic cycle in desaturase and understand key physico-chemical properties of the active site that control desaturation over hydroxylation in this system. The project also includes a comparison with relative systems such as ribonucleotide reductase (**Chalupský, et al J. Am. Chem. Soc. 2014**). Our contribution to this work: design of the project, QM/MM calculations, preparation of the manuscript as a co-corresponding author).

Research direction 4: Molecular dynamics simulations of biophysical and photochemical processes

The line of research involving molecular dynamics simulations is mainly focused on biologically relevant systems (Dr. Lukasz Cwiklik). The work in this direction in the Department of Theoretical Chemistry was initiated in 2011 and since this time resulted in 23 published papers, three successful grant proposals, involvement of several students, and both international and internal collaboration. The following four main research topics are explored:

1) Structure and dynamics of biological lipid membranes

Lipid membranes are fundamental structures forming not only cell membranes but also various intracellular organelles and bodies. While their basic role is compartmentalization they also serve as platforms of action of numerous proteins. They act under various and dynamically changing conditions and hence both their structure and dynamics are crucial for understanding their biological role. Molecular dynamics simulations are well suited for studying lipid membrane properties at the molecular level with the biological context taken into account. Within this line of research in our department several well separated subtopics can be characterized:

a) basic characteristics of lipid bilayers in their environments

In these studies we concentrated on the influence of the varying external factors as well as internal composition of lipid membrane properties. More specifically, *influence of the biologically relevant ions*, mostly sodium and potassium, was widely studied (for instance, **Jurkiewicz, et al. BBA Biomembranes 2012**). Modulation of membrane properties by the ions was demonstrated and characterized in detail. This work was done in collaboration with experimental group of Prof. Martin Hof (fluorescent microscopy, JH Institute) and with the theoretical group of Prof. Pavel Jungwirth (IOCB); molecular dynamics simulations were conducted in our department. Membrane composition was explored by means of binding of cholesterol, one of major components of mammalian cell membranes, that was investigated in collaboration with the group of Prof. Thorsten Hugel (AFM, TU Munich) with free energy calculations performed in the department. We estimated stabilization free-energy of cholesterol in liquid ordered and liquid disordered membranes. Molecular-level details of lipid membrane hydration were studied in collaboration with experimental group of Prof. Martin Hof (fluorescent microscopy, JH Institute, Department of Biophysical Chemistry) (**Jurkiewicz, et al. Biochimie 2012**).

b) role of lipid oxidation on properties of membranes

This work was initiated within the framework of the Euromembrane EU grant in close collaboration with the group of Prof. Martin Hof (fluorescent microscopy, JH Institute, Department of Biophysical Chemistry), the theoretical group of Prof. Pavel Jungwirth (IOCB) as well as two group from Technical University in Wroclaw. Among several topics explored, our department had a major input into exploration of membrane permeability upon oxidation (**Lis, et al. Phys. Chem. Chem. Phys. 2011**) as well as investigation of possible apoptotic pathways via flip-flop of negatively-charged lipids (**Volinsky, et al. Biophys. J. 2011**). In these projects, comprehensive MD simulations were performed by our department in collaboration with the group of Prof. Pavel Jungwirth (IOCB) and with the involvement of students from Wroclaw.

c) lateral organization of lipid membranes

The lateral arrangement of lipids in lipid membranes is in recent years recognized as an important factor influencing not only the properties of membranes but also modulating the action of membrane proteins. However, typical MD simulations are unable to cover the range of time- and length scales relevant for this issue. We developed a mixed molecular dynamics – lattice Monte Carlo simulation approaches which deals with this issue by use of Graphical Processing Units (**Lis, et al. J. Chem. Theory Comput. 2012**). We intensively continue the work in this direction including the issue of membrane protein lateral arrangement.

2) Lipid monolayers

In our work on phospholipid monolayers we focus on such systems as plausible models of the lung surfactant. This project is a part of the current GACR grant proposal (2013-2015) in collaboration with Dr. Martina Roeselova (IOCB). It also involves direct collaboration with the group of Prof. Heather Allen (Ohio State Univ) and Prof. Jacek Korchowiec (Jagiellonian University in Krakow). First, we investigated consequences of lipid oxidation for monolayer properties. We demonstrated that oxidized lipids undergo reorientation and other oxidation products may reside in the monolayer (**Khabiri, et al. Chem. Phys. Lett. 2012**). Currently we work on multicomponent monolayer systems as well as the systems that include non-lipid biologically relevant constituents (**Griffith, et al. J. Phys. Chem. B 2015**).

3) Tear Film Lipid Layer

In this project we aim at getting a molecular-level understanding of biophysical properties of the human tear film lipid layer (TFLL). This work is performed in collaboration with the experimental group of Prof. D. Robert Iskander from Technical University in Wroclaw as well as with the group of Prof. Martin Hof (JH Institute, Department of Biophysical Chemistry). This project is currently financed by the GACR grant (2015-2016). First, we introduced a realistic coarse grained model of the tear film and investigated its main structural properties (**Wizert, et al. PLOS ONE 2014**). Presently, we examine the same system in the presence of tear proteins as well as possible drug molecules.

4) Fluorescent probes in biological environments

By combining advanced methods of quantum chemistry with classical MD simulations, we study photophysical properties of fluorescent probes in biological environments. This project is currently supported by a GACR grant. First, in collaboration with M. Barbatti and H. Lischka we developed efficient methods for surface hopping molecular dynamics which computes the non-adiabatic couplings from overlaps of wave functions at various levels of theory and performed assessment of the resulting methods on selected photochemical processes: at CASSCF level (**Barbatti et al. Chem. Phys. 2010, Pederzoli et al. J. Phys. Chem. A 2011**), as well as at TDDFT and ADC(2) level (**Plasser et al. J. Chem. Theor. Comp. 2014**). These developments became part of the MD software package Newton-X (**Barbatti et al. Wiley Interdisc. Revs. 2014**). Second, we developed the and intensively tested the methodology, including the software, for mixed quantum-classical calculations (**Cwiklik, et al. J. Phys. Chem. A 2011**). Third, we characterized the fluorescent probe PRODAN at atomistic level in various environments which allowed us for explanation of the experimentally observed solvatochromism (**Pederzoli, et al. Chem. Phys. Lett. 2014**). Presently we study different fluorescent probes (Laurdan, C-Laurdan) in the context of the ordered-disordered phases in phospholipid membranes.

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