



# SEMINÁŘ STUDENTŮ ÚFCH JH 2019



**J. Heyrovský Institute  
of Physical Chemistry**

# **Seminář studentů ÚFCH JH 2019**

## **Sborník příspěvků**

**ze studentské konference konané  
29.-30. dubna 2019  
v Konferenčním centru AVČR Liblice**

# **Seminar of Students of JHI 2019**

## **Collection of abstracts**

**of all lectures given at the student conference  
held on 29-30 April 2019  
in Conference centre of AS CR in Liblice**

**Seminář studentů ÚFCH JH 2019**  
**Sborník příspěvků ze studentské konference**  
**konané 29.-30. dubna 2019**  
**v Konferenčním centru AV ČR Liblice**

Kolektiv autorů

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# SEMINÁŘ STUDENTŮ ÚFCH JH 2019

PROGRAM 1. dne konference - pondělí 29.4.2019

**Odjezd autobusu z parkoviště před ústavem v 8:45 hodin.**

*Předpokládaný příjezd do Konferenčního centra AV ČR v zámku  
v Liblicích okolo 9:45 hodiny.*

## SEMINAR OF STUDENTS JHI 2019

PROGRAM - Monday April 29, 2019

**April 29, 2019 - Departure from the parking place (in front of the JHI building) - 8:45**

Čas	Předseda- jící/ Chairman	Přednášející/ Lecturer	Název/ Title of the presentation
<b>9:45 -10:40</b>		Ubytování - v recepci, ihned po příjezdu. <b>OBČERSTVENÍ PŘED ZAHÁJENÍM KONFERENCE</b> (káva, nápoje, zákusek - v 1. patře, na ochozu) <b>Coffee break (1st floor)</b>	
<b>10:45</b>		<b>Zahájení konference „Seminář studentů ÚFCH JH 2019“</b> <i>Opening of the Annual conference "Seminar of Students JHI 2019"</i>	
10:50-11:05	<b>Adam Pastorek</b>	David DUNLOP (bakalář, školitel M. Lamač)	EXPLORING CYTOTOXIC TITANOCENE DIHALIDES
11:05-11:20		Jana HRNČÍŘOVÁ (diplomantka, školitel M. Ferus)	SYNTHESIS OF CANONICAL NUCLEOBASES OVER CLAYS UNDER CONDITIONS OF EARLY EARTH
11:20-11:45		Martin JINDRA (bakalář, školitel O. Frank)	M-DROPLET SPECTROELECTROCHEMISTRY OF GRAPHENE (EDGES VS. BASAL PLANE, COMBINATION WITH MECHANICAL LOADING)
11:45-12:00		Jan SVOBODA (bakalář, školitel J. Ludvík)	ELEKTROCHEMICKÉ A SPEKTROMETRICKÉ STUDIUM TITANOCÉN DIHALOGENIDŮ
<b>12:00-12:30</b>		<b>PŘESTÁVKA</b> <i>Break- (v rámci přestávky si účastníci, kteří se neubytovali ráno po příjezdu, zajistí UBYTOVÁNÍ v recepci hotelu)</i>	
12:30-12:45	<b>Jaroslava Řáhová</b>	Matyáš KOUT (bakalář, školitel M. Horáček)	REAKCE MODIFIKOVANÝCH FERROCENŮ SE SENDVIČOVÝMI KOMPLEXY IV. SKUPINY
12:45-13:00		Antonín KNÍŽEK (PhD student, 1. ročník, školitelé S. Civiš a M. Ferus)	FORMATION OF (PER)CHLORATES ON MARS
13:00-13:15		Ghulam ABBAS (PhD student, 1. ročník, školitel O. Frank)	IN-SITU SPECTROELECTROCHEMISTRY OF FUNCTIONAL MATERIALS FOR RECHARGEABLE ALUMINUM BATTERIES
13:15-13:30		Anna KŘIVKOVÁ (diplomantka, školitel M. Ferus)	VÝKONOVÉ LASERY VE VÝZKUMU PRVKOVÉHO SLOŽENÍ MEZIPLANETÁRNÍ HMOTY PRO APLIKACE V KOSMONAUTICE A ASTRONOMII

<b>13:30 -15:00</b>	<b>OBĚD</b> <i>Lunch in the restaurant - 13:30-15:00</i> (podává se v restauraci v přízemí)		
15:00-15:15	<b>Dávid</b>  <b>Hvizdoš</b>	Sofia TVORYŇSKA (PhD studentka, 1. ročník, školitel B. Josypčuk)	THE DEVELOPMENT OF FLOW ELECTROCHEMICAL CHOLINE BIOSENSOR BASED ON THE ENZYMATIC CHOLINE OXIDASE REACTOR
15:15-15:30		Lukáš PETERA (diplomant, školitel M. Ferus)	IDENTIFIABLE SPECTRAL FEATURES PREDICTED FOR TRANSMISSION SPECTRA OF YOUNG EXOPLANETS UNDERGOING HEAVY BOMBARDMENT
15:30-15:45		Kristýna POKORNÁ (středoškolská stáž v proj. Tři nástroje, školitel M. Horáček)	THE CENTRAL ATOM EFFECT ON GEOMETRY OF TRANSITION METAL COMPLEXES CONTAINING GUANIDINATE LIGAND
		Ukončení prezentací I. kategorie, navazují prezentace doktorandů z kategorie II.	
15:50-16:10		Michaela OBLUKOVÁ (PGS studentka, školitel R. Sokolová)	ELECTROCHEMISTRY AND UV-VIS AND IR SPECTROELECTROCHEMISTRY OF 1-PENTYL- 3-(1-NAPHTOYL)INDOLE AND 1-PENTYL-3-(2- METHOXY-PHENYLACETYL)INDOLE
<b>16:10-16:30</b>	<b>PŘESTÁVKA NA KÁVU</b> (1.patro, ochoz) <i>Coffee break (1st floor)</i>		
16:30-16:50	<b>Antonín</b>  <b>Knížek</b>	Anna NĚMEČKOVÁ (MAKRLÍKOVÁ) (PGS studentka, školitel T. Navrátil)	DETERMINATION OF TUMOR BIOMARKERS USING FLOW INJECTION ANALYSIS WITH AMPEROMETRIC DETECTION AT BORON DOPED DIAMOND ELECTRODE
16:50-17:10		Mariia LEMISHKA (PGS studentka, školitel J. Dědeček)	SELECTIVE OXIDATION OF METHANE TO METHANOL OVER DISTANT BINUCLEAR CATIONIC CENTERS IN ZEOLITES
17:10-17:30		Martin PIŽL (PGS student, školitel S. Zálíš)	TIME-RESOLVED VIBRATIONAL SPECTRA OF Ru AND Re DIIMINE COMPLEXES: AN ANHARMONIC CALCULATIONS
17:30-17:50		Štěpánka SKALOVÁ (PGS studentka, školitel T. Navrátil)	USING OF A DUAL GLASSY CARBON ELECTRODE FOR AMPEROMETRIC DETERMINATION OF ANTHRAQUINONE -2- SULFONATE
<b>17:50-18:00</b>	<b>PŘESTÁVKA</b> <i>Break</i>		
18:00-19:30	Presentation of project "ERA Chair at J. Heyrovsky Institute of Physical chemistry AS CR – The institutional approach towards ERA" (project No. 810310 in Horizon 2020, 2018-2023)		
18:00-19:00	RNDr. Štefan VAJDA CSc., Dr.habil.	Catalysis and Electrocatalysis by Size and Composition Selected Clusters	
19:00-19:30	RNDr. Juraj JAŠÍK, Ph.D.	Forming of He <sub>n</sub> -C <sub>60</sub> <sup>3+</sup> "Snowballs" in Cryogenic Ion Trap	
<b>19:30</b>	<b>Ukončení prvního dne konference</b> <b>VEČEŘE v RESTAURACI - začátek v 19:30</b> <i>(Dinner in the restaurant - 19:30)</i>		

PROGRAM 2. dne konference - úterý 30.4.2019

PROGRAM - Tuesday April 30, 2019

Čas	Předseda- jící/ Chairman	Přednášející/ Lecturer	Název/ Title of the presentation
<b>8:15</b>	<b>Zahájení druhého dne konference</b>		
8:20-8:40	<b>Jan  Brandejs</b>	Jaroslava ŘÁHOVÁ (PGS studentka, školitel O. Frank)	LOCAL PHOTOCURRENT CHARACTERIZATION OF GRAPHENE-SILICON HETEROJUNCTION
8:40-9:00		Adam PASTOREK (PGS student, školitel S. Civiš)	THE EXPLORATION OF THE GAMMA RADIATION EFFECT ON PRIMORDIAL FORMAMIDE-BASED SOLUTIONS
9:00-9:20		Rebecca PITTKOWSKI (PGS studentka, školitel P. Krtil)	SYNERGISTIC EFFECTS IN OXYGEN EVOLUTION ACTIVITY OF MIXED IRIIDIUM-RUTHENIUM PYROCHLORES
9:20-9:40		Kristián SKÁLA (PGS student, školitel R. Šachl)	NOVEL APPROACH FOR PREPARATION OF PROAPOPTOTIC PROTEIN BAX
<b>9:40-10:10</b>	<b>PŘESTÁVKA NA KÁVU</b> (1.patro, ochoz) <span style="float: right;"><i>Coffee break (1st floor)</i></span>		
10:10-10:30	<b>Rebecca  Pittkowski</b>	Roman NEBEL (PGS student, školitel P. Krtil)	SrTiO <sub>3</sub> NANO-CUBE PARTICLE SIZE TUNING: ACTIVITY AND SELECTIVITY CONTROL FOR PHOTO-ELECTROCHEMICAL WATER OXIDATION
10:30-10:50		Dávid HVIŽDOŠ (PGS student, školitel R. Čurík)	FURTHER DEVELOPMENT OF DISSOCIATIVE RECOMBINATION THEORY FOR DIATOMIC CATIONS
10:50-11:10		Miroslava GURICOVÁ (PGS studentka, školitel J. Ludvík)	ELECTROCHEMICAL CHARACTERIZATION OF FISCHER CARBENE COMPLEXES OF GROUP 6 METALS BEARING CONDENSED HETEROCYCLIC SUBSTITUENTS
11:10-11:30		Jan BRANDEJS (PGS student, školitel L. Veis)	SENSOR NETWORKS METHODS FOR STRONGLY CORRELATED SYSTEMS IN QUANTUM CHEMISTRY AND ITS COUPLED CLUSTERS EXTENSIONS
<b>11:30-13:00</b>	<b>PŘESTÁVKA NA OBĚD</b> (podává se v restauraci od 11:30 do 13 hodin) <i>Lunch in the restaurant</i> <span style="float: right;"><b>11:30-13:00</b></span>		
13:00-13:20	<b>Roman  Nebel</b>	Ivo S. VINKLÁREK (PGS student, školitel M. Fárník)	VIBRATIONALLY MEDIATED PHOTO- DISSOCIATION DYNAMICS OF PYRROLE
13:20-13:40		Vladislav BURAVET (PGS student, školitel P. Krtil)	SURFACE SENSITIVITY OF THE CO <sub>2</sub> REDUCTION ON TiO <sub>2</sub> CATHODES
13:40-14:00		Daniel BÍM (PGS student, školitel M. Srnec)	REACTIVITY OF THE BINUCLEAR NON-HEME IRON ENZYME Δ <sup>9</sup> -DESATURASE FROM THEORETICAL PERSPECTIVE
<b>14:00-14:10</b>	<b>PŘESTÁVKA</b> <span style="float: right;"><i>Break</i></span>		
14:10-14:30	<b>Kristián</b>	Kamila RIEDLOVÁ (PGS studentka, školitel L. Cwiklik)	INFLUENCE OF BENZALKONIUM CHLORIDES ON HUMAN TEAR FILM LIPID LAYER MODELS

14:30-14:50	<b>Skála</b>	Michal LACKO (PGS student, školitel P. Španěl)	A COMBINED SIFT-MS AND IMS STUDY OF PHTHALATES ISOMERS
<b>14:50-15:30</b>	<b>PŘESTÁVKA NA KÁVU A ZÁKUSEK</b> (1.patro, ochoz) <i>Coffee break (1st floor)</i>		
<b>15:30-16:00</b>	<b>15:30 - SLAVNOSTNÍ VYHLÁŠENÍ VÝSLEDKŮ</b> <b>SOUTĚŽNÍ KONFERENCE - V KONFERENCEČNÍM SÁLE</b> <b>UKONČENÍ KONFERENCE</b> <i>Closing ceremony - Results announcement (in conference hall)</i>		
<b>16:15</b>	<b>Odjezd do Prahy - autobusem z parkoviště u zámku v 16:15</b> <i>(autobus bude přistaven na 16:00 hodin)</i> <b>Departure from the parking place (in front of the chateau) - 16:15</b>		



# Seznam prezentujících studentů (29)

## List of participants (29)

### Kategorie I (10)

#### Diplomanti, magistři a zájemci z řad bakalářů (7)

**Dunlop David**

(bakalář, PřF UK, školitel M. Lamač)

**Hrnčířová Jana**

(diplomantka, PřF UK, školitel M. Ferus)

**Jindra Martin**

(bakalář, VŠCHT Praha, školitel O. Frank)

**Kout Matyáš**

(bakalář, PřF UK, školitel M. Horáček)

**Křivková Anna**

(diplomantka, PřF UK, školitel M. Ferus)

**Petera Lukáš**

(diplomant, PřF UK, školitel M. Ferus)

**Svoboda Jan**

(bakalář, VŠCHT Praha, školitel J. Ludvík)

#### Studenti 1. ročníku PGS (3)

**Abbas Ghulam** (školitel O. Frank)

**Knižek Antonín** (školitel S. Civiš a M. Ferus)

**Tvoryňska Sofii**a (školitel B. Josypčuk)

#### Ukázka středoškolské stáže:

**Pokorná Kristýna** - Gymnázium Roudnice nad Labem, stáž v projektu Tři nástroje, lektor M. Horáček

### Kategorie II (18)

#### Studenti ostatních PGS ročníků

**Bím Daniel** (školitel M. Srnec)

**Brandejs Jan** (školitel L. Veis)

**Buravet Vladislav** (školitel P. Krtíl)

**Guricová Miroslava** (školitel J. Ludvík)

**Hvizdoš Dávid** (školitel R. Čurík)

**Lacko Michal** (školitel P. Španěl)

**Lemishka Mariia** (školitel J. Dědeček)

**Němečková (Makrlíková) Anna**  
(školitel T. Navrátil)

**Nebel Roman** (školitel P. Krtíl)

**Obluková Michaela** (školitel R. Sokolová)

**Pastorek Adam** (školitel S. Civiš)

**Pittkowski Rebecca** (školitel P. Krtíl)

**Pižl Martin** (školitel S. Záliš)

**Riedlová Kamila** (školitel L. Cwiklik)

**Řáhová Jaroslava** (školitel O. Frank)

**Skála Kristián** (školitel R. Šachl)

**Vinklárek Ivo S.** (školitel M. Fárník)

**Skalová Štěpánka** (školitel T. Navrátil)

#### Hodnotící komise:

Štefan Vajda  
Eva Krupičková - Pluhařová  
Otakar Frank







# IN-SITU SPECTROELECTROCHEMISTRY OF FUNCTIONAL MATERIALS FOR RECHARGEABLE ALUMINUM BATTERIES

**Ghulam Abbas**

*supervisor: Mgr. Otakar Frank, Ph.D.*

It is crystal clear from the predictable facts about present energy resources that world is on the track towards energy crisis in future [1]. Currently, due to the requisite of portable electrical and electronic devices, electrochemical energy storage systems such as batteries have achieved tremendous attraction. Rechargeable Aluminum ion batteries (RABs) owing to high energy densities and no scarcity of depletion of Al unlike Li, could be the one of the best alternatives rather than monovalent  $\text{Li}^{1+}$  ion batteries. Recently, extensive efforts have been devoted for the development of inexpensive; much safer and emerging Al ion batteries comprising Al as anode with potential cathode material and ionic liquid organic electrolytes but still it is believed that Al ion batteries are far away from laboratory scale to the practicability due to multiple challenges.

The unrevealed demonstration about the reaction mechanism for intercalation, electrolyte stability, determination of novel cathode material to achieve the ultimate capacity, stability of current collector and side reaction of electrolyte with separator and binder are the crucial obstacles that need the eminent consideration for the development of Al ion batteries. Above all, the interpretation of the real picture of reaction mechanism is the major concern that deserves tremendous attention from researchers. Recently, In-Operando X-Ray diffraction technique has been used to study the in-situ electrochemical reaction mechanism during charging/discharging process for Rechargeable Al batteries [2]. One of the most appealing concern about reaction mechanism in which we are mainly interested, is the clear justification about intercalation species whether  $\text{Al}^{3+}$  or  $\text{AlCl}_4^-$  will be the responsible during charge storage intercalation process for RABs.

The charge storage reaction mechanism for RABs will be revealed by using In-Situ spectroelectrochemistry for graphene and other 2D transition metal dichalcogenides by using different electrolytes. First of all, charge transfer mechanism for monolayer exfoliated and CVD graphene will be studied by using a micro-droplet Raman spectroelectrochemical technique and further spectroelectrochemistry of TMDCs by using aprotic and aqueous electrolyte will also be studied by using standard classical cell to demonstrate the reaction mechanism for RABs in true sense. Furthermore, In-situ tip enhanced spectroelectrochemistry will be eventually tested to figure out more details about the reaction mechanism for RABs.

## References:

1. F. Umbach, *Energy Policy*, 2010, **38**, 1229-1240.
2. C. J. Pan, C. Yuan, G. Zhu, Q. Zhang, C. J. Huang, M. C. Lin, M. Angell, B. J. Hwang, P. Kaghazchi and H. Dai, *Proc Natl Acad Sci U S A*, 2018, **115**, 5670-5675.



## REACTIVITY OF THE BINUCLEAR NON-HEME IRON ENZYME $\Delta^9$ -DESATURASE FROM THEORETICAL PERSPECTIVE

Ing. Daniel Bím

*supervisor: RNDr. Martin Srnec, PhD.*

Mono- and binuclear non-heme iron sites in proteins serve as efficient catalysts of a broad set of oxidation reactions, including activation of unreactive C–H bonds of organic substrates for subsequent desaturation, hydroxylation, halogenation, peroxidation, electrophilic aromatic substitution, etc. A prominent example of such class of enzymes is the soluble  $O_2$ -dependent stearyl-acyl carrier protein  $\Delta^9$ -desaturase ( $\Delta^9D$ ), which is capable of inserting a double bond into an alkyl chain of stearic acid *via* two sequential H-atom abstractions. Building on a detailed investigation of the initial stages of  $O_2$  activation reaction in the  $\Delta^9D$  active site reported earlier by our group,<sup>[1-2]</sup> the catalytic cycle is completed, employing the hybrid QM(DFT)/MM methodology. Energetics of key reaction intermediates are carefully examined at the level of advanced multi-configurational methods, and the selectivity of  $\Delta^9D$  toward desaturation (at the expense of more thermodynamically favored hydroxylation) is clarified.

### **References:**

[1] Srnec, M.; Rokob, T. A.; Schwartz, J. K.; Kwak, Y.; Rulíšek, L.; Solomon, E. I. *Inorg. Chem.* **2012**, *51*, 2806-2820.

[2] Chalupský, J.; Rokob, T. A.; Kurashige, Y.; Yanai, T.; Solomon, E. I.; Rulíšek, L.; Srnec, M. *J. Am. Chem. Soc.* **2014**, *136*, 15977-15991.



# TENSOR NETWORKS METHODS FOR STRONGLY CORRELATED SYSTEMS IN QUANTUM CHEMISTRY AND ITS COUPLED CLUSTERS EXTENSIONS

Mgr. Jan Brandejs

*supervisor: RNDr. Libor Veis, Ph.D.*

Tensor networks-based approaches have proved successful for strongly correlated systems both in quantum chemistry and in solid state physics. The effective description is achieved by encoding the correlation into the product of matrices, or more generally, into the contraction of tensors. In chemistry, this approach led to the development of the Density Matrix Renormalization Group Method (DMRG). DMRG is the method of choice for systems with strong static correlation, otherwise known as the multireference systems. Although the approach is efficient for the static correlation, it fails to describe the dynamic correlation, that is the effects of the correlated movement of electrons.

To address this drawback, we have extended DMRG by the means of Coupled Clusters theory (CC). CC effectively captures the dynamic correlation and makes the computations more precise than ever for a specific class of molecular systems. Successful applications include hexachlorodocuprate anion  $[\text{Cu}_2\text{Cl}_6]^{2-}$  [1], tetramethyleneethane (TME) [2], and cyclobutadiene  $[\text{C}_4\text{H}_4]$  [3].

Aside from these applications, we currently work to extend our DMRG implementation into a massively parallel version, designed for distributed calculations on supercomputers. The new implementation will allow us to compute significantly larger systems, with potential applications reaching the scale of FeMo cofactor complex [4], a system crucial to efficient artificial nitrogen fixation. Once it is finished, our software, released under the name of MOLMPS, will become an integral part of the NWChem package [5].

## **References:**

- [1] Orms, N.; Krylov A., *Phys. Chem. Chem. Phys.* **2018**, *20*, 19, 13095-13662.
- [2] Veis, L.; Antalík A. et al., *J. Chem. Theory Comput* **2018**, *14*, 5, 2439-2445.
- [3] Eckert-Maksić M. et al., *J. Chem. Phys.* **2006**, *125*, 6, 064310.
- [4] Reiher, M. et al., *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 29, 7555-7560.
- [5] Valiev, M. et al., *Comput. Phys. Commun.* **2010**, *181*, 9, 1477-1489.



# SURFACE SENSITIVITY OF THE CO<sub>2</sub> REDUCTION ON TiO<sub>2</sub> CATHODES

Vladislav Buravet, MSc

*supervisor: Doc. Ing. Petr Krtil, CSc.*

Carbon dioxide (CO<sub>2</sub>) emitted from fossil fuels represents the largest anthropogenic contribution to the climate change. Although there are chemical technologies capable of converting the CO<sub>2</sub> to valuable chemicals like fuel (e.g. Fischer-Tropsch process), they remain dependent on fossil fuels both for energy and for the source of hydrogen.

The electrochemical conversion can be performed under ambient temperature and pressure conditions, in aqueous solutions and the required electricity can be obtained from renewable energy sources. However, use of electrochemical methods for CO<sub>2</sub> reduction on an industrial scale remains a challenge. The development of an efficient catalyst in terms of lifetime, overpotential and selectivity is required. In addition, the reaction mechanism is not exactly known in most cases and has to be illuminated. The state-of-the-art catalysts are based on Cu and Ag, the potential of non-metal catalyst is poorly understood so far.

TiO<sub>2</sub> has received great attention as a catalyst due to its high efficiency, low cost and lack of toxicity. It was shown that TiO<sub>2</sub> (anatase) with different surface orientation possess different catalytic activity in water splitting process<sup>[1]</sup>.

The role of surface orientation on electrochemical reduction of CO<sub>2</sub> on TiO<sub>2</sub> in aqueous solutions will be demonstrated. Experiments were performed on nanocrystalline TiO<sub>2</sub> - anatase dominated by {001} and {101} surface orientations in 0.1M KHCO<sub>3</sub> and 0.1M NaClO<sub>4</sub> aqueous solutions, saturated with CO<sub>2</sub>. The products of CO<sub>2</sub> reduction were detected online using differential electrochemical mass spectrometry (DEMS) technique. As water serves as the main source of hydrogen in this process, a set of experiment in heavy water (D<sub>2</sub>O) was performed to elucidate the reaction products.

The reduction of carbon dioxide in aqueous solution is accompanied by vigorous hydrogen evolution reaction (HER). Based on the DEMS data of the experiments in D<sub>2</sub>O, the source of hydrogen is not confined only to water but could be obtained from the introduced ions of HCO<sub>3</sub><sup>-</sup> and is sensitive to the applied potential. Methane is shown to be the product of CO<sub>2</sub> reduction on TiO<sub>2</sub> anatase.

## **References:**

1. Minhová-Macounová, K.; et. al., *The J. Phys. Chem. C* **2017**, 121(11), 6024-6032.



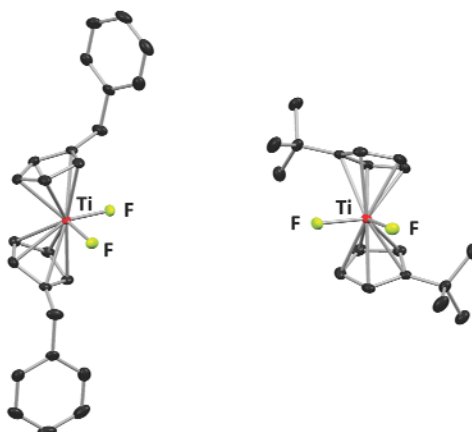
# EXPLORING CYTOTOXIC TITANOCENE DIHALIDES

David Dunlop

supervisor. RNDr. Martin Lamač, Ph.D.

Various metallocenes have been shown to possess interesting cytotoxic activity, making them potential anti-tumor agents. The cytotoxic properties of the so called „sandwich complexes” are strongly dependent on both the metals and the fine tuning of their ligands.

The goal of this talk is to share the challenges posed by synthesis of selected titanocene dihalides and the approaches we have applied to their solution, the results of NMR and X-ray diffraction analysis of the isolated complexes and some of the results of their cytotoxic parameters.



## **References:**

Zhang, P.; Sadler, P. J., *Journal of Organometallic Chemistry*, **2017**, 839, 5-14.  
Hartinger, G. C.; Metzler-Nolte, N.; Dyson P. J., *Organometallics*, **2012**, 31, 5677-5685.  
Cini, M.; Bradshaw, T. D.; Woodward, S., *Chemical Society Reviews*, **2017**, 46, 1040-1051.  
Hodík, T.; Lamač, M.; Červenková Štastná, L.; Karban, J.; Koubková, L.; Hrstka, R.; Císařová, I.; Pinkas J., *Organometallics*, **2014**, 33, 2059-2070.

## **Acknowledgements**

This work has been supported by the Czech Science Foundation (project no. 17-05838S).



# ELECTROCHEMICAL CHARACTERIZATION OF FISCHER CARBENE COMPLEXES OF GROUP 6 METALS BEARING CONDENSED HETEROCYCLIC SUBSTITUENTS

Ing. Miroslava Guricová

*supervisor: prof. RNDr. Jiří Ludvík, CSc.*

Carbene complexes are characterized by presence of a formally double bond  $M=CR_2$ . In electrophilic carbenes of Fischer type, the  $M^{\delta-} = C^{\delta+}$  polarity of this bond is typical. An extended study of mononuclear complexes  $(CO)_nM = C(NR')R$  showed that there are presented two rather independent redox active centers: oxidation is aimed on the metal atom, reduction on the carbene moiety.

The molecules were studied using cyclic voltammetry on GC and Pt electrode and by IR spectroelectrochemistry. The results were compared with those find at molecules substituted by simple heterocycles, N-methylpyrrol (MePyr), furyl (Fur), and thienyl (Thi) <sup>[1], [2], [3]</sup>.

Oxidation potential is mostly influenced by the central metal nature. The oxidation process is quasi-reversible, it proceeds in two steps and oxidation potentials of the compounds with the same central atom lay within 50 mV range, depending on the substituent. The inductive influence of the heterocycle itself (heteroatom) is evident: the oxidation potential increases in sequence  $II < I < III$ . The only difference was found in  $E_{ox}$  of the compounds I and Ia (derivatives with the heterocycle bond in position 2- and 3-, resp.),  $E_{ox}(I)$  is by 120 mV higher than  $E_{ox}(Ia)$ ; no similar result was found for 2-MePyr and 3-MePyr substituents. This may be caused by different delocalization of  $\pi$ -electron system in I and Ia.

Reduction of the presented compounds, which is impacted by substituents of the carbene carbon, proceeds at higher potential (easier) compared with the heterocycle substituted compounds, and the difference of  $E_{red}$  is not so pronounced (range about 200 mV instead of 400 mV). Presence of the larger  $\pi$ -electron system makes the reduction easier by stabilizing the reaction intermediate and, at the same time, in some extent overlays the different inductive effect of the heteroatoms. This effect can be shown also from  $E_{red}$  sequence:  $II > I > III$ .

Acknowledgement: Financial support from GACR 17-21770S and from specific university research (MSMT No 20-SVV/2018) is gratefully acknowledged.

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# SYNTHESIS OF CANONICAL NUCLEOBASES OVER CLAYS UNDER CONDITIONS OF EARLY EARTH

**Bc. Jana Hrnčířová**

*supervisor: RNDr. Martin Ferus, Ph.D*

The origin of life represents a longstanding enigma for generations of scientists and philosophers. Basic brick stones of the genetic code are very likely central for the formation of the first living structure. A. I. Oparin formulated the first theory explaining origin of life as abiogenesis - formation of the first living system from abiotic substances. He introduced a scientific abiogenesis as a process of formation of prebiotic molecules from abiotic substances. These molecules have been abundant on early Earth and Oparin called their mixture as a primordial soup. These compounds could form coacervates a sort of clusters of chemical compounds.<sup>1</sup> This theory of abiotic origin of life was 30 years after publication of Oparin theory experimentally proven by Miller, who demonstrated preparation of amino acids in electric discharge.<sup>2</sup> This rather easy formation of nucleic bases was in basal disagreement between the ideas of evolutionary and molecular biologists and chemists. In their opinion, the first living structure was more probably established on self-replicating entity of RNA (ribonucleic acid). However, chemical experiments pointed synthesis of nucleobases as really complicated under prebiotic conditions.

In our explorations, we simulate conditions on early terrestrial planets. We are investigating thermochemistry of fundamental prebiotic feedstock molecule: formamide, in presence of various catalytic materials, such is meteorite dust, a wide range of clays with heavy atoms in their crystal lattice. Surface early Earth or Mars contained minerals, very likely iron-rich clays, which could play a significant catalytic role in remarkable chemical reactions leading to abiotic heat-induced formation of nucleobases, amino acids and other biomolecules.<sup>3,4</sup>

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## FURTHER DEVELOPMENT OF DISSOCIATIVE RECOMBINATION THEORY FOR DIATOMIC CATIONS

RNDr. Dávid Hvizdoš

*supervisor: Mgr. Roman Čurík, Ph.D.*

The neutralization and subsequent breakup of molecular ions by incoming electrons is an important and key process in molecular plasma dynamics. This process is called dissociative recombination (DR) and attempts to calculate its probabilities and cross sections often face many quantitative difficulties (owing to complexities caused by the presence of a long-range Coulomb interaction). Thus most theoretical calculations use an approximative approach.

In the previous years we have reported on our tests [1] to determine the validity of a widely accepted yet not rigorously tested approximative method for calculating DR cross sections for a model case of  $H_2^+$  by comparison with an exact numerical model. This method adapts frame transformation [2] to calculate DR cross sections using Siegert pseudostates [3]. We have first shown how a simplified model yields decently correct results. Then replacing the Siegert basis with an exterior complex scaling basis [4] and upgrading the approach to consider the energy dependence of quantum defects has shown to yield significantly better results. This second approach still contains several simplifications and ad hoc assumptions. We present how to improve it further and at the same time make the approach more physically correct with more mathematic rigour.

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# **$\mu$ -DROPLET SPECTROELECTROCHEMISTRY OF GRAPHENE (EDGES VS. BASAL PLANE, COMBINATION WITH MECHANICAL LOADING)**

**Martin Jindra**

*supervisor: Mgr. Otakar Frank, Ph.D*

Graphene is well known for its unique electrical properties. Previous measurements of spectroelectrochemistry of graphene were commonly performed with electrochemical cell where electrolyte was spread on whole sample. Because of that charge can flow through the edges and basal plane simultaneously. Development of the  $\mu$ -droplet electrochemistry method [1] allow us to investigate the behavior of graphene edges and basal planes separately. Also very small areas can be investigated. Limit for the investigated area is the size of the droplet, which can be as small as  $10\ \mu\text{m}$  in diameter. It is also possible to combine graphene spectroelectrochemistry with mechanical loading. Raman spectroscopy is used for the characterization of graphene in these types of experiments, where is very important to distinguish the contribution of charge doping and strain through vector analysis [2].

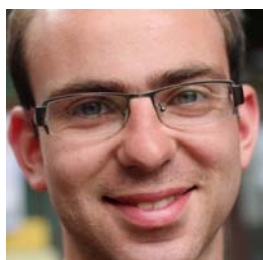
Graphene was prepared by direct exfoliation of graphite crystals on a Si/SiO<sub>2</sub> wafer or on polymer beam, for combination with mechanical loading. Contact on graphene flake were handmade with silver paste.

Graphene bilayers were polarized through basal plane and interface between bilayer and monolayer. Raman spectra were measured up to 1.2 V. Also combination with mechanical loading were measured. Different adhesion of graphene to substrate under the droplet and out of the droplet was measured.

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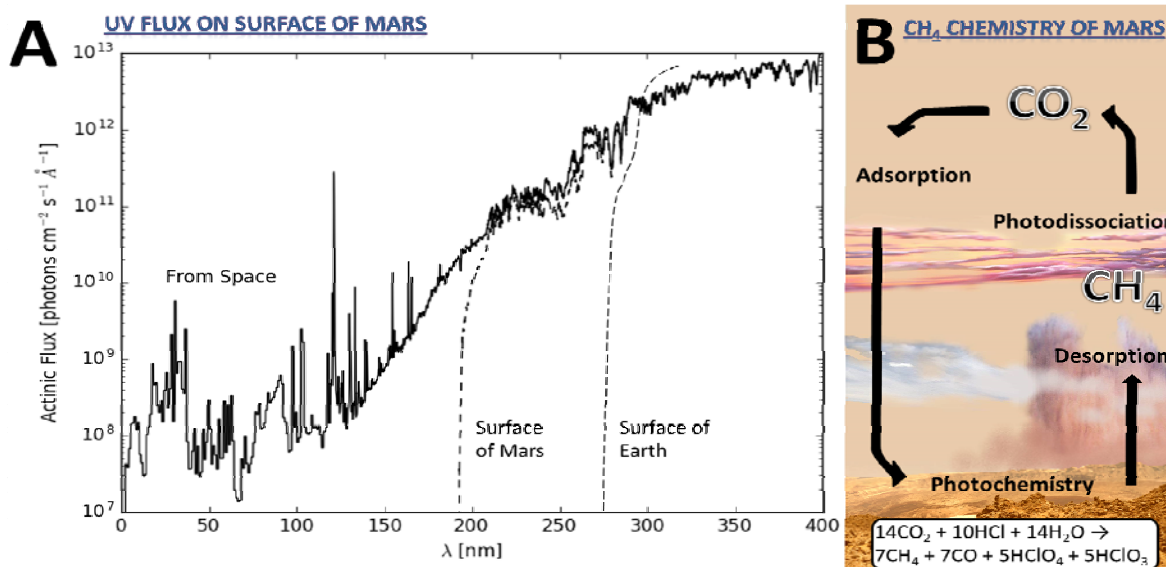
## FORMATION OF (PER)CHLORATES ON MARS

Mgr. Antonín Knížek

supervisors: RNDr. Martin Ferus, Ph.D

prof. RNDr. Svatopluk Civiš, DSc.

The origin of methane, perchlorates, chlorates and chlorinated alkanes on Mars has never been explained, even though their presence has been confirmed by the Viking and Curiosity Rovers. In our experiments (1, 2), we performed photocatalytic reduction of  $\text{CO}_2$  and  $\text{HCl}$  over  $\text{TiO}_2$ , montmorillonite and the Nakhla meteorite and other catalysts by irradiating the sample for up to 3500 hours. After FT-IR and XPS analyses, we observed the formation of perchlorates, chlorates, methane and chlorinated methane. The experiment was performed at ambient temperature and at liquid nitrogen boiling point temperature. Based on these findings, we propose that this process may be the reason for the observed presence of methane on Mars as well as perchlorates and chlorates. Furthermore, perchlorates are stable in Martian conditions and therefore could have accumulated on the surface for billions of years. We estimate that this mechanism would be sufficient to accumulate perchlorate in the Martian soil in 0.1 – 1 wt. % in 5 – 50 cm depth. This proposed gradient may be observed by Insight over, which is the substitute rover for Curiosity.



UV flux on Mars (panel A) and an overview of the  $\text{CH}_4$  chemistry according to our results.

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# REAKCE MODIFIKOVANÝCH FERROCENŮ SE SENDVIČOVÝMI KOMPLEXY IV. SKUPINY

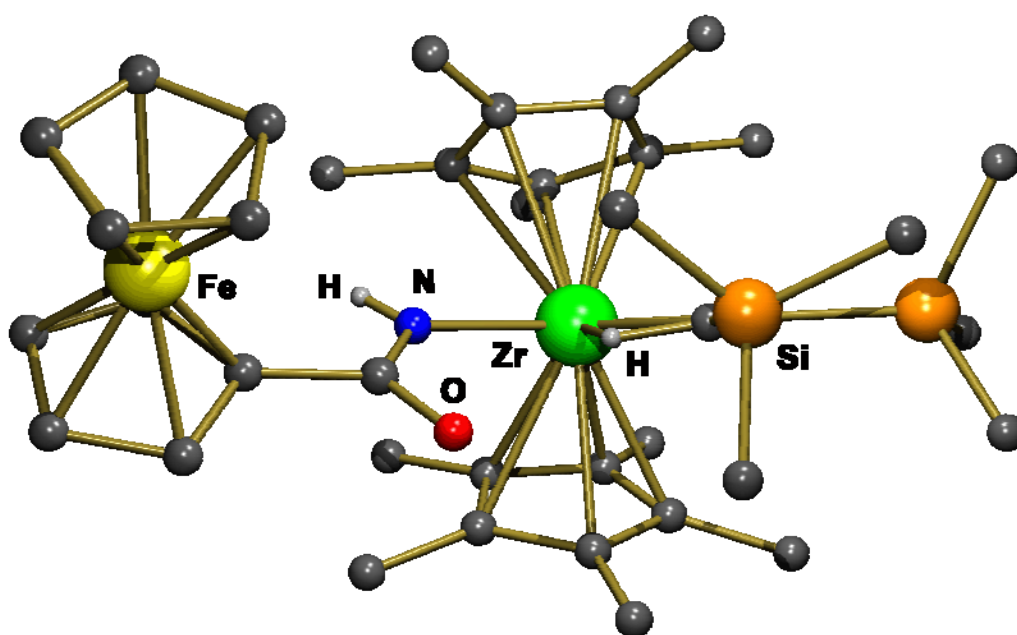
**Matyáš Kout**

*školitel: Mgr. Michal Horáček PhD.*

Dnes známe celé spektrum derivátů ferrocenu, které obecně mají specializovaná využití, založená na jejich neobvyklé struktuře a vlastnostech. Některé z derivátů jsou uplatnitelné v průmyslové syntéze léčiv a agrochemikálií.

Sloučeniny podobné ferrocenu na bázi titanu (titanocenyl) a zirkonia (zirkonocenyl) byly od konce 80. let minulého století zkoumány pro své katalytické schopnosti. Byla studována redukce čtyřmocných sendvičových komplexů a jejich stabilizace v nižších mocenstvích elektronově bohatými ligandy. Využití titanocenů a zirkonocenů spočívá nejčastěji v katalytických reakcích olefinů, ale lze je rovněž využít pro organickou syntézu, zejména pro specifické alkylační reakce.

V této přednášce budou shrnuty experimentální výsledky z mé bakalářské práce vycházející z průniku obou výše zmíněných typů sloučenin. Titanocenové a zirkonocenové komplexy stabilizované bis(trimethylsilyl)acetylenem ochotně reagují s amidovou skupinou na modifikovaném ferrocenovém skeletu a poskytují heterokovové sloučeniny. Vznik těchto sloučenin, jejich charakterizace, stabilita a prostorové uspořádání atomů v molekule bude diskutováno.



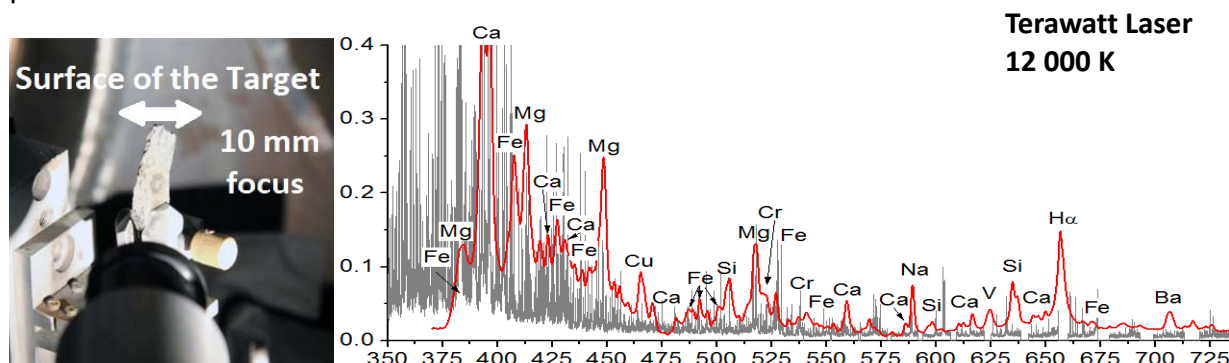


# VÝKONOVÉ LASERY VE VÝZKUMU PRVKOVÉHO SLOŽENÍ MEZIPLANETÁRNÍ HMOTY PRO APLIKACE V KOSMONAUTICE A ASTRONOMII

**Bc. Anna Křivková**

*školitel: RNDr. Martin Ferus, Ph.D.*

Výzkum aplikace výkonových laserů má potenciál významně přispět k rozvoji celé řady badatelských záměrů, které sahají od zkoumání prvkového složení těles meteoroidů spektrální analýzou plazmatu meteorů a tím k poznání mineralogie a distribuce meziplanetární hmoty, zkoumání chemické evoluce sluneční soustavy, pátrání po mechanismech vedoucích ke vzniku života až po témata směřující k aplikacím snad dostupným v budoucnosti, jako je prospekce a těžba nerostného bohatství na asteroidech či mírového využití pro destrukci potenciálně nebezpečných těles, jako jsou blízkozemní planety a kosmické smetí. Naším výzkumným záměrem je aplikace výkonových laserů v oblasti simulace meteorů, využití LIBS v kosmických satelitech a výzkum fyzikálního působení laserů určených pro případný odklon/urychlení až destrukci těles o modelové velikosti až 10 mm (kosmické smetí). Prvním úkolem je určit potřebné škálování pro odklonění/urychlení těles o daných rozměrech, extrapolovat parametry potřebné pro lasery schopné působit na větší objekty, tj. ověřit základní parametry laserových pulzů (délka pulzu, prostorový profil, intenzita atd.) tak, aby byla dosažena maximální absorpce laserového záření jednotlivými vzorky reálných meteoritů. Výzkum povede zejména k optimalizaci parametrů laserového svazku. Vedlejším výsledkem také bude zjištění parametrů laserového svazku pro napodobení plazmatu meteorů.



Vzorek meteoritu, připravený pro experiment (vlevo), vysoce rozlišené (šedá) a níže rozlišené (červená) spektrum naměřené pomocí terawattového laseru (vpravo).

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## A COMBINED SIFT-MS AND IMS STUDY OF PHTHALATES ISOMERS

**Mgr. Michal Lacko, PhD.**

*supervisor: prof. RNDr. Patrik Španěl, Dr. rer.nat.*

Phthalates (esters of phthalic acid) are used as plasticizers in production of plastics. However, their negative health effect are now understood (Halden, 2010). Several the most dangerous phthalates (diethylhexyl phthalate, dibutyl phthalate, benzylbutyl phthalate, diisononyl phthalate, diisodecyl phthalate, and di-n-octyl phthalate) are under the EU regulations (EC, 2005) or are tracked by European Chemical Agency (EHCA). However, the regulations do not cover daily use plastic products other than toys.

Several analytical techniques are used for detection of phthalates; mainly based on the liquid or gas chromatography – mass spectrometry (GC-MS / LC/MS) (Russo et al., 2015), witch is time consuming and for phthalates has a low selectivity. Soft chemical ionization (SCI) techniques providing high selectivity used mainly in real time detection of VOCs at trace levels (Smith and Španěl, 2011) can be potentially used for real time and accurate detection of phthalates contamination in plastics. Ion mobility spectrometry (IMS) is a suitable SCI technique for detection of phthalates. IMS is a device using operational pressure near atmospheric and can be used for detection of traces of molecules present at very low partial pressures such as explosives (Sabo et al., 2014).

To describe the possibility of phthalate detection in the IMS, we have to understand the ion chemistry occurring during the detection. Therefore, we have carried out a combined IMS-MS and SIFT-MS study of phthalates DMP, DMIP and DMTP with focus on the phthalate ion chemistry with  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  primary ions. Formation of water clusters strongly depends on isomerization of phthalates. Results were confirmed by study of chemical kinetic using SIFT-MS. According to different position of phthalate esters, for 1,2 position is water attachment impossible, for 1,3 position can phthalate effectively attach two water molecules, and for 1,4 position is effective only attachment of one water molecule.

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## SELECTIVE OXIDATION OF METHANE TO METHANOL OVER DISTANT BINUCLEAR CATIONIC CENTERS IN ZEOLITES

Mgr. Mariia Lemishka

*supervisor: Mgr. Jiří Dědeček, DSc.*

Zeolites are key materials of the chemical production (heterogeneous catalysis, gas separation and purification). They are used as catalysts in a wide range of acid-catalyzed reactions for the transformations of hydrocarbons in the petrochemical industry [1]. Metal containing zeolites represents redox catalysts for NO/NO<sub>x</sub> elimination from diesel exhausts and N<sub>2</sub>O abatement. Fe-containing zeolites are exceptional due to their ability to decompose N<sub>2</sub>O and form unique type of highly active oxygen (so called α-oxygen) [2]. This α-oxygen form is able to selectively oxidize methane to methanol [3]. However, Fe species active in the formation of α-oxygen are difficult to be prepared and unstable.

This study aimed in targeted preparation of the binuclear Fe(II), Co(II), Ni(II) structures in zeolite ferrierite and testing their activity in N<sub>2</sub>O decomposition, formation of active α-oxygen and selective oxidation of methane. The catalysts with high loading of binuclear structures (Me = Fe, Co, and Ni) were prepared using ion exchanged method (Co) or impregnation (Fe and Ni). The presence of divalent cations (Fe, Co, and Ni) in cationic position of the zeolite matrix was confirmed by FTIR spectroscopy. FTIR results showed that in all prepared Me-zeolites, the majority of metal cations has to be present as binuclear M(II) cations due to the dominant presence of bare M(II) ions. In-situ FTIR studies confirmed the interaction of M(II)-zeolites with N<sub>2</sub>O at RT, reflected in the shift of the skeletal vibrations, which was assigned to atomic oxygen ([M(III)-O]<sup>2+</sup>) stabilized on metal cations (Co, Fe or Ni). The introduction of CH<sub>4</sub> at 220 °C to oxidized M-zeolites containing active oxygen, confirms the complete reduction of the [Me(III)-O]<sup>2+</sup> species by CH<sub>4</sub>. Moreover, the FTIR spectra of M-zeolites after oxidation and methane treatment showed new vibrations typical for methanol and other oxidation products. Titration of the α-oxygen by methane monitored by MS detection showed that methanol represents the main product of methane oxidation.

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## **SrTiO<sub>3</sub> NANO-CUBE PARTICLE SIZE TUNING: ACTIVITY AND SELECTIVITY CONTROL FOR PHOTO-ELECTROCHEMICAL WATER OXIDATION**

**Ing. Roman Nebel**

*supervisor: Doc. Ing. Petr Krtil, CSc.*

Hydrogen produced by photo-electrochemical splitting of the water is envisioned as a convenient medium for storing of renewable (namely solar) energy into energy of chemical bonds. [1] The overall reaction can be divided into two parts: cathodic reduction of hydrogen and anodic oxidation of oxygen. However, due to its lifeless kinetics, the oxygen evolution reaction (OER) is the limiting step. Finding a cost-effective stable n-semiconductor catalyst suitable for photoanodic evolution of oxygen and optimization of its activity is therefore of an immense importance.

Low temperature, carbonate free synthesis of perovskite SrTiO<sub>3</sub> nano-cubes [2] and comparison of the photo-electrochemical behavior for differently sized SrTiO<sub>3</sub> nano-cubes will be presented. Photo-electrochemical experiments were carried out in chronoamperometric mode using three-electrode setup in argon and oxygen saturated perchloric acid and sodium hydroxide solutions. Experiments held in argon saturated solutions were also accompanied with differential electrochemical mass spectroscopy (DEMS) method for online semi-quantitative determination of the (gaseous) reaction products.

Activity of prepared SrTiO<sub>3</sub> nano-cubes towards photo-electrochemical water splitting is promoted as the size of the particles increases. Overall photoelectrochemical activity is strongly affected by protonation/deprotonation reactions occurring at the catalyst surface, and therefore is suppressed by increasing the pH of the electrolyte. Low dimensionality sites (i.e.) edges and vertices of the nanocubes accommodate hydrogen peroxide formation via oxygen reduction reaction, whilst {100} faces are selective towards oxygen evolution reaction as well as for production of ozone.

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## DETERMINATION OF TUMOR BIOMARKERS USING FLOW INJECTION ANALYSIS WITH AMPEROMETRIC DETECTION AT BORON DOPED DIAMOND ELECTRODE

RNDr. Anna Němečková

*supervisor: Doc. Ing. Tomáš Navrátil, PhD.*

Homovanillic (HVA) and vanillylmandelic (VMA) are products of catecholamine metabolism excreted in urine; normal concentrations in urine are from 8.2 to 41.0  $\mu\text{mol}\cdot\text{l}^{-1}$  for HVA and from 11.6 to 28.7  $\mu\text{mol}\cdot\text{l}^{-1}$  for VMA [1]. Increased urinary HVA and VMA levels are found in patients with tumors, pheochromocytoma and neuroblastoma [2]. This contribution is devoted to the determination of HVA and VMA using flow injection system with amperometric detection at a commercially available boron doped diamond electrode (3 mm in diameter).

Results of flow injection analysis with amperometric detection at boron doped diamond electrode in optimum medium of Britton-Robinson buffer (0.04  $\text{mol}\cdot\text{l}^{-1}$ , pH 3.0) will be presented with the use of this method for the determination of HVA (in the presence of VMA) and VMA (in the presence of HVA).

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# ELECTROCHEMISTRY AND UV-VIS AND IR SPECTROELECTROCHEMISTRY OF 1-PENTYL-3-(1-NAPHTOYL)INDOLE AND 1-PENTYL-3-(2-METHOXY-PHENYLACETYL)INDOLE

Mgr. Michaela Obluková

supervisors: Mgr. Romana Sokolová, Ph.D.  
doc. RNDr. Radomír Čabala, Ph.D.

The electrochemistry properties of 1-pentyl-3-(1-naphtoyl)indole (hereinafter referred to as “JWH-018”) and 1-pentyl-3-(2-methoxyphenylacetyl)indole (hereinafter referred to as “JWH-250”) were studied. These compounds belong to heterogenous group of synthetic cannabinoids, which have been appeared in the drug market recently. These substances are abused for their psychoactive effect and serve as alternative to classical drugs (heroin, cocaine, ecstasy) due to their legal status. In human organism, JWH-018 and JWH-250 are rapidly and completely metabolized and thus parent compounds are often undetectable. To detection of these compounds is necessary to know their metabolism pathway.

In view of the fact that the electron transfer reactions play an important role in metabolic pathways, this study is focused on electrochemical investigation of oxidation and reduction of JWH-018 including *in situ* UV-Vis and IR spectroelectrochemical research.

This report is based on cyclic voltammetry and electrolysis in non-aqueous media combined with HPLC-ESI-MS/MS detection of reactions products.

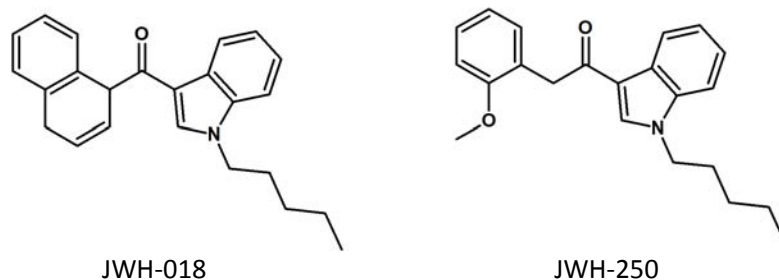


Figure 1: Chemical structure of JWH-018 and JWH-250

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## **Acknowledgement**

This work is supported by the Czech Science Foundation (GAČR 19-03160S).



# THE EXPLORATION OF THE GAMMA RADIATION EFFECT ON PRIMORDIAL FORMAMIDE-BASED SOLUTIONS

Ing. Adam Pastorek

*supervisor: prof. RNDr. Svatopluk Civiš, DSc.*

Many experiments in the past have proven some simple molecules under specific conditions and enough amount of external energy can possibly form more complex biogenic compounds such as nucleobases, amino acids or sugars. One of those molecules is formamide, the simplest amide possible, which yields all the canonical nucleobases and other compounds as well upon simple heating.

Nowadays, one of current trends is to observe different types of external energy which could have possibly influenced early prebiotic chemistry. Researchers tried electric discharge [1], high energy lasers [2], shockwaves [3] or even proton [4] and heavy nuclei [5] bombardment. Nevertheless, the role of ionising radiation itself remains a mystery since there are only few scientists involved in this extremely difficult topic.

In my presentation I will highlight urea as the main product of  $\gamma$  radiolysis of formamide and I will show its high importance in prebiotic chemistry. A certain amount of focus will also be aimed on the importance of nuclear chemistry itself and its remarkable role in origin of life theories.

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# IDENTIFIABLE SPECTRAL FEATURES PREDICTED FOR TRANSMISSION SPECTRA OF YOUNG EXOPLANETS UNDERGOING HEAVY BOMBARDMENT

**Bc. Lukáš Petera**

*supervisor: RNDr. Martin Ferus, Ph.D.*

The chemical environments of young planets are assumed to be largely influenced by impacts of bodies lingering on unstable trajectories after the dissolution of the protoplanetary disk. We explore the chemical consequences of impacts within the contexts of several model planetary atmospheres. A terawatt high-power laser was used in order to simulate the airglow plasma and blast wave surrounding the impactor. The chemical results of these experiments were then applied to a theoretical atmospheric model. We predict that acetylene absorption bands are observable on exoplanets with reducing atmospheres that have recently undergone their own „Heavy Bombardments,“ with prominent features at 3.05  $\mu\text{m}$  and 10.50  $\mu\text{m}$ . Furthermore, we demonstrate that impact reprocessing of volcanic atmospheres leads to a formation of carbonyl sulfide (OCS) and carbon disulfide ( $\text{CS}_2$ ). These results show that impact plasma is the driving force of atmospheric chemistry on young planets and can lead to the formation of marker molecules that can be predicted through laboratory experiments<sup>1</sup>.

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## SYNERGISTIC EFFECTS IN OXYGEN EVOLUTION ACTIVITY OF MIXED IRIDIUM- RUTHENIUM PYROCHLORES

**Rebecca Pittkowski, M.Sc.**

*supervisor: doc. Ing. Petr Krtil, CSc.*

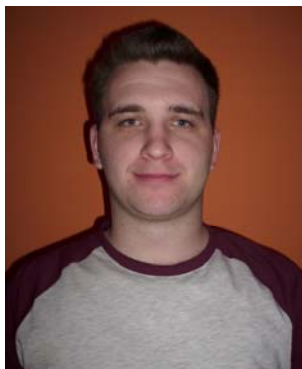
Efficient energy storage solutions are of vital importance to allow for the replacement of fossil fuels to renewable electricity sources.<sup>1</sup> Hydrogen is deemed as suitable for large-scale energy storage and energy conversion using electrochemical devices such as electrolyzers.<sup>2</sup> The technology is, however, limited by the sluggish kinetics of the electrocatalytic oxygen evolution reaction (OER).<sup>3</sup> To improve the current state-of-the-art catalyst's feasibility, one may either aim at optimizing the surface orientation or at reducing the costly catalyst components. Here, the latter approach is outlined on the benchmark oxygen evolving systems for acid media, based on rutile structured RuO<sub>2</sub> and IrO<sub>2</sub>. A decrease of noble metal content can conveniently be achieved if one moves from binary to ternary phases. Cubic pyrochlores of the A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> type have been studied as promising catalysts to replace conventional IrO<sub>2</sub> and RuO<sub>2</sub> OER catalysts. For catalytically active Ru or Ir occupying B-sites, the A-sites can be occupied by many lanthanides. These rare earth elements are subject to the effect of lanthanide contraction, differing in ionic radius. Hence, different lanthanide cations change the unit cell parameter and, consequently, the metal-to-metal distance between the transition metal cations. This again influences the position of the catalyst's d-band center.<sup>4</sup>

This work presents the synthesis and characterization of a new set of rare earth pyrochlore catalysts of the general structure Ln<sub>2</sub>(Ru<sub>x</sub>Ir<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> (Ln = Yb, Gd, Nd), introducing different ratios of iridium and ruthenium as B-site cations. The motivation to use cation mixing is the positive effect the Ir/Ru coexistence has on the catalyst's performance in the mixed binary oxides: Iridium is known to stabilize RuO<sub>2</sub> in mixed oxide electrodes, and the effect has been studied thoroughly.<sup>5,6</sup> By introducing iridium into ruthenium oxide, however, the catalytic activity in OER is slightly lessened.

The catalysts were synthesized *via* the spray-freeze freeze-dry approach and the obtained materials were characterized by XRD, SEM, and EDX. The new catalyst reported here all exhibit an unprecedented improvement of OER activity compared to the previously described catalysts without mixing of Ru/Ir, as well as benchmark IrO<sub>2</sub>. The local structure of the materials was analyzed using X-ray absorption fine structure (EXAFS) analysis and related to the observed improved catalytic activity.

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## TIME-RESOLVED VIBRATIONAL SPECTRA OF Ru AND Re DIIMINE COMPLEXES: AN ANHARMONIC CALCULATIONS

Ing. Martin Pižl

supervisor: Ing. Stanislav Záliš, CSc.

Vibrational properties of Ru and Re complexes were used for characterization of their photophysical properties. Anharmonic calculations are important for better understanding of time-resolved IR spectra and detailed description of experimental data by calculated results. Anharmonic frequencies were calculated by second-order perturbation theory (VPT2) in the frame of DFT methodology using Gaussian 16 program package. Resonances were treated by generalized VPT2 procedure (GVPT2).

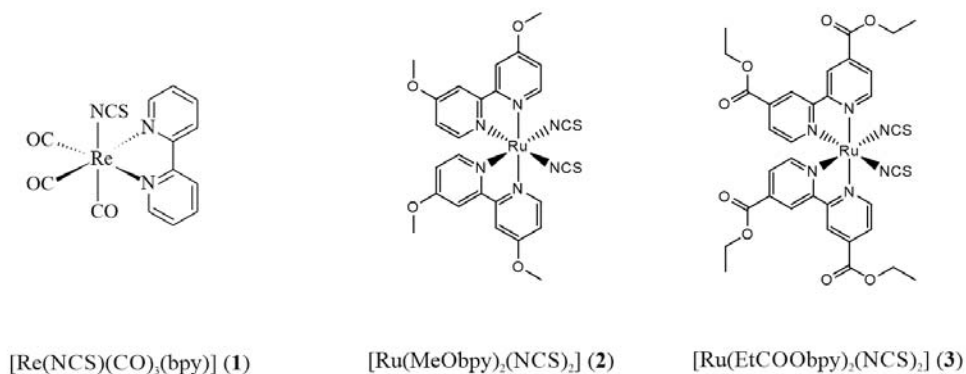


Figure 1 Structure of complexes under study.

The simulated harmonic and anharmonic difference IR spectra between excited and ground state of [Re(NCS)(CO)<sub>3</sub>(2,2'-bipyridine)] (1) describes changes in the experimental TRIR spectrum. The second part of this work is focused on an application of the anharmonic approach for estimating of diagonal and off-diagonal anharmonicities in 2DIR spectra of Ru complexes – [Ru(4,4'-di-R-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub>] (R= OMe (2) and CO<sub>2</sub>Et (3)). Anharmonic vibration analysis also well interprets shifts of  $\nu(\text{N-C})$  stretching frequencies upon the excitation and oxidation/reduction of Ru complexes. Structures of complexes 1-3 are depicted on Fig.1. Calculated matrix elements of Y matrix point out to couplings of NC vibrations.

**Acknowledgements** This work was supported by the Czech Science Foundation (GAČR) grant 17-011375 and the MOLIM COST action.



# THE CENTRAL ATOM EFFECT ON GEOMETRY OF TRANSITION METAL COMPLEXES CONTAINING GUANIDINATE LIGAND

**Kristýna Pokorná**

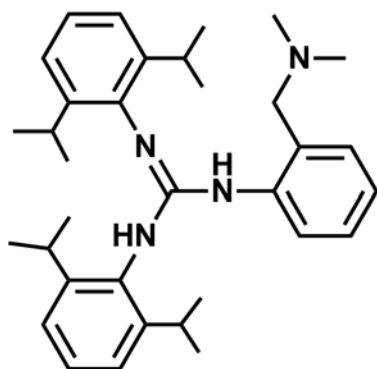
secondary school internship,  
Gymnázium Roudnice nad Labem

*supervisor: Mgr. Michal Horáček, Ph.D.*

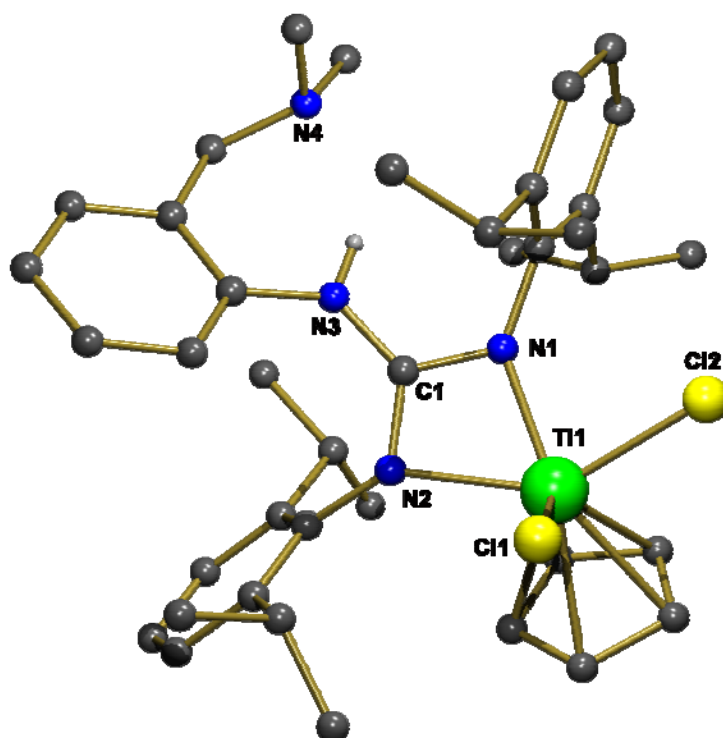
The aim of this student's project is to compare structural and electronic effects in transition metal complexes containing different elements such as titanium, zirconium, hafnium, and iron with the bonded guanidinate ligand.

For solving this project it was necessary to find the right way for complexes preparation and isolation in the cleanest form. The guanidinate compound used for this study contains two diisopropylphenyl and dimethylaminoaniline groups on central  $N_3C$  skeleton ( $LNNH_2$  molecule). This ligand was bonded into titanium, zirconium, hafnium, and iron precursors by a straight reaction using metal amides, or by transmetallation reaction of its lithium salt.

The obtained material was characterized by different spectroscopic techniques with the aim to find out molecular structures and compositions of newly prepared substances. The results displaying different/similar physical and chemical properties of used metals on the structure of the complexes with  $LNNH$  ligand will be discussed.



$LNNH_2$  molecule





## LOCAL PHOTOCURRENT CHARACTERIZATION OF GRAPHENE- SILICON HETEROJUNCTION

**Mgr. Jaroslava Řáhová**

*supervisor: Mgr. Otakar Frank, Ph.D.*

Many 2D materials like graphene and TMDCs exhibit compelling optoelectronic properties, which make them interesting for future use in photovoltaics. Heterostructures build-up of these materials and 3D crystals benefit from exceptional features of thin layered materials and already established production know-how of 3D materials. Even though there are reliable macroscopic methods for heterojunction characterisation, deeper understanding of fundamental photo-induced effects at the heterojunctions is needed to investigate the effects of number of layers of 2D material, defects, ionic doping or ageing.

Our study is targeted on the characterisation of photovoltaic properties of exfoliated graphene (2D)/n-silicon (3D) heterostructures by advanced Atomic Force Microscopy (AFM) based techniques: current measurement by conductive AFM mapping (C-AFM) complemented by local I-V characterisation; and surface potential measurement by Kelvin Probe Force Microscopy (KPFM). Obtained results were supplied by additional information provided by Raman spectroscopy and photoluminescence characterisation and compared to results given by macroscopic surface potential measurement by Scanning Kelvin Probe Microscopy (SKP).

We further show the importance of systematic characterisation of the bare p and n doped silicon substrate to distinguish the influence of carrier diffusion through silicon and photoeffects generated at the heterojunction.



## **INFLUENCE OF BENZALKONIUM CHLORIDES ON HUMAN TEAR FILM LIPID LAYER MODELS**

**Mgr. Kamila Riedlová**

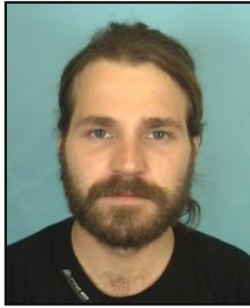
*supervisor: Doc. Lukasz Cwiklik, Ph.D.*

The tear film is a thin aqueous layer residing at the surface of the cornea. It is covered by a lipid structure – Tear Film Lipid Layer (TFLL). The main role of TFLL is to reduce the surface tension of the tear film. It is also hypothesized that tear lipids prevent tear evaporation. Importantly, TFLL is the first eye structure that is exposed to topical ophthalmologic drugs.

Benzalkonium chloride mixtures (BAK) traditionally used to preserve eye drops through their bactericidal and bacteriostatic properties. They are composed of aliphatic (C8, C12) quaternary ammoniums. The compounds of BAK have an amphiphilic and surface active character hence it can be assumed that on the ocular surface they interact and alter TFLL properties. We hypothesize that by influencing polar lipids, BAK can modulate the details of molecular-level interactions between individual species of TFLL and indirectly affect the organization and stability of the tear film.

To assess molecular-level interactions between BAK species and Tear Film Lipid Layer models, we employed *in silico* molecular dynamics (MD) simulations. Apart from BAK, we are also considering other components used in topical ophthalmologic drug formulations, such as cetalkonium chloride and short-chain triglycerides.





## NOVEL APPROACH FOR PREPARATION OF PROAPOPTOTIC PROTEIN BAX

**Mgr. Kristián Skála**

*supervisor: RNDr. Radek Šachl, Ph.D.*

Protein Bax is a member of bcl-2 family proteins that can regulate the permeability of the outer mitochondrial membrane. Stress factors cause accumulation of Bax on the membrane and subsequent formation of oligomers that can form a pore. Cytochrome c is subsequently released from the mitochondria, which triggers a reaction cascade leading to the apoptosis of cells.

In the first phase of the project, the main aims are to recombinantly express the protein Bax in bacteria, purify it and label a mutated version of the protein with a fluorescent probe. To increase the yields of this approach, we established a new construct where Bax has been fused with GST protein. This approach should lower the toxicity of Bax against bacteria. In the next phase, we plan to examine the impact of the lipid composition and the activator of Bax tBid on the oligomerization of Bax in model lipid bilayers. The project also aims at finding out a possible relation between the oligomerization of Bax and formation of pores induced by this protein.

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## USING OF A DUAL GLASSY CARBON ELECTRODE FOR AMPEROMETRIC DETERMINATION OF ANTHRAQUINONE -2-SULFONATE

Mgr. Štěpánka Skalová

*supervisor: Doc. Ing. Tomáš Navrátil, Ph.D.*

Anti-cancer drug dosages are commonly based on estimation of the physician. Therefore, they frequently do not correspond to requirements of patients suffering from cancer. One of the way, how to improve the cancer therapy, is the optimization of dosage on the base of determination of drug level in blood of particular patients [1].

For monitoring of anti-cancer drugs in blood, we have developed a flow system with an electrochemical cell connected with direct dialysis of drugs.

The electrochemical arrangement was employed: the dual working glassy carbon electrode (GCE), the Ag|AgCl (3 mol L<sup>-1</sup> KCl) reference electrode, and the stainless steel capillary auxiliary electrode. Natrium anthraquinone-2-sulfonate (AQS) was chosen as model substance for anthraquinone anticancer drugs. It was dissolved in a carrier solution – saline (physiological) solution (154 mmol L<sup>-1</sup> of NaCl).

Described arrangement was used for AQS amperometric determination. At the first GCE, reduction of AQS was carried out at optimized potential of -1200 mV. Subsequently, oxidation of AQS reduction product was performed at the optimized potential of -900 mV. With this experimental design, we have successfully increased the signal/noise ratio, which led to improvement of determination sensitivity.

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## ELEKTROCHEMICKÉ A SPEKTROMETRICKÉ STUDIUM TITANOCÉN DIHALOGENIDŮ

Jan Svoboda

školitel: prof. RNDr. Jiří Ludvík, CSc.

Cisplatina ( $cis\text{-}[\text{PtCl}_2(\text{NH}_3)_2]$ ) je stále považována za jedno z neúčinnějších cytostatik.[1] Nicméně ona a její deriváty vykazují celou řadu nežádoucích účinků. Proto vzrůstá zájem o výzkum a vývoj nových protirakovinných léčiv neobsahujících platinu. Jednou ze zkoumaných alternativ je skupina organometalocenových dihalogenidů založených na atomech přechodných kovů (Ti, Zr). Titanocen dichlorid ( $[\text{Cp}_2\text{TiCl}_2]$ ,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) byl první koordinační sloučeninou neobsahující platinu, která podstoupila klinické zkoušky jako lék při chemoterapii. I přes ukončení klinických testů pro jeho nedostatečnou účinnost (*in vivo*) a nízkou rozpustnost zůstávají deriváty titanocenu nadějnými kandidáty pro léčbu. [2]

V našem oddělení (dr. Jiří Pinkas) byla nedávno připravena nová série titanocén dihalogenidů, kde atomy chloru byly nahrazeny fluorem a cyklopentadienové kruhy byly methylovány. Je zřejmé, že oxidačně-redukční vlastnosti těchto látek budou hrát roli v jejich biologické aktivitě. [3] V literatuře lze najít pouze omezené informace o elektrochemickém výzkumu titanocen dihalogenidů, a proto bylo prvním úkolem tohoto projektu doplnit mezeru v poznání těchto sloučenin, nově připravené látky prostudovat elektrochemicky (pomocí dc-polarografie, cyklické voltametrie a voltametrie na rotující diskové elektrodě) v kombinaci s UV-vis spektrometrií a zjistit též případnou korelaci mezi naměřenými elektrochemickými a spektrometrickými daty.

Elektrochemická redukce všech studovaných látek je difuzí řízená, nezávisí na materiálu elektrody (Hg, Pt, GC) a probíhá ve dvou až třech krocích. První krok je ireverzibilní, zřejmě jednoelektronový. Fluoridové ligandy znesnadňují redukci, která probíhá na halogenidech (bylo detegováno odštěpení halogenidu) a nikoliv na Ti. Je překvapivé, že redukce plně methylovaných  $\text{Cp}^*_2\text{TiX}_2$  a nemethylovaných  $\text{Cp}_2\text{TiX}_2$  neprobíhají podle analogického mechanismu. Ukázalo se též, že chlorované titanoceny reagují spontánně se rtuťí za uvolnění chloridových iontů (potvrzeno UV-vis spektrometrií).

Elektrochemická oxidace u všech studovaných látek je též difuzí řízená, opět nezávisí na materiálu elektrody (Hg, Pt, GC) a probíhá v jednom až ve dvou krocích. První krok však vykazuje dvojnásobný proud oproti redukci (RDE, CV). Fluorované titanoceny při oxidaci tvoří zřejmě polymery, které blokují elektrodu (pozorováno při preparativní elektrolýze).

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## THE DEVELOPMENT OF FLOW ELECTROCHEMICAL CHOLINE BIOSENSOR BASED ON THE ENZYMATIC CHOLINE OXIDASE REACTOR

**Mgr. Sofiia Tvorynska**

*supervisor: Bohdan Josypčuk, Ph.D.*

Choline (Ch) plays an essential role in human health as a precursor to neurotransmitter acetylcholine, reducing the amount of last one in human body leads various neurological disorders, including Parkinson's disease, Alzheimer's disease, and schizophrenia. Moreover, Ch is a quite important for healthy functioning of liver and in woman's health during the pregnancy. Therefore, there is an ever increasing demand for methods of its detection in biological samples and pharmaceutical products.

In this work, a perspective type of the selective and stable flow amperometric biosensor based on enzyme choline oxidase (ChOx) bioreactor and a solid amalgam detector for the determination of Ch has been developed for the first time. The distinctive feature of the proposed biosensor laid in the separation of the enzymatic (reactor) and detection (working electrode) parts. Two types of the mesoporous silica powders, MCM-41 and SBA-15, have been utilized and compared as the filling materials in the reactor. The enzyme ChOx was covalently immobilized with glutaraldehyde to filling material surface, which was previously covered by  $\text{NH}_2$ -groups. The detection of Ch is based on amperometric monitoring of oxygen consumption in the enzymatic reaction, which is directly proportional to Ch concentration. Two arrangements of an electrolytic cell in flow injection analysis, namely wall-jet with working silver solid amalgam electrode covered by mercury film and flow-through cell with tubular detector of polished silver solid amalgam were compared. A number of the parameters (e.g., pH of the mobile phase, flow rate, detection potential, injection volume of Ch, concentration of the enzyme solution, time required for the recovery of ChOx activity, volume of ChOx-SBA15 reactor) effecting on the properties of the amperometric biosensor has been optimized.

Under the optimized conditions, the proposed choline biosensor showed the linear response range  $2.0 \times 10^{-5} - 3.0 \times 10^{-4} \text{ mol l}^{-1}$  with limit of detection  $9.0 \times 10^{-6} \text{ mol l}^{-1}$ . The biosensor with the elaborated enzymatic ChOx-SBA15 reactor lost 50 % of its initial response after its 700 uses over an investigated period of 100 days, indicating high stability of the biosensor. Moreover, the developed biosensor exhibited excellent selectivity, good repeatability and reproducibility. As a result, it has been successfully applied for the determination of Ch in two commercial pharmaceuticals with complex matrix produced in the Czech Republic.

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## VIBRATIONALLY MEDIATED PHOTODISSOCIATION DYNAMICS OF PYRROLE

**Mgr. Ivo S. Vinklársek**

*supervisor: doc. Mgr. Michal Fárník, DSc. Ph.D.*

Photodissociation of pyrrole molecules with IR excited N-H bond stretching vibration ( $\nu_1 = 1$ ,  $\nu_{\text{IR}} = 3532 \text{ cm}^{-1}$ ) was investigated in a velocity map imaging experiment upon photodissociation at  $\lambda_{\text{UV}} = 243 \text{ nm}$ . The velocity map images show the bimodal structure of fast and slow H-fragments. In the UV+IR experiment, the fast peak is shifted to 1.04eV compared to 0.81eV of the UV-only photodissociation, which means that approximately 53% of additional vibrational energy (0.44eV) is deposited into H-fragment kinetic energy. The IR pre-excitation also exhibits enhanced H-fragment signal with respect to UV-only experiment due to a more favourable Franck-Condon factor of transition from the vibrationally excited pyrrole. [1] The UV+IR spectra were further compared with isoenergetic UV-only experiments. Upon excitation at  $\lambda_{\text{UV}} = 224 \text{ nm}$ , the fast peak maximum shifts 0.15eV towards lower energies and only 61 % of total available energy converts into H-fragment kinetic energy in respect to 72% of UV+IR photodissociation, which demonstrates efficient coupling of the excited N-H vibration to the bond dissociation and fragment kinetic energy. The observation corresponds to spectra of Cronin et al. [2] measured with excitation of  $\lambda_{\text{UV}} = 220 \text{ nm}$  and  $\lambda_{\text{UV}} = 228 \text{ nm}$  with similar lower conversion to fragment kinetic energy of 56% and 70%. Finally, we measured the time-resolved nanosecond experiment by pump-probe approach. The H-fragment signal shows similar intensification and kinetic energy distribution independently on the delay of IR pulse up to 150 ns, which illustrates preservation of the vibrational excitation in various degrees of freedom of pyrrole that enhances the UV photodissociation. [3]

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