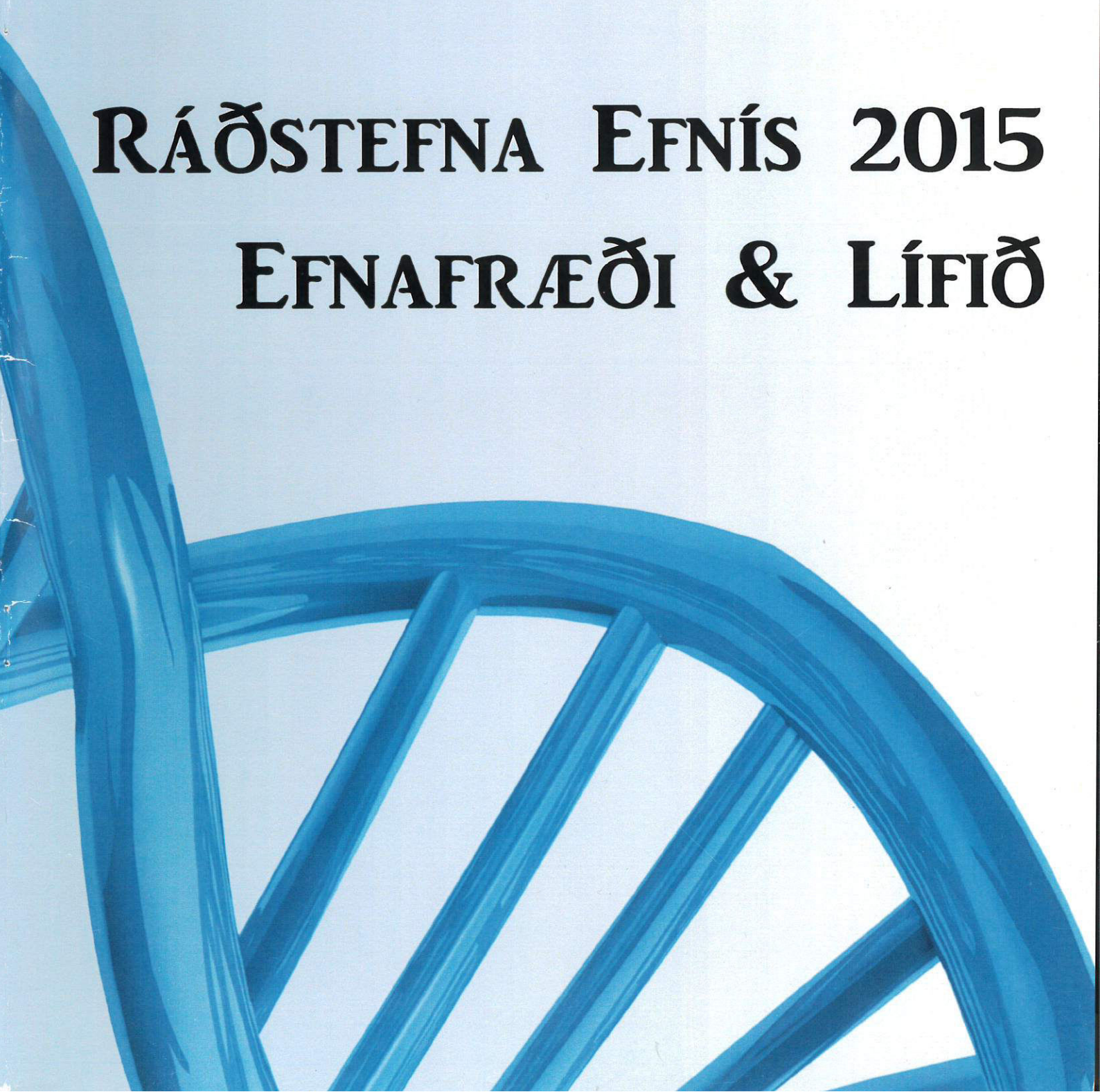
Efnafræðifélag Íslands
The Icelandic Chemical Society

Ráðstefna Efnís 2015

Efnafræði & Lífið



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Ráðstefna Efnís 2015 – Efnafræði og lífið

Dagskrá

Tími	Fyrirlesari og Kynning
09:00 – 09.10	**Helgi Rafn Hróðmarsson** *– Setning Ráðstefnu Efnafræðifélags Íslands 2015*
09:15 – 09:45	**Ágúst Kvaran** *– Um Efnafræði í Alheimi og Sitthvað Fleira á 30 Mínútum*
09:50 – 10:10	**Sesselja Ómarsdóttir** *– "Biophilia", Biodiversity, and Bioprospecting in Natural Product Drug Discovery in Iceland*
10:20 – 11:00	Kaffihlé & Veggspjaldakynning
11:00 – 11.30	**Gissur Örlygsson** *– Lífstoðefni*
11:35 – 11: 50	Örfyrirlestrar 1 og 2
12:00 – 13:05	Hádegismatur
13:05 – 13:35	**Egill Skúlason** *– Sjálfbær Framleiðsla á Eldsneyti og Áburði til Matvælaræktunar*
13:40 – 14:10	**Ásta Margrét Ásmundsdóttir** *– Röntgengeislar – Hvernig Hið Ósýnilega varð Sýnilegt*
14:15 – 14:30	Örfyrirlestrar 3 og 4
14:40 – 15:10	Kaffihlé & Veggspjaldakynning
15:10 – 15:25	Örfyrirlestrar 5 og 6
15:30 – 16:00	**Valgeir Valgeirsson** *– Notkun Ómaltaðs Íslenskts Byggs til Bjórgerðar með Viðbættum Ensímum*
16:00 – 17:00	Veggspjaldakynningar og Mixer
17:00 – 19:00	Hlé
19:00 –	Árshátíð Efnís

Schedule

Time	Lecturer and presentation
09:00 – 09.10	**Helgi Rafn Hróðmarsson** *– Introduction to the Icelandic Chemical Society's conference 2015*
09:15 – 09:45	**Ágúst Kvaran** *– Chemistry of life in the universe and related matters in 30 minutes*
09:50 – 10:10	**Sesselja Ómarsdóttir** *– "Biophilia", Biodiversity, and Bioprospecting in Natural Product Drug Discovery in Iceland*
10:20 – 11:00	Coffee break and poster presentations
11:00 – 11.30	**Gissur Örlygsson** *– Biomaterials*
11:35 – 11: 50	Short lectures 1 and 2
12:00 – 13:05	Lunch
13:05 – 13:35	**Egill Skúlason** *– Sustainable production of fuels and fertilizers*
13:40 – 14:10	**Ásta Margrét Ásmundsdóttir** *– X-rays – how the invisible became visible*
14:15 – 14:30	Short lectures 3 og 4
14:40 – 15:10	Coffee break and poster presentations
15:10 – 15:25	Short lectures 5 og 6
15:30 – 16:00	**Valgeir Valgeirsson** *– The use of unmalted barley in beer brewing without additional enzymes*
16:00 – 17:00	Poster presentations and mixer
17:00 – 19:00	Intermission
19:00 –	Efnís banquet

Ágrip fyrirlestra
Lecture abstracts

Fyrirlestur 1

Chemistry of life in the universe and related matters in 30 minutes

Ágúst Kvaran

Fundamental, basic chemistry and relevant physics behind possible formation of „earth like life" in the universe will be discussed. The importance of interactions between radiation and matter will be highlighted. Ongoing related studies, within University of Iceland, will be introduced and relevant research methodologies presented....., all within 30 minutes!

Fyrirlestur 2

"Biophilia", biodiversity, and bioprospecting in natural product drug discogvery in Iceland

Sesselja Ómarsdóttir

"Biophila" means love of life or living systems and the biophilia hypothesis introduced by E.O. Wilson is defined as "the innate tendency to focus on life and life like processes"[1]. Natural product chemists, as many others, are innately attracted to nature, through their scientific investigations of plants, animals and microbes that hold potential for sustainable sources of natural products of high chemodiversity. Natural products are represented in over a third of the drugs in Western pharmacopeias, and new compounds are being discovered continuously. Our research program at the University of Iceland is directed towards one of the first systematic investigation of natural product diversity of the Icelandic biota, especially lower plants, lichens – and more recently marine organisms – for their potential for drug-lead discovery in several key therapeutic areas. Iceland is a volcanic island in the North Atlantic Ocean, which hosts both hot- and cold-adapted organisms. Iceland's natural products are relatively unexplored. The unique of Iceland, including hydrothermal vent sites, are of particular interest for bioprospecting. To date, several new natural compounds of different chemical classes e.g. alkaloids, terpenoids, nucleosides, lipids, carbohydrates and phenolic compounds have been isolated and their structures elucidated using spectroscopic techniques. These new compounds, together with previously identified natural products, showed interesting *in vitro* biological activity. Expanded investigations of unique and pharmacologically active compounds from Icelandic flora and fauna complements traditional approaches to natural products-based drug discovery from temperate and tropical zones.

1. Wilson, Edward O. (1984). *Biophilia*. Cambridge: Harvard University Press.

Fyrirlestur 3

Lífstoðefni

Gissur Örlygsson

Lífstoðefni (biomaterials) eru hverskyns efni önnur en lyf, náttúruleg eða manngerð, sem laga, auka, eða er skipt út fyrir eða koma í stað hverskyns vefja, líffæra eða virkni líkamans í lengri eða skemri tíma í þeim tilgangi að viðhalda lífsgæðum eða auka lífsgæði einstaklings[1]. Þörfin fyrir lífstoðefni er rík þar sem marga sjúkdóma, áverka og einkenni er ekki hægt að meðhöndla með öðrum meðferðum eða aðferðum. Sem dæmi má nefna endurnýjun á líkamshlutum sem hafa glatað virkni sinni (mjaðmarliður, hjartaloka), leiðréttingu á afbrigðilegu ástandi (hryggur), bætingu á virkni (gangráður, æðavíkkun) og aðstoð við lækningu/græðslu (stuðningur, saumþráður). Lífstoðefni geta verið af margvíslegu tagi, svo sem málmar, keramik og glerefni, fjölliðuefni, náttúrulegar fjölliður og samsett efni.

Nýsköpunarmiðstöð hefur tekið þátt í fjölmörgum verkefnum á sviði lífstoðefna. Hér verða nokkur þeirra nefnd: Þróun og greining á beingræðsluefnum úr kítósanafleiðum og kalsíumfosfati ásamt rannsóknum á virkni þeirra í dýratilraunum. Þróun á húðun á títani og títanígræðlingum með kítósanafleiðum til að flýta og bæta festu í beini[2]. Húðunaraðferðir á slétta fleti hafa verið þróaðar[3] sem og einfaldar aðferðir á borð við „dip coating" en einnig fengist við rafdráttarhúðun (electrophoretic deposition). Þróun á nýstárlegri liðskál úr samsettu keramik- og glerkeramikefni í mjaðmagerviliði var unnin í evrópsku samstarfsverkefni[4]. Röntgensneiðmyndagreining á sýnum úr dýratilraunum og úr annarri vinnu með lífstoðefni hefur einnig verið fyrirferðamikil[5,6].

Í erindinu verður farið almennt yfir lífstoðefni og greint frá rannsóknar- og þróunarverkefnum sem Nýsköpunarmiðstöð hefur tekið þátt í.

1. B.D. Ratner et al. (Eds.) Biomaterials Science; An introduction to materials in medicine, 3rd edition, 2013, Elsevier Inc., xxv-xxxix.

2. R. Lieder, M. Darai, M. B. Thor, C.-H. Ng, J. M. Einarsson, S. Gudmundsson, B. Helgason, V. S. Gaware, M. Másson, J. Gíslason, G. Örlygsson and Ó. E. Sigurjónsson. J. Biomed. Mater. Res. Part A, 100A(12) 2012, 3392-3399.

3. R. Lieder, M. Darai, G. Örlygsson and O. E. Sigurjonsson. Biological Procedures Online 2013, 15:11.

4. F. Baino, J. Minguella, N. Kirk, M. A. Montealegre, C. Fiaschi, F. Korkusuz, G. Örlygsson, C. Vitale-Brovarone. Submitted to Acta Biomaterialia.

5. A. Czenek, R. Blanchard, A. Dejaco, O.E. Sigurjonsson, G. Orlygsson, P. Gargiulo, C. Hellmich. J.Mater.Res., 29(23), 2014, 2757-2772.

6. P. Hasslinger, V. Vass, A. Dejaco, R. Blanchard, G. Örlygsson, P. Gargiulo, C. Hellmich. Under review by International Journal for Computational Methods in Engineering Science and Mechanics.

Fyrirlestur 4

Sjálfbær framleiðsla á eldsneyti og áburði til matvælaræktunar

Egill Skúlason

Á næstu örfáum áratugum þarf að finna nýjar leiðir til að knýja bæði vélar og menn áfram til að hægt sé að viðhalda lífi og bæta lífsgæði fyrir alla jarðarbúa. Olían er að hverfa, gróðurhúsaáhrifin aukast og mannfólkinu fjölgar. Vísindamenn keppast um að finna lausnir á orkumálunum, og þar hefur endurnýting á CO_2 verið eitt mest lofandi viðfangsefnið. Nú er hægt að fanga CO_2 úr andrúmsloftinu í tonnavís, en einnig er hægt að endurnýta CO_2 úr útblæstri verksmiðja og borhola frá jarðhitasvæðum og framleiða úr því eldsneyti á borð við metan eða metanól. Í dag þarf að setja upp verksmiðjur þar sem vetnisgas er fyrst framleitt en síðan er það hvarfað við CO_2 við háan hita og mikinn þrýsting líkt og Carbon Recycling International framleiðir metanól hér við Svartsengi á Suðurnesjunum. Þar er vetnið framleitt með rafgreiningu vatns sem er hægt hér á landi vegna ódýrrar og grænnar raforku. Keimlíkt dæmi er hvernig áburður er framleiddur í dag fyrir matvælaræktun, með svokallaðri Haber-Bosch aðferð, þar sem lykilskrefið í átt að áburðarframleiðslu er að framleiða ammóníak. Þar er nitur andrúmsloftsins tekið og hvarfað við H_2 við enn meiri hita og þrýsting en þarf fyrir CO_2 afoxunina. Þetta er risastór iðnaður en þetta ferli er talið ástæðan fyrir þeirri fólksfjölgun sem hefur átt sér stað síðustu 100 árin. Hér er vetnisgasið yfirleitt framleitt úr jarðgasi, sem er þverrandi orkulind, en það ferli er einnig það dýrasta og mengar hvað mest í allri áburðarframleiðslunni. Ef hægt væri að afoxa CO_2 eða N_2 beint í rafsellum, væri hægt að búa til eldsneyti og áburð hvar sem er, með litlum og ódýrum búnaði. Þá væri hægt að framleiða eldsneyti á ferð og flugi, í heimahúsum sem og við CO_2 uppsprettur eða útblástur. Áburðinn þyrfti ekki lengur að flytja á milli heimshorna með tilsvarandi mengun og kostnaði heldur gætu bændur í þróunarlöndunum sem og almenningur heima hjá sér útbúið sinn eigin áburð við rætur plantnanna. Rannsóknahópur minn við Háskóla Íslands hefur lagt hönd á plóg við bæði verkefnin. Rannsóknirnir byggja að mestu leiti á kennilegum reikningum þar sem við notum samhliða tölvureikninga sem byggja á grundvallarjöfnum eðlisfræðinnar, skammtafræðinni, til að spá fyrir um eiginleika og framvindu efnahvarfa á yfirborði rafskauta í raflausn. Þegar grundvallarskilningur hefur náðst, útbúum við einföld lögmál til að hjálpa okkur við leit að nýjum efnahvötum fyrir þessi rafefnahvörf. Þeir rafefnahvatar sem eru mest lofandi eru síðan búnir til á rannsóknarstofu og prófaðir í rafefnafræðilegum tilraunum.

Fyrirlestur 5

Röntgengeislar - Hvernig hið ósýnilega varð sýnilegt

Ásta Margrét Ásmundsdóttir

Þýska eðlisfræðingnum W.C. Röntgen varð strax ljóst að hinir dularfullu geislar sem hann uppgötvaði fyrir tilviljun þann 8. nóvember 1895, myndu hafa mikla þýðingu ekki aðeins fyrir vísindin heldur fyrir allt mannkynið. Það verður samt að teljast ólíklegt að hann hafi séð fyrir þá atburðarás sem fylgdi í kjölfarið.

Uppgötvun Röntgens vakti athygli langt út fyrir vísindasamfélagið og menn sáu strax hvaða byltingu hún boðaði t.d. í læknisfræði. Líklega hafa fáar vísindalegar uppgötvanir verið hagnýttar svo fljótt og það áður en menn höfðu hugmynd um hvaða fyrirbrigði þetta var sem Röntgen sjálfur kallaði X geisla. Margt átti eftir að koma í ljós og uppgötvun Röntgens, hagnýting hennar og þáttur í þróun vísindanna er áhugaverður hluti af sögu tuttugustu aldar. Sú saga snertir á siðferðilegum og efnahagslegum álitamálum sem endurspegla tíðarandann hverju sinni, þó mörg þeirra séu viðfangsefni okkar enn í dag. Síðast en ekki síst er þetta saga framfara í vísindum og aukinna lífsgæða fyrir almenning a.m.k. í hinum vestræna heimi.

Í fyrirlestrinum verður sagt frá uppgötvun röntgengeisla seint á 19. öld og hvaða þýðingu hún hafði. Farið verður yfir þróun röntgentækninnar framan af 20. öldinni og hvaða þátt hún átti í mörgum merkustu uppgötvunum vísindanna.

Fyrirlestur 6

Notkun ómaltaðs íslenskts byggs til bjórgerðar með viðbættum ensímum

Valgeir Valgeirsson

Á Íslandi hafa aðstæður til kornræktunar ekki verið góðar undanfarnar aldir, ólíkt því sem áður var. En núna með ögn hagstæðara veðurfar, nútíma landbúnað og kynbótaræktun hefur kornræktun náð góðri fótfestu á Íslandi og fer vaxandi. Langmest af því korni sem hér er ræktað er bygg sem hefur meira og minna verið nýtt í skepnufóður. Bændur hafa verið að leita leiða til að auka verðmæti korns og nýting þess til manneldis hefur því farið vaxandi. En bygg er jafnframt helsta korntegundin í bjórgerð og því lá ljóst fyrir að kanna nýtingu þess til innlendrar bjórframleiðslu.

Bjór er drykkur sem hefur fylgt mannkyninu frá örófi alda. Framleiðsluaðferðir hafa verið æði misjafnar gegnum tíðina en eiga það alltaf sameiginlegt að niðurbrot á dextrínum úr ýmsum korntegundum hefur verið lykilatriði ásamt gerjuninni sjálfri með gertegundinni *Saccaromyces cerevisiae*. Dextrín eru ógerjanlegar fjölliður glúkósasameinda og við niðurbrot þeirra þarf á ensímum að halda. Þessi ensím eru til staðar í flestum tegundum korns en myndast aðallega við náttúrulega spírun kornsins. Hægt er að stýra spírunarferli korns með vinnsluaðferð sem kallast möltun. Kornið er þá látið spíra við stýrðar aðstæður. Spírunin er svo stöðvuð þegar kornið er komið á það stig sem er hagkvæmast til bruggunar og kallast þá malt.

Vegna eiginleika íslensks byggs og vegna skorts á möltunaraðstöðu hér á landi, þá er ekki hægt að malta íslenskt bygg og því ekki hægt að brugga bjór á hefðbundinn hátt úr því. Fyrirtækið Novozime hefur þróað ensímblöndu sem nýtist í bruggun þannig að hægt er að brugga úr ómöltuðu byggi. Blandan inniheldur ýmsa próteasa sem brjóta m.a. niður hörðu próteinbygginguna í korninu og losa þannig um aðgengi að dextrínunum. Dextrín niðurbrotsensím sem kallast α- og β amylasar eru einnig í blöndunni og brjóta löngu dextrín fjölliðurnar niður í einfaldari sykrur sem eru; einsykruna glúkósa, tvísykruna maltósa, þrísykruna maltótríósa og lengri sykrur kallaðar maltódextrín. Próteasarnir sjá jafnframt um að brjóta ýmis prótín niður í form sem nýtist gernum.

Ávinningar af því að brugga bjór á þennan hátt geta verið margþættir. Þetta er umhverfisvænna ferli þar sem möltunarferlinu er sleppt en þannig minnkar heildarlosun gróðurhúsalofttegunda. Jafnframt er fjárhagsleg hagræðing bæði vegna kostnaðar við möltun og vegna þess að nýtingin á kornin er aðeins meiri. Hér á Íslandi bætist við markaðslegur ávinningur af því að geta nýtt innlent bygg. Aukin notkun á íslensku byggi eykur veltu hjá ræktendum og stuðlar vonandi að auknum gæðum sem á endanum mun auka notkunina enn frekar. En til marks um gæði íslensks byggs og bjórs sem er bara bruggaður úr því með viðbættum ensímum má nefna bjórinn Snorra frá Borg brugghúsi. Snorri vann til gullverðlauna í sínum flokki í stórri alþjóðlegri keppni árið 2014.

Ágrip veggspjalda
Poster abstracts

Veggspjald 1

Phospholipid composition of lipid rafts from rat heart

Edda Benediktsdóttir[1] and Adam Bauer[1].

Lipid rafts (LR) in the plasma membrane of eukaryotic cells have been defined as microdomains enriched in cholesterol, sphingolipids and phospholipids with saturated fatty acids. LR are either flat or caveolar structures and serve as platforms for efficient signal transduction. In cardiomyocytes, LR are predominantly in the caveolar form and among residents there are α_1- and β_2 adrenergic receptors, partly the β_1 adrenergic receptor and their signal transduction systems and effectors. The phospholipid composition of LR has been reported in several cell types, but to our knowledge the lipid composition of LR from heart muscle has not been reported. The aim of this project was to investigate the phospholipid composition of LR from heart.

LR from rat hearts were isolated on a sucrose gradient with a detergent-free method. LR marker proteins and ganglioside GM1 were analyzed with western blots and dot blots, respectively. Cholesterol was measured with a spectrophotometric assay. Lipids were extracted with the Folch method and the phospholipid composition was analyzed with ^{31}P-NMR spectroscopy.

LR markers were isolated in fractions 4-6 (of 12), counted from the top of the gradient and those fractions were defined as LR. ^{31}P-NMR analysis of the LR phospholipids showed that compared to the composition in total membranes of rat heart, LR were enriched in sphingomyelin, phosphatidylinositol and phosphatidylserine. Total phospholipid content in LR was 1,60 micromoles/mg protein and the cholesterol:phospholipid molar ratio was estimated to 1:3. Comparison to reported results about phospholipid composition of LR from three different cell types revealed a considerable cell type variation, especially in sphingomyelin content.

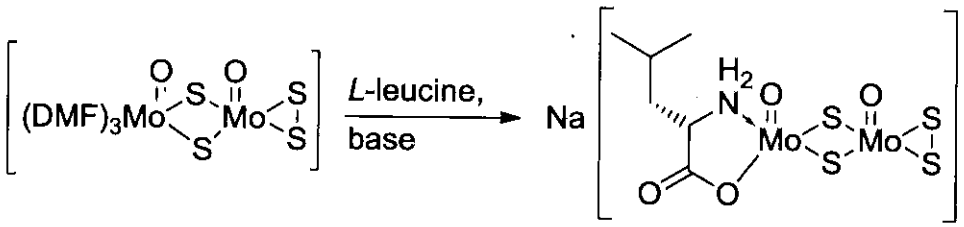
Veggspjald 2

Study of the Catalytic Conversion of Cyanide by the Novel Na[(*Leu*)$Mo_2O_2S_4$]-complex

Philipp Scharf, Thorvaldur Snæbjörnsson, and Sigríður G. Suman*

Aqueous cyanides are a concern because of their toxicity and potential impact on public health.[1] Development of methods to remove cyanides from the environment, and development of emergency treatments for cyanide poisoning has high impact on our future.

While most of the current treatments have to be given intravenously, an orally or intramuscular administration is desirable to simplify the treatment. The presented molybdenum complex and related compounds are promising candidates for a safe and effective treatment.



1 **2**

Catalytic cyanide conversion of the novel [(Leu)$Mo_2O_2S_4$]$^-$ anionic complex was quantified using spectroscopic methods. The complex is an active catalyst in vitro and shows promise for future devleopment. The preliminary data obtained will be presented.

Financial support from Icelandic Centre of Research (Rannís grant nr. 140945-051) is gratefully acknowledged.

References:

[1] F. P. Simeonova, L. Fishbein, *Hydrogen Cyanide and Cyanides: Human Health Aspects*, World Health Organization, Geneva, **2004**

Veggspjald 3

Synthesis and Structural Characterization of Co(II) Complex With a Glutathione Derivative.

Lindsey Monger, Sigríður Suman*

Glutathione (GSH) is a tripeptide with the amino acid sequence γ-glutamate-cysteine-glycine and it is considered one of the most important biological thiols. Because of its reduction abilities, it provides protection for cell components against oxidation. This also makes glutathione an attractive ligand for complexation. There have been previous attempts to synthesize cobalt(II)-GSH complexes. These synthetic routes have involved using aqueous solutions of $CoCl_2$ and GSH and stirring in a 1:1 molar ratio, then adding NaOH[1]. Another route involved using an aqueous solution of GSH and LiOH and adding $Co(ClO_4)_2$[2].

Recently we explored using a methylated derivative of glutathione ($GS(CH_3)_3$) for complexation, as this will change the properties of the ligand, possibly preventing dimerization.

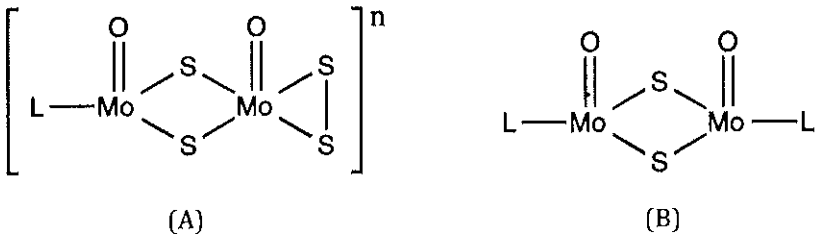
We will present the synthesis and structural characterization of a Co(II)- ($GS(CH_3)_3$) complex. We will present evidence that the cobalt binds to the ligand via the amide and amine groups.

Veggspjald 4

Spectroscopic Studies of Molybdenum-Sulfur Complexes with Amino Acid Ligands

Johanna M. Gretarsdottir and Sigridur G. Suman*

A set of Molybdenum-Sulfur complexes with different amino acid ligands were synthesized as potential cyanide treatment compounds *in vivo*. Complexes with bidentate amino acid ligand (L) coordinated to the dinuclear molybdenum sulfur bridged metal centre in ratios of 1:1 as well as 2:1 are reported, where L = leucine, methionine, serine and threonine.[1] The tridentate 1:1 cysteine complex was synthesised as well.[2] The 2:1 cysteine complex of the dinuclear $[Mo_2O_2S_2]^{2+}$ cation was reported previously as a model compound for xanthine oxidase [3], and it's crystal structure has been studied in great detail.[4]



(A) (B)

Figure 1. Molybdenum-Sulfur complexes with amino acid ligand to metal centre ratio for (A) and (B), respectively. L = leucine, methionine, serine and threonine, n= -1. L = cysteine for (A), n= -2.

The physical properties of these complexes were studied and the properties of the 1:1 complexes compared to those of the 2:1 complexes. The 1:1 complexes can be distinguished from the 2:1 complexes using electronic and infrared spectra.

We thank the Icelandic Centre of Research for financial support: grant nr. 140945-05

References

1. S. G. Suman; J. M. Gretarsdottir. *Manuscript in preparation.*
2. S. G. Suman, J. P. Gunnarsson. *Manuscript in preparation.*
3. A. Kay, P.C.H. Mitchell, Nature, Vol. 219 (1968) 267-268.
4. a) J.R. Knox, C.K. Prout, Acta Cryst. B25 (1969) 1857-1866. b) R. Yoshida, S. Ogasahara, H. Akashi, T. Shibahara, Inorganica Chimica Acta. *383 (2012)* 157-163.

Veggspjald 5

A highly buried and conserved tryptophan residue close to the dimer interface in a cold-adapted phosphatase is phosphorescent and important fro activity

Jens G. Hjörleifsson and Bjarni Ásgeirsson

Alkaline phosphatase (AP) from Vibrio G15-21 is a cold-adapted dimeric enzyme with one of the highest catalytic efficiency reported for known APs. It contains five intrinsic tryptophan (Trp) residues and one additional Trp located on the C-terminal StrepTag used for expression and purification. In this study, we made several single Trp-substitutions to determine the role of each of the Trp in the fluorescence emission spectrum. We also determined their solvent exposure by acrylamide fluorescence quenching. The results indicate that Trp301, Trp460 and Trp475 are mostly responsible for the fluorescence emission. Quenching experiments with acrylamide indicated that all the Trp residues were about equally accessible for quenching, except Trp460 which was shown to be highly buried in the core of the protein. Interestingly, the enzyme was found to be highly phosphorescent at 10 °C, having two phosphorescence lifetimes. The longer lifetime is due to Trp460. Trp460 is located close to the dimer interface and points towards a helix in the active site where His277 binds an active-site zinc ion. In other APs, an aromatic amino acid is conserved in the location occupied by the Trp460 residue. In most cases for cold-adapted APs it is indeed a Trp. Interestingly, the mutation of the Trp460 to a phenylalanine affected both stability and activity of the enzyme. kcat/KM was 10-fold lower than for wild-type. Overall, this study reveals that Trp460 can be used as a phosphorescent probe of local dynamics and could possibly also serve to study the dimer-monomer equilibrium due to proximity to the dimer interface, an area clearly crucial for enzyme activity and stability.

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Covalent Attachment of Biradicals to Surfaces for DNP Experiments

Snædís Björgvinsdóttir, Johanna Münkemer, Hartmut Oschkinat, Torsten Gutmann, Gerd Buntkowsky & Snorri Th. Sigurdsson

Dynamic nuclear polarization (DNP) can be used to enhance NMR signal intensities through electron spin polarization transfer from paramagnetic centres to nuclear spins of the sample of interest. This is usually attained by doping the sample with a paramagnetic polarizing agent, such as a stable organic radical. The sample is then irradiated with microwaves to transfer polarization of the unpaired electrons of the radicals to the sample nuclei. Under the experimental conditions used for solid-state DNP NMR, high magnetic field and low temperature, the most dominant mechanism for polarization transfer is the cross effect (CE). The CE is a three spin process where two electrons couple with one nucleus and each other. This makes biradicals, typically consisting of two TEMPO moieties tethered together, the most efficient polarizing agents for solid-state DNP NMR experiments. The current work is focused on synthesis and covalent attachment of biradicals to a variety of surfaces. The resulting spin labeled surfaces will then be used in DNP NMR experiments.

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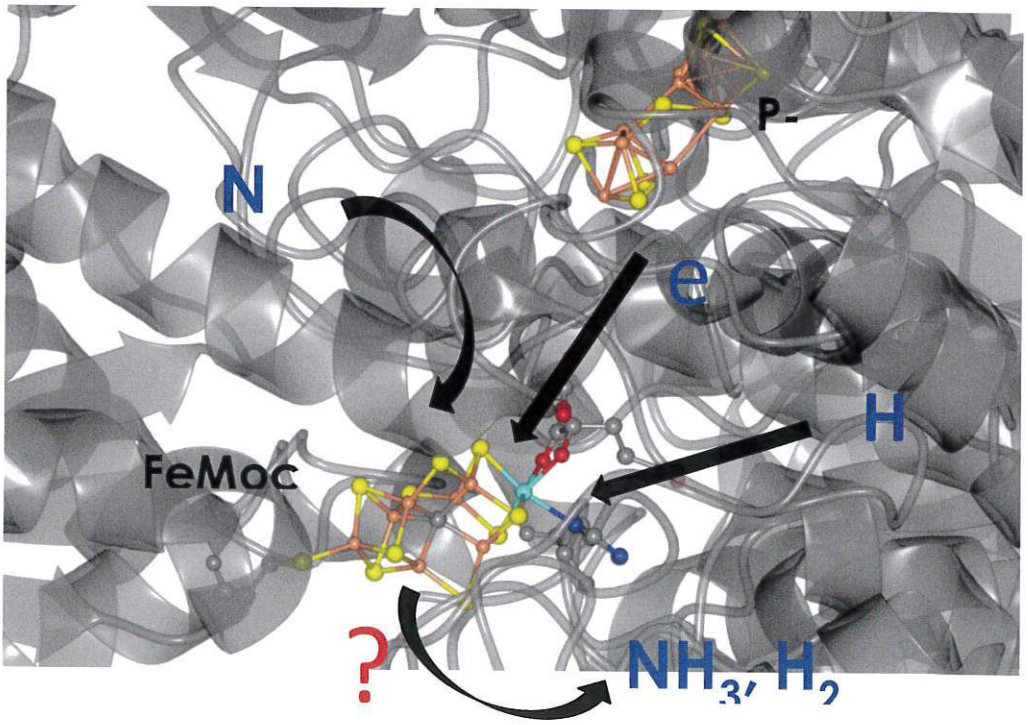
Understanding biological nitrogen reduction using advanced quantum chemical calculations

Ragnar Björnsson

The reduction of dinitrogen (N_2) to ammonia (NH_3) is a fundamental reaction in the nitrogen cycle and nitrogen is a building block in all organisms. Nitrogenase is the only biological system that activates dinitrogen and the complex metal-sulfide cofactor (FeMoco) used for this process is unique as it has structural features not known in any other enzyme. Understanding how the enzyme activates the strong bond of dinitrogen at ambient temperature and electrochemically produces ammonia is of fundamental importance and crucial for any attempt at bioinspired nitrogen catalysis. Despite decades of research, crucial structural and mechanistic information about the cofactor such as the binding site of N_2 remain unknown.

We here present recent quantum chemical modelling efforts from our group. A quantum mechanics/molecular mechanics model of the enzyme has recently been created that we hope will be able to uncover the mechanism of N_2 reduction and H_2 production. The mechanistic aspects of model [$MoFe_3S_4$] cubane compounds that bear structural similarities and shares catalytic aspects to the FeMoco cluster, have also been studied and sheds light on the structure-activity relationship that may be relevant to the chemistry of the enzyme.



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Copper(II) metallogel of 4-pyridyl nicotinamide in crystallization of pharmaceuticals

Dipankar Ghosh

The existence of different crystal forms such as polymorphs, solvates, salts or co-crystals have different bioavailability and solubility characteristics, and the crystal morphology and structure of pharmaceuticals can significantly affect their solubility, processing and tableting behaviour. Hydrogels and polymers have also been used to crystallize organic and inorganic compounds such as pharmaceuticals drugs and the crystallization of pharmaceuticals from metallogels is highly underexplored. We are interested in crystallizing selective polymorphs of organic and inorganic compounds by using designed metallogels. In this context, we have synthesized a series of metal complexes of pyridyl amide ligands and the gelation studies revealed that copper(II) complexes selectively formed gels. The selective gelation of all the copper(II) salts compared to the other metal salts may be attributed to Jahn-Teller distorted nature of copper(II), which weakens water binding in all copper(II) salts. The crystallization of organic and inorganic compounds using these metallogels are in progress.

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CO_2 Fixation by Catalytically Active MOFs based on Metalloligand

Dipankar Ghosh

Developing improved methods for the capture of carbon dioxide (CO_2) and its conversion to useful organic compounds is an area of current interest due to increasing percentage of CO_2 in the atmosphere, one of the most important factors of global warming and climate change. Metal organic frameworks (MOFs) are an excellent class of materials employed for CO_2 capture/separation and catalysis but there are only limited examples showing both CO_2 adsorption and catalytic conversion mainly due to the lack of catalytically active sites in MOFs. In this work we aim to synthesize a mixed MOF that can selectively adsorb CO_2 and will also catalytically convert CO_2 to useful organic products. We have incorporated catalytic active metal sites namely metalloligand, which are catalytically active metal centres with functional ligands into MOFs. MOFs developed by this method have large surface area and uniform micropores, which will lead to efficient and selective adsorption and the well-ordered arrangement of the catalytic centre will lead to effective catalysis of adsorbed CO_2 to desired product.

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Rational design of the cold active subtilisin-like serine protease VPR with improved catalytic properties and thermal stability.

Kristinn R. Óskarsson, Sigridur H. Thorbjarnardóttir, Magnús M. Kristjánsson.

On the basis of research done on the subtilisin-like serine proteinase VPR, from a psychrophilic *Vibrio* species and its thermophilic structural homologue, aqualysin I (AQUI) from *Thermus aquaticus,* we set out to design a mutant of VPR which would be more thermostable, but would retain the high catalytic activity of the wild type enzyme. Our starting protein template was a previously stabilized mutant containing two inserted proline residues close to the N-terminus of VPR (N3P/I5P). This VPR_N3P/I5P mutant was shown to have a significantly increased thermal stability but displayed a concomitant tenfold loss of catalytic efficiency. From our previous studies we selected two mutations, one which increased catalytic activity (Q142K) of the enzyme significantly and another which stabilized the protein against thermal denaturation (N15D). The N15D mutation had been shown to introduce a salt bridge into the structure of the cold adapted proteinase, yielding higher stability but without negative effects on activity. The Q142K exchange had been shown to double the turnover number (k_{cat}) to that of the wild type enzyme. Insertions of these selected mutations into the VPR_N3P/I5P mutant were according to predictions; the Q142K increased the k_{cat} tenfold, and the N15D mutation increased the thermal stability. In the combination mutant, VPR_N3P/I5P/N15D/Q142K, thermal stability was increased by 8 °C and 10 °C, in terms of T_m and $T_{50\%}$, respectively. Furthermore, the catalytic activity of the mutant was somewhat higher than that of the wild type enzyme.

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Total synthesis of stearidonic, eicosapentaenoic and docosahexaenoic acids

Svanur Sigurjónsson, Þóra Katrín Kristinsdóttir og Guðmundur G. Haraldsson

The n-3 PUFAs stearidonic acid (SDA), eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) were synthesized from 6-heptynoic, 5-hexynoic and 4-pentynoic acids, respectively. These precursors were converted into the corresponding ethyl esters by use of EDCI coupling agent and subsequently into the key diyne ethyl ester headgroups by condensation of their terminal acetylenes with propargyl bromide, promoted by copper(I) iodide in the presence of sodium iodide and potassium or cesium carbonate in DMF at room temperature. Similar polyyne propargyl halide building block strategy was followed to prepare di-, tri- and tetrayne tail groups possessing the n-3 framework that were attached to the appropriate headgroups using the same copper(I) mediated strategy. The resulting tetrayne (SDA), pentayne (EPA) and hexayne (DHA) ethyl esters were finally submitted to the crucial stereoselective Lindlar catalyst based semi-hydrogenation step to accomplish the intended n-3 PUFAs.

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NONCOVALENT SPIN-LABELING OF UNMODIFIED RNA USING APTAMER-LIGAND INTERACTION

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ABSTRACT

In our quest for spin-labeling of unmodified RNA, spin-labeled derivatives malachite green were synthesized and one of them was found to bind substantially to the well-known malachite green RNA aptamer by EPR and UV experiments.

INTRODUCTION, RESULTS AND DISCUSSION, CONCLUSION

Since it became evident that nucleic acids are indispensible constituents of all life forms, it has become more and more essential to determine the structure and dynamics of nucleic acids in order to understand their entire range of functions. Despite the existence of high resolution techniques like NMR, FRET and X-ray, EPR spectroscopy has been attaining increased attention and importance in recent years primarily owing to its sensitivity, simplicity of operation and for the fact that only unpaired electrons or paramagnetic species show EPR activity. Thus, has minimal background interferences.

After achieving promising results with covalent [1] and non-covalent [2] labeling of 'modified' nucleic acids, the next step was to develop a method for noncovalent spin-labeling of unmodified nucleic acids. To this end, we decided to utilise aptamers. Aptamers are artificial nucleic acids that are capable of strongly binding and distinguishing specific target ligands. They have been often described as nucleic acid version of antibodies and are also known to occur in nature in the form of riboswitches. Aptamers can be identified by the *in vitro* selection called **S**ystematic **E**volution of **L**igands by **Ex**ponential Enrichment (SELEX). This method utilises enrichment of a combinatorial library of DNA or RNA and several rounds of selection to generate aptamers for a given ligand.

The malachite green aptamer is one of the most well-known and well-studied aptamers (**Figure 1**) and binds to known dyes of the malachite green family with strong affinity. The binding mode has been coined as 'adaptive binding' because both the ligand and the RNA undergo changes in conformation upon binding. Our principle strategy was to attach paramagnetic spin-labels (SL) to malachite green and to the most promising derivative of the malachite green family, viz., tetramethylrosamine (TMR) [3]. Multi-step synthetic schemes were employed to synthesize the desired spin probes (**Figure 2**).

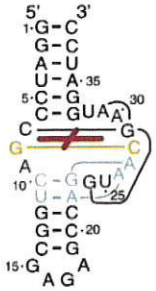

Figure 1. Secondary structure of the malachite green binding RNA aptamer (the binding position of the ligand is denoted by red) [3]

EPR binding of one of the spin labeled probes showed substantial and specific binding to the aptamer even at room temperature, although some unbound spin label (fast moving component) also seemed to be present. However, UV binding experiments [4] proved that the spin label had indeed bound fully and specifically to the aptamer (data not shown). Thus, we have taken the first step towards labeling unmodified RNA and further studies along similar lines are in progress.

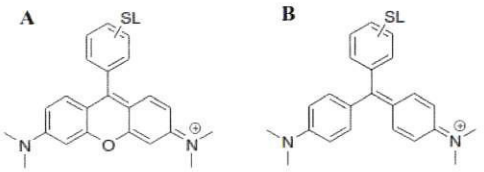

Figure 2. Generic structures of the synthesized spin labeled derivative of **(A)** tetramethylrosamine (TMR) **(B)** malachite green

REFERENCES

1. Barhate, N., Cekan, P., Massey, A.P. and Sigurdsson, S.T., *Angew. Chem. Int. Ed.*, **2007**, *119*, 2709-2712.
2. Shelke, S.A. and Sigurdsson, S.T., *Angew. Chem. Int. Ed.*, **2010**, *49*, 7984-7986.
3. Baugh, C., Grate, D. and Wilson, C., *J. Mol. Biol.*, **2000**, *301*, 117-128.
4. Grate, D. and Wilson, C., *P. Natl. Acad. Sci.*, **1999**, 96, 6131-6136.

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THE CH($A^2\Delta$) SPECTRA FOLLOWING REMPI OF CH_mBr_{4-m}; m = 1,2,3: LONG-TERM PUZZLE REVISITED

ARNAR HAFLIÐASON, HUASHENG WANG, AND ÁGÚST KVARAN*

**Raunvísindastofnun, Háskóli Íslands, Dunhagi 3, 107 Reykjavík, Ísland*

Dissociation of bromoform ($CHBr_3$) caused by two-photon resonance excitations to molecular Rydberg states forms the fragment CH* in the excited state $A^2\Delta(v'=0)$ as well as carbon and bromine atoms in the ground and first excited states, C/C* and $^iBr/^iBr^*(i = 79,81)$. Further excitation of the CH* fragment brings it into the energy region of concern by (1 + 1)[a] REMPI[b], whereas the atom fragments were identified by further (2 + 1) REMPI. Analysis based on simulations [1] and comparison with others data [2-4] allowed identification and partial characterization of spectra due to transitions to highly excited bound states for the molecular fragment (CH**($D^2\Pi$; v'= 0)).(Fig.1)

REMPI uses high energy photons to excite electrons to higher excited states. Radiation, generated by an excimer laser, is directed through a dye laser and a second harmonic generator and subsequently diverted by a Pellin Broca prism into an ionization chamber, where it is focused onto a pulsed molecular beam. Ions, formed, are directed through a time-of-flight tube and detected by a Micro Channel Plate (MCP) detector. Mass signals as a function of laser excitation wavenumber are recorded by a digital oscilloscope.(Fig.2)

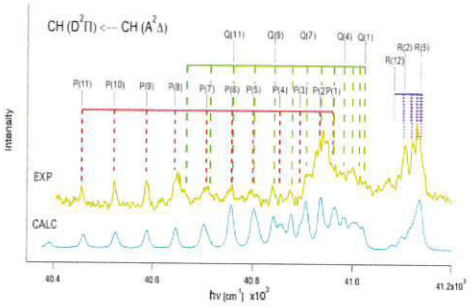

Figure 1. Experimental spectrum, with assigned rotational lines, P, Q and R (top). Simulation of CH*($A^2\Delta$; v'= 0) (1 + 1)REMPI spectrum due to the resonance transition to the CH**($D^2\Pi$; v'= 0) state.

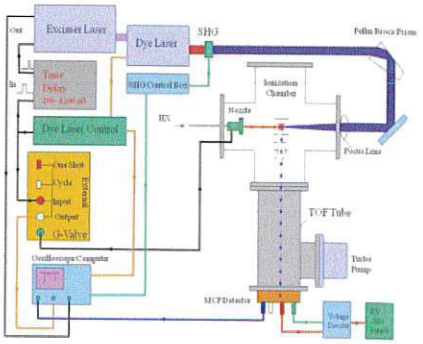

Figure 2. REMPI-TOF experimental setup. Detection for positive ions.

References

1. C. M. Western, *PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol,* http://pgopher.chm.bris.ac.uk University of Bristol 2003-2015.
2. G. Herzberg and J. W. C. Johns, *The Astrophysical Journal*, 1969, **158**, 399-418.
3. E. F. van Dishoeck, *J. Chem. Phys.*, 1986, **86**, 196-214.
4. Y. Chen, J. Jin, L. Pei, X. Ma and C. Chen, *Journal of Electron Spectroscopy and Related Phenomena*, 2000, **108**, 221-224.

[a] (1_f+1_i): 1st photon stands for resonance, 2nd photon stands for ionization.

[b] REMPI: Resonance-Enhanced-Multi-Photon-Ionization

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Dissociative electron attachment to $HFeCo_3(CO)_{12}$

Ragesh Kumar T P and Oddur Ingólfsson

$HFeCo_3(CO)_{12}$ is a bimetal precursor molecule used in Focused electron beam induced deposition (FEBID) to fabricate CoFe alloy magnetic nanostructures [1]. During FEBID of $HFeCo_3(CO)_{12}$, large number of secondary electrons generating from the substrate and deposit dissociate $HFeCo_3(CO)_{12}$. In the current study we investigated the dissociation of $HFeCo_3(CO)_{12}$ by the resonant interaction of low energy electrons (0 to 25 eV). We performed this experiment using a crossed electron and molecule beam mass spectrometric set up. Clear resonance peak was observed for sequential loss of all CO ligands. Parent anion $HFeCo_3(CO)_{12}^-$ and loss of one to two CO ligands was observed at ~0 eV. Formation of $Fe(CO)_4^-$ through the bonding of $Fe(CO)_3$ and one CO was also observed at ~0 eV with considerable intensity. Complete loss of CO ligands was occurred above the ionization threshold of molecule. It is quite unusual to observe a resonance peak above the ionization potential of molecule. Most prominent DEA channel is the loss of two CO ligands. Using those observed resonance peaks we discussed the fragmentation of $HFeCo_3(CO)_{12}$ by low energy electrons. To our knowledge this is the first study of low energy interaction with bimetal precursor molecule. This study might help to understand the electron induced fragmentation of $HFeCo_3(CO)_{12}$ occurred during FEBID process.

Acknowledgments: This work was supported by Icelandic Centre for Research (RANNIS). R K. T. P gratefully acknowledges a PhD grant from the The University of Iceland's Research Fund

References

[1] Porrati, F., et al. "Direct writing of CoFe alloy nanostructures by focused electron beam induced deposition from a heteronuclear precursor." *arXiv preprint arXiv:1506.07311* (2015).

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Revealing photofragmentation dynamics through interactions between Rydberg states: REMPI of HI as a case study

Helgi Rafn Hróðmarsson and Ágúst Kvaran

High energy regions of molecular electronic states are largely characterized by the nature and involvement of Rydberg states. Whereas the number of observed dynamical processes that are due to interactions between Rydberg and valence states, reports on corresponding effect of Rydberg-Rydberg state interaction, in the literature are scarce. Here we report, for the first time, a detailed characterization of the effects of interactions between two Rydberg states on photofragmentation processes, for a hydrogen halide molecule. Perturbation effects, showing as rotational line shifts, intensity alterations and line-broadenings in REMPI spectra of HI, for two-photon resonance excitations to the $j^3\Sigma^-(v' = 0)$ and $k^3\Pi_1(v' = 2)$ Rydberg states, are analyzed. The data reveal pathways of further photofragmentation processes involving photodissociation, autoionization and photoionization affected by the Rydberg-Rydberg state interactions as well as the involvement of other states, close in energy. Detailed mechanisms of the involved processes are proposed.

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Illuminating hidden states through perturbations: New observations in high energy REMPI of HI

Helgi Rafn Hróðmarsson, Huasheng Wang and Ágúst Kvaran

The electronic spectra of the hydrogen halides are of particular interest in molecular spectroscopy due to the clarity and resolution of their observed spectral structures. They provide epitomizing examples of interactions between Rydberg states and ion-pair states, due to the varying strengths of spin-orbit couplings that arise from the halogen atoms. These perturbations elucidate the photodynamics of fragmentations and ionization pathways.

In this work, several Rydberg states and ion-pair states in hydrogen iodide were studied via two-photon resonance enhanced multiphoton ionization (REMPI) with respects to perturbation efffects in order to locate so-called hidden states which are indirectly observed through unexplained perturbation effects.

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Direct-write nanofabrication: writing nanostructures with an electron-beam "pen"

Rachel Thorman*, Oddur Ingólfsson

Nanofabrication methods are used to create a wide variety of products, from integrated circuits to nanoscale sensors and drug delivery methods. While many common techniques, such as the various forms of lithography and etching, use a top-down approach to fabrication, other techniques – such as chemical synthesis, self-assembly, and molecular deposition –utilize bottom-up approaches. Focused electron beam induced depositon (FEBID) is one such bottom-up technique, in which an electron beam is used to directly write 3-dimensional nanostructures of nearly any geometry on 3-dimensional surfaces. This talk will cover the basics of FEBID, and connect it to fundamental gas phase work involving the interactions of low-energy electrons with FEBID precursors currently taking place in Oddur Ingófsson's lab at the University of Iceland.

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