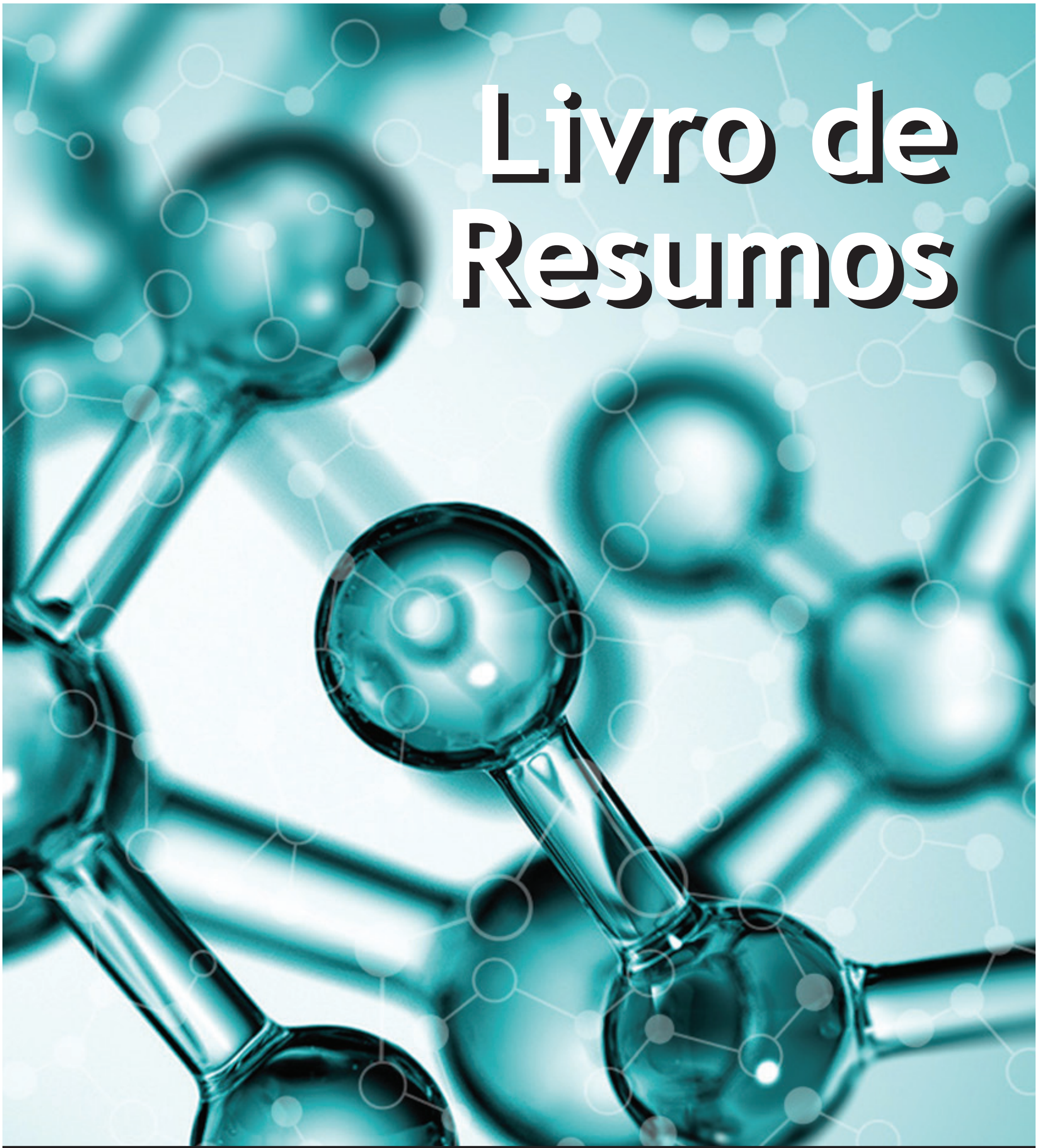
Livro de Resumos



XIX SBQT

Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Apoio

USP

UNICAMP

CNPq
Conselho Nacional de Desenvolvimento
Científico e Tecnológico

CAPES

FAPESP
FUNDAÇÃO DE AMPARO À PESQUISA
DO ESTADO DE SÃO PAULO

FAPEMIG

FAPERJ
Fundação Carlos Chagas Filho de Amparo
à Pesquisa do Estado do Rio de Janeiro

Patrocínio

AR
Intelligence for Technology

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PARTNER
PLATINUM

silix

SEAGATE

versatus
HPC

Sumário

Boas Vindas:

Sejam bem vindos ao XIX Simpósio Brasileiro de Química Teórica!

Esta é a décima nona edição do SBQT (http://www.sbqt2017.if.usp.br) e ocorre no Hotel Majestic em Água de Lindoia no período de 12 a 17 de novembro de 2017.

Neste evento reunimos cerca de 380 participantes, o que representa uma parte considerável da comunidade de Química Teórica e Física Atômica e Molecular do Brasil. Esta edição envolve 57 instituições de ensino e pesquisa, com uma distribuição regional de 5% do Norte, 15% do Nordeste, 14% do Centro-Oeste, 63% do Sudeste e 14% do Sul. Sendo os seguintes estados do Sudeste os que têm mais participantes: São Paulo (27%), Minas Gerais (19%) e Rio de Janeiro (16%). Também contamos com a participação de pesquisadores estrangeiros da Argentina, Chile, Colombia, Dinamarca, Equador, França, Inglaterra, México, Portugal, Suécia, Suíça e Uruguai. O perfil dos participantes está distribuído em 40% de pesquisadores doutores, 44% de pós-graduando (26% de doutorando e 18% de mestrando) e 16% de estudantes de graduação.

Para bem receber os estrangeiros e manter o carater nacional do simpósio as atividades serão em inglês nas manhãs e em português nas tardes. Num total teremos: 9 palestras plenárias, 24 palestras, 21 comunicações oral e 286 painéis divididos em duas seções noturnas. A tarde de quarta-feira será livre para que os participantes tenham tempo para discussões. Os trabalhos que serão apresentados são teóricos e vão deste desenvolvimentos de métodos e algoritmos até aplicações em áreas acadêmicas buscando compreender conceitos básicos e áreas tecnológica identificando características de materiais de interesse tecnológico, usando mecânica quântica e mecânica clássica dentro de uma ampla variedade de métodos e algoritmos. Este ano particularmente, teremos a palestra de abertura de um pesquisador experimental, Prof. Majed Chergui da Ecole Polytechnique Federale de Lausanne/Suíça, que falará sobre espectroscopia ultrarrápida que é um tema bastante importante e atual, desafiador para pesquisas teóricas. Desejamos a todos um bom simpósio.

Kaline Coutinho

Profa. Kaline Coutinho
Comitê Organizador

Comitê Organizador:

Profa. Kaline Coutinho (coordenadora) (USP)
Profa. Elizete Ventura do Monte (vice-coordenadora) (UFPB)

Prof. Alberto dos Santos Marques (UFAM)
Profa. Alessandra Albernaz Vilela (UNB)
Prof. Itamar Borges Jr. (IME)
Profa. Juliana Angeiras (UFPE)
Prof. Luiz Antonio Sodre Costa (UFJF)
Prof. Nelson Morgon (UNICAMP)
Prof. Paulo Augusto Netz (UFRGS)

Comitê Científico:

Prof. Alfredo Mayall Simas (UFPE)
Prof. Antonio Carlos Borin (USP)
Prof. Helio Anderson Duarte (UFMG)
Prof. Marco Antonio Chaer do Nascimento (UFRJ)
Prof. Rogério Custódio (UNICAMP)
Prof. Sylvio Canuto (USP)
Prof. Wagner Batista de Almeida (UFF)

MASTER CLASS
Eventos e Viagens

Programa Científico

As atividades desenvolvidas no período da manhã serão em inglês e no período da tarde em português.

The activities in the morning will be in English and in the afternoon in Portuguese.

	Domingo 12/Nov	Segunda 13/Nov	Terça 14/Nov	Quarta 15/Nov	Quinta 16/Nov	Sexta 17/Nov
07h00-09h00		Café da manhã	Café da manhã	Café da manhã	Café da manhã	Café da manhã
09h00-09h25 (20+5min)		Palestra PA.01 L. Pettersson	Palestra PA.08 R. Bruns	Palestra PA.15 R. Long	Palestra PA.18 A. Reyes	
09h25-09h50 (20+5min)		Palestra PA.02 C. Domene	Palestra PA.09 A. Formiga	Palestra PA.16 J. Torres	Palestra PA.19 M. Varella	
09h50-10h35 (20+5min)		Plenária PL.02 K. Mikkelsen	Plenária PL.04 G. Aucar	Plenária PL.06 B. Cabral	Plenária PL.08 S. F-Alberti	
10h35-11h00		Coffee Break	Coffee Break	Coffee Break	Coffee Break	
11h00-11h45 (35+10min)		Plenária PL.03 J. Contreras	Plenária PL.05 S. Sauer	Plenária PL.07 M. Skaf	Plenária PL.09 A. Borin	
11h45-12h10 (20+5min)		Palestra PA.03 G. Merino	Palestra PA.10 A. Giussani	Palestra PA.17 M. Pickholz	Palestra PA.20 L. Costa	
12h10-14h00		Almoço	Almoço	Almoço	Almoço	
14h00-14h25 (20+5min)	Check-in e registro	Palestra PA.04 T. Soares	Palestra PA.11 P. Chaudhurt		Palestra PA.21 B. Souza	
14h25-14h50 (20+5min)		Palestra PA.05 P. Netz	Palestra PA.12 V. C-Silva		Palestra PA.22 J. Politi	
14h50-15h35 3x(12+3min)		Comunicações CO.01-CO.03	Comunicações CO.09-CO.11		Comunicações CO.17-CO.19	
15h35-16h00		Coffee Break	Coffee Break	Discussão livre	Coffee Break	
16h00-16h25 (20+5min)		Palestra PA.06 M. Pinheiro	Palestra PA.13 J. Lino		Palestra PA.23 A. Kuznetsov	
16h25-16h50 (20+5min)		Palestra PA.07 G Seabra	Palestra PA.14 A. Arapiraca		Palestra PA.24 S. Galembeck	
16h50-18h05 5x(12+3min)		Comunicações CO.04-CO.08	Comunicações CO.12-CO.16		Comunicações CO.20-CO.24	
18h05-18h30	Abertura	Jantar	Jantar	Jantar	Jantar	
18h30-19h30 (50+10min)	Abertura PL.01 M. Chergui					
20h00-22h00 (2h)	Jantar e Confraternização	Painéis:PN.001 até PN.164	Painéis: PN.165 até PN.328	Confraternização	Assembléia	

Domingo 12/11

14h00-18h00
Check-in nos hotéis e registro no evento.

Coordenadora:
Profa. Kaline Coutinho

18h00-18h30
Abertura

18h30-19h30
Plenária de abertura: PL.01
Prof. Majed Chergui, "Ultrafast molecular dynamics in solutions", da Ecole Polytechnique Federale de Lausanne/Suíça.

20h00-23h00
Jantar e depois confraternização na piscina do Hotel Majestic
(Dinner and after drinks at the pool of Hotel Majestic)

Segunda-feira 13/11

07h00-09h00
Café da manhã (Breakfast)

Coordenador: Prof. Sylvio Canuto

09h00-09h25
Palestra PA.01
Prof. Lars Pettersson, "Combining Spectral and Scattering Data to Determine Liquid Water Structure", da Stockholms Universitet/Suécia.

09h25-09h50
Palestra PA.02
Profa. Carmen Domene, "Mechanistic insight into oxygen diffusion in prolyl", da University of Bath/Inglaterra.

09h50-10h35
Plenária PL.02
Prof. Kurt Mikkelsen, "Capture and Storage of Solar Radiation", da University of Copenhagen/Dinamarca.

10h35-11h00
Coffee Break

Coordenador:
Prof. Helio Anderson Duarte

11h00-11h45
Plenária PL.03
Profa. Julia Contreras,
"Using bond analysis for the rational design of photoswitches . . .
and it worked!", da Pierre and Marie Curie University/França.

11h45-12h10

Palestra PA.03
Prof. Gabriel Merino, “Planar Hypercoordinate Atoms”, da Cinvestav Mérida/México.

12h10-14h00

Almoço (Lunch)

Coordenador: Prof. Nelson Morgon

14h00-14h25

Palestra PA.04
Thereza A. Soares, “Early Stages of Antimicrobial Peptides Binding to Resistant and Susceptible Bacterial Outer Membrane Chemotypes from Atomistic MD simulations”, Universidade Federal de Pernambuco, UFPE/PE.

14h25-14h50

Palestra PA.05
Paulo A. Netz, “Docking, molecular dynamics and ensemble docking in the study of petrobactin biosynthesis inhibition in Bacillus anthracis”, Universidade Federal do Rio Grande do Sul, UFRGS/RS.

14h50-15h35

Comunicação CO.01:
Adalberto V. Sanches de Araújo, “Electronic Structure and Absorption Spectra of Fluorescent Nucleoside Analogues”, Instituto de Química, USP/SP.

Comunicação CO.02:
Antonio G. S. de Oliveira-Filho, “Multireference Coupled-Cluster Benchmark for Transition Metal Molecules: Comparison with Experimental Data and Assessment of Standard Coupled-Cluster and Kohn–Sham DFT”, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, FFCLRP-USP/SP.

Comunicação CO.03:
Antonio R. da Cunha, “Experimental and Theoretical Investigations of Barbaloin in a DMPC Bilayer”, Universidade Federal do Maranhão, Campus Balsas, UFMA/MA.

15h35-16h00

Coffee Break

Coordenadora:
Profa. Juliana Angeiras

16h00-16h25

Palestra PA.06
Max Pinheiro Jr, “Chemical doping based design of oligoacenes for tuning the biradical character and excitation properties”, Universidade do Estado do Rio de Janeiro, UERJ/RJ.

16h25-16h50

Palestra PA.07
Gustavo de Miranda Seabra, “Inhibitors for Zika Virus NS5 RdRp”, Universidade Federal de Pernambuco, UFPE/PE.

16h50-18h05

Comunicação CO.04:
Eufrásia de Sousa Pereira, Theoretical investigation of the reduction potential of ruthenium(III/II) complexes with potential antitumor activity and their interactions with biological targets”, Universidade Federal de Minas Gerais, UFMG/MG.

Comunicação CO.05:
Felipe Cesar Torres Antonio, “Study of the dynamics of aggregation and behavior in the solution of substituted phthalocyanines”, Universidade Federal do ABC, UFABC/SP.

Comunicação CO.06:
Flávia Cristina Assis Silva, “Structure and Dynamics of Poly(urethaneurea) from Molecular Dynamics Simulations”, Universidade Federal Fluminense, UFF/RJ.

Comunicação CO.07:
Flávio Olimpio Sanches Neto, “A novel assessment of the role of the methyl radical and water formation channel in the CH_3OH + H reaction”, Universidade Estadual de Goiás, UEG/GO.

Comunicação CO.08: SEAGATE, “Tecnologia Seagate para armazenamento de dados de alta performance”.

18h00-20h00

Jantar (Dinner)

20h00-22h00

Seção de Painéis:
PN.001 até PN.164

Terça-feira 14/11

07h00-09h00
Café da manhã (Breakfast)

Coordenador: Prof. Marco Chaer

09h00-09h25
Palestra PA.08
Roy E. Bruns, "Quantum Theory of Atoms in Molecules charge-charge transferdipolar polarization classification of infrared intensities", Universidade Estadual de Campinas, UNICAMP/SP.

09h25-09h50
Palestra PA.09
André Formiga, "Unveiling the active species for oxygen atom transfer reactions promoted by manganese porphyrins", Universidade Estadual de Campinas, UNICAMP/SP.

09h50-10h35
Plenária PL.04
Prof. Gustavo Adolfo Aucar, "Atomic and molecular response properties within a relativistic framework", da Universidad Nacional del Nordeste/Argentina.

10h35-11h00
Coffee Break

Coordenador:
Prof. Rogério Custódio

11h00-11h45
Plenária PL.05
Prof. Stephan Sauer, "Atomistic Modelling of Hadron Radiation Damage to DNA:
from Stopping Powers to Reaction Kinetics", da University of Copenhagen/Dinamarca.

11h45-12h10
Palestra PA.10
Angelo Giussani, "Photophysics and photochemistry of nitrobenzene and 1-nitronaphthalene performing CASPT2//CASSCF static computations and DD-vMCG dynamics", University College London/Inglaterra.

12h10-14h00
Almoço (Lunch)

Coordenador:
Prof. Luiz Antonio Sodre Costa

14h00-14h25
Palestra PA.11
Puspitapallab Chaudhuri, “A molecular approach towards the atmospheric implications of aerosol formation”, da Universidade Federal do Amazonas, UFAM/AM.

14h25-14h50
Palestra PA.12
Marcos S. Amaral, “High-performance molecular dynamics at constant pH and constant redox potential using AMBER”, Universidade Federal de Mato Grosso do Sul, UFMS/MS.

14h50-15h35
Comunicação CO.09:
Gabriel Costa A. da Hora, “Investigating the Mechanism of Action of Pediocin-Plantaricin Antimicrobial Peptide using Atomistic Molecular Dynamics Simulations”, Universidade Federal de Pernambuco, UFPE/PE.

Comunicação CO.10:
Gabriel L. C. de Souza, “Dimerization effects on the e--
(H2CO)2
scattering cross sections”, Universidade Federal de Mato Grosso, UFMT/MT.

Comunicação CO.11:
Henrique Brandão Cerqueira de Azevedo, “Stability structures of acetonitrile ionic clusters for astrochemical implications”, Universidade Federal do Rio de Janeiro, UFRJ/RJ.

15h35-16h00
Coffee Break

Coordenadora:
Profa. Alessandra Albernaz Vilela

16h00-16h25
Palestra PA.13
Jéssica Boreli dos Reis Lino, “The value of NMR parameters and DFT calculations for Quantum Information Processing utilizing Phosphorus Heterocycles”, Universidade Federal de Lavras, UFLA/MG.

16h25-16h50
Palestra PA.14
Antônio F. C. Arapiraca, “The dipole moments of deuterated endofullerenes isotopologues HD@C60 and HT@C60”, Centro Federal de Educação Tecnológica de Minas Gerais, CEFET/MG.

16h50-17h50

Comunicação CO.12:
João Guilherme Siqueira Monteiro, "Assessing the molecular basis of the fuel octane scale: A detailed investigation on the rate controlling steps of the autoignition of heptane and isooctane", Universidade Federal Fluminense, UFF/RJ.

Comunicação CO.13:
Leonardo Silva Dias, "Stochastic Chiral Symmetry Breaking Process", Universidade Federal de Sao Carlos, UFSCar/SP.

Comunicação CO.14:
Lucas Chuman Santana, "Evaluation of Intermolecular Potentials for Carboplatin and Oxaliplatin in Aqueous Solution", Universidade Federal de Itajubá, UNIFEI/MG.

Comunicação CO.15:
Marcelo Hidalgo Cardenuto, "A Sequential-QM/MM study of the electronic spectra of molecular switches", Instituto de Física, USP/SP.

Comunicação CO.16: SILIX, "Servidores e Storages para computação científica"

18h00-19h30

Jantar (Dinner)

20h00-22h00

Seção de Painéis
PN.165 até PN.328

Quarta-feira 15/11

07h00-09h00
Café da manhã (Breakfast)

Coordenador:
Prof. Wagner Almeida

09h00-09h25
Palestra PA.15
Ricardo Longo, "The Activity Coefficient from a Solvation Thermodynamics Perspective", Universidade Federal de Pernambuco, UFPE/PE.

09h25-09h50
Palestra PA.16
Prof. F. Javier Torres, "Computational Study of the C-X (X = F, Cl, Br, and I)
Bond Cleavage Mediated by Cob[N]alamin", da Universidad San Francisco de Quito/Equador.

09h50-10h35
Plenária PL.06
Prof. Benedito J. Costa Cabral, "Electronic properties in liquid phase: combining many-body energy decomposition schemes with first principles molecular dynamics", da Universidade de Lisboa/Portugal;

10h35-11h00
Coffee Break

Coordenador:
Prof. Paulo Augusto Netz

11h00-11h45
Plenária PL.07
Prof. Munir Skaf, "Ion-Mobility Mass Spectrometry: Shooting Proteins into a Buffer Gas", da Universidade Estadual de Campinas/Brasil.

11h45-12h10
Palestra PA.17
Profa. Monica Pickholz, "Coarse grain approaches to study drug delivery systems", da University of Buenos Aires/Argentina.

12h10-14h00
Almoço (Lunch)

14h00-18h00
Discussões livres

18h00-19h30
Jantar (Dinner)

20h30-23h30
Confraternização, música e dança (Confraternization, music and dance)

Quinta-feira 16/11

07h00-09h00
Café da manhã (Breakfast)

Coordenador: Prof. Alfredo Simas

09h00-09h25
Palestra PA.18
Prof. Andrés Reyes, "Antimatter binding matter: The covalent positron bond", da Universidad Nacional de Colombia/Colombia.

09h25-09h50
Palestra PA.19
Marcio Varella, "Suppression of electron-induced degradation in methylated nitroimidazoles", Instituto de Física, USP/SP.

09h50-10h35
Plenária PL.08
Prof. Sebastian Fernandez-Alberti, "Photodynamics of light harvesting molecules: energy transfer, localization, molecular scrambling and state-specific vibrations", da Universidad Nacional de Quilmes/Argentina.

10h35-11h00
Coffee Break

Coordenador: Prof. Itamar Borges Jr

11h00-11h45
Plenária PL.09
Prof. Antonio Carlos Borin, "Light and Nucleobases: A Healthy Relationship", da Universidade de São Paulo/Brasil.

11h45-12h10
Palestra PA.20
Luciano Tavares da Costa, "Local environment structure and dynamics of CO2 in the 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide and related ionic liquids", Universidade Federal Fluminense, UFF/RJ.

12h10-14h00
Almoço (Lunch)

Coordenadora:
Profa. Elizete Ventura do Monte

14h00-14h25
Palestra PA.21
Bernardo de Souza, "On new methods for predicting photophysical constants and spectra using the path integral approach: implementations on ORCA", Universidade Federal de Santa Catarina, UFSC/SC.

14h25-14h50
Palestra PA.22
José Roberto dos Santos Politi, "Study of Dimers via Quantum Monte Carlo", Universidade de Brasília, UnB/DF.

14h50-15h35
Comunicação CO.17:
Paulo Fernando Gomes Velloso, "A computational probe for molecular environments", Universidade Federal de Minas Gerais, UFMG/MG.

Comunicação CO.18:
Ricardo Oliveira, "HDO reaction mechanism of fatty acid model over molybdenum carbide", Universidade Federal do Rio de Janeiro, UFRJ/RJ.

Comunicação CO.19:
Rodolfo Goetze Fiorot, "Investigation of 1,3-dipolar cycloaddition mechanism: which orbital is active?", Instituto Federal do Rio de Janeiro, IFRJ/RJ.

15h35-16h00
Coffee Break

Coordenador:
Prof. Alberto dos Santos Marques

16h00-16h25
Palestra PA.23
Aleksey E. Kuznetsov, "Computational Design of Novel Building Blocks for Nanotechnology Based on Core-Modified Metalloporphyrins", Instituto de Química, USP/SP.

16h25-16h50
Palestra PA.24
Sérgio Emanuel Galembeck, "The nature of the interactions between Ag+ and benzene", Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, FFCLRPUSP/SP.

16h50-18h05
Comunicação CO.20:
Selma Fabiana Bazan, “Estudo teórico das propriedades eletrônicas e estruturais do azul da prússia”, Universidade Federal de Minas Gerais, UFMG/MG.

Comunicação CO.21:
Vinícius Manzoni, “Solvatochromic reversal: is it really possible?”, Universidade Federal de Alagoas, UFAL/AL.

Comunicação CO.22:
Luís P. Viegas, “Computational strategies in finding greener CFC replacements”, Aarhus University/Dinamanca.

Comunicação CO.23:
AR IT e DELL, “Tecnologia está em nosso DNA e a evolução está em nosso sangue”.

Comunicação CO.24:
Sergio Galembeck, “Latin American Conference on Chemical Bond 2018”.

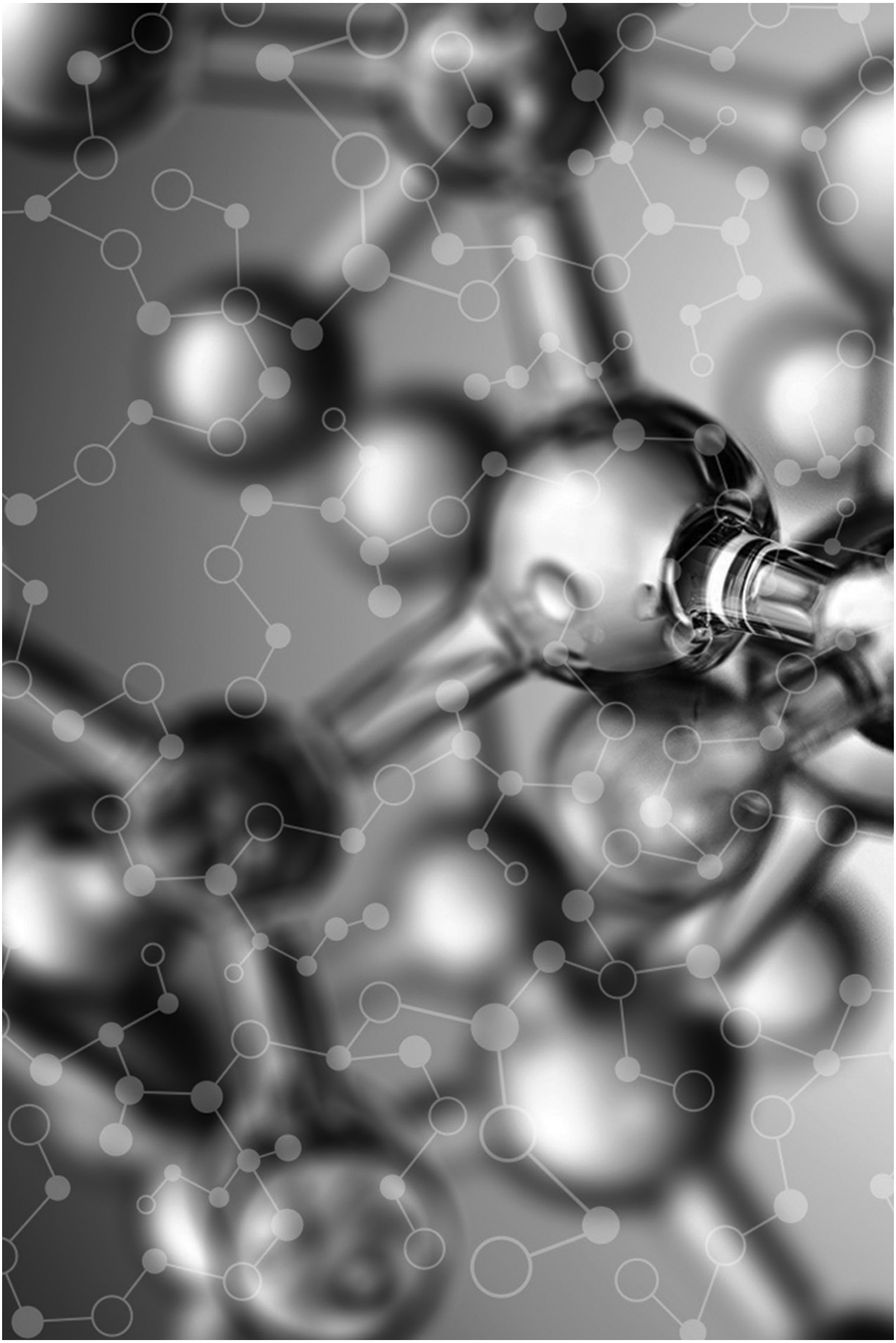
18h00-20h00
Jantar (Dinner)

20h30-23h30
Assembleia

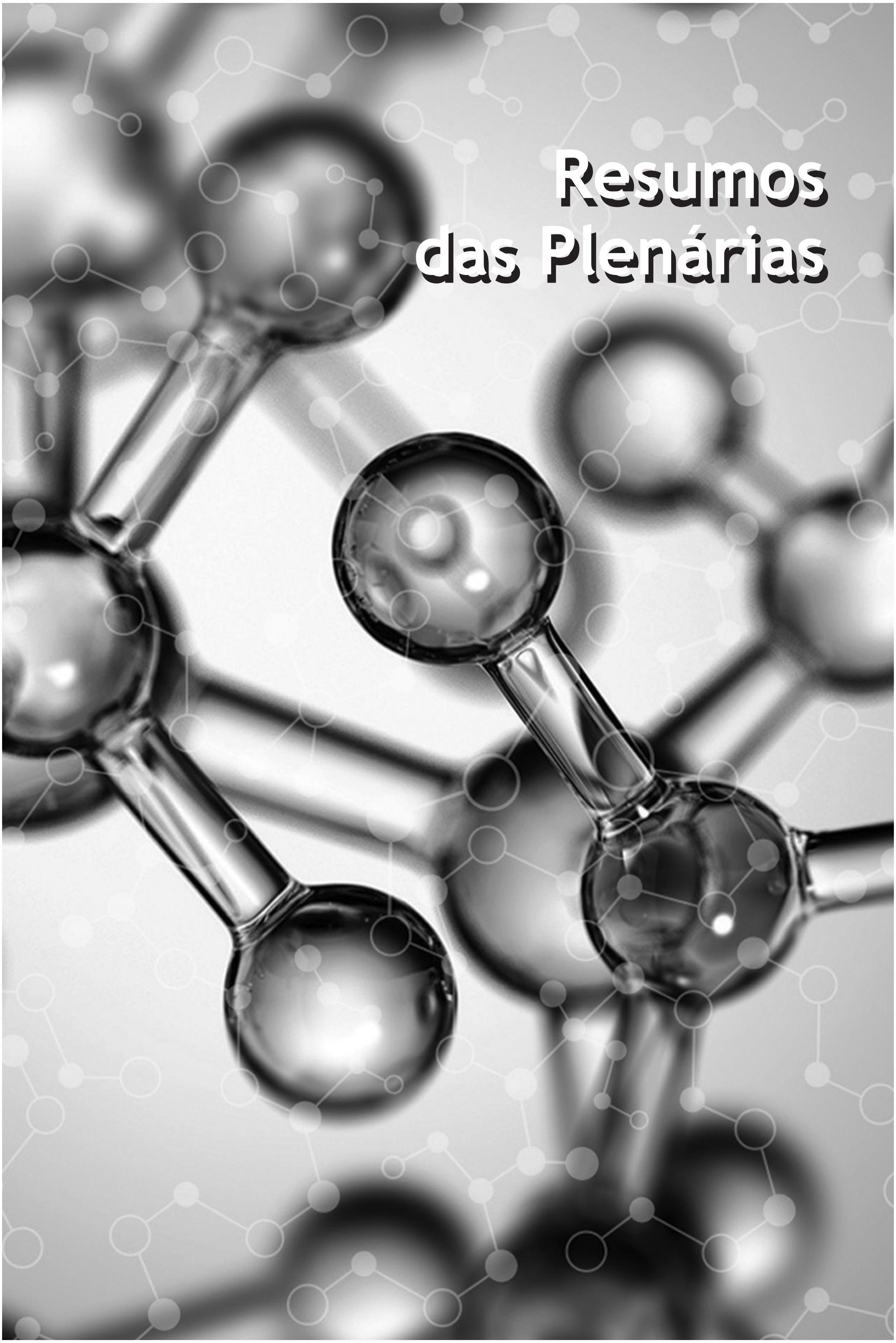
Sexta-feira 17/11

07h00-09h00
Café da manhã (Breakfast)

09h00-11h00
Check-out e Partida



Resumos das Plenárias



Plenária 01|PL.01

Ultrafast molecular dynamics in solutions

Majed CHERGUI

Lab. of Ultrafast Spectroscopy (LSU) and
Lausanne Centre for Ultrafast Science (LACUS)
Ecole Polytechnique Fédérale de Lausanne
ISIC, FSB, Station 6
CH-1015 Lausanne, Switzerland

Abstract: In this talk, I will present case studies of the photophysical and photochemical dynamics of coordination chemistry complexes using a toolbox of ultrafast methods: transient absorption from the infrared to the deep-ultraviolet, X-ray absorption and emission spectroscopy and photoelectron spectroscopy of liquid solutions. The systems that will be discussed include: ferric Iron hexacyanide showing an impulsive electronic-to-vibrational energy conversion,1 ferrous Iron hexacyanide showing the mechanism of photoaquation2 and diplatinum complexes with an emphasis on transfer of vibrational coherence in intersystem crossing events.3 Implications for the study of sensitized solar cells and perspectives for studies at Free Electron lasers will be discussed.

Key-words: Femtosecond, picosecond, metal complexes, 2-dimensional spectroscopy, core-level spectroscopy, infrared spectroscopy

Support: This work has been supported by NCCR:MUST

References:

[1] Ojeda, J.; Arrell, C. A.; Longetti, L.; Chergui, M.; Helbing, J.: Charge-transfer and impulsive electronic-to-vibrational energy conversion in ferricyanide: ultrafast photoelectron and transient infrared studies. Phys Chem Chem Phys 2017.
Reinhard, M.; Auböck, G.; Besley, N. A.; Clark, I. P.; Greetham, G. M.; Hanson-
[2] Heine, M. W. D.; Horvath, R.; Murphy, T. S.; Penfold, T. J.; Towrie, M.; George, M. W.; Chergui, M.: Photoaquation Mechanism of Hexacyanoferrate(II) Ions: Ultrafast 2D UV and Transient Visible and IR Spectroscopies. Journal of the American Chemical Society 2017, 139, 7335-7347.
[3] Monni, R.; Capano, G.; Aubock, G.; Gray, H. B.; tavernelli, I.; Vlcek, A.; Chergui, M.: Ultrafast solvent-dependent intersystem crossing and vibrational coherence transfer in di-platinum complexes. Nat Chem 2017, under review.

Capture and Storage of Solar Radiation

Kurt V. Mikkelsen

Department of Chemistry,
University of Copenhagen, Copenhagen, Denmark
Contact: kmi@chem.ku.dk

Abstract: The Sun delivers within an hour to Earth an amount of energy similar to that consumed by all humans in one year. One major challenge for society is to be able to store solar energy.

Our fundamental hypothesis is that we can store energy in chemical bonds via lightinduced isomerization reactions of photoactive molecules as illustrated in Fig. 1. Upon irradiation, molecule A is converted to the high-energy photo-isomer B, which upon a certain trigger will return to A and release the absorbed energy as heat. This corresponds to a closed-energy cycle of light-harvesting, energy storage and release, with no emission of CO2. The overall purpose of this project is to develop suitable organic molecules for such cycles based on fundamental structure-property relationships (SPRs).

We will focus on the dihydroazulene (DHA) – vinylheptafulvene (VHF) couple (Fig. 2), being attractive as only the DHA to VHF reaction is photoinduced.

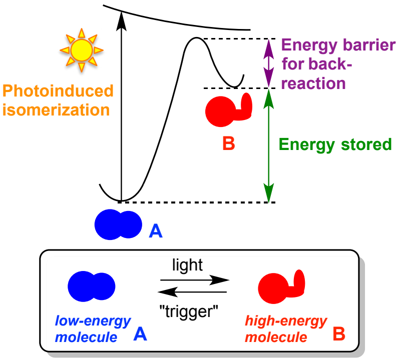


Fig. 1: Energy storage using photoswitch.

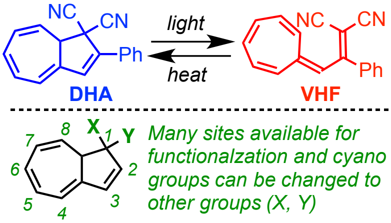


Fig. 2: DHA-VHF couple and numbering.

Using bond analysis for the rational design of photoswitches...and it worked!

J. Contreras-García[1], Joaquín Calbo[2]

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Abstract: Photoswitchable compounds, which can be reversibly switched between two isomers (E and Z) by light, continue to attract significant attention for a wide array of applications: from molecular motors, memory, and manipulators to solar thermal storage.[1] Azoheteroarenes represent a relatively new but understudied type of photoswitch, where one of the aryl rings from the conventional azobenzene class has been replaced with a five-membered heteroaromatic ring. Initial studies have suggested the azoheteroarenes –the arylazopyrazoles in particular– to have excellent photoswitching properties (quantitative switching and long Z isomer half-life).[2]

Here we present a systematic computational study to elucidate the origin of the long thermal half-lives and excellent addressability of the arylazopyrazoles, and apply this understanding to determine important structure-property relationships for a wide array of comparable azoheteroaryl photoswitches. We identify compounds with Z isomer half-lives ranging from seconds to hours, to days and to years, and variable absorption characteristics; all through tuning of the heteraromatic ring. On the one hand, the compounds with the longest isomerization half-lives adopt a T-shaped ground state Z isomer conformation and proceed through a T-shaped isomerization pathway. On the other hand, the most complete photoswitching is achieved for compounds that have a twisted (rather than T-shaped) Z-isomer conformation. By balancing chemical bonding factors, we report on a new azopyrazole, which has been experimentally demonstrated to quantitatively switch between Z and E isomers, and has a very long half-life for thermal isomerisation (t1/2 = 74 d at 25 °C).[3]

Keywords: photoswitches, inverse design, chemical bond

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Atomic and molecular response properties within a relativistic framework

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Abstract: The relativistic quantum chemistry, RQC, is at the moment the best theoretical framework that one have at hands when wants to describe the atomic and molecular quantum world. Even though it is not usually necessary to consider the influence of relativistic effects on the description of the chemistry world, when accuracy is involved or heavy-atoms (belonging to the 4th or lower rows of the periodic table) are part of such a world, there is no option, one should work within a relativistic framework.

Almost 40 years ago few authors (being Pekka Pyykkö the central figure) started to highlight the fact that relativistic effects can strongly influence many chemical properties of the heavier elements. [1, 2] It was in the early 1990s that an small community of theoretical chemist started to do some fundamental contributions to the RQC which so grew faster than previously by the development of new theories and its implementations in computational codes. Several specific books appeared since then. [3 - 8] Today RQC is a mature field lead by european research teams, though there are also some experts spread out in all continents. In South America there are only few consolidated teams working in this quickly evolving field.

The importance of including relativistic effects on the studies of response atomic and molecular properties compelled the theoretical chemists to develop new specific relativistic theories and models. It is not only the accuracy but also the physics behind those properties which must be considered. Few examples: i) the four well known non relativistic, NR, mechanisms of the NMR indirect J-coupling are unified in one; ii) diamagnetic and paramagnetic terms of the NMR magnetic shielding are also unified and iii) some NR relationships among molecular properties, like the Flygare relation between spin-rotation constants and NMR magnetic shieldings must be modified.[9] New mechanisms and so, new physics is behind all this.[3, 8, 10, 11]

In this presentation I will briefly describe the state of the art of one of the most active areas of the RQC, that of response properties. In this area one can apply methods that are wave-function-based, DFT-based or based on polarization propagators. I will focus in the relativistic polarization propagator formalism, which is the one I was engaged in during the last 25 years.[10] I will also briefly expose another two-component model, known as linear response elimination of small component [11] from which one can grasp new insights about the electronic mechanisms that underlies molecular properties.

Atomistic Modelling of Hadron Radiation Damage to DNA: from Stopping Powers to Reaction Kinetics

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Abstract: Hadron therapy, i.e. the use of protons and C6+ ion beams instead of photon beams in radiation therapy, is an upcoming new way of treating cancer. Compared to standard radiation therapy it offers the advantage of reduced damage to the surrounding tissues. Over the recent years, we have been trying to cast light on some of the molecular processes which will finally lead to the strand breaks in DNA.

We have on one hand focused on the initial, physical interaction of the ion beam with different kind of molecules in a cell. This involves an energy transfer to the target molecule leading to its ionization or fragmentation and a slowing down of the ion beam projectiles. The key property in this process is the stopping power of the target, which in the Bethe theory [1] is directly related to the mean excitation energy of the target. The latter can accurately be calculated from the poles and residues of the linear response function of the electric dipole moment operator. In my talk I will illustrate this for several classes of molecules [2-6]. One of the most important target molecules is water, whose fragmentation leads to the formation of OH-radicals. In a second line of research we have studied possible reactions of the OH-radical with DNA. In my talk I will present first results of our atomistic modelling of the reaction of OH-radicals with the five nucleobases and discuss the importance of several aspects of the ab initio calculations of these reactions [7-9].

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Electronic properties in liquid phase: combining manybody energy decomposition schemes with first principles molecular dynamics

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Abstract: The dynamics and electronic properties of systems in liquid phase are of fundamental interest for understanding chemical reactivity in solution. One important issue concerns the limitations of classical force fields for representing the interactions in liquid phase. Despite some progress, the accurate representation of polarization effects, dispersion interactions, and charge transfer processes in solution remains a challenge. First principles molecular dynamics, where the dynamics is generated with forces derived from electronic structure calculations is an interesting possibility to exploit. However, in this case, the results will be dependent on the adopted methodology for solving the electronic structure problem, which is usually based on density functional theory. The implementation, in liquid phase, of high accuracy ab initio methods, that can be currently applied to the calculation of gas-phase properties needs further theoretical developments. In this sense, the combination of many-body energy decomposition schemes (MBE) with first principles molecular dynamics should be considered as a promising alternative [1-3]. In this presentation, applications of first principles approaches for studying the structure, dynamics and electronic properties in liquid phase will be reviewed. Some emphasis will be given to the MBE/Molecular dynamics methodology for the calculation of the electronic spectra in liquid phase.

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Ion-Mobility Mass Spectrometry: Shooting Proteins into a Buffer Gas

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Abstract: Ion Mobility-Mass Spectrometry (IM-MS) is becoming an increasingly popular and powerful tool to investigate structure, conformational dynamics, and folding properties of proteins and other biomacromolecules. In short, an IM-MS experiment separates molecular ions of arbitrary shapes and sizes (ranging from small molecules up to megadalton protein complexes) based on their differential mobility through a buffer gas. Measurement of the molecule's time-of-flight through the drift chamber is readily related to the rotationally-averaged collisional cross-section of the target molecule with the buffer gas, from which valuable information can be extracted regarding its structural features. In this talk, I will present a detailed view of the molecular processes that take place in an IM-MS experiment from the structural perspective of the protein using Molecular Dynamics simulations. I will also show how the cross-section can be effectively computed from simulations and compared to experimental data.

Key-words: Ion Mobility-Mass Spectrometry, Collision Cross Section,
Molecular Dynamics Simulation

Support: This work has been supported by CNPq and Fapesp
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Plenária 08 | PL.08

Photodynamics of light harvesting molecules: energy transfer, localization, molecular scrambling and state-specific vibrations

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Abstract: Solar energy conversion starts with the harvest of light, and its efficacy depends on the spatial transfer of the light energy to where it can be transduced into other forms of energy. Harnessing solar power as a clean energy source requires the continuous development of new synthetic materials that can harvest photon energy and transport it without significant losses.

Firstly, we investigate photoexcited dynamics and relaxation pathways in a variety of lightharvesting molecules using Non-Adiabatic Excited State Molecular Dynamics (NA-ESMD). We aim to achieve a detailed comprehension of the ultrafast intramolecular electronic and vibrational energy transfer that takes place after photoexcitation. Within our NA-ESMD framework[1], direct nonadiabatic molecular dynamics simulations can be applied to describe photoinduced dynamics in large organic conjugated molecules involving multiple coupled electronic excited states. Such NA-ESMD simulations are performed by combining the molecular dynamics with quantum transitions (MDQT) approach with "on the fly" analytical calculations of excited state energies, gradients, and non-adiabatic couplings terms.

With chemically-controlled branched architectures, dendrimers are ideally suited for light harvesting, since they consist of arrays of chromophores with relative positioning and orientations to create energy gradients and to spatially focus excitation energies. The spatial localization of the energy delimits its efficacy and has been a point of intense research for synthetic light harvesters. We therefore present results of combined theoretical experimental studies elucidating ultrafast electronic energy transfer on different phenylene-ethynylene dendrimers (PPE), leading to either unidirectional energy transfer onto an energy sink including an ultrafast collapse of the photoexcited wave function[2], and exciton self-trapping on different units including an ultrafast spatial scrambling among isoenergetic chromophore units[3]. Besides, the use of multiconfigurational Ehrenfest method[4] is discussed and compared to surface-hopping approach[4] in this kind of molecules.

Secondly, we study the internal conversion and vibrational relaxation processes in chlorophylls[5]. Excited state trajectories are analyzed in terms of the ground state equilibrium normal modes[6]. Our analysis of the time evolution of the average mode energies uncovers that only a small subset of the medium-to-high frequency normal modes actively participate in the electronic relaxation processes. These active modes are characterized by the highest overlap with the non-adiabatic coupling vectors (NACRs) during the electronic transitions. Further statistical analysis of the nonadiabatic transitions reveals that the electronic and vibrational energy relaxation occurs via two distinct pathways with significantly different time scales. Besides, we investigate excitation energy transfer and exciton localization dynamics in a chlorophyll dimer system at the interface of two monomers of light-harvesting complex II (LHCII) trimer. The energy relaxation occurs more efficiently in the the dimer than the monomer. The strength of thermal fluctuations

exceeds intraband electronic coupling between the states belonging to a certain band, producing localized states on the individual chromophores.

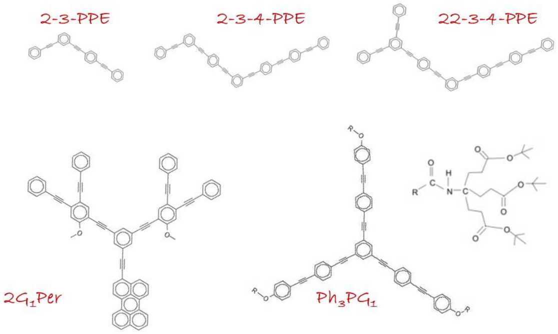

Figure 1. Models of PPE dendrimers

Therefore, time evolution of spatial electronic localization during internal conversion reveals transient trapping on one of the Chla monomers participating in the events of intermonomeric energy exchange. At the moment of quantum transition, the states become near-degenerate promoting Frenkel-exciton-like delocalization and inter-chromophore energy transfer. As energy relaxation occurs, redistribution of the transition density between two monomers leads to the final spatial scrambling of the exciton.

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Light and Nucleobases: A Healthy Relationship

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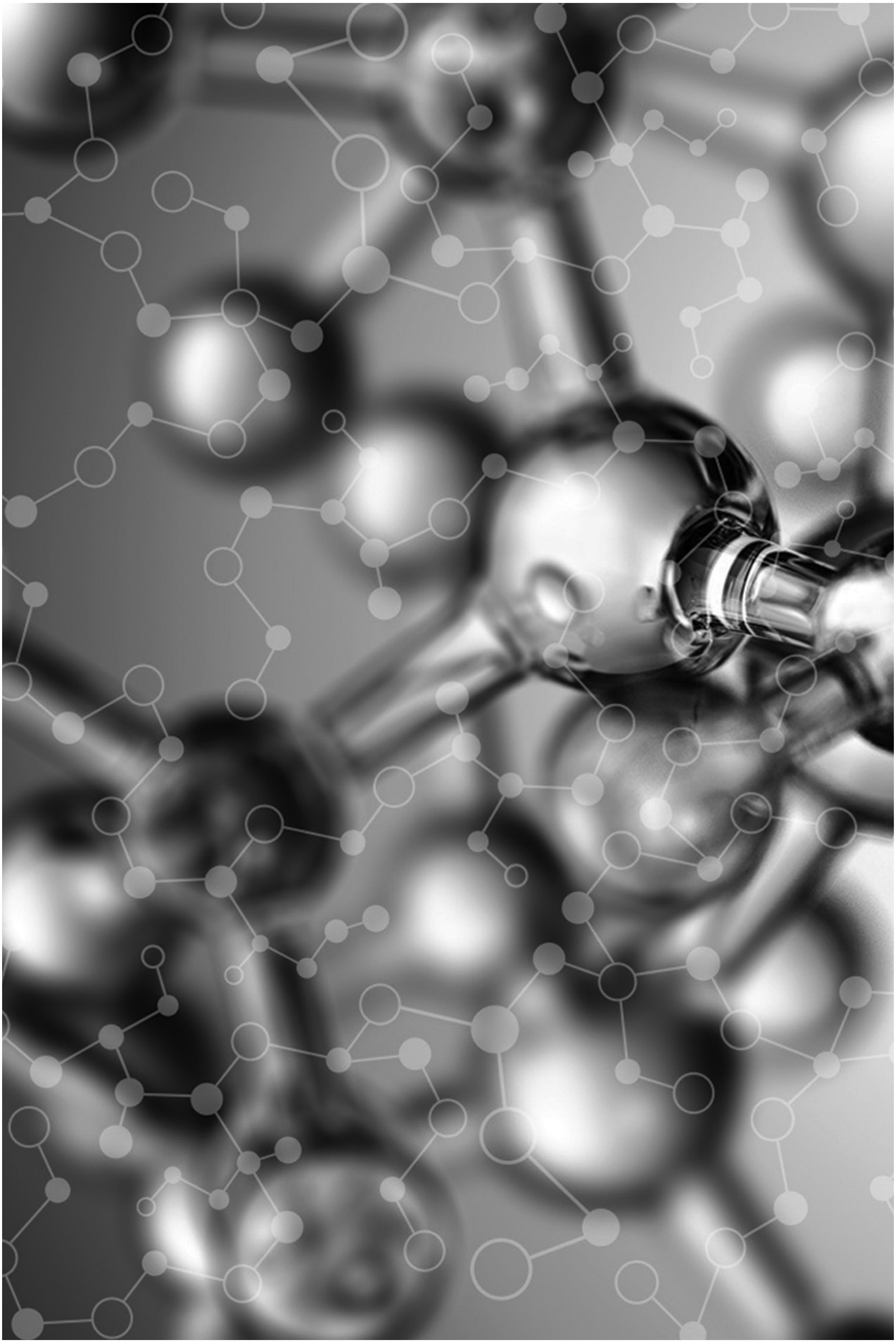
Abstract: We are used to thinking that light, especially in the ultraviolet region, is not good for us because it has a destructive influence on DNA and RNA; UV radiation, for instance, is the main agent for DNA mutagenic effects. Nonetheless, they (nucleobases and radiation) co-exist since ancient times, even without the protective ozone. So, we may wonder: how did the nucleobases survive under such extreme conditions? Is it due to a kind of natural protection mechanism? Answering this question is important, because if we understand the photochemical mechanisms behind this longstanding relationship, we can learn how to minimize the damage and maximize the profit. The canonical nucleobases are photostable due to extremely efficient nonradiative photochemical pathways, which makes them very low fluorescent species. Which are the photochemical pathways responsible for ultrashort lifetimes of the canonical nucleobases?

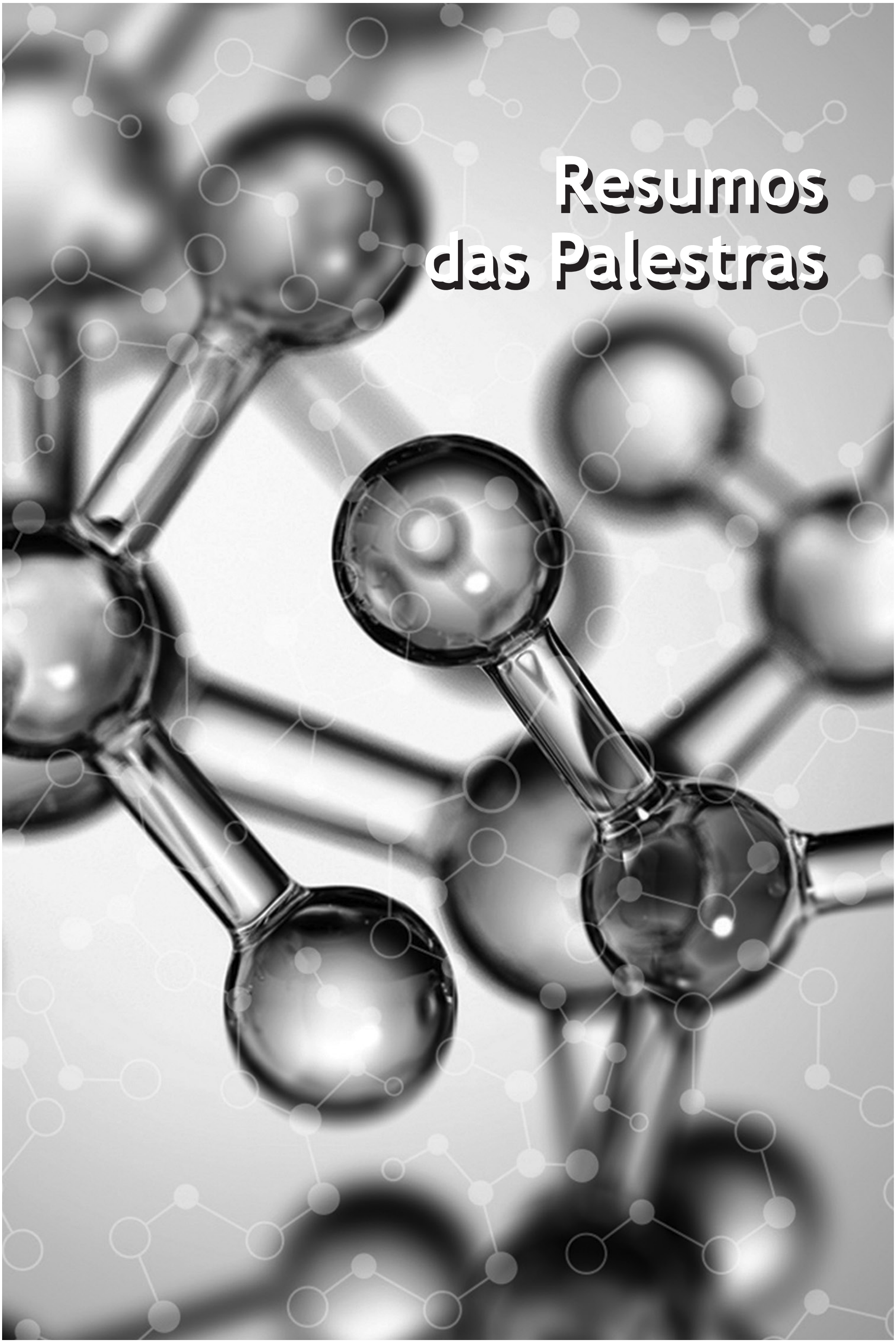
On the other hand, a good way for studying DNA/RNA structure and dynamics is to use fluorescence spectroscopy; but, if the canonical nucleobases are not fluorescent, how is it possible to employ fluorescence spectroscopy? The answer is on fluorescent natural and non-natural modified nucleobases, especially those that are isomorphic to the canonical species, which besides fluorescent probes can be employed to artificially expand the genetic code. Which are the photochemical mechanics and nature of their excited states?

In this work, we will present an overview of the photochemistry of modified and canonical nucleobases, based on results derived with the aid of high level, state of the art ab initio multiconfigurational methods. By exploring similarities and differences, we can better understand the fundamental aspect behind the interaction of light and nucleobases and, in some sense, make proposals for how to obtain fluorescent species.

Key-words: Canonical nucleobases, modified nucleobases, photochemical mechanisms, luminescence, multiconfigurational ab initio methods

Support: This work has been supported by CNPq and FAPESP





Resumos das Palestras

Combining Spectral and Scattering Data to Determine Liquid Water Structure

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Abstract: I will discuss recent experimental and simulation data of liquid water and the picture of fluctuations between high-density (HDL) and low-density (LDL) liquid this has led to [1,2]. I will especially focus on the temperature dependence in the O-O pairdistribution function at intermediate range (< 18 Å), which has recently been measured with good statistics [3-5], as well as x-ray spectroscopic and scattering data and simulations with far-reaching implications for our understanding of structure and dynamics in water. Finally, I will discuss recent experiments following the liquid-liquid (HDL to LDL) transition in ultraviscous water [6].

Key-words: Liquid water, x-ray scattering, x-ray spectroscopy, simulations

Support: This work has been supported by the Swedish Research Council through grant number VR 2016-04875

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Mechanistic insight into oxygen diffusion in prolyl hydroxylase domain-2 by equilibrium and nonequilibrium,classical and ab initio molecular dynamics simulations

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Abstract: The human oxygen sensing cycle characterizes the physiological regulation and detection of oxygen levels in mammals. It is now well-established that a relationship between the misregulation of human oxygen sensing and disease exists, including many types of cancers, ischemic and autoimmune diseases. In this computational study, molecular oxygen diffusion and the interactions of two key components of this cycle have been studied. The hypoxia-inducible factor (HIF) is the central signaling peptide of the cycle, regulated by a trans-4-hydroxylation reaction. Among the various proteins that are involved is prolyl hydroxylase domain-2 (PHD2), a member of the 2OG-dependent dioxygenase family of enzymes that uses molecular oxygen to catalyze a posttranslational hydroxylation reaction in the human oxygen sensing cycle.

A combined approached involving classical molecular dynamics simulation trajectories comprising equilibrium and non-equilibrium MD together with ab initio molecular dynamics and QM/MM calculations has been employed to characterize oxygen transport and the mechanism of reaction of HIF and PHD2; a slow rate of was obtained, involving oxygen diffusion through an 8.0 Å wide oxygen pathway into the PHD2 active site lined by hydrophobic residues. The kinetic model proposed compares with experimental kcat(PHD2:O2)/KM(PHD2:O2) estimates, and provides a framework for the understanding at the atomistic level of the oxygen-sensing properties of a prototype oxygenase.

Key-words: oxygen sensing; oxygenases; PHD; HIF; ABF; metadynamics

Support: This work has been supported by DECI and PRACE initiatives by providing computational resources in European computational facilities. This project has made use of time on ARCHER granted via the UK High-End Computing Consortium for Biomolecular Simulation, HECBioSim (www.hecbiosim.ac.uk), supported by EPSRC (grant no. EP/L000253/1).

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Planar Hypercoordinate Atoms

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Abstract: Thinking about a planar tetracoordinate carbon atoms (ptC) (or even planar pentacoordinate carbon atom) may look like an aberration in organic chemistry or simply a figment of the imagination of a theoretician, but in the last forty years, a plethora of such compounds have been synthetized or detected experimentally. As mentioned by Roald Hoffmann, "the purpose of studying nonclassical molecules is to learn from the abnormal… the making of molecules that are untypical or abnormal test our understanding of that fundamental yet fussy entity –the chemical bond" and the ptC is one of the best examples.
Here I will discuss some of our contributions in this field and the computational tools used to analyse such type of compounds and the extention to other main group elements.1-5

Key-words: Hypercoordination, multicenter bonding, nonclassical carbon systems

Support: This work is supported by Conacyt (Grant CB-2015--252356)

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Early Stages of Antimicrobial Peptides Binding to Resistant and Susceptible Bacterial Outer Membrane Chemotypes from Atomistic MD simulations

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Abstract: Lipopolysaccharides (LPS) are the major constituent of bacterial outer membranes, acting as an effective permeability barrier against xenobiotic agents and a potent activator of the mammalian immune system in amounts as little as fmol. Compounds that bind Lipid-A can limit this inflammatory process. The cyclic cationic antimicrobial peptide polymyxin B (Pmx-B) is one of the simplest molecules capable of selectively bind to Lipid-A. Gram-negative bacteria resistance to Pmx-B relies on chemical modifications of the LPS structure, which lead to major changes in the physical-chemical properties of the outer membrane. We have previously developed and validated atomic parameters for classical simulations of different LPS chemotypes.[1, 2] These parameters have been used to investigate the structural dynamics,[3, 4] hydration[5] and electrostatic properties6 of bacterial outer membranes. In this work, we have performed a systematic investigation of Pmx-B binding to outer membrane models composed of distinct LPS chemotypes experimentally shown to be either resistant or susceptible to the peptide. Molecular dynamics simulations were carried out for Pmx-B bound to the penta- and hexa-acylated forms of Lipid-A and Lipid-A modified with 4- amino-4-deoxy-L-arabinose as well as the penta-acylated form of LPS Re.7 Our simulations show that upon binding to the bacterial outer membrane surface, Pmx-B promotes cation displacement and structural changes in membrane curvature and integrity as function of the LPS chemotype susceptibility or resistance to the antimicrobial peptide. These findings reproduce experimental trends while providing atom-level structural information on the molecular basis of resistance and susceptibility of Gram-negative bacteria to Pmx-B.

Key words: vicinal proton-proton coupling constants, peptide-induced membrane curvature, peptide-induced cation displacement, mechanism of action, GROMOS force-field.

Support: This work has been financially supported by the Brazilian Funding agencies CAPES-BioMol and FACEPE) and the Swedish funding agency STINT. Computational resources were provided by the High Performance Computing Center North (HPC2N), Sweden.

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Docking, molecular dynamics and ensemble docking in the study of petrobactin biosynthesis inhibition in Bacillus anthracis

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Abstract: Bacillus anthracis is a large, gram-positive, aerobic, rod-shaped bacterium responsible for a systemic, acute and lethal infection known as anthrax. Under adverse environmental conditions, these bacteria are capable of forming dormant spores that are resistant to drying, cold, radiation, heat, and disinfectants, remaining viable for centuries. These spores can be found in soils all over the world and can enter mammals through either cutaneous, gastrointestinal or respiratory routes.[1] Inhalational anthrax has a lethality superior to 80% in humans, what makes B. anthracis a well-known bioweapon with a high potential of use as a bioterrorism agent.[2]

Three factors play a primary role in the pathogenesis and lethality of B. anthracis: a capsule; production of two exotoxins (lethal and edema); and its ability to quickly achieve high microbial concentrations in infected hosts.[3] This high virulence is related with the bacteria's capacity to acquire iron, an essential micronutrient, through the release of high-affinity iron chelating molecules named siderophores. Petrobactin has shown to be the first siderophore released by the bacteria in iron depletion conditions.[4] It is not recognized by siderocalin, a siderophore sequestrating enzyme found in the immune system, and has an affinity for iron 100 times higher than transferrin, the iron-carrier protein found in blood.[5]

The biosynthetic pathway of petrobactin involves six enzymes (AsbA-F), and within these, the asbF gene encodes a dehydroshikimate dehydratase responsible for the synthesis of the 3,4-dihydroxybenzoic acid groups that serve to coordinate iron within the siderophore itself.6 Kinetic parameters of the enzyme have been elucidated and a high resolution crystal structure of AsbF has also been published.7 This, coupled with the fact that this enzyme has no known homologues in humans makes it an attractive target for antibiotic intervention.

In this work, a set of compounds with experimentally known inhibitory potential against AsbF were studied through molecular docking and molecular dynamics (MD) simulations aiming a deeper understanding about the processes and mechanisms related with the enzymatic inhibition, which can guide the rational design of new compounds with improved potency, selectivity and with possible application as new therapies against anthrax.

Dockings with Autodock Vina8 was able to reproduce the binding mode for

3,4-DHB as found in the crystal structure with a RMSD of 2,2 Å. This binding mode is 12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil shared by several compounds with inhibitory activity and include important hydrogen bonding between carboxylate moiety in the ligands and active site residues like Arg102, Tyr70 and Tyr217 as well as between hydroxyl groups and residues like His144, His175 and Phe211.

Molecular dynamics simulations were performed with Gromacs9 4.5, with Amber03 force field for receptor and GAFF with AM1-BCC charges for ligands. DM results showed that hydrogen bonding with Arg102 and His175 are the major anchors for ligands in the active site and that the inhibitory potential can be related with the maximization in the number of interactions with active-site residues while keeping these two main hydrogen bonds.

Furthermore, the MD simulations were also used to obtain a set of distinct structures of AsbF, which are representative of the different conformational "substates" this enzyme can achieve in solution as well as to sample conformational changes induced by the presence of ligands.

The inclusion of receptor's flexibility through docking with these structures (ensemble docking) allowed an improvement in the linear correlation between docking scores and experimental free energies of binding, from r^2 of 0.13 (PCC=0.36) for docking in the crystallographic structure to r^2 of 0.34 (PCC=0.58) for the ensemble docking when all the experimental ligands are considered and from r^2 of 0.57 (PCC=0.75) to a r^2 of 0.86 (PCC=0.93) when considering the 10 most active compounds. This allowed the development of a model for the quantitative prediction of inhibitory potency and for the virtual screening of new compounds, the current step of this research.

Key-words: petrobactin, anthrax, enzyme inhibition, docking, molecular dynamics

Support: This work has been supported by CAPES and CNPq

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Chemical doping based design of oligoacenes for tuning the biradical character and excitation properties

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Abstract: The idea of combining semiconducting and open-shell properties in organic materials has attracted the attention of many researchers towards the study of polyaromatic hydrocarbons (PAHs) [1]. In particular, the acenes are interesting models of PAHs that evolve towards polyradical structures with thermally accessible triplet excited states as the size increases [2,3]. From the theoretical viewpoint, this feature impose a significant challenge since the emergence of strong electron correlation in such larger acenes requires to go beyond the usual single-determinant mean-field approximations [3,4]. Recently, we have shown that doping acenes with boron (B) or nitrogen (N) atoms leads to a large modulation in its biradicaloid nature [5]. Here we extend the previous study to the case of asymmetric substitutions with a BN-pair and also explores the consequences of the chemical doping on the excitation properties of oligoacenes based on Time-dependent Density Functional Theory (TD-DFT) and multireference configuration interaction (MRCI) calculations. Moving the dopants from the terminal to the central benzene rings leads to a remarkable increase in the singletsinglet and singlet-triplet (π-π*) energy gaps that is also accompanied by a quenching of the acenes biradical character. These results are interpreted in terms of aromaticity changes and a π-charge transfer effect. Finally, through a rational molecular design, our study provides new insights towards developing high-spin organic materials with efficient singlet fission for solar cell applications.

Key-words: mutireference, biradical, unpaired electrons, excited states, acenes
Support: Brazilian funding agencies CNPq, CAPES-ITA and FAPESP.

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Inhibitors for Zika Virus NS5 RdRp

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Abstract: Although having been discovered in 1947 in the Zika Forest, Uganda, Zika virus (ZIKV) remained largely ignored until the recent outbreak of ZIKV in South and Central Americas was linked to an increase in cases of microcephaly. It has since been determined that ZIKV can attack fetuses' immature neural cells during gestation, leading to Congenital Zika Syndrome, an umbrella term to encompass the neurological, ophthalmological, audiological and skeletal abnormalities caused by ZIKV. [1] Since then, a new wave of research has focused on vector eradication, vaccines and specific drug development.

One of us (LJP) has recently identified a small molecule, 6MMPR, capable of inhibiting the activity of ZIKV NS5 RNA dependent RNA polymerase (NS5 RdRp), which crystal structure has been recently determined at 1.9Å resolution. [2] Starting from 6MMPR and the NS5 crystal structures, we used molecular docking to identify how 6MMPR binds the protein. Based on those results, we were able to build a pharmacophore model of the most important 6MMPR features responsible for the interaction with the NS5. This model was used to filter a database of >1,800 compounds already approved for human use, [3] resulting in 944 compounds that share some pharmacophoric features with 6MMPR. We then used the FlexX algorithm to dock each one to the NS5 RdRp, [4] and identified 117 compounds predicted to show higher receptor affinity than 6MMPR. The 10 compounds with highest NS5 RdRp affinities were rescored using the Hydrogen bond and dehydration energies method (HYDE), useful to eliminate false-positives. After rescoring, three compounds still showed predicted receptor affinities higher than that of 6MMPR. The compounds are now being purchased for in vitro testing against ZIKV.

Keywords: Zika; NS5 RdRp; Inhibitor; Virtual Screening

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Quantum Theory of Atoms in Molecules charge-charge transfer-dipolar polarization classification of infrared intensities

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Abstract: Fundamental infrared intensities of gas-phase molecules are sensitive probes of changes in electronic structure accompanying small molecular distortions. Models containing charge, charge transfer and dipolar polarization effects are necessary for a successful classification of the C-H, C-F and C-Cl stretching and bending intensities. C-H stretching and in-plane bending vibrations involving sp3 carbon atoms have small equilibrium charge contributions and are accurately modeled by the charge transfer- counterpolarization contribution and its interaction with equilibrium charge movement. Large C-F and C=O stretching intensities have dominant equilibrium charge movement contributions compared to their charge transfer-dipolar polarization ones and are accurately estimated by equilibrium charge and the interaction contribution. The C-F and C-Cl bending modes have charge and charge transfer-dipolar polarization contribution sums that are of similar size but opposite sign to their interaction values resulting in small intensities. Experimental in-plane C-H bends have small average intensities of 12.6±10.4 km mol-1 owing to negligible charge contribuions and charge transfer-counterpolarization cancellations, whereas their average out-of-plane experimental intensities are much larger, 65.7±20.0 km mol-1,as charge transfer is zero and only dipolar polarization takes place. The C-F bending intensities have large charge contributions but very small intensities. Their average experimental out-of-plane intensity of 9.9±12.6 km mol-1 arises from the cancellation of large charge contributions by dipolar polarization contributions. The experimental average in-plane C-F bending intensities, 5.8±7.3 km mol-1 is also small owing to charge and charge transfer-counterpolarization sums being cancelled by their interaction contributions. Models containing only atomic charges and their fluxes are incapable of describing electronic structure changes for simple molecular distortions that are of interest in classifying infrared intensities. One can expect dipolar polarization effects to also be important for larger distortions of chemical interest.

Key-words: Charge transfer , polarization, infrared intensities, QTAIM.

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Palestra 09|PA.09

Unveiling the active species for oxygen atom transfer reactions promoted by manganese porphyrins

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Abstract: Cytochrome P450 is a class of monooxygenases present in a variety of living organisms playing an important role in oxygen atom transfer (OAT) reactions to hydrophobic substrates. Generally, their catalytic sites contain a prosthetic iron porphyrin group coordinated to a cysteine residue in a hydrophobic pocket. Over the years, several biomimetic manganese counterparts revealed to be also active for OAT and, in some cases, with catalytic activities similar to those found in natural enzymes. Despite the similarity in geometry and catalytic activities, manganese porphyrins react differently from iron porphyrins and the nature of the active species is yet to be determined. A high-valent Mn complex was claimed to be responsible by the OAT. This is mainly due to the experimental detection of a diamagnetic Mn(V)-Oxo species in 1997 with a remarkable stability in alkaline medium.[1] This stability contrasts with the expected high reactivity an active species should have. However, DFT calculations confirmed the possibility of a diamagnetic state for this Mn(V)-Oxo species and the inertness toward OAT was claimed to be a consequence of a low oxyl character for this state.[2] This debate on the nature of the active species is still open and two important questions must be answered. What is the role of the oxyl character for reactivity? If the diamagnetic Mn(V)-Oxo ground state is unreactive, what is the true nature of the active species? Recently, we have used two model systems to investigate the relative energies of low-lying electromeric states of these Mn-Oxo species using the multiconfigurational ab initio CASPT2 and RASPT2 methods.[3] We have found that two states are possible candidates to be the active species, a MnVO(P)+ triplet state and a MnIVO(P•)+ quintet state. We have also showed that meso substitution is responsible to change the energy difference between these two states showing that a multistate reactivity pattern cannot be ruled out. We have used the RASPT2 results as a benchmark for a variety of pure and hybrid functionals in DFT calculations. From this benchmark study we have extended our investigation to more complex molecules with meso-substituted groups like phenyl and penta-fluoro-phenyl groups.

Key-words: manganese porphyrin, CASSCF, spin state energetics

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Photophysics and photochemistry of nitrobenzene and 1-nitronaphthalene performing CASPT2//CASSCF static computations and DD-vMCG dynamics

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Abstract: Nitrobenzene (NB) and 1-nitronaphthalene (1NN) can be regarded as the most simple nitroaromatic compounds, and yet they are characterized by a complex photophysics and photochemistry. Both molecules are common pollutants of urban atmosphere due to their production as a consequence of incomplete combustions [1], while NB is also an important model of energetic materials [2] and it has applications in the drug delivery sector [3]. NB' photophysics is characterized by three lifetimes (100 fs, 6 ps, and 480 ps)[4] and by a particularly high value of the triplet quantum yield, equal to 0.67 [5]. Under UV radiation the system can photoreact leading to the formation of different photoproducts, as NO2, NO and O [6]. 1NN is also characterized by a first lifetime equal to 100 fs, attributed to the decay into the triplet manifold and consequently making 1NN the organic compound with the fastest multiplicity change ever measured, [7] and by a high value of the triplet quantum yield (0.63) [5], while only the formation of NO has been reported as a consequence of its UV-induced photodegradation [8]. The photophysics and photochemistry of these two similar but yet different compounds have been studies by means of static CASPT2// CASSCF computations in the framework of the so-called "photochemical reaction path approach" [9,10], and performing dynamics simulations with the direct dynamics variational multi-configurational Gaussian (DD-vMCG) method, which is a full quantum dynamics methodology, allowing the resolution of the time-dependent nuclear Schrödinger equation variationally [11]. A comparison of the photophysical and photochemical reaction paths characterized for the systems highlighting the differences and similarities in relation to the know experimental data on the molecules will be presented, together with the dynamics results obtained up to date.

Key-words: nitrobenzene, nitronaphthalene, CASPT2//CASSCF, DD-vMCG

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Palestra 11|PA.11

A molecular approach towards the atmospheric implications of aerosol formation

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Abstract: In last few years we observe a growing interest in the study of aerosol particles as they strongly influence the environmental processes both at local and global scale. Formally, atmospheric aerosols can be defined as microscopic solid particles or liquid droplets suspended in air for an atmospherically meaningful period of time, ranging from minutes to days for particles in the lower tropospheric atmosphere to years for stratospheric aerosols [1]. Atmospheric aerosol particles can be produced by natural means or artificially by anthropogenic activities like agricultural activities, biomass burning etc. They are either emitted directly into the atmosphere (primary aerosols) or formed by secondary processes (secondary aerosols) through the transformation of gaseous inorganic or organic precursors [1,2]. Atmospheric aerosols may participate in the process of climate change altering the natural cycles of precipitation and cloud formation, which, as a consequence, may alter the nature of the local ecosystem. They may also affect the quality of air causing pollution and adverse effects on human health. Depending on the size, atmospheric aerosol particles may influence the radiative balance of the earth's atmosphere directly by scattering solar radiation altering the atmospheric visibility, or, by absorbing the same to warm the atmosphere and indirectly by acting as cloud condensation nuclei (CCN) controlling the process of formation and lifetime of clouds and, thereby, influencing the local hydrological cycle. Although the importance of atmospheric aerosol particles are more or less well understood, current knowledge on the physical and chemical processes involving the mechanisms of their formation, chemical composition and morphology, and evolution of their composition and properties during their atmospheric lifetime is still insufficient [1]. Sulfuric acid (H_2SO_4) is known to play a fundamental role in aerosol particle formation [3-5]. However, Atmospheric bases, such as ammonia and amines, as well as other organic compounds and ions can significantly enhance sulfuric acid driven particle for-

mation and alter their active participation in environmental processes [6,7]. In fact, there are only a few inorganic precursors (SO_2, NO_2, NH_3) compared to the large spectrum of volatile organic compounds that contribute to secondary organic aerosol formation [1]. Understanding how these particles are formed and how they alter the atmospheric characteristics is of paramount importance for the sustainable development of social projects and implementation of proper environmental policies [8-10].

In the present seminar, we will present an overview of the use of molecular modelling and quantum chemical approaches to the study of atmospheric aerosol formation and their properties with particular application to the interaction of methanesulfinic acid (CH_3SO_2H) and methanesulfonic acid (CH_3SO_3H) with atmospheric nucleation precursors such as H_2SO_4 and NH_3.

Key-words: atmospheric aerosol, atmospheric nucleation precursor, volatile organic compunds, molecular modelling

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Palestra 12|PA.12

High-performance molecular dynamics at constant pH and constant redox potential using AMBER

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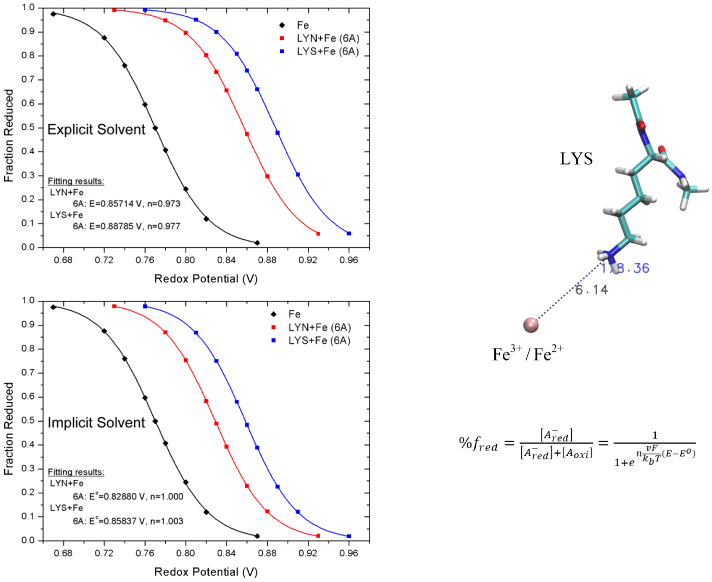
Abstract: Protein function is intrinsically related to structure and dynamic. Solution pH often has a dramatic impact on protein systems, since pH can affect the charge distribution within these biomolecules.[1] Understanding how pH-dependent conformation changes take place is key to the development of drugs targeting pH sensors, to the success of computational drug discovery strategies, and so forth.[2] Hence, accurate computational models designed to treat such systems must somehow account for pH effects. While the traditional approach of assigning a fixed protonation state for each titratable residue at the beginning of the simulation is still the most common approach, numerous methods have been developed in an attempt to treat pH effects in biomolecules more quantitatively.[1] For this purpose, Swails et al.[1] presented a new method of performing Constant pH Molecular Dynamic simulations in explicit solvent using discrete protonation states, which predicted pK_a values agreed well with experiment.

On the other hand, redox reactions, like protonation reactions, represent the simplest chemistry, involving only transfer of electrons. The source of the pH dependence of protein stability is the changing ionization state of protein residues. Redox reactions are usually coupled to some redistribution of protons within the protein, as the charge change at the redox center modifies the pK_{as} of the surrounding residues. In the same way, modifications of protonation states with pH influence redox site midpoint redox potential (E^0).[3]

A group of versatile and important proteins incorporate hemes as cofactors (heme-proteins). The in situ heme E^0 determines the role the protein will play. Many of the methods that analyze heme E^0 in proteins are conceptually similar to those that calculate residue pK_{as} in proteins, analyzing how the protein shifts the proton affinity of a site. However, proteins are found to shift heme E^0 over a much larger range than amino acid pK_{as}.[4]

Thus, the aim of this study was to extend replica exchange molecular dynamics for constant pH and electrochemical potential calculations. The implementation was done on AMBER Computational Package and have been tested and validated with some model systems (Figure 1), including the microperoxidase-8 peptide (Bis-His-NAcMP8), an 8-residue peptide with one heme c as cofactor. By making use of CUDA implementation, we obtain a high-performance code that can be used in simulations of large systems. We also show how our results are in agreement with theoretical/experimental expectations, and how computational benchmarks show the high-performance of calculations using GPU in comparison with serial or MPI calculations for large systems.



$$\%f_{red} = \frac{[A^{-}_{red}]}{[A^{-}_{red}]+[A_{oxi}]} = \frac{1}{1+e^{n\frac{vF}{k_bT}(E-E^{O})}}$$

Figure 1. Computational results and graphical representation for an iron ion in the presence of lysine peptide. The figure shows the fraction of reduced species (%fred) as a function of the redox potential by using explicit and implicit solvent representations, with the respective fittings by equation for %fred. Results in blue are for when the peptide is protonated (LYS), and results in red are for the deprotonated peptide (LYN).

Key-words: Molecular Dynamic; cytochrome; CEMD; REMD; CpHMD

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The value of NMR parameters and DFT calculations for Quantum Information Processing utilizing Phosphorus Heterocycles

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Abstract: Quantum computing is the field of science that uses quantum-mechanical phenomena, such as superposition and entanglement, to perform operations on data. The fundamental information unit used in quantum computing is the quantum bit or qubit [1-2]. The principal difference between a qubit and a classical computing bit is: A quantum bit can be in any of a potentially infinite number of states and quantum systems can be simultaneously in superposition with many of the basis states [2]. That makes the computational basis vastly increased, because a series of operations can be performed nearly simultaneously; and, theoretically, solve problems much more quickly than any classical computers [2-3]. Currently, the first and still the most successful implementations of quantum information processing (QIP) have been based on nuclear spins in liquids [3]. However, molecules that enable many qubits NMR QIP implementations should meet some conditions: have large chemical shifts and be appropriately dispersed for qubit addressability, appreciable spin-spin coupling between any pair of spins, and a long relaxation time [4]. In this line, Benzyldene-2,3-dihydro-1H-[1,3]diphosphole (BDF) derivatives have been theoretically tested for maximizing large chemical shifts, spin-spin coupling, and minimizing the hyperfine coupling constant. The NMR spectroscopic parameters (δ and J) were calculated with six different DFT functionals. The τ-HCTH/6-31G(2d) level is in better agreement with the experimental data of 31P and 13C chemical shifts. While PCM-B3LYP/cc-pVDZ level shows a decrease on deviation between calculated and experimental values for NMR properties. Finally, the Surface Response technique was employed to rationalize how the hyperfine constant varies with the chemical shifts and coupling constants values. From our findings, BDF-NO2 was the best candidate for NMR quantum computations (NMR-QC) among the studied series.

Key-words: 31P NMR, NMR parameters calculations, quantum computation

Support: This work has been supported by the Brazilian agencies FAPEMIG, CAPES, and CNPq. This work was also supported by Excellence project FIM.

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Palestra 14|PA.14

The dipole moments of deuterated endofullerenes isotopologues HD@C60 and HT@C60

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Abstract: The encapsulation of chemical species - atoms, ions or molecules - in nanostructures such as fullerenes and nanotubes has attracted much attention [1], since it has potential applications, for example, in the contexts of medicine and electronics, allowing intelligent drugs and devices to be developed. To understand the charge distributions in these systems is essential for the development of future applications, so the accurate prediction of the electrical properties of these endohedral nanostructures is an important research topic. In addition, modelling the isotopic effect associated with hydrogen substitution by deuterium or tritium may contribute to the description of these systems. In this work we report a theoretical and computational methodology that computes the dipole moments of the deuterated molecular complexes $HD@C_{60}$ and $HT@C_{60}$. This approach was used previously to predict the isotopic effect on dipole moments in a variety of apolar and polar molecules [2][3][4]. Here, we observed that the presence of HD and HT induces a polarization in the C_{60} cage, causing the dipoles of the complexes to decrease considerably with respect to the dipoles of the isolated molecules. Despite of the lack of the experimental studies to the dipole moment of these systems, this finding is compatible with theoretical [5] and experimental predictions in the literature for the $H_2O@C_{60}$ [6] and $HF@C_{60}$ [7] complexes and provides good quantitative insights opening perspectives in the study of the isotopic effect on the dipole moments of deuterated endohedral systems.

Key-words: Endohedral fullerenes, dipole moments, isotopic effects

Support: This work has been supported by FAPEMIG, CNPq and CAPES

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Palestra 15|PA.15

The Activity Coefficient from a Solvation Thermodynamics Perspective

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Abstract: Activity is a central concept and quantity in thermodynamics because it unifies the description of several relevant functions and properties as well as it retains the simple logarithm form of the chemical potential. Because the activity is related to the concentration via the activity coefficient, the relationship between the chemical potential and the concentration is then established and the limit to ideal solution can be obtained by setting the activity coefficients to one. Thus, for real solutions, the activity coefficient embodies a wealth of information regarding the solute-solvent and solute-solute interactions and correlations as well as some other terms related to the choice of the standard state. The activity coefficient is then related to the solvation of a species (e.g., solute) in a given environment (e.g., solution). Thus, the proper definition of solvation and its use is relevant to interpret and quantify the activity coefficient. In this context, the solvation thermodynamics [1-3] formalism has been successful in defining solvation and removing several ambiguities in the conventional standard thermodynamic quantities.

The solvation thermodynamics is a molecular based description of the solvation concept and it provides a proper distinction from other processes such as liberation (momentum, volume sampling and indistinguishability). The main quantity in this formalism is the pseudo-chemical potential, $\mu_{i,\alpha}^{*}$, that represents the work to transfer the molecule i from a fixed position and orientation in the ideal gas phase to a fixed position and orientation within phase α, where for flexible molecules the conformation in the gas phase is maintained in phase α. Therefore, $\mu_{i,\alpha}^{*}$ quantifies the interactions between a reference molecule and its surroundings, which gives the proper meaning and expression for the solvation of this reference molecule.

We have shown that within the classical statistical mechanics, $\mu_{i,\alpha}^{*}$ can expressed exactly as, $\mu_{i,\alpha}^{*} = -k_{\mathrm{B}}T \ln\{q_i \langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha}\}$, where k_{B} is the Boltzmann constant, T the temperature, $\beta = (k_{\mathrm{B}}T)^{-1}$, q_i the internal partition function of i, and $E_{i,\alpha}$ is the binding energy defined as the difference between the potential energy of the system with i molecule inside, U_{N+i}, and the potential energy of the system without it, U_N, $E_{i,\alpha} \coloneqq U_{N+i} - U_N$. It is noteworthy that this is exact and does not invoke the pairwise approximations in the definition and calculation of $E_{i,\alpha}$ present in previous derivations [1-4]. The activity coefficient, $\gamma_{i,\alpha}^{\mathrm{ss}}$, of i in phase α given the standard state ss is then expressed as $\gamma_{i,\alpha}^{\mathrm{ss}} \coloneqq \exp\left[\left(\mu_{i,\alpha}^{*} - \mu_{i,\mathrm{ss}}^{*}\right)/(RT)\right] = \langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha} / \langle e^{-\beta E_{i,\mathrm{ss}}} \rangle_{N',\mathrm{ss}}$. The ensemble averages $\langle e^{-\beta E_{i,\alpha}} \rangle_{N,\alpha}$ and $\langle e^{-\beta E_{i,\mathrm{ss}}} \rangle_{N',\mathrm{ss}}$ involves different number of molecules

(N, N'), because the environment of the standard state (ss) is distinct from that of the phase of interest (α), which can be evaluated from experimental solvation energy data $\Delta G^*_{i,\alpha}$, because $\langle e^{-\beta E_{i,\alpha}}\rangle_{N,\alpha} = e^{-\beta \Delta G^*_{i,\alpha}}$, or from liquids theories or from molecular simulations (Monte Carlo, molecular dynamics).

In addition, the expression $\gamma^{\text{ss}}_{i,\alpha} = \langle e^{-\beta E_{i,\alpha}}\rangle_{N,\alpha} / \langle e^{-\beta E_{i,\text{ss}}}\rangle_{N',\text{ss}}$ is the starting point to approximated approaches to calculate the activity coefficient, for instance, using the primitive model to describe electrolytic solutions or the small fluctuation approximation that allows the separation of the average binding energies $\langle E_{i,\alpha}\rangle_{N,\alpha}$ and $\langle E_{i,\text{ss}}\rangle_{N',\text{ss}}$ into a cavity and non-cavity contributions [5]. The cavity term can be described by analytical expressions based on scale particle theory [6], whereas the non-cavity contribution can be estimated from the interaction potential using the pairwise approximation or from implicit solvation models. Alternatively, this expression can be the starting point of a rigorous and feasible approach based on perturbation theory. For electrolytic solutions, the primitive model provides simple expressions for the activity coefficients of ions with the proper dependence with the concentration.

In addition to providing rigorous, general and alternative expressions and approaches, this formalism can give insightful and original interpretation for the activity coefficient. For instance, the difference in the average binding energies of species i within phases α and ss can be related to the activity coefficient, which provides a clear interpretation of how the distinct environments affect the activity of a given species.

This new formalism, interpretations and some applications will be explored during the presentation.

Key-words: binding energy, perturbation theory, solvation thermodynamics, activity.

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Palestra 16|PA.16

Computational Study of the C—X (X = F, Cl, Br, and I) Bond Cleavage Mediated by Cob[N]alamin

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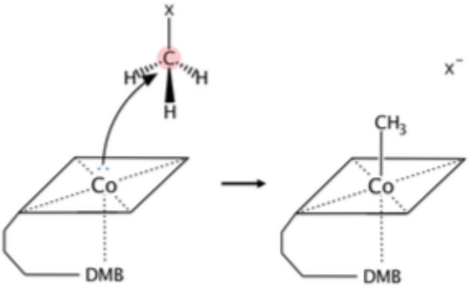
Abstract: Cob[N]alamin, Cbl, is a macrocyclic complex (~ 200 atoms/molecule) composed of a cobalt atom of variable oxidation state (*i.e.,* Co^{1+}, Co^{2+}, or Co^{3+}) located at the center of an almost- flat deprotonated corrin ring [1, 2]. This macromolecule is well-known for its relevance in different metabolic processes occurring at the cellular level. However, recent experimental evidence has demonstrated that, beyond its biological importance, Cbl plays a fundamental role in the reductive dehalogenation of halocarbon compounds [3, 4]. In the present work, the C— X (X = F, Cl, Br, and I) bond cleavage process mediated by Cbl is thoroughly studied by the computational description of the a SN2 model reaction:



A DFT/SemiEmpirical ONIOM scheme was adopted, where different functional and basis-set combinations were tested together with the PM6 method. The results of the first stage of the study showed that the employed ONIOM approach is well-suited for describing the different forms of Cbls, being the computed geometric and electronic properties comparable with results obtained from a full DFT description by adopting state-of-the-art dispersion-corrected methods [5]. Regarding the Cbl potential to cleave the different C—X bonds, various methodologies for the analysis of chemical reactions such as: the reaction force concept, the natural bond orders and charges, the reaction synchronicity, among others, suggested that both the oxidation state and the coordination number of the Co atom are determinant factors in the efficiency of reaction.

Key-words: DFT, Cob[N]alamin, Reductive Dehalogenation, Halocarbons

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Coarse grain approaches to study drug delivery systems

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Abstract:

Computer simulations, such as Molecular Dynamics simulations, are a very powerfull tool to understand biomolecular processes. In this direction, Coarse Grain (CG) models - where atoms are grouped in specific sites - allow simulation time and length scales of the systems beyond what is achievable with traditional atomistic models [1]. In this work, we go over different application of this methodology to Drug delivery systems (DDS) carried out in the group.

DDS - a formulation or a device that enables the introduction of a therapeutic substance in the body and improves its efficacy and safety by controlling the rate, time, and place of release of drugs - are an important component of drug development and therapeutics [2]. Biocompatible nanoparticles are materials in the nanoscale emerged as important players in this direction, improving efficacy of aproved drugs, for example. In this direction, the molecular understanding of the encapsulation process could be very helpful to guide the nanocarrier for a specific system.

Here we discuss different aplications of drug delivery carriers, such as liposomes, polymeric micelles and polymersomes using CG molecular dynamics simulations, based on Martini forcefield [3]. In particular we investigate [4]:

- The encapsulation of sumatriptan – an antimigraine drug - with polymeric micelles. We based the drug parametrization on atomistic simulations. We found that the drug escentially partition between the hydrophilic crown and water phase.
- The interaction of Prilocaine, a local anesthetic, in liposomes and poly(ethylene oxide)-poly(butadiene) di-block copolymer polymersomes. For the di-block copolymers, we also run bilayer systems under different ensembles. In this consition, we were are to reproduce key structural and mechanical experimental for different length chains with a similar weight fraction.
- The differential interaction of amphiphilic antimicrobial peptides with 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) lipid structures. We simulated the peptide/lipid system from different initial configurations. The peptides used for our simulations are aurein 1.2 and maculatin 1.1, two well-known AMPs from the Australian tree frog, molecules that present different membrane-perturbing behaviors. Our results showed for each peptide a different pathway for the peptide-induced membrane leakage and in good agreement with experimental observations.

Keywords: Molecular Dynamics, Coarse grain, Drug delivery systems, MARTINI forcefield

Support: This work has been supported by CONICET, ANPCyT and Universidad de Buenos Aires

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Antimatter binding matter: The covalent positron bond

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Abstract: We have previously employed a number of theoretical methodologies developed within the any particle molecular orbital (APMO) approach [1] to study the binding of positrons to atoms and molecules [2-3].

The present study is a little different. Here, we provide sufficient theoretical evidence, obtained at different level of theory within the APMO approach, revealing that one or more positrons are responsible for chemically binding two or more repelling anions.

Key-words: any particle molecular orbital, covalent bond, positron.

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Palestra 19|PA.19

Suppression of electron-induced degradation in methylated nitroimidazoles

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Abstract: Nitroimidazoles are efficiently decomposed by low energy electrons. This process, known as dissociative electron attachment (DEA), is believed to account, at least partly, for the radiosensitizing bioactivity of nitroimidazoles [1,2]. Since the DEA reactions are typically initiated by the formation of transient negative ions, or resonances, obtaining the anion spectra of nitroimidazoles is a key step to better understand their electron-induced degradation, and ultimately their application as sensitizers in the radiation and heavy-ion treatment of cancer cells.

The recently reported DEA measurements of Tanzer *et al.* [3] revealed that 4-nitroimidazole (4NI) has a very rich fragmentation spectrum below 2V, comprising single-bond cleavages and more complex reactions. Despite the low collision energies, several dissociation channels were observed, producing the H, OH and NO_2 radicals, besides HNO_2 and CN^-. However, the most striking experimental result was the complete suppression of these reactions in 1-methyl-4-nitroimidazole (1M4NI), along with a significant quenching of higher energy dissociation reactions, around 3 eV. The DEA suppression was also observed for 1-methyl-5-nitroimidazole (1M5NI) in subsequent experiments [4]. As the DEA yields show a series of narrow peaks for H abstraction below 1 eV, Tanzer *et al.* consistently argued that vibrational Feshbach resonances (VFRs) would trigger the H-elimination reaction. Since the methylation at the N1 site would be expected to completely quench this reaction, in view of the unfavorable energetics of C–H bond cleavages, those authors further considered that VFRs would also be doorways for more complex reactions, involving the cleavage of the C4–NO_2 bond.

We report a theoretical study on the anion state spectra of 4NI, 1M4NI and 1M5NI, based on electron scattering and bound state calculations. Our results point out five anion states that would be relevant for the DEA dynamics in 4NI, namely a dipole bound state (DBS), a valence bound state and three resonances, the latter formed by electron attachment into either π^* or σ^* virtual orbitals. While the DBS binding energy and the fundamental frequency of the ν_{NH} stretch mode are consistent with the VFR progression for H elimination, as previously suggested, our calculations strongly indicate that a π^* shape resonance would be the initial step for the cleavage of both the N1–H and C4–NO_2 bonds around 1.5 eV. The calculated integral cross sections, obtained with the Schwinger Multichannel Method [5] at the equilibrium geometries of the target molecules, also point out that the lifetime of the π^* resonance is about four times smaller in 1M4NI and 1M5NI than in 4NI. We believe the shorter-lived resonances, which strongly favor autoionization with respect to vibrational relaxation in the methylated species, would be responsible for the observed DEA suppression around 1.5 eV. Our results are also consistent with the DEA signals for several fragments around 3 eV, where we found a higher lying π^* resonance.

Key-words: Rediosentizers; Radiation Therapy, Resonances, Dissociative Electron Attachment; Electron Scattering.

Support: This work was supported by FAPESP (grants no. 2015/23792-5 and 2014/10012-9) and CNPq (grant no. 305672/2014-2). The calculations were partly performed using resources at LCCA/USP.

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Local environment structure and dynamics of CO_2 in the 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and related ionic liquids

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Abstract: Ionic liquids (ILs) have been considerated as advanced materials for different applications, due to the ability to be tuned and, as consequence new physical and chemical properties can be reached, such as low steam pressure, low flammability, chemical and thermal stability as well as good solubility of greenhouse gases. The combination of these specific properties makes of the ionic liquids good candidates for CO2 capture technologies.[1] In this present work molecular dynamics (MD) were carried out in order to correlate the effect of the gas absorption in the local liquid structure and its correlations with the dynamical properties of the system.[2] It were simulated three different ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide $[C_2mim][Tf2N]$, 1-ethyl-3-methylimidazolium acetate $[C_2mim][Ac]$ and 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [BMpyr][Tf2N] with six different concentrations of CO_2 at 1 atm and 313 K. In Figure 1 can be seen the a combinated distribution function (CDF) of the g(r) of H9-S and the angle of H9-O-S for the neat $[C_2mim][Tf2N]$ and the mixture $[C_2mim][Tf2N]/CO_2$ with 50 gas molecule. It is possible to see a slightly change in the orientation of the cation and anion, which was correlated to the detachment of the ions in order to create an empty space to receive the carbon dioxide. However no change was observed in the g(r) on the top of the figure, evidencing that these changes occur just in the local structure of cation and anion.

Figure 2 shows that the addition of CO_2 in the ionic liquid has shown an increase for the diffusivity of ions, which was related to the decrease of cation-anion interaction strength caused by the presence of the gas between the ions. The transport properties results showed that the addition of CO_2 in the IL generates a fluidization[3] of the system, decreasing the viscosity as a consequence of the local environment structure changing. Likewise, the effect of the type of anion and cation on the systems properties was studied considering $[Ac]^-$ and $[BMpyr]^+$ ions, showing large effects by the change of anion to $[Ac]^-$ which rise from the strong $[C_2mim]$--$[Ac]$ interaction, which conditions the solvation of ions by CO_2 molecules.

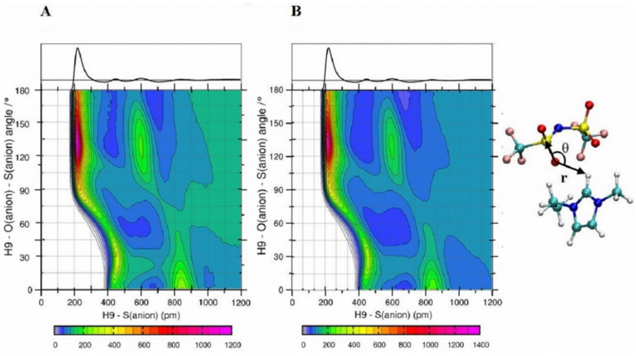

Figure 1 - Combined Distribution Function (CDF) joining the angle and distance distribution for the H9-O(anion)-S(anion) and H9-S(anion), respectively, for the cation-anion interaction in (a) neat [C_2mim] [Tf2N], and (b) fraction 0.24 [C_2mim][Tf2N]/CO_2 at 313 K with a snapshot representing this interaction from MD simulations.

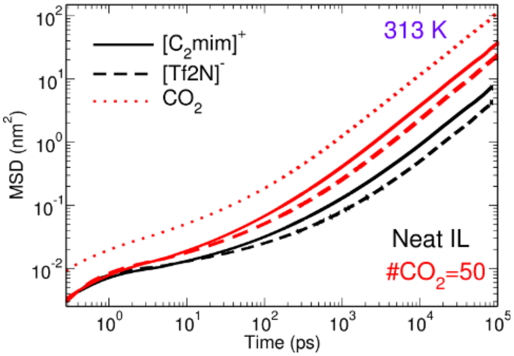

Figure 2 - Mean square displacement of [C_2mim]$^+$ and [Tf 2 N]$^-$ in neat ionic liquid and mixture containing 50 molecules of CO_2 at 313 K.

Key-words: Molecular Dynamics, CO_2, Ionic Liquids

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Palestra 21|PA.21

On new methods for predicting photophysical constants and spectra using the path integral approach: implementations on ORCA

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Abstract: Considering the recent developments in photophysics and photochemistry, particularly on the areas of Solar Cells, OLEDs, artificial photosynthesis and photodynamic therapy, the need for an efficient theoretical method capable of predicting the dynamics of excited states is ever more pressing. Much has been done in solving the time-independent Schrödinger equation, but for relevant predictions on these applications it is necessary to go beyond the static picture. Although there are methods that consider the solutions for the time-dependent Schrödinger equation in more or less approximate ways, the current methods such as the MCTDH[1] and surface hopping[2] are, in general, very costly and applicable only to small systems of about less than 20 atoms. In this work, we propose a new approach where it is possible to obtain these rates in a simpler way. Assuming a harmonic potential energy surface and using the solutions for the path integrals of the harmonic oscillator, it is possible to demonstrate that an analytic solution is obtainable[3]. The theory for the computation of transition rates such as fluorescence, phosphorescence and intersystem crossing was developed and implemented in the free software ORCA in a way that allows for systems of more than 100 atoms with excellent results. In this derivation it is also possible to include temperature and higher order effects such as vibronic coupling and Duschinsky rotations. Also, as the rates are proportional to the observed spectral intensities, the method can be used to predict very accurate absorption and emission spectra with real vibronic resolution. The same theory was also extended to compute the resonant Raman polarizability from the Douglas-Kramers-Heiseberg formula and permits simulation of rRaman spectra including transitions from fundamentals, overtones and combination bands, also including vibronic coupling and mode rotations.

As an example of the capabilities of this new module, named ORCA_ESD (from Excited State Dynamics), we present the absorption and emission spectra for benzene (Fig. 1), as predicted using data from B3LYP/DEF2-TZVP calculations. The module extracts data automatically from the other modules of ORCA and computes the rates in many different levels of approximation. It is important to consider that, in the case of benzene, the S_0-S_1 transition is symmetry-forbidden and all of the intensity observed is due to vibronic coupling. The calculated rate in hexane at 298 K, is 1.63 $\times 10^6$ s^{-1} while its best experimental value is 1.76 $\times 10^6$ s^{-1}[4].

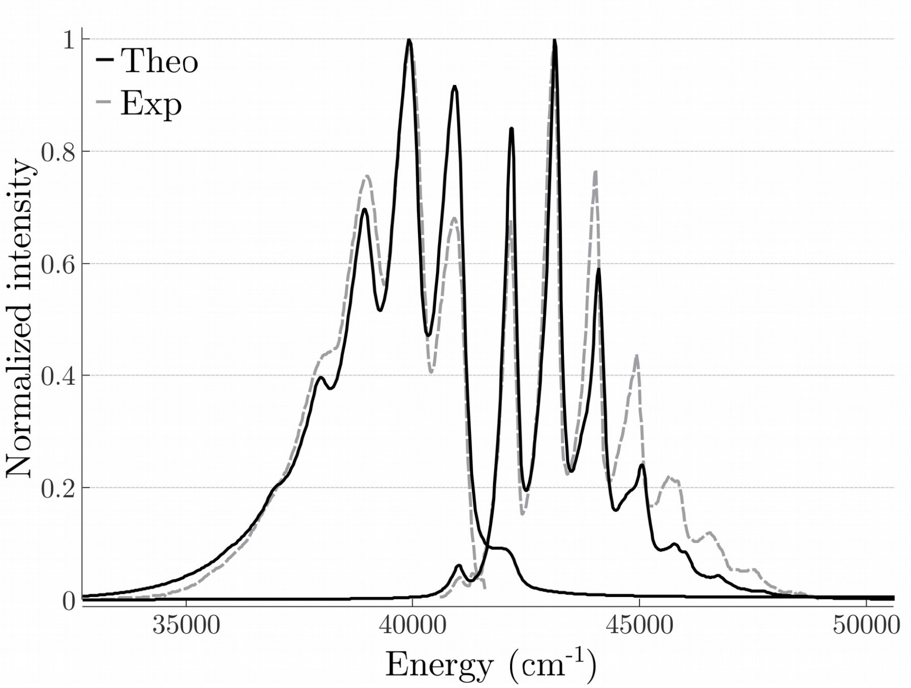

Figure 1. Predicted (in solid black) versus experimental (dashed grey) absorption (right) and emission (left) spectra for the S_0-S_1 transition of benzene in hexane solution at 298 K.

Key-words: excited state dynamics, photophysics, fluorescence, phosphorescence, intersystem crossing.
Support: This work has been supported by CAPES, the Alexander von Humbolt Foundation and the Max-Planck Gesellschaft.

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Palestra 22|PA.22

Study of Dimers via Quantum Monte Carlo

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Abstract: Monte Carlo method is a statistical method used to calculate integrals by means of random samplings. When this method is applied to calculate quantum properties of atomic and molecular systems, it is called Quantum Monte Carlo (QMC) [1]. The two most commonly used QMC methods are: Variational Monte Carlo and Diffusion Monte Carlo [2]. In this work, QMC was used for the calculation of interaction energy of dimers, specifically dimers of CH_4 that have an expressive van der Waals interactions contribution. The studied dimers were: CH_4-CH_4, CH_4-HF, CH_4-H_2O. These dimers have great importance in astrophysical and spectroscopic applications [3,4,5,6]. Thus, the main objective of this work is to evaluate the QMC method to calculate the interaction energy of van der Waals dimers. To perform the calculations, it was used wave functions generated by two *ab initio* methods - Hartree Fock (HF) and DFT – in order to analyze the quality of the wave functions to be used as guide function in QMC. The Gaussian09 program was used to perform the HF and DFT calculations and the two wave functions were used as input of QMC method in Casino software. By analyzing the results of the energies of the molecules and the dimers, it was observed that all of them were in line with the referential values. Also, it was confirmed that the effects included in the DFT did not impact the wave function when it was used in QMC and the same basis set did not induce the same proportional energy improvement in the dimer and in separated molecules. In other words, the quality of the wave function is not equal for the dimer and for the molecules that composed it. Another important characteristic observed was that the deviations of the interaction energy increase with the number of electrons difference between the two molecules that formed the dimer. Finally, it was observed that the quality of the results generated by QMC does not depend on the nature of the interaction.

Key-words: Monte Carlo, dimers, van der Waals interactions
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Computational Design of Novel Building Blocks for Nanotechnology Based on Core-Modified Metalloporphyrins

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The sizes, shapes, electronic properties, and binding abilities of metalloporphyrins can be broadly tuned by replacing one or more pyrrole nitrogens with other elements, for example, C, Si, chalcogens (O-Te), or P. This type of the porphyrin core-modification is a highly promising approach for tuning the properties as well as reactivity of porphyrin species. Also, metalloporphyrins are able to form numerous covalently and non-covalently linked arrays/stacks with each other as well as complexes with fullerenes and semiconductor nanoparticles (NPs). These building nanotechnology blocks have been extensively explored due to their tremendous potential in applications such as photovoltaic dyes, near-infrared dyes, nonlinear optical materials, nanoelectronics devices, medicine, etc. Stimulated by these facts, along with our recent reports on metalloporphyrins with all the four N's replaced with P, $MP(P)_4$, M = Sc-Zn [1-4], we formulated the following extremely interesting questions to be addressed: (i) Could core-modified porphyrins form stacks without any linkers/substituents? (ii) How strong will core-modified porphyrins interact with fullerenes? (iii) Are core-modified porphyrins able to make complexes with NPs? We present the recent results of the computational design of several novel building nanoblocks based on core-modified metalloporphyrins: (i) stacks; (ii) complexes with fullerenes; and (iii) complexes with small semiconductor NPs and small metal clusters.

Key-words: porphyrins, core-modification, nanotechnology, complexes.
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The nature of the interactions between Ag+ and benzene

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Abstract: The interaction of transition metal cations with aromatic compounds is of utmost importance to modulate the properties of materials or to modify the action of biomolecules. There are few works that study the interaction of Ag^+ with benzene, the standard aromatic compound. None of them explore the nature of this interaction. In this work all conformations of the Ag^+ - benzene system was determined, and for each the nature of cation-pi interactions was analyzed by energy decomposition and by electron density techniques of analysis.

The geometry optimization and vibrational frequency analysis were made by MP2/def2-TZVPP-SDD computational model, by using Orca 4.0.0 software. Some tests were made with DKH2 relativistic approximation, but results are similar to those obtained with SDD ECP. Single point calculations were made with CCSD(T)/def2-QZVPP-SDD, using Turbomole 6.3. NBO analysis was obtained by NBO 6.0 interfaced with Orca 4.0.0 by B3LYP/def2-TZVPP-SDD. AIMAll (17.01.25) was used for QTAIM and interacting quantum atoms (IQA) analysis. SAPT2+(CCD)/TZP was made by PSI4 1.1.

After an extensive search in the potential energy surface, there are three structures for the complexation of Ag+ with benzene, η^2, η^3 and η^6, Figure 1. Kim et al. found also a η^1 complex [1], in contrast with our results.

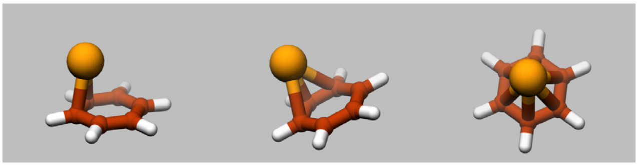
(a) (b) (c)

Figure 1 – Ag+-benzene complexes. (a) η^2; (b) η^3; (c) η^6.

Our best results indicate that the interaction energy is around 41 kcal/mol, and the complexes are nearly isoenergetic. The difference between η^2 and η^3 is only 0.05 kcal/mol, and for η^2 and η^6, 0.42 kcal/mol. All methods indicate a donation of electron density from the pi system of benzene to the cation. According to NBO, the main interaction is π(C-C) → s(Ag). A d(Ag) → π^*(C-C) is also observed, but is much less important. NRT indicates secondary quinoidal dipolar resonance structures, instead of Dewar structures. The molecular graphs obtained by QTAIM show that all bond paths (BP) are topologically unstable, because they are curved and the ellipticities are very high. Parameters of the bond critical point (BCP), as the electron density and its Laplacian indicate that Ag-C are closed shell interactions. In contrast, the total electron density and its components reveal that Ag-C interaction for η^1 is covalent, or at least with a large covalent character, and closed shell for η^2 and η^6, with a very small covalent character. The largest component of E_{IQA} is the exchange-correlation, not the classical energy. This suggests that all Ag-C interactions have a polar and covalent character. The largest stabilizing components of SAPT2+(CCD) are electrostatic, and dispersion. This shows that metal-carbon contacts have ionic and covalent components, and this is confirmed by sizable charge transfer energies.

In conclusion an extensive search in the potential energy surface indicates that there are three Ag^+-benzene complexes, nearly isoenergetic. The metal-carbon interactions are polar, with a covalent component.

Key-words: cation-pi interactions, EDA, NBO, QTAIM, SAPT.

Support: This work has been supported by CAPES, CNPq (Grants 304447/2010-2 and 308254/2016-3), FAPESP (Grants 2008/02677-0 and 2014/50265-3).

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Resumos das Comunicações Orais

Comunicação Oral 01|CO.01

Electronic Structure and Absorption Spectra of Fluorescent Nucleoside Analogues

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Due to the emissive nature of some modified nucleobases, new fluorescent nucleosides, nucleotides, and oligonucleotides have been used to investigate fundamental biochemical transformations observed in DNA and RNA, facilitating the understanding of structural changes taking place due to environmental changes or interaction with light [1]. Recently, a second generation of a new emissive RNA alphabet, based on the isothiazolo[3,4-d]-pyrimidine structure, was synthetized [2] (Figure 1). These new molecules present not only isomorphism with the canonical ones, but also exhibit an isofunctional character making them prone for the above mentioned applications. The experimental absorption spectra were obtained in 1,4-dioxane and water. However, the molecular nature of the absorption and emission bands were not fully analyzed. To better understand these physical chemical properties we carried out a systematic investigation employing quantum chemical and molecular mechanics tools.

Solvent effects were taken into account combining the Sequential QM/MM methodology [3] with an average electrostatic embedding (ASEC) [4] and the Free Energy Gradient method (FEG) [5], called the ASEC-FEG method [6]. Furthermore, the absorption spectra were computed with the state of the art CASPT2 model. The molecular nature of the ground and excited states, charge distribution, geometries and hydrogen bonding in gas phase, dioxane and water were also studied. With these computational methods, we are able to carry out an atomistic treatment the solvent as well as a statistical treatment for the geometries and hydrogen bonding configurations.

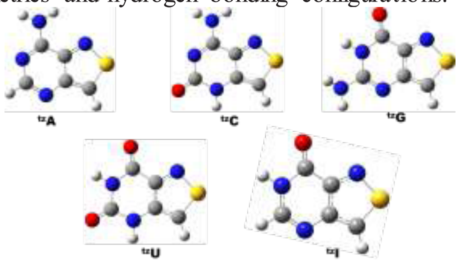

Figure 1: New fluorescent nucleobases obtained from isothiazolo[4,3-d]pyrimidine (sugar was substituted by hydrogen atoms).

Analysis of the atomic charges showed that no significant difference was noticed between the gas and dioxane media. In water, the charge redistribution is larger, leading to a significant increase in the dipole moment for all cases, ranging from 1.9 D for ^{tz}I to 5.0 D for ^{tz}G. The computed absorption spectra are in good agreement with those observed experimentally; however special attention was needed to reproduce the results obtained in 1,4-dioxane, probably because of its lower dielectric constant in comparison to water. In addition, the changes in geometry when changing from the gas to the condensed media are especially noticeable in the pyramidalization of the $-NH_2$ group for ^{tz}A and ^{tz}C, on which the amino group is placed in position 6 of the ring. The pyramidalization of the $-NH_2$ group, is not observed in ^{tz}G, in which the group is in position 2. All molecules are hydrogen bond donors and acceptors, but only water exhibits the same characteristic, with dioxane acting as an acceptor only. In respect to the number of hydrogen bonds obtained, the following trend was obtained: $^{tz}I < {}^{tz}A < {}^{tz}U < {}^{tz}C < {}^{tz}G$.

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Multireference Coupled-Cluster Benchmark for Transition Metal Molecules: Comparison with Experimental Data and Assessment of Standard Coupled-Cluster and Kohn-Sham DFT

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Abstract: We present Coupled-Cluster (CC) and Kohn–Sham Density Functional Theory (DFT) calculations of dissociation energies (D_e), equilibrium bond distances (R_e), and harmonic vibrational constants (ω_e) for 60 diatomic molecules containing 3d, 4d, and 5d transition metals and compare to experimental data. To arrive at accurate benchmark values, we employ a CC based composite approach with basis set extrapolation, inclusion of core-valence correlation, and corrections for relativistic and multireference effects. The latter correction was obtained from internally contracted multireference Coupled-Cluster (icMRCC) theory. In accordance with previous studies on a subset of molecules[1-3], we find that multireference corrections are rather small in many cases and CCSD(T) can provide accurate reference values, if the complete basis set limit is explored. In addition, the multireference correction improves the results in cases where CCSD(T) is not a good approximation. For a few cases, however, strong deviations from experiment persist, which cannot be explained by the remaining error in the computational approach. We suggest that these experimentally derived values require careful revision. We also tested ten DFT functionals for the molecules in the present data set against experimental and calculated reference values.

Key-words: CCSD(T), MRCC, ab initio, transition metals, DFT
Support: This work has been supported by FAPESP and DFG

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Experimental and Theoretical Investigations of Barbaloin in a DMPC Bilayer

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Barbaloin (10-glucopyranosyl-1,8-dihydroxy-3-(hydroxymethyl)-9(10H)-anthracenone, BBH), is the major anthraquinone glycoside of the Aloe vera. It can be extracted from plants of the family Asphodelaceae such as Aloe vera, Asphodelus and Asphodeline, which are widely used in the food, cosmetic and pharmaceutical industries [1]. Barbaloin has been found to have several pharmacological activities, such as laxative, antimicrobial, anti-inflammatory, antioxidant, antifungal and anticancer activities [2]. Previous studies have shown that barbaloin present strong inhibitory effects on histamine release from human mast cells [3]. This inhibitory effect of barbaloin is much higher than of some anti-inflammatory drugs. Due these effects, more and more scientific workers devote themselves to studying the structural and electronic properties of this molecule and its interactions with the biological environment [4,5]. In a recent work [6], we discussed the absorption spectra of emodin (a small antraquinone) in different solvents and its chemical processes in aqueous solution, such as protonation/deprotonation and tautomerism. These processes changes the molecular properties and its interactions with the environment. In this work, we report a study experimental and theoretical of Barbaloin into solvents and lipid bilayer addressed to examine the partition, location and interaction of this molecule in these environments. As experimental, we present the UV/Visible spectra of these species in solvents of different polarity (range from water to benzene) and in lipid dispersions of DMPC in two pH conditions acid and alkaline. Additionally, we performed molecular dynamics (MD) simulations of Barbaloin in fully hydrated lipid bilayers of DMPC to investigate at atomic detail the molecular mechanism of the interaction of this molecule with lipid membrane and its preferred location and orientation in these environments. In addition, we investigate the partition, orientation and mobility of barbaloin in the bilayer. As main results, we obtained that barbaloin have a strong tendency to insert into the lipid bilayer, collecting near the head groups of DMPC, with the anthracene almost fully oriented parallel to the membrane normal axis and the glucose moieties anchored in the head groups of DMPC. Analysis of various structural properties (area per lipid, electron density profile and order parameters of the phosphatidylcholine tails) showed that the barbaloin causes a stronger disorder in phosphatidylcholine tails of the lipids.

Support: FAPESP, FAPEMA, CNPq, CAPES, Rede Nanobiotec and INCT de Fluidos Complexos.

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Theoretical investigation of the reduction potential of ruthenium(III/II) complexes with potential antitumor activity and their interactions with biological targets

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Abstract: Complexes of Ruthenium (II and III) have attracted the interest of the scientific community as potential antitumor drugs, thanks to their low toxicity and ability to overcome drug resistance [1]. Although Ru metallodrugs exhibit antitumor activity in both oxidation states, the Ru (III) metal ion is likely to be reduced to Ru (II) in vivo. In this way, Ru (III) complexes would act as a prodrug, which is activated byreduction in vivo to bind more efficiently to the biological target . There are currently two antitumor compounds of ruthenium(III) in the clinical phase, thanks to their ample anti-neoplastic activity: *trans*-tetrachloro (dimethylsulfoxide) imidazole ruthenate(III) [Im]trans-[RuCl4(Im)(DMSO)] (NAMI-A) and *trans*-[tetrachlorobis (1H-indazole) ruthenate(III) [IndH]trans-[RuCl4(Ind)2] (KP1019). It is believed that in the mechanism associated with these Ru(III) complexes, activation by reduction and exchange of chloride ligands by water molecules of the solvent (hydrolysis or aquation) are two important steps for the antitumor function of such metallodrugs Based on experimental observations, three events are connected with the biological activity of NAMI-A and KP1019: i) Reduction of the Ru(III) center, (ii) chloride exchange reaction with water molecules of the solvent medium and (iii) interaction with the biological targets. The sequence of the events will depend, on the kinetics of these reactions and also on the reduction potential of the species, chloride concentration and thermodynamic stability of the complexes formed. In this work we employed the Density Functional Theory (DFT), at the TPSSh/Def2-TZVP level, in combination with the SMD continuum solvation model, to investigate the electrochemistry of NAMI-A, KP1019 and their

hydrolysis products as well as the thermodynamics of their interactions with S-donor (cystine (Cys), glutathione (GSH)) and N-donor (guanine at the coordination sites N3 and N7) biological molecules. Our results show that the compounds exhibit different electrochemical behavior upon hydrolysis. The reduction potential of NAMI-A is sensitive to the degree of hydrolysis, increasing with the number of chloride ligands replaced by water. On the other hand, the reduction potential of KP1019 does not vary with the hydrolysis and remains almost constant. The calculations showed that for both complexes the thermodynamics of the hydrolysis processes are extremely favorable and the Gibbs free energy calculations for the successive hydrolysis reactions revealed that all chloride ligands can be favorable replaced by water. Interestingly, the Gibbs free energy for the chloride exchange by water varies linearly with the number of water, that is, the ΔG for the second hydrolysis is twice the valor for the first hydrolysis and the free energy for the third hydrolysis is three times the value for the first hydrolysis. This trend is observed for both the NAMI-A and KP1019 complexes. Our results shows that thermodynamically, the NAMI-A and KP1019 complexes are reduced first and undergoes hydrolysis after, since the free energy involved in the reduction process of the complexes is more negative. Our results are shows that the NAMI-A complex have more affinity for the S-donor ligand glutathione (ΔGsol = -24.5 kcal/mol and ΔGsol = -30.8 kcal/mol for the circular and extend forms, respectively) than for the guanine base (ΔGsol = -0.4 kcal/mol for the interaction at the N7 site). On the other hand, for the KP1019 complex, the only favorable interaction in solution is with guanine at the N7 site, with ΔGsol = -4.8 kcal/mol. Interaction with the S-donor ligands are unlikely to happen, with for the interaction with cysteine and 11,01 and 18.6 kcal/mol for the interaction with glutathione extend and circular form, respectively.

Key-words: **NAMI-A, KP1019, electrochemical behavior, biological activity**

Support: CNPq, CAPES, FAPEMIG e INCT-Catálise.

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Study of the dynamics of aggregation and behavior in the solution of substituted phthalocyanines

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Abstract: The study of electronic properties of photosensitizing compounds, in which the derivatives of porphyrins, phthalocyanines and naphthalocyanines are focused here, has attracted the interest of the academic community recently thanks to the wide range of applications as, e.g., in energy conversion for solar cells or in photodynamic therapy (PDT). [1,2] Using quantum methods to study part of this class of compoundswere carried out in order to obtain electronic properties, aiming their use as photosensitizers in PDT. For such application, electronic transition may occur in the region between 600 and 800 nm.[2,3] However, previous studies by our research group and other researchers emphasized the importance of understanding the aggregations of these compounds and their electronic implications. [4,5] Thus, this work proposes to study the dynamics of aggregation of Zn(II)-Phthalocyanines (ZnPc) and Zn(II)-Naflococyanines (ZnNc) and their tetrasubstituted variations with tert-butyls. As cells of the dynamics were modeled with approximately 4000 SPC water molecules using the GROMOS 53a6 force field. The 200 ns times in MD simulations were adopted to extract representational inputs to analyze the solvation layer and its interference where applicable In TD-DFT using BLYP and 6-311G(d). The molecular dynamics calculations were performed using the GROMACS 4.5 package.

Key-words: ZnNc, ZnPc, Molecular Dynamics, Aggregation
Support: This work has been supported by FAPESP, CAPES, CNPQ and UFABC.

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Structure and Dynamics of Poly(urethane-urea) from Molecular Dynamics Simulations

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Abstract: Polymer based membranes for gas capture and separation have been investigated as alternative to the conventional systems, mainly in processes applied by petrochemical and refinery areas [1]. Due to their versatility, poly(urethane) (PU) and poly(urethane-urea) (PUU) have been studied as good candidates to be applied on gas capture/separation [2,3]. Molecular dynamics (MD) simulations not only give support to the experiment, but also can predict structural, dynamical and thermodynamic properties. In this work, a new approach for the point charge model development for polymers simulations is performed, based on a sampling of the conformations and DFT calculations. The intramolecular force field is based on the GAFF parameters using Antechamber and ACPYPE tools. This methodology has been used to generate the topology and subsequent validation by molecular dynamics simulations, using as reference the density and the structure of the pure PUU. The density average obtained in the simulations with a value of 1.06 $g.cm^{-3}$ agrees with data from the literature [4]. Structural calculation by the radial distribution function (RDF) allowed the characterization of microphase separation. The model developed for PUU proved to be satisfactory to represent the studied systems and promising for future works involving polymer membrane simulation.

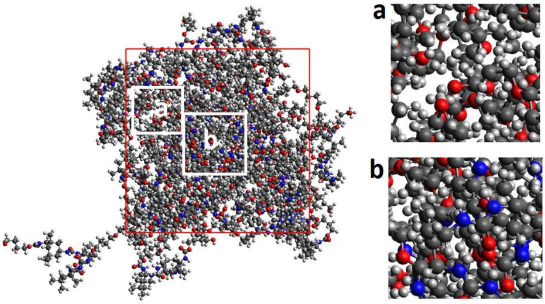

Figure 1 - System framework demonstrating a micro-phase separation

Key-words: **polymer, molecular dynamics, simulation, gas separation**

Support: This work has been supported by Capes and FAPERJ

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Comunicação Oral 07|CO.07

A novel assessment of the role of the methyl radical and water formation channel in the CH3OH + H reaction

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Abstract: A number of experimental and theoretical papers have accounted only for two H-abstraction channels in the reaction of methanol with atomic hydrogen (R1 and R2 channels) [1,2]. Recently, several astrochemical studies have claimed the importance of another channel for this reaction, which is crucial for kinetics simulations related to the abundance of molecular constituents in planetary atmospheres: methyl radical and water formation (R3 channel) [3,4]. Here, motivated by the lack of and uncertainties about the experimental and theoretical kinetic rate constant for the third channel, we developed a first-principle Car-Parrinello molecular dynamics thermalized at two significant temperatures – 300 and 2500 K. Furthermore, the kinetic rate constant of all three channels was calculated from a high-level *deformed*-Transition State Theory (*d*-TST) [5] at a benchmark electronic structure level. *d*-TST shows to be suitable to describe the overall rate constant for CH_3OH + H reaction (archetype of moderate tunnelling regime) with the precision required by pratical aplications. Considering experimental ratios at 1000 K, $k_{R1}/k_{R2} = 0.84$ and $k_{R1}/k_{R3} \approx 15 - 40$, we provided a better estimate when compared with previous theoretical work: 7.47 and 637, respectively. The combination of these procedures explicitly demonstrates the role of the third channel in a significant range of temperatures and indicates its importance considering the thermodynamic control to estimate methyl radical and water formation. We expect that our results can help to shed new light on the fundamental kinetic rate equations for the CH_3OH + H reaction.

Key-words: CH_3OH + H reaction, reaction rate constants, *d*-TST.

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Investigating the Mechanism of Action of Pediocin-Plantaricin Antimicrobial Peptide using Atomistic Molecular Dynamics Simulations

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Hybrid antimicrobial peptides (AMPs) are designed for novel or enhanced antimicrobial activity, broad-spectrum targeting, decreased induction of antibiotic resistance, and reduced hemolytic activity and mammalian cytotoxicity.[1] A hybrid peptide sequence has been synthesized from the antimicrobial peptides pediocin A (N-terminal)[2] and plantaricin 149A (C-terminal).[3] Previous studies of circular dichroism and fluorescence spectroscopic studies have shown a disordered to ordered conformational transition of the peptide upon binding to POPG but not to POPC membranes. Optical microscopy measurements have indicated that at low concentrations the peptide causes the disruption of POPG membrane of vesicles and formation of small, heterogeneous complexes of phospholipids and peptides. In order to investigate the molecular mechanism of the hybrid peptide, molecular dynamics (MD) simulations were carried out using the GROMOS parameter set 54A7 at atomistic level and NpT ensemble. The simulated systems were analyzed with respect to time-dependent (peptide secondary structure and lipid tilt angle), and average properties (density profiles and deuterium order parameters). The peptide concentration was also taken into account to investigate the effect over the membranes.

The present simulations show that the peptide adsorbs on both PG and PC membranes via electrostatic interactions. Only upon binding to the PG surface there is an increase of helical content compared to the peptide in solution. Higher helical content is also observed for the single peptide embedded in PG compared to PC membranes, which is in agreement with experimental data. The density of the membrane medium makes conformational transition of the peptide embedded slower than on the surface of the membrane. The results suggest that PA–Pln149 does not form nanopores, but rather promotes the breakdown of membrane integrity through peptide aggregation followed by induction of negative membrane curvatures and membrane transition from a lamellar to a non-lamellar arrangement. Our data points to a mechanism of membrane disruption without deep penetration of the peptide and from a given peptide concentration threshold. Evidence for that comes from increased disorder of the membrane and persistent interactions between the peptide and membrane headgroups throughout the membrane disruption process (Figure 1). Our findings suggest that the hybrid peptide disrupt the membrane via a carpet-like mechanism (in a V-shape) which has also been postulated for the action of Pediocin A and Plantaricin 149A.[4]

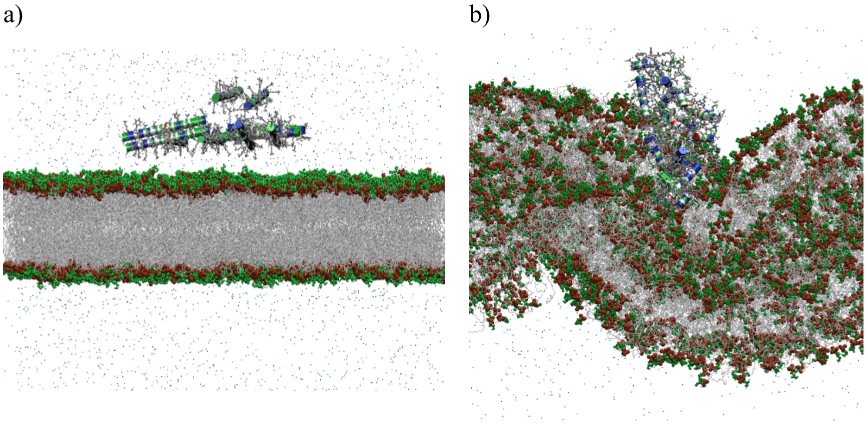

Figure 1 Structural evolution of the system with ten peptide units interacting with a 100% POPG bilayer. Snapshots were taken from (a) 0 ns and (b) 100 ns of simulation. At the membrane, the glycerol groups are represented in green, the acyl chains are in green, and the oxygen atoms of the phosphate groups are represented in red. Water molecules were hidden to better visualization.

Key-words: **antimicrobial peptide, mechanism of action, MD simulations, carpet.**

Support: This work has been financially supported by the Brazilian Funding agencies CAPES-BioMol, FACEPE and CNPq) and the Swedish funding agency STINT. Computational resources were provided by the High Performance Computing Center North (HPC2N) and the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory, a scientific user facility sponsored by the U.S. Department of Energy.

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Dimerization effects on the e^{-}-$(H_2CO)_2$ scattering cross sections

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Abstract: Electron-induced DNA damaging have been associated to subionization and subexcitation processes [1]. Hence, several studies on electron scattering with biological molecules have appeared in the literature in the recent past, however quite a few explored weakly bound systems [2,3]. Formaldehyde dimer $(H_2CO)_2$ present one of the simplest examples of systems containing a C-H...O interaction, that is often found in the structures of important biomolecules such as amino acids, sugars, DNA and RNA. Therefore, the system can serve as a prototype for investigations about the damage caused by low-energy electrons when interacting with larger biochemical units present in living tissue.

In this work we present a theoretical investigation on e^{-}-$(H_2CO)_2$ scattering. Several cross sections of the two most stable structures reported by Dolgonos [4] (the Cs and the C_2h ones) were computed in the 1-50 eV energy range. For comparison purposes, all the cross sections of the monomeric system were also determined.

The EPolyScatD suite of codes (originally developed by Gianturco *et al.* [5] and modified by de Souza *et al.* [6]) was employed to perform all the scattering-related computations. In the referred package, a complex optical potential (COP) is used to represent the collision dynamics and a single-center expansion method combined with the Padé approximation is used to solve the scattering equations. The COP incorporated in EPolyScatD is given by:

$$V_{opt} = V_{st} + V_{ex} + V_{cp} + iV_{ab}\,.$$

In the above equation, V_{st} and V_{ex} are the static and the exchange components, respectively. V_{cp} is the correlation-polarization contribution obtained in the framework of the free-electron-gas model [7], and V_{ab} is the improved model absorption potential developed by our group [8].

In Fig. 1 we show our calculated results of the Momentum Transfer Cross Sections (MTCS).

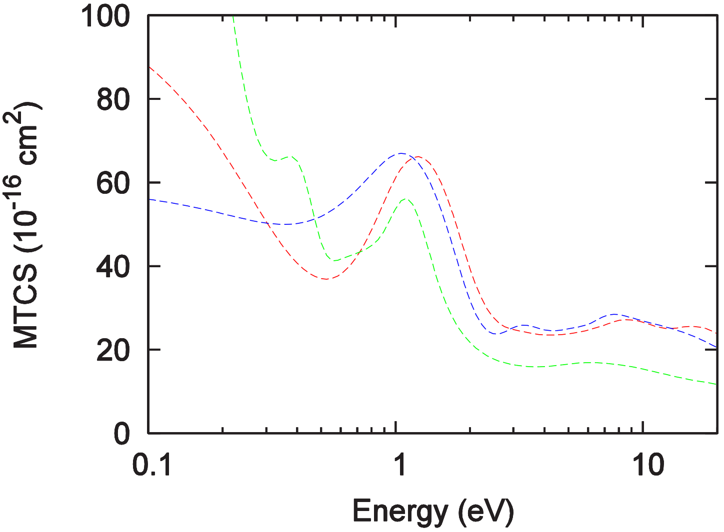

Figure 1. MTCS of the electron scattering. Green dashed curve, results of e^--formaldehyde monomer; red dashed curve, results of e^--(Cs dimer); blue dashed curve, results of e^--(C_2h dimer).

It is possible to notice the occurrence of a shape resonance (around 1.0 eV) in all three species. Interestingly, the feature seen in the Cs dimer presents a blue shift (about 0.3 eV) when compared to the monomer, while the C_2h dimer show the feature at the same energy (or slightly red shifted by 0.05 eV). Additional results will be presented at the Conference.

Key-words: Electron scattering, formaldehyde, cross sections
Support: This work has been supported by CNPq.

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Comunicação Oral 11|CO.11

Stability structures of acetonitrile ionic clusters for astrochemical implications

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Abstract: Acetonitrile, CH_3CN, was first detected on the Sgr A and Sgr B molecular clouds, and since then had been detected in a lot of galactic sources, as Titan's atmosphere, comets, molecular clouds, protoplanetary disks and proto-stars.[1] Its relevance as an important astrophysical molecule is due to its high dipole moment (3.9 Debye), what makes it possible to estimative the temperature and density of molecular clouds by means of its emission lines due to rotational transitions.

Inside molecular clouds, at about 10K, the formation of acetonitrile ice on dust grains, forming ice mantles, is expected. Such mantles are exposed to different forms of radiation, as UV, X-rays, cosmic rays, stellar winds and charged particles.[2] These agents unleash several chemical reactions on the ice surface and desorption of molecules to gas-phase, being a good explanation for the molecular abundance on molecular clouds.

The objective of this work is to study ionic clusters of acetonitrile with hydrogen, CH_xCN (x= 4 to 8), which has already been detected experimentally by the TOF-MS technique.[3] The structures of these clusters were determined at Density Functional Theory (DFT), with M06 functional and cc-pVTZ basis. The relative energies and vibration frequencies of the cluster were calculated and correlated with the intensity of the TOF-MS spectrum obtained in such conditions as to mimic the astrophysical environment.

Key-words: acetonitrile, astrochemistry, stability structures

Support: This work has been supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)

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Comunicação Oral 12|CO.12

Assessing the molecular basis of the fuel octane scale: A detailed investigation on the rate controlling steps of the autoignition of heptane and isooctane

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Abstract: N-heptane and isooctane are the primary reference fuels and key species in the modelling of ignition of hydrocarbon based fuel formulations. The octane rating scale is defined as the fraction of isooctane in a mixture of isooctane and n-heptane. It is employed to access the quality of different fuels used in spark-ignition engines. Isooctane is knock-resistant while n-heptane is a very knock-prone hydrocarbon. In the low-temperature mechanism of autoignition, the parent alkane molecule is converted to an alkyl radical, which can subsequently reacts with O_2 forming an alkylperoxy (ROO•) intermediate. The ROO• can internally transfer a hydrogen atom to form a hydroalkylperoxy (•QOOH) or decompose directly to an olefin and HO_2. [1] The •QOOH species are directly related to chain-branching in the low-temperature autoignition chemistry. It has been suggested that interconversion of alkylperoxy and hydroalkylperoxy species via hydrogen-transfer isomerization reaction is the key step to understand the different knocking behavior of alkanes. [2] In this work, the kinetics of unimolecular hydrogen-transfer and HO_2 elimination reactions of n-heptylperoxy and isooctylperoxy are determined using canonical variational transition state theory (CVT) and multidimensional small curvature tunneling (SCT). [3] The rate coefficients are calculated in the temperature range 300−900K, relevant to low-temperature autoignition. The relations between the rate constants and tunneling corrections to the geometrical parameters of the species involved are discussed. The concerted HO_2 elimination is an important reaction that competes with some H-transfer and is associated with chain termination, since the lowly reactive HO_2 radical is formed. The branching ratio between elimination and isomerization channels constitutes an important parameter to understand the knock propensity. Variational and multidimensional tunneling effects on the reaction coordinate cannot be neglected for the H-transfer reaction. In particular, in the small curvature approximation the 'corner cutting' effect may considerably enhance the reaction rate. The SCT and ZCT (zero curvature tunneling) transmission coefficients are compared to the Wigner and Eckart models. For the HO_2 elimination, we show that it is the endothermicity of the reaction and not the higher mass that is responsible for its low tunneling probability. Internal rotations of reactants and saddle points are taken explicitly into account in the molecular partition function.[4] At the transition state of the H-transfer isomerization reaction, several internal rotations of the reactant are hindered. Thus, the entropy of activation and hence the rate constant are strongly affected by changes in the vibrational partition

function. In particular, the constraints of alkyl rotations are found to be particularly effective in decreasing reactant entropy. The segmented reference Pitzer-Gwin method (SRPG) [5] is used to calculate the hindered rotor partition functions. A recently proposed generalized Arrhenius function is used to study the temperature dependence of the rate constants. [6] The activation energy calculated using this model function has the correct asymptotic behavior at absolute zero. In addition, this model is found to yield a lower fitting error as compared to the widely used model: $k = AT^n \exp(-E/RT)$. The H-transfer pre-exponential and activation energy vary strongly with temperature. This is a direct consequence of the increase tunneling transmission at temperatures below 500 K. Based on our results, a consistent model for the reasons for different knock behavior observed for n-heptane and isooctane is proposed.[7]

Key-words: Octane Rating, Autoignition, Transition-State Theory, Peroxy-radicals, Tunneling, conformation analysis, unimolecular reactions
Support: CENPES-Petrobrás

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Comunicação Oral 13|CO.13

Stochastic Chiral Symmetry Breaking Process

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Abstract: Chiral symmetry breaking is the process of unequal formation of enantiomers with different configuration [1]. This phenomenon is directed related to life, which is well exemplified by the absolute presence of L-amino acids in proteins and D-carbohydrates in sugars [2]. Many theoretical works have been developed in order to understand the reasons of that unexpected break. Most of these works were performed considering deterministic approaches and they concluded that chemical systems composed by autocatalytic and competition reactions, under small perturbations as initial enantiomeric excess, are able to reach asymmetric final states.

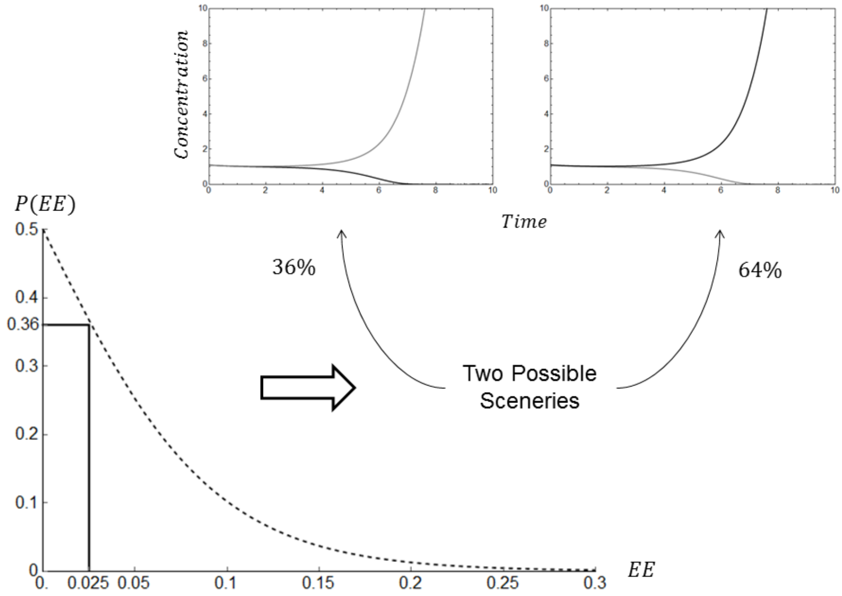

FIG. 1. Probability of the two possible final states, $P(EE)$, as function of Enantiomeric Excess (EE), where $EE = [L] - [D]$ and $\alpha = 21.78$. Considering initial excess $EE = 0.025$, the probability of enantiomer D dominates the final state is 36%, whereas the probability of the enantiomer L dominates the final state is 64%. The component L is represented by black line and D by gray line.

Moreover, following these results, the configuration of the final state is always the same of the chemical specie with initial enantiomeric excess *(EE)* [3-5]. However, in Nature the last consideration is not true [6]. The enantiomer with initial excess is probabilistic favored if statistical fluctuation is present. From that, stochastic approaches can offer a complete description of chiral symmetry breaking by taking into account the initial enantiomeric excess and the statistical fluctuation [7]. So, considering the Frank`s model we obtained the law $P(EE) = 1/(e^{\alpha EE} + 1)$, where the favoring probability (P) decreases exponentially with the initial enantiomeric deficiency (*ED*=-*EE*) mediated by statistical fluctuation, see FIG. 1. Concluding, this work breaks to the widespread idea that the configuration of the final asymmetric state is defined by the initial enantiomeric excess.

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Key-words: Homochiral states, statistical fluctuations, nonequilibrium conditions.

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Comunicação Oral 14|CO.14

Evaluation of Intermolecular Potentials for Carboplatin and Oxaliplatin in Aqueous Solution

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Abstract: Platinum complexes are widely studied due to their anticancer activity. The first step of mechanism of action is the hydrolysis reaction, which takes places in water environment. Aiming to study cisplatin hydrolysis in first place, two different intermolecular parameters sets were developed by Lopes[1,2]. Transferability for carboxylate analogous as Carboplatin and Oxaliplatin, however, were not tested at that time and are presented in this work. First of all, both molecules were optimized using 6-31g(d,p) basis set for the light atoms, while for Pt the LANL2DZ basis set were used. The atomic charge was calculated by ChelpG method. Geometries and charges were also evaluated in solution by means of IEFPCM. All quantum mechanical calculations were performed using Gaussian09 software and for Monte Carlo simulations, DICE[3] software was used. In MC simulations two LJ parameters were settled[1,2], so as two different charges (gas, IEFPCM), resulting in 4 combinations. A system was defined as a cubic box and filled with 1.10^3 molecules of solvent. The system was equilibrated in a 5.10^5steps on first stage and then followed by a simulation stage of 1.10^6 steps, both in a NPT ensemble. The **Fig. 1** shows snapshots of MC simulation with first LJ parameters developed for cisplatin[1].

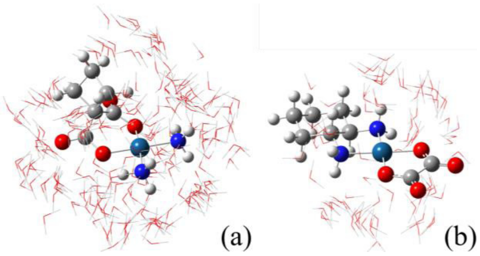

Figure 1 – MC Simulations snapshots for one uncorrelated configuration first solvation shell of Carboplatin**(a)** and Oxaliplatin**(b)**.

Water distribution around the Carboplatin is described by RDF of center of masses interactions in **Fig. 2**. **Fig. 3** shows the same data respective to Oxaliplatin.

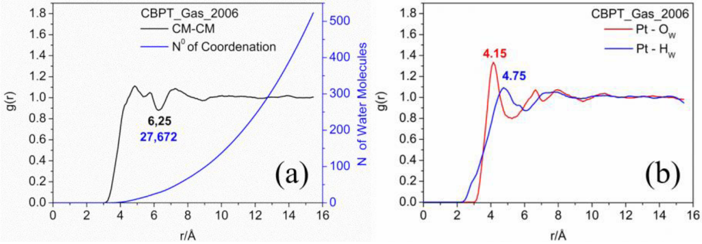

Figure 2 – RDFs of MC simulation of Carboplatin. **(a)** Center of mass pair correlation function. **(b)** RDFs Pt···O_W and Pt···H_W.

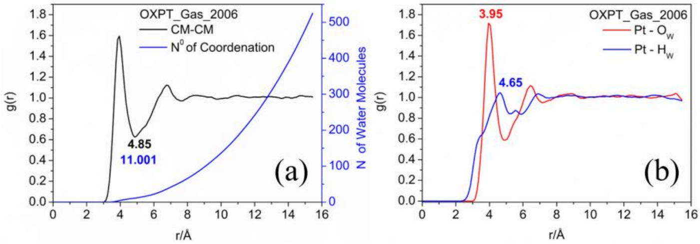

Figure 3 – RDFs of MC simulation of Oxaliplatin. **(a)** Center of mass pair correlation function. **(b)** RDFs Pt···O_W and Pt···H_W

Analysis g(r) solute-solvent center of masses (CM), **Fig. 2(a)**, one can see the solvation shell finishing at 6.2 Å, the coordination number (NC) calculated for this shell were 28 water molecules. To Oxaliplatin, **Fig. 3(a)**, was verified the first shell finishing at 4.85 Å and NC for the first shell were 11 water molecules which indicates that carboplatin is more stable in aqueous solution. The g(r) Pt···O_W and Pt···H_W pair correlation functions, to Carboplatin, **Fig. 2(b)**, two peaks centered at 4.15 and 4.75 Å, to Oxaliplatin, **Fig. 3(b),** two peaks centered at 3.95 and 4.65 Å, so the O_W in average stay closer than H_W, however, H_W shows closer distance to Pt atom, indicating a stronger interaction with it. To execute QM calculation, as reference to parametrization process, the structure of complex with one water interaction was extracted of the simulations. With the correlation processes 100 configurations was selected to Carboplatin in water and 140 configurations to Oxaliplatin. These configurations were used as base for Scan calculations. In **Fig. 4** shows one configuration of Scan calculations for carboplatin and the classical curve with the two parameters of literature[1,2] with different atomic charges. Classical curve has a significant difference, indicating that a new and specific set of parameters is necessary to Carboplatin. To make the parametrization all the 100 different Potential Energy curves will be used on a specific program, for fitting these values with the adjust a new set of LJ parameters will be defined. Carboplatin scan calculations are already finished; Oxaliplatin scan calculations are still running.

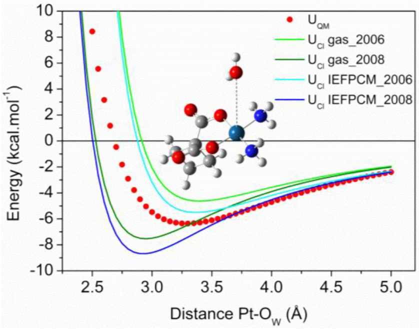

Figure 4 – QM and classical potential energy curves calculated for the Carboplatin-water interaction.

Key-words: Platinum compounds, Monte Carlo simulation, Parametrization.
Support: This work has been supported by Capes, FAPEMIG, CNPQ.

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A Sequential-QM/MM study of the electronic spectra of molecular switches

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In this work we present a theoretical study of a photochromic molecular switch. The target molecule is composed by two units of the dihydroazulene (DHA)/Vinylheptafulvene (VHF) covalently linked by a benzene ring. We use a sequential Quantum Mechanics/Molecular Mechanics (S-QMMM) [1] methodology to investigate the solvent effects on the electronic spectra of these molecules. Four isomers of this molecule are studied depending on the open/close forms of the DHA/VHF unit. Classical Monte Carlo simulations are performed to obtain the liquid structures of the solvent and then quantum mechanics calculations are used to obtain the electronic spectra at Density Functional Theory level. The solvent effect is considered both as an electrostatic embedding composed by the point charges of the solvent molecules (acetonitrile) as well as the closest explicit acetonitrile molecules. The shifts of the absorption band in relation to the isolated molecules are calculated and the inhomogeneous broadening are obtained in good agreement with the experiment [2].

This work has been supported by São Paulo Research Foundation (FAPESP).

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Title: A computational probe for the study of molecular electric fields

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Abstract: We propose the use of a fictitious isotopic probe, similar to the HD molecule, to investigate molecular environments, independently of the accurate representation of the electronic density and its gradient. HD has a small dipole moment due to its mass asymmetry. We explore the possibility of handling the finite nuclear masses with our code ISOTOPE [1, 2] in electronic calculations, to introduce a fictitious probe with a large and a small nuclear mass, and freeze the "internuclear" distance, so to create an appropriate the dipole probe.

As the probe interacts with a molecule, we subtract the Born-Oppenheimer energy from the total energy, so that the interaction energy is reduced to two classical terms: the interaction of the dipole moment with the molecular electric field and the polarization of the molecule by the dipole, the second being usually much smaller than the first. These two energy terms can be isolated either by rotating the dipole or by their behaviour with the distance.

The probe can evaluate, for example, the vector electric field created by a molecule in specific points. For this we just flip the dipole from its position of least energy (field direction), calculate the energy difference, and divide it by the dipole moment (field strength). Applications will be presented for H_2, H_2O clusters and other systems.

Key-words: Molecular electric field, isotopic probe
Support: This work has been supported by FAPEMIG and CNPq
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HDO reaction mechanism of fatty acid model over molybdenum carbide

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Abstract: Transition metal carbides could replace more expensive noble metal catalyst, such as platinum and palladium, in hydrogenation and other related reaction. Molybdenum carbide (Mo_2C) was recently used for a several reactions with Pt-like catalytic behavior, high activity and selectivity and CO and sulfur compounds poisoning resistance. Molybdenum carbide was used for hydrogenation, decomposition and hydrodeoxygenation (HDO) reactions [1-2].

It is not clear how HDO reaction over Mo_2C occurs in fatty acids formed by thermal cracking of triglycerides in bio-oil and biomass, because there are only a few microscopy experimental evidences of this system [1]. Thus, the aim of this work is to propose a reaction mechanism of acrylic acid, a molecular model for fatty acid over orthorhombic 001-Mo_2C surface. For this, DFT calculations were performed with Generalized Gradient Approximation (GGA) functional PBE with periodic boundary condition (PBC). The energy cutoff for plane wave basis set was 410 eV. Calculations were done in the projector augmented wave (PAW) approximation in Vienna Ab-Initio Simulation Package (VASP). All reactants, products, reaction intermediates, and main transition state structures were obtained until formation of propane.

Results are compatible with experimental ones. The first step of reaction is the hydrogen addition to CO group, and there is no formation of carbon monoxide and propanoic acid [1].

Key-words: molybdenum carbide, DFT, heterogeneous catalysis, HDO, fatty acid

Support: This work has been supported by CNPq.

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Investigation of 1,3-dipolar cycloaddition mechanism: which orbital is active?

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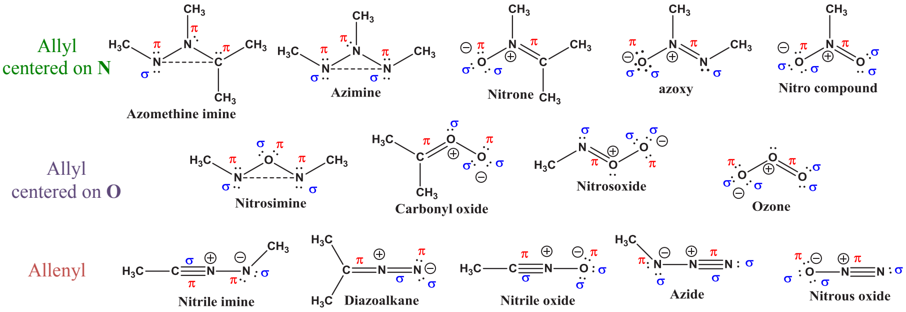
1,3-dipolar cycloaddition (1,3-DC) is a type of reaction that occurs between a 1,3-dipole and a dipolarophile yielding 5-membered heterocycles. It became very popular and important in organic synthesis due to its versatility, once there are many suitable types of 1,3-dipoles and dipolarophiles. Recently, much advance in asymmetric 1,3-DC has been accomplished, enhancing even more the interest in it [1]. Since its discovery in the late 19th century, studies focused on understanding the mechanism have been developed. Currently the proposal made by Huisgen is the most accepted by the scientific community: a concerted, often asynchronous, pericyclic cycloaddition [2], involving a symmetry-allowed $\pi^4s + \pi^2s$ six-electron transition state (TS) in which the extent of the reactivity of the 1,3-dipole is directly influenced by the frontier molecular orbitals (FMO). However, our observations indicate that not always a π-electron system is involved in the TS and σ non-bonded electrons can take relevant part in the reaction.

The aim of the present work is to correlate the orbital's symmetries of different 1,3-dipoles with bond formation to ethene, as well as the energetic profile. The dipoles were divided into 3 groups: allyl-type centered on N; allyl-type centered on O; and allenyl-type. Geometry optimizations and MO calculations of 1,3-dipoles were made with the post-Hartree-Fock MP2 method and the 6-31G(d) basis set. Natural bond orbital (NBO) analysis was employed to determine the structure with major contribution to the hybrid and to describe the symmetry of the FMO between σ (orbitals in the molecular plane) and π (out of plane orbitals). Initial complexes (IC), TS and products were optimized. Frequencies were calculated to characterize the nature of the stationary points. Kinetic and thermodynamic data are shown in **Scheme 1**.

For allyl cases, π orbitals are involved in bond formation. The FMO related with adequate symmetries are HOMO/LUMO, except for the dipoles with less favorable energetic profiles (nitro compound and ozone). In those cases, the LUMO shows the right π symmetry, while HOMO-2 and HOMO-3, less accessible electronic states, have the right symmetry. For azomethine imine, azimine and nitrosimine, π interaction between atoms 1 and 3 of the dipole was observed. Those dipoles also showed the lowest activation barriers and highest negative values of ΔE and ΔG, indicating a high instability of the starting material.

Surprisingly, for all allenyl dipoles, σ symmetry was observed in the bond formation. The only exception was the diazoalkane, which has no σ orbital available on the carbon atom of the dipole. This observation goes against what is argued in the literature: the σ non-bonded electrons instead of π, are directly involved in bond formation.



Type of dipole	Dipole	Kinetic data [kcal mol^{-1}]		Thermodynamic data [kcal mol^{-1}]		TS Symmetry	FMO
		DE‡	DG‡	DE	DG		
Allyl centered on "N"	Azomethine imine	2.19	6.25	-51.81	-42.37	π	HOMO/LUMO
	Azimine	8.42	13.12	-31.98	-23.26	π	HOMO/LUMO
	Nitrone	10.62	16.29	-30.82	-20.97	π	HOMO/LUMO
	Azoxy	17.93	22.55	-13.33	-5.65	π	HOMO/LUMO
	Nitro compound	26.60	32.37	24.95	32.38	π	HOMO-2/HOMO-3 /LUMO
Allyl centered on "O"	Nitrosimine	4.47	8.12	-47.42	-39.80	π	HOMO/LUMO
	Carbonyl-oxide	6.37	9.97	-63.55	-55.18	π	HOMO/LUMO
	Nitrosoxide	6.49	9.72	-45.54	-38.63	π	HOMO/LUMO
	Ozone	8.97	9.57	-45.13	-39.53	π	HOMO-2/HOMO-3 /LUMO
Allenyl	Nitrile-imine	0.83	3.70	-67.10	-57.60	σ	HOMO/LUMO
	Diazoalkane	4.63	8.82	-43.53	-34.60	π	HOMO/LUMO+1
	Nitrile-oxide	8.94	13.82	-42.98	-32.89	σ	HOMO/LUMO
	Azide	15.25	19.99	-23.25	-14.66	σ	HOMO-1/LUMO
	Nitrous-oxide	28.80	33.92	-0.10	7.14	σ	HOMO/HOMO-1 LUMO

Scheme 1. Kinetic and thermodynamic data for 1,3-DC of different dipoles at 298 K.

Key-words: 1,3-dipolar cycloaddition, 1,3-dipole, transition state, symmetry.
Support: This work has been supported by FAPERJ, CNPq and PPGQ-UFF.

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Comunicação Oral 20|CO.20

Estudo teórico das propriedades eletrônicas e estruturais do azul da prússia

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Introdução: As baterias recarregáveis são estudadas desde 1859 e são baseadas na capacidade de um metal oxidar e reduzir, de forma reversível, sendo um processo dependente de um cátodo e um ânodo. O interesse deste trabalho é estudar a reação que ocorre apenas no cátodo, o material escolhido foi o azul da prússia (PB), que em 1978 descobriu-se sua capacidade de oxidar e reduzir por meio dos átomos de ferro em estados de oxidação (II) e (III) e, desde então, trabalhos são desenvolvidos a partir do mesmo [1]. O PB possui fórmula geral $Fe^{III}_4[Fe^{II}(CN)_6]_3$ e sua estrutura está representada na Fig. 1.

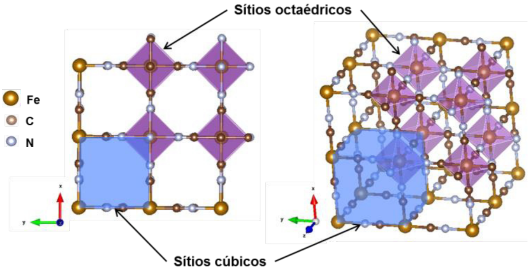

Fig. 1: Estrutura cúbica primitiva do PB com os respectivos sítios octaédricos e sub-cubos. [3]

Nos sub-cubos pretende-se incluir átomos de sódio. Baterias baseadas nesse metal são amplamente utilizadas em energia renovável, tais como eólica e solar [2]. O objetivo deste trabalho é modelar a parte catódica da bateria de forma a descrever eletronicamente e estruturalmente a reação que ocorre na mesma.

Utilizou-se o *software* Quantum Espresso para cálculos de otimização de geometria, análise vibracional e densidades de estados (DOS), aplicando o método DFT / ondas planas com o funcional PBE.

Resultados e Discussão: A estrutura inicial considerada foi retirada do COD, e a partir da mesma realizou-se os testes para a determinação da melhor malha de pontos K e melhor energia de corte nas ondas planas. Ambos os gráficos estão apresentados na Fig. 2 e percebe-se que a malha de pontos K 2x2x2 possui uma diferença de energia em relação à malha 4x4x4 próxima de 1 mRy e, portanto, pode ser utilizada. Analisando a energia de corte, a diferença de 1 mRy foi obtida quando usado 60 Ry na energia de corte. Assim os parâmetros de cálculos adotados foram: malha de pontos K 2x2x2 e energia de corte 60 Ry nas ondas planas.
Utilizando essas condições, os parâmetros de rede e a geometria do sólido foram otimizados e o DOS calculado (Fig. 3).

Como pode-se observar na Fig. 3, há um comportamento de um material condutor, no entanto de acordo com a literatura o azul da prússia é um semicondutor com band gap de 1,75eV [4] o que é possível afirmar que a metodologia utilizada não descreve o adequadamente esse gap de energia.

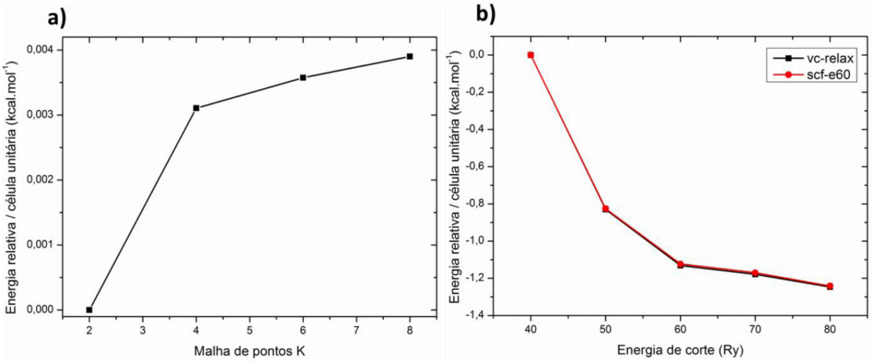

Fig. 2: Gráfico a) de malha de pontos K; b) de energia de corte

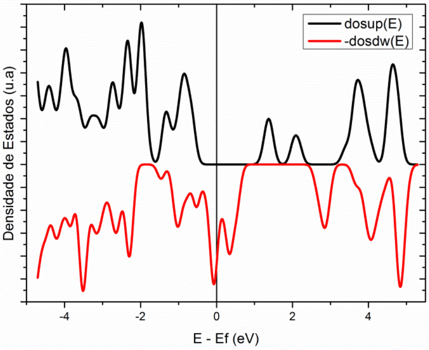

Fig. 3: Gráfico de densidade de estados referente ao azul da prússia

Na tentativa de resolver este problema, novos modelos, considerando moléculas de água completando o sítio de coordenação de átomos de ferro estão sendo tentados e os resultados serão apresentados. Como perspectivas futuras, espera-se que o novo modelo adotado seja condizente a um semicondutor para que com tais resultados seja possível iniciar a inclusão do átomo de sódio na estrutura de interesse e posteriormente realizar o estudo da reação catódica.

Agradecimentos: Os autores agradecem à FAPEMIG, CNPq, CAPES e ao INCT-Acqua.

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Solvatochromic reversal: is it really possible?

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Abstract: Several theoretical and experimental studies have shown that organic dyes may show solvatochromic reversal in the visible region with respect to the solvent polarity. This controversial non-monotonic behavior is still not well understood. This has been analyzed here using the merocyanine of Brooker as the working example. Sometimes the solvatochromic reversal is attributed to self-aggregation.[1] In spite of this, some works discard the aggregation origin and point to structural changes of resonance hybrid between the neutral (quinoid) and the zwitterionic (benzenoid) canonical structures.[2,3,4,5,6]. Also it is argued that the flow direction of the charge transfer in the merocyanine dye plays an important role.[7] A better understanding of the real possibility of solvatochromic reversal is both timely and relevant. Considering an electric field to model the solvent polarity a solvatochromic reversal is obtained with a single solute without aggregation. Thus the reversal behavior is obtained as the result of a competition between structural changes and intramolecular charge transfer. [8] This change of regime, held responsible for the solvatochromic reversal, affects in a similar way the ^{13}C magnetic shielding constant. [8]

Key-words: Solvatochromic reversal, Merocyanine of Brooker, Absorption spectrum, Solvent effect.

Support: This work has been supported by the Brazilian research agencies CNPq, CAPES, FAPESP, FAPEAL and the projects BioMol, INCT-FCx and NAP-FCx(USP).

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Computational strategies in finding greener CFC replacements

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Abstract: For many years CFCs were used in a vast range of applications, but the adverse environmental impact of their release into the atmosphere [1,2] has led to an international effort to replace them with acceptable alternatives. The Montreal Protocol [3] led to the phase out of CFCs in industrialized countries because of their elevated ozone depletion and global warming potentials (ODP and GWP). Development of suitable replacements with lower tropospheric lifetimes thus became a priority, with HCFCs firstly selected as alternatives on the basis of their higher reactivity towards OH radicals and similar physical chemical properties with CFCs. However, besides the nonzero ODP due to the presence of chlorine, these first-generation replacements were also found to maintain a high GWP. Development of environmentally friendly secondgeneration replacements for CFCs and HCFCs based on fluorocarbon derivatives thus became an urgent priority, with HFCs and PFCs appearing as a preferred choice. However, because of their high GWP, they were targeted by the Kyoto Protocol on climate change [4]. Consequently, renewed efforts to design and develop useful alternatives were put into practice, with hydrofluoroethers (HFEs) and hydrofluoropolyethers (HFPEs) appearing as promising third-generation replacements because of their zero ODP and even lower GWP. Finding such replacements has become increasingly important since October 2016, when nearly 200 countries adopted the Kigali Amendment to the Montreal Protocol, which phases-down production and use of HFCs and is considered by the United Nations Environment Programme (UNEP) "the single largest contribution the world has made towards keeping the global temperature rise well below 2 degrees Celsius, a target agreed at the Paris climate conference last year." [5]

Here, we will provide a detailed insight behind the computational strategies involved in designing and developing greener replacements according to Green Chemistry principle #10 (Design for Degradation), which states that "chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment". We will place empha-

sis in two critical steps of the process: 1) cost-effective calculation of the highly multidimensional potential energy surfaces [6-9] for the reactions between the targeted replacements and the OH radical and 2) prediction of the associated forward rate constants through multiconformer transition state theory [10], where we will analyze the key factors determining their values such as a) the magnitudes of quantum tunneling corrections and barrier heights and b) the pivotal interplay between the conformational sampling of reactants and transition states with their associated Boltzmann weight factors. These strategies will be contextualized while comparing two specific classes of the HFPEs family, a,w-dihydrofluoropolyethers (DH-FPEs) and the more recent and promising a,w-dialkoxyfluoropolyethers (DA-FPEs), in a pioneering bottom-up-like approach projected to unveil the fundamental theoretical aspects of the unestablished atmospheric chemistry of HFPEs and other compounds. Hopefully, the gained theoretical knowledge will serve as an important tool to boost the design and development of new greener CFC alternatives.

Key-words: atmospheric chemistry, conformational sampling, density functional theory, hydrofluoropolyethers, model chemistry

Support: This work has been supported by the AIAS-COFUND Marie Curie program, Grant/Award Number 609033

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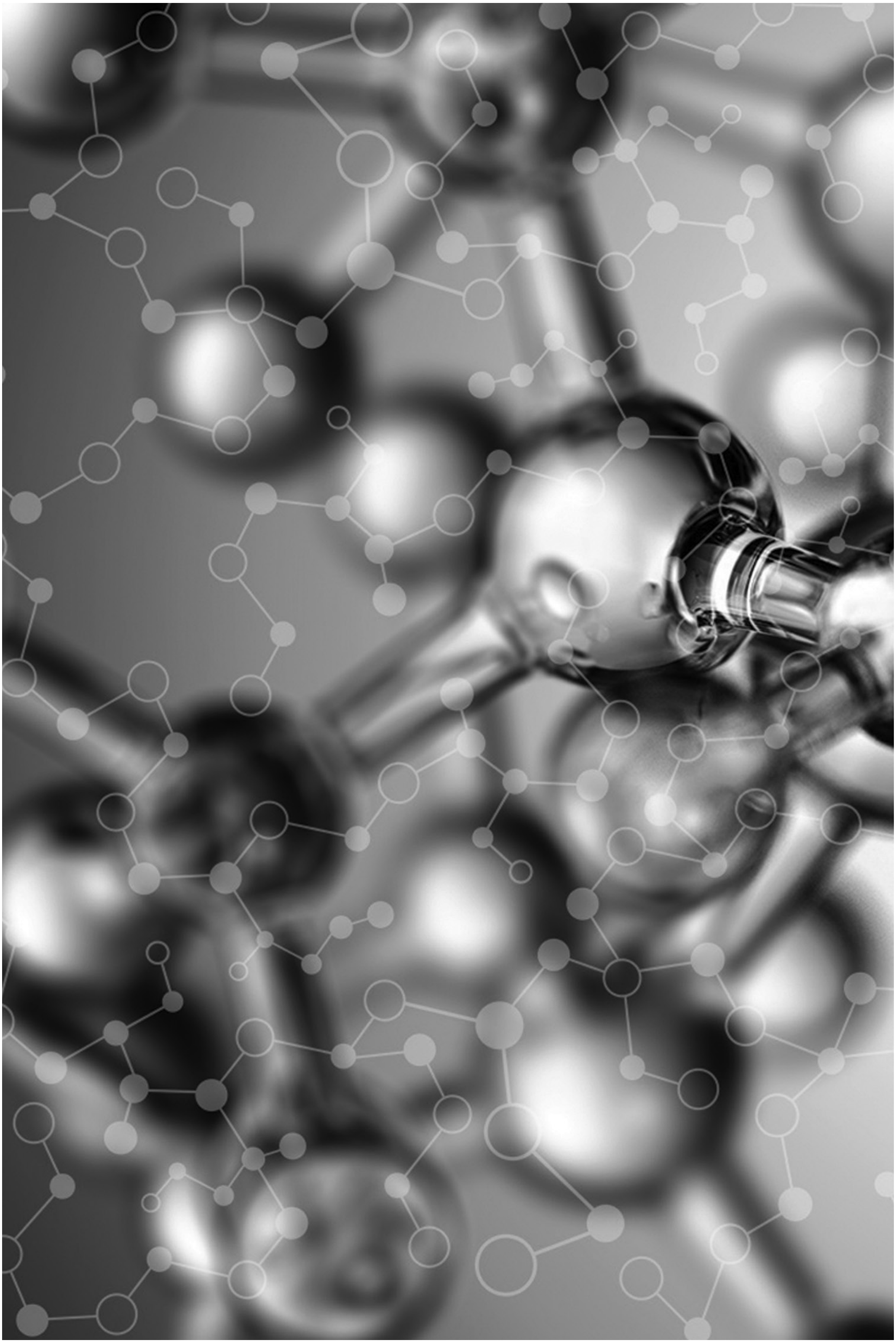

Lista dos Trabalhos apresentados na forma de Painel

Segunda-feira 13/11 das 20h às 22h

Painel	Apresentador	Título do trabalho
PN.001	Acassio Rocha Santos	Semiempirical ΔHbind calculations for interactions between the RTA and RTB subunits and ricin inhibitors
PN.004	Alberto dos Santos Marques	Theoretical study of the molecular and electronic structures of β-carbolines and MAO substrates using the theory of density functional
PN.005	Alejandro Lopez Castillo	Bond metamorphosis between coordinate (dative) and single covalent bonds: BN-ethylamine molecule
PN.006	Alessandra Albernaz	Kinetics of the O + HCN Reaction
PN.007	Alexandre B. Rocha	Total photoabsorption cross sections with square integrable basis set
PN.008	Alexandre Carvalho Bertoli	DFT approach of uranyl species originating from acid mine drainage and its interaction with ion exchange resin
PN.009	Alexandre Coelho Rodrigues Gomes	Aluminum-silicon nanoalloys: search for the most stable structures up to 13 atoms.
PN.010	Alexandre Costa	Azulene and naphthalene polymers
PN.011	Alexandre N. M. Carauta	Study of the interaction between resins and albite by MM/QM methods.
PN.012	Alexandre O. Ortolan	Anion Recognition by Heterocalixarenes: Understanding the Physical Nature of the Interaction
PN.013	Alexsander Carvalho Vendite	Theorical Studies of CO2 Capture in Structured and Humid Nanopores
PN.014	Aline de Oliveira	Structural and electronic properties of MOF-74
PN.015	Alyson Celson M. de Oliveira	Hydrogen Absorption/Desorption in Palladium and Metal Hydrides
PN.016	Amanda F. Gouveia	Analysis of the interaction of water with TiO2 nanotubes
PN.017	Amanda Ziviani de Oliveira	Segmented all-electron Gaussian basis sets of double and triple zeta qualities for Fr, Ra, and Ac
PN.018	Amauri Francisco da Silva	Theoretical and experimental study of lanthanide ion complexes: Spectroscopy and chemical bond analysis
PN.019	Ana Claudia P.S. CRUZ	The spherical-harmonics representation for the interaction between H2O-HX molecules, with X = H, F, Cl and Br atoms.
PN.020	Ana Débora Porto Silveira	Aluminium-Silicon nanoalloys: structures and stabilities
PN.021	Ana Paula de Lima Batista	Computational Investigation of Ligand Influence on the Insertion of Allene into Cu-B (Boryl) Bond
PN.023	Anderson José Lopes Catão	On the Degradation Pathway of Glyphosate and Glycine
PN.024	André F. de Moura	Thermodynamic and Kinetic Study of Germanium Crystal Growth by Computer Simulations
PN.025	André Pacheco de Oliveira	Electron-Molecule Collision Calculations Based On The First Born Approximation and EOM-CCSD
PN.026	Andresa Messias	Polymorphism of Lipid A bilayers in presence of Al3+ at different ionic concentrations of NaCl and AlCl3
PN.027	Angelita Nepel	Substituent effect on 1JCH in benzaldehyde derivatives
PN.028	Antônio Carlos Amaro de Faria Jr	A critical review of some underlying concepts involving both Arrhenius equation and the transition state theory
PN.029	Antônio Cláudio Pinheiro Barbosa	Adsorbents for Carbon Capture: A Quantum-chemical Investigation of the Adsorption of CO2 and N2 on Pure-silica Chabazite
PN.030	Antonio João da Silva Filho	Mesoionic Heterocyclics: Theoretical Study of the Structural Stability of Oxazoles (C3H3NO-R) and Thiazole (C3H3NS-R), with R = O and S

Painel	Apresentador	Título do trabalho
PN.031	Antonio Ricardo Belinassi	A theoretical exploration on the 1[H, Se, I] potential energy surface: energetics, structures, IR spectra, and heats of formation
PN.032	Arnaldo F. Silva	FFLUX: Adding Dispersion to a Quantum Mechanical Force-Field through Machine Learning and Electronic Correlation
PN.035	Augusto Batagin-Neto	Electronic structure calculations for the study of polyaniline-based chemical sensors
PN.037	Bárbara Maria T. Costa Peluzo	Theoretical Study of the Structure and Reactions of Uranium Fluorides
PN.038	Brenda S. D. Frachoni	Computational study of zinc phthalocyanine mobility in a phospholipid bilayer containing cholesterol
PN.039	Bruna Luana Marcial	Theoretical Calculation of pKa Values of Amidines in Aqueous Solution Using an Implicity Solvation Model
PN.040	Bruna Thalita de Lima Pereira	Exploring EPR Parameters of 99Tc Complexes for Designing new MRI Probes: Coordination Environment, Solvent, and Thermal Effects on the Spectroscopic Properties
PN.041	Bruno Edson Santana de Freitas	Quasiclassical Trajectory Study of the Kinetics and Dynamics of the O + HBr Reaction
PN.042	Bruno Henrique de M. Mendes	Influence of Molecular Dynamics in the Docking of Dialkylphosphorylhydrazones in Leishmania braziliensis Hexokinase
PN.043	Bruno Moraes Servilha	A DFT Study on the non-covalent interaction control on enantioselective Heck-Matsuda Reactions
PN.044	Bruno Vilella de Faria	Structural and electronic modeling of Cuprum Oxide
PN.045	Caio César Ferreira Florindo	On the description of the orientation state in mesophase pitch-based carbon fibers
PN.046	Calisa Carolina da S. D. de Oliveira	Aflatoxin B1: An Inactivation Proposal.
PN.047	Lilian T. F. M. Camargo	Structure-Activity Relationship of Tacrine and Analogous Against Alzheimer´s disease
PN.048	Maximiliano Segala	DFT models for first step of the Chemoselective Hydrogenation of Substituted Aldehydes Using Silver Nanoparticles as Catalyst
PN.049	Camila M. B. Machado	Nugget Hydrocarbons CnHn with Six Four-membered Rings and their growth as 3D-Scaffolds
PN.050	Camila Rocha de Andrade Neves	Estudo DFT da organização estrutural de hidratos formados pelos gases, H2S, CH4, N2, CO2, C2H6 e C3H8

Segunda-feira 13/11 das 20h às 22h

Painel	Apresentador	Título do trabalho
PN.051	Carla Grijó Fonseca	DFT investigation of Montmorillonite edge surfaces stability and their acid-basic properties in Biodiesel production context
PN.052	Carlos Cruz	Amino acid polymorphisms in the fibronectin-binding repeats affect the fibronectin bond strength
PN.053	Carlos Eduardo da Silva	Theoretical investigation of the metallic bismuth growth on the semiconductor surfaces by electron irradiation
PN.055	Chiara Valsecchi	Imidazolium/imidazolate pi-pi stacked ions pair simulations in chloroform
PN.056	Cleiton Maciel	Polarization of Methylene Blue in aqueous solutions: impact over the Hydrogen Bonds
PN.057	Cleuton de Souza Silva	Accurate pKa Determination of Alcohols with BMK And G3(MP2)//B3-CEP
PN.059	Daiana T. Mancini	Excited-State Proton Transfer Can Tune the Color of Protein Fluorescent Markers
PN.060	Daniel Angelo Polisel	Modeling nmr parameters of oximes in water and ionic liquids – implications of solvation shell structure
PN.062	Daniel Garcez S. Quattrociocchi	DFT study of the interaction between neutral ligands and metal cations (M = Ca2+, Mg2+, Li+, Ni2+, Pb2+): Taking an insight into the interaction strength
PN.063	Daniel Mungo Brasil	Investigação teórica do complexo de monocarboxilato de praseodímio (III)
PN.064	Danillo Valverde	Theoretical Investigation of the Emission Spectra and Stokes Shift of Modified Canonical Nucleobases in Gas Phase, 1,4-dioxane and Water
PN.065	David Wilian Oliveira de Sousa	One-electron bonds from the quantum interference perspective
PN.066	Dayse Silva	Identification of flavonoid with potential for inhibitor Enoyl-ACP Reductase in Plasmodium falciparum by hierarquical virtual screening
PN.067	Denys Ewerton da Silva Santos	SuAVE: a computational tool for the assessment of curved surfaces
PN.068	Diego José Raposo da Silva	Conformational Analysis of 1,2-Dichloroethane in Implicit Solvent (SMD) through Solvation Thermodynamics
PN.069	Diego Nascimento de Jesus	Conformational Analysis and pKa Calculations of Glycine in Aqueous Solution
PN.071	Douglas de Souza Gonçalves	Molecular Signature of Atmospheric Organic Aerosols
PN.073	Éderson D'M. Costa	Improved calculations of the sensitivity density between phase shift and potential energy function
PN.075	Eduardo Campos Vaz	Can molecular hydrogen reduce cytotoxic hydroxyl radical reactivity in aqueous environment? Combined ab-initio molecular dynamics and electronic structure investigation.
PN.076	Eduardo da Conceição	NMR spectra interpretation of diastereomeric MacMillan imidazolidinones by DFT calculation of indirect spin-spin coupling constants
PN.077	Eduardo Dias Vicentini	Potential energy surface and kinetics of reaction between CO2 and Iron
PN.078	Egon Campos dos Santos	Stability, structure, and electronic properties of the pyrite/arsenopyrite solid-solid interface- A DFT study
PN.079	Elaine Cesar do C. A. de Souza	Theoretical Investigation of the Ozonolysis Mechanism of Monoterpenes: Reaction Path and Rate Coefficients

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PN.080	Elder Taciano Romão da Silva	Bistability and oscillation raised by recombination between dimers
PN.081	Eliziane S. Santos	Molecular Wires Formed from Polypyrroles and Beta-Cyclodextrins: A Theoretical Investigation.
PN.082	Ellen V. Dalessandro	Automated Fast Computational Screening of Solvents for Extraction of Organic Chemicals from Aqueous Solution Using SMD Solvation Free Energies
PN.083	Érica Cristina Moreno Nascimento	Multivariate Analysis and Fuzzy Analysis of Acetylcholinesterase Inhibitors: Correlating Inhibition Mechanism and Ligands Properties with Pharmacophoric Profile.
PN.084	Erica T. Prates	Computational Study of Enzymatic Lignin beta-O-4 cleavage
PN.085	Erick G. França	Computational and experimental study of cholesterol influence on the activity of liposomal zinc phthalocyanine
PN.086	Ericson H. N. S. Thaines	A structural study of Ni/NiO interface materials by Rietveld Refinement and DFT calculations
PN.087	Evanildo Lacerda Jr	Theoretical Study of the Xenon NMR Chemical Shift in Supercritical Condition: many-body, electron-correlation and relativistic effects
PN.088	Ewerton Ferreira da Silva Souza	Theoretical Study of the Reactivity of C2 - C5 Alkenes Towards Ozone
PN.089	Igor B. Ferreira	All-electron Gaussian basis sets of double zeta quality for the actinides
PN.090	Fabio Luiz Paranhos Costa	Protocol for Calculating 13C NMR Chemical Shifts of Flexible Organic Molecules
PN.091	Fabrício Bracht	Molecular dynamics of a highly secreted α-L-arabinofuranosidase (GH62) from Aspergillus nidulans grown on sugarcane bagasse
PN.092	Fátima M.P. de Rezende	Constante de acoplamento de longo alcance 4J em cicloexanona e cicloexationa 2-flúor-substituídas
PN.093	Felipe Curtolo	Static correlation effects in flavin mediated hydride transfer
PN.094	Felipe Fantuzzi	Moving Protons with Pendant Amines in Niobium-Based Electrocatalysts
PN.095	Felipe O. Ventura	Determinação do comprimento de espalhamento para colisões H-H, H-D, H-T, D-D, D-T, T-T nos estados eletrônicos (X1Σ+) e (b3Σ+) usando um método variacional
PN.096	Felipe S. S. Schneider	A theoretical investigation on the synthesis of aromatic polyimides
PN.097	Felippe Mariano Colombari	Electronic Circular Dichroism of Gamma-valerolactone dimers extracted from Monte Carlo liquid phase simulation.
PN.099	Fernando da Silva	Molecular dynamics and electronic properties of pyridinium-iodide charge-transfer complexes in acetonitrile solution
PN.100	Fernando Marques Lisboa	Uso da Expansão de Redlich-Kister e do Modelo SMD para Prever Equilíbrio de Fases em Misturas Binárias
PN.101	Fernando R. Ornellas	Thermodynamic stable diatomic dications: the case of SrO2+
PN.102	Fernando Steffler	Keggin polyoxometalates: An Electronic structure perspective based on TDDFT
PN.103	Filipe Belarmino	Thiophenol: Photoinduced Hydrogen Migration

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Painel	Apresentador	Título do trabalho
PN.104	Filipe Camargo D. Alves Lima	Adsorption of Benzoic Acid on Carbonate Surfaces
PN.105	Flávio M.B. Oliveira	Modelos de Nanoestruturas baseadas em Geometrias de Projeções Geométricas do R7
PN.106	Francisco Antonio Martins	Theoretical study on the anomeric, exo-anomeric and reverse anomeric
PN.107	Francisco B. C. Machado	The singlet excited states of N-acenes (N=0-5): A CASSCF/CASPT2 study of the La and Lb bands
PN.108	Frederico Pontes	Structural transition in Lipid A bilayers driven by physical and chemical factors.
PN.109	Frederico Teixeira Silva	New genetic algorithm paradigms applied to atomic and molecular clusters studies
PN.110	Gabriel Aguiar de Souza	A DFT Benchmark Study on Ionic Liquids
PN.111	Gabriel Ernesto Jara	Catalytic mechanism of conversion of ATP to cyclic-AMP catalyzed by the Edema Factor of Anthrax: a QM/MM study
PN.112	Gabriel Freire Sanzovo Fernandes	Electronic structure and thermochemistry of Sin clusters(n=2-11)
PN.113	Gabriel Heerdt	High Performance Collision Cross Section Calculation - HPCCS
PN.114	Gabriel Jordy Cascardo Araujo	Estudo das Propriedades Físico-Químicas do Líquido Iônico 1-Butil-3-Metil-Imidazólio Bis(Trifluormetanosulfonil)Imida ([BMIm][Tf2N]) Puro e em Solução Aquosa
PN.115	Gabriel L S Rodrigues	Theoretically understanding the exchange of NO and the nature of the Ru-NO bond in ruthenium-nitrosyl metallic complexes.
PN.116	Gabriel Modernell Zanotto	Charge Transfer descriptors application: TD-DFT protocol for analysis on DMABN transitions and push-pull effect on D-π-A dyes.
PN.117	Gabriel S. S. Brites	Conformational Analysis of Alanine, its Radical Cation and Anion
PN.119	Gabriela Volpini Soffiati	Molecular Modelling of Polyol Electro-Oxidation Reaction on Pt Surfaces
PN.120	Gerd Bruno Rocha	Aplicação do método RM1 em complexos de Eu3+, Gd3+ e Tb3+ contendo ligantes com anéis Porfirina
PN.121	Gerlane Bezerra da Silva	Assessing Dunning's basis set along with the G3(MP2)//B3 theory for ionization energies
PN.123	Gisele Franco de Castro	Calculations of the electronic state TICT of the diphenyl polyenes P,P'- and O,O'- di-substituted using the functional density theory
PN.124	Giseli Maria Moreira	Effect of microsolvation in low-energy positron collisions with formaldehyde-water complexes.
PN.125	Giuliano de Mesquita Cordeiro	Estudo da reação entre wustita e água durante o processo de loop químico utilizando a teoria do funcional de densidade
PN.126	Gladson de Souza Machado	Kinetic Analysis of Acetone Combustion Reactions
PN.127	Glauco Favilla Bauerfeldt	Calculations of Rate Coefficients for the Uni and Bimolecular Reactions of Dimethyl Ether and Improvement of its Combustion Mechanism
PN.128	Glauco Fonseca Silva	Estudo de Adsorção de Água em Wustita para Aplicação Catalítica na Produção de H2 Combustível
PN.129	Guedmiller Souza de Oliveira	Design of immunosensors assisted by computer simulations

Painel	Apresentador	Título do trabalho
PN.130	Guilherme Arantes Canella	Entanglement in disordered systems via DFT calculations
PN.131	Guilherme Augusto Batista Soares	Competition for βCD cavity on inclusion complex of antihypertensive drugs and Excipient
PN.133	Guilherme de S. Tavares de Morais	Polycarbonitrile: a DFT investigation of structural stability
PN.134	Guilherme Luiz Chinini	CBS-QB3 Composite Method Along with Pseudopotential for the Calculation of Standard Enthalpy of Formation
PN.135	Gustavo Gomes de Sousa	Estudo Teórico do Mecanismo e da Cinética da Reação Atmosférica HF + OH→H2O + F
PN.137	Gustavo Juliani Costa	Fully Anharmonic Resonance Raman Spectra of Diatomic Systems Through Variation Quantum Monte Carlo Simulations
PN.139	Henrique de Oliveira Euclides	Reaction Rate of H2CO = H2+CO
PN.140	Henrique Musseli Cezar	Implementation of Configurational Bias Monte Carlo Method to Sample Flexible Solute in Solvent Media
PN.141	Hugo de Oliveira Batael	Ground State Energy for Confined Hydrogen Molecule
PN.142	Hugo Gontijo Machado	Homochiral salt of S-Fluoxetine Oxalate: Theoretical Insights on Preferential Crystallization of RS-Fluoxetine Antidepreessant
PN.143	Igo Tôrres Lima	Molecular Modeling of Azo-Enaminone Derivatives in Solvent Medium: Investigation of the Nonlinear Optical Properties
PN.144	Igor Araujo Lins	Metastability of the low-lying electronic states of CBr2+: A CASSCF/MRCI Study
PN.145	Igor Barden Grillo	Study of Local Reactivity of Ricin Toxic A chain Based on Conceptual Density Functional Theory
PN.146	Isabella D. M. S. Rosado	Theoretical and Computational Description of Equivalent Chemical Bonds
PN.147	Isadora Aurora Guerra	Ensemble docking studies of interaction between pesticides and acetylcholinesterase of mosquito and homo sapiens
PN.148	Italo Curvelo Anjos	Evaluation of α-lapchones Reduction Sites through DFT and QTAIM calculations
PN.149	Itamar Borges Jr.	Correlation between molecular eletronic structure, sensitivy to explosion and chemical stability of energetic materials: nitramines
PN.150	Iuri N. Soares	A comparative DFT study on antioxidant-related properties of myricetin
PN.151	João Carlos O. Guerra	Estudo comparativo de diferentes métodos de ensemble generalizado em simulações computacionais de polímeros de pequenos comprimentos
PN.153	Janay Stefamy Carneiro Araújo	Molecular dynamics simulations of Plasmodium falciparum Fe-superoxide dismutase
PN.154	Javier Oller	Global and local reactivity descriptors based on quadratic and linear energy models in alpha, beta-unsaturated systems
PN.155	João Gabriel Farias Romeu	Electronic structure and spectroscopic properties of the scandium monosulfide, ScS
PN.157	João Paulo Ataide Martins	A new approach for sampling descriptors in 4D-QSAR methodology using computational geometry
PN.158	João Paulo Cascudo Rodrigues	Vibrational and Electronic Properties of Carbon Dioxide Absorbed in Graphene Nanosheets

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Painel	**Apresentador**	**Título do trabalho**
PN.161	João Vitor Afonso Borges	Simulation of the AHAS-imazaquin system by Molecular Dynamics to design an enzyme-based AFM nanobiosensor
PN.162	Jorge Leonardo O. Santos	Theoretical Study of ion mobility of isomers in different drift gases
PN.163	José Diogo L. Dutra	Development of Models for the Calculation of Collision Cross Section
PN.164	Josefredo R. Pliego Jr.	Cluster Expansion Method for Solvation Free Energy Calculations: Theoretical Development

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Painel	Apresentador	Título do trabalho
PN.165	Josene Maria Toldo	New insights on Photo-Fries rearrangement: a model for photodegradation of carbamate pesticides
PN.166	Josimar Fernando da Silva	Different ways to compute the ground state of electronic energy of ion hydrogen molecule confined via variational method.
PN.167	Joyce Karoline Daré	Conformational Dependence of the Hydrophobicity of Fluorine-containing Agrochemicals
PN.168	Juliana Cecília de Carvalho Gallo	Hierarchical virtual screening for identification of Leishmania braziliensis N-myristoyltraferase inhibitors
PN.169	Juliana O. Mendes	Azoles molecules as potential corrosion inhibitors: A DFT study.
PN.170	Júlio C. S. da Silva	Olefins Hydroformylation Reaction Catalyzed by Rhodium Complexes of the Type HRh(PÇP)(CO)2: A DFT and ab initio Study
PN.171	Julio Cesar Guedes Correia	Pi-Pi Stacking Interactions between Asphaltene and Aggregation Inhibitors: A Study by Density Functional Theory.
PN.172	Kahlil Schwanka Salome	The Perlin Effect in terms of molecular orbitals
PN.173	Kelly Fernandes Pessôa	Study of the interaction between resins and albite by MM/QM methods.
PN.174	Larissa de Mattos Oliveira	Pharmacophore and docking-based hierarchical virtual screening to identify Leishmania major farnesyl pyrophosphate synthase inhibitors
PN.175	Larissa F. VasconceLos	Computational study of glycerol/guanidine associative system for CO2 capture
PN.176	Larissa Lavorato Lima	Structural and thermodynamic analysis of the compound {[Zn(2,5-pdc)(H2O)2].H2O}n and its dehydrated and delaminated forms.
PN.177	Laurent Emmanuel Dardenne	DockThor 2.0: a Free Web Server for Protein-Ligand Virtual Screening
PN.178	Leandro Rezende Franco	Photophysics and Thermoquemistry of 1-8- Naphthalimide in solvents
PN.179	Leonardo A. De Souza	DFT calculations of spectroscopic properties of drug delivery systems formed by oxidized carbon nanostructures
PN.180	Leonardo Baptista	Estudo da Dissociação de Espécies Aniônicas e Catiônicas do Metano e Sua relação com a Irradiação de Gelos Astrofísicos
PN.182	Leonardo dos Anjos Cunha	Efficient molecular design of nanoporus mebranes: the role of intermolecular interactions
PN.183	Leonardo Gois Lascane	Electronic structure calculations for the study of polyfuran-based chemical sensors: evaluation of local reactivities
PN.184	Leonardo Henrique de Morais	Molecular and Electronic Structure Elucidation of a New Class of Cannabisin. An Experimental and Theoretical study
PN.185	Leonardo José Duarte	Quantum Theory of Atoms in Molecules charge-charge transfer-dipolar polarization classification of infrared intensities
PN.186	Letícia C. Assis	Theoretical studies of PP5-Mg2+ with potential inhibitors and H304A mutation
PN.187	Letícia Maia Prates	Effect of the Metal–Support Interaction on the Adsorption of NO on Pd4/γ-Al2O3
PN.188	Letícia Rodrigues Chaparro Corrêa	Comparative study of the photochemical properties of silole, thiophene and furan

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Painel	Apresentador	Título do trabalho
PN.189	Lisandra P. dos Santos	Influência da oxigenação da cadeia carbônica na energia de dissociação C-C
PN.190	Ljiljana Stojanovic	Nonadiabatic dynamics of cycloparaphenylenes
PN.191	Lourival Rodrigues de Sousa Neto	validation of the chitin parameterization in the OPLS force field
PN.192	Lucas C. Ducati	NMR J-Coupling Constants of Tl−Pt Bonded Metal Complexes in Aqueous Solution: Ab Initio Molecular Dynamics and Localized Orbital Analysis
PN.193	Lucas Modesto-Costa	On the electronic origin of the high-efficiency of the PTB series donor polymers for organic photovoltaics
PN.194	Lucas N. Trentin	A Computational Study of The Wetting of Nanocrystalline Cellulose
PN.195	Lucas Pereira Mendes	Structural, electronic, elastic and vibrational properties of zinc sulfide nanotubes: a DFT approach
PN.196	Luciano N. Vidal	Fully Anharmonic Resonance Raman Spectrum of Diatomics Through Vibrational CI Calculations
PN.197	Luciano Ribeiro	Spectroscopic Analysis of the C70_2 Dimer on Different Relative Configurations
PN.198	Luciano T. Costa	Modelling the Polymer Electrolyte/Li-Metal Interface by Molecular Dynamics simulations
PN.199	Luis Maurício da Silva Soares	Molecular modeling in the inhibition of M. tuberculosis enzymes
PN.201	Luiz Felipe Guain Teixeira	Density Functional Calibration for Indirect Spin-Spin Coupling Constant Calculations
PN.202	Luiz Fernando de Araujo Ferrão	Copper Acetylacetonate Intermolecular Interactions with Conjugated Polymers
PN.203	Luiz Henrique Medeiros da Costa	The Selectivity of the O-/N-Nitroso Aldol Reactions
PN.204	Lyzette G. Moraes de Moura	Theoretical-experimental study of asphaltene properties
PN.205	Felipe A. La Porta	First-principle calculations and ab initio direct dynamics study on the molecular mechanism of the 1,3-dipolar cycloaddition reactions
PN.206	Maiara Oliveira Passos	Estados eletrônicos de mais baixa energia da molécula CI2+
PN.207	Maíra dos Santos Pires	Theoretical study of the methane decomposition catalyzed
PN.208	Malucia M. Soeiro	DFT Calculations of Spectroscopic Properties for Zn (II) - Kaempferol Complexes
PN.210	Marcelo A. P. Pontes	Thermochemistry calculations of farnesane biofuel
PN.211	Marcelo Andrade Chagas	Cd(II)-Cd(II) Metal-Substitued Phosphotriesterase: Theoretical Analysis of A New Enzymatic Mechanisms to Paraoxon Phosphate Triester Hydrolysis
PN.213	Marcelo Mota Reginato	Molecular orbital analysis of the halogen dependence of nuclear magnetic shielding in PX3 and POX3 (X = F, Cl, Br, I)
PN.214	Marcia K. D. Belarmino	Gas Storage in MOFs: A Friendly Strategy to Predict the Ability of Molecule Insertion
PN.215	Márcio Oliveira Alves	Explicitly Correlated Calculations in the CNO System
PN.216	Marco Antonio de Mecenas Filho	Computational studies of potential inhibitors to the protein aurora b kinase
PN.217	Marco Aurélio Euflauzino Maria	Molecular dynamic study on graphene-based chemical sensors: adsorption studies and substrate effect
PN.218	Marcos Paulo de Oliveira	Estados Excitados e Fotoquímica da Desoxiribose

Painel	Apresentador	Título do trabalho
PN.220	Marcus Vinícius Juliaci Rocha	Structure and bonding in triorganotin halides complexes: a perspective by Energy Decomposition Analysis
PN.221	Maria Carolina N. Barbosa Muniz	Sudden Changes in Atomistic Mechanisms for the Cl- + CH3I SN2 Reaction with Increasing Collision Energy
PN.222	Mariana Toretti Caldeira	Development of a Composite Method Based Exclusively on The Density Functional Theory
PN.223	Marina Pelegrini	Reactions of hypergolic pair N2H4 and NO2
PN.224	Marina Pinheiro Dourado	Estudo de Propriedade-Estrutura para Cadeias Orgânicas Conjugadas Ramificadas via Análise de Componente Principal
PN.225	Marina Purri Brant Godinho	Zn(II)-Zn(II) and Cd(II)-Cd(II) Metal-Substituted Phosphotriesterase (pdPTE): Theoretical Analysis of the Structure the Active Site and Interaction with Phosphate Triester Paraoxon
PN.226	Mateus A. M. Paiva	Theoretical calculations on the OSiS molecule and its interstellar relevance
PN.227	Mateus Aquino Gonçalves	Comparing structure and dynamics of solvation of different iron oxide phases for enhanced mr imaging
PN.229	Mateus R. Lage	DFT study of the self-aggregation of asphaltene model compounds
PN.230	Mateus Xavier Silva	Multi-Electronic-State Approach of Tetranitrogen
PN.231	Mateus Zanotto	A study of different oxidation states of Zinc(II)-Phthalocyanines
PN.232	Matheus J. Lazarotto	Computer Simulations to Study the Efficiency of Solvents in the Synthesis of Benzilidenethiazolidinedione in Micro-reactor
PN.233	Matheus Ruas Miranda Signorelli	Study of new Azo Dyes for DSSCs using DFT
PN.234	Mauricio A. Vega-Teijido	A study on the reaction of hydroselenyl (HSe.) and selenenic (HSeO.) radicals
PN.236	Mauricio D. Coutinho-Neto	Large amplitude motion affects cleavage reaction barrier in HIV protease
PN.237	Maurício P. Franco	A DFT study on Mor-DalPhos ligand in ammonia monoarylation by Buchwald-Hartwig amination
PN.238	Max Nunes Pereira	Estudo teórico de aglomerados moleculares de interesse da indústria petroquímica
PN.239	Michele A. Salvador	Computational study of photosensitizing IR780 and its interaction with transition metals cations
PN.240	Michell O. Almeida	Study of Molecular Dynamics, NBO and QTAIM for inhibitors of ALK-5
PN.241	Milene Aparecida R. de Oliveira	Theoretical study of cis and trans structures [Zn(dmso)2 (H2O) (fum)], where dmso = dimethylsulfoxide fum = fumaric acid
PN.242	Milton Massumi Fujimoto	Averaged electron collision cross sections for thermal mixtures of beta-Alanine conformers in the gas phase
PN.243	Mirele Bastos Pinto	Theoretical Study of Cleavage Surfaces and Water Adsorption on B-Nb2O5
PN.244	Mirian Chaves Costa Silva	The use of ensemble docking to evaluate the inhibition of the dDat enzyme by the sugar compared with cocaine
PN.245	Munique Rodrigues Pereira	Abordagem por métodos de estrutura eletrônica no processo de ESIPT em derivados de 2-(2'-hidroxifenil)benzazóis
PN.246	Naiara Letícia Marana	Theoretical analysis of IGP-ZnO and IGP-ZnO nanotubes

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Painel	Apresentador	Título do trabalho
PN.247	Natália Aparecida Rocha Pinto	Computational investigation of the OH initiated oxidation of C6 unsaturated alcohols
PN.248	Natalie Mounteer Colodette	Development of an empirical binding free energy model for phosphatidylinositol 4-kinase inhibitors.
PN.249	Natieli Alves da Silva	Analysis of charge, charge flux and dipole flux contributions for infrared intensities of the OH stretching mode in carboxylic acid dimers
PN.251	Nelson H. Morgon	Brønsted Acid Catalyzed O- to N-Alkyl Migratory Rearrangement in Pyridine
PN.252	Neubi F. Xavier Junior	Computational Study of Glycine and its Radical Cation and Contributions to the Interstellar Chemistry
PN.253	Orlando Roberto Neto	Variational Transition State Theory Calculations of the Hydrogen Abstraction Reactions O (3P) + cis-CH3OCHO: Effects of Multidimensional Tunneling on the Rate constants and Branching Ratio
PN.254	Osmair Vital de Oliveira	Theoretical study of hydration free energy of the C60, Li+@C60, Na+@C60 and K+@C60
PN.255	Patricia R. P. Barreto	Theoretical Study of HCO + O Reactions
PN.256	Paúl Pozo	Activation of polar bonds by electric fields: An Electron Localization Perspective
PN.257	Paula do Nascimento Goulart	Theoretical Investigation of the Oxidation Reactions of Primary Alcohols to Aldehydes using o-iodoxybenzoic acid Reagent.
PN.258	Paula Homem-de-Mello	Excited-State Intramolecular Proton Transfer in triphenylimidazolic compounds
PN.260	Paulo Henrique Ribeiro Amaral	Core-valence stockholder AIM analysis and its connection to non-adiabatic effects in small molecules
PN.261	Paulo Roberto G. Gonçalves Jr.	DFT study of water adsorption on (001) Mn3O4 surface
PN.264	Pedro Ivo R. Moraes	Ab initio Investigation of Layered Double Hydroxides with Intercalated Herbicides
PN.265	Pedro Oliveira Mariz de Carvalho	2D, 3D and Hybrid QSAR Studies for a Set of 3-Benzyl-(arylmethylene)furan-2(5H)-ones and Their Herbicide Activity
PN.266	Pollyanna P. Maia	Encapsulation process of p-Cymene into Beta-Cyclodextrin: A Theoretical Study
PN.267	Rafael Oliveira Lima	Study of Excited States of Polycyclic Aromatic Hydrocarbons (PAHs)
PN.269	Raphael S. Alvim	Aggregation of Asphaltenes Using a Top-down Molecular Modeling Hierarchical Approach
PN.270	Raquel Costabile Bezerra	Glycerol adsorption energy onto Pt and PtSn (001) surfaces using density functional theory and vdW corrections
PN.272	Régis Casimiro Leal	Theoretical Calculations on Diels-Alder Reactions: Case Study of Cyclopentadiene and Alkyl Acrylate
PN.273	Regis Tadeu Santiago	Relativistic effects on the noble gas chemistry: A study of the HNgF → Ng + HF (Ng = Ar, Kr, Xe and Rn) decomposition reaction
PN.274	Renato C. da Silva	Parâmetros Estruturais e Eletrônicos para o Cálculo da Temperatura Crítica de Supercondutores do tipo A2BC60 (A e B: Na, K, Rb e Cs)
PN.275	Rênica Alves de Morais Rocha	Pentacyclic Triterpenes isomers 13C NMR Chemical Shift Prediction Using GIAO-mPW1PW91/3-21G//PM7 Level of Theory

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PN.276	Rhuiago Mendes de Oliveira	Combination of Electronic Structure Calculations and Rovibrational Spectroscopic Constants for Enhancement of Lennard-Jones Potential in the Description of Molecules Involving Gas-Nobles
PN.277	Ricardo de Almeida	The influence of dopants elements at the electronic properties of Pd12M Clusters: A DFT study
PN.278	Ricardo de Lima	Electronic and structural properties of supercritical fluids. Evaluation of force fields for the description of the absorption spectrum of paranitroanilina in supercritical CO2
PN.279	Ricardo Fagundes da Rocha	Inhibitors of Salicylic Acid Binding Protein 2 (SABP2) Design by Docking and Molecular Dynamics
PN.280	João B. L. Martins	H-S…Pi interactions
PN.281	Roberta P. Dias	Effect of counterion on the self-assembly of N-hydroxy alkyl ammonium surfactants
PN.282	Rodrigo A. L. Silva	Energy and rovibrational spectroscopic constants for fullerenes dimers (C20)2 , (C24)2 , (C36)2 , (C60)2 , (C70)2 and (C84)2
PN.283	Rodrigo A. Mendes	Probing the antioxidant potential of phloretin and phlorizin through a computational investigation
PN.284	Rodrigo Fraga de Almeida	Basis Functions Search for the Electronic Spectra Simulations of Polypyridyl Ruthenium Sensitizers Applied on DSSCs
PN.285	Rogério José da Costa	Theoretical study of the adsorption of alcohols on H-ZSM-5 zeolite
PN.286	Rogério Vaz A. Jr	The role of hydrogen bonds and solvent effects on mechanical behavior of mortar coatings applied on the facades of structural masonry buildings
PN.287	Roiney Beal	Estudo da Fotólise da Acetanilida por métodos multiconfiguracionais
PN.288	Rosemberg Fortes N. Rodrigues	Theoretical investigations of nonlinear optical properties of two heterocyclic chalcones.
PN.291	Sarah Arvelos	Adsorption of CO2-C3H8 mixtures on Na-ZSM-5: a molecular simulation study
PN.292	Shawan K. de C. Aldeida	Probing the effect of sugar substitution on the antioxidant-related properties of flavonols
PN.293	Silviana Corrêa	Theoretical study of the molecular fragmentation mechanism of the hybrid δ-FeOOH/PMMA
PN.294	Sinkler Tormet G.	Molecular Dynamics Simulations of a new family of Glycoside Hydrolase (GH-X)
PN.295	Taís Christofani	Ruthenium(II) Polypyridine Complexes: Photophysics and Electrochemistry
PN.296	Tamires Lima Pereira	Optimally Tuned Functional Methods as a Way of Improvement in the Description of Optical and Electronic Properties of Phthalocyanines Complexes
PN.297	Tárcius N. Ramos	THE ROLE OF CHARGE TRANSFER IN THE TWO-PHOTON ABSORPTION CROSS SECTION
PN.298	Tatiane Nicola Tejero	Theoretical Investigation of the Biginelli Reaction Mechanism: When Knoevenagel is a Possible Mechanism Pathway
PN.299	Taylane da Silva Araújo	De novo design of novel Mycobacterium tuberculosis pantothenate synthetase inhibitors
PN.300	Telles Cardoso Silva	Oxidative insertion and activation of the C-H bond of methane by niobium oxides NbOmn+ (m=1, 2; n=0, 1, 2)

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PN.301	Teodorico C. Ramalho	The Quantum Description of Halogen Bonds via a Generalized Empirical Potential
PN.302	Thaís Forest Giacomello	Structural determination of polyphenols by quantum mechanical calculations of ^{13}C NMR chemical shifts: development of a parameterized protocol using a set of chalcones
PN.303	Thayana Maria Lopes de Lima	Estudo teórico do estado iônico da molécula do HCFC-133a
PN.304	Thayane Paula Dias Caldeira	Metal–Support Interaction Effect on the Nucleation of Pdn particles (n=1-6) on (110C) γ-Al2O3 surface
PN.306	Thiago de Souza Duarte	Theoretical Study of Interactions between Drugs and Metal-Organic Frameworks
PN.308	Tiago Espinosa de Oliveira	Computational studies on the temperature- induced transition in PNnPAm hydrogels.
PN.310	Uallisson Silva Santos	Computational Study of the Interactions between TiO2 Anatase Nanoparticles
PN.312	Ulisses José de Faria Junior	Multiconfigurational Study of X2S+ and A2P States of BeF, MgF and CaF molecules
PN.313	Verlucia Amanda M. de Freitas	Molecular properties of N-benzoyl-2-hydroxybenzamide derivatives related to Plasmodium falciparum inhibition
PN.314	Verônica M. Nascimento	Abertura seletiva de epóxidos com Metil Selenolato de Litio
PN.315	Victor A. V. Ferreira	Solamargine and Solamarine: Why so different?
PN.316	Victor Augusto Santana da Mata	Theoretical Study on Electron Collisions with Methylamine
PN.317	Victor Hugo Malamace da Silva	DFT Study of the interaction between the [Zn(H2O)6]+2, [Cd(H2O)4]+2, [Hg(H2O)2]+2 aquacomplexes and monodentate O-, N- and S-donor ligands
PN.318	Vinícius Bonatto	Conformational analysis of molecules with potential antileishmania activity
PN.319	Vinícius Nunes da Rocha	Comparative Kinetic Analysis of Hydrogen Abstraction Reactions by OH Radicals: Dimethyl Ether and Diethyl Ether
PN.320	Stella Maris Resende	Thermochemistry of monoterpene β-ocimene
PN.321	Virginia Camila Rufino	Thermochemistry of the atmospheric decomposition of β-ocimene initiated by OH radical
PN.322	Vitor H. Menezes da Silva	Theoretical Study on Selectivity Trends in (N-heterocyclic carbene)-Pd Catalyzed Heck reactions: Exploring Density Functionals Methods and Models
PN.324	Wagner Eduardo Richter	On the negative dipole moment derivatives of HNgX molecules
PN.325	Washington de Almeida Pereira	Electronic-structural study of the interaction of inhibitors of the protein Abl-Bcr tyrosine kinase in mutated form against the wild-type
PN.326	Yago Francisco Lopes	Estudo teórico da reação de hidroformilação utilizando a molécula de (-)-isopulegol parte (II).
PN.327	Yago Silva de Sousa	Description of multiple pathways on rearrangement the H atom on methylchlorocarbene
PN.328	Yeny Y. P. Valencia	Computational Simulations of POPG Aggregates in presence of the Antimicrobial Peptide LL37