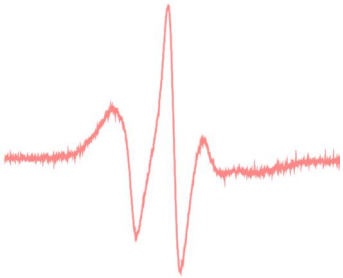
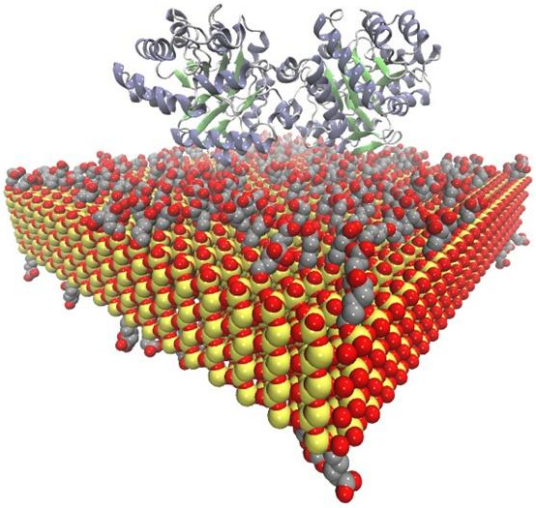
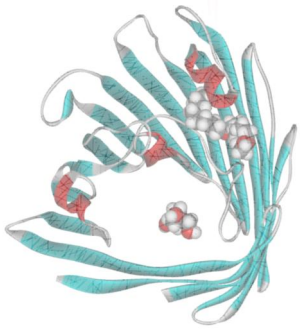
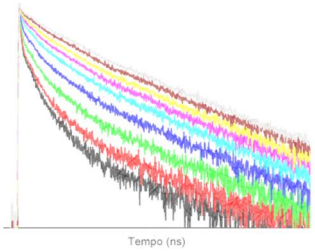
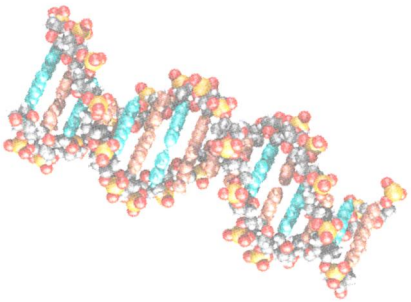


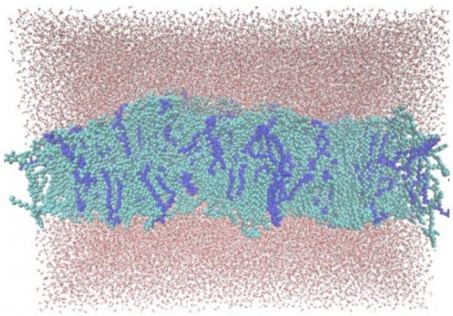




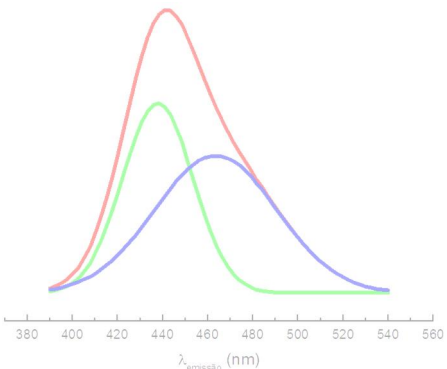
Workshop on Biomolecular Theory-Experiment Interplay (WBioTEI)







November, 21st and 22nd
IFUSP
São Paulo – Brasil



Organizers

Profa. Kaline Coutinho (Coordinator)
Dra. Cíntia C. Vequi-Suplicy

Support

Program

Thursday, 21st	
9:00-9:20	**Opening Session**
9:20-10:10	P01: **Prof. Wilfred F. van Gunsteren** (ETH/Zurique/Suíça) "Comparing Simulation with Experimental Results"
10:10-10:50	P02: **Prof. Roberto Salinas** (IQ/USP) "NMR studies on the type IV secretion system of Xanthomonas citri"
10:50-11:10	**Coffee Break**
11:10-11:50	P03: **Prof. Roberto Lins** (DQF/UFPE) "Molecular Glycoscience Across Scales"
11:50-12:30	P04: **Prof. Hernan Chaimovich** (IQ/USP) "Experimental and simulation insights on ion specificificity in amphiphilic aggregates: the triflate case"
12:30-14:00	Lunch Break
14:00-14:40	P05: **Prof. M. Teresa Lamy** (IF/USP) "Structural properties of cationic diC14-amidine vesicles";
14:40-15:20	P06: **Prof. André Silva Pimentel** (DQ/PUCRJ) "Molecular Dynamics of Lung Surfactant Systems Interacting with Polyciclic Aromatic Hydrocarbons"
15:20-16:00	P07: **Prof. Cristiano Oliveira** (IF/USP) "Investigating Biological Systems by Scattering Methods
16:00-16:20	**Coffee Break**
16:20-17:00	P08: **Prof. Amando Ito** (FFCLRP/USP) "Model membranes and peptides membrane: simulation and fluorescence studies"
17:00-18:30	**Poster Session**

Program

Friday, 22nd	
9:00-9:40	P09: **Prof. Hubert Stassen** (DQ/UFRGS) "Ionic Liquids interacting with Model Membranes"
9:40-10:20	P10: **Prof. Shirley Schreier** (IQ/USP) "Membrane-peptide interaction. Conformational, functional, and physicochemical aspects"
10:20-10:40	**Coffee Break**
10:40-11:20	P11: **Prof. Thereza Soares** (DQF/UFPE) "Computational Simulations of LPS membranes: chemotypes, temperature and cations."
11:20-12:00	P12: **Prof. Hans Agren** (KTH/Stockholm/Sweden) "Multiscale modelling - the 2013 Nobel prize in Chemistry"
12:00-12:10	**Closing Session**

Poster Abstracts

P1

Theoretically describing the ^{17}O magnetic shielding constant of biomolecular systems. Uracil and 5-fluorouracil in water environment

Rodrigo M. Gester, Carlos Bistafa*, Herbert C. Georg, Kaline Coutinho, Sylvio Canuto
IFUSP, IF-UFG, Faculdade de Física da UFPA

The nuclear magnetic resonance chemical shielding of 17O is of great important for bio-molecular characterization in water environment. In these systems oxygen atoms occupy important positions and are involved in hydrogen bonds with the water environment. In this work, different solvation models are used for the theoretical determination of the 17O chemical shielding of the nucleobase uracil and the substituted 5-fluorouracil in aqueous environment. Continuum, discrete and explicit solvent models are used and an analysis is made of the role played by the solute polarization by the solvents. The best results are obtained using the sequential Quantum-Mechanics/Molecular-Mechanics methodology using an iterative procedure for the solute polarization but a good compromise is obtained by using the electronic polarization provided by the polarizable continuum model. Quantum mechanical calculations of the chemical shieldings are made using density-functional theory in two different exchange-correlation approximations. Using an iterative procedure for the solute polarization and the mPW1PW91/aug-pcS-2 model in the electrostatic approximation we obtained magnetic shielding constants of 57.2 ppm and -13.5 ppm for the two O atoms of uracil in very good agreement with the experimental results of 55.5 ppm and -13.5 ppm, respectively. For 5-fluorouracil the theoretical results, with the same model, are 56.5 ppm and -12.6 ppm, again in good agreement with the experimental values of 57.5 ppm and -6.5 ppm. An analysis of the influence of the solute-solvent hydrogen bonds in the chemical shielding of uracil case is also made and it is concluded that the most important contribution to the calculated shielding derives from the electrostatic contribution to the solute-solvent interaction.

Support: FAPESP, CNPq, CAPES, nBioNet, INCT-FCx

P2

Avaliação teórica quantitativa estrutura-atividade (QSAR) em derivados de cetonatiossemicarbazonas com potencial inibitório a melanogênese

Karina Anunciada Barros*
Universidade Federal de Pernambuco (UFPE)

Neste trabalho foi realizada uma previsão teórica da concentração inibitória (IC50) do potencial de inibição a melanogenesis em alguns derivados de cetonatiossemicarbazonas utilizando descritores eletrônicos obtidos através de cálculos computacionais de química quântica. As cetonatiossemicarbazonas utilizadas neste trabalho foram do grupo de pesquisa do pesquisador Pillaiyar Thanigaimalai. O trabalho de pesquisa foi feito por meio de um estudo quantitativo de estrutura atividade (QSAR)tomando como base o modelo matemático da regressão múltipla linear (RLM). O método químico quântico computacional para obtenção dos parâmetros eletrônicos foi a Teoria do Funcional de Densidade (DFT) com o funcional hibrido de densidade B3LYP e a função de base 6-311G(d,p). Os descritores eletrônicos calculados foram: afinidade eletrônica adiabática (EA), gap de energia ΔE(HOMO-LUMO), atração cargas de Mulliken dos atómos (N1, N2, N3 e S)e a permeabilidade da membrana celular através do momento de dipolo (μ) e o logartimo do coeficiente de partição octanol/água (LogP).

Support: Fundação de Amparo à Ciência e Tecnologia de Pernambuco (FACEPE)

P3
Theoretical Study of the Absorption Spectra of Photosynthetic Pigments

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The first stage of the photosynthetic process is the extraordinary efficiency of sunlight absorption in the visible region [1]. This region corresponds to the maximum of the spectral radiance of the solar emission. The efficient absorption of visible light is one of the most important characteristics of photosynthetic pigments. In chlorophylls, for example, the absorptions are seen as a strong absorption in the region 400-450 nm in connection with other absorptions with small intensities in the region of 500-600 nm.

Understanding the absorption spectrum of photosynthetic pigments will allow the design of new artificial photosynthetic pigments with appropriate response to the absorption of light and energy. Thus, this comprehension is also in the development line of solar cells [2], and also in the development of sensors for the treatment of cancer by photodynamic therapy [3]. These studies have gained tremendous interest in recent years.

This work aims at understanding the essential features of the absorption spectrum of photosynthetic pigments, in line with several theoretical studies in the literature [4,5].

The first pigments studied were Porphyrins and Phthalocyanines, in-medium and in gas phase. For the isolated optimized geometries benchmarkings were made for the electronic absorption spectrum in comparision with experimental data for gas phase, and also to infer the influence of dimerization. Molecular Dynamics were done to analyze the influence of thermal effects in the spectrum.

[1] R.E. Blankenship; “Molecular Mechanisms of Photosynthesis”, Blackwell Science (2002).
[2] A. Kay, R. Humphry-Baker and M. J. Gr¨atzel; J. Phys. Chem., 98, 952 (1994).
[3] A. E. H. Machado; Qu´ımica Nova, 23, 237 (2000).
[4] P. Jaramillo, K. Coutinho, B.J.C. Cabral and S. Canuto; Chem. Phys. Lett., 516, 250 (2011).
[5] L. Petit, A. Quartarolo, C. Adamo and N. Russo; J. Phys. Chem. B, 110, 2398 (2006).

Support: CNPq, Fapesp, inctFCx

P4
Cell membrane models containing capsaicin and surface analysis of wood modified with antifungal

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Instituto de Física de São Carlos - Universidade São Paulo (USP), São Carlos, SP, Brazil

Wood is composed of cellulose and hemicelluloses, being therefore food for an important group of extremely active organisms - xylophages. Owing to the recurrent problems of wood biodeterioration, especially in tropical countries, the adoption of treatment techniques using preservative substances becomes necessary when this material is intended for construction. A more acceptable alternative, from an ecological point of view, is the use of natural biocides in the treatment of wood. Examining molecules that present a low environmental impact is the main goal of the current research. The substances of natural origin are often safer than synthetic ones, and do not leave residues in the environment. The application of chemical preservatives provides an increase in wood resistance to xylophages. This study evaluated the efficacy of oleoresin capsaicin, extracted from the peppers Malagueta, Red Savina and Bhut Jolokia, applied to wood Pinus sp. In specimens of size 3.0 x 2.0 x 1.0 (cm) under attack of the Paecilomyces variotti fungus and utilized the Langmuir technique to better understand the interaction of capsaicin, ergosterol and DPPG which is present in fungi membranes and has as main objective the study of interactions between drugs and membrane models for obtaining information on the molecular level of possible actions related to physiological activity. The two major modes of action of drug / membrane models is the penetration in the membrane by changing the packaging of the lipid bilayer creating pores and changes in elasticity of the diaphragm induced by the drug. The surface pressure isotherms for ergosterol/capsaicin and DPPG/capsaicin were more expanded than for neat ergosterol and DPPG with monotonic increase in the minimum area. This effect should be associated with the insertion of capsaicin in the monolayer of ergosterol e DPPG.

Support: CAPES e FAPESP

P5
Captopril and it's N-domain ACE complex molecular modeling

Flávio Araújo Pousa Paiva*, Dr. Odonírio Abrahão Jr., Dr. Milton Taidi Sonoda
Universidade Federal do Triângulo Mineiro

Angiotensin Converting Enzyme (ACE) is a zinc metalloprotease found in many human body tissues, as lung, epithelial tissue, testicles and pericardial fluid, among others, and it's best known function is blood pressure regulation. Consisting by two catalytic domains, known as N and C domains, ACE has been recognized as the major target for cardiovascular therapies and hypertension.

Captopril was the first developed and still is one of the main commercial ECA inhibitor However it was developed without the knowledge of the ECA domains structure, resulting in a low domain selectivity, observed by experimental dissociation constant data, producing undesirable side effects such as cough, renal failure, among others.

Molecular Docking is a valuable tool in the drug discovery process. The main objective is to predict the receptor-ligand complex structure, where the receptor is generally a protein, and the ligand a small molecule, peptides or other proteins. In this work Lamarckian Genetic Algorithm molecular docking were employed to model Captopril complexed with ACE, whose experimental structure were not determined. The Captopril structure were energy minimized and Merz-Kollman partial charges computed through quantum chemistry DFT/B3LYP calculations at 6-31g(d,p) level of theory. These charges were used in ligand model in docking simulations.

Generally, the ligand orientation and specific interactions with aminoacids in the binding pocket were the same as the Captopril-C-domain complex, whose x-ray structure has been determined, accounting for the relatively low ACE domain selectivity. This result is expected since Captopril is relatively small when compared to other ACE inhibitors, such as lisinopril and enalaprilat, whose size and volume allow to occupy other binding pocket subsites.

Support: FAPEMIG

P6
Experimental and Theoretical Studies of Emodin in Lipid Bilayer

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Emodin (1,3,8-trihydroxy-6-methyl-9,10-anthraquinone, EMH), is one of the most abundant anthraquinone derivatives found in nature. It can be extracted from different plant sources such as Aloe vera, Polygonum hypoleucum and rhubarb, which is widely used in the cosmetic and pharmaceutical industries [1]. Emodin is known to have antibacterial, antiviral, anti-inflammatory, antioxidant, antifungal and anticancer activities [2]. Due these biological and pharmacological activities, several scientific researches examined the structural and electronic properties of this molecule and it interactions with the biological environment [3]. In recent investigation some chemical processes of EMH in alcoholic solutions, such as deprotonation and tautomerism, has been analyzed [4]. These processes change the molecular properties and its interactions with the environment. In this work, we report a study experimental and theoretical of protonated (EMH) and deprotonated (EM-¬) emodin into solvents and lipid bilayer addressed to examine the location and interaction of both species of emodin 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 both species in fully hydrated lipid bilayers of DMPC to investigate at atomic detail the interaction mechanism of these species with lipid membrane and its preferred location and orientation in these environments. In addition we investigate the lateral diffusion of EMH and EM- in lipid bilayer in order to examine the dynamics and fluidity of both species in these environments. As mean results we obtained that both species of emodin have a tendency to insert into the lipid bilayer, collecting near the glycerol group of DMPC, with species molecules mostly oriented parallel to the membrane normal axis. Our results also show that the effect of EM- specie in the lipid bilayer structure is stronger than the EMH.

References:

[1] R. H. Thomson, Naturally Occurring Quinones, 2nd ed. Acad. Press, London, (1971).
[2] D.O.Andersen, et al., Antivirial Res.16, 185(1991).
[3] E.L.Duarte, et al., Langmuir 24, 4041(2008).
[4] S.C.Nguyen, et al., Chem.Phys. 352, 167 (2008).

Support: FAPESP, CNPq, CAPES, Rede Nanobiotec and INCT-Fluidos Complexos

P7
Interactions and Elastic Properties of Lipid Membranes: The Role of a Cosurfactant

Rafael Leite Rubim*, Kévin Bougis, Barbara Gerbelli, Emerson Silva, Cristiano Oliveira, Laurence Navailles, Frédéric Nallet, Elisabeth Andreoli de Oliveira
Institute of Physics, University of São Paulo - São Paulo - Brazil,
University of Bordeaux 1 - Research Centre Paul Pascal - Pessac - France

In this work we investigate interactions between lipid membranes and their elastic properties, with the incorporation of ethoxylated fatty acids, commercially known as Simulsol. Small Angle X-ray Scattering (SAXS) experiments were carried out in lamellar phases in order to obtain structural information and using a model to the scattered radiation, we can obtain the thickness of the membrane and the Caillé parameter, which is related to the flexibility of the membrane. Applying an osmotic pressure to the membranes we can access information about the interactions between the bilayers and evaluate the effect of changing their flexibility and the interface. Combining the information obtained from both methods it is possible to characterize the elastic parameters of the membrane. We observe that the insertion of the cosurfactant increases the flexibility of the membranes, as well as the diluted and repulsive interactions. This study brings a new method to evaluate interactions between membranes and characterize its elastic properties.

Support: This work was supported by FAPESP, process number 2011/16149-8, and INCT-FCx.

P8

Molecular modeling of pyridinium-iodide complexes in acetonitrile solution: donor-acceptor interactions and charge-transfer excitations

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Universidade Estadual de Maringá, Maringá-PR

In this work, we have been studing theoretically charge-transfer complexes (CTC) formed by pyridinium derivatives with iodide. The formation of CTC is characterized by the appearance of a new absorption band on electronic spectra, in organic polar solvents like acetonitrile[1,2]. These type of systems have recently received much interest in a broad variety of fields, for example, organic electronics, nonlinear spectroscopy, medical biochemistry, pharmaceutical industry, etc. We have performed quantum mechanical calculations with Density Functional Theory associated with the Polarizable Continuum Model in order to obtain stable complexes in vacuum and in acetonitrile solution. Charge transfer excitation energies have been calculated using Time Dependent Density Functional Theory with long range corrected functionals. We also investigated the solvent effects on the geometry stabilisation and excitation energies of the CTC using multiscale methods, such as hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) method.

[1] E. M. Kosower and J. A. Skorcz, J. Am. Chem. Soc. 82, 2195 (1960).
[2] F. R. Carvalho and N. Hioka. Master Dissertation, Universidade Estadual de Maringá, PR,Brasil (2010).

Support: CNPq, CAPES, FAPESP, INCT-FCx and nBioNet

P9

Molecular dynamics simulations Fasciola hepatica cathepsin B complexes with CA074, a dipeptidyl nitriles and PubChem BioAssays potential selective inhibitors

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Cathepsin B (fCatB), the major secreted protease from the juvenil stage of Fasciola hepatica, is a relevant chemotherapeutic target to treat fascioliasis. However the three-dimensional (3D) structure of fCatB have not been experimentally solved yet. This constitutes an important drawback for the structure-based design of novel inhibitors using virtual screening approaches. fCatB inhibitors abrogated the parasite life cycle and have a low selectivity towards human (hCatB) and bovine (bCatB), the related host proteases. We predict putative selective inhibitors of fCatB by combining comparative modeling (multiple structures complex template), molecular docking (CA074, a dipeptidyl nitriles and PubChem BioAssays compounds) and molecular dynamics simulations. A cavities prediction, ligand's interactions and a molecular dynamic simulations assay were made. Also, 13 residues potentially determinant in the substrate specificity was identified from wish its suggest that tree of them could enhances the design of selective cathepsin B Fasciola hepatica's inhibitors regarding to mammalian' cathepsins.

Support: CAPES, International Foundation for Science (IFS)

P10
Structure-activity relationship of analogues of the antimicrobial peptide gomesin: The role of peptide hydrophobicity in its interaction with model membranes

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Division of Biophysical Chemistry (Biozentrum, University of Basel, Basel, Switzerland)

Antimicrobial peptides are molecules of the immune system of animals and plants that exhibit antibacterial and antifungal activity. Among several related mechanisms of action, most antimicrobial peptides induce membrane permeabilization. Gomesin (Gm) was originally obtained from the spider Acanthoscurria gomesiana, and has 18 amino acid residues (ZCRRLCYKQRCVTYCAGR-NH2), among which 6 cationic residues and 4 cysteines that form two disulfide bounds, which result in a b-hairpin structure. The aim of this study is to investigate the influence of the hydrophobicity of Gm in its ability to interact with biomimetic membranes. For that purpose, different analogues were synthesized with substitution of specific amino acid residues by alanine to modify the peptide hydrophobicity. Large unilamellar vesicles (LUVs) composed of mixtures of POPG and POPC (3:7) were used to mimic bacterial membranes. The interaction of Gm and its analogues was studied by isothermal titration calorimetry (ITC), static light scattering (SLS) and kinetics of carboxyfluorescein (CF) leakage. From ITC results, the thermodynamic parameters of the lipid-peptide interaction (DH, DS, DG and K) were assessed. SLS results were used to evaluate the extent of peptide-induced vesicle aggregation. The percentage of CF leakage was used to quantify and obtain the kinetics of membrane permeability induced by peptides. The results show that the magnitude of the effects caused by the different peptides is related to a hydrophobicity scale. It may be concluded that: i) the increase in peptide hydrophobicity increases the magnitude of DH, DG and K and the total CF leakage induced; ii) the extent of peptide-induced vesicle aggregation is mainly related to the electric charge of the peptide, increasing with the peptide charge; iii) the kinetics of CF leakage exhibits two characteristic times (one on the order of few seconds and another on the order of several minutes), and the first process becomes faster and more important upon increasing the hydrophobicity of the peptide.

Support: FAPESP, CAPES, CNPq, INCT-FCx

P11
Molecular Simulation of the Potential Surface of Langmuir films

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Langmuir films are of interest for their own purpose and because their molecular architecture makes it possible to create materials very promising from the point of view of their applications in molecular electronics. The change in the concentration of a surfactant in a Langmuir film results in numerous phase transformations and surface potential changes whose nature and fundamental underlying physical chemistry of which are still unclear for many systems. The surface potential technique is one of the most frequently used method for characterizing Langmuir films. It provides valuable information on important monolayer effects related to molecular orientation. Unfortunately, the interpretation of surface potential measurements has been afflicted with two problems: many discrepancies exist between the measured and expected dipole moments and the measured surface potentials for expanded films do not have usually a good reproducibility. A great extent of these problems has been overcome by using models and better techniques but some gaps are still not understood, at least for the first problem.

The models provide imprecise values of the monolayer normal dipole moment because the dielectric constant of the monolayer is experimentally unapproachable, the group dipole moments are assumed to be the sum of group dipole moments, and the partial charges are not well defined in models. A simple approach to calculate the dipole moment in a more realistic way is to use molecular dynamics. Once the tool is applied to surfactants conformational information of the system can be drawn from the analysis of the results, such as changes of orientation and dipole moment as a function of packaging of the surfactant molecules. In this work the dipole moments of stearic acid (SA), octadecylamine (OA), dipalmitoylphosphatidylcholine (DPPC), and dipalmitoylphosphatidylethanolamine (DPPE) monolayers were calculated to try reconciling theory and experiment.

Oliveira, O. N. JR. and Bonardi, C.. Langmuir 1997, 13, 5920-5924.

Support:CAPES, CNPq, FAPERJ

P12
Molecular Dynamics Simulations and Free Energy Calculations on the Dissociation of Hypericin from a Peptide Nanotube

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Diphenylalanine (FF) nanotubes were synthetized firstly by Görbitz by the self-assembly process. The tubes formed by FF earned most attention because this is a important sequence on the formation of amyloid fibrils and one of their most interesting application was their use like templates to metallic nanowires production. Many questions regarding the process of self-assembly of those molecules are still being investigated. Besides that, the stability of the structures already formed is another question to be considered. Thus, on this work we performed simulations regarding the stability of structures formed by these diphenylalanine nanotubes.

Support: FAPESP

P13
Characterization and Absorption Spectrum of Mg:Tetracycline Complexes in Aqueous Environment - A Theoretical Study

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The complex formed by the tetracycline (TC) molecule with the Mg ion is able to prevent the replication of the genetic material in the bacterial ribosome, making an excellent antibiotic. In general, the absorption and emission spectra of TC are very sensitive to the host ions and the pH of the solvent that the set is immersed. However, the theoretical absorption spectrum available in the literature is scarce and limited to simple models that do not consider the fuctuations of the liquid. Our aim is to obtain the electronic absorption spectrum of TC and the complex Mg:TC in the ratio 1:1 and 2:1. Moreover, we analyze the changes in intensity and shifts of the bands in the systems listed. We performed the simulation using the classical Monte Carlo technique with the Lennard-Jones plus Coulomb potential applied to each atom of the both TC molecule and the Mg:TC complexes in water. The electronic absorption spectrum was obtained from the time-dependent density functional theory using diferent solvent models. In general, we obtained a good qualitative description of the spectra when compared with the experimental results. The Mg atom shifts the first band by 4 nm in our models, in excellent agreement to the experimental result of 4 nm. The second absorption band is found here to be useful for the characterization of the position where the ion attaches to the TC.

Support: CNPq, CAPES, FAPESP, INCT-FCx

P14
Electric dipole moments of the fluorescent probes Prodan and Laurdan: experimental and theoretical evaluations

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Several experimental and theoretical approaches can be used for a comprehensive understanding of solvent effects on the electronic structure of solutes. In this review, we revisit the influence of solvents on the electronic structure of the fluorescent probes Prodan and Laurdan, focusing on their electric dipole moments. These biologically used probes were synthetized to be sensitive to the environment polarity. However, their solvent dependent electronic structures are still a matter of discussion in the literature. Prodan and Laurdan absorption and emission spectra in different solvents indicate that the two probes have very similar electronic structures, in both the ground and excited states. Theoretical calculations confirm that their electronic ground states are very much alike. This review discuss the ground and excited states electric dipole moments calculated using the largely applied Lippert-Mataga equation, using both spherical and spheroid prolate cavities for the solute. The dimensions of the cavity were found to be crucial for the calculated dipole moments. These values are compared to those obtained by quantum mechanics calculations, considering Prodan in vacuum, in a polarizable continuum solvent, and using a hybrid quantum mechanics-molecular mechanics methodology. Theoretical approaches make evident that Prodan dipole moment can change even in the absence of solute-solvent specific interactions, what is not taken into consideration with the experimental Lippert-Mataga method. Moreover, in water, for electric dipole moment calculations, it is fundamental to consider hydrogen-bonded molecules.

Support: Work supported by FAPESP, CNPq, CAPES, NAP-FCx, INCT-FCx and nBioNet. Additionally, CCV-S acknowledges a fellowship from FAPESP and MTL and KC research fellowships from CNPq.

Annotations

Annotations

Annotations