analyses. We found that not only was the composition of the cell wall dramatically altered, but the overall structure of the cell wall was affected demonstrating the flexibility of plant polysaccharide organization to compensate for changes within the cell wall.

3006-Pos Board B776
FTIR Study of Temperature and pH Effects on Amino Acid Side-Chains
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Analysis of protein amide I IR bands can be complicated by absorption of side-chain groups. Side-chain IR spectra have been previously studied at acidic (pH ~2.3) and neutral (pH ~7) conditions, which take account of the protonated and deprotonated states of the carboxylic groups, but only at room temperature. It is expected that in thermal denaturation experiments these side-chain absorptions will change in both frequency and intensity with respect to temperature. This will additionally convolute the Amide I spectra unless corrected for. In order to attain these corrections an equilibrium study of temperature effects on amino acid side-chain absorptions has been conducted at both pH's for the amino acids glutamine, glutamic acid, asparagine, aspartic acid, and arginine. Experiments were carried out in a 1mM deuterated phosphate buffer. Deuterated amino acids were dissolved (1mg Amino Acid/60μL Buffer) in the buffer and scanned using a Bruker Tensor 27 FTIR. Samples were heated via a software controlled water bath from 0C to 87C, with scans taken every 3C. The collected temperature and pH dependent side-chain absorptions were normalized, to published room temperature data, and fit to pseudo-Voigt functions. It was found that both frequency and intensity exhibit linear changes with respect to temperature, though direction and magnitude varied between amino acids. These known shifts can thus be accounted for in the Amide I spectra analysis of proteins.

3007-Pos Board B777
A Co-Translationally Insertable Donor-Acceptor Pair for the Real Time Study of Vibrational Energy Transfer in Proteins
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Vibrational energy flow in biological macromolecules can be nicely studied by ultrafast pump-probe spectroscopy, given that suitable chromophors for injecting and tracking energy flow are present. Here we present a study on a new donor-acceptor pair consisting of two artificial aminoacids, with an azulene chromophore as a ''donor'', that can be excited at 600 nm and injects vibrational energy into the peptide or protein investigated. An azide chromophore is serving as an ''acceptor'', which can be monitored at 2100 cm-1 to track energy flow in the system. These labels combine a set of very favourable properties for the study of IVR in biological macromolecules. Co-translational incorporation of each of the labels into proteins has been demonstrated in the form of beta-(1-azulenyl)-L-alanine and L-azido-homo-alanine. To investigate the performance of the azulene-azide donor-acceptor pair, we designed a model peptid (Aaa-Tyr-Asn-Aha-Gly) inculding both chromophores and additional protein marker modes, such as tyrosine, asparagine and glycine providing the c-terminal carboxyl. We performed Vis-pump IR-probe experiments on the peptide, covering the range from 1200 cm-1 to 2120 cm-1. While in azulene-containing monomers, studied for comparison, the infrared signals reached their maximum within 2ps, we found for the peptide a pronounced correlation between the through-bond distance of a vibrating group from the azulene chromophore and the time until the IVR induced signal of this group becomes maximal. The signal of the azide band of our ''acceptor'' azido-homo-alanine is the dominating contribution at 9-10 ps. Even over a distance of four residues, it reaches a signal size comparable to the total amide I intensity of the peptide. In the light of the presented results the application of the azulene-azide donor-acceptor pair for IVR studies in proteins appears very promising.

3008-Pos Board B778
Molecular Structure and Stability of Phospholipid Monolayers Probed by Vibrational Sum Frequency Spectroscopy (VSFS)
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Deposited and floating monolayers of phospholipids are commonly used as model systems for biological membranes, since their complex structure make spectroscopic investigations difficult. In this research, the surface specific technique Vibrational Sum Frequency Spectroscopy (VSFS) was applied to investigate the molecular structure, packing properties, and hydrating water of Langmuir-Blodgett monolayers of *1,2-distearoyl-sn-glyerco-phosphatidylcholine* (DSPC, 18:0 PC), its deuterated analog (18:0 PC-d83), and *1,2-distearoyl-sn-glyerco-phosphatidylserine* (DSPS, 18:0 PS) deposited on CaF_2 substrates at a surface pressure of 35 mN/m. The CH and CD stretching regions, the water region, and the lower wavenumber region, containing phosphate, ester, carboxylate, and amine signals, thus partly covering the fingerprint region, were probed to obtain a complete map of the molecules. All phospholipids formed well ordered, stable monolayers. Probing the water region revealed significant differences in hydration of the different headgroups. The tilt angle of the aliphatic chains relative to the surface normal was estimated to 4° to 10° based on orientational analysis of the antisymmetric methyl stretch, and the result of a qualitative orientational analysis of the ester C=O groups was consistent with the tilt angle of the aliphatic chains.
Additionally, the stability of Langmuir monolayers of 18 PC with various degrees of unsaturation in the aliphatic chains was studied *in situ*. To monitor the degradation of the phospholipids the time dependent change of the Langmuir monolayer area at constant surface pressure and the SF intensity of the vinyl CH stretch were measured. While monolayers of fully saturated phospholipids formed stable, well ordered films at the water surface, phospholipids containing unsaturated aliphatic chains showed a significantly lower stability and rapid degradation. Nitrogen purging of the ambient air inhibited the breakdown, attributed to spontaneous degradation by oxidation mediated by reactive species in the air.

3009-Pos Board B779
Digital Parallel Acquisition in Frequency Domain for the Characterization of Tissue Spatial Heterogeneities
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Near-infrared (NIR) (650-1000 nm) optical properties of turbid media can be accurately quantified noninvasively using methods based on diffuse reflectance or transmittance, such as frequency domain photon migration (FDPM). For instance, Diffuse Optical Spectroscopy (DOS) is a noninvasive technique that is commonly used to provide biochemical information on hemoglobin, bulk lipids and water concentration by NIR tissue absorption and scattering. DOS does not require exogenous contrast, and rapidly provides quantitative, functional information about tumor biochemical composition. Conventional FDPM techniques are based on white-light steady-state (SS) measurements and the acquisition of frequency-domain (FD) data at several wavelengths using laser diodes, to measure broadband NIR scatter-corrected absorption spectra of turbid media. These techniques are limited by the number of wavelength points used to obtain the FD data. We developed a new method to improve the acquisition of optical parameters of the examined tissues, based on digital parallel acquisition in FD. With our system, both FD and SS measurements are performed using a super-continuum white laser alone. Moreover, the white laser allows a continuous scan of frequencies in the spectral medical window, thus providing additional wavelength information. At each wavelength, we extract what we refer to be as the tissue phasor. The estimated absorption and scattering coefficients are obtained by fitting phase shift and demodulation with a mathematical model for a semi-infinite geometry. In previous works we showed the possibility of non-invasively predicting chemotherapy response prior to treatment based on biomarkers obtained from tumor spatial heterogeneities of spectral features measured using a conventional DOS instrument. With the method here presented, we expect to improve the characterization of breast tumor spatial heterogeneities and the prediction of chemotherapy outcome. Work supported by NIH-P41-RR003155.

Computational Methods II

3010-Pos Board B780
Cross-Talk and Information Transfer in Mammalian and Bacterial Signaling
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In both mammalian cells and bacteria, simple phosphorylation circuits play a very important role in cellular function. Bacteria have hundreds of two-component signaling systems that involve phosphotransfer between a receptor kinase and a response regulator. In mammalian cells a similar pathway is the crucial TGF-beta signaling pathway, where extracellular levels of TGF-beta family ligands lead to activation of receptors that phosphorylate Smad proteins, which in turn activate many genes. In TGF-beta signaling the multiplicity of external ligands begs the question as to how cells distinguish signals coming from different extra-cellular ligands, but transduced through a small set of Smads. Here we use information theory with stochastic simulations of simple networks to address this question. We find that when signals are transduced through the same Smad, the cell cannot distinguish between different levels