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Unraveling the Photophysical Properties of Organic Semiconductors (Grammaticakis-Neumann Award Lecture 2015)

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Organic semiconductors offer numerous advantages compared to their inorganic counterparts, such as low-cost manufacturing, flexibility and lightweight. One important application is their use in new generation solar cells (Figure 1). The active layer of such photovoltaic devices often consists of a conjugated polymer, blended with a fullerene derivative in a solid-state thin film. In order to understand how those solar cells work and to improve their performance, it is important to investigate the light-matter interactions of the organic materials. We have done so by using a palette of experiments, spanning from ultrafast spectroscopy, via Stark effect methods, terahertz techniques, photocurrent measurements, to mobility characterization.

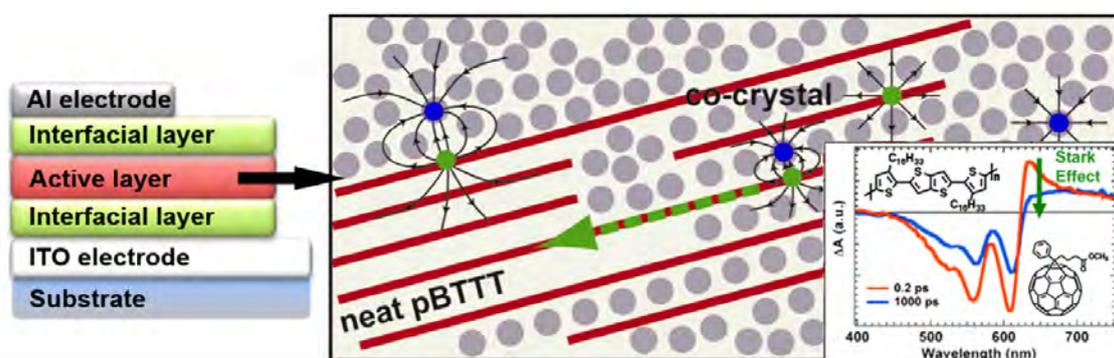


Figure 1: Typical organic solar cell, with zoom on the active layer nanoscale structure, and transient absorption spectra of polymer pBTTT blended with fullerene PCBM, showing a Stark signature due to photogenerated charges

In the first part of the talk, I will present our insights about the excited-state properties of conjugated polymers, which display a fascinating behavior in-between that of small molecule systems and that of bulk semiconductors [1,2]. I will then move on to discuss the correlation between the phase-morphology of polymer:fullerene blends and the photogeneration of free charge carriers [3-5]. Indeed, our work has shown that this essential step in solar cell functioning is largely determined by the way in which the polymer and fullerene arrange at the nanoscale (Figure 1). Finally, I will give an overview of our most recent studies about organic and hybrid semiconductors, not just applied to photovoltaics, but also to transistors and biological sensors.

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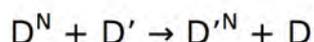
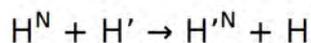
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Kinetic Isotope Effects on Exchange Rates of H^N and D^N in TryptophanE. Canet^{1,2}, P. Kadeřávek^{1,2}, P. Pelupessy², G. Bodenhausen^{1,2*}¹EPF Lausanne, ²ENS Paris

We have quantified the exchange rates between indole protons in tryptophan with the protons of the aqueous solvent, and compared the exchange rate of the analogous process when hydrogen is replaced by deuterium, so that we could determine the H/D kinetic isotope effect (KIE).



The measurement of H/H and D/D exchange rate constants of H^N and D^N on the indole ring in tryptophan is of obvious interest. The isotope effect is considered to be one of the most sensitive tools for the study of reaction mechanisms as it can give insight into free energies and other thermodynamic parameters that describe the stability of hydrogen-bonded structures in different environments.

We have extended our method originally designed for measuring very fast proton exchange rates^{1,2,3} to deuterium exchange rates. The effects of scalar relaxation caused by the exchanging H^N or D^N nuclei is determined by detecting the decay of the coherence of a ¹⁵N nucleus that has a scalar coupling ¹J(¹⁵N, ¹H) or ¹J(¹⁵N, ²D) to the exchanging nuclei under a multiple-refocusing CPMG pulse train in the presence or absence of proton or deuterium decoupling.

The exchange rates were found to lie in the range from 17 to 10 000 s⁻¹ for pH from 2.2 to 11.8 and temperature from 290 to 320 K. The logk_D vs. pH plot indicates a combination of specific base catalysis at high pH, un-catalyzed exchange at intermediate pH, and specific acid catalysis at low pH, which becomes more important at higher temperatures.

The kinetic isotope effect k_H/k_D was found to lie in the range from 0.22 to 14.99 for pH from 6.3 to 10.5 and temperature from 300 to 320 K. The kinetic isotope effect increases with increasing pH and temperature.

Altogether we can say that in the base-catalyzed mechanism the rate-limiting step of the exchange is the removal of the proton or deuteron from the amide, while for the acid-catalyzed mechanism it is the donation of a proton or deuteron by H₃O⁺, respectively D₃O⁺. From the small values of the kinetic isotope effect we can conclude that the H^N/D^N bonds are elongated, and not totally broken in the transition state, the H/D atom being more tightly bound to the donor N atom of tryptophan than to the acceptor D₂O or OD⁻.

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Photoinduced Stark effect in colloidal systems: a case study with MAPbBr₃ and AQU/nC₆₀

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Understanding the mechanisms of charge carrier generation and transport in photovoltaic systems is a key to get to efficient devices. The primary step towards such an understanding is a thorough analysis of the electronic structure and properties of those systems, yielding more targeted designs. Among several effects, the electronic modifications arising from the presence of an electric field is of great interest in such a framework: indeed, optical excitations tend to generate excitons, and those excitons create a transient electric field. This excitonic field in turn perturbs the electronic structure of the surrounding species, yielding a shift in their optical properties: it is a case of photoinduced (optical) Stark effect.

Ideal systems for the study of such optical Stark shifts are colloidal suspensions. Nanoparticles actually allow an extensive delocalization of the created exciton compared to molecules in solution, which creates a favorable environment for observation of a photoinduced Stark effect. Moreover, control on nanoparticle size is another advantage of the system compared to solid-state films.

Herein, we aim at studying those electro-optical shifts in two colloidal systems: methylammonium lead-bromide perovskites (MAPbBr₃) and hydrated fullerene C₆₀ (AQU/nC₆₀), using ultrafast transient absorption (TA) and electroabsorption (EA) measurements. Via the application of an external electric field, the latter method gives a direct insight into the features of the Stark signal for a given sample (electroabsorption spectrum). Then, on the basis of EA results, transient absorption experiments allow to directly assess the presence or absence of Stark-related features in our systems. As well, it gives us the associated dynamics, which informs us about delocalization of excitonic states.

EA measurements were performed on the solid-state film counterparts of our two colloidal systems. We show that both MAPbBr₃ and AQU/nC₆₀ colloids exhibit significant Stark shifts in their transient absorption spectra. As well, hints at a possible system size dependence of such a signal were obtained, that should be thoroughly considered in further studies.

High resolution infrared spectroscopy and theory of parity violation and tunneling for dithiine as a candidate for measuring the parity violating energy difference between enantiomers of chiral molecules

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In the framework of ordinary “electromagnetic” quantum theory the ground states of the enantiomers of chiral molecules are energetically equivalent. However, with the electroweak quantum chemistry and parity violation, one predicts a small “parity violating” difference $\Delta_{PV}E$ on the order of 100 aeV, typically, depending on the molecule, corresponding to a reaction enthalpy of stereomutation of about 10^{-11} J mol⁻¹ [1,2]. So far, this effect has never been observed experimentally. In our paper, we report exploratory spectroscopy and theory in view of a possible use of the chiral C₂-symmetric molecule dithiine (C₄H₄S₂) for detecting molecular parity violation using a current experimental setup in our laboratory [3]. Using high resolution FTIR spectroscopy [4] we were able to provide a first rovibrational analysis of two bands, one centered at 623.3121 cm⁻¹ consisting of c-type transitions and the second centered at 1308.8724 cm⁻¹ consisting of a-type transitions. The assignments have been verified by combination differences. In parallel we calculated parity violating potentials using our recent coupled cluster approach [5] and tunneling using our quadiabatic channel reaction path Hamiltonian approach [6]. The implication of our results for the study of molecular parity violation will be discussed.

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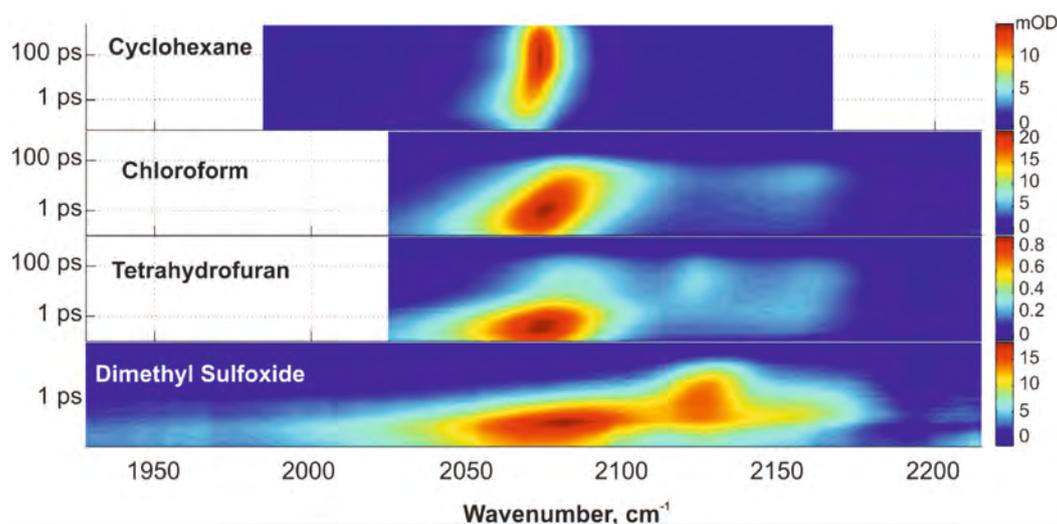
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Symmetry-Breaking Phenomena Detected with Ultrafast Time-Resolved Infrared Spectroscopy

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Quadrupolar molecules with a D- π -A- π -D molecular architecture are known to show large cross-sections for two-photon absorption processes. A search for such systems is stimulated by a growing need of photoinitiators for two-photon initiated photopolymerization. This field has been intensively developing in the last decade. Such molecules possess a small net dipole moment due to symmetry reasons, but the solvent dependence of their emission shows that they behave like highly dipolar molecules in polar environment. This remarkable behavior points to a localization of the optical excitation on one side of the molecule, i.e. to symmetry-breaking. Whereas electronic transient absorption of such molecules does not provide wealth of information about this phenomenon, a rich insight can be obtained by ultrafast time-resolved infrared spectroscopy. Using this technique we have monitored excited-state vibrational modes located on both branches of a D- π -A- π -D molecule. Directly after the optical excitation the same frequency is observed for both branches independently on the solvent polarity. At later time in polar solvents new bands develop reflecting the localization of the charge-transfer excited state on one side of the molecule. To the best of our knowledge it is the first spectroscopic visualization of such symmetry-breaking process in quadrupolar molecule.

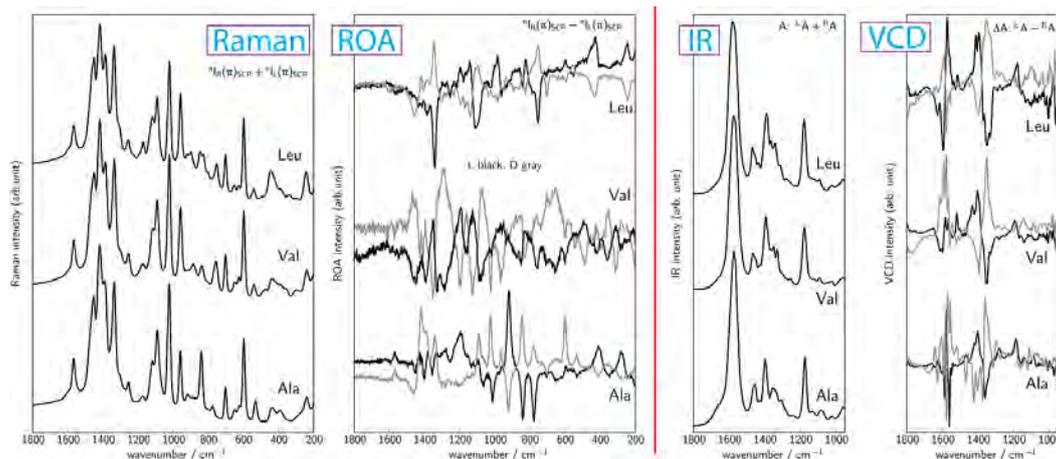


Vibrational Optical Activity (VOA) of Chiral Ionic Liquids (CILs)

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The synthesis of CILs from amino acids with 1-ethyl-3-methyl-imidazolium ([Emim]) as cation was presented a decade ago[1]. We have synthesized and recorded the Raman scattering and absorption spectra, and their optical activity for both techniques, for the L-/D-pairs of alanine, valine, and leucine ([L-/D-Ala][Emim], [L-/D-Val][Emim], and [L-/D-Leu][Emim]), see Figure below.



The spectra are analyzed by comparison to literature[2], and with the support of new calculations for both the anions and the cation.

Additional insight into the origin of observed spectral bands was obtained for the sample case of [L-Ala][Emim] through a Born-Oppenheimer molecular dynamics (BOMD) simulation[3]. The simulation box comprises 20 [L-Ala][Emim] pairs. In total three different sets of four [L-Ala][Emim] pairs and five different sets of one [L-Ala][Emim] pair were used to investigate the influence of the conformation on the optical activity of this CIL.

The emphasis is set on the dependence of molecular conformation and effects of the anion/cation interaction in regard to the generated optical activity.

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Characterization of Gd(III) chelators and combination of paramagnetic NMR with Gd(III)-nitroxide DEER in studies of biomacromolecules

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We applied the double electron-electron resonance (DEER) technique with Gadolinium(III) ions and nitroxide radicals as spin labels to measure nanometre-range distances on proteins [1] and peptides [2]. This relatively new approach [3] utilizes two spectroscopically and/or chemically orthogonal (non-identical) tags. It allows to benefit from extended spectroscopic information content, and from the combination with further techniques in studies of biomacromolecules.

We characterized several Gd(III) macrocycle chelators as labels for dipolar spectroscopy applications and observed an effect of the hyperfine interaction on their performance. [4] As an example of orthogonal labelling, we show that the pairs of non-identical spin labels could be introduced into an enzyme (hCAII) using an inhibitor derivative for the nitroxide and cysteine chemistry for the lanthanide label. The labelled hCAII of known X-ray structure was used to test the combination of paramagnetic relaxation enhancement and pseudo contact shift NMR with DEER measurements for structure determination. Correspondences between NMR and EPR constraints are analyzed and a guideline for a joint use of those data is presented. Noteworthy, orientation selection experiments were sufficient to extract the nitroxide orientation with respect to the protein at 35 GHz (Q-band). This example reveals that Gd(III)-nitroxide DEER is a versatile tool in studies of bio-macromolecules and potentially allows for addressing more complex biological systems than before.

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Experimental study of the ion-molecule reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ at low collision energies

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H_2 molecules in a skimmed supersonic beam are excited to nonpenetrating $n = 30$, $M_j = 3$ Rydberg-Stark states belonging to series converging to a selected rotational level ($N^+ = 0, 1, 2$ or 3) of the $X^2\Sigma_g^+$ ($v^+ = 0$) ground state of H_2^+ . The beam of Rydberg molecules is then deflected and velocity selected using a bent surface decelerator [1] and merged with another supersonic beam of ground state H_2 . In $n = 30$, $M_j = 3$ Rydberg-Stark states, the Rydberg electron is completely decoupled from the H_2^+ ion core motion and acts as a spectator when the H_2^+ ion core reacts with an H_2 molecule located within the Rydberg-electron orbit [2]. The experimental apparatus has been conceived so that the relative velocities of the two beams can be adjusted, making the study of the reaction at collision energies below 10 meV possible. The reaction products are monitored on an imaging microchannel-plate detector following extraction with a pulsed electric field. The information contained in the ion time-of-flight (TOF) distributions and in the distributions of H_3^+ product ions on the images are used to determine the relative cross section in dependence of the collision energy and the selected rotational state of the H_2^+ ion core. A typical TOF spectrum showing H_3^+ ions formed from the reaction of $\text{H}_2^+(v^+ = 0, N^+ = 0)$ at a collision energy of 6 meV is displayed in the Figure as illustration.

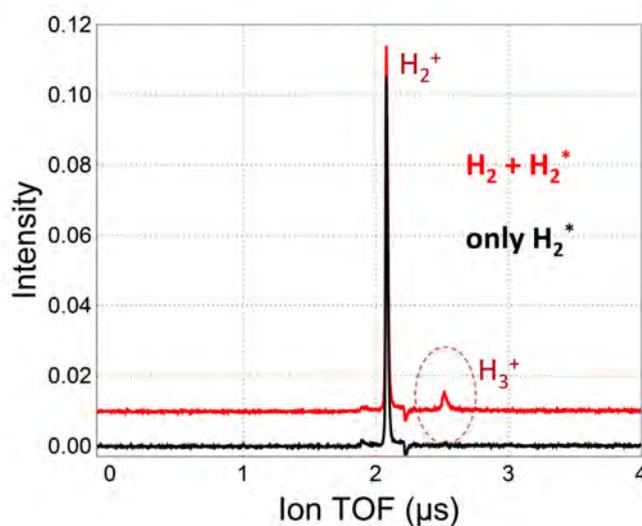


Figure 1: TOF spectrum showing H_2^+ ions (main peak) produced by pulsed field ionization of the initially prepared $n = 30$, $M_j = 3$ Rydberg states and H_3^+ ions resulting from the $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ reaction at 6 meV collision energy.

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ClHO₃S as a prototype system for studying photo-dissociation induced by OH stretching overtone excitation

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Sulphur containing compounds play an essential role in atmospheric chemistry. Especially the photo-dissociation of sulphuric acid into water and sulphur trioxide is of interest, due to its role in tropospheric aerosol layer formation.^[1] It was found that this reaction can be induced by excitation of OH stretching overtones, rather than by absorption of ultra violet radiation.^[2] Experimental analysis of this reaction is experimentally difficult. This is due to the fact that H₂SO₄ is, in gas phase, in equilibrium with its two fragments (H₂O + SO₃) and it possesses an extremely low vapour pressure.^[3]

For that reason related compounds were considered as a model system. It was suggested to use ClHO₃S as a prototype system for the experimental investigation of vibrationally induced photo-dissociation.^[4] Using several thousands points at the MP2/6-311G++(2d,2p) level of theory and fitting to a parameterised force field, extensive reactive MD simulations were run. For the analysis of the photo-dissociation of sulfurochloridic acid multi-surface adiabatic reactive molecular dynamics (MS-ARMD)^[5] simulations were performed. This method enables us to follow the H transfer, as well as the HCl elimination after the excitation of the OH-stretching mode. Final state analysis of several thousands of trajectories of the two fragments show distinct distributions for translational, rotational, and vibrational degrees of freedom.^[6]

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Cold Chemistry on a multi-functional ion trap chip

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Chip-based trapping techniques present novel possibilities for precise experiments with cold, quantum-state controlled particles with potential applications in mass spectrometry, chemistry, quantum information science, and spectroscopy [1-7]. We have designed and characterized a multi-functional monolithic miniaturized device for shuttling and manipulation of sympathetically cooled molecular ions [8-9] using accurately shaped electric fields above the surface of the chip. The chip consists of quadrupolar and octupolar surface-electrode RF traps featuring a few experimental sites that are connected via two optimized junction structures. The experiment aims to shuttle translationally cold N_2^+ , CaH^+ , and CaO^+ with laser-cooled $^{40}Ca^+$ ions in the millikelvin range. However, our design based on a mass-independent normalized optimization presents a universal surface pattern structure applicable to any other mass as well as trapping parameters.

This compact, flexible technology will progressively impact on experiments with hybrid quantum systems [10-11] as well as highly integrated experiments with molecular ions combining various tasks such as chemistry and spectroscopy, which have thus far been in the domain of costly and complex guided-ion beam machines [12].

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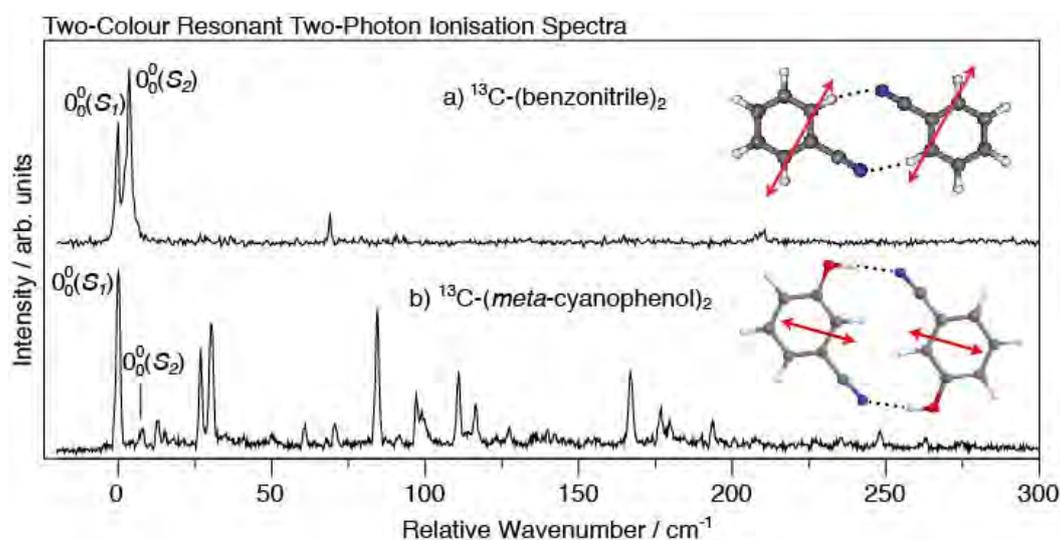
(Benzonitrile)₂ and (meta-Cyanophenol)₂: Influence of a Hydroxy Group on the Excitonic Splitting

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The benzonitrile dimer (BN)₂ is C_{2h}-symmetric with two antiparallel CN⋯H bonds. Its S₀ → S₁ (¹A_g → ¹A_g) transition is inversion-symmetry forbidden, and only the S₀ → S₂ (¹A_g → ¹B_u) transition is observed. In the ¹³C-isotopomer the monomers are inequivalent, rendering both the S₀ → S₁ and S₀ → S₂ transition allowed as shown in Figure (a). The S₁/S₂ splitting of the ¹³C-isotopomer is 3.9 cm⁻¹ and consists of an excitonic contribution (Δ_{exc}=2.0 cm⁻¹) and a ¹³C-isotope effect (Δ_{iso}=3.3 cm⁻¹). [1]

Substituting the H-atom at the *meta*-position of benzonitrile (BN) with an OH-group changes the H-bond pattern, see Figure (b). The presence of the hydroxy-group also rotates the transition dipole moments within the mCP unit by 40° to an almost collinear/anti-collinear alignment in the dimer, leading to an allowed S₀ → S₁ (¹A_g → ¹A_u) transition and a forbidden S₀ → S₂ (¹A_g → ¹A_g) transition. ¹³C-substitution renders both transitions allowed and the excitonic S₁/S₂ splitting was determined to be Δ_{exc}=7.1 cm⁻¹.



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Aqueous Catholyte for Rechargeable Li-O₂ and Li-Water Batteries

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Lithium is the lightest metal with the most negative potential (-3 V vs. SHE). Combining oxygen and water as a cathode as well as an electrolyte with lithium, the resulting rechargeable Li-O₂ and Li-water batteries provide 10-20 times higher energy densities than the conventional Li-ion batteries.

However, the reversibility of the redox reactions and hence the cyclability of those batteries are far below the requirements. Among several structures of Li-O₂ batteries, using an aqueous electrolyte provides a higher efficiency and cyclability due to the high ionic mobility and the solubility of discharge products [1]. A schematic of hybrid (organic/solid/aqueous) electrolyte-based Li-O₂ cell is shown in Fig. 1. During charging and discharging, the pH value changes so extremely that current membranes are damaged [2,3]. It was also reported that the saturated discharge product (LiOH) blocks the pores of the membrane, where Li⁺ ions should be able to pass through [4].

To avoid such extreme change of pH in an aqueous electrolyte, buffer solutions (PO₄³⁻ and SO₄²⁻) are useful. The pH values, the discharge products and ionic conductivity are evaluated in the process of charging and discharging. Accordingly, the electrochemical reactions are monitored to investigate the properties of electrolyte.

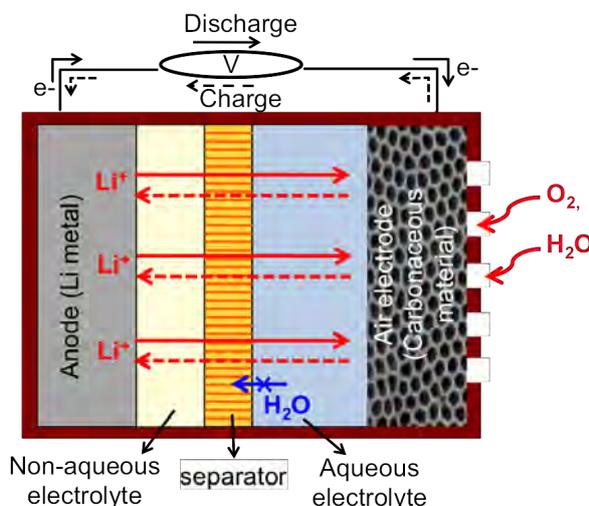


Fig. 1. Schematic of hybrid (organic/solid/aqueous) electrolyte-based Li-O₂ cell.

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Quantifying Equilibrium Binding Affinity using 2D IR Spectroscopy and Non-native Amino Acids

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Azidohomoalanine (Aha) is a very versatile label that can be incorporated into proteins. It absorbs in the non-congested part of protein IR spectra and the center frequency is sensitive to the environment [1]. The combination of ultrasensitive 2D IR spectroscopy and Aha labelling of proteins gives rise to new possibilities of investigating biological structures and their dynamics with very low sample demands. With voice coil flexure guided delay stages and automated exchange of buffer and protein samples it is possible to measure Aha labelled proteins down to a concentration of 0.5 mM with good signal to noise ratio. This is demonstrated with equilibrium binding studies of Aha-labelled peptide with its associated wild-type protein binding domain PDZ2. Upon binding, the Aha band redshifts by $\sim 15 \text{ cm}^{-1}$ and can clearly be resolved from the unbound fraction. For a fixed ligand concentration of 0.5 mM, analysis of fractional binding recovered from 2D IR spectra collected at various protein concentrations allows for the direct observation of the binding affinity.

[1] Robbert Bloem, Klemens L. Koziol, Steven A. Waldauer, Brigitte Buchli, Reto Walser, Brighton Samatanga, Ilian Jelesarov, Peter Hamm, *J. Phys. Chem. B*, **2012**, 116, 13705-13712