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Time-resolved X-ray absorption spectroscopy indicates a new photodissociation mechanism of dissolved CBr_4

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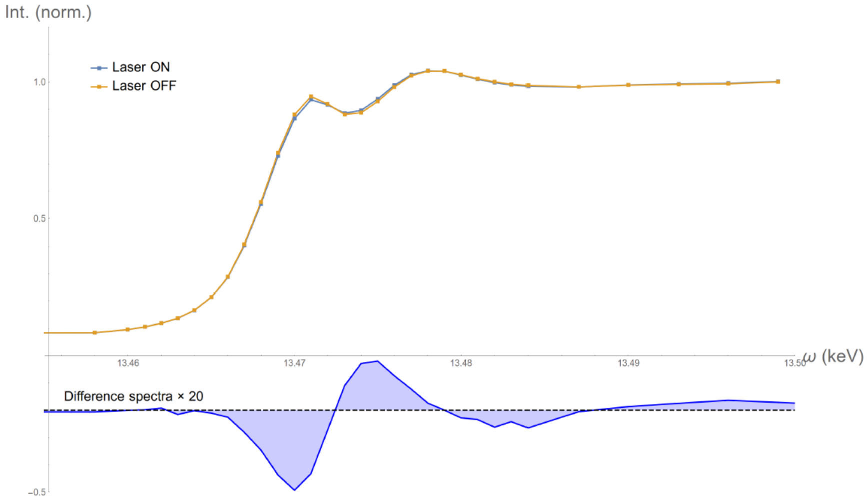
Commercial catalytic reactions can be improved by optimizing the slowest reaction step in the catalytic cycle. Nucleophilic substitution, in which one bond is broken and another bond is created, often represents the rate determining reaction step, as for instance in the Monsanto process in which acetic acid is synthesized from carbon monoxide and methanol. Understanding the initial carbon-halogen bond breakage of halogenated methanes in such reactions is therefore of utmost importance.

Photodissociation of dissolved CBr_4- a prototype bond breaking reaction - has been extensively investigated innumerous time-resolved studies. As the reaction mechanisms involves several intermediates and final products, the identification of individual species represents a challenging problem. In particular, previous studies have shownsomewhat contradictory results regarding the formation of final products [1, 2]. In order to elucidate the dissociation mechanism of dissolved CBr_4 on the ns - µs time scale, associated with the formation of final states,we have performed time-resolved X-ray absorption spectroscopy (XAS) measurements. Because XAS is only sensitive to the specific element probed and consequently to its chemical environment, it is often the preferred method for determining reaction mechanisms of photo-initiated chemical reactions [3].

In our study we have found that Br_2, formed ns after the UV excitation, is not stable in the solvent (methanol) and reacts within the first 1 µs upon photodissociation of CBr_4. On the other hand C_2Br_6, previously considered to be an intermediate decaying into Br_2 and C_2Br_4 [2], is found to be the final decay product. These findings are well supported by our ab initio DFT calculations which also indicate that other decay products are likely to contain HBr and CH_3Br in agreement with other studies [4]. Finally, we have extracted recombination rate constants from the experimental data and with this the missing ns - µs part of CBr_4photodissociation kinetics.



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Reaction-detected infrared spectroscopy of state-selected molecular ions

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First results are presented obtained using an experimental setup developed to record IR spectra of rotationally state-selected ions. The method we use is a state-selective version of a method developed by S. Schlemmer, D. Gerlich and coworkers (Int. J. Mass. Spec. **185**, 589 (1999); J. Chem. Phys. **117**, 2068 (2002)) to record IR spectra of ions.

Ions are produced in specific rotational levels using mass-analysed threshold ionisation spectroscopy combined with single-photon excitation of neutral molecules in supersonic expansions with a vacuum-ultraviolet laser. The ions generated by pulsed-field ionisation of Rydberg states of high principal quantum number ($n \approx 200$) are extracted toward an octupole ion guide containing a neutral target gas. Prior to entering the octupole the ions are excited by an IR laser. The target gas is chosen so that only excited ions react to form product ions. These product ions are detected mass selectively as function of the IR laser wavenumber.

To illustrate this method, we present IR spectra of $C_2H_2^+$ in selected rotational levels of the $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$ spin-orbit components of the electronic ground state.

From non-relativistic pre-Born-Oppenheimer theory to molecular structure

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The central paradigm of present day theoretical and computational chemistry consists in treating the nuclei as distinguishable particles in the Born and Oppenheimer (BO) approximation[1], as they define a framework geometry unambiguously even if formally dentical. Electrons, however, are described by an antisymmetric wavefunction, as it is appropriate for indistinguishable fermions. There are no doubts that the BO approximation can be considered as the backbone of modern quantum chemistry but, although it proved to be satisfactory for many purposes, the fundamental questions about the very concept of molecular structure for an isolated molecule prevals.[2] Essentially there are no reasons to believe that the probabilities for all possible nuclear configurations are the same and maxima of radial and angular densities may be taken as an indication for some underlying structure.[3] However, when nuclear permutation symmetry is not ignored, the undistinguishability of nuclei becomes the main obstacle toward the reconstruction of the classical structure.[4,5] While trying to translate those traditional chemical notions, such as molecular structure, chirality and isomerism, into the formalism of quantum mechanics, calculations in the pre-BO regime also provide highly accurate energy levels[6,7] that contribute to a deeper understanding of different phenomena in molecular physics.

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Towards hybrid trapping of cold molecules and cold molecular ions

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Hybrid systems of cold atoms and ions have been studied intensively in recent years. The simultaneous trapping of atoms with ions has opened up new possibilities for the investigation of interactions between the two species and has greatly contributed to the understanding of collisional and chemical processes at low temperatures [1].

Here, we report on the development of an advanced hybrid trapping technique which aims at trapping neutral molecules and molecular ions simultaneously. A translationally cold package of neutral molecules is produced by means of Stark deceleration. This deceleration technique exploits the Stark effect experienced by polar molecules in switched inhomogeneous electric fields, thereby producing a molecular package at translational temperatures T_{trans} › 1 mK [2]. During the last deceleration stage, the molecular package is loaded into a magnetic trap, which is incorporated into an RF ion trap. With this set-up, the superposition of cold neutral molecules with molecular ions allows for quantum-state selective investigations of elastic, inelastic and reactive collisions at low translational energies. Initial experiments will focus on $OH + Ca^+$, $OH + N_2^+$ and $OH + H_2O^+$ as collision systems.

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State-to-state scattering of methane from Ni(111) and epitaxial graphene on Ni(111)

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In recent years the dissociation reaction of CH_4 on Ni(111) has been studied extensively both by quantum state resolved experiments and by first principles theory.[1-4] In these dissociation studies, it was observed that typically a large fraction of the incident methane molecules does not dissociate but scatters from the surface even if their incident energy is significantly above the minimum barrier of ~0.8 eV.

Such inefficient dissociation can be explained either by a very narrow transition state, requiring a specific deformation of the reactant, or by fast vibrational energy transfer between the incident reactant and the metal surface through electron-hole pair excitation in the metal which competes with the dissociation reaction. Efficient vibrational energy transfer in gas/surface collisions has been reported for NO and HCl on Au(111)[5, 6] but has never been investigated for collisions of methane with transition metal surfaces .

To study ro-vibrational energy transfer in methane/surface collisions, we have developed a state-to-state molecular beam/surface scattering machine. The experiments use infrared laser excitation to prepare methane incident on a Ni(111) surface sample in a specific rovibrationally excited quantum state and probes the quantum state distribution of the scattered molecules by a cryogenic bolometer detector in combination with infrared laser tagging.

Using this setup, we have prepared incident methane with one quantum of antisymmetric C-H stretch vibration $CH_4(\nu_3)$ and measured the rovibration state distributions of the scattered molecules. We detect both vibrationally elastic and inelastic scattering of CH_4 and quantify the probabilities for the different channels. Efficient vibrational energy transfer is observed for incident $CH_4(\nu_3)$ leading to scattered $CH_4(\nu_1)$ and CH_4 (v=0).

Through chemical vapor deposition of hydrocarbons, a well ordered monolayer of carbon (graphene) can be grown on the Ni(111) surface. Scattering of a state prepared beam of $CH_4(\nu_3)$ from this C/Ni(111) surface shows a distinctly different scattering probability for both vibrationally elastic and inelastic scattering than for the clean Ni(111) surface. These new results, as well as the developed method, will be discussed.

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Study of the $N(^4S)+NO(^2\Pi)$ reactive collision at extreme temperatures relevant to the hypersonic flight regime.

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The NO molecule plays a major role in the chemistry near the surface of vehicles for atmospheric re-entry in the hypersonic flight regime. Therefore, the reactions of this system with the most common atmospheric gases, e.g. N and O, must be considered in the design of spacecraft. At the extremely high temperature typical of this regime, the experiments are difficult and expensive. Consequently, the theoretical studies became vital for the correct comprehension of the energy transfer of such molecular collisions. This work focuses on the study of the $N(^4S)+NO(^2\Pi)$ reaction using classical and quantum methods to describe the nuclear dynamics, which occur entirely in the triplet manifold. Most studies of the dynamics of this collision [1,2] have used the $^3A'$ and $^3A''$ potential energy surfaces (PESs) computed at the CASPT2 level [3]. Only very recently, new $^3A'$ and $^3A''$ PESs have been presented at the MRCI level [4]. However, these surfaces only could be used for the reverse $N_2(^1\Sigma)+O(^3P) \rightarrow N(^4S)+NO(^2\Pi)$ channel because they do not have the correct long-range behavior. Here, we develop PESs for the two lowest triplet states at the MRCI+Q level, where the correct R^{-6} asymptotic behavior is taking into account in the fitting procedure. Quasi-classical trajectory calculations have been carried out for the $N(^4S)+NO(^2\Pi)$ reaction using both PESs. Then thermal rate coefficients are determined in the 100-20000 K temperature range. Furthermore, time-independent quantum reactive scattering calculations were performed. The probabilities of reaction at several energies are reported. Finally, the results using both, classical and quantum methods, are compared.

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Spectroscopic separation of ^{13}C NMR spectra of complex isomeric mixtures by the CSSF-TOCSY-INEPT experiment

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Among the most critical parameters for NMR experiments are spectrometer stability and sensitivity. The spectrometer hardware for optimal results will depend strongly on the application used. The presentation will cover probe choice and probe design for high resolution NMR applications. The impact of the sensitivity gain by CryoProbes[1] for ^{13}C detection will be illustrated with an example of a complex mixture analysis using the CSSF-TOCSY-INEPT experiment[2].

This experiment uses the resolving power of a chemical shift selective filter (CSSF) to separate strongly overlapped ^{1}H NMR signals in complex mixtures. The selectivity of the CSSF is then amplified via magnetization transfer from the excited proton(s) to all other protons within the same coupling network during TOCSY isotropic mixing. Subsequent refocused INEPT transfer from proton to carbon spins allows then the acquisition of proton-decoupled ^{13}C sub-spectra.

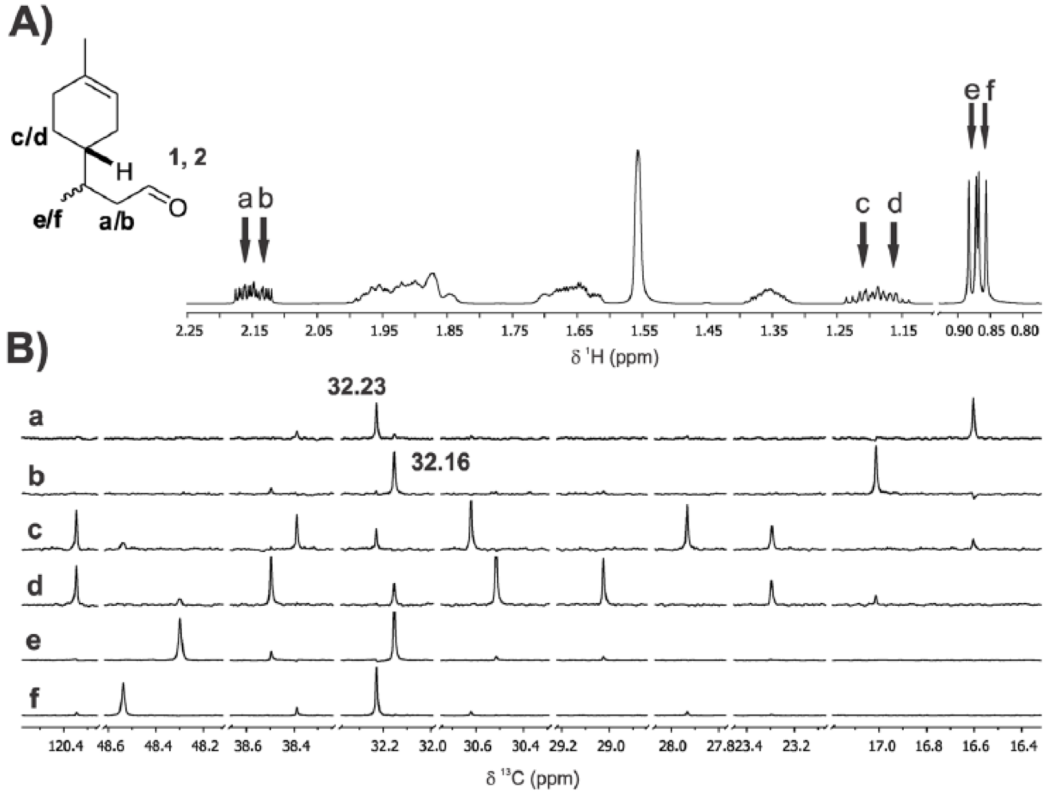

Figure: Spectroscopic separation of a 1:1 mixture of diastereomers **1** and **2** (~360mM each). (A) Selection of ^{1}H chemical shifts for selective excitation. (B) CSSF-TOCSY-INEPT experiments with ^{1}H selective excitation of a–f generate six ^{13}C NMR sub-spectra.

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Ultrafast spectroscopy as a tool to investigate the microstructure of donor-acceptor blends for organic photovoltaics

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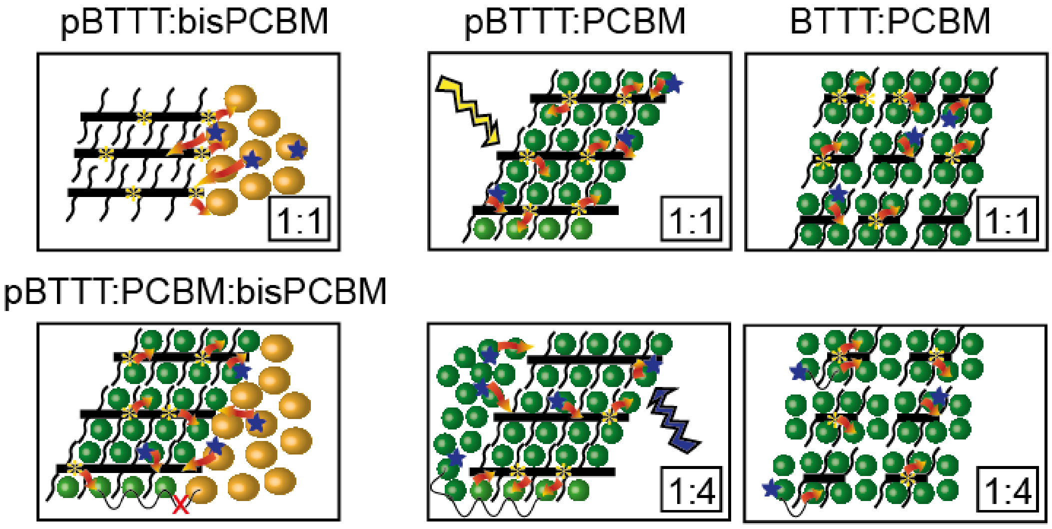
The active layer of organic solar cells consists of blends of an electron donor and an electron acceptor, known as the bulk heterojunction (BHJ). Understanding he phase morphology, i.e. the co-existence of an intermixed donor-acceptor phase with neat donor and neat acceptor domains, is important in view of its significant impact on the photovoltaic performance. In this respect, results from time-resolved spectroscopy do not only allow following charge transfer dynamics between the donor and the acceptor and the charge generation process, but, additionally, they provide information on the BHJ microstructure, which is necessary to optimise organic solar cells.
We have monitored ultrafast processes at the interface between the donor component (poly- and oligothiophene derivatives, pBTTT and BTTT respectively) and a range of fullerene acceptors (PCBM, bisPCBM and ICBA), which are different with respect to size, conjugation and electron accepting properties. Moreover, different fullerene concentrations in the blends (D:A ratio of 1:1 or 1:4 by weight) and combinations of two fullerene units with the donor in ternary systems have been investigated, in order to further address the effect of donor-acceptor phase separation.
Femtosecond transient absorption data demonstrates distinct spectral features and evolutions for the different blends, which we correlate to the diverse phase morphologies of each system. Our observations highlight how alternative acceptors and, in particular blend composition, have a specific impact on the miscibility of the acceptor with the donor and on the tendency to form fullerene domains that act as energetic sinks. The latter favours the spatial charge separation of photo-generated electron-hole pairs, playing a key role during the charge generation and collection processes.



Surface-Enhanced 2D Attenuated Total Reflectance IR Spectroscopy for Studying Surface-Sensitive Ultrafast Vibrational Dynamics

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Dynamics and structures of molecules at solid-liquid interfaces are of significant importance in chemistry and physics. To study ultrafast vibrational properties of samples near solid-liquid interfaces, we recently developed two-dimensional attenuated total reflectance infrared spectroscopy (2D ATR IR)[1-4]. 2D ATR IR spectroscopy is a third-order nonlinear method which employs short-range (sub-µm) evanescent fields at reflecting planes of an ATR crystal, guaranteeing maximum light intensity at the interface and the well-known surface-sensitivity of the ATR technique. We focus on the two most recent major developments of 2D ATR IR. Firstly, we use ultrathin (~nm) noble metal layers to immobilize molecules at the ATR interface and to enhance the weak nonlinear signals[3] from sub-monolayer surface coverages[2]. Using polarization-dependent 2D ATR IR signals, we clarify the mechanisms of signal enhancement and evaluate contributions from electromagnetic and chemical contributions[3]. We demonstrate that s-polarization (solid lines, Fig. 1 (a)) optimally enhances 2D ATR IR signals from voids between metal nanoparticles (NPs, Fig. 1 (b) – (c)), while p-polarization (dashed lines, Fig. 1 (a)) enhances signals from outside the voids with different degrees of enhancement. Secondly, we report on a combination of 2D ATR IR spectroscopy with spectroelectrochemistry (SEC), using the ultrathin conductive layers at the ATR interface as electrodes [4]. We outline experimental key-points in the development of 2D ATR IR SEC and use vibrational Stark-shift spectroscopy of carbon monoxide (CO) adsorbed to platinum (Pt) NPs to demonstrate the electrochemical performance of the electrode surfaces (Fig. 1 (d) – (g)). Furthermore, we characterize potential-dependent ultrafast vibrational relaxation as well as spectral diffusion of surface-bound CO (Fig. 1 (h)).

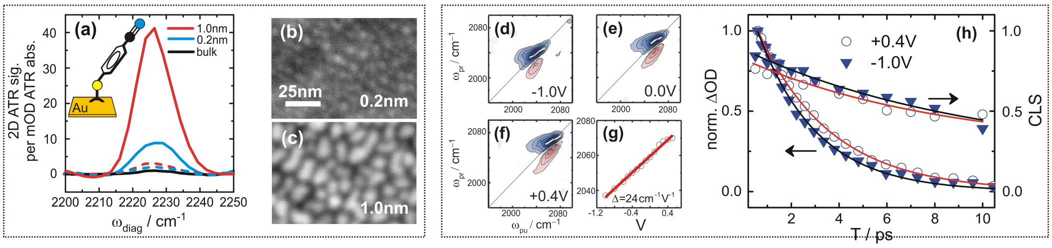

Figure 1. (a) – (c) Characterization of surface-enhancement mechanisms with diagonal 2D ATR IR signals (a) and electron-microscopy analysis (b) – (c) of different surfaces from Gold NPs. (d) – (f) 2D ATR IR SEC signals of CO adsorbed ot Pt NPs at different electrode potentials. (g) Ground-state bleach vibrational Stark-shoft signals of CO. (h) Potential-dependent vibrational relaxation (left scale) and spectral diffusion (CLS, right scale) of surfacebound CO. In (g) and (h), open symbols are experimental data, solid lines represent linear- or exponential fits.

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Direct visualization of excited-state symmetry breaking by ultrafast time-resolved infrared spectroscopy

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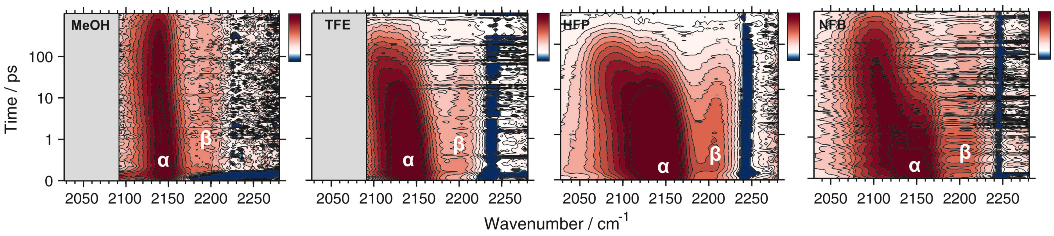
An overwhelming majority of quadrupolar and octupolar charge-transfer molecules designed for various two-photon absorption applications behave in the electronic excited state as if they were dipolar although they demonstrate the expected multipolar character in the ground state. We show that femtosecond time-resolved infrared spectroscopy spectacularly reveals symmetry breaking occurring in the excited state. This breaking leads to a rapid transformation from an initially prepared quadrupolar excited state with evenly distributed electronic excitation to a symmetry-broken state where the density of electronic excitation is different in the identical branches of the molecule. This transformation is driven by the solvent fluctuations and the rearrangement of the polar environment during the solvation of excited chromophore. We demonstrate that in highly polar solvents the process proceeds even further causing the complete localization of the electronic excitation on a single branch of the molecule. TRIR unveils the disparate spectral signatures of symmetrical, symmetry-broken and localized states and provides an unprecedented accuracy in following its dynamics. This effect is general and originates from non-specific interaction with the solvent molecules. However, we demonstrate that specific hydrogen-bonding interactions with the solvent can be utilized to enhance it even further. The dynamics of these interactions is slower than of non-specific ones and it provides an easier way to follow this process in real time. When H-bonding to the solvent is very strong it can cause the reactivity of the different identical branches within a single molecule to be vastly different. This provides means of controlling the photochemical reactivity at the different sites of the same molecule.



TRIR contour maps of the quadrupolar probe molecule in H-bonding solvents (MeOH - methanol, TFE - trifluoroethanol, HFP - hexafluoroisopropanol, NFB - nonafluorotert-butanol). Band designations are shown for early pump-probe delays. Symmetry-breaking enhancement as well as formation of stoichiometrically bound H-bonded complex are clearly seen.

Rational Design of Nitroxide Biradicals for Efficient Cross-Effect Dynamic Nuclear Polarization

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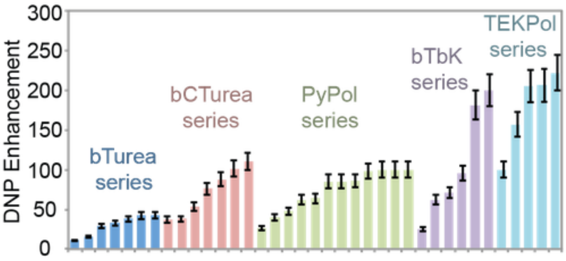
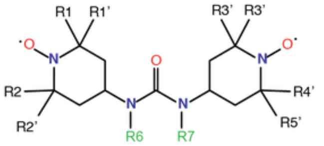
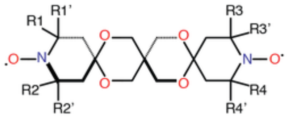
Dynamic nuclear polarization (DNP)[1-3] currently attracts considerable attention as one of the most efficient methods to increase the sensitivity of NMR experiments.

In particular, it can boost the sensitivity of magic-angle spinning (MAS) solid-state NMR experiments at low temperatures by several orders of magnitude.[4] Typically, the samples are dissolved or impregnated with a solution of stable biradicals, acting as polarizing agents capable of transferring the electron hyperpolarization through the cross-effect. Here, a series of 41 bi-nitroxide radicals has been prepared and their performance studied as polarizing agents in cross-effect DNP NMR experiments at 9.4 T and 100 K in bulk solution. We observe that in this regime the DNP performance is strongly correlated with the electron and nuclear spin relaxation times, with longer relaxation times leading to better enhancements. We observe that deuteration of the radicals generally leads to better DNP performance. One of the new radicals introduced here provides the best performance obtained so far under these conditions. In similar conditions we show that over a two-fold improvement in DNP enhancements can achieved be simply incorporating solid particles into the sample. Enhancements up to $\varepsilon_H = 515$ are obtained in this way, corresponding to 78% of the theoretical maximum.[5]





bTurea, bCTurea and PyPol series backbone



bTbK and TEKPol series backbone

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Microhydration of N1-Cytosine Derivatives

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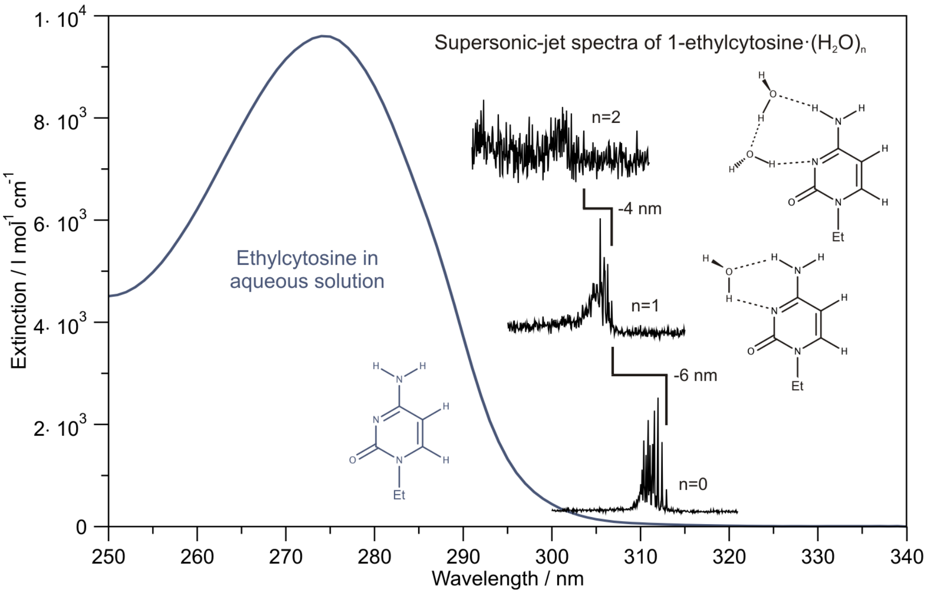
The $S_0 \rightarrow S_1$ electronic transition of cytosine as well as different N1-substituted derivatives in the gas phase, 1-methylcytosine, 1-ethylcytosine and 1-isopropylcytosine, are between 313 and 315 nm [1,2]. In contrast the red edge of the UV absorption of cytosine and N1-substituted cytidines in solution are blue shifted by ~15 nm to ~300 nm [3].

To investigate the influence of stepwise microhydration on the $S_0 \rightarrow S_1$ electronic transitions, we measured the mass-selective two-color resonant two-photon ionization and UV-UV hole-burning spectra of supersonic jet-cooled 1-ethylcytosine·$(H_2O)_n$ and 1-methyl-5,6-trimethylenecytosine·$(H_2O)_n$ with n=0-2. The n=1 clusters shift by -6 nm compared to the monomers, the n=2 clusters shift further to the blue (-4 nm) resulting in a blue shift of -10 nm compared to the bare N1-cytosines.

The most stable isomers of 1-ethylcytosine·$(H_2O)_n$ calculated at the SCS-CC2/aVDZ level are shown in the figure. Their calculated $S_0 \rightarrow S_1$ electronic origins are blue-shifted relative to the monomer and are in very good agreement with the experimental values.



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