

4.18 Project part P18

Femto-chemical physics in complex molecules: from electronic coherence and nuclear wavepackets to populations

Principal investigators:

Harald F. Kauffmann
Institut für Physikalische Chemie, Universität Wien
Währingerstr. 42, A-1090 Wien, Austria
Phone: +43 1 4277 52429
Fax: +43 1 4277 9524
Email: harald.f.kauffmann@univie.ac.at

Eberhard Riedle
LS für BioMolekulare Optik
Department für Physik
Ludwig-Maximilians-Universität München
Oettingenstraße 67, D-80538 München
Phone: +49 89 2180 9210
Fax: +43 89 2180 9202
Email: riedle@physik.uni-muenchen.de

Allocation to technical disciplines (according to code of OeStat*)

1	%	2	%	3	%
1327	50	1230	30	1311	20

4.18.1 Summary

The relaxation of the electronic phase due to its coupling to nuclear dynamics is a crucial and unexplained issue in the primary dynamics after femtosecond excitation of molecular systems. In the project P18 new concepts and experiments were developed and technical strategies devised to measure molecular coherence and, from coherence loss (decoherence) experiments, to tackle electronic inter-site coupling and electron-phonon coupling in molecular many bodies. Special emphasis was placed on the electronic coherence problem in conjugated polymeric/oligomeric site arrays.

The high-repetitive Coherent RegA pump source was successfully coupled to a specially adapted noncollinear optical parametric amplifier (NOPA). This combination – pulses of some 100 nJ with sub-20 fs temporal width, 200 kHz repetition rate and tunability in the region from 470 to 720 nm - is particularly novel and opens a new frontier in the instrumentation of photo-echo techniques. A great deal of expertise has been acquired that now enables access to the aimed measurement of photon-echo $P^{(3)}$ signals. Various photon-echo experiments have been performed with this system and with pulses as short as 8 fs from a 1 kHz NOPA. For the kHz system major improvements were achieved in the compression of visible pulses to below 10 fs, the conversion to 7 fs UV pulses by achromatic phase matching and the full analysis of all pulses by the novel ZAP-SPIDER. Phase-locked pulse trains at three independently chosen wavelengths were used for gated heterodyne detected CARS microscopy.

Systematic photon-echo studies have been made on the electronic phase-relaxation of low molecular weight dye-type oligomers in fluid solutions and on the coherence loss in conjugated polymers, both in liquid solution and in the solid state. Rigid, segment-type dye model compounds (PERY, Nile-Blue, DTCI) in solution show long-lived vibrational beating (which survive on early picosecond scales), whereas flexible model compounds (stilbene-type homologs, Rhodamine B) with soft torsional coordinates demonstrate strong damping. For polymers, however, the nuclear oscillations are totally eroded on a scale of a few hundred femtoseconds. The echo peak-shifts are, however, quite large which strongly points to inter-segmental excitonic coupling as the predominant correlation mechanism. The fluorescence in NH_2 -substituted N-Aminoperylene-3,4:9,10-tetra-carboxyl-bisimide was found to be quenched by Pauli-blocking within 1 ps. The generated mini-polaron decays in 3.5 ps by hole back transfer.

The achievements made in the ADLIS II program will have strong impact on the key heterodyning experiments in the follow-up ADLIS III-program and hence ensure the long-term significance of forthcoming 2-D molecular excitonics.

4.18.2 Results and discussion

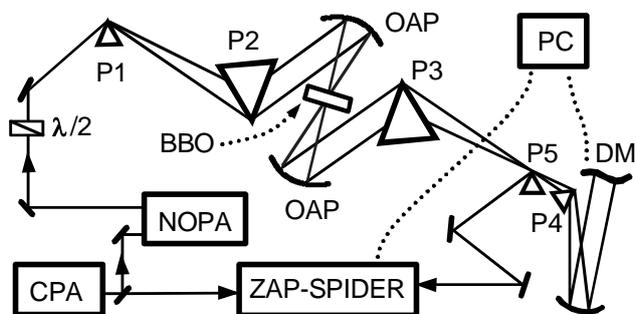
The focus of the proposed research was the experimental investigation of electronic & nuclear coherences (wavepackets) and their dephasing into uncorrelated populations. Electronic coherences in condensed phase molecular systems dephase in tenths of femtoseconds and vibrational coherences on the timescale of a picosecond. The essential prerequisite for all investigations is therefore the availability and control of ultrashort pulses with a duration down to 10 fs at the visible and UV absorption wavelengths of the systems under investigation. Noncollinear optical parametric amplifiers (NOPAs) serve as the prime source and major efforts were undertaken to incorporate these into the spectroscopic experiments.

Tunable sub-10-fs visible pulses

The generation of sufficiently broad pulse spectra to support sub-10-fs pulses throughout the visible was demonstrated previously. In these experiments a deformable mirror was used for control of the residual spectral phase deviation left by a prism compressor. The deformable mirror led, however, to significant lateral displacement of individual spectral components in the beam. The same was found for a permanently deformed mirror of proper shape. The envisioned use of a programmable dispersive filter (Dazzler) proved impractical, since it is not yet available with sufficient bandwidth in the blue-green part of the visible spectrum. The previously available chirped mirror designs with near normal incidence that are highly successful in many parts of ADLIS were found to display unfavorable dispersion oscillations at the desired short wavelengths. We therefore turned to a recently proposed idea of Brewster angled chirped mirrors (Steinmeyer2003). A combination of a fused silica prism compressor and typically 32 reflections on the Brewster chirped mirrors allows the generation of 5.6 fs pulses or alternatively nearly Fourier limited 10-fs pulses tunable throughout most of the visible (Baum2005a).

7 fs UV pulses

Ultrashort UV pulses cannot be generated directly but rather primary sources in the visible have to be converted by nonlinear optics. The second harmonic generation from visible NOPAs renders insufficient spectral bandwidth for 10-fs pulses in the UV even for very thin nonlinear crystals. We therefore used achromatic phase matching in the geometry shown in the



accompanying figure to generate UV pulse spectra sufficient to support a 2.9 fs pulse (Baum2004a and 2004b). Slightly limited spectra were compressed to an unprecedented level of 7.1 fs or to tunable 10-fs UV pulses.

ZAP-SPIDER

Conventional FROG and SPIDER (spectral phase interferometry for direct electric-field reconstruction) setups require ultrabroadband beam splitters and introduce additional dispersion by the substrates. These problems are particularly detrimental in the UV and full characterizations of ultrashort UV pulses were hitherto not possible. We developed a novel spectral-shearing interferometry setup with **Z**ero **A**dditional **P**hase that avoids all the aforementioned problems by using the unaltered pulse to be measured and suitably modified auxiliary pulses from the Ti:sapphire regenerative amplifier. ZAP-SPIDER can precisely characterize sub-10 fs pulses in the UV and the visible within the same setup (Baum2004c and 2005b).

Pulse shaping

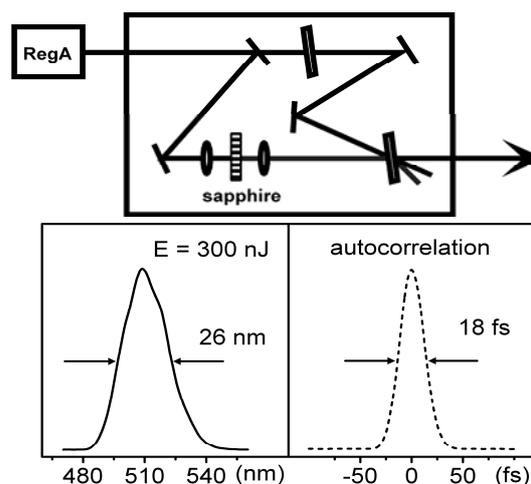
Shaping of ultrashort pulses in the visible and NIR is now an established technique used in many laboratories. Typically, the pulses are transversally dispersed in a 4-f setup and an LCD or acousto-optic modulator is used in the Fourier plane. This is not possible in the UV since the available modulators have no sufficient transmission in this spectral region. We developed a scheme to transfer shaped tunable visible pulses from a NOPA to the UV by sum frequency mixing with chirped pulses from the Ti:sapphire regenerative amplifier (Schriever2005). In this way arbitrarily structured UV pulses with substructures as short as 20 fs can be generated.

Phase control and heterodyne detection

A triple NOPA was developed that generates three independently tunable pulse trains with locking of the phase to better than 250 mrad (Baum2005c). This high degree of interpulse coherence was measured by gated heterodyne detected Coherent Antistokes Raman Scattering (GH-CARS). The pulses were already used for CARS microscopy with a high degree of suppression of the nonresonant background signal (Greve2005).

Tunable visible sub-20 fs pulses at 200 kHz

At the time of the project application we envisioned that it would be possible to pump a NOPA with the output of a commercially available kHz multipass amplifier delivering sub-30 fs pulse around 800 nm and thus provide the needed sub-20 fs visible pulses in the Vienna laboratory. Unfortunately, this approach did not prove to be successful due to insufficient quality of the pump beam. An alternative approach was therefore successfully implemented.



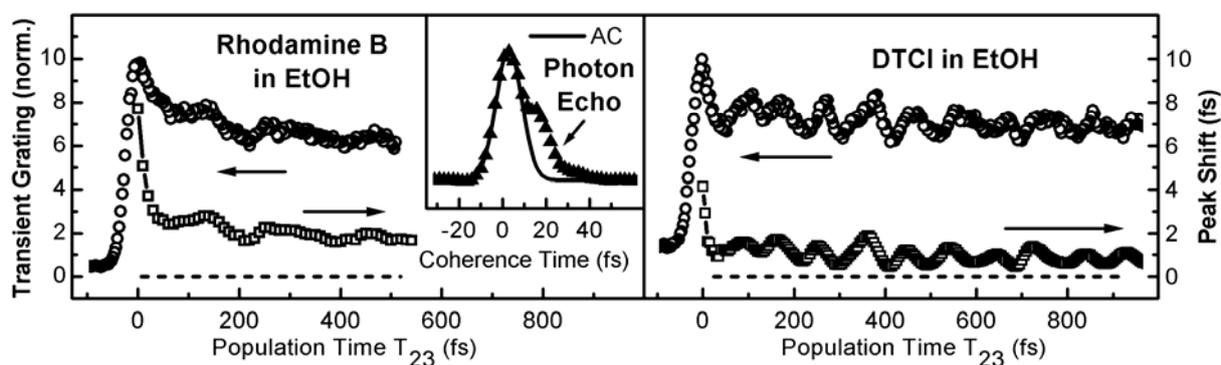
As shown in the accompanying figure, a 200-kHz Ti:sapphire amplifier (RegA, improved stability due to a recently procured VERDI 18W pump laser) that delivers 6 μ J pulses with 40 fs duration is used as pump source for a one-stage NOPA. The beam propagation within this low pump power, high repetition rate NOPA is redesigned from the standard 1 kHz, high pump power system. In addition, the usual 3 mm sapphire plate used for the seed continuum generation is replaced by a 1 mm plate to further reduce dispersion and increase the spectral bandwidth. In this way we obtain fully tunable pulses with up to 300 nJ energy and a sub-20 fs duration in the orange red/part of the spectrum. In the blue green part that is particularly important for the experiments on polymers (see below) we can still reliably generate 20 fs pulses. In the figure 26 nm wide pulses centered at 510 nm are shown with an extremely clean pulse shape of 18 fs duration.

The resulting new pulse source is ideally suited to the highly demanding photon echo experiments due to the following properties: 1) Highest stability due to all solid state laser pumping. 2) 200 kHz repetition rate that allows lock-in detection of 3-pulse PEs in twin-configuration for the peak shift measurements and therefore an extremely high detection sensitivity. 3) Dramatically reduced pulse length and increased pulse energy compared to the commercially available collinear OPA. 4) Extremely stable operation and ease of alignment.

Photon-Echo experiments with tunable sub-20 fs pulses

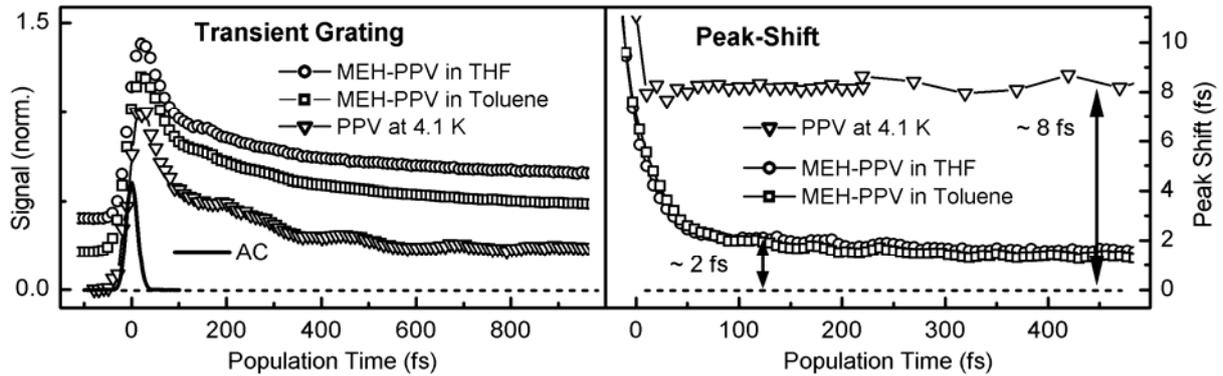
The method of choice for the investigation of the ultrafast electronic coherence in condensed phase molecules are photon-echo (PE) experiments in various complexities. Such experiments have been successfully performed with 10 to 20 fs pulses from Ti:sapphire systems, i.e. around 800 nm center wavelength. This approach is, however, not applicable for the molecules in the focus of our interest. We therefore explored the possibilities to

perform such measurements with a high demand on the stability of the light source with the output of NOPAs.



First experiments were jointly performed between members of the Vienna subgroup and the Munich one in the Munich laboratory at 1 kHz repetition rate. With various dyes in liquid solution as test samples for absorbers throughout the visible, PE peak shift and transient grating (TG) measurements were performed. In systematic 3-pulse peak-shift experiments (PEPS) with extremely clean (Gaussian shaped) 20 fs pulses the soft coordinates of torsional motion that are believed to be the predominant channel for structural dephasing have been studied by varying π -conjugated segmental model-compounds from *flexible* to *rigid*. In the figure TG (circles) and 3-pulse PEPS (squares) are compared for Rhodamine B and DTCl. The measurements show that:

- The TG-profiles are characterized by pronounced vibronic oscillations on top of the spectral diffusion (population decay). In the *flexible* Rhodamine B the vibronic coherences are damped on a 500 fs scale, whereas in the more *rigid* DTCl the nuclear coherences (main frequencies at 170, 350 and 580 cm^{-1}) are hardly affected in this time regime and can be measured as persistent oscillations up to 5 ps!
- The PEPS signals display essentially the same patterns as the TG profiles both with regard to the oscillatory and the damped part, thus clearly indicating an intra-molecular origin.
- The effect of the solvent – solute scattering is only weak, so torsional / vibrational coupling from typically internal molecular ‘phonons’ is the predominant mechanism of coherence loss.
- In addition, distinctively asymmetric 2-pulse PE decays (with 8 fs excitation) at room temperature revealed the *electronic* intra-solute dephasing on a sub 50 fs time scale ($T_2 \sim 45$ fs for Rhodamine B). The measurements confirm the working-hypothesis: *The more flexible the molecular structures, the shorter the dephasing times!*



Decoherence in disordered, multi-site conjugated polymers

As soon as the 200 kHz NOPA became available, it was integrated into the 3-pulse PE set-up and used for the investigation of the hitherto unknown coherence, decoherence phenomena in the disordered, segmental multi-site system of the conjugated polymer PPV at low phonon temperatures. We find that this novel combination is the ideal setup for comparative measurements of the electronic phase relaxation at cryogenic temperatures and at room temperature. Correlated fluorescence interferometry had previously been used to detect coherent kernels in the DOS-bottom-states of PPV, i.e. *below* the migrational threshold, where the site-site energy transfer is negligible (Milota2004a). The approximate 130 fs damping of the interferogram was interpreted as the formation of the structurally relaxed exciton in PPV (Milota2004b). In conjunction with these previous results on homogeneous site dephasing, we performed time integrated 1-D PEPS and TG measurements as well as 2-D homodyned 3-pulse PEs on various polymer samples. In the above figure traces are shown for MEH-PPV in room temperature solutions and for PPV at 4.2 K. We could demonstrate that

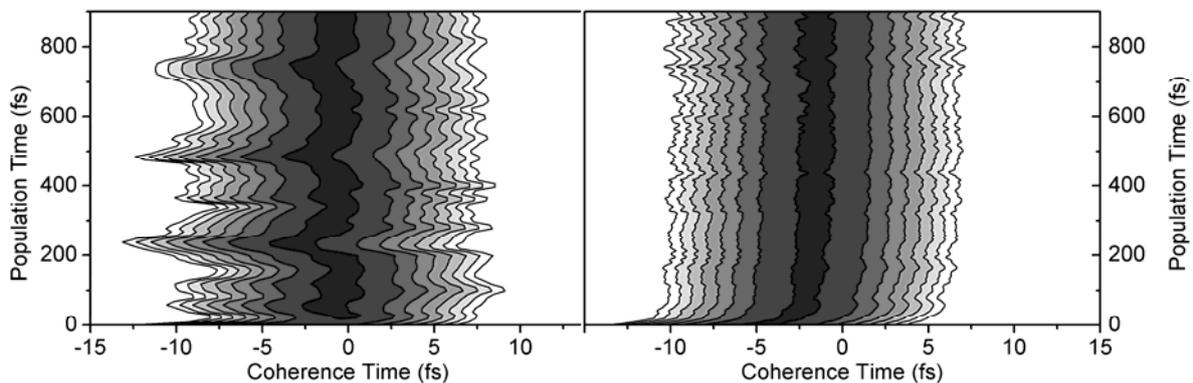
- the electronic coherence decay ($\tau = 20$ fs) can be resolved, for the first time, from the initial steep slope of the peak-shift relaxation.
- the absolute value of the initial peak-shift σ is substantially larger than those of molecular model dyes, clearly indicating *excitonic coupling*.
- for PPV at 4.2 K the initial peak-shift value of more than 11 fs pronouncedly exceeds those obtained for bulk PPV at RT (~ 7 fs) and for MEH-PPV in solutions at RT (~ 2 fs) which gives strong impact on the destructive role of thermal polymer-intrinsic phonons on the strength of initial coherent exciton coupling.
- generally, a residual σ -value is observed for conjugated polymers which evidences the inhomogeneity of the site-ensemble (residual inhomogeneous broadening). It is

small at RT ($\sigma = 1$ to 2 fs, motional narrowing), but very significant under quasi-static site-energy disorder and at 4.2 K ($\sigma = 8$ to 10 fs).

- The observed peak-shifts measured with the 20 fs pulses and discussed above directly report on *excitonic couplings* !

From the TG-patterns of the conjugated polymers we learned:

- the first observation of a significant nuclear coherence (beating mode $\sim 350 \text{ cm}^{-1}$) which is dominating the sub-1 ps temporal regime of the population decay.
- although strongly eroded, the oscillations are still observable for the MEH-PPV derivative dissolved in THF and toluene. Both internal (predominantly, polymer-intrinsic motions controlling the decay) and external phonon-reservoirs (site-solvent scattering, to a minor extent) cannot completely damp out the wavepacket on this timescale.



Finally, the above figures depict 2-D homodyned 3-pulse PE profiles, both inter-pulse delays T_{12}, T_{23} are varied in this time integrated technique which probes the square of the third – order polarization signal pulse $|P^{(3)}(T_{12}, T_{23})|^2$. The curves (left: the rigid PERY dye with persistent oscillations, right: the totally flexible, overdamped MEH-PPV) show in a 2D fashion what is, in principle, already known from the corresponding 1-D plots above, but the representation in two time-axes allows one to appreciate the enormous potential of this method, if, in lieu of the square, the amplitude and the phase of the diffracted electric field can be measured (cf. P18, proposal-book).

Vibrational coherence in excited state proton transfer (ESIPT)

A high degree of vibronic wavepacket contribution to the ultrafast pump-probe signal was recently demonstrated in a number of model compounds (Lochbrunner2004). In collaboration with P09 and the group of de Vivie-Riedle (Dept. Chemie, LMU München) benchmark calculations were now performed to interpret these findings. For HBT and 10-HBQ time dependent DFT calculations were used to obtain a 2D potential energy surface for the ground and first excited electronic state with full optimization of all other intramolecular coordinates. The minimum energy path (MEP) in S_1 and on-the-fly molecular dynamics simulations clearly show that slow nuclear motions are decisive for the transfer of the highly mobile proton. Additional normal mode analyses along the MEP and quantumdynamic wavepacket propagation including laser excitation reveal that the vibrational coherence is to a large part generated by the reactive process and not just the optical excitation.

Intramolecular exciton dynamics

For the investigation of the primary relaxation processes in medium size molecules we used various substituted N-Aminoperylene-3,4:9,10-tetra-carboxyl-bisimides (perylene dyes) synthesized by Langhals and coworkers, in particular the NH_2 -substituted J-57 (Mohr2000). We find that all relevant spectral signatures of the perylene dyes lie within the fundamental tuning range of the NOPA and the continuum generated in a sapphire plate. The dyes absorb between 450 and 540 nm, fluoresce between 520 and 630 nm and a significant transient absorption of the S_1 state is centered around 700 nm. We used these various signatures to show that for perylene dyes with high fluorescence quantum yield (close to unity) only a picosecond vibrational relaxation is found. On the contrary, for J-57 no significant fluorescence was reported and we determined a 1.0 ps decay of the fluorescence. The transient absorption does, however, decay with the slower time of 3.5 ps. By comparison with the reported spectrum of the perylene radical anion we can conclude, that this slower transient is due to the spectral superposition of the neutral and anion perylene. The 1.0 ps time corresponds to the transfer of a HOMO electron from the NH_2 to the hole generated by the optical excitation in the perylene HOMO. The relevant process for the fluorescence quenching is therefore identified as Pauli blocking. The generated mini-polaron decays in 3.5 ps by electron-hole recombination.

Cooperation with Shaul Mukamel's group

For the typically "ill-condensed" conjugated polymers like MEH-PPV, with dynamic fluctuations on early fs-scales (internal and external phonons/torsio-vibrations, structural dephasing), and static site-disorder in energy space and off-diagonal coupling, the intimate interrelation between experimental NL observables and theoretical, optical response averages is indispensable (Zhang1999). The nonlinear exciton equations (Chernyak1998) in conjunction with the coupled electron-oscillator (CEO)-quantum-chemical method (Mukamel1997, Schulz2000) provide such a framework. We have demonstrated the utility of these equations by applying them to the pump-probe simulation of quantum-stochastic excitation funneling in a (rigid) dendrimer (Tortschanoff2002). J. Sperling (coworker in P18) currently works in Mukamel's group and is analyzing our experimental photon-echo data. The combined experimental and theoretical findings are beginning to give a consolidated understanding of the dephasing dynamics and a joint manuscript about the results is in preparation.

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P18 - Femto-chemical physics in complex molecules: from electronic coherence and nuclear wavepackets to populations (Kauffmann/Riedle)

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4.18.3 Collaboration within and beyond the SFB

- Discussions with scientists from P02 were most helpful in the design of novel – Brewster angle based – chirped mirrors that allowed the convenient compression of the tunable output from the NOPA to sub-10 fs duration. Techniques of the broadband noncollinear optical parametric amplification that is used in the NOPAs are now also advanced in the generation of high pulse energy phase stabilized pulses (P02).
- Potential energy hypersurfaces were calculated by P09 for ES IPT systems measured in Munich. These allow for the first time the ab-initio simulation of the ultrafast proton transfer dynamics with extremely good agreement between theory and experiment.
- Fruitful discussions with P12 (G. Reider) about the use of diffractive optics to be implemented into the 3-pulse delay line of the photon-echo experiment – phase-locked pulses via Fourier optics have been, meanwhile, achieved.
- Quite useful overlaps with P09 (H. Lischka/W. Jakubetz): translate the photon-echo phase loss measurements of PPV-units into a chemical picture - extension on the chemical background of the structural relaxation process by quantum-chemical calculation and simulation.

- The problems of implementing free-standing probes in photon-echo spectroscopy, discussion on strategies toward manufacturing nanoscopic two-site systems (P06, G. Strasser).
- Preliminary discussions with P03 (Ch. Spielmann) on the spatio-temporal dynamics of electron-phonon coupling – methodological comparison: sub-100 fs structural relaxation (3-PPEs) versus its structural analog (Time-resolved optical pump/X-ray probe spectroscopy).