

Publications using Clark-MXR Lasers

Ultrafast Energy Transfer between the $^3\text{MLCT}$ State of $[\text{Ru}^{\text{II}}(\text{dmb})_2(\text{bpy-an})]^{2+}$ and the Covalently Appended Anthracene

Jon R. Schoonover, Dana M. Dattelbaum, Anton Malko, Victor I. Klimov, and Thomas J. Meyer, David J. Styers-Barnett, Erika Z. Gannon, Jeremy C. Granger, W. Steven Aldridge, III, and John M. Papanikolas

The time scale for triplet-triplet energy transfer (EnT) between a Ru(II) chromophore and a ligand bound anthracene acceptor in $[\text{Ru}^{\text{II}}(\text{dmb})_2(\text{bpy-an})]^{2+}$ (dmb = 4,4'-dimethyl-2,2-bipyridine; bpy-an = 4-(9-anthrylethylene), 4-methyl-2,2-bipyridine) has been measured using femtosecond transient absorption spectroscopy. The appearance of the anthracene excited state is monitored following photoexcitation to a metal-to-ligand charge transfer (MLCT) state via the $\pi\pi^*$ absorption of the triplet excited state of anthracene. Our time-resolved experiments show the presence of fast, sub-100 ps energy transfer to the anthracene occurring on two characteristic time scales of 23 and 72 ps.

J. Phys. Chem. A 2005, 109, 2472-2475

Ultrafast optical and magneto-optical studies of III-V ferromagnetic semiconductors

J. WANG, G. A. KHODAPARAST, J. KONO, A. OIWA and H. MUNEKATA

We use ultrafast optical techniques to investigate the dynamics of charge and spin carriers and coherent phonons as well as magnetic order in III-V ferromagnetic semiconductors. We observe a rich array of dynamical phenomena that are absent in traditional nonmagnetic semiconductors or metallic ferromagnets. Very short charge and spin lifetimes of the photoinjected carriers (~ 2 ps) and multi-level charge decay dynamics are observed, which are attributed to a large density of mid-bandgap states introduced during low temperature molecular beam epitaxy (LT-MBE) growth and highly p-type Mn doping. During the very short free carrier lifetime, the coercivity of the system is seen to be reduced. We attribute this photo-induced 'softening' to the transient modification of carrier-mediated ferromagnetic exchange coupling between Mn spins. After the photogenerated free electrons are trapped by defects, periodic oscillations appear in differential reflectivity due to the coherent generation of acoustic phonon wavepackets.

Journal of modern optics, 10 november-15 december 2004 vol. 51, no. 16-18, 2771-2780

Trimming phase and birefringence errors in planar lightwave circuits with deep ultraviolet femtosecond laser

Q. Chen, K.P. Chen, M. Buric and S. Nikumb

A deep ultraviolet femtosecond laser was employed to trim phase and birefringence errors in silica planar lightwave circuits. A permanent refractive index change of $\sim 3.8 \times 10^{-4}$ and a birefringence change of 1.08×10^{-4} were induced in hydrogen-free Mach-Zehnder planar waveguide circuits. The ultrafast laser enhances the ultraviolet photosensitivity response in silica waveguides by two orders of magnitude greater than that of a nanosecond 248 nm KrF excimer laser.

Stability of High-Density One-Dimensional Excitons in Carbon Nanotubes under High Laser Excitation

G. N. Ostojic, S. Zaric, and J. Kono, V. C. Moore, R. H. Hauge, and R. E. Smalley

Through ultrafast pump-probe spectroscopy with intense pump pulses and a wide continuum probe, we show that interband exciton peaks in single-walled carbon nanotubes (SWNTs) are extremely stable under high laser excitations. Estimates of the initial densities of excitons from the excitation conditions, combined with recent theoretical calculations of exciton Bohr radii for SWNTs, suggest that their positions do not change at all even near the Mott density. In addition, we found that the presence of lowest-subband excitons broadens all absorption peaks, including those in the second-subband range, which provides a consistent explanation for the complex spectral dependence of pump-probe signals reported for SWNTs.

PHYSICAL REVIEW LETTERS, 94, 097401 (2005)

Tunable femtosecond pulses in the near-ultraviolet from ultrabroadband parametric amplification

Pancho Tzankov, Torsten Fiebig, Ivan Buchvarov

Using an ultrabroadband amplification technique in a **b**-barium borate noncollinear optical parametric amplifier, pumped by the third harmonic of a 1 kHz Ti:sapphire laser, we generate tunable femtosecond pulses in the range of 335–480 nm with energies of a few hundred nJ. The developed setup is an amplification source with a bandwidth of more than 200 THz and provides femtosecond pulses in the near-ultraviolet spectral range using coherent amplification. Parts of the amplified white-light continuum spectrum were compressed to 24–35 fs using a prism pair. Further improvements could make it possible to generate tunable ultraviolet pulses as short as 4–5 fs.

APPLIED PHYSICS LETTERS, Vol. 82, No. 4, January 27, 2003

Investigation of nonlinear absorption processes with femtosecond light pulses in lithium niobate crystals

O. Beyer, D. Maxein, K. Buse, B. Sturman, H. T. Hsieh and D. Psaltis

The propagation of high-power femtosecond light pulses in lithium niobate crystals (LiNbO₃) is investigated experimentally and theoretically in collinear pump-probe transmission experiments. It is found within a wide intensity range that a strong decrease of the pump transmission coefficient at wavelength 388 nm fully complies with the model of two-photon absorption; the corresponding nonlinear absorption coefficient is $\beta_p \approx 3.5$ cm/GW. Furthermore, strong pump pulses induce a considerable absorption for the probe at 776 nm. The dependence of the probe transmission coefficient on the time delay Δt between probe and pump pulses is characterized by a narrow dip (at $\Delta t \approx 0$) and a long (on the picosecond time scale) lasting plateau. The dip is due to direct two-photon transitions involving pump and probe photons; the corresponding nonlinear

absorption coefficient is $\beta_r \approx 0.9$ cm/GW. The plateau absorption is caused by the presence of pump-excited charge carriers; the effective absorption cross section at 776 nm is $\sigma_p \approx 3.5 \times 10^{-18}$ cm². The above nonlinear absorption parameters are not strongly polarization sensitive. No specific manifestations of the relaxation of hot carriers are found for a pulse duration of ≈ 0.24 ps.

PHYSICAL REVIEW E 71, 056603 s2005d

Femtosecond time-resolved absorption processes in lithium niobate crystals

O. Beyer, D. Maxein, K. Buse, B. Sturman, H. T. Hsieh and D. Psaltis

Femtosecond pump pulses are strongly attenuated in lithium niobate owing to two-photon absorption; the relevant nonlinear coefficient β_p ranges from ~ 3.5 cm/GW for $\lambda_p = 388$ nm to ~ 0.1 cm/GW for 514 nm. In collinear pump-probe experiments the probe transmission at the double pump wavelength $2\lambda_p = 776$ nm is controlled by two different processes: A direct absorption process involving pump and probe photons ($\beta_r \approx 0.9$ cm/GW) leads to a pronounced short-duration transmission dip, whereas the probe absorption by pump-excited charge carriers results in a long-duration plateau. Coherent pump-probe interactions are of no importance. Hot-carrier relaxation occurs on the time scale of ≤ 0.1 ps.

OPTICS LETTERS, Vol. 30, No. 11, June 1, 2005

Direct measurement of the group-velocity mismatch and derivation of the refractive index dispersion for a variety of solvents in the ultraviolet

Ida Z. Kozma, Patrizia Krok, and Eberhard Riedle

A new method, to our knowledge, for use in the ultraviolet spectral range was developed for the direct measurement of the group-velocity mismatch (GVM) between two ultrashort pulses. It is based on a standard pump-probe spectroscopic arrangement. From the measured wavelength dependence of the GVM, the refractive-index dispersion can be determined if refractive-index data at one reference wavelength are known. The GVM was measured, and dispersion formulas were derived at room temperature in the 230 to 640 nm spectral range for 2-propanol, acetonitrile, cyclohexane, dimethyl sulfoxide, ethanol, ethyl acetate, ethylene glycol, methanol, *n*-hexane, toluene, and water. The results obtained for water show a good agreement with available experimental data.

J. Opt. Soc. Am. B, Vol. 22, No. 7, July 2005

Ultrafast excited-state proton transfer and subsequent coherent skeletal motion of 2-(2'-hydroxyphenyl)benzothiazole

S. Lochbrunner, A. J. Wurzer, and E. Riedle

The excited-state intramolecular proton transfer of 2-(2'-hydroxyphenyl)benzothiazole was investigated with 30 fs temporal resolution. The proton takes 60 fs to arrive at its S₁ equilibrium position and the electron distribution changes on the same time scale. The molecule cannot adjust to the new structure of the H-chelate ring equally fast and starts to strongly vibrate in four low-frequency skeletal modes. This coherent wave packet motion is the cause of the experimentally observed strong signal oscillations that are only weakly damped despite the solvent environment.

pH-Dependent Photoisomerization of Retinal in Proteorhodopsin

Robert Huber, Thomas Koehler, Martin O. Lenz, Ernst Bamberg, Rolf Kalmbach, Martin Engelhard and Josef Wachtveitl

The early steps in the photocycle of the bacterial proton pump proteorhodopsin (PR) were analyzed by ultrafast pump/probe spectroscopy to compare the rate of retinal isomerization at alkaline and acidic pH values. At pH 9, the functionally important primary proton acceptor (Asp97, $pK_a \approx 7.7$) is negatively charged; consequently, a reaction cycle analogous to the archaeal bacteriorhodopsin (BR) is observed. The excited electronic state of PR displays a pronounced biphasic decay with time constants of 400 fs and 8 ps. At pH 6 where Asp97 is protonated a similar biphasic decay is observed, although it is significantly slower (700 fs and 15 ps). The results indicate, in agreement to similar findings in other retinal proteins, that also in PR the charge distribution within the chromophore binding pocket is a major determinant for the rate and the efficiency of the primary reaction.

Biochemistry 2005, 44, 1800-1806

A Fast Photoswitch for Minimally Perturbed Peptides: Investigation of the trans \rightarrow cis Photoisomerization of N-Methylthioacetamide

Jan Helbing, Harald Bregy, Jens Bredenbeck, Rolf Pfister, Peter Hamm, Robert Huber, Josef Wachtveitl, Luca De Vico, and Massimo Olivucci

Thio amino acids can be integrated into the backbone of peptides without significantly perturbing their structure. In this contribution we use ultrafast infrared and visible spectroscopy as well as state-of-the-art ab initio computations to investigate the photoisomerization of the trans form of N-methylthioacetamide (NMTAA) as a model conformational photoswitch. Following the S_2 excitation of trans-NMTAA in water, the return of the molecule into the trans ground state and the formation of the cis isomer is observed on a dual time scale, with a fast component of 8-9 ps and a slow time constant of ~ 250 ps. On both time scales the probability of isomerization to the cis form is found to be 30-40%, independently of excitation wavelength. Ab initio CASPT2//CASSCF photochemical reaction path calculations indicate that, in vacuo, the trans \rightarrow cis isomerization event takes place on the S_1 and/or T_1 triplet potential energy surfaces and is controlled by very small energy barriers, in agreement with the experimentally observed picosecond time scale. Furthermore, the calculations identify one S_2/S_1 and four nearly isoenergetic S_1/S_0 conical intersection decay channels. In line with the observed isomerization probability, only one of the S_1/S_0 conical intersections yields the cis conformation upon $S_1 \rightarrow S_0$ decay. A substantially equivalent excited-state relaxation results from four T_1/S_0 intersystem crossing points.

J. AM. CHEM. SOC. 2004, 126, 8823-8834

Femtosecond transient absorption spectroscopy of single-walled carbon nanotubes in aqueous surfactant suspensions: Determination of the lifetime of the lowest excited state

J.-P. Yang, M. M. Kappes, H. Hippler and A.-N. Unterreiner

Femtosecond one- and two-colour pump–probe spectroscopy of single-walled carbon nanotubes (SWNTs) individual in aqueous surfactant suspensions has been used to assess the “intrinsic” lifetime of the lowest excited states. We demonstrate that such measurements can be perturbed by several competing photophysical processes thus making lifetime deconvolution difficult. Furthermore we show how these effects, arising primarily from sample heterogeneity, can be reduced. Measurements of induced transients in the near IR yield lifetimes of (35 ± 10) ps and (56 ± 10) ps, for nanotubes having mean diameters of 0.95 and 1.2 nm, respectively. Furthermore, a fast decay component in the ps to sub-ps regime is also observed. We tentatively attribute this to relaxation in SWNT bundle components.

Phys. Chem. Chem. Phys., 2005, 7, 512 – 517

Interligand Electron Transfer Determines Triplet Excited State Electron Injection in RuN3-Sensitized TiO₂ Films

Gabor Benko, Jani Kallioinen, Pasi Myllyperkio, Florentina Trif, Jouko E. I. Korppi-Tommola, Arkady P. Yartsev, and Villy Sundstrom

Electron injection from the transition metal complex $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ (dcbpy = 2,2'-bipyridine-4,4'-dicarboxylate) into a titanium dioxide nanoparticle film occurs along two pathways. The dominating part of the electron injection proceeds from the initially excited singlet state of the sensitizer into the conduction band of the semiconductor on the sub-hundred-femtosecond time scale. The slower part of the injection occurs from the thermalized triplet excited state on the picosecond time scale in a nonexponential fashion, as was shown in a previous study (Benko, G.; et al. *J. Am. Chem. Soc.* 2002, 124, 489). Here we show that the slower channel of injection is the result of the excited state being localized on a ligand of the sensitizer that is not attached to the semiconductor; hence, the electron cannot be injected directly from such an excited state into the semiconductor. Before being injected, it has to be transferred from the non-surface-attached ligand to the attached one. The results show that the interligand electron-transfer time is on the picosecond time scale, depends on the relative energies of the two ligands, and controls the electron injection from the excited triplet state of the sensitizer. The findings provide information relevant to the design of molecular-based assemblies and devices.

J. Phys. Chem. B 2004, 108, 2862-2867

Photochemistry of 2-(2'-Hydroxyphenyl)benzothiazole Encapsulated in Nanosized Zeolites

S. Mintova, V. De Waele, M. Holzl, U. Schmidhammer, B. Mihailova, E. Riedle, and T. Bein

The in situ incorporation and characterization of 2-(2'-hydroxyphenyl)benzothiazole (HBT) in the cages of nanosized FAU zeolites is reported. We demonstrate the advantage of using colloidal zeolite solutions to perform subpicosecond transient experiments on nanosized host/guest systems. FAU molecular sieve is prepared from precursor solutions containing as organic template only tetramethylammonium hydroxide (TMA) or both molecules HBT and TMA, using a hydrothermal treatment at 90 °C for 70 h. In situ dynamic light scattering investigations of the precursor solutions and the crystalline suspensions are performed with the original sample concentrations using a backscattering mode. The radius of the amorphous entities formed in the TMA-containing precursor solutions is about 25 nm, while that of the amorphous species in the HBT/TMA precursor solution is about 15 nm. The final particle size of FAU and HBT/FAU colloidal

zeolites is 100 and 80 nm, respectively. The encapsulation of HBT with different concentrations into the large pore FAU molecular sieve host is confirmed by Raman, infrared, and ^{13}C solid-state NMR spectroscopies. The spectroscopic data reveal that the HBT molecules are incorporated in the nanosized zeolite particles, thus leading to changes in the environment of the TMA ions as well as in the local atomic arrangements of the FAU structure. At high concentration of HBT, a large fraction of the sodalite cages are destroyed, and the HBT and TMA molecules are located in the subsequently formed cavities. Steady-state UV-vis spectra also reveal the presence of the keto HBT-conformers inside the FAU zeolite nanocrystals. Upon UV excitation, the HBT molecules occluded in the zeolite nanoparticles undergo ultrafast intermolecular proton transfer within 1.5 ps.

J. Phys. Chem. A 2004, 108, 10640-10648

Femtosecond fluorescence up-conversion spectroscopy of adenine and adenosine: experimental evidence for the $\pi\sigma^*$ state?

Thomas Pancur, Nina K. Schwalb, Falk Renth, Friedrich Temps

Femtosecond time-resolved fluorescence up-conversion spectroscopy has been used in a study of the excited electronic state lifetimes of the purine base adenine (Ade) and its ribonucleoside adenosine (Ado) in aqueous solution. The molecules were excited at wavelengths in the range $245 \leq \lambda_{\text{exc}} \leq 280$ nm using tunable UV pulses from a frequency doubled non-collinear optical parametric amplifier (NOPA). The observed biexponential temporal fluorescence profiles of Ade could be fitted using a fast decay time between $\tau_1 = (0.34 \pm 0.07)$ ps at the shorter excitation wavelengths and $\tau_1 = (0.67 \pm 0.14)$ ps at the longer excitation wavelengths and, independent of the excitation wavelength, a slow decay time of $\tau_2 = (8.4 \pm 0.8)$ ps. The two values were assigned to the "canonical" 9H-ade tautomer (τ_1) and the less stable 7H-Ade tautomer (τ_2) which are known to be present in aqueous solution. The excited state lifetime of 9H-Ade in H₂O is thus sub-picosecond even around the electronic origin of the first excited $\pi\pi^*$ state, in contrast to a report for the 0-0 level in the gas phase (≥ 9 ps). The fluorescence decay profiles of Ado, in which the 9H atom is substituted by the ribose, could be described assuming monoexponential behavior with a lifetime $\tau = (0.31 \pm 0.05)$ ps. The results are consistent with fast radiationless electronic relaxation from the excited $\pi\pi^*$ to the S₀ ground state. The apparent step in the lifetime of 9H-Ade centered at $\lambda_{\text{exc}} \approx 265$ nm might be interpreted as evidence for the opening of an additional radiationless electronic relaxation pathway, which could arise from the $\pi\sigma^*$ state predicted at about that energy.

Chemical Physics 313 (2005) 199-212

Ultrafast Quenching of the Xanthone Triplet by Energy Transfer: New Insight into the Intersystem Crossing Kinetics

H. Satzger, B. Schmidt, C. Root, W. Zinth, B. Fierz, F. Krieger, T. Kiefhaber, and P. Gilch

The formation and quenching of the triplet state of xanthone are studied by femtosecond techniques. As revealed by femtosecond fluorescence spectroscopy, the primarily excited $^1\pi\pi^*$ state decays within 1.5 ps. In a transient absorption experiment, this time constant is associated with a partial rise of a triplet signature. This rise has a second and slower component with a time constant of 12 ps. In the presence of high concentrations of the quencher 1-methylnaphthalene,

the slow 12 ps rise component is absent. This finding gives strong evidence that the biphasic rise of the triplet absorption of xanthone is due to a sequential mechanism, namely, a $^1\pi\pi^* \rightarrow ^3n\pi^*$ with fast intersystem crossing followed by a $^3n\pi^* \rightarrow ^3\pi\pi^*$ internal conversion. Furthermore, an analysis of the concentration dependence of the quenching kinetics allows one to pin down the intrinsic transfer time of the triplet energy from xanthone to 1-methylnaphthalene to ~ 1 ps.

J. Phys. Chem. A **2004**, *108*, 10072-10079

Zero-additional-phase SPIDER: full characterization of visible and sub-20-fs ultraviolet pulses

Peter Baum, Stefan Lochbrunner, and Eberhard Riedle

We demonstrate a novel spectral-shearing interferometry setup for characterizing the temporal amplitude and phase of ultrashort optical pulses over an extremely wide wavelength region. By the mixing of two strongly chirped auxiliary pulses with the pulse to be characterized, two spectrally sheared replicas are generated, and their spectral interference is evaluated. We fully characterize 10-fs pulses in the visible region by sum-frequency mixing and 19-fs pulses in the ultraviolet region by difference-frequency mixing. The scheme is self-referencing and highly sensitive. The zero-additional-phase scheme does not alter the unknown pulses and yields the pulse shape at the interaction point of a spectroscopic experiment.

OPTICS LETTERS, Vol. 29, No. 2, January 15, 2004

Real time observation of the photo-Fries rearrangement

S. Lochbrunner, M. Zissler, J. Piel, E. Riedle, A. Spiegel and T. Bach

The photo-Fries rearrangement of 4-*tert*-butylphenyl acetate dissolved in cyclohexane is investigated by two-color femtosecond pump probe spectroscopy. The spectral transmission changes are characterized in the visible and ultraviolet spectral region and allow for the first time to temporally resolve the primary reaction steps. We find that the photoinduced homolytic cleavage of the CO bond occurs within 2 ps and that the geminate recombination of the generated radical pair to the intermediate substituted cyclohexadienone takes 13 ps. The experimental results support a model in which the initial reaction proceeds from the originally excited $\pi\pi^*$ state via a barrier to a dissociative $\pi\sigma^*$ state.

J. Chem. Phys., Vol. 120, No. 24, 22 June 2004

Evidence of ultrafast optical switching behaviour in individual single-walled carbon nanotubes

H. Hippler, A.-N. Unterreiner, J.-P. Yang, S. Lebedkin and M. M. Kappes

The ultrafast photophysics of D₂O/sodium dodecylbenzene sulfonate surfactant dispersions of single-walled carbon nanotubes enriched in individual tubes (versus tube bundles) were studied by femtosecond pump-probe spectroscopy in the near-IR (NIR) spectral range. Measurements at 920 nm excitation and variable probe wavelengths showed evidence of superimposed transient bleaching as well as induced absorption behaviour. Our results indicate that such nanotube samples manifest ultrafast pump-induced switching of probe transmission with switching times of

less than 1 ps under appropriate conditions. Given their high photochemical and photophysical stability these materials may be suitable candidates for the development of ultrafast NIR optical switches and logic gates.

***Phys. Chem. Chem. Phys.*, 2004, 6, 2387 – 2390**

Terahertz optical properties of thin doped contact layers in GaAs device structures

Tobias Bauer, Johanna S Kolb, Ernst Mohler, Hartmut G Roskos and Klaus Kohler

We investigate the transmittance of thin doped GaAs layers in the terahertz (THz) frequency range taking into account multiple reflections. Our experimental and theoretical study aims at providing a guideline for designing the top-side contact layers for THz emitters and receivers with direct, antenna-free coupling of the radiation. It is shown that the surface conductivity of the contact layer is the determining factor for the THz transmittance.

***Semicond. Sci. Technol.* 18 (2003) 28–32**

Generation of tunable 7-fs ultraviolet pulses: achromatic phase matching and chirp management

P. Baum, S. Lochbrunner, E. Riedle

Ultraviolet pulses with a duration of 7 fs are efficiently generated by frequency doubling the output of a noncollinear optical parametric amplifier. The ultraviolet pulses are tunable between 275 to 335 nm. The acceptance bandwidth of the doubling crystal is increased by a factor of 80 through high order achromatic phase matching. The chirp of the visible pulses and the dispersion introduced along the beam path are compensated partially before and partially after the doubling crystal. For the design of the dispersion management, we investigate the second harmonic generation of pulses with mixed orders of chirp and explicitly discuss the transfer of the spectral phase in frequency doubling. A simple analytic theory is derived that correctly describes frequently observed spectral narrowing effects. We find that chirped SHG avoids spectral narrowing and allows for precompression of dispersion encountered in the ultraviolet beam path. We apply chirped SHG to generate 18.7 fs ultraviolet pulses in an extremely simple setup.

***Appl. Phys. B* 79, 1027–1032 (2004)**

50-fs Photoinduced Intramolecular Charge Separation in Triphenylmethane Lactones

Tanja Bizjak, Jerzy Karpiuk, Stefan Lochbrunner, and Eberhard Riedle

Upon excitation of their structural subunits, phenolphthalein and malachite green lactone undergo ultrafast intramolecular charge separation with formation of a long-lived charge-transfer state (intramolecular “radical ion pair”). The kinetics of the primary charge separation in these molecules in aprotic solvents has been studied using femtosecond pump-probe spectroscopy. The phenol radical cation is formed by electron transfer within 50 fs after excitation of phenolphthalein to the S₁ state. In malachite green lactone the products of charge separation are observed 150 fs after excitation to the S₂ state. The results demonstrate that electron transfer in

these molecules occurs faster than the time scale of inertial solvation dynamics. An intramolecular vibrational mode to promote charge separation is indicated.

J. Phys. Chem. A, Vol. 108, No. 49, 2004

Electronic Structure, Photophysics, and Relaxation Dynamics of Charge Transfer Excited States in Boron-Nitrogen-Bridged Ferrocene-Donor Organic-Acceptor Compounds

M. D. Thomson, M. Novosel, H. G. Roskos, T. Mueller, M. Scheibitz, and M. Wagner, F. Fabrizi de Biani and P. Zanello

We present a study of the electronic, photophysical, and picosecond excited-state relaxation characteristics of a class of derivatives comprised of multiple bipyridylboronium acceptors covalently linked to a ferrocene donor. These compounds exhibit a broad visible absorption band, which we attribute to a metal-to-ligand charge transfer transition between the donor and the acceptor. A comparison of optical absorption, spectroelectrochemical, and theoretical results confirms the assignment of the band and provides information on the degree of electron delocalization between the donor and the acceptor. Picosecond transient absorption measurements reveal that the back-electron transfer relaxation is critically dependent on the structural flexibility of the bridging bonds between the donor and the acceptor. In the case where the acceptor substituents are free to rotate about the bridging bonds between the boron and the cyclopentadienyl rings of the ferrocene, a significant portion of the excited state decays directly back to the ground state on a time scale of ~18 ps, whereas in the case where an additional ansa-bridge that connects acceptor substituents enforces a more rigid conformation, the ground-state recovery proceeds only on a ~800-ps time scale. This demonstrates the importance of conformational degrees of freedom for the internal conversion and back-electron transfer in these systems.

J. Phys. Chem. A 2004, 108, 3281-3291

Real-time characterization and optimal phase control of tunable visible pulses with a flexible compressor

P. Baum, S. Lochbrunner, L. Gallmann, G. Steinmeyer, U. Keller, E. Riedle

The output pulses of a noncollinearly phasematched optical parametric amplifier (NOPA) are fully characterized by spectral phase interferometry for direct electric-field reconstruction (SPIDER). The SPIDER setup has been optimized for online diagnosis of tunable visible pulses with a 1 kHz repetition rate and 10–40 fs duration. The compression of the NOPA pulses by different prism sequences and commercially available chirped mirrors is investigated. For flexible phase control the end mirror of a fused-silica prism compressor has been replaced by a deformable mirror. With an evolutionary strategy guided by the spectral phase information of the SPIDER, optimal compression of the NOPA pulses to a 7.6 fs duration is achieved.

Appl. Phys. B 74 [Suppl.], S219–S224 (2002)

Remote identification of protrusions and dents on surfaces by terahertz reflectometry with spatial beam filtering and out-of-focus detection

Noboru Hasegawa, Torsten Loeffler, Mark Thomson, and Hartmut G. Roskos

We propose two terahertz reflectometry modalities that are optimized to be sensitive to the curvature of surface features. The first is a dark-field technique that allows the detection of protrusions and dents on surfaces with high sensitivity. It cannot distinguish, however, between convex and concave shapes. This becomes possible with the second technique, which combines out-of-focus imaging with suitable beam filtering. Both methods may be of interest for surface inspection in fabrication environments; for example, for online monitoring during metal processing.

Appl. Phys. Lett., Vol. 83, No. 19, 10 November 2003

Ultrafast singlet energy transfer competes with intersystem crossing in a multi-center transition metal polypyridine complex

Johan Andersson, Fausto Puntoriero, Scolastica Serroni, Arkady Yartsev, Torbjorn Pascher, Tomas Polivka, Sebastiano Campagna, Villy Sundstrom

Transition metal polypyridine complexes are finding widespread applications within many areas of chemistry. For their lightinduced processes, the generally accepted picture is that all function emanates from triplet states because the singlet states initially prepared by light absorption are depopulated via intersystem crossing on the 100-fs time scale, before they are significantly involved in chemical reactions. Here we show that this is not always true. With ultrafast spectroscopy applied to a (ruthenium)₃-osmium complex we show that transition metal polypyridine complexes can be designed where energy transfer between excited singlet states located on different metal centers efficiently competes with intersystem crossing, thus decreasing population of the lower-lying triplet states and concomitant energy loss.

Chemical Physics Letters 386 (2004) 336–341

Ultrafast excitation transfer and trapping in a thin polymer film

Mette M.-L. Grage, Yuri Zaushitsyn, Arkady Yartsev, Mirianas Chachisvilis, Villy Sundstrom, and Tonu Pullerits

Transient absorption anisotropy of a polythiophene polymer in a thin film was studied on a femtosecond time scale. The anisotropy has a non-exponential decay on the sub-picosecond time scale, with a fastest component characterized by an ~ 40 fs time constant. To simulate the anisotropy decay an incoherent energy migration model has been used. Comparison between the simulated and experimental kinetics enabled us to estimate the nearest-neighbor pair wise hopping time ($\tau_h = 1 \pm 0.1$ ps), the fraction of the interchain aggregates ($\sim 10\%$) and the structural disorder of the polymer. The initial ~ 30 fs anisotropy decay does not originate from incoherent hopping energy transfer but from some other relaxation among electronic excited states within a spectroscopic unit.

PHYSICAL REVIEW B 67, 205207 (2003)

Widely tunable sub-30 fs ultraviolet pulses by chirped sum frequency mixing

Ida Z. Kozma, Peter Baum, Stefan Lochbrunner and Eberhard Riedle

A novel scheme for the generation of UV pulses in the 295 - 450 nm range is presented. Sum frequency mixing of the chirped visible pulses from a noncollinear optical parametric amplifier with deliberately chirped pulses from the Ti:sapphire amplifier ensures efficient energy conversion and easy tunability. Pulse energies as high as 5.5 μJ at 295 nm, and $>2 \mu\text{J}$ in most of the tuning range are obtained with highly symmetric and smooth spectra. They are compressed to sub-30 fs throughout the entire tuning range (20 fs at 348 nm) with a newly designed prism compressor.

OPTICS EXPRESS, 17 November 2003, Vol. 11, No. 23. 3110-5

12-fs pulses from a continuous-wave-pumped 200-nJ Ti:sapphire amplifier at a variable repetition rate as high as 4 MHz

R. Huber, F. Adler, A. Leitenstorfer, M. Beutter, P. Baum, and E. Riedle

We demonstrate a novel compact femtosecond Ti:sapphire laser system operating at repetition rates from 10 kHz to 4 MHz. The scheme is based on the combination of a broadband cavity-dumped oscillator and a double-pass Ti:sapphire amplifier pumped by a low-noise cw solid-state laser. Amplified pulses with an extremely smooth spectrum, a duration of only 12 fs, and less than 0.25% rms fluctuation are generated in a beam with $M^2 < 1.2$. A maximum pulse energy of 210 nJ and an average output power of as much as 720 mW are achieved. This output energy is sufficient to generate a stable continuum in a sapphire disk.

OPTICS LETTERS, Vol. 28, No. 21, November 1, 2003

Femtosecond Fluorescence and Absorption Dynamics of an Azobenzene with a Strong Push-Pull Substitution

B. Schmidt, C. Sobotta, S. Malkmus, S. Laimgruber, M. Braun, W. Zinth, and P. Gilch

The ultrafast photoisomerization of a push-pull substituted azobenzene (4-nitro-4'-(dimethylamino)azobenzene, NA) is studied by means of femtosecond fluorescence and absorption spectroscopy. The fluorescence dynamics is biphasic. The initial fluorescence with a narrow and intense spectrum decays in ~ 100 fs. This decay is accompanied by the rise of broad red-shifted and much weaker emission. The same time constants recur in the transient absorption spectra which hold additional information on the ground-state dynamics. The ground state recovers in 0.8 ps, demonstrating that only the longer time constant is associated with an internal conversion process. Small spectral changes occurring thereafter (~ 5 ps) point to vibrational cooling in the ground state. The results are analyzed in comparison with the behavior of the parent compound azobenzene. Though the push-pull substitution of azobenzene strongly alters the character of its excited states, the photodynamics are surprisingly robust with respect to that substitution.

J. Phys. Chem. A 2004, 108, 4399-4404

On the way to 'optical doping' of electronically low-dimensional polymer systems with strong charge and spin correlations

M. Thomson, H. Roskos, M. Wagner

We discuss the concept of optical manipulation of the charge and spin density in polymer systems with strong correlation phenomena by attaching pendant chromophores to the polymer backbone. In the process of identifying suitable functional groups for future inclusion in polymers, we study here boron–nitrogen-linked ferrocene derivatives. We investigate the metal-to-ligand charge transfer between a ferrocene donor and π -acceptor units across the B–N bridges. On the basis of photophysical measurements, including picosecond time-resolved spectroscopy, we identify that the initial relaxation of the excited states depends critically on the degree of structural rigidity, and can be tuned by more than an order of magnitude (~ 20 –800 ps).

Appl. Phys. A **78**, 477–481 (2004)

Bichromophoric Interactions and Time-Dependent Excited State Mixing in Pyrene Derivatives. A Femtosecond Broad-Band Pump-Probe Study

M. Raytchev, E. Pandurski, I. Buchvarov, C. Modrakowski, and T. Fiebig

Femtosecond broad-band pump-probe spectroscopy has been used to study intramolecular bichromophoric coupling and structural relaxation in pyrene and aryl pyrene derivatives in solution. The influence of aryl substituents on the $S_2 \rightarrow S_1$ internal conversion process, which occurs with a time constant of ~ 75 fs in pyrene, has been investigated. While in 1-phenylpyrene the internal conversion is faster than 50 fs, it is slower in 1-biphenyl-4-yl-pyrene (105 fs). The temporal evolution of the transient absorption spectrum indicates strong mixing of several "zero-order" electronic configurations which evolve separately with times in the S_1 and the S_2 states. The time-resolved spectra are interpreted within the framework of an adiabatic state model which includes interchromophoric electronic coupling. In this paper we give a full description of the experimental setup, the data acquisition procedure, and several experimental details about the characterization of the broad-band femtosecond white light source.

J. Phys. Chem. A **2003**, *107*, 4592-4600

Carrier-envelope phase fluctuations of amplified femtosecond pulses: characterization with a simple spatial interference setup

P. Baum, S. Lochbrunner, E. Riedle

We demonstrate a direct and versatile scheme to determine the carrier-envelope phase fluctuations of tunable ultrashort optical pulses. The spatial interferogram between the high frequency components and the parametrically amplified and frequency doubled low frequency components of an octave broad white light continuum is measured for every single pulse. It directly reveals the carrier-envelope phase fluctuations of the pump pulses from the regenerative amplifier, as well as of the white light and the tunable pulses generated from it.

Appl. Phys. B **77**, 129–132 (2003)

Electron Injection into DNA: Synthesis and Spectroscopic Properties of Pyrenyl-Modified Oligonucleotides

Nicole Amann, Evgeni Pandurski, Torsten Fiebig, and Hans-Achim Wagenknecht

The nucleoside 5-(1-pyrenyl)-2'-deoxyuridine (**1**) was prepared by a Suzuki-Miyaura cross-coupling reaction and subsequently used as a DNA building block in order to prepare a range of modified oligonucleotides using phosphoramidite chemistry. The DNA duplexes contain a pyrenyl group covalently attached to the nucleobase uracil. Upon excitation at 340 nm an intramolecular electron transfer from the pyrenyl group to the uracil moiety takes place which represents an injection of an excess electron into the DNA base stack. Based on the results obtained by steady-state fluorescence and time-resolved pump-probe laser spectroscopy it was possible to show that base-to-base electron transfer can occur from the Py-dU group only to adjacent thymines.

Chem. Eur. J. **2002**, *8*, No. 21

Visualization and classification in biomedical terahertz pulsed imaging

Torsten Löffler, Karsten Siebert, Stephanie Czasch, Tobias Bauer and Hartmut G Roskos

'Visualization' in imaging is the process of extracting useful information from raw data in such a way that meaningful physical contrasts are developed. 'Classification' is the subsequent process of defining parameter ranges which allow us to identify elements of images such as different tissues or different objects. In this paper, we explore techniques for visualization and classification in terahertz pulsed imaging (TPI) for biomedical applications. For archived (formalin-fixed, alcohol-dehydrated and paraffin-mounted) test samples, we investigate both time- and frequency-domain methods based on bright- and dark-field TPI. Successful tissue classification is demonstrated.

Phys. Med. Biol. **47** (2002) 3847–3852

Phase-coherent generation of tunable visible femtosecond pulses

P. Baum, S. Lochbrunner, J. Piel, and E. Riedle

Stable interference between the outputs of two noncollinearly phase-matched optical parametric amplifiers seeded by separate white-light continua has been observed. This means that the tunable visible pulses have a well-defined relative phase and that the temporal jitter between them is less than 1 fs. The residual phase variations are due to fluctuations of the pump power.

OPTICS LETTERS, Vol. 28, No. 3, February 1, 2003

Femtosecond dynamics in directly linked pyrenyl donor-acceptor systems: orbital control of optical charge transfer in the excited state

Evgeni Pandurski, Torsten Fiebig

The ultrafast charge transfer (CT) dynamics in two directly linked pyrenyl donor-acceptor systems has been studied using femtosecond broadband pump-probe spectroscopy. This method allows to capture complex chemical dynamics by measuring the time-resolved spectral evolution of transient absorption and stimulated emission induced by femtosecond optical pumping. After

electronic relaxation, an optical CT transition between two excited states was found in both systems. Although the excited state CT occurs adiabatically significant differences in the electronic coupling are deduced from the band intensities. The results are discussed in terms of an adiabatic state model and compared with predictions from orbital topology arguments.

Chemical Physics Letters 357 (2002) 272–278

Broadband optical parametric amplification in the near UV–VIS

P. Tzankov, I. Buchvarov, T. Fiebig

An optical parametric amplification scheme yielding a broad bandwidth in a BBO crystal (Type I) pumped by the third harmonic of a femtosecond Ti:Sapphire laser has been investigated theoretically and experimentally. A broad amplification bandwidth of 205 THz between 346 and 453 nm is obtained in a noncollinear geometry of parametric interaction. The bandwidth of the amplification is reduced significantly when the pump–signal angle is changed by only 0.1°. A UV-extended white-light continuum is used as a signal seed. Several materials for white-light generation – such as CaF₂, MgF₂ and LiF – have been investigated.

Optics Communications 203 (2002) 107–113

Tunable sub-10-fs ultraviolet pulses generated by achromatic frequency doubling

Peter Baum, Stefan Lochbrunner, and Eberhard Riedle

Tunable UV pulses shorter than 10 fs are generated by achromatic frequency doubling of a noncollinear optical parametric amplifier. With a suitable two-prism sequence we achieve first- and second-order achromatic phase matching and increase the natural bandwidth of the nonlinear crystal by a factor of 80. Extremely broad UV spectra with a Fourier limit of 2.9 fs are generated in a 360- μ m-thick β -barium borate crystal at a conversion efficiency of 20%. We compensate for the angular dispersion and the first-order chirp of the highly stable UV pulses with a second prism sequence and fully characterize the temporal pulse shape with zero-additional-phase spectral phase interferometry for direct electric-field reconstruction (ZAP-SPIDER). Pulses as short as 7 fs are generated by controlling the higher-order chirp with a deformable mirror.

OPTICS LETTERS, Vol. 29, No. 14, July 15, 2004

Zero-additional-phase SPIDER: full characterization of visible and sub-20-fs ultraviolet pulses

Peter Baum, Stefan Lochbrunner, and Eberhard Riedle

We demonstrate a novel spectral-shearing interferometry setup for characterizing the temporal amplitude and phase of ultrashort optical pulses over an extremely wide wavelength region. By the mixing of two strongly chirped auxiliary pulses with the pulse to be characterized, two spectrally sheared replicas are generated, and their spectral interference is evaluated. We fully characterize 10-fs pulses in the visible region by sum-frequency mixing and 19-fs pulses in the ultraviolet region by difference-frequency mixing. The scheme is self-referencing and highly

sensitive. The zero-additional-phase scheme does not alter the unknown pulses and yields the pulse shape at the interaction point of a spectroscopic experiment.

OPTICS LETTERS, Vol. 29, No. 2, January 15, 2004

Femtosecond Spectroscopic Investigation of the Carrier Lifetimes in Digenite Quantum Dots and Discrimination of the Electron and Hole Dynamics via Ultrafast Interfacial Electron Transfer

Yongbing Lou, Xiaobo Chen, Anna C. Samia, and Clemens Burda

For the Cu_xS system there exists several known solid phases such as Cu_2S (chalcocite), $\text{Cu}_{1.8}\text{S}$ (digenite), $\text{Cu}_{1.96}\text{S}$ (djurleite), and CuS (covellite). All of these phases have been identified as p-type semiconducting materials due to copper vacancies within the lattice, which is responsible for their usefulness as optoelectronic materials. The different Cu_xS phases show reportedly low band gap energies of ≥ 1.2 eV for the bulk, which makes them potentially ideal for application purposes of photoinduced voltaics or catalysis where activation through visible light is desired. In this study, we report on the femtosecond carrier dynamics of digenite copper sulfide quantum dots. Digenite quantum dots were prepared by a single source precursor type process and the optical transitions and dynamic properties of the photoinduced charge carriers in these novel nanomaterials characterized by femtosecond time-resolved spectroscopy. It is found that the larger quantum dots have longer excited-state lifetimes, which implies a strong surface-induced effect on the relaxation dynamics. In addition, the dynamics of the electron was differentiated from that of the hole by employing the technique of rapid (< 100 fs) electron trapping at adsorbed organic electron acceptors such as benzoquinone.

J. Phys. Chem. B, Vol. 107, No. 45, 2003

Semiconductor Quantum Dots for Photodynamic Therapy

Anna C. S. Samia, Xiaobo Chen, and Clemens Burda

Photodynamic therapy (PDT) is an emerging cancer treatment that takes advantage of the interaction between light and a photosensitizing agent to initiate apoptosis of cancer cells. In PDT, the photosensitizing agent becomes activated by light but does not react directly with cells and tissues. Instead, it transfers its triplet state energy to nearby oxygen molecules to form reactive singlet oxygen ($^1\text{O}_2$) species, which cause cytotoxic reactions in the cells. The increasing popularity of this treatment method is largely due to its selectivity: only tissues that are simultaneously exposed to the photosensitizer and light, in the presence of oxygen, are the ones subjected to the cytotoxic reactions during PDT. Thus, under ideal circumstances only diseased tissues are eradicated, leaving the surrounding healthy cells undamaged.

J. AM. CHEM. SOC. 2003, 125, 15736-15737

Ultrafast photoinduced softening in a ferromagnetic semiconductor

J. Wang, G. A. Khodaparast, J. Kono, T. Slupinski, A. Owia, and H. Munekata

Two-color time-resolved magneto-optical Kerr spectroscopy is used to manipulate and detect the dynamics of carrier-induced ferromagnetism in III-V ferromagnetic semiconductors. Our data demonstrates that magnetic properties, e.g., the coercivity, can be tuned reversibly and nonthermally on subpicosecond time scale.

Quantum Electronics and Laser Science Conference, OSA Technical Digest (Optical Society of America, 2003), QThB6.

Mid-infrared Ultrafast Optical Manipulation of Ferromagnetism in InMnAs/GaSb

J. Wang, G. A. Khodaparast, J. Kono, T. Slupinski, A. Oiwa, and H. Munekata

We have used two-color time-resolved magneto-optical Kerr Effect spectroscopy to study the dynamics of spin/magnetic order in InMnAs. We observed ultrafast photo-induced softening due to spin-polarized transient carriers. This transient *softening* persists only during the carrier lifetime (~ 2 ps). Our data clearly demonstrates that magnetic properties can be strongly modified in an ultrafast manner.

Conference Digest of the 28th International Conference on Infrared and Millimeter Waves (2003) : 359-360.

Ultrafast Softening in InMnAs

J. Wang, G. A. Khodaparast, J. Kono, T. Slupinski, A. Oiwa, and H. Munekata

We have used two-color time-resolved magneto-optical Kerr Effect (MOKE) spectroscopy to manipulate and detect dynamic processes of spin/magnetic order in a ferromagnetic semiconductor InMnAs. We observed ultrafast photo-induced "softening" (i.e., transient decrease of coercivity) due to spin-polarized transient carriers. This transient softening persists only during the carrier lifetime (~ 2 ps) and returns to its original value as soon as the carriers recombine to disappear. Our data clearly demonstrates that magnetic properties, e.g., coercivity, can be strongly and reversibly modified in an ultrafast manner. We attribute the origin of this unusual phenomenon to carrier-mediated ferromagnetic exchange interactions between Mn ions. We discuss the dependence of data on the time delay, pump polarization, pump intensity, and sample temperature. Our observation opens up new possibilities for ultrafast optical manipulation of ferromagnetic order as well as providing a new avenue for studying the dynamics of long range collective processes in strongly-correlated many-body systems.

Physica E 20, 412 (2004)

Ultrafast photoinduced above-bandgap transparency in GaAs due to the Dynamic Franz-Keldysh effect

A. Srivastava and J. Kono

We report the dynamic Franz-Keldysh effect in bulk GaAs. Ultrafast changes in transmission spectra near the band edge, including the first observation of photoinduced transparency as large as 40%, are observed.

*Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference,
Technical Digest (Optical Society of America, 2003), paper QFD2*