Publications:

Pub 25:

Kozich, V; Moguilevski, A; Heyne, K

**High energy femtosecond OPA pumped by 1030 nm Yb:KGW laser**

OPTICS COMMUNICATIONS 2012, 285 (21), p. 4515-4518;

We present a traveling-wave-type optical parametric amplifier (OPA) pumped at 1.03 μm by a Yb:KGW laser that produces tunable high-energy pulses of 6.5-4 μJ in the mid-infrared (mid-IR) region from 3.6 to 7 μm. Pumping with negatively chirped pulses generates nearly transform-limited (TL) mid-IR pulses of 300-330 fs length. Pumping with TL pulses of 200 fs not only decreases the output energy by a factor of 1.5, but also decreases the mid-IR pulse-length to 160 fs after additional compression. The compact and simple OPA setup is ideal for femtosecond infrared experiments in the fingerprint region.

DOI 10.1016/j.optcom.2012.06.077

Pub 24:

Yang, Y; Jones, D; von Haimberger, T; Linke, M; Wagnert, L; Berg, A; Levanon, H; Zacarias, A; Mahammed, A; Gross, Z; Heyne, K

**Assignment of Aluminum Corroles Absorption Bands to Electronic**

**Transitions by Femtosecond Polarization Resolved VIS-Pump IR-Probe**

**Spectroscopy**

JOURNAL OF PHYSICAL CHEMISTRY A 2012, 116(3), p. 1023-1029;

We combine femtosecond polarization resolved VIS-pump IR-probe spectroscopy with DFT and TD-DFT calculations to identify and assign absorption bands to electronic transitions for corroles. These macrocycles and their corresponding metal complexes are receiving great attention because of their utility in many field, while many of their spectroscopic features have not yet been fully described. Analysis of the perturbed free induction decay provides information about the bleaching signal at time zero and allows for determination of overlapping excited state and bleaching signal amplitudes. The S0 -> S1 and S0 -> S2 transitions in the Q-band of the hexacoordinated Al(tpfc)(py)2 and Br(8)Al(tpfc)(py)2 absorption spectra are explicitly assigned. Angles between these electronic transition dipole moments (tdms) with a single vibrational transition dipole moment of (53 ± 2 degrees) and (34 ± 2 degrees) when excited at 580 and 620 nm for hexacoordinated Al(tpfc)(py)2 and (51 ± 2 degrees) and (43 ± 2 degrees) when excited at 590 and 640 nm for hexacoordinated Br(8)Al(tpfc)(py)2 were determined. The relative angles between the two lowest electronic tdms are (90 ± 8 degrees) and (94 ± 3 degrees) for Al(tpfc)(py)2 and Br(8)Al(tpfc)(py)2, respectively. Angles are determined before time zero by polarization resolved perturbed free induction decay and after time zero by polarization resolved transients. Comparison of corrole's wave functions with those of porphine show that the reduced symmetry in the corrole molecules results in lifting of Q-band degeneracy and major reorientation of the electronic transition dipole moments within the molecular scaffold. This information is necessary in designing optimal corrole-based electron and energy transfer complexes.

DOI 10.1021/jp211970j

Pub 23:

Yang, Y; Linke, M; von Haimberger, T; Hahn, J; Matute, R; Gonzalez, L; Schmieder, P; Heyne, K

**Real-Time Tracking of Phytochrome's Orientational Changes During Pr**

**Photoisomerization**

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2012, 134(3), p.1408-1411;

Photoisomerization of a protein bound chromophore is the basis of the light sensing and signaling responses of many photoreceptors. Z-to-E photoisomerization of the Pr Cph1 Δ2 phytochrome has been investigated by polarization resolved femtosecond visible pump-infrared probe spectroscopy, which yields structural information on the Pr excited (Pr\*), Pr ground, and lumi-R product states. By exhaustive search analysis, two photoreaction time constants of (4.7 ± 1.4) and (30 ± 5) ps were found. Ring D orientational change in the electronic excited state to the transition state (90 degrees twist) has been followed in real-time. Rotation of ring D takes place in the electronically excited state with a time constant of 30 ± 5 ps. The photoisomerization is best explained by a single rotation around C-15=C-16 methine bridge in the Pr\* state and a diffusive interaction with its protein surrounding.

DOI 10.1021/ja209413d

Pub 22:

Rubin, T; von Haimberger, T; Helmke, A; Heyne, K

**Quantitative determination of metabolization dynamics by a real-time**

**13CO2 breath test**

JOURNAL OF BREATH RESEARCH 2011, 5, p. 027102-027108;

We have developed a flow-through fast liver investigation packet (FLIP) to quantitatively measure the amount of exhaled 13CO2, as a result of liver metabolization processes. The FLIP system allows investigation of every single breath in real time. Line width variations due to interactions with other gas components disturb traditional measurements and limit their sensitivity to the ppm range. Detection of the complete breath volume and the spectrally fully resolved line shape allows sensitivity in the ppb range with a standard deviation of approximately 80 ppb, a prerequisite to quantitatively analyze liver metabolization processes.

DOI 10.1088/1752-7155/5/2/027102

A

Pub 21:

Lauer, A; Dobryakov, AL; Kovalenko, SA; Fidder, H; Heyne, K

**Dual photochemistry of anthracene-9,10-endoperoxide studied by**

**femtosecond spectroscopy**

PHYSICAL CHEMISTRY CHEMICAL PHYSICS 2011, 13, p. 8723-8732;

The dual photochemistry of anthracene-9,10-endoperoxide (APO) was investigated in a fs UV pump-supercontinuum probe experiment, along with anthracene (AC) and anthraquinone (AQ) for comparison. Excitation of APO at 282 nm leads to 100% product formation by two competing photoreaction channels. Cycloreversion generates with a similar to 25% quantum yield (QY) O2 and AC vibrationally excited in the singlet electronic ground state (hot AC). 1-2% of the AC is generated in the lowest triplet state, but no AC is generated in electronically excited singlet states. Generation and cooling of hot AC are modeled using solution phase and broadened gas-phase AC absorption spectra at various temperatures. Results indicate ultrafast generation of hot AC within 3 ps, much faster than reported before for derivatives of anthracene endoperoxide, and subsequent cooling with an 18 ps time constant. The homolytic O-O cleavage pathway generates a biradical, which converts into electronically excited diepoxide (DE). Our data indicate a 1.5 ps time constant that we tentatively assign to the biradical decay and DE formation. Cooling of DE in this electronically excited state takes place with a similar to 21 ps time constant. Excitation of AQ at 266 nm is followed by an ultrafast population of the T1(nπ\*) triplet state of AQ with a time constant of (160 ± 60) fs.

DOI 10.1039/c0cp02218gp

Pub 20:

Linke, M; Theisen, M; von Haimberger, T; Madjet, MEA; Zacarias, A; Fidder, H; Heyne, K

**Determining the Three-Dimensional Electronic Transition Dipole Moment**

**Orientation: Influence of an Isomeric Mixture**

CHEMPHYSCHEM 2010, 11(6), p. 1283-1288;

A new mixed experimental and theoretical approach for determining the exact three-dimensional orientation of electronic transition dipole moments (tdms) within the molecular frame is discussed. Results of applying this method on Chlorophyll *a* and the dye Coumarin 314 (C314) are presented. For C314 the possible influence of a mixture of E- and Z-isomers in the sample on the determined electronic tdm is investigated. Moreover, the robustness of the method is investigated with the C314 data.

DOI 10.1002/cphc.200900888

Pub 19:

Theisen, M; Linke, M; Kerbs, M; Fidder, H; Madjet, MEA; Zacarias, A; Heyne, K

**Femtosecond polarization resolved spectroscopy: A tool for determination**

**of the three-dimensional orientation of electronic transition dipole**

**moments and identification of configurational isomers**

JOURNAL OF CHEMICAL PHYSICS 2009, 131, p. 124511-124519;

A method is presented that combines femtosecond polarization resolved UV/visible pump-IR probe spectroscopy and density functional theory calculations in determining the three-dimensional orientation of an electronic transition dipole moment (tdm) within the molecular structure. The method is demonstrated on the approximately planar molecule coumarin 314 (C314) dissolved in acetonitrile, which can exist in two ground state configurations: the E- and the Z-isomer. Based on an exhaustive search analysis on polarization resolved measurement data for four different vibrational modes, it is concluded that C314 in acetonitrile is the E-isomer. The electronic tdm vector for the electronic S0→ S1 transition is determined and the analysis shows that performing the procedure for four vibrational modes instead of the minimally required three reduces the 1 σ probability area from 2.34% to 2.24% of the solution space. Moreover, the fastest rotational correlation time τc for the C314 E-isomer is determined to be 26 ± 2 ps.

DOI 10.1063/1.3236804

Pub 18:

Stockmann, M; Lock, JF; Riecke, B; Heyne, K; Martus, P; Fricke, M; Lehmann, S; Niehues, SM; Schwabe, M; Lemke, AJ; Neuhaus, P

**Prediction of Postoperative Outcome After Hepatectomy With a New Bedside**

**Test for Maximal Liver Function Capacity**

ANNALS OF SURGERY 2009, 250(1), p. 119-125

Objective: To validate the LiMAx test, a new bedside test for the determination of maximal liver function capacity based on 13C-methacetin kinetics. To investigate the diagnostic performance of different liver function tests and scores including the LiMAx test for the prediction of postoperative outcome after hepatectomy.

Summary Background Data: Liver failure is a major cause of mortality after hepatectomy. Preoperative prediction of residual liver function has been limited so far.

Methods: Sixty-four patients undergoing hepatectomy were analyzed in a prospective observational study. Volumetric analysis of the liver was carried out using preoperative computed tomography and intraoperative measurements. Perioperative factors associated with morbidity and mortality were analyzed. Cutoff values of the LiMAx test were evaluated by receiver operating characteristic.

Results: Residual LiMAx demonstrated an excellent linear correlation with residual liver volume (r = 0.94, P < 0.001) after hepatectomy. The multivariate analysis revealed LiMAx on postoperative day I as the only predictor of liver failure (P = 0.003) and mortality (P = 0.004). AUROC for the prediction of liver failure and liver failure related death by the LiMAx test was both 0.99. Preoperative volume/function analysis combining CT volumetry and LiMAx allowed an accurate calculation of the remnant liver function capacity prior to surgery (r = 0.85, P < 0.001).

Conclusions: Residual liver function is the major factor influencing the outcome of patients after hepatectomy and can be predicted preoperatively by a combination of LiMAx and CT volumetry.

DOI 10.1097/SLA.0b013e3181ad85b5

Pub 17:

Fidder, H; Lauer, A; Freyer, W; Koeppe, B; Heyne, K

**Photochemistry of Anthracene-9,10-endoperoxide**

JOURNAL OF PHYSICAL CHEMISTRY A 2009, 113(22), p. 6289-6296

The wavelength dependence of the photochemistry of anthracene-9,10-endoperoxide (APO) in acetonitrile was quantitatively investigated at 5° C, with excitation varied from 240 to 450 nm. Anthracene (AC) and a diepoxide (DE) were identified as the main primary photoproducts. After short exposure times DE was at all wavelengths the dominating photoproduct, while AC was only formed for λ <= 320 nm. The maximum AC quantum yield of 29% was reached at 270 nm. Anthraquinone (AQ) and a bicyclic acetal (BA) were identified as the main secondary products. Formation of AQ and BA occurred both from DE and from ground-state APO. Formation of BA from ground-state APO involved excited DE or BA itself, while formation of BA from DE required UV excitation of DE. Room-temperature thermolysis of APO only produced AQ. For λ <= 310 nm the total photochemistry quantum yield was, within error margins, constant and close to unity. Between 300 and 450 nm, the tail of the APO absorption spectrum, a more or less monotonic decrease of the total photochemistry quantum yield was observed.

DOI 10.1021/jp901073s

Pub 16:

Linke, M; Lauer, A; von Haimberger, T; Zacarias, A; Heyne, K

**Three-Dimensional Orientation of the Q(y) Electronic Transition Dipole**

**Moment within the Chlorophyll a Molecule Determined by Femtosecond**

**Polarization Resolved VIS Pump-IR Probe Spectroscopy**

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2008, 130(45), p. 14904-14905

Chlorophyll *a* (*Chl* *a*) is the most abundant pigment on earth. In all plants, algae, and cyanobacteria, it plays a pivotal role as an antenna and reaction center pigment in the primary steps of photosynthesis. In the past, a true three-dimensional (3D) experimental determination of the Qy electronic transition dipole moment orientation could not be obtained. With combined femtosecond polarization resolved VIS pump-IR probe experiments and theoretical calculations of the infrared transition dipole moments (tdm's) in the electronic ground state, we determined the 3D orientation of the Qy electronic tdm of Chl a within the molecular structure. Polarization resolved experiments provided angles of the Qy electronic tdm with three different infrared tdm's, whose orientations within the molecular structure were taken from our theoretical calculations. The orientation of the Qy tdm results from the intersection of all three angles and was found to have an angle of (78 ± 3)degrees with the x-axis, (12 ± 3)degrees with the y-axis, and (86 ± 2)degrees with the z-axis.

DOI 10.1021/ja804096s

Pub 15:

Heyne, K; Krishnan, GM; Kühn, O

**Revealing anharmonic couplings and energy relaxation in DNA oligomers by**

**ultrafast infrared Spectroscopy**

JOURNAL OF PHYSICAL CHEMISTRY B 2008, 112(26), p. 7909-7915

The identification and characterization of NH2 hydrogen-bonded stretching vibrations (v(NH2)) in DNA oligomers is usually hampered by the all-dominating absorption of the water stretching band in the spectral range of 3050-3600 cm-1. Here, we use the two-color IR pump-probe technique to overcome the limitations of linear absorption spectroscopy by exciting adenine-thymine A-T oligomer vibrations in the fingerprint region and analyzing induced transient spectral changes in the v(NH2) spectral region. These transient changes are related to anharmonic couplings to the modes excited in the fingerprint region and to modes populated by intra- and intermolecular energy redistribution and relaxation. The combination of calculated anharmonic coupling parameters and experimental transient IR data allows the assignment of a transition at 3215 cm-1 to the v(NH2) vibration of adenine in dA20-dT20 DNA oligomers.

DOI 10.1021/jp711262y

Pub 14:

Corral, I; Gonzalez, L; Lauer, A; Freyer, W; Fidder, H; Heyne, K

**Identifying the low-lying electronic states of anthracene-9,10-endoperoxide**

CHEMICAL PHYSICS LETTERS 2008, 452(1-3), p. 67-71

The electronic excited states of anthracene-9,10-endoperoxide giving rise to singlet oxygen generation (1O2) or homolytic O-O cleavage have been unambiguously characterized using multi-configurational second order perturbation theory MS-CASPT2/CASSCF, with inclusion of solvent interactions, femtosecond polarization resolved UV/IR pump-probe, and steady-state fluorescence experiments. The S1 state, responsible for homolytic O-O cleavage, is observed at 34400 cm-1. Determination of the transition dipole moment direction of the 37000 cm-1 band, confirms the assignment of the S4 state, from which 1O2 is generated, and allows assigning the other electronic states. Furthermore, it is demonstrated that APO can emit after electronic excitation.

DOI 10.1016/j.cplett.2007.12.013

Pub 13:

Elsaesser, T; Huse, N; Dreyer, J; Dwyer, JR; Heyne, K; Nibbering, ETJ

**Ultrafast vibrational dynamics and anharmonic couplings of**

**hydrogen-bonded dimers in solution**

CHEMICAL PHYSICS 2007, 341(1-3), p. 175-188

Hydrogen-bonded molecular pairs and dimers represent important structural motifs in nature. They display highly complex vibrational spectra reflecting their equilibrium structure and structural dynamics. Femtosecond nonlinear vibrational spectroscopy provides direct insight into vibrational dynamics and the underlying intra- and intermolecular couplings. In this article, we discuss recent experimental and theoretical results on the ultrafast vibrational response of carboxylic acid and 7-azaindole dimers. Distinct femto- and pico-second time scales are found for the vibrational dephasing of OH/NH stretching excitations and low-frequency hydrogen bond motions, respectively. Anharmonic couplings giving rise to Fermi resonances are determined quantitatively and separated from couplings between stretching and low-frequency modes. In 7-azaindole dimers, the prominent role of Fermi resonances for the NH stretching lifetime is demonstrated.

DOI 10.1016/j.chemphys.2007.06.036

Pub 12:

Heyne, K; Mohammed, OF; Usman, A; Dreyer, J; Nibbering, ETJ; Cusanovich, MA

**Structural evolution of the chromophore in the primary stages of**

**trans/cis isomerization in photoactive yellow protein**

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2005, 127(51), p. 18100-18106

We have studied the structural changes induced by optical excitation of the chromophore in wild-type photoactive yellow protein (PYP) in liquid solution with a combined approach of polarization-sensitive ultrafast infrared spectroscopy and density functional theory calculations. We identify the v(C8- C9) marker modes for solution phase PYP in the P and I0 states, from which we derive that the first intermediate state I0 that appears with a 3 ps time constant can be characterized to have a cis geometry. This is the first unequivocal demonstration that the formation of I0 correlates with the conversion from the trans to the cis state. For the P and I0 states we compare the experimentally measured vibrational band patterns and anisotropies with calculations and find that for both trans and cis configurations the planarity of the chromophore has a strong influence. The C7=C8-C9=O-S moiety of the chromophore in the dark P state has a trans geometry with the C=O group slightly tilted out-of-plane, in accordance with the earlier reported structure obtained in an X-ray diffraction study of PYP crystals. In the case of I0, experiment and theory are only in agreement when the C7=C8-C9=O-S moiety has a planar configuration. We find that the carboxylic side group of Glu46 that is hydrogen-bonded to the chromophore phenolate oxygen does not alter its orientation on going from the electronic ground P state, via the electronic excited P\* state to the intermediate I0 state, providing conclusive experimental evidence that the primary stages of PYP photoisomerization involve flipping of the enone thioester linkage without significant relocation of the phenolate moiety.

DOI 10.1021/ja051210k

Pub 11:

Usman, A; Mohammed, OF; Heyne, K; Dreyer, J; Nibbering, ETJ

**Excited state dynamics of a PYP chromophore model system explored with**

**ultrafast infrared spectroscopy**

CHEMICAL PHYSICS LETTERS 2005, 401(1-3), p. 157-163

We perform ultrafast polarization sensitive visible pump-infrared probe spectroscopy on deprotonated trans-S-phenyl-thio-p-hydroxycinnamate, a model compound for photoactive yellow protein. We derive structural information from the observed bleach signals by comparison of the experimental frequency positions and anisotropies with results from quantum chemical calculations. The electronically excited state decays with 8 or 15 ps time constants for 1:1 or 10:1 DMSO:buffer, respectively, with a quantum yield for isomerization product formation less than 5%. Comparison of our results with earlier reported work on model compounds and on photoactive yellow protein (PYP) suggests an intricate tuning mechanism of the protein environment for the relaxation dynamics of PYP.

DOI 10.1016/j.cplett.2004.11.032

Pub 10:

Heyne, K; Nibbering, ETJ; Elsaesser, T; Petkovic, M; Kühn, O

**Cascaded energy redistribution upon O-H stretching excitation in an**

**intramolecular hydrogen bond**

JOURNAL OF PHYSICAL CHEMISTRY A 2004, 108(29), p. 6083-6086

Femtosecond two-color pump-probe experiments in the mid-infrared range demonstrate that excitation energy of the hydrogen-bonded O-H stretching oscillator of phthalic acid monomethyl ester is redistributed on a subpicosecond time scale along the O-H bending vibration. The O-H stretching and O-H bending lifetimes are 220 and 800 fs, respectively. Quantum dynamical model calculations of the energy flow induced by O-H stretching excitation reveal a relaxation mechanism involving cascaded energy redistribution along the O-H bending vibration and two O-H out-of-plane deformation modes at similar to700 and 800 cm-1.

DOI 10.1021/jp048653f

Pub 9:

Heyne, K; Huse, N; Dreyer, J; Nibbering, ETJ; Elsaesser, T; Mukamel, S

**Coherent low-frequency motions of hydrogen bonded acetic acid dimers in**

**the liquid phase**

JOURNAL OF CHEMICAL PHYSICS 2004, 121(2), p. 902-913

Ultrafast vibrational dynamics of cyclic hydrogen bonded dimers and the underlying microscopic interactions are studied in temporally and spectrally resolved pump-probe experiments with 100 fs time resolution. Femtosecond excitation of the O-H and/or O-D stretching mode gives rise to pronounced changes of the O-H/O-D stretching absorption displaying both rate-like kinetic and oscillatory components. A lifetime of 200 fs is measured for the v=1 state of the O-H stretching oscillator. The strong oscillatory absorption changes are due to impulsively driven coherent wave packet motions along several low-frequency modes of the dimer between 50 and 170 cm-1. Such wave packets generated via coherent excitation of the high-frequency O-H/O-D stretching oscillators represent a clear manifestation of the anharmonic coupling of low- and high-frequency modes. The underdamped low-frequency motions dephase on a time scale of 1-2 ps. Calculations of the vibrational potential energy surface based on density functional theory give the frequencies, anharmonic couplings, and microscopic elongations of the low-frequency modes, among them intermolecular hydrogen bond vibrations. Oscillations due to the excitonic coupling between the two O-H or O-D stretching oscillators are absent as is independently confirmed by experiments on mixed dimers with uncoupled O-H and O-D stretching oscillators.

DOI 10.1063/1.1762873

Pub 8:

Zemojtel, T; Rini, M; Heyne, K; Dandekar, T; Nibbering, ETJ; Kozlowski, PM

**NO-bound myoglobin: Structural diversity and dynamics of the NO ligand**

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY 2004, 126(7), p. 1930-1931

We used femtosecond infrared polarization spectroscopy and density functional theory in a study on the key signaling molecule nitric oxide (NO) bound to myoglobin. Our results show that after photolysis, a substantial fraction of NO recombines within the first few picoseconds. We discovered that the diatomic ligand is severely tilted in the protein and present evidence that the Fe−NO moiety can sample a wide range of off-axis tilting and bending conformations.

DOI 10.1021/ja039086x

Pub 7:

Heyne, K; Huse, N; Nibbering, ETJ; Elsaesser, T

**Ultrafast relaxation and anharmonic coupling of O-H stretching and**

**bending excitations in cyclic acetic acid dimers**

CHEMICAL PHYSICS LETTERS 2003, 382, p. 19-25

The relaxation and anharmonic coupling of vibrational O-H stretching and O-H bending excitations of hydrogen-bonded acetic acid dimers in solution is studied by femtosecond two-color pump-probe spectroscopy in the mid-infrared. The O-H stretching and O-H bending population lifetimes are 200 and 250 fs. After excitation of the stretching mode, anharmonic coupling leads to pronounced absorption changes of the bending mode, without involving relaxation induced excess populations of the bending mode. On a longer picosecond time scale, a similar reshaping of the vibrational spectra is induced by anharmonically coupled modes which are populated through vibrational relaxation.

DOI 10.1016/j.cplett.2003.09.145

Pub 6:

Huse, N; Heyne, K; Dreyer, J; Nibbering, ETJ; Elsaesser, T

**Vibrational multilevel quantum coherence due to anharmonic couplings in**

**intermolecular hydrogen bonds**

PHYSICAL REVIEW LETTERS 2003, 91, p. 197401-197404

Femtosecond three-pulse photon-echo studies of acetic acid dimers in solution reveal multilevel coherence of O-H stretching excitations caused by the anharmonic coupling between the high-frequency stretching and low-frequency hydrogen-bond motions. We demonstrate for the first time that such multilevel coherence determines the nonexponential decay of the macroscopic O-H stretching polarization, whereas spectral diffusion processes play a minor role. The dephasing time of individual vibrational transitions contributing to the overall polarization is approximately 200 fs.

DOI 10.1103/PhysRevLett.91.197401

Pub 5:

Heyne, K; Huse, N; Nibbering, ETJ; Elsaesser, T

**Ultrafast coherent nuclear motions of hydrogen bonded carboxylic acid**

**dimers**

CHEMICAL PHYSICS LETTERS 2003, 369, p. 591-596

Real-time vibrational dynamics of the cyclic dimer of deuterated acetic acid in solution, a model system for hydrogen-bonded units of biomolecules, are elucidated by ultrafast infrared spectroscopy. Upon excitation of the O-D stretching mode, we demonstrate coherent nuclear motions along several intermolecular low-frequency modes of the dimer. The anharmonic coupling of the fast O-D stretching and slow low-frequency motions is isolated in the nonlinear vibrational response whereas other couplings are suppressed. The large-amplitude motions persist for several pico-seconds, potentially allowing for optical control of (bio)chemical dynamics.

DOI 10.1016/S0009-2614(03)00023-X

Pub 4:

Heyne, K; Huse, N; Nibbering, ETJ; Elsaesser, T

**Coherent vibrational dynamics of intermolecular hydrogen bonds in acetic**

**acid dimers studied by ultrafast mid-infrared spectroscopy**

JOURNAL OF PHYSICS-CONDENSED MATTER 2003, 15, p. 129-136

Ultrafast vibrational motions and the underlying microscopic couplings in hydrogen-bonded cyclic dimers. of acetic acid are studied by pump-probe and photon echo experiments in the mid-infrared. Upon femtosecond excitation of the O-H stretching mode, we demonstrate coherent nuclear motions along the in-plane dimer stretching mode which persist for picoseconds. The anharmonic coupling of the O-H stretching and the low-frequency mode is isolated in the nonlinear vibrational response, whereas other couplings are suppressed. Three-pulse photon echo experiments demonstrate a dephasing of O-H stretching excitations on a femtosecond timescale and quantum beats due to the anharmonically coupled dimer stretching mode.

DOI 10.1088/0953-8984/15/1/316

Pub 3:

Herbst, J; Heyne, K; Diller, R

**Femtosecond infrared spectroscopy of bacteriorhodopsin chromophore**

**isomerization**

SCIENCE 2002, 297(5582), 822-825

The vibrational dynamics of the retinal chromophore all-trans-to-13-cis photoisomerization in bacteriorhodopsin has been studied with mid-infrared absorption spectroscopy at high time resolution (about 200 femtoseconds). After photoexcitation of light-adapted bacteriorhodopsin, the transient infrared absorption was probed in a broad spectral region, including vibrations with dominant C-C, C=C and C=NH stretching mode amplitude. All photoproduct modes, especially those around 1190 cm-1 that are indicative for a 13-cis configuration of the chromophore, rise with a time constant of ~0.5 picosecond. The results presented give direct vibrational-spectroscopic evidence for the isomerization taking place within 0.5 picosecond, as has been suggested by previous optical femtosecond time-resolved experiments but questioned recently by picosecond time-resolved vibrational spectroscopy experiments.

DOI 10.1126/science.1072144

Pub 2:

Heyne, K; Herbst, J; Stehlik, D; Esteban, B; Lamparter, T; Hughes, J; Diller, R

**Ultrafast dynamics of phytochrome from the cyanobacterium Synechocystis,**

**reconstituted with phycocyanobilin and phycoerythrobilin**

BIOPHYSICAL JOURNAL 2002, 82(2), 1004-1016

Femtosecond time-resolved transient absorption spectroscopy was employed to characterize for the first time the primary photoisomerization dynamics of a bacterial phytochrome system in the two thermally stable states of the photocycle. The 85-kDa phytochrome Cph1 from the cyanobacterium Synechocystis PCC 6803 expressed in Escherichia coli was reconstituted with phycocyanobilin (Cph1-PCB) and phycoerythrobilin (Cph1-PEB). The red-light-absorbing form Pr of Cph1-PCB shows an ~150 fs relaxation in the S1 state after photoexcitation at 650 nm. The subsequent Z-E isomerization between rings C and D of the linear tetrapyrrole-chromophore is best described by a distribution of rate constants with the first moment at (16 ps)-1. Excitation at 615 nm leads to a slightly broadened distribution. The reverse E-Z isomerization, starting from the far-red-absorbing form Pfr, is characterized by two shorter time constants of 0.54 and 3.2 ps. In the case of Cph1-PEB, double-bond isomerization does not take place, and the excited-state lifetime extends into the nanosecond regime. Besides a stimulated emission rise time between 40 and 150 fs, no fast relaxation processes are observed. This suggests that the chromophore-protein interaction along rings A, B, and C does not contribute much to the picosecond dynamics observed in Cph1-PCB but rather the region around ring D near the isomerizing C-15==C-16 double bond. The primary reaction dynamics of Cph1-PCB at ambient temperature is found to exhibit very similar features as those described for plant type A phytochrome, i.e., a relatively slow Pr, and a fast Pfr, photoreaction. This suggests that the initial reactions were established already before evolution of plant phytochromes began.

Pub 1:

Heyne, K; Herbst, J; Dominguez-Herradon, B; Alexiev, U; Diller, R

**Reaction control in bacteriorhodopsin: Impact of arg82 and asp85 on the**

**fast retinal isomerization, studied in the second site revertant**

**arg82ala/gly231cys and various purple and blue forms of**

**bacteriorhodopsin**

JOURNAL OF PHYSICAL CHEMISTRY B 2000, 104, 6053-6058

Femtosecond time-resolved optical absorption experiments reveal that the changes of the excited electronic state dynamics observed between bacteriorhodopsin wild type and the single mutant R82A are completely reversed in the double mutant R82A/G231C. Thus, the bacteriorhodopsin double mutant R82A/G231C is shown to be a second site revertant with respect to the primary ultrafast all-trans to 13-cis photoisomerization of the retinal cofactor. The results imply that in R82A/G231C a cofactor binding pocket is realized in which, at physiological pH, the arginine residue in position 82 (R82) is not, but a deprotonated D85 is needed for a wild-type-like fast retinal photoisomerization. The revertancy found for R82A/G231C and further results on the single mutants R82A, R82C, R82Q, and G231C at various pH values and ion concentrations confirm and broaden the range of applicability of the known correlation between the protonation state of aspartic acid 85 (D85) and the time constants of the excited electronic state decay. Among the bR mutant systems investigated, species with D85 deprotonated exhibit an excited electronic state decay time constant of τ1 = 0.52 ± 0.05 ps whereas systems with D85 protonated show a biphasic decay with τ1 = 1.7 ± 0.3 and τ2  ranging from 6 to 12 ps. It is noted that the distribution of the τ2 times is much wider than that of the τ1 times.

DOI 10.1021/jp992877u