



• *Excited-State Symmetry Breaking in a Quadrupolar Molecule Visualized in Time and Space*

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The influence of the length of the push-pull branches of quadrupolar molecules on their excited-state symmetry breaking was investigated using ultrafast time-resolved IR spectroscopy. For this, the excited-state dynamics of an A-D-A molecule was compared with those of an ADA analogue, where the same electron donor (D) and acceptor (A) subunits are directly linked without a phenylethynyl spacer. The spatial distribution of the excitation was visualized in real time by monitoring ^{13}C and ^{15}N vibrational modes localized in the spacer and acceptor units, respectively. In nonpolar solvents, the excited state is quadrupolar and the excitation is localized on the D center. In medium polarity solvents, the excitation spreads over the entire molecule but is no longer symmetric. Finally, in the most polar solvents, the excitation localizes on a single D-A branch, contrary to the ADA analogue where symmetry breaking is only partial.

• *Specific Monitoring of Excited-State Symmetry Breaking by Femtosecond Broadband Fluorescence Upconversion Spectroscopy*

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Most quadrupolar molecules designed for large two-photon absorption cross section have been shown to undergo symmetry breaking upon excitation to the S_1 state. This was originally deduced from their strong fluorescence solvatochromism and later visualized in real time using transient infrared spectroscopy. For molecules not containing clear IR marker modes, however, a specific real-time observation of the symmetry breaking process remains lacking. Here we show that this process can be resolved using broadband fluorescence upconversion spectroscopy by monitoring the instantaneous emission transition dipole moment. This approach is illustrated with measurements performed on two quadrupolar molecules, with only one of them undergoing excited-state symmetry breaking in polar solvents.

• *Direct Observation of a Photochemical Alkyne-Allene Reaction and of a Twisted and Rehybridized Intramolecular Charge-Transfer State in a Donor-Acceptor Dyad*

Bogdan Dereka, Denis Svechkarov, Arnulf Rosspeintner, Maximilian Tromayer, Robert Liska, Aaron M. Mohs and Eric Vauthey
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The excited-state dynamics of an aniline- π -triazine electron donor-acceptor dyad with an alkyne spacer has been investigated using a combination of ultrafast broadband mid-IR and visible transient absorption and fluorescence spectroscopies. The transient IR data reveal the occurrence of an efficient alkyne to allene isomerization of the spacer with a time constant increasing from a few hundreds of femtoseconds to a few picoseconds with solvent viscosity. This process is faster than the vibrational cooling of the Franck-Condon excited state, indicative of nonequilibrium dynamics. The transient electronic absorption and fluorescence data evidence that this transformation is accompanied by a charge separation between the donor and the acceptor subunits. The allene character of the spacer implies an orthogonal orientation of the donor and acceptor moieties, similar to that proposed for twisted intramolecular charge-transfer states. Such states are often invoked in the excited-state dynamics of donor-acceptor dyads, but their involvement could never be unambiguously evidenced spectroscopically. The alkyne-allene isomerization involves not only a torsional motion but also a bending of the molecule due to the sp to sp^2 rehybridization of one of the alkyne carbon atoms. This twisted and rehybridized intramolecular charge transfer (π - π^*) state decays back to the planar and linear alkyne ground state on a time scale decreasing from a few hundred to ten picoseconds upon going from weakly to highly polar solvents. The different solvent dependencies reveal that the dynamics of the allene buildup are controlled by the structural changes, whereas the decay is limited by the charge recombination step.

• *Influence of Solvent Relaxation on Ultrafast Excited-State Proton Transfer to Solvent*

Tatu Kumpulainen, Arnulf Rosspeintner, Bogdan Dereka and Eric Vauthey
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A thorough understanding of the microscopic mechanism of excited-state proton transfer (ESPT) and the influence of the solvent environment on its dynamics are of great fundamental interest. We present here a detailed investigation of an ESPT to solvent (DMSO) using time-resolved broadband fluorescence and transient absorption spectroscopies. All excited-state species are resolved spectrally and kinetically using a global target analysis based on the two-step Eigen-Weller model. Reversibility of the initial short-range proton transfer producing excited contact ion pairs (CIP*) is observed unambiguously in fluorescence and must be explicitly considered to obtain the individual rate constants. Close inspection of the early dynamics suggests that the relative populations of the protonated form (ROH*) and CIP* are governed by solvent relaxation that influences the relative energies of the excited states. This constitutes a breakdown of the Eigen-Weller model, although the overall agreement between the data and the analysis using classical rate equations is excellent.

• *Solute-Solvent Interactions and Excited-State Symmetry Breaking: Beyond the Dipole-Dipole and the Hydrogen-Bond Interactions*

Bogdan Dereka and Eric Vauthey
The Journal of Physical Chemistry Letters **8** (16) 2017, p3927-3932 DOI:10.1021/acs.jpcllett.7b01821

Symmetry breaking of the excited state of a linear quadrupolar acceptor-donor-acceptor molecule was investigated using time-resolved infrared spectroscopy in 55 solvents allowing the influence of several solute-solvent interactions to be examined separately. No symmetry breaking was found in nonpolar solvents irrespective of their refractive index, indicating that differences in dispersion interactions between the two arms of the molecule do not suffice to induce an asymmetric distribution of the excitation. However, symmetry breaking was observed in nondipolar but quadrupolar solvents like benzene to an extent that can be as large as that found in medium dipolar solvents like THF. Whereas larger symmetry breaking occurs in the most dipolar solvents, the strongest are observed in protic solvents due to hydrogen bonding. Strong evidence of the formation of halogen bonds in the excited state is also presented, confirming the idea of symmetry-breaking-induced asymmetrical photochemistry.

• *Direct Local Solvent Probing by Transient Infrared Spectroscopy Reveals the Mechanism of Hydrogen-Bond Induced Nonradiative Deactivation*

Bogdan Dereka and Eric Vauthey
Chemical Science **8** (7) 2017, p5057-5066 DOI:10.1039/C7SC00437K

The fluorescence quenching of organic dyes via H-bonding interactions is a well-known phenomenon. However, the mechanism of this Hydrogen-Bond Induced Nonradiative Deactivation (HBIND) is not understood. Insight into this process is obtained by probing in the infrared the O-H stretching vibration of the solvent after electronic excitation of a dye with H-bond accepting cyano groups. The fluorescence lifetime of this dye was previously found to decrease from 1.5 ns to 110 ps when going from an aprotic solvent to the strongly protic hexafluoroisopropanol (HFP). Prompt strengthening of the H-bond with the dye was identified by the presence of a broad positive O-H band of HFP, located at lower frequency than the O-H band of the pure solvent. Further strengthening occurs within a few picoseconds before the excited H-bonded complex decays to the ground state in 110 ps. The latter process is accompanied by the dissipation of energy from the dye to the solvent and the rise of a characteristic hot solvent band in the transient spectrum. Polarization-resolved measurements evidence a collinear alignment of the nitrile and hydroxyl groups in the H-bonded complex, which persists during the whole excited-state lifetime. Measurements in other fluorinated alcohols and in chloroform/HFP mixtures reveal that the HBIND

efficiency depends not only on the strength of the H-bond interactions between the dye and the solvent but also on the ability of the solvent to form an extended H-bond network. The HBIND process can be viewed as an enhanced internal conversion of an excited complex consisting of the dye molecule connected to a large H-bond network.

- *A simple model of solvent-induced symmetry-breaking charge transfer in excited quadrupolar molecules*

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Keywords: solvents • dielectric constant • excited states • charge transfer • band models

A simple model has been developed to describe the symmetry-breaking of the electronic distribution of $A_L\hat{\sigma}^*D\hat{\sigma}^*A_R$ type molecules in the excited state, where D is an electron donor and A_L and A_R are identical acceptors. The origin of this process is usually associated with the interaction between the molecule and the solvent polarization that stabilizes an asymmetric and dipolar state, with a larger charge transfer on one side than on the other. An additional symmetry-breaking mechanism involving the direct Coulomb interaction of the charges on the acceptors is proposed. At the same time, the electronic coupling between the two degenerate states, which correspond to the transferred charge being localised either on A_L or A_R , favours a quadrupolar excited state with equal amount of charge-transfer on both sides. Because of these counteracting effects, symmetry breaking is only feasible when the electronic coupling remains below a threshold value, which depends on the solvation energy and the Coulomb repulsion energy between the charges located on A_L and A_R . This model allows reproducing the solvent polarity dependence of the symmetry-breaking reported recently using time-resolved infrared spectroscopy.

- *Exploring Fluorescent Dyes at Biomimetic Interfaces with Second Harmonic Generation and Molecular Dynamics*

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Langmuir **33** (14) **2017**, p3373-3383 DOI:10.1021/acs.langmuir.7b00403

The adsorption of a DNA fluorescent probe belonging to the thiazole orange family at the dodecane/water and dodecane/phospholipid/water interfaces has been investigated using a combination of surface second harmonic generation (SSHG) and all-atomistic molecular dynamics (MD) simulations. Both approaches point to a high affinity of the cationic dye for the dodecane/water interface with a Gibbs free energy of adsorption on the order of ~ 45 kJ/mol. Similar affinity was observed with a monolayer of negatively charged DPPG (1,2-dipalmitoyl-*sn*-glycero-3-phospho-*rac*-(1-glycerol)) lipids. On the other hand, no significant adsorption could be found with the zwitterionic DPPC (1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine) lipids. This was rationalized in terms of Coulombic interactions between the monolayer surface and the cationic dye. The similar affinity for the interface with and without DPPG, despite the favorable Coulombic attraction in the latter case, could be explained after investigating the interfacial orientation of the dye. In the absence of a monolayer, the dye adsorbs with its molecular plane almost flat at the interface, whereas in the presence of DPPG it has to intercalate into the monolayer and adopt a significantly different orientation to benefit from the electrostatic stabilization.

- *Probe dependence on polar solvation dynamics from fs broadband fluorescence*

Tatu Kumpulainen, Arnulf Rosspeintner and Eric Vauthey

Physical Chemistry Chemical Physics **19** (13) **2017**, p8815-8825 DOI:10.1039/C7CP00706J

Polar solvation dynamics of six 7-aminocoumarins and 4-aminophthalimide (**4AP**) are investigated using broadband Fluorescence UP $\hat{\sigma}$ conversion Spectroscopy (FLUPS) combined with a global analysis based on time-dependent band-shape functions. The solvation dynamics of the coumarins in ethanol exhibit only minor differences but are, however, significantly different from that of **4AP**. The band-shape parameters, width and asymmetry, exhibit much larger variation even among the coumarins and are correlated with the amount of excess excitation energy. Differences in the solvation dynamics of **4AP** and a selected coumarin, **C151**, are also observed in dimethyl sulfoxide demonstrating the molecularity of solvation i.e. solvation depends on the solute and does not solely reflect the dynamic properties of the solvent. These differences are attributed to specific solute-solvent interactions due to hydrogen bonding. In a weakly interacting solvent, benzonitrile, the solvation dynamics of **4AP** and **C151** are nearly identical.

- *Looking at Photoinduced Charge Transfer Processes in the IR: Answers to Several Long-Standing Questions*

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Because of its crucial role in many areas of science and technology, photoinduced electron transfer is the most investigated photochemical reaction. Despite this, several important questions remain open. We present recent efforts to answer some of them, which concern both inter- and intramolecular processes. The decisive factor that allowed these issues to be successfully addressed was the use of time-resolved infrared (TRIR) spectroscopy. Many different transient species, such as tight and loose ion pairs (TIPs and LIPs) and exciplexes, have been invoked to explain the dynamics of intermolecular photoinduced charge separation reactions (i.e., electron transfer between two neutral species) and the production of free ions. However, their structures are essentially unknown, and their exact roles in the reaction mechanism are unclear. Indeed, the commonly used transient electronic absorption spectroscopy does not give much structural insight and cannot clearly distinguish ion pairs from free ions, at least in the visible region. Unambiguous spectral signatures of TIPs, LIPs, and exciplexes could be observed in the IR using electron donor/acceptor (D/A) pairs with adequate vibrational marker modes. The ability to spectrally distinguish these intermediates allowed their dynamics to be disentangled and their roles to be determined. Structural information could be obtained using polarization-resolved TRIR spectroscopy. Our investigations reveal that moderately to highly exergonic reactions result in the formation of both TIPs and LIPs. TIPs are not only generated upon direct charge-transfer excitation of DA complexes, as usually assumed, but are also formed upon static quenching with reactant pairs at distances and orientations enabling charge separation without diffusion. On the other hand, dynamic quenching produces primarily LIPs. In the case of highly exergonic reactions, strong indirect evidence for the generation of ion pairs in an electronic excited state was found, accounting for the absence of an inverted region. Finally, weakly exergonic reactions produce predominantly exciplexes, which can evolve further into ion pairs or recombine to the neutral ground state. The high sensitivity of specific vibrational modes to the local electronic density was exploited to visualize the photoinduced charge flow in symmetric $A\hat{\sigma}^*(\hat{\sigma}^*D)_2$ - and $D\hat{\sigma}^*(\hat{\sigma}^*A)_2$ -type molecules developed for their two-photon absorption properties. The electronic ground state and Franck-Condon S_1 state of these molecules are purely quadrupolar, but the strong solvatochromism of their fluorescence points to a highly dipolar relaxed S_1 state. This has been explained in terms of excited-state symmetry breaking induced by solvent and/or structural fluctuations. However, real-time observation of this process was missing. Direct visualization of symmetry-breaking charge transfer was achieved using TRIR spectroscopy by monitoring vibrations localized in the two arms of these molecules. A transition from a purely quadrupolar state to a symmetry-broken state on the timescale of solvent relaxation could be clearly observed in polar solvents, indicating that symmetry breaking occurs primarily via solvent fluctuations. In the case of the $D\hat{\sigma}^*(\hat{\sigma}^*A)_2$ molecule, this breaking results in different basicities at the two A ends and consequently in different affinities for H-bonds, which in turn leads to the formation of an asymmetric tight H-bonded complex in highly protic solvents.

- *Simulations of the Ultrafast Transient Absorption Dynamics of a Donor-Acceptor Biaryl in Solution*

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The Journal of Physical Chemistry A **121** (2) **2017**, p471-481 DOI:10.1021/acs.jpca.6b11581

A model for simulating the transient electronic absorption spectra of donor-acceptor dyads undergoing ultrafast intramolecular charge transfer in solution has been developed. It is based on the stochastic multichannel point-transition approach and includes the reorganization of high-frequency intramolecular modes (treated quantum mechanically) and of low frequency intramolecular and solvent modes (described classically). The relaxation of the slow modes is assumed to be exponential with time constants taken from experiments. The excited-state dynamics is obtained by simulating the population distribution of each quantum state after optical excitation and upon electronic and vibrational transitions. This model was used to simulate the transient electronic absorption spectra measured previously with a pyrylium phenolate in acetonitrile. A very good agreement between the simulated and measured spectra was obtained assuming a three-level model including the ground state, the optically excited state, and a dark state with large charge-transfer character and a substantially different geometry relative to that of the optically excited state. The merit of this approach to disentangle the contributions of both population changes and relaxation processes to the ultrafast spectral dynamics will be discussed.

- *Ultrafast Elementary Photochemical Processes of Organic Molecules in Liquid Solution*

Tatu Kumpulainen, Bernhard Lang, Arnulf Rosspeintner and Eric Vauthey

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Ultrafast photochemical reactions in liquids occur on similar or shorter time scales compared to the equilibration of the optically populated excited state. This equilibration involves the relaxation of intramolecular and/or solvent modes. As a consequence, the reaction dynamics are no longer exponential, cannot be quantified by rate constants, and may depend on the excitation wavelength contrary to slower photochemical processes occurring from equilibrated excited states. Such ultrafast photoinduced reactions do no longer obey the Kasha-Vavilov rule. Nonequilibrium effects are also observed in diffusion-controlled intermolecular processes directly after photoexcitation, and their proper description gives access to the intrinsic reaction dynamics that are normally hidden by diffusion. Here we discuss these topics in relation to ultrafast organic photochemical reactions in homogeneous liquids. Discussed reactions include intra- and intermolecular electron- and proton-transfer processes, as well as photochromic reactions occurring with and without bond breaking or bond formation, namely ring-opening reactions and cis-trans isomerizations, respectively.

- *A biocompatible macromolecular two-photon initiator based on hyaluronan*

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Polymer Chemistry **8** (2) **2017**, p451-460 DOI:10.1039/C6PY01787H

The possibility of the direct encapsulation of living cells via two-photon induced photopolymerization enables the microfabrication of hydrogel scaffolds with high initial cell loadings and intimate matrix-cell contact. While highly efficient water-soluble two-photon initiators based on benzylidene ketone dyes have been developed, they exhibit considerable cyto- and phototoxicity. To address the problem of photoinitiator migration from the extracellular matrix into the cytosol, a two-photon initiator bound to a polymeric hyaluronan backbone (**HAPI**) was synthesized in this work. **HAPI** exhibited a distinct improvement of cytocompatibility compared to a reference two-photon initiator. Basic photophysical investigations were performed to characterize the absorption and fluorescence behavior of **HAPI**. Laser scanning microscopy was used to visualize and confirm the hindered transmembrane migration behavior of **HAPI**. The performance of **HAPI** was tested in two-photon polymerization at exceedingly high printing speeds of 100 mm s⁻¹ producing gelatin-based complex 3D hydrogel scaffolds with a water content of 85%. The photodamage of the structuring process was low and viable MC3T3 cells embedded in the gel were monitored for several days after structuring.

- *Ultrafast transient IR spectroscopy and DFT calculations of ruthenium(II) polypyridyl complexes*

Qinchao Sun, Bogdan Dereka, Eric Vauthey, Latevi Max Lawson Daku and Andreas Hauser

Chemical Science **8** (1) **2017**, p223-230 DOI:10.1039/C6SC01220E

Ultrafast time-resolved infrared spectroscopy of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine), [Ru(mbpy)₃]²⁺ (mbpy = 6-methyl-2,2'-bipyridine), and [Ru(mphen)₃]²⁺ (mphen = 2-methyl-1,10-phenanthroline) in deuterated acetonitrile serves to elucidate the evolution of the system following pulsed excitation into the ¹MLCT band at 400 nm. Whereas for [Ru(bpy)₃]²⁺ no intermediate state can be evidenced for the relaxation of the corresponding ³MLCT state back to the ground state, for [Ru(mbpy)₃]²⁺ and [Ru(mphen)₃]²⁺ an intermediate state with a lifetime of about 400 ps is observed. The species associated IR difference spectra of this state are in good agreement with the calculated difference spectra of the lowest energy ³dd state using DFT. The calculated potential energy curves for all the complexes in the triplet manifold along the metal-ligand distance show that for [Ru(bpy)₃]²⁺ the ³dd state is at higher energy than the ³MLCT state and that there is a substantial barrier between the two minima. For [Ru(mbpy)₃]²⁺ and [Ru(mphen)₃]²⁺, the ³dd state is at lower energy than the ³MLCT state.