

4.9 Project part P09

Femtochemistry – Theory

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

1	%	2	%	3	%
1317	70	1311	20	1327	10

4.9.1 Summary

The objective of this project part is to develop methods and models for the investigation of processes induced by the interaction of molecules with laser pulses, and the microscopic control of molecular processes. These concepts are then applied in the simulation and interpretation of current experiments. The research in the 2nd period focused on (i) the complete high-level *ab initio* treatment of small systems, (ii) the dynamics and control of molecular model systems, including the role of the carrier envelope phase, and (iii) the development and assessment of approximate methods and their application to larger molecular systems.

(i) The work comprises the determination of highly accurate molecular energy surfaces in electronically excited states including nonadiabatic coupling vectors, the discussion of conical intersections and nonadiabatic dynamics. Significant breakthrough has been achieved in several ways. The analytic computation of energy gradients and coupling vectors has been implemented in the distribution version of our public domain COLUMBUS program system. 'On-the-fly' non-adiabatic dynamics could be performed for the first time with high-level quantum chemical methods and novel views of standard photodynamic processes could be given. These investigations laid the basis for the treatment of larger systems in item (iii).

(ii) Molecular isomerization in the electronic ground state can be driven by one-cycle pulses and by pairs of time-delayed half-cycle pulses. The dynamics of these processes are dipole-driven and give rise to an extremely strong CEP-dependence. This behaviour opens up new possibilities for level switching in dipolar molecular systems. Control scenarios utilizing phase adjusted pulse pairs and phase-incremented pulse trains have been developed for the suppression of background state population in molecular multiphoton excitation.

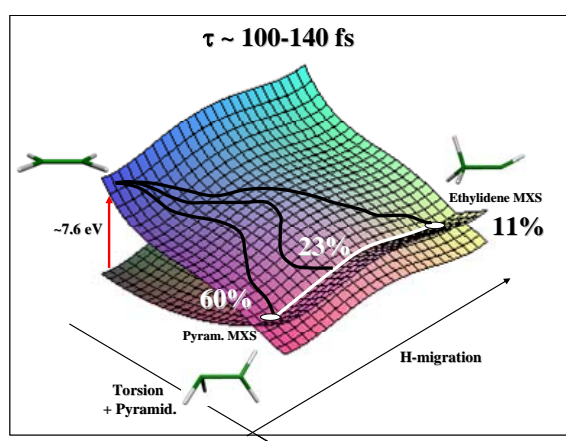
(iii) A stepwise strategy was used to assess computational methods for the calculation of energy surfaces of compounds, which are of interest for the experimental groups in P18. Excited-state intramolecular proton transfer (ESIPT) was investigated in collaboration with the group of E. Riedle concentrating on 2-(2'-hydroxyphenyl)benzothiazole and 10-hydroxybenzo[h]quinoline. Analysis of the experimental femtosecond investigations resulted in the picture of a coupling of low-frequency vibrational modes with the hydrogen-transfer process. The combination of classical dynamics calculations, wave packet dynamics calculations and the femtosecond experiments provides a picture of the ESIPT dynamics in a detail never achieved before. In cooperation with H. Kauffmann, π -conjugated oligomers, such as oligo-fluorenes and oligo-p-phenylenes, have been investigated by RI-CC2 and

TDDFT methods. In the next step, this work will lead to a dynamical treatment similar to that already achieved for the ESIPT processes.

4.9.2 Results and discussion

The aim of this project is the development of methods for the theoretical investigation and the microscopic control of molecular processes induced by laser pulses, the application of these approaches to molecular dynamics simulation and the interpretation of current or future experiments. Our plan for the second ADLIS phase was (i) the complete ab initio high-level treatment of small systems, (ii) the dynamics and control of molecular model systems, (iii) the development and assessment of approximate methods and their application to larger molecular systems.

The different conceptual and procedural steps necessary for the solution of the just-mentioned tasks are characterized in the figure below, in which results from our simulations of the photodynamics of ethylene (Barbatti 2005a) are displayed.



The figure shows two energy surfaces (S_0 and S_1), the extension of the intersection seam over a wide range of molecular structures, examples of trajectories and the computed efficiency of the seam in terms of these structures. One of the biggest problems in the overall theoretical treatment of the photodynamics of molecular systems is the computation of excited-state surfaces since the required wave functions have a complicated multireference structure and conical intersection will occur at which the fundament of Quantum Chemistry, the Born-Oppenheimer, is breaking down. However, it is especially this intersection region, which is of particular importance since there ultrafast femtosecond transitions from one electronic state to the other will occur. The performance of dynamics calculations on such surfaces is also not straightforward. Quantum dynamics calculations are limited to a few internal degrees of freedom and usually require the pre-computation of the energy surfaces. Therefore, as an alternative, classical on-the-fly surface-hopping dynamics calculations can

be performed. The on-the-fly strategy implies that only those points on the energy surfaces need to be considered, which are actually accessed during the dynamics. No pre-computation is required and all internal degrees of freedom are taken into account. However, it is necessary to keep in mind that the classical approach will not be able to reproduce all features of a quantum mechanical dynamics.

(A) *Ab initio treatment of small systems*

Procedures for the computation of analytic MR-CI gradient and nonadiabatic coupling vectors have been implemented into the COLUMBUS program system. COLUMBUS (see <http://www.univie.ac.at/columbus>) is a set of program modules developed by our group in cooperation with R. Shepard (Argonne National Laboratory), I. Shavitt (Ohio State University) and R. M. Pitzer (Ohio State University). It is especially well-suited for such difficult cases as excited-state calculations or extensive scans of energy surfaces including bond-breaking processes. The development of quantum chemical methods for the just-mentioned analytic computation of MR-CI gradient and nonadiabatic coupling vectors is quite involved (Lischka 2004, Dallos 2004). All respective program work has been finished and all features are available in the standard distribution set of COLUMBUS. Our program package is the only one worldwide providing these analytic MR-CI gradient/nonadiabatic coupling vector properties.

Using these possibilities a wide variety of calculations on energy surfaces of interesting chemical problems have been performed. From these we want to mention here the calculations on charge exchange between singly charged ions and a LiF surface (Wirtz 2003) in cooperation with the group of J. Burgdörfer (P10). In particular, the structure of nonadiabatic processes and avoided crossings has been studied. Furthermore, systematic investigations on polar π -systems, namely ethylene (Barbatti 2004, 2005ab), fluoroethylene (Barbatti 2005c), silaethylene (Pitonak 2005, Zechmann 2005) and the formiminium cation (Lischka 2005, Barbatti 2005d), excited-state protonation processes of formaldehyde (Antol 2003) and formamide (Antol 2004a) and the bond-stretch isomerism in the benzo[1,2:4,5]dicyclobutadiene system (Antol 2004b) have been carried out.

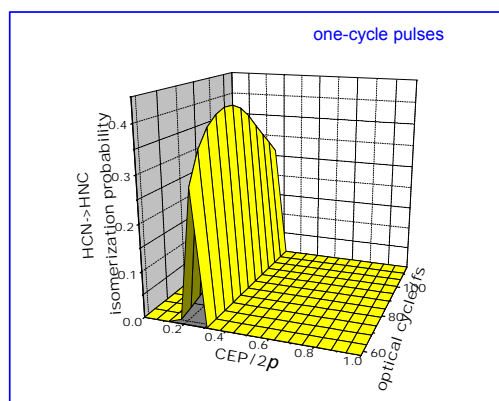
Quantum dynamical wave packet investigations were performed for the S_1 and S_2 transitions in acetylene in collaboration with the group of H. Köppel, University of Heidelberg, Germany (Schubert 2005). Whereas the S_1 spectrum is quite well understood, much less is known about the transitions to the S_2 state. Our previous calculations had shown that an asymmetric minimum-energy structure existed on the S_2 surface. However, we had also located an intersection with the S_1 state nearby. The wave packet simulations were performed in a first step for the isolated S_1 and S_2 surfaces. They gave good agreement with

the experimental S_1 spectrum and a first access to the interpretation of the S_2 transitions. Wave packet calculations including nonadiabatic interactions between the S_1 and S_2 states are in progress.

On-the-fly surface-hopping dynamics calculations have been performed for the aforementioned series of polar π -systems. In these calculations the MR-CI method has been used due to the availability of analytic gradients and nonadiabatic coupling vectors. These calculations represent a real breakthrough in this field, since before only much less reliable methods, such as the complete active space self consistent field (CASSCF) method could be used. In these calculations very interesting, but also quite unexpected results were obtained (Barbatti 2005c, Zechmann 2005). They demonstrated clearly the need of dynamics investigations for the clarification of photochemical reaction mechanisms. These investigations are currently extended to larger systems, such as protonated Schiff bases, which - in the form of retinal - are responsible for the primary processes of vision. These full ab initio investigations formed also the basis for our calculations on larger molecular systems, where this extensive quantum chemical treatment was not possible any more.

(B) The dynamics and control of molecular model systems

These investigations are stimulated by the progress and achievements of projects P02 and P03 and attempt to carry over these pulse concepts and techniques to molecular systems. One branch of this research deals with the application of few-cycle, one-cycle and half-cycle pulses to photochemical processes in molecular ground states, and in particular with the role and the control properties of the carrier envelope phase (CEP).

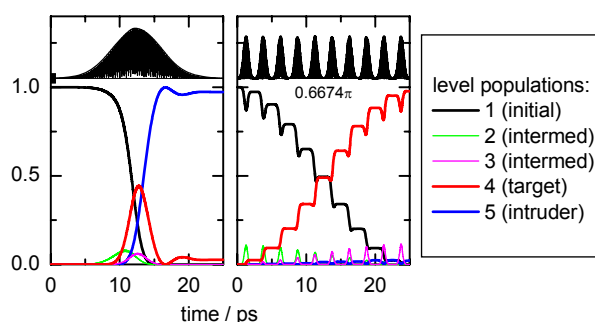


The Figure shows the strong CEP-dependence of the HCN→HNC isomerization yield that arises if the reaction is driven with ir one-cycle pulses (Uiberacker 2004ab). Isomerization can also be driven by pairs of time-delayed half-cycle pulses, in which case the

timing depends crucially on the polarization direction of the lobes. The generic mechanism of population transfer in both cases is the preparation by the pump pulse of a wavepacket involving delocalized states above the barrier, followed by the motion of the delocalized part of wavepacket across the barrier, and the de-excitation by the dump pulse (or lobe) to states in the product well. The CEP-dependent timing is determined by the recurrence properties of the wavepacket, which depend not only on the potential, but are also linked to the dipole moments of the molecular system. A marked dependence on pulse duration, caused by possible self-quenching of the recurring wavepacket, is again linked to the molecular dipole properties.

In the sub-one-cycle regime the usual frequency- (energy-) driven dynamics is thus replaced by dipole-driven dynamics (Uiberacker 2005). For an arbitrarily shaped sub-one-cycle pulse interacting with a two-level system a dipole resonance condition can be derived, and a Rabi-type π -pulse behavior applies for the transition between the two levels. Numerical work shows that with some limitations such conditions are approximately valid for N -level systems. These conditions determine the optimal amplitude and pulse duration for a driving pulse. Since the dipole resonance depends on the sign of the field, a pair of oppositely polarized half-cycle pulses has very different effects on the molecule. In the most common case, a transition, which is resonantly driven by a suitable half-cycle pulse, will not be driven by the sign-reversed pulse. This represents an extreme case of CEP-dependence and implies that interesting cases of level switching may be devised for molecular systems. Furthermore, in an N -level system half-cycle pulses with different CEPs and/or different amplitudes may select between transitions to different levels, thus generating the possibility of a multiple switch.

Continuing the investigations on the loss of selectivity in multiphoton (MP) excitations by background state participation, we found that the intruder state not only does the resonance leak into the background state, the background state also may act as a sink for population in extended frequency ranges, which in the unperturbed system are dark. We introduced several control strategies suppressing the leaking to intruder states (Lan 2004).



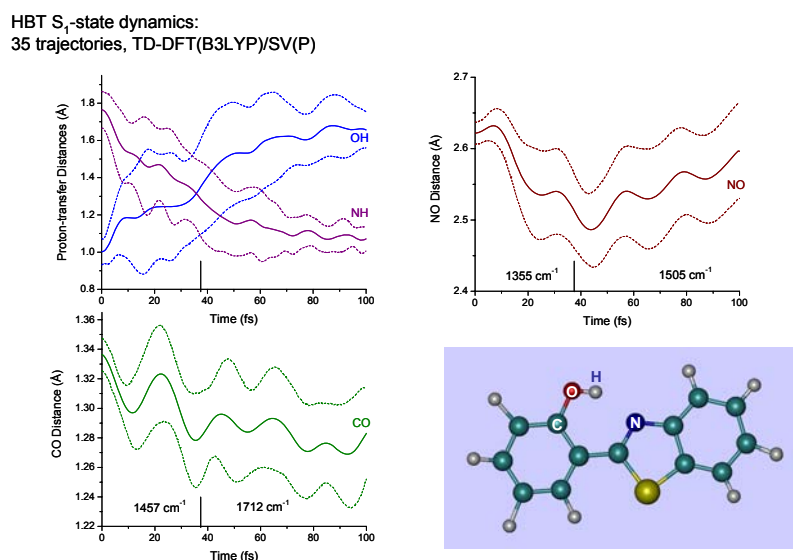
Using phase-adjusted pulse pairs, a ‘control-by-repair’ method employs back-pumping of the intruder population to the target state by a pulse acting after the end of the original one, and a constructive method employs two interfering fractional π -pulses. The applicability of both methods to realistic molecular systems has been demonstrated. Another strategy employs a counterdiabatic correction to the field suppressing population in the intruder state as soon as emerges (Etinski 2005a). Finally, phase incremented pulse trains can also be used to control leaking resonances (Etinski 2005b). The figure shows how a 10-pulse sequence with a phase increment of $2\pi/3$ restores the transition to the target state, which is almost completely quenched for an equivalent single π -pulse (the top inserts represent the amplitude of the field envelope). Pulse train methods appear to have potential for the control of situations involving near-degenerate transitions or overlapping resonances even in cases of strong coupling.

(C) Larger molecular systems

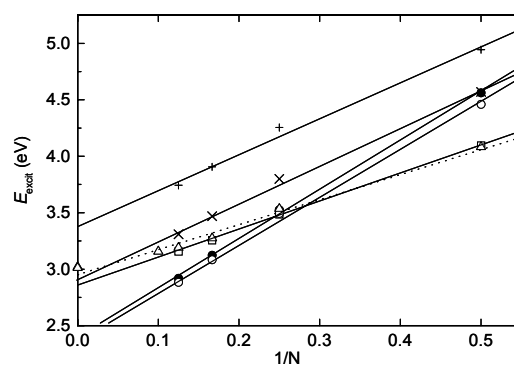
In this section the collaboration with the ADLIS members E. Riedle and H. Kauffmann (P18) concerning a joint experimental and theoretical investigation and characterization of photochemical systems will be described. The chemical systems of interest are far too large for high-level MR-CI calculations as described in Sec. 4.2.A. Therefore, a stepwise strategy was used by connecting as much as possible classes of molecules affordable within the MR-CI approach with those of interest here. Moreover, several other quantum chemical methods were considered in order to assess their reliability. This strategy will be exemplified in the case of excited-state intramolecular proton transfer (ESIPT). Systematic benchmark calculations on malonaldehyde, o-hydroxybenzaldehyde, salicylic acid, 7-hydroxy-1-indanone and 2-(2'-hydroxyphenyl)benzothiazole (HBT) were performed and extended by 10-hydroxybenzo[h]quinoline (HBQ) (Aquino 2005). HBT and HBQ were the actual goals because of the work of the Riedle group. For malonaldehyde MR-CI and MR-AQCC calculations were performed (Andrade do Monte 2003) and compared to resolution-of-the-identity coupled cluster to second order (RI-CC2) and time-dependent density functional theory (TDDFT) results (Aquino 2005). DFT is certainly one of the most popular methods in Quantum Chemistry. However, it requires support by other methods, especially for excited states, since the available density functionals might show deficiencies, the extent of which is not always easily predictable in a particular case. The RI-CC2 and MR-AQCC calculations were performed in order to provide this support. Comparison of results showed quite good agreement for excited-state geometries and energy profiles. Nevertheless, certain discrepancies were observed, which have to be clarified by ongoing calculations. Finally, TDDFT/B3LYP was selected as appropriate method for performing calculations on HBT and HBQ. Analysis of the experimental femtosecond investigations performed in the group of Riedle resulted in the picture of a coupling of low-frequency vibrational modes with the

hydrogen-transfer process. The elucidation of the character of these low-lying modes was the major goal.

The figure below displays the temporal behavior of selected bond distances for the HBT dynamics. Full lines show the average values and broken lines indicate standard deviations. The NO bond distance shows a systematic decrease first, in line with the findings by de Vivie-Riedle (2003). After the proton transfer it increases again. The CO frequency shows an increase demonstrating gain of partial double-bond character. In combination with the wave packet dynamics calculations being performed by R. de Vivie-Riedle and the experimental femto second measurements by E. Riedle we will be able to give for the first time a picture of the ES IPT dynamics in a detail, which has never been achieved before (Schriefer, to be submitted).



Using a similar strategy, π -conjugated oligomers such as oligo-fluorenes and oligo-p-phenylenes have been investigated by means of the RI-CC2 and TDDFT methods (Lukeš 2005). The figure below shows the extrapolation of the excitation energies of fluorene oligomers for $N \rightarrow \infty$ using different methods in comparison to experimental data. It can be seen that for RI-CC2 and ZINDO/S the extrapolation limits agree well with experimental data from films, but that TDDFT/B3LYP significantly underestimates the limiting value. This behavior has to be kept in mind when other similar systems are investigated.



Dependence of the vertical excitation energy to the lowest excited state (1^1B_2) on the number of phenylene rings (N): TDDFT/SVP (solid circles); TDDFT/TZVP (open circles), RI-CC2/SVP (plus symbols), RI-CC2/SVP+ (x symbols), ZINDO/S (open square) and the experimental data for in thin films (open up triangles).

A very important question is the characteristics of torsional potential energy curves and their influence on the broadening of spectra in comparison to the influence of environmental effects. The torsional broadening has been investigated in detail for biphenyl (Beenken 2005). Extended investigations are in progress for larger p-phenylene systems. This work should lead to a better understanding of oligomer energy surfaces of conjugated π systems and, in the next step, to a dynamical treatment similar to what has been achieved for the ESIPT processes.

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4.9.3 Collaboration within and beyond the SFB

- Excited-state intramolecular proton transfer (ESIPT): E. Riedle (P18): benchmark investigations on the dynamics of ESIPT processes for larger organic molecules
- Excited-state properties of conjugated polymers: H. Kauffmann (P18): systematic quantum chemical investigation on excited states (UV absorption and fluorescence spectra) of realistic molecular models
- Nonadiabatic effects in charge-transfer processes: J. Burgdörfer (P10): first basic investigations on charge transfer processes on a LiF surface
- Nonadiabatic interactions – static properties: R. Shepard (Argonne National Laboratory), D. R. Yarkony (Johns Hopkins University Baltimore), P. G. Szalay (Eötvös Lorand University Budapest): Worldwide first implementation of analytic MRCI energy gradients and nonadiabatic couplings in COLUMBUS
- Nonadiabatic interactions – dynamics: M. Persico (University of Pisa), J. Pittner (Czech Academy of Sciences), V. V. Bonačić-Koutecký: breakthrough in nonadiabatic

on-the-fly photodynamics calculations on the basis of extended quantum chemical methods

- Excited-state proton transfer and structure of conjugated π -systems: M. Eckert-Maksič, Z. Maksič (Rudjer Bošković Institute Zagreb): highly accurate quantum chemical calculations on important systems in bio-organic chemistry
- Conjugated organic polymers: V. Lukeš (Technical University Bratislava): benchmark investigations on oligomer models for conjugated polymers in cooperation with H. Kauffmann (P18)
- Excited-state intramolecular proton transfer (ESIPT): R. de Vivie-Riedle (Ludwig-Maximilian University Munich): elucidation of the details of ESIPT processes
- Control of molecular many-level systems: B. Lan (Monash University of Malaysia): suppression of background state population by phase-adjusted pulse pairs