5.1 General information about the finished project C1

5.1.1 Title:

Theory for the control of chemical reactions by ultra-short laser pulses

5.1.1 Research areas:

Theoretical Chemistry – Coupled Electron and Nuclear Dynamics, Reactions, and Laser Control

5.1.3 Principal investigators:

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5.2 Project development report

Back in 1998, our project started as TP C1 Manz/Saalfrank/Gerber, with four subprojects:

UP1: Theory for laser pulse control of separation of ligands from organo-metallics

UP2: Theory for laser pulse control of dynamics of matrix-isolated molecules

UP3: Theory for laser pulse control of proton transfer

UP4: Theory for laser pulse control of photodesorption

P. Saalfrank received and followed a call to University College London, however, already for the winter semester 1998/99. Fortunately, after taking the next position as Professor of Theoretical Chemistry at the University of Regensburg, he became Professor of Theoretical Chemistry at the University of Potsdam, so that he could finally “come home” to Sfb 450 with his own project TPC7 Saalfrank/Nest, for the third period of support. In any case, as a consequence, we did not pursue UP4 which was tailored to him. Instead, we focused on UP1, UP2, and UP3. Initially, these sub-projects were guided by R. B. Gerber (primarily UP2) and by J. Manz. During the second period, young scientists Leticia González as well as Oliver Kühn became leaders of UP1 and UP3, respectively; in addition, they made important contributions to UP3 and to UP2, respectively. It was appropriate, therefore, to promote both Oliver Kühn and – on special recommendation of the referees – also Leticia González to co-project leaders. That means that TP C1 Manz/Gerber mutated to TP C1 Manz/Kühn/Gerber/González for the third period of support. Towards the end of that period, Oliver Kühn and Leticia González were promoted to project leaders of their own new TP C9 González/Kühn. Subsequently, they received and followed calls to new positions: Leticia González became Professor of Theoretical Chemistry at Friedrich-Schiller-Universität Jena; Oliver Kühn became Professor of Theoretical Physics at Universität Rostock. As a consequence, TP C1 was back to only two project leaders, specifically TP C1 Manz/Gerber, but now in a new situation, that means without the expertises of Leticia González and Oliver Kühn for the previous sub-projects UP 1 and UP 3. In this situation, it was decided to replace those UPs by new ones that means during the final period of support, TP C1 Manz/Gerber had

UP1: Theory for laser pulse control of electric ring currents in vibrating molecules

UP2: Theory for laser pulse control of dynamics of matrix-isolated molecules (as before)

UP3: Theory for laser pulse control of isomerization of phenylalanine

The new UP1 was motivated, on one hand, by the developments of PhD student Ingo Barth working with J. Manz, in the frame of the previous project Ma 515/23-1 “Models for selective quantum dynamics of electrons driven by attosecond laser pulses”; for the details see below, UP1. On the other hand, UP1 was also strongly motivated by the development of new technology in TP A1 Wöste/Bernhardt/Lindinger during the third period of support, specifically the formation of ultrafast circularly polarized laser pulses – the necessary pre-requisite for experimental applications of the theory. Gratifyingly, the referees supported this switch of themes – in practice this meant that the previous project Ma 515/23-1 mutated to the new UP1 of TP C1, as integral part of Sfb 450. Let us express with gratitude that this

courageous decision of the referees was rewarded, last but not least, by the Carl-Ramsauer award of the Deutsche Physikalische Gesellschaft zu Berlin for Ingo Barth, for one of the four best PhD Thesis in Physics (2009) of the four Berlin plus Potsdam Universities – this reflects the interdisciplinary character of the new UP1, between Theoretical Chemistry and Theoretical Physics. The success of Ingo Barth is even more remarkable, in view of the fact that he is deaf. The PhD thesis of Dr. I. Barth contains all the details for the publications co-authored by him, as quoted below for UP1.

UP1 also profited from the enormous impacts of three senior research awardees of the Alexander-von-Humboldt foundation in the group of J. Manz: Dr. Guennaddi K. Paramonov (Institute of Physics, Minsk) developed invaluable numerical techniques for propagations of laser driven nuclear, electronic, and coupled electron and nuclear wavepacket dynamics. Prof. Tamar Seideman (Northwestern University, Evanston; co-invitation with M. Wolf, TP A6) paved the way to laser pulse pre-orientation or pre-alignment, followed by laser pulse control of the sequel processes. Prof. André Bandrauk (Université de Sherbrooke) opened new horizons for analysis and control, from nuclear to electron dynamics, and from femto- to attosecond chemistry, see also [BMV09]. These were explored, in depths, together with visiting Prof. Dennis J. Diestler (University of Nebraska, Lincoln). Sfb 450 also supported repeated visits of Dr. G. K. Paramonov as well as Dr. Mikhail V. Korolkov (Institute of Physics, Minsk), who carried out most of the quantum dynamics simulations for the Cl + para-H_2 reaction in solid para- H_2, cf. UP2.

Likewise, the new UP3 was motivated, on one hand, by encouraging experimental results for laser driven isomerizations of phenylalanine, achieved as part of the successes of TP B7 von Helden/Meijer during the third period of support, and on the other hand, by developments of theoretical methods for analysis of the system, by the group of R. B. Gerber. The plan had been to combine this with multi-dimensional quantum dynamics simulations of laser control, based on MCTDH technology of the Heidelberg group and possibly on its further development by the group of V. May (TP C3), as well as on concepts of IR laser pulse control by the group of J. Manz.

In view of the previous and new UP1, UP2 and UP3 of TP C1, it is quite difficult to nominate our “three highlight” papers during four periods of support. Choosing three ones automatically means an injustice to others. With this caveat, we would like to point, with

gratitude for the farsightedness of the referees catalyzing support by DFG during 12 years, to the following “highlights” of TP C1:

*[1] C. Daniel, J. Full, L. González, C. Lupulescu, J. Manz, A. Merli, Š. Vajda and L. Wöste: Deciphering the Reaction Dynamics Underlying Optimal Control Laser Fields, Science, **299**, 536-539 (2003)*

The first deciphering of the reaction dynamics underlying optimal laser fields, achieved during the second period of support, in cooperation of TP A1 (experiment) and TP C1 (theory).

*[2] M. V. Korolkov and J. Manz: Coherent spin control of matrix isolated molecules by IR+UV laser pulses: Quantum simulations for ClF in Ar, J. Chem. Phys., **120**, 11522-11531 (2004)*

The prediction of coherent control of the “fifth dimension” in molecular processes, i.e. laser pulse control of the spin of molecular wavepackets, together with ultrafast (sub-10 fs) temporal and ultra-high (sub-Å) spatial resolutions. This may be considered as a culmination of the developments during the first to third periods of support, stimulated by cooperation of the Jerusalem and Berlin sub-groups TP C1 with the experimental one TP A3 Schwentner on laser pulse control of matrix-isolated molecules.

*[3] R. B. Gerber: Formation of Novel Rare-Gas Molecules in Low-Temperature Matrices, Annu. Rev. Phys. Chem., **55**, 55-78 (2004)*

The prediction of a large class of new molecules containing rare gas atoms may be considered as an offspring of our cooperation with TP A3 Schwentner, in the frame of Sfb 450, during the first to third periods of support.

Similarly, we consider the survey article

[BaM in press]
*I. Barth and J. Manz: Quantum Switching of Magnetic Fields by Circularly Polarized Re-optimized π Laser Pulses: From One-Electron Atomic Ions to Molecules, in Progress in Ultrafast Intense Laser Science VI, eds.: K. Yamanouchi, A. D. Bandrauk and G. Gerber, **in press** (Springer, Berlin, 2010)*

as very important contribution of TP C1 during the final period of support. According to the general theme of this period, it includes the design of laser pulses for control of an instrument (“Werkzeug”), see UP1.

We do not want to close this introduction to our report without also pointing to serious difficulties which were imposed on the Berlin sub-group of TP C1, by unexpected financial constraints on the Institut für Chemie und Biochemie, as part of the Fachbereich Biologie, Chemie und Pharmazie at Freie Universität Berlin. As a consequence, one of the previous

three positions for system administration at the Institut was cancelled, even though the workload of services for altogether 15 large groups had grown monotonously. Hence it was dictated that Dr. Holger Naundorf had to serve – with highest priority – as system administrator not only for my group (gratifyingly, he did that perfectly), but also for too many other groups – in practice that became his exclusive task, irrespective of the fact that according to his official working contract, his first priority duty should have been to carry out scientific computing for projects of the Manz group, specifically for TP C1 of Sfb 450. The situation did not improve when he reached the fatal Buhlmahn's limit of "twelve years after PhD", implying that he was removed from my group at the end of 2009. In practice, that meant that the planned work of Dr. Naundorf for UP3 of TP C1 Manz/Gerber, could not be carried out. The resume is that we cannot present any results for MCTDH simulations of the multi-dimensional laser driven wavepacket dynamics of phenylalanine. We say this with a sense of anger about the "stolen" coworker, with frustration about the financial restrictions at Freie Universität Berlin, and also with shame, both to our experimental partners as well as to the referees.

5.2.1 Report

UP1: Control of electric ring currents in vibrating molecules

5.2.1a State of the Art and Plans at the Last Application

This subproject was based on discoveries made together with PhD student Ingo Barth in the frame of another project Ma 515/23-1 "Models for selective quantum dynamics of electrons driven by attosecond laser pulses", also supported by DFG. There the goal had been to investigate electron dynamics, specifically electronic ring currents and circulations, as well as the induced magnetic fields, driven by means of circularly polarized laser pulses with durations of few fs to sub-fs that means in the time domain when the nuclei are essentially frozen, and that also means beyond the scope of Sfb 450. The results of project Ma 515/23-1 had already discovered three general trends: (1) Laser pulse excitation of ring currents and induced magnetic fields are typically two orders of magnitude more efficient than traditional excitations by static magnetic fields. (2) Excitations of ring currents offer the possibility of laser control, with the laser pulses acting as "traffic light" for regulations of electron fluxes through different chemical bonds. (3) In accord with the quantum mechanical version of the Biot-Savart law, the induced magnetic field increases with increasing mean value of electronic flux (= circulating charge per time) and with decreasing mean value of the radius of

the ring current. On this basis, the goal of sub-project UP1 has been to extend the discoveries of project Ma 515/23-1 from the atto- to the femtosecond time domain of Sfb 450, including not only electronic but also nuclear motions, in particular concerted electronic and nuclear motions. An important motivation has been the development of ultrafast circularly polarized laser pulses, in TP A1 Wöste/Bernhardt/Lindinger, during the third period of support: This provided the necessary pre-requisite as well as encouraging prospects for experimental applications of our theory. In view of the trend (3), we focused on laser pulse control of ring currents in small systems, typically diatomic molecules, offering small radii of toroidal ring currents. The goal has been to discover laser pulse control of giant induced magnetic fields. According to the general theme of Sfb 450 during the final period, this should contribute ultimately to laser pulse control of an instrument ("Werkzeug").

5.2.1b Results

Selective excitations of strong ring currents and induced magnetic fields (max = 8 Tesla) in AlCl by means of circularly polarized laser pulses were predicted in [BMS08a]. Extensions to a combination of laser driven pre-orientation followed by selective excitation of ring currents and even stronger induced magnetic fields (max = 52 Tesla) in BeO are documented in [BSS09]. Extrapolation from selective excitations of electronic ring currents to nuclear ones, by means of circularly polarized laser pulses in the infrared (IR) spectral domain instead of the ultraviolet (UV) or visible (vis) one, opened a new possibility of laser control of rather strong (max = 11 Tesla) induced magnetic fields in pseudorotating molecules, e.g. in FHF^- [BMP08a]. As a by-product, Ref. [BMP08a] also discovers a new type of hydrogen bond that means the toroidal hydrogen bond, in pseudorotating FHF^-. Extension to laser driven pseudorotations of the metal dihydride CdH_2, with highly charged nucleus ^{114}Cd circulating on a very small radius (mean value $\langle R_{Cd} \rangle = 0.0048\ a_0$) with short period ($\tau = 53$ fs), allowed the prediction of the present "world record" of induced magnetic fields in molecules (318 Tesla) [BMS08b]. This example also provided the criteria for systematic searches for possibly even stronger magnetic fields in pseudorotating molecules – ideal systems include metal polyhydrides with large values of the nuclear charge Z, implying large ratios of the masses of the metal versus hydrogen atoms and, therefore, small mean values of the radius of the nuclear ring current, combined with short periods of pseudorotations corresponding to coherent superpositions of degenerate vibrations. Accordingly, we are proud to announce already the next "world record", that means 1552 Tesla in pseudorotating OsH_4 (manuscript

in preparation). For comparison, the world's strongest permanent magnet (in Dresden-Rossendorf) produces “only” less than 100 Tesla!

Ultrafast laser pulse control of giant magnetic fields may be developed further to laser control of a new instrument for analysis, i.e. pump-probe neutron scattering with femtosecond time resolution. The concept is as follows: Well designed circularly laser pulses switch on and off, or reverse giant induced magnetic fields close to heavy nuclei, within few hundreds of femtoseconds. Neutron scattering off the nuclei is influenced by these magnetic fields. That means that the direction of neutron scattering is manipulated by laser pulses, mediated by switches of pseudorotations in molecules, in the femtosecond time domain. As a consequence, one can prepare two (or more) neutron pulses which sweep over samples, with controllable time delays. This offers the possibility of pump-probe neutron scattering, in the femtosecond time domain! The concept is in the survey [BaM in press].

The results for laser control of electronic ring currents [BMS08a, BSS09, BaM in press] suggested extended explorations of laser driven electron currents, including elementary processes such as ionization, electron re-scattering, and high harmonic generation (HHG). Investigations towards this goal started with a wrong way, i.e. our attempt to provide six criteria that should serve as firm basis for the validity of the so-called single active electron (SAE) model of ionization, or in chemical language the time-dependent extension of Koopman’s picture for ionization by a laser pulse [BMP08b]. Our predictions for ultrafast laser ionization of $H_2(B^1\Sigma_u^+)$ were tested systematically by accurate evaluations of the laser driven wavepacket dynamics by A. Saenz and coworkers, TP C6. The resume is that our quantum dynamics simulations by means of the SAE model are qualitatively correct but quantitatively wrong, because we had overlooked another criterion; for the details see [4]. We concluded that we should not extend applications of the SAE model to larger systems (even though we had already developed the theory and implemented the codes, with application to AlCl), because one will hardly find any real system that satisfies seven (and possibly more?) criteria. This is an example of cooperation in Sfb 450 which preserved us from wrong investments of the most valuable i.e. human resources. Alternative routes turned out to be more rewarding:

Using a one-dimensional model of H_2^+, we investigated competing effects of electronic and nuclear motions during attosecond photo-ionization of a coherent superposition of bound and dissociative molecular states, implying concepts for laser control of electron localization in competing photo-fragments [BCC09]. At the same time, visiting Prof. D. J. Diestler re-

investigated the fundamental theory of HHG, by means of the quantum-electrodynamical approach to the photon-number spectrum; surprisingly, he discovered that adequate measures of HHG signals are provided neither by the familiar dipole nor by the dipole acceleration, but by the dipole velocity presentations [5]. Joint applications of his theory of HHG, by means of accurate numerical simulations of HHG spectra of the hydrogen atom, were published in [BCD09]. This served as spring-board for the design of laser pulses for uni-directional electron re-scattering [BCD08]. The underlying role of electron wavepacket phases in ionization and re-scattering processes by intense laser pulses are documented in [BMY09]. For comparison with laser driven re-scattering, we also developed the theory for attosecond electron diffraction [BMS10], complementary to the experimental concept of P. Baum and A. H. Zewail. This means an alternative to laser pulse control in molecular attosecond dynamics [6].

A common theme of Refs. [BMS08a, BSS09, BMP08a, BMS08b, BaM 10, BMP08b, BCD08] has been selective electronic or nuclear fluxes induced by laser pulses, or by electron diffraction [BMS10]. Accordingly, we developed the theory for concerted effects of electronic AND nuclear fluxes in molecules [BHI09], with subsequent special attention centred on the initial-state dependence [KMP10].

Last but not least, the experience gained with all kinds of fluxes – pantha rhei! – allowed us to discover a surprising effect in double proton transfer DPT, with application to the model porphine. This application brings us back to the original topic of UP3! In any case, our results add a new twist to the never-ending debate of the mechanisms that means whether DPT proceeds synchronously or sequentially. The analysis of double proton fluxes demonstrate that the mechanism may actually switch from synchronous DPT during the forward reaction to sequential DPT for the back reaction, depending on the preparation for the reactants [ABK in press].

5.2.1c Relation to other work in Sfb 450

Concerning the new UP1, we are grateful to A. Saenz (TP C6) for very helpful feedback [4] which stopped our wrong way [BMP08]. We are also very grateful, and in fact we are happy and a bit proud that our predictions for laser driven ring currents have already stimulated five experimental investigations worldwide, including searches for various effects of laser-driven ring currents. First beautiful results, i.e. three-dimensional mappings of the toroidal structures of electron densities carrying ring currents, have been published by the group of T. Baumert

[7]. We are also aware of several theory groups who are working on extensions; exemplarily, the group of H. Kono (Tohoku University Sendai) could predict fascinating effects of electron circulations in near-degenerate excited electronic states, coupled to vibrations [8]. We are also pleased with the high appreciation of our theory for attosecond electron diffraction, by our experimental partner, P. Baum (young scientist in the group of F. Krausz at MPI für Quantenoptik, Garching).

The results of Refs. [BHI09], complemented by [KMP 10], serve as basis for the new project Ma 515/25-1 supported by DFG, "Unravelling the secret of the organic chemist's rule for fluxes of electrons in electrocyclic reactions by quantum dynamics simulations", guided by J. Manz and B. Paulus in cooperation with H. Kono (Tohoku University Sendai, supported by JSPS).

UP2: Control of dynamics of matrix-isolated molecules

5.2.1a State of the Art and Plans at the Last Application

This subproject has been advanced by both the Jerusalem and Berlin groups. In general, it is on the analysis and control of ultrafast photodissociation processes in cryogenic matrices. Previous research on this topic by the Jerusalem group focused on: (1) Diatomics-in-Molecules (DIM) modelling of the potential energy surfaces and nonadiabatic couplings for dihalogens in noble-gas matrices; (2) Semiclassical (surface-hopping) treatment of nonadiabatic transitions between different electronic states, in photochemistry in matrices; (3) Selective role of electronic quantum numbers on the femtosecond timescale, e.g., the ultrafast spin-flip effect that was found and was the topic of extensive cooperation with the groups of J. Manz and N. Schwentner (TP A3); (4) Study of reduced dimensionality models for photodissociation in matrices (as developed by J. Manz), their usefulness and limitations, by comparison with multidimensional, many-atom surface hopping simulations of the processes in matrices. The plans called for further exploration of these topics, with extensions for additional systems and searches for new interesting effects.

The Berlin group planned to extend the theory and applications to two systems which had been suggested to us by our experimental partner, N. Schwentner (TP A3), namely Br_2@Ar and Cl_2@para-H_2. A special challenge of the rather heavy system Br_2@Ar has been to extend the DIM method to adequate spin and angular momentum couplings according to Hund's case c. This step had already been mastered at the end of the previous period of support, by O. Kühn as co-project leader of the previous TP C1 Manz/Kühn/Gerber/González. On this basis, the work plan for the final period has been to simulate the laser driven dynamics for analysis and control of the system, in cooperation with the experimental group of N. Schwentner, and the theory group of O. Kühn, now Professor of Theoretical Physics at Rostock University and

co-project leader of TP C9 González/Kühn. The other extension to Cl_2@para-H_2 aimed at the first quantum simulations of laser induced reactions in quantum solids. This possibility had been demonstrated experimentally by Prof. D. T. Anderson, a guest scientist of N. Schwentner during part of the final period. The plan has been to develop the theory which should explain his experiment, and on this basis to predict new effects which should stimulate experimental investigations by means of very short laser pulses, by the joint groups of D. T. Anderson and N. Schwentner (TP A3). Reactions in quantum solids offer fascinating perspectives, complementary to the previous investigations of reactions of molecules embedded in rare gas matrices, the topic of the Jerusalem group during the previous periods of support, which culminated in the prediction of the formations of many new molecules containing rare gas atoms, see the “highlight” [3].

5.2.1b Results

The work by the Jerusalem group continued to focus for the most part on F_2 in Ar. A number of several interesting new effects were found in the nonadiabatic “surface hopping” Molecular Dynamics (MD) simulations. These simulations were carried out by Arik Cohen, a PhD student of Benny Gerber at the time. One of these results is the prediction of ultrafast g $\leftrightarrow$ u transitions between these two symmetry-types of states for F_2@Ar [CoG07a, CoG08]. Another interesting prediction is an extremely fast, single femtosecond timescale spin-flip in the photolysis of HF in solid Ar [CoG07b]. Finally, we examined quantum-mechanical reduced dimensionality calculations against multi-dimensional “surface hopping” MD simulations for F_2 in solid Ar [SCG09]. Close agreement is found for short timescales, especially for the spin-flip effect. For longer times, the two approximate treatments diverge, since the reduced dimensionality model cannot describe energy transfer to the matrix. On the other hand, the reduced dimensionality model predicts coherent quantum effects that semiclassical MD cannot describe. The important conclusion is that a combined study, using reduced dimensionality for quantum effects and semiclassical MD for handling energy transfer seems an advantageous approach for condensed-phase dynamics at the present state of the art [BCG07].

The work of the Berlin group for Br_2@Ar was carried out by two PhD students, A. Borowski and A. Accardi of the Manz group, guided – as previously – by O. Kühn. Accordingly, the progresses which have been achieved in close cooperation with TP A3 Schwentner are as follows: A diatomics-in-molecules description of the valence states of the Hund's case c Br_2 embedded in solid Ar served as the basis for the development of a tailored reaction surface-

vibronic coupling Hamiltonian in [BoK07]. Using this Hamiltonian quantum dynamics simulations have been performed (four and five coordinates, four electronic states) to unravel the role of matrix cage deformations for the B to C state predissociation [BoK08]. In Ref. [ABK09] it was shown, using optimal control theory, how a vibrationally hot electronic ground state can be prepared, whose subsequent excitation to the B state leads to enhanced B to C predissociation.

The theory for the experiments of laser driven chemical reactions in quantum solids, specifically the reaction Cl + H_2 → HCl + H in solid para-H_2, has been published in tandem with the experimental paper by the group of D. T. Anderson (both with acknowledgement to DFG support for Sfb 450!), see Ref. [KMS09]. Extended analyses showed that the reaction profits from a resonance; we also provided experimental criteria for discovering resonances in reactions in quantum solids [KoM10], different from reactions in the gas, compare with Ref. [9]. A characteristic property of the reaction in the "soft" quantum solid is the rather large amplitude zero point motion of the molecular reactant H_2, much larger than the amplitudes of rare gas atoms in "hard" rare gas matrices, but of course much smaller than the quasi infinite amplitude in the gas [KMS10]. This property implies unique effects of reactions in quantum solids, different from analogous reactions in the gas, or in rare gas matrices. Predictions of altogether six isotope effects of the reactions Cl + H_2 → HCl + H in solid para-H_2 versus Cl + D_2 → DCl + D in solid ortho-D_2 confirm the general trends [KMS in press].

5.2.1c Relation to other work in Sfb 450

The cooperation of R. B. Gerber, J. Manz and coworkers in TP C1 was a strong one, reflected both in the joint publication [BCG07], and in close exchange of ideas otherwise. The comparison and combination of reduced dimensionality treatment (due to Manz) with "surface hopping" MD by the Gerber group is an important example. Also the interaction with the experiments of N. Schwentner and his group, e.g., [BCG07, KMS09], was very central for the achievements of the project. The femtosecond experiments of TP A3 also inspired ideas for some of our new predictions. Very fruitful interactions and exchange of ideas also took place with O. Kühn (TP C9). This dealt mostly with the connection between quantum and semiclassical ("surface hopping") treatments, and the development of the extended Einstein model for para-H_2 or ortho- D_2 crystals, as basis for the theory of reactions in quantum solids [KMS10]. This is complemented by recent cooperation with B. Schmidt, TP C5 Schütte/Schmidt/Lasser, on the interaction of Cl_2 in Einstein cells for para-H_2.

UP3: Control of isomerization of phenylalanine

5.2.1a State of the Art and Plans at the Last Application

This subproject was motivated in part by experiments in TP B7 (v. Helden/Meijer) aiming at controlling transitions between conformers of small biological molecules. A strategy proposed previously by J. Manz suggests the possibility of controlling conformational transitions by IR pulses. The objectives of the Jerusalem group in this framework included (1) Spectroscopic calculations to help characterize specific conformers of the molecule; (2) Calculation of the PES, especially the reaction path between the conformers, and the modes that couple strongly to the path; (3) Classical calculations of the dynamics. Such calculations should be helpful for future quantum treatments of the dynamics and of coherent control of the process, along the lines suggested by J. Manz.

5.2.1b Results

In a joint experimental-theoretical study with the group of Meijer and von Helden (TP B7), the vibrational spectra of several low energy conformers of phenylalanine were characterized [HCB08]. The calculations used the anharmonic VSCF method of the Gerber group. The calculations were done by Dr. Brina Brauer, a postdoc working with Benny Gerber. Very good agreement between theory and experiment was found, supporting the quantitative accuracy of the PES used, and throwing light on the spectroscopic differences between conformers.

A new version of VSCF, based on using internal coordinates was developed by Suwan and Gerber [SuG in press]. The method is especially suitable for treating torsional mode vibrations that are much better described by angular variables than by normal modes. So far, only test calculations for small molecules were carried out, but applications for biomolecules are under way, specifically for aminophenol. This study was stimulated by experimental separation of isomers of aminophenol [10], achieved by J. Küpper, G. von Helden and coworkers, associated to TP B7. Our preliminary collaborative results for this system were presented as a poster entitled “Dynamics of Conformational Transitions in Biological Molecules” and co-authored by J. Šebek, I. Barth, R. B. Gerber, J. Manz at the Sfb 450 ACU Symposium “Analysis and Control of Ultrafast Photoinduced Reactions”, Berlin, Oct. 8/10, 2009. But unfortunately, the group of J. Manz was unable to carry out the necessary multi-dimensional extensions by means of MCTDH simulations of the laser driven system, see the Introduction to this report.

On another aspect of the project, direct dynamics calculations using the semi-empirical PM3 potential were carried out for conformational transitions in glycine, following vibrational excitation of the OH stretch [SMG accepted]. The results show that for the CW excitation used, extensive IVR takes place on a 10 ps timescale, and conformational transitions take place only in the wake of this. Thus, CW excitation merely heats the system in this case, calling for ultrashort laser pulses in order to induce selective conformational transitions. These calculations were carried out by Michaela Shmilovits-Ofir, a PhD student in the Gerber group.

A study by Adesokan *et al*. [APF07] explored the spectroscopies of 3 intermediate states of the chromophore of PYP in the photocycle of this system. The project involved cooperation between the Gerber group and the experimental group of R. A. Mathies (Berkeley). The results lead to characterization of the spectra of the three intermediates, and to reliable, anharmonic-level calculations of the PES in the vicinity of each structure. The findings should be useful in following the photocycle in time. The system could be suitable for control experiments, as the different structures can be identified and resolved.

An article by Segev *et al*. [SWB08] explores the structural changes in the electrospray process of ubiquitin +13. The high charging state drives dramatic changes from the initial folded structure to a final linear structure. The processes in ubiquitin +13 are not ultrafast, but suggest that similar structural changes should be much faster in small peptides.

5.2.1c Relation to other work in Sfb 450

Spectroscopic calculations for conformers of phenylalanine were carried out in cooperation with experiments by von Helden, Meijer and coworkers of TP B7. As noted, this led to a joint paper, [HCB08], but – as explained in the Introduction – we were unable to achieve the ultimate goal for this sub-project.

Acknowledgement

At the end of this report, we would like to express our gratitude to our colleague and friend, Prof. Ludger Wöste, together with his superb team for the administration, for creating the wonderful environment of the collaborative research Sfb 450 on analysis and control of ultrafast photo-induced reactions during 12 years, including also 9 years of wonderful and very fruitful cooperations on the original UP1; to the referees for their farsighted and most encouraging decisions, to Deutsche Forschungsgemeinschaft for very helpful support during

12 years; and last but not least to all coworkers and partners who contributed to the success of TP C1 in Sfb 450.

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[8] M. Kanno, H. Kono, Y. Fujimura and S. H. Lin: Nonadiabatic Response Model of Laser-Induced Ultrafast π-Electron Rotations in Chiral Aromatic Molecules, *Phys. Rev. Lett.*, **104**, 108302 (4 pages) (2010)

[9] Y. T. Lee: Molecular Beam Studies of Elementary Chemical Processes, Nobel lecture, *Angew. Chem. Int. Ed.*, **26**, 939-951 (1987)

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5.2.2 List of publications resulting from the TP C1 since the last proposal

(all with explicit acknowledgements to DFG in the frame of Sfb 450)

I. Published (2007-2010)

[BMS10] P. Baum, J. Manz and A. Schild: *Quantum Model Simulations of Attosecond Electron Diffraction*, Sci. China Ser. G, **53**, 987-1004 (2010)

[KMP10] A. Kenfack, F. Marquardt, G. K. Paramonov, I. Barth, C. Lasser and B. Paulus: Initial-State Dependence of Coupled Electronic and Nuclear Fluxes in Molecules, *Phys. Rev. A*, **81**, 052502 (7 pages) (2010)

[KMS10] O. Kühn, J. Manz and A. Schild: *Quantum Effects on Translational Motions in Solid para-Hydrogen and ortho-Deuterium: Anharmonic Extension of the Einstein Model*, J. Phys. Condens. Matter, **22**, 135401 (8 pages) (2010)

[KoM10] M. V. Korolkov and J. Manz: *Resonant versus off-resonant quantum reaction dynamics in quantum solids: Model simulations for* $Cl + H_2 \rightarrow ClH_2^* \rightarrow HCl + H$ *in solid para-hydrogen*, in Festschrift E. Pollak, Chem. Phys., **370**, 159-167 (2010)

[ABK09] A. Accardi, A. Borowski and O. Kühn: *Nonadiabatic Quantum Dynamics and Laser Control of* Br_2 *in Solid Argon*, in Festschrift R. B. Gerber, J. Phys. Chem. A, **113**, 7491-7498 (2009)

[BaL09] I. Barth and C. Lasser: *Trigonometric Pulse Envelopes for Laser-Induced Quantum Dynamics*, J. Phys. B, **42**, 235101 (8 pages) (2009)

[BCC09] A. D. Bandrauk, S. Chelkowski, P. B. Corkum, J. Manz and G. L. Yudin: *Attosecond Photoionization of a Coherent Superposition of Bound and Dissociative Molecular States: Effect of Nuclear Motion*, J. Phys. B, **42**, 134001 (7 pages) (2009)

BCD09] A. D. *Bandrauk, S. Chelkowski, D. J. Diestler, J. Manz and K.-J. Yuan: Quantum Simulation of High-order Harmonic Spectra of the Hydrogen Atom*, Phys. Rev. A, **79**, 023403 (14 pages) (2009)

[BHI09] I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt and G. K. Paramonov: *Concerted Quantum Effects of Electronic and Nuclear Fluxes in Molecules,* Chem. Phys. Lett., **481**, 118-123 (2009)

[BMV09] A. D. Bandrauk, J. Manz, M. J. J. Vrakking (eds.): *Attosecond Molecular Dynamics,* Chem. Phys., **366**, 1-150 (2009), with 17 contributions.

[BMY09] A. D. Bandrauk, J. Manz and K.-J. Yuan: *Electron Wavepacket Phases in Ionization and Rescattering Processes by Intense Laser Pulses, Special Issue in Honor of N. B. Delone*, Laser Physics, **19**, 1559-1573 (2009)

[BSS09] I. Barth, L. Serrano-Andrés and T. Seideman: *Nonadiabatic Orientation, Toroidal Current, and Induced Magnetic Field in BeO Molecules,* J. Chem. Phys., **129**, 164303 (12 pages) (2008), Erratum: *J. Chem. Phys.*, **130**, 109901 (1 page) (2009)

[KMS09] M. V. Korolkov, J. Manz and A. Schild: *The Cl + H_2 ↔ HCl + H Reaction Induced by IR + UV Irradiation of Cl_2 in solid para-H_2: Quantum Model Simulation*, in Festschrift R. B. Gerber, J. Phys. Chem. *A*, **113**, 7630-7646 (2009)

Note: Published in tandem with the experimental investigation of Prof. D. T. Anderson in the group of N. Schwentner (TP A3): S. Kettwick, P. L. Raston, D. T. Anderson, in Festschrift R. B. Gerber, J. Phys. Chem. *A*, **113**, 7621-7629 (2009)

[SCG09] M. Shukarev, A. Cohen, R. B. Gerber and T. Seideman: *Ultrafast Nonadiabatic Photodissociation Dynamics of F_2 in Solid Ar, Special Issue in Honor of N. B. Delone,* Laser Physics, **19** , 1651-1659 (2009)

[BCD08] A. D. Bandrauk, S. Chelkowski, D. J. Diestler, J. Manz and K.-J. Yuan: *Quantum-mechanical Models for Photo-Ionization: Uni-directional Electron Re-scattering by a Laser Pulse*, in Festschrift E. Illenberger, Int. J. Mass Spectrom., **277**, 189-196 (2008)

[BMP08a] I. Barth, J. Manz, G. Pérez-Hernández and P. Sebald: *Towards Toroidal Hydrogen Bonds*, in Festschrift H.-H. Limbach, *Z.* Phys. Chem., **222**, 1311-1331 (2008)

[BMP08b] I. Barth, J. Manz and G. K. Paramonov: *Time-dependent Extension of Koopmans' Picture for Ionisation by a Laser Pulse: Application to H_2 ($B^1\Sigma_u^+$),* in Festschrift R. D. Levine, Mol. Phys., **106**, 467-483 (2008)

[BMS08a] I. Barth, J. Manz and L. Serrano-Andrés: *Quantum Simulations of Toroidal Electric Ring Currents and Magnetic Fields in Linear Molecules Induced by Circularly Polarized Laser Pulses*, in Festschrift W. Domcke, Chem. Phys., **347**, 263-271 (2008)

[BMS08b] I. Barth, J. Manz and P. Sebald: *Spinning a Pseudorotating Molecular Top by Means of a Circularly Polarized Infrared Laser Pulse: Quantum Simulations for $^{114}CdH_2$*, in Festschrift P. Botschwina, Chem. Phys., **346**, 89-98 (2008)

[BoK08] A. Borowski and O. Kühn: *Nonadiabatic Quantum Dynamics of Br_2 in Solid Ar: A Four-dimensional Study of the B to C State Predissociation,* in Festschrift W. Domcke, Chem. Phys., **347**, 523-530 (2008)

[CoG08] Cohen and R. B. Gerber: *Dynamical u ↔ g Electronic State Transition in Matrix Photochemistry: Photodissociation of F_2 in Solid A*r, Chem. Phys. Lett., **453**, 173-177 (2008)

[HCB08] G. von Helden, I. Compagnon, H. N. Blom, M. Frankowski, U. Erlekam, J. Oomens, B. Brauer, R. B. Gerber and G. Meijer: *Mid-IR Spectra of Different Conformers of Phenylalanine in the Gas Phase*, Phys. Chem. Chem. Phys., **10**, 1248-1256 (2008)

[SWB08] E. Segev, T. Wyttenbach, M. T. Bowers and R. B. Gerber: *Conformational Evolution of Ubiquitin Ions in Electrospray Mass Spectrometry: Molecular Dynamics Simulations at Gradually Increasing Temperatures*, Phys. Chem. Chem. Phys., **10**, 3077-3083 (2008)

[APF07] A. A. Adesokan, D. Pan, E. Fredj, R. A. Mathies and R. B. Gerber: *Anharmonic Vibrational Calculations Modeling the Raman Spectra of Intermediates in the Photoactive Yellow Protein (PYP) Photocycle*, J. Am. Chem. Soc., **129**, 4584-4594 (2007)

[BCG07] M. Bargheer, A. Cohen, R. B. Gerber, M. Gühr, M. V. Korolkov, J. Manz, M. Y. Niv, M. Schröder and N. Schwentner: *Dynamics of Electronic States and Spin-Flip for Photodissociation of Dihalogens in Matrices: Experiment and Semiclassical Surface-Hopping and Quantum Model Simulations for F_2 and ClF in Solid Ar*, in Festschrift S. H. Lin, J. Phys. Chem. *A.*, **111**, 9573-9585 (2007) Note: Listed as "In Preparation" in the report from 2007.

[BoK07] A. Borowski and O. Kühn: *Towards a Quantum Mechanical Description of the Photochemistry of Dihalogens in Rare Gas Matrices*, *J. Photoch. Photobio. A*, **190**, 169-176 (2007), special issue on Theoretical Aspects of Photoinduced Processes in Complex Systems Note: Listed as "Submitted" in the report from 2007

[CoG07a] A. Cohen and R. B. Gerber: *Photodissociation of F_2 in Solid Ar: Electronic State Distribution in Cage-Exit*, in Festschrift J. Manz, Chem. Phys., **338**, 200-206 (2007)

[CoG07b] A. Cohen and R. B. Gerber: *A 1fs Spin-Flip in a Chemical Reaction*: *Photodissociation of HF in Solid Ar,* Chem. Phys. Lett., **441**, 48-52 (2007)

II. Accepted

[ABK10] A. Accardi, I. Barth, O. Kühn and J. Manz: *From Synchronous to Sequential Double Proton Transfer: Quantum Dynamics Simulations for the Model Porphine*, in Festschrift K. Müller-Dethlefs, *J. Phys. Chem. A*, **in press** (2010)

[BaM10] I. Barth and J. Manz: *Quantum Switching of Magnetic Fields by Circularly Polarized Re-optimized π Laser Pulses: From One-Electron Atomic Ions to Molecule*s, in Progress in Ultrafast Intense Laser Science VI, eds.: K. Yamanouchi, A. D. Bandrauk and G. Gerber, **in press** (Springer, Berlin, 2010)

[KMS10] M. V. Korolkov, J. Manz and A. Schild: *Isotope Effects of Reactions in Quantum Solids Initiated by IR + UV Lasers: Quantum Model Simulations for $Cl(^2P_{3/2})$ + $X_2(v) \rightarrow XCl + X$ in X_2 Matrices (X = H,D)*, in Festschrift R. Schinke, J. Phys. Chem. *A*, **in press** (2010)

[SuG10] I. Suwan and R. B. Gerber: *VSCF in Internal Coordinates and the Calculation of Anharmonic Torsional Mode Transitions*, Chem. Phys., **in press** (2010)

[SMG 10] M. Shmilovits-Ofir, Y. Miller and R. B. Gerber: Conformational Transitions of Glycine Induced by Vibrational Excitation of the OH Stretch, *Phys. Chem. Chem. Phys.*, **in press** (2010)

5.3 Bewilligte Mittel für die laufende Förderperiode

Das Teilprojekt wurde im Sonderforschungsbereich von 07/1998 bis 06/2010 gefördert.

Haushalts-jahr	Personalmittel	Sachmittel	Investitionsmittel	Gesamt
2007/2	51.5	0	12.0	63.5
2008	103.0	0	0	103.0
2009	103.0	0	0	103.0
2010/1	51.5	0	0	51.5
Summe	309.0	0	12.0	321.0

(Alle Angaben in Tausend EUR)

5.3.1 Personal im Teilprojekt

	Name, akad. Grad, Dienststellung	engeres Fach des Mitarbeiters	Institut der Hochschule oder der außeruniv. Einrichtung	im SFB tätig von (Monat / Jahr) bis (Monat / Jahr)	Entgelt-gruppe
Grundausstattung					
wissenschaftl. Personal (einschl. Hilfskräfte)	1. Manz, Jörn, Prof. Dr.	Theoretical Chemistry	Inst. f. Chem., FUB	07/1998 – 06/2010	
	2. Gerber, Robert, Benny, Prof. Dr.	Theoretical Chemistry	Hebrew Univ., HUJ	07/1998 – 06/2010	
	3. Shemesh, Dorit, Dr.	Theoretical Chemistry	Hebrew Univ., HUJ	01/2009 – 06/2010	
	4. Shmilovits-Ofir, Mihaela, Doktorandin	Theoretical Chemistry	Hebrew Univ., HUJ	07/2007 -–06/2010	
	5. Brauer, Brina, Dr	Theoretical Chemistry	Hebrew Univ., HUJ	07/2007-– 12/2008	
	6. Accardi, Antonio, Doktorand	Theoretical Chemistry	Inst. f. Chem., FUB	01/2008 – 06/2010	
	7. Borowski, Alexander, Dr.	Theoretical Chemistry	Inst. f. Chem., FUB	01/2004 – 07/2008	
Ergänzungsausstattung					
wissenschaftl. Personal (einschl. Hilfskräfte)	8. Sebek, Jirka, Dr.	Theoretical Chemistry	Hebrew Univ., HUJ	07/2007 – 06/2010	BAT IIa0.35
	9. Suwan, Iyad, Dr.	Theoretical Chemistry	Hebrew Univ., HUJ	07/2007 – 06/2010	BAT IIa0,35
	10. Barth, Ingo, Dr.	Theoretical Chemistry	Inst. f. Chem., FUB	07/2007 – 06/2010	BAT IIa1/1