

# Chapter 6

## Conclusions and Outlook

### 6.1 Enantio-selective laser control

In this work the selective preparation of pure enantiomers from a pre-oriented racemate by means of ultra-short laser pulses has been demonstrated for molecular models using quantum *ab initio* calculations. Neither the incident light nor the initial molecular system, the racemate, need to be chiral, but chiral discrimination and the selective enhancement of the population of one enantiomer over the other in a racemic mixture is possible. Several laser control strategies based exclusively on the laser-dipole interaction have been developed to accomplish selective control over molecular chirality. The conversion of one chiral form into the other is accomplished by laser induced isomerization of the molecule around its chiral axis described by an symmetric *ab initio* double well potential. All laser control mechanisms developed in this thesis require laser coupling to two dipole components of different symmetry, i.e. one component which is *symmetric* and one which is *anti-symmetric* with respect to the inversion center of the conversion path from one chiral form to the other. Therefore, the pulsed laser fields are polarized such that coupling to the two different dipole components is possible. This is accomplished by series of linearly polarized laser pulses, with each pulse coupling to the symmetric or anti-symmetric dipole component, or by single linearly polarized laser fields, each coupling to both dipole components simultaneously, or by circularly polarized pulses. In any case, the polarization direction of the laser field with respect to the orientation of the molecules was found to be critical for the enantio-selectivity of the laser pulses.

Based on preliminary results [61, 127, 126], an enantio-selective five step laser control

mechanism, called the “parking” mechanism, was developed for the pre-oriented model system H<sub>2</sub>POSH, inheriting axial chirality in the limit of low temperature. This was the first demonstration of the purification of a racemate by means of analytical linearly polarized laser pulses for a molecular model system based on *ab initio* calculations [128]. In an extended model, allowing free molecular rotations around the chiral axis, it was shown that the enantiomer selectivity of the control mechanism is slightly reduced, and circularly polarized laser pulses instead of linearly polarized pulses are required [136] (see also ref. [163]).

For the enantio-selective control mechanism intermediate states with either symmetric or antisymmetric symmetry are required. These intermediate states can lie in the electronic ground or in electronic excited states [125]. The extension of the “parking” control scheme to intermediate states in the first electronic excited state also gave rise to the development of an adiabatic strategy introducing a new half-STIRAP process [125] (cf. ref. [164]). This STIRAP variant of the “parking” mechanism is more robust to variations of the applied laser field than the parking mechanism. Additional modifications of the five step “parking” mechanism allowed to derive the simpler two step enantio-selective pump-dump scheme which yields a more direct interconversion from one enantiomer into the other [137], see section 4.7.1. In this form of laser control, the polarization direction of the linearly polarized laser pulses controls the enantio-selectivity of the laser-dipole interaction and allows to discriminate both enantiomers in a pre-oriented system [137, 139].

In order to overcome restrictions of the molecule H<sub>2</sub>POSH in terms of experimental availability and stability with respect to racemization a more realistic model system, the molecule (4-methyl-cyclohexylidene)fluoromethane, possessing axial chirality even at room temperature, was investigated. Because of the high barrier between the chiral conformers in the electronic ground state the choice of an appropriate intermediate state for enantiomer control is restricted to electronic excited states which are less accessible to direct laser excitation. The control mechanism was adapted to this demand by applying an enantio-selective laser excitation using localized “enantiomer” states as intermediate states [130]. Once the population of the undesired enantiomer is excited to the electronic excited state and hence, the energetic degeneracy of both chiral forms in the racemate is lifted, several scenarios for the purification of the racemate may be applied, as e.g. photodestruction of the undesired enantiomer [130] or “laser distillation” [58].

The one-dimensional model system for (4-methyl-cyclohexylidene)fluoromethane was extended to two coupled degrees of freedom. In this two-dimensional model enantio-selective excitation was accomplished by exciting the degree of freedom, in an intermediate step, which does not support the interconversion between both chiral forms of the molecule [165]. Again the polarization directions of the linearly polarized laser pulses are important for controlling the enantio-selectivity in this system. In addition, the orientation of the

molecules is vital for the success of the enantio-selective laser control. Therefore, in order to partly overcome the restriction of molecular orientation, a control mechanism consisting of two perpendicular propagating enantio-selective laser pulses was developed, allowing to maintain selectivity to a small extent (ca. 10%) provided unidirectional orientation of the molecules is assumed [166].

From the results obtained in this work the possibilities but also some restrictions of laser control for the selective preparation of pure enantiomers from a racemate were revealed. Using the here presented mechanisms, molecular chirality can be controlled by laser induced isomerization as long as the initial orientation of the molecules is restricted. The more uniform the molecules are orientated initially, the higher the enantio-selectivity of the laser control will be.

## 6.2 Proposed experimental realization

The experimental verification of the proposed theoretical results still remains open. Especially, the demand of oriented molecules makes the experimental realization difficult. However, all required experimental techniques are available, hence, an experiment is, in principle, possible.

Concerning the need for polarization-shaped femtosecond laser pulses, Brixner *et. al.* recently presented a new technique of computer-controlled pulse shaping, where intensity, momentary frequency, and light polarization can be varied as a function of time, even allowing the generation of elliptically polarized pulses [167].

Concerning the need for molecular orientation, several methods for the alignment and the unidirectional orientation of molecules by means of laser fields have been demonstrated theoretically [168, 159, 161, 169, 162] and experimentally [160, 170, 171]. On the theoretical front, the alignment of molecules with near-resonant or nonresonant, intense linearly polarized laser pulses were presented by Seideman [168, 161] and Friedrich and Herschbach [159], respectively. For unidirectional orientation of polar molecules along the pulse field direction Fujimura and coworkers reported a quantum control theory based on analytical [169] or optimal [162] laser pulses. Indeed, this technique has been applied recently for numerical simulations on the enantiomeric enrichment of a randomly oriented racemic mixture<sup>1</sup> of H<sub>2</sub>POSH [172]. The experimental alignment of polar and nonpolar neutral molecules by means of strong nonresonant nanosecond linearly polarized laser

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<sup>1</sup>Note that after the unidirectional orientation a fixed angular configuration was picked for enantio-selective control.

pulse was reported by Stapelfeldt *et. al.* [160, 170]. Recently, Stapelfeldt, Seideman and coworkers also demonstrated theoretically and experimentally that an intense, elliptically polarized, nonresonant laser field can simultaneously force all three axes of a molecule to align along given axes fixed in space, thus inhibiting the free rotation in all three Euler angles [171].

The alignment of chiral molecules on a surface has also been studied experimentally proving that enantiomers form domains of unique chirality on the surface [173, 174]. Ernst and coworkers, for example, found an unique azimuthal alignment in the saturated monolayer of chiral heptahelicene on a copper surface [175].

All in all, orientation of chiral molecules by laser fields or on surfaces are promising approaches for the experimental realization of the proposed enantio-selective laser control. As a matter of fact, Schwentner and coworkers are now preparing a proposal which is based, in part, on this thesis, cf. chapter 5. They plan to identify surfaces which allow orientation of weakly physisorbed chiral olefines. Then, by applying enantio-selective laser excitation to a racemic mixture of oriented molecules one enantiomer should be desorbed, while the other enantiomer remains pure on the surface [176].

## 6.3 Possible extensions

The theoretical investigations presented in this work are based on several assumptions and approximations. Therefore, extensions of the model system – especially in view of an experimental realization – covering (a) temperature effects and IVR, (b) relaxation from the electronic excited state, (c) molecular alignment and orientation, and (d) the application of the enantio-selective laser control to other chiral molecules should be considered:

- (a) The low temperature limit guarantees a perfect initial state for the enantio-selective control mechanism, higher temperature, however, might reduce the efficiency of the laser control. Likewise, dissipative effects could reduce the efficiency of the racemate purification. Therefore, the energetic coupling between the considered intramolecular motions and the other degrees of freedom, especially in case of the cyclohexyl ring, should be investigated for experimental practicable temperatures.
- (b) Spontaneous relaxation of the system could be considered in order to test the efficiency of a laser distillation scenario. In addition, extended *ab initio* calculations of the electronic excited state of (4-methyl-cyclohexylidene)fluoromethane can reveal possible conical intersections which could also be used for relaxation.

- (c) Quantum simulations including the laser controlled alignment and orientation of the molecule as well as quantum chemical studies on the orientation of chiral molecules on surfaces should be carried out. Even the role of molecular orientation for the laser controlled chiral discrimination is not entirely understood. Further studies on how chiral information is transformed by the laser-dipole interaction to a chiral molecule are necessary.
- (d) The here developed laser control is valid for a change in molecular chirality by isomerization around a chiral axis. Therefore, it would be interesting to perform further investigations with molecular model systems possessing e.g. a chiral center or a chiral plane. For a molecule with a chiral center a control mechanism similar to those presented here could be designed, inducing selective dissociation of the undesired enantiomer in a racemate.

Other aspects of the developed enantio-selective laser control, only briefly mentioned in this thesis, are being studied by Shibl and Mehdaoui based on the here presented model systems, i.e. the enantio-selective dissociation of the undesired enantiomer in a racemic mixture of pre-oriented H<sub>2</sub>POSD molecules and the enantio-selective excitation of a controlled unidirectional rotational motion in racemic (4-methyl-cyclohexylidene)fluoromethane, respectively. Related to the latter topic, the recent theoretical investigations on chiral molecular motors driven by linearly polarized laser pulses presented by Fujimura and coworkers [177] and the experimental realization of unidirectional rotation around a central C=C double bond in a chiral helical alkene by means of linearly polarized lasers reported by Feringa *et. al.* are inspiring [178, 179].

Finally, the results obtained throughout this work provide new insights on the interaction of chiral molecules with ultra-short laser pulses. Based on these results further theoretical (Shibl, Medaoui) and experimental [176] investigations have been already stimulated. In the future, this research may also serve as basis for experimental application such as the development of chiral optical switches [180, 181] or chiral catalysators controlled by enantio-selective laser pulses.