

# Chapter 5

## Summary and outlook

In this work, we presented a detailed study of the mechanism of double proton tautomerization in porphycene. Moreover, we demonstrated how to control tautomerization reactions, in particular, the separation of enantiomers using laser pulses. We focus, first, on the study of the tunneling splitting of porphycene (section 3.2) to infer the overall behaviour of the ground state (2D) wave function, see Fig. 3.16. Second, we investigate the geometric H/D isotope effect (section 3.3) to probe the cooperativity in double hydrogen bonds of porphycene in a way such as to highlight the tautomerization mechanism. In addition, kinetic H/D isotope effect was reported to establish a correspondence between the geometric and kinetic H/D isotope effects which determines the tautomerization mechanism in porphycene. Finally, we designed a laser pulse to selectively prepare a pure enantiomer from a pre-oriented racemate of H<sub>2</sub>POSD model system.

In the first part of the thesis, quantum chemical potential energy surface calculations with a multi-configuration time-dependent Hartree solution of the nuclear Schrödinger equation was combined to compute the ground state wave function for the double hydrogen bond in porphycene, see section 3. Furthermore, the tunneling splitting of concerted proton transfer reaction in porphycene and its double deuterated analogue have been calculated. The calculations of the potential energy surface were done with DFT/B3LYP and the 6-31G(d,p) basis set. The tunneling splitting was predicted to be 1.2 cm<sup>-1</sup> for normal species and 0.03 cm<sup>-1</sup> for double deuterated species, see Fig. 3.16. The obtained value for non-deuterated species is in relatively good agreement with the experimental value (4.4 cm<sup>-1</sup>), see section 3.2.1 and Fig. 3.8. The mean field calculations of the ground state wave function were compared to the exact calculations. We found that the mean field approximation is not enough to reproduce the coupling in the potential energy surface, see

Figs. 3.15 and 3.16. The strongest coupled mode (describes the change in the NN distance) to the reaction coordinates has been calculated which was found to be in accord with the experimental fluorescence spectra investigation [167], see section 3.3. The reaction coordinates as well as the coupled modes were correlated to the so-called Cartesian reaction plane coordinates. It was found that the compact Cartesian reaction plane coordinates covers the reaction Cartesian coordinates as well as some of the strongly coupled modes to the reaction coordinates.

In order to infer the properties of the wave function in the vicinity of the equilibrium geometry, an anharmonic multidimensional potential energy surface in terms of normal coordinates was evaluated. As a consequence of the combined effect of zero point energy and anharmonic mode coupling, expectation values of interatomic distances deviate strongly from classical predictions giving rise, for instance, to a quantum mechanically induced strengthening of the hydrogen bonds. Since the zero point energy depends on the nuclear masses, one observes an isotope dependence of the hydrogen bond distances, that is, the hydrogen bond strength is modified. Comparing this geometric isotope effect for symmetric (HH/DD) and asymmetric (HD) isotopomers it was found that already single substitution causes a simultaneous contraction of both hydrogen bonds. The theoretical predictions are in accord with NMR experimental data [170]. For the primary geometric isotope effect we find an excellent agreement between theory and experiment. Although this agreement deteriorates for the secondary geometric isotope, the comparison is still reasonably good if one takes into account theoretical and experimental error sources. Thus we can conclude that the two hydrogen bonds in porphycene are cooperative. In summary, we have demonstrated that geometric isotope effects can in principle be used to address the issue of cooperativity of coupled intramolecular hydrogen bonds. The favorable almost quantitative comparison between experiment and theory for a system of this size is rather encouraging, see Fig 3.28. Returning to our working hypothesis, our findings for porphycene do not yet support the conclusion that the cooperativity expressed in the geometrical changes also leads to a preference for concerted double hydrogen transfer. In order to address this point and to establish a firm relation between the quantum effects on the geometry and the kinetics of hydrogen bonds further studies, namely, the kinetic H/D isotope effect was necessary. In this respect, concerted and stepwise tautomerization mechanisms of porphycene had been explored using as a tool the distinct way in which the rates of each of these mechanisms is influenced by deuteration. For the calculated potential en-

ergy surface, proton-transfer rates were then calculated by Z. Smedarchina using the approximate instanton method. The results were compared with experimental rate constants and activation energies. Fitting these data requires empirical adjustment of the potential, the adjustment being disproportionately large for the stepwise but modest for the concerted mechanism, which is therefore favoured. Therefore, studying the geometric isotope H/D effect indicates that the two hydrogen bonds in porphycene are cooperative referring to a concerted motion of the two protons. This was scrutinized by kinetic H/D isotope effect which predicts a concerted mechanism assuming that the two mechanism are independent. This gives a conclusion (theoretically) that the double proton transfer in porphycene might proceeds concertedly. For the final conclusion, experimental investigations of kinetics for HD and DD cases will be performed by Limbach and co-workers.

In the future, since we have the multidimensional anharmonic potential energy surface, we intend to investigate deeply the vibrational motions (infrared study) which enables us to get an insight into the strength of intramolecular couplings, which is the key to understanding the mechanisms of double proton transfer in porphycene. Furthermore, this may help to solve the general problem of porphycene, that is, the disappearance of the NH stretching vibration in the experimental IR spectra which is the strongest peak in all the theoretical calculations performed so far. In addition, we shall use the Cartesian reaction plane coordinates (more compact coordinates) as well as strongly coupled modes to construct the multidimensional potential energy surface which we can use in the calculation of the tunneling splitting. We can use the same potential energy surface in a more sophisticated kinetics calculations, namely, quantum rates for concerted and stepwise mechanisms in porphycene [201].

In the second part of the thesis, two-dimensional quantum dynamical simulations on the model system  $H_2POSD$  have been employed to demonstrate that optical resolution of oriented enantiomers taking advantage of selective photodissociation is feasible, see section 4. The reactive coordinates taken into account are the torsion of the D atom around the P-S bond (Fig 4.4), which defines the interconversion between (L) and (R) enantiomers, and the P-S stretching mode, which is strongly affected upon irradiation to the electronic singlet excited state. The employed strategy relies on using two components of a linearly polarized laser field which define a polarization direction which makes the interaction with one of the enantiomers vanishing. The relation between the two field components is determined by choosing the dipole interaction so as to minimize one of the lo-

calized functions but constructively enhance the other one. In this way, only one enantiomer is excited to some intermediate state while the other remains mostly unexcited in the electronic ground state. Since the intermediate state is a repulsive electronic excited state, the excited enantiomer dissociates, while the counterpart does not, see Fig. 4.12. Repeated applications of the laser pulses accumulate the target enantiomer while dissociating the other one, separating completely the racemic mixture, see Fig 4.14.

In the separation of enantiomers using laser pulses, we have assumed a preoriented racemate, so one can extend this work to design a previous laser pulse(s) to orient the molecule in the racemate before applying the separation pulse. Moreover, we assumed that the simulation has been performed at very low temperature, so that only the lowest vibrational state is populated. One can consider a higher temperature and calculate the population for the second vibrational doublet for which a laser pulse can be then designed in similar way to selectively excite one enantiomer to the first electronic excited state. Then, a combination between these pulses might provide a new procedure for the separation of enantiomers at high temperature. The combination of two separate pulses, to achieve the same separate goals, is not trivial and may need further adjustment of both pulses.