

# Chapter 5

## Summary and Outlook

The work at hand deals with an investigation of hydrogen motion within medium sized molecules that contain an intramolecular hydrogen bond. We investigated two types of systems, first one whose PES is characterized by a single minimum (PMME) and was embedded in a liquid environment, and second a double minimum system (SA) in the gas phase. Concerning the PMME molecule, attention was paid to the relaxation dynamics through intra- and intermolecular couplings. In the case of SA, the intramolecular interactions were studied for the protonated and the deuterated species, and the possibility to control a hydrogen transfer reaction was addressed.

Keeping in mind the importance of the anharmonic couplings when describing hydrogen bonded systems, two approaches were implemented for the investigation of interactions between different degrees of freedom on the system dynamics: the *Anharmonic Force Field* (AFF) and the *Cartesian Reaction Surface* (CRS) method. The AFF approach rests on the calculation of the anharmonic force fields which are defined as higher order derivatives of the PES. We restricted our calculations on establishing the cubic and the quartic anharmonicities. In principle, they should provide a good approximation of the PES close to the global minimum, where the truncation of the Taylor expansion of the potential at the 4<sup>th</sup> order should be valid. The CRS method enables investigation of systems in full dimensionality. It treats the selected (reactive) coordinates exactly, while the other DOFs are studied within the harmonic approximation. It has a few advantages over the AFF method:

- (i) It allows straightforward investigation of different isotopic species, i.e., upon isotope replacements new quantum chemical calculations are not required as would be the case for the AFF method.
- (ii) The required quantities for defining the Hamiltonian (PES, forces, Hessian) are calculated on a grid, and therefore the anharmonicity of reactive coordin-

ates is treated more rigorously.

- (iii) It gives a more compact picture due to the fact that the CRS modes do not include the motion of reactive atoms. The resulting model is simpler than the one that would be obtained by the AFF method, as has been shown for the SA molecule. For this special case, the 9D AFF model is to be contrasted to the 7D CRS model. Nevertheless, this double minimum system has a rather anharmonic PES, so for systems characterized by less pronounced anharmonic couplings the AFF approach might be more appropriate, since it would require lower numerical effort (the force fields need to be calculated only, and not the second derivatives of the potential on the grid).

Further, we employed the diabatic representation, which proved to be useful for both methods. Within both approaches it considerably decreased the computational effort, concerning the AFF method for the diagonalization of the total Hamiltonian, and for the CRS approach it enabled investigation of the relevant region of the PES only.

Turning to specific systems, the first investigated molecule was PMME. The investigation was motivated with stimulating experimental results of the relaxation of the OH stretching vibration that is shown to proceed via the OH in plane bending mode and is, in addition, influenced by a low frequency hydrogen bond mode. Taking this as a starting point, we performed calculations of the anharmonic force fields that included those three modes and identified two additional DOFs that influence the relaxation dynamics. They have an OH out of plane bending character. This resulted in a 5D model. The two-mode couplings between the first three DOFs was treated explicitly (on the grid), whereas other couplings are included through anharmonic force fields. Further, it was necessary to include dissipation in order to reproduce the experimentally measured relaxation time. The calculations were based on the Redfield approach within the Bloch limit. In that respect, two molecular modes are included that form the internal bath and in addition the interaction with the solvent is accounted for. The system-bath interaction has previously been established through classical molecular dynamics simulations [65]. The calculations show that the relaxation of the OH stretching vibration represents a cascading process that includes four additional molecular degrees of freedom, that gives rise to energy redistribution within the molecule. The presence of the bath was essential for modelling the fast relaxation.

The SA molecule was investigated in the gas phase. First, we compared the results from the AFF and the CRS approach. The calculations showed that systems with highly anharmonic potentials, as is this double minimum system, cannot properly be studied by including only the two lowest anharmonic terms in

the AFF. That is, one would have to include also higher derivatives of the potential. Another possibility would be to treat the couplings between most strongly coupled modes explicitly, on a grid, as has been done for the PMME molecule. We have not done that, since we aimed at a comparison of the CRS method with the AFF method alone. Next, we investigated the dynamics after an excitation of the OH/OD bending and stretching vibration for the protonated/deuterated species. It was shown that different modes couple to the hydrogen and the deuterium atom, although in both cases the motion of the reactive atom is strongly influenced by skeleton modes. Finally, we discussed the possibility of controlling the hydrogen transfer reaction by means of a sequence of ultrashort IR laser pulses. The nature of the zero-order states (in the diabatic representation) suggested that the SA-D molecule is a better candidate than SA-H for accomplishing the control over this process, since the target state of this molecule is better localized in the well that corresponds to the local minimum due to its higher mass. This is important, since as a result of the excitation, it is likely that the product would be obtained in an excited state and the wave packet might cross the barrier and end up in the global minimum. However, competition with the energy redistribution might aggravate or even disable this task. Therefore, simple pulses would probably not be able to localize the wave packet in the product well, which prompts necessity for applying optimal control theory [109]-[117]. Current progress in constructing and analyzing optimized laser pulses justifies a growing interest in both theoretical and experimental research in this field.