6 Summary

In the scope of this thesis, laser spectroscopic examinations of small aromatic aggregates were carried out. A detailed examination of the isolated chromophores anisole-h8, anisole-d3 and anisole-d8 formed the basis for the examination of intermolecular interactions.

First steps were taken to get a deeper understanding of the influence of intermolecular interactions (especially hydrogen bonding) on the vibrational structure of the chromophore in the first excited state. For the examination of the hydrogen bonding, the isotopomeres of anisole with ammonia were used. For the systematic examination of the hydrogen bonding, they were compared with other intermolecular interactions. I used anisole-clusters with argon and carbon dioxide for this purpose. The system anisole/dinitrogenmonoxide could only be used to some extent due to its complexity.

The following results were achieved:

1. Anisole and its molecular aggregates were created with the seeded-beam-technique and investigated by mass spectroscopy, REMPI spectroscopy and resonant-2-photon spectroscopy.
2. As the basis for a solution to the scientific question, anisoles were examined in detail in the electronic ground state (S_0) and in the first excited state (S_1). A special interest was taken in the observed shift during the excitation from the S_0-state into the S_1-state, the geometry and the normal vibrations.

3. All 42 normal vibrations of the three anisoles: $C_6H_5OCH_3$ (Anisol-h8), $C_6H_5OCD_3$ (Anisol-d3) and $C_6D_5OCD_3$ (Anisol-d8) were assigned for the first time in the S_1-state. The previous assignment of some normal vibrations in the S_0-state could be revised.
4. The assignment of normal modes is based on the comparison with other chromophores and especially on the isotope effects going from anisole-h8 to anisole-d3 and anisole-d8. The classification of overtones and combinations based on the spectrum confirms the assignment of the fundamental vibrations given in this thesis.
5. REMPI-spectra of all three isotopomeres of anisole with ammonia were measured. All intermolecular vibrations could be assigned completely for the first time, as well as almost all intramolecular normal modes of anisole in the cluster.
6. The intermolecular interactions in the system anisole/ammonia were analyzed in detail. It was shown that anisole can work as a proton acceptor as well as a weak proton donor. It was found that the N-H•••O hydrogen bonding dominates next to electrostatic interactions.
7. It was shown on the basis of frequency-shifts of normal modes of anisole in the cluster, that the intermolecular interactions can have an influence on the intramolecular normal vibrations. For the out-of-plane-C-H-vibrations and the ether group, a remarkable increase in the frequency of the vibrations in the cluster in comparison to the isolated chromophor was observed. This is an interesting result because until now in present literature, this kind of influence has been less explored.
8. To compare the hydrogen bonding with other intermolecular interactions, the REMPI-spectra of anisole/carbon dioxide were also measured. In this system, the quadrupole-dipole interaction dominates. In comparison to the hydrogen bonding, this interaction leads to only small shifts in the intramolecular modes. Intermolecular vibrations as well as some

fundamental modes in both systems were compared, and the similarities and differences of both dominating interactions were highlighted.

9. REMPI-spectra of anisole-argon were also measured. No influence of intermolecular interactions on intramolecular modes of anisole could be determined in this system.
10. The REMPI- spectra of the 1:1-cluster of anisole/dinitrogenmonoxide show three structures. These spectra could not be analyzed satisfactorily so far.
11. For all systems mentioned in this thesis, quantum chemical model calculations for the S_0-state and the S_1-state were performed with the packet GAUSSIAN 98.
12. Additionally, photo-electronic-spectra of the systems anisole-h8/ammonia, anisole-d3/ammonia and anisole-d8/ammonia were measured. This, however, would go beyond the scope of this thesis and was therefore excluded from this work.