Summary

The purpose of the investigations was to gain an insight in magnitude and sign of π-electron orbital angular moments of negative ions of aromatic hydrocarbons. These quantities are an important help in the assignment of spectroscopic transitions. The sign and magnitude may give direct information about the excited state symmetry and possible processes affecting the molecule (electrostatic interaction, Jahn-Teller effect). Especially negative ions were investigated because of their unique properties. They may have for instance, in contrast to neutral aromatics, an orbitally degenerate ground state, provided the symmetry is threefold or higher. Besides, the lowest excited states in negative ions have a comparatively long wavelength, because the levels in the MO-scheme are more than half-filled (IR and visible region). The consequence of this is a relatively large interaction between these states, caused by the magnetic field.

For the measurement of the quantities mentioned, the spectroscopic methods magnetic circular dichroism (MCD) and optical absorption were used. MCD is a method in which a difference-spectrum is measured, in this case the difference in absorption of left and right circularly polarized light. When the Zeeman splitting is small compared with the bandwidth of the absorption bands, MCD is a very sensitive technique for the determination of angular moments. In order to perform MCD and absorption under identical circumstances (wavelength, temperature etc), an apparatus has been built, that can do these measurements simultaneously. The signal-to-noise ratio and the spectral bandwidth are better than those of commercially available instruments. In the first paragraph of chapter II the apparatus is described, together with the underlying theory.

Measurements were done on the mono- and divalent negative ions of [16]annulene (chapter III), the neutral molecule and the mononegative ion of tribenzo[12]annulene (chapter IV), and the anion of triphenylene (chapter V). In the case of the [16]annulene (1-) ion a low lying state (about 500 cm⁻¹) could be shown from the intensity of the MCD spectrum with respect to the absorption spectrum.
In the spectra of the (2-) ion a weak optical transition is characterized by a very intense MCD signal; its orbital angular momentum is determined as 2.3 $\hbar$. The presence of A-terms in the MCD spectra confirms the fourfold symmetry of the ions. From the temperature dependence of the absorption signal of a solution, that contains the neutral molecule as well as both kinds of ions, some thermodynamical quantities and the dipole strengths of the ion bands are determined. The MCD spectrum of the negative ion of triphenylene is clearly temperature dependent, which indicates the presence of an orbital angular momentum in the ground state. Also the influence of an interaction with the counterion can be seen, which causes a decreasing of the splitting of the ground state at lower temperatures. The absolute magnitude of the parameter C/D, which is only one third of the calculated value, indicates a dynamic Jahn-Teller effect. The signs of the MCD parameters for one of the bands in the spectrum led to a reassignment of a previous result. In the case of the neutral tribenzo[12]annulene the MCD measurements show that the first, weak absorption band must be assigned to two optical transitions and also that in the intense band a second transition is hidden. The spectra of the negative ion of tribenzo[12]annulene are measured and the influence of the solvent is studied. The interpretation of the spectra is done with the aid of semi-empirical $\pi$-electron calculations (PPP method), where the perturbation, caused by the positive alkali metal ion, could be taken into account (chapter II, §5).