

Kapitel 16

Summary

The research presented in this thesis is focussed on the characterization of small clusters containing aromatic molecules using excited state photoelectron spectroscopy and REMPI spectroscopy.

To carry out this task a special experimental setup was constructed and built, which consists of a supersonic molecular beam, a Nd-YAG pumped dye laser and a time of flight spectrometer. The spectrometer is a combination of a magnetic bottle-type photoelectron spectrometer and a linear TOF mass spectrometer. The energy resolution of the photoelectron spectrometer was determined to be 10 meV at 0.5 eV electron energy. The $R_{50\%}$ mass resolution is approx. 300. The laser system has limited the energy resolution which could be achieved in the REMPI spectra to 0.26 cm^{-1} - 1 cm^{-1} .

The characterization was performed by measuring mass spectra, REMPI- and photoelectron efficiency spectra and excited state photoelectron spectra of the following systems. The clusters containing toluene and rare gases (Ar, Kr, Xe), anisole and argon, anisole and ammonia or anisole and carbondioxide. The homogeneous anisole dimers were also investigated.

REMPI spectra yielded in the absorption spectra of the clusters. The shift of the $S_1 \leftarrow S_0$ transition energy with respect to the pure aromatic cluster compound and intermolecular vibrations were determined. The shifts of the transition energy of the aromatic molecule rare gas clusters are linearly proportional to the rare gas polarizabilities. They also increase with the dipole moment of the aromatic molecule. The transition energy of the anisole ammonia (1:1) and the anisole carbondioxide (1:1) clusters is shifted to smaller and bigger values respectively. This last shift is an unexpected result. Obviously the shift is influenced by the cluster structure. Considering the results of ab initio calculations all intermolecular vibrations of the (1:1) clusters could be assigned. The experimental vibrational energies are in a good agreement with the calculated values and it was therefore possible to determine the cluster structures.

The unexpected shift of the $S_1 \leftarrow S_0$ transition energy of the anisole carbondioxid (1:1) cluster demand the investigation of the cluster structure in detail. This was done by a comparison of the rotational fine structure of the $S_1 \leftarrow S_0$ transition with the simulated spectra of three different calculated structures. The comparison led to the conclusion that in the structure of the (1:1) cluster, the carbondioxide molecule is not found to be on top of the aromatic ring but side on coordinated in plane of the ring. Two weak hydrogen bonds contribute to the intermolecular bond. For such kind of cluster systems this is a new type of structure which has never been observed before.

Up to now only a limited number of excited state photoelectron spectra of clusters were published. Ionization energies, intramolecular and some intermolecular vibrations of the above-mentioned systems were determined. The measurement of the intramolecular vibrations of clusters was not possible with the ZEKE photoelectron spectroscopy previously. Most of the vibrational modes were assigned. Almost all the ionization energies stated on this thesis were measured for the first time. Compared to the ionization energies of the pure aromatic molecules, the ionization energies of the clusters are shifted to smaller values. In the case of the aromatic molecule rare gas clusters the shift is linearly proportional to the rare gas polarizability. The shift of the other systems showed a reliance of the cluster structure. For example the new cluster structure of the anisole carbondioxide (1:1) cluster lead to a very small shift. The shape of the photoelectron spectra also show the intracuster dynamic. It has been shown exemplary for the anisole ammonia (1:1) cluster how the reorientation of the ion following the Franck Condon transition broadened the spectra. The coupling between the intra- and intermolecular vibrations is shown as an example for the toluene rare gas clusters. It should also be mentioned here, that it is possible to extract the excess energy of the cluster ion from the excited state photoelectron spectra.

In the photoelectron spectra of the anisole dimer a special structure with two maxima was observed. This is explained by the interaction of two identical molecules with dipole moments. It was possible to define the dimer structure and determine the intermolecular binding energies with the photoelectron spectrum and a cyclic process.