Structure and dynamics of large molecules and their van der Waals complexes by high resolution UV laser spectrocopy.

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The combination of a supersonic molecular beam expansion and a narrow band UV laser is a powerful tool in experimental molecular spectroscopy. It provides detailed information about the dynamics and structure of molecules and molecular complexes. Expanding volatilized organic molecules seeded in a carrier gas produces a cooling of the vibrational and rotational degrees of freedom. The low internal temperatures permit the stabilization of structural variants (tautomers or conformers) and the stabilization of molecular clusters (van der Waals and hydrogen bonded complexes).

Analysis of rotationally resolved laser induced fluorescence (LIF) spectra provides the molecular constants in both the ground and the electronically excited state, giving access to information about intramolecular and intermolecular bond lengths and their changes upon excitation.

In addition to the geometrical information, one can determine the orientation of the electronic transition moment vector in the molecular frame from the high resolution spectrum. This vector provides insight in the electronic charge migration or displacement that occurs during the transition. It is therefore related to the probability distribution functions in the involved electronic states.

Another interesting interaction is caused by the coupling of an internal hindered rotation with the overall rotation of the molecule. Full analysis of the spectra provide values for the barrier heights in the ground state and the excited state. The extent of complexity of the spectra depends strongly on the barrier heights, the direction of the internal rotation axis with respect to the overall inertial axis, and the (optical) selection rules (type of transition).

In the present talk first a short description is given of the experimental setup. A number of examples will be discussed to demonstrate the power of the method amoung others the triphenylamine and its van der Waals complex with argon, the 1-cyanonaththalene—triethylene complex, the tautomers of benzotriazole and the hydrogen bonded phenol—water complex.