ELECTRONIC SPECTROSCOPY OF PHENOL(WATER)$_{1-12}$ CLUSTERS: STRUCTURES AND INTERMOLECULAR VIBRATIONS

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The structures and intermolecular vibrations of jet cooled phenol$(H_2O)_n$ were investigated in the electronic ground state by dispersed fluorescence and in the electronically excited state by mass resolved resonant two-color/two-photon ionization, spectral hole burning and rotationally resolved laser induced fluorescence. Vibronic spectra up to a cluster size of n = 12 could be taken via excitation just above the ionization thresholds and were discriminated for isomers via spectral hole burning.
The measured rotational constants, the analysis of the (electronic) spectral shifts, the ionization potentials and the comparison of measured and *ab initio* calculated intermolecular vibrations are used to determine the structures of these two-, three- and (partially) tetra-coordinated H-bridge systems. The n = 1 cluster exhibits a trans-linear hydrogen bond.[a] The aggregates with n = 2 - 4 H_2O are cyclic H-brigded systems with single H-donor units, whereas double H-donor H_2O presumably form a cage structure in the case of n = 5. The vibronic spectra of the n = 8 and n = 12 cluster are especially prominent.
The experimental data point to H-bridge assoziation of phenol to cube-like $(H_2O)_8$ and $(H_2O)_{12}$ clusters, exhibiting the tendency of a particular high cluster stability for a maximum number of planar $(H_2O)_4$ rings. The spectral shifts point to a structure with $(H_2O)_4$ assiziated to the water molecules of the cyclic phenol$(H_2O)_4$.

[a] G. Berden, W.L. Meerts, M. Schmitt and K. Kleinermanns *J. Chem. Phys.* **102**, 972 (1996)