ELECTRONIC SPECTROSCOPY OF PHENOL(WATER)$_n$ CLUSTERS: STRUCTURES AND INTERMOLECULAR VIBRATIONS

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The structures and intermolecular vibrations of jet cooled phenol(H$_2$O)$_n$ 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. The aggregates with $n = 2 - 4$ H$_2$O are cyclic H-bridged systems with single H-donor units, whereas double H-donor H$_2$O 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 association of phenol to cube-like (H$_2$O)$_8$ and (H$_2$O)$_{12}$ clusters, exhibiting the tendency of a particular high cluster stability for a maximum number of planar (H$_2$O)$_4$ rings. The spectral shifts point to a structure with (H$_2$O)$_4$ associated to the water molecules of the cyclic phenol(H$_2$O)$_4$.