STRUCTURE AND MOLECULAR DYNAMICS OF THE HYDROGEN-BONDED PHENOL-METHANOL COMPLEX FROM HIGH RESOLUTION ELECTRONIC SPECTROSCOPY AND AB INITIO THEORY.[a]

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The rotationally resolved spectrum of the electronic origin of the hydrogen bonded phenol-methanol cluster in a molecular beam at 35933 cm^{-1} has been analyzed. Due to the internal rotation of the methyl group in the methanol moiety the spectrum is split into A and E sub-torsional bands separated by 3.558 GHz. From a perturbation analysis of the torsional-rotational structure the V_3/F values of the threefold barriers to internal rotation of the methyl group could be determined to be 32.16 in the S_0 and 27.65 in the S_1 state, respectively. The determination of barrier heights from these ratios is discussed, and the obtained barrier heights are compared to bare methanol and other methanol clusters. The perturbation analysis also yields the angle between the internal rotor axis and the inertial axes of the cluster, which allows the determination of the geometry of the hydrogen bond in both electronic states. From the obtained data parameters of the intermolecular structure of the cluster as well as for the torsional potential of the methyl rotation are determined.
The structure, energetics and barrier to internal rotation of the cluster are calculated at different levels of theory (HF, DFT, and MP2) and compared to the experimental results. The structure of the phenol-methanol cluster is determined by the hydrogen bonding interaction and the (mostly) dispersive interaction of the methyl group with the aromatic ring. To account for the correct balance between these two attractive forces, methods have to be employed which include electron correlation. Furthermore *ab initio* normal mode analyses are compared to experimental intermolecular vibrational frequencies for both electronic states.
The results obtained for phenol-methanol are compared to the phenol-water cluster,[a] in which also the phenol moiety acts as proton donor. This cluster shows distinct differences to the phenol-methanol cluster in structure and molecular dynamics and the reasons for these different behaviours are discussed.

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[a]G. Berden, W.L. Meerts, M. Schmitt and K. Kleinermanns, *J. Chem. Phys.* **104**(1996), 972