The rotationally resolved UV spectra of the electronic origins of five isotopomers of the phenol dimer and the most abundant isotopomer of the benzonitrile dimer have been measured. The complex spectra are analyzed using a genetic algorithm based fitting strategy. For the phenol dimer we determined from the inertial parameters the intermolecular geometry parameters for the electronic states \( S_0 \) and \( S_1 \) and compared them to the results of \textit{ab initio} calculations. In the electronic ground state \( S_0 \) a larger hydrogen bond length than in the \textit{ab initio} calculations is found and a smaller tilt angle of the aromatic rings, showing a more pronounced dispersion interaction. In the electronically excited state \( S_1 \) the hydrogen bond length decreases, as has been found for other hydrogen bonded clusters of phenol and the two aromatic rings are tilted less toward each other.

For the benzinitrile dimer we found that the electronic ground state has a \( C_{2h} \) symmetric structure in which the permanent dipole moments of the benzonitrile monomers are aligned anti-parallel. The orientation of the transition dipole moment could be shown to be parallel to the orientation in the monomer moiety. The distance between the two monomer moieties decreases slightly upon electronic excitation and the symmetry of the benzonitrile dimer changes from \( C_{2h} \) in the electronic ground state to \( C_2 \) in the electronically excited state. This break of symmetry is probably caused by the local excitation of only one benzonitrile moiety in the cluster due to the weak electronic coupling between the cluster moieties.

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