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Intermolecular vibrational couplings in the phenol$(H_2O)_1$ cluster

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The intermolecular vibrations of the binary cluster phenol$(H_2O)_1$ are characterised by anharmonicities and strong couplings. Therefore a one-dimensional and harmonic approximation is not suitable to explain the intermolecular parts of the experimental vibrational spectra of the electronic ground state (S_0) and the first excited state (S_1). In a first step, three normal modes were chosen to perform a three-dimensionally coupled vibrational analysis of the above-mentioned system. The normal modes τ (torsional motion), β_2 (symmetric in-plane wagging motion) and ρ_1 (asymmetric out-of-plane rocking motion) were selected because the transition state of the torsion of the water molecule can be expressed with these coordinates.

An *ab initio* potential energy surface has been calculated by elongations along the τ, β_2, and ρ_1-coordinates. The eigenvalues of this PES were determined via the Ritz variational method. The eigenvalue spectrum as well as intensities which were obtained by the calculation of Franck-Condon factors were used to interpret experimental data. Simulated transitions were correlated with experimental bands in a frequency region of 90 to 140 cm^{-1}. The analysis of couplings depending on torsional symmetry gave valuable information about the height of the torsional barrier.

In order to simulate the intermolecular vibrations of the phenol$(H_2O)_1$ cluster completely, we started to perform a full six-dimensional calculation. An important basis for this is an *ab initio* potential energy surface at a high level of theory. The hamiltonian to solve the eigenvalue problem will include monomer parts and coupling terms to describe the couplings between the motions of the two monomers as well as interactions with the overall rotation [1].

[1] C. Leforestier, L. B. Braly, K. Liu, M. J. Elrod, R. J. Saykally, *J. Chem. Phys.* **106** (1997) 8527