COMPUTATIONAL HIGH-FREQUENCY OVERTONE SPECTRA OF THE WATER AMMONIA COMPLEX

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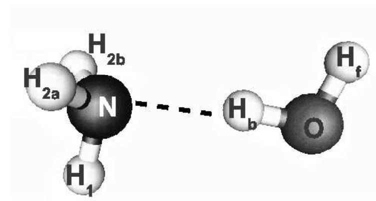

We have computed vibrational high-frequency overtone spectra of the water ammonia complex, $H_2O - NH_3$, and its isotopomers. The cluster has been modelled as two independently vibrating monomer units. Our internal coordinate Hamiltonians for each monomer unit have been constructed using exact gas phase kinetic energy operators. The potential energy and dipole moment surfaces have been calculated with the explicitly correlated coupled cluster method CCSD(T)-F12A and valence triple zeta VTZ-F12 basis around the equilibrium geometry of the complex. The vibrational eigenvalues are calculated variationally. The eigenfunctions obtained are used to compute the relative absorption intensities.

In $H_2O - NH_3$, water molecule acts as the proton donor and its symmetry is broken. The hydrogen bonded OH_b bond oscillator undergoes a large redshift and intensity enhancement compared to the free hydrogen bond. Broken degeneracy of the asymmetric vibrations, quenched inversion splittings, and blueshift of the symmetric bend are the most visible changes in the ammonia unit.

Our vibrational model is anharmonic. Therefore, we have been able to calculate not only high-frequency fundamentals but also overtones and combination levels that for this complex have not been detected experimentally. The calculated fundamentals agree well with matrix isolation and helium droplet measurements except for the bonded OH_b stretching of the water unit where our model overestimates the clustering induced shift. The same has previously been seen in the bonded OH_b stretch of the water dimer and is probably due to the couplings with the low-frequency modes.