CALCULATED OH STRETCHING VIBRATIONAL BAND INTENSITIES OF SMALL WATER CLUSTERS

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We have calculated fundamental and overtone OH-stretching vibrational band intensities of the small water clusters. The intensities were determined with a simple harmonically coupled anharmonic oscillator (HCAO) local mode model and ab initio dipole moment functions. The dipole moment functions were calculated at the self-consistent-field Hartree- Fock and quadratic configuration interaction including single and double excitations levels of theory with the 6-31G(d), 6-311+G(d,p), and 6-311++G(2d,2p) basis sets. The overtone spectra of the dimer and trimer have not been observed and a method of obtaining local mode parameters from scaled ab initio calculations has been suggested. Our calculations show that the total overtone intensity of the dimer and trimer, although distributed differently, is close to two and three times the total intensity of the monomer for a given region. One significant difference between the monomer and the dimer and trimer is the appearance of the red shifted hydrogen bonded OH-stretching band in the dimer and trimer spectra. We suggest that these red shifted bands are ideal for attempts to observe the water dimer in the atmosphere. The method presented can provide an accurate estimate of the OH-stretching intensities for molecules for which vibrational spectra have not been observed. Such calculations are of importance in atmospheric solar energy absorption models.