

COMPUTATIONAL FRAMEWORK FOR ANALYSIS OF HYDROGEN BONDING IN THE OH STRETCH REGION

LAURA C. DZUGAN, ANNE B McCOY, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA.*

There are two types of bands in the OH stretch region of the vibrational spectra of hydrogen-bonded complexes; narrow peaks due to isolated OH stretches and a broadened feature reflecting the OH stretches involved in strong hydrogen bonding. This second region can be as wide as several hundred wavenumbers and is shifted to the red of the narrow peaks. In this work we focus on $(\text{CaOH})^+ \cdot (\text{H}_2\text{O})_n$ and $(\text{MgOH})^+ \cdot (\text{H}_2\text{O})_n$ systems.¹ When $n < 4$, the spectra are characterized by only the narrow peaks near 3700 cm^{-1} . When $n \geq 4$, there is an additional band that is several hundred cm^{-1} wide, which is attributed to hydrogen bonding. This breadth arises from coupling between the OH stretches in the water molecules and the low frequency modes of the complex. To understand the broadening observed in the spectra, we have developed a computational framework in which we sample displacement geometries from the equilibrium structure based on the ground state harmonic wavefunction. Then we combine the harmonic spectra in the OH stretch region for each computed geometry to generate the spectrum for this complex. As the calculated spectra agree well with the experimental spectra, we then investigated which geometric parameters in the system are correlated to the size of the red-shift of the frequencies. The hydrogen-bonded OH stretches were found to be very sensitive to how the water molecules were arranged around the hydroxide group.

1. Leavitt, C.M.; Johnson, C.J.; Johnson, M.A. Unpublished work.