ORIGINS OF IR INTENSITY IN OVERTONES AND COMBINATION BANDS IN HYDROGEN BONDED SYSTEMS

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As the infrared spectra of an increasing number of hydrogen bonded and ion/water complexes have been investigated experimentally, we find that they often contain bands with significant intensity that cannot be attributed to fundamental transitions. In this talk, we explore several sources of the intensity of these overtone and combination bands. A common source of intensity is mode-mode coupling, as is often seen between the proton transfer coordinate and the associated heavy atom vibration. A second important mechanism involves large changes in the dipole moment due the loss of a hydrogen bond. This results in intense overtone transitions involving non-totally symmetric vibrations as well as the introduction of intense combination bands involving intramolecular bending coupled to hindered rotations. These effects will be discussed in the context of several systems, including the spectra of complexes of argon atoms with H_3O^+,[a] $F^-\cdot H_2O$,[b] $Cl^-\cdot H_2O$,[c] protonated water clusters,[a] and HOONO.[d]

[a] T. Guasco, S. Olesen and M. A. Johnson, private communication

[b] S. Horvath, A. B. McCoy, J. R. Roscioli and M. A. Johnson, *J. Phys. Chem. A*, **112**, 12337-44 (2008)

[c] S. Horvath, A. B. McCoy, B. M. Eliot, G. H. Weddle, J. R. Roscioli and M. A. Johnson, *J. Phys. Chem. A*, **115**, 1556-68 (2010).

[d] A. B. McCoy, M. K. Sprague and M. Okumura, *J. Phys. Chem. A*, **115**, 1324-33 (2010)