HYDROGEN BONDING EFFECTS ON THE INFRARED INTENSITIES OF HALIDE-WATER COMPLEXES

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The implications of H-bonding in halide-water complexes and its effects on infrared spectra have been of long standing interest, with studies focusing mainly on the OH stretching region. Until recently only the low-energy portion of the $X^-(H_2O)$ spectra had been probed experimentally (X = F, Cl, Br).[a,b] An interesting feature in this low-energy region, especially noticeable in the $Cl^-(H_2O)$ spectrum,[b] is the large intensity of the overtone for the out-of-plane bending mode. The potential and dipole moment surfaces along this internal coordinate are calculated at the MP2 level of theory (aug-cc-pVTZ basis), and the X^- vibrational wave functions and energies are the result of one-dimensional variational calculations.[c] Our results reproduce the experimental findings very well, and we determine that the overtone intensities reflect the large shifts in charge distribution along the heavy-atom axis when the hydrogen moves out of the plane. This method, although only one-dimensional, shows excellent agreement with experiment and accurately explains the essential physics that give rise to these spectral features.

[a] G. M. Chaban, S. S. Xantheas, and R. B. Gerber, J. Phys. Chem. A 107, 4952 (2003).
[b] E. G. Diken et al., J. Phys. Chem. A 109, 571 (2005).
[c] D. T. Colbert and W. H. Miller, J. Chem. Phys. 96, 1982 (1992).