

## 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 ( $X = F, Cl, Br$ ).<sup>a,b</sup> An interesting feature in this low-energy region, especially noticeable in the  $Cl^-$  ( $H_2O$ ) spectrum,<sup>b</sup> 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.<sup>c</sup> 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.

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<sup>a</sup>G. M. Chaban, S. S. Xantheas, and R. B. Gerber, *J. Phys. Chem. A* **107**, 4952 (2003).

<sup>b</sup>E. G. Diken et al., *J. Phys. Chem. A* **109**, 571 (2005).

<sup>c</sup>D. T. Colbert and W. H. Miller, *J. Chem. Phys.* **96**, 1982 (1992).