UNDERSTANDING THE INTERMOLECULAR BENDING VIBRATIONS OF $(^{1,2}H_2O)X^-$ [X=F, Cl, Br, I]

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Halide-water complexes have been the subject of numerous experimental studies over the last few years.[a,b] Recently spectroscopists have been able to probe the intermolecular bending region (below 1000 cm^{-1}) and have noticed some interesting features, such as spectral evidence for tunneling through the barrier in the in-plane bend coordinate that interconverts the two hydrogens.[a] An analysis of the in-plane bend is complicated because of the coupling between this mode and the water bend. This interaction is illustrated by the harmonic frequencies of the in-plane bend, which do not display a simple H/D mass dependence: 366 cm^{-1} for $(HOH)Cl^-$, 310 cm^{-1} for $(HOD)Cl^-$, 297 cm^{-1} for $(DOH)Cl^-$, and 264 cm^{-1} for $(DOD)Cl^-$. In order to capture the isotopic trend, we need to incorporate this coupling in our model in at least an average way. To do this we use a reaction path formulation[c] that allows us to incorporate the zero point energies in the remaining degrees of freedom, thereby generating an effective potential energy surface.

We investigate the underlying motions associated with the in-plane bend for these halide-water systems by calculating the electronic energy and dipole moment surface at the MP2 level of theory using aug-cc-pVTZ basis sets. The subsequent vibrational energies and wave functions are determined using a one-dimensional finite basis set representation in sines and cosines. Our initial theoretical results reproduce the experimental and electronic structure trends well and provide insight into the interesting mass dependence of this molecular vibration.

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[a] J. R. Roscioli, E. G. Diken, M. A. Johnson, S. Horvath, and A. B. McCoy, *J. Phys. Chem. A*, 110, 4943 (2006).
[b] E. G. Diken *et al.*, *J. Phys. Chem. A*, 109, 571 (2005).
[c] W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.*, 72, 99 (1980).