UNRAVELING THE INTENSITY PATTERNS IN THE INFRARED SPECTRA OF $X^-(^{1,2}HO^{1,2}H)$ [X=F,Cl]

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The distortions from equilibrium and changes in the infrared spectra of a single water molecule when it is complexed with a halide ion (F^-, Cl^-, and Br^-) have been of great interest for the past several years.[a,b] In these systems the bonded hydrogen stretch (ν_2), the so-called "proton-transfer" mode, as well as the in-plane (ν_4) and the out-of-plane (ν_6) bending modes have displayed unexpected intensity patterns in the experimental infrared spectra.[c] An example of such anomalies can be seen in the ν_2 mode of $F^-(H_2O)$. This vibrational mode exhibits significant intensity in the fundamental transition, over ten times that of any other fundamental, and its frequency is shifted by nearly 1500 cm^{-1} to the red of the free OH stretch. Analysis of the first and second overtones in ν_2 indicates that anharmonicity is not as significant as one might expect from such a large redshift of the fundamental.

We investigate the underlying motions associated with the ν_2, ν_4, and ν_6 modes by calculating the potential energy and dipole moment surfaces at the MP2 level of theory using aug-cc-pVTZ basis sets. The $X^-(H_2O)$ vibrational energies and wave functions are determined using one- and two-dimensional[d] variational calculations. Our theoretical results reproduce the experimental findings extremely well and provide insight into the physics behind these intriguing spectral features.

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[b] E. G. Diken et al., J. Phys. Chem. A 109, 571 (2005).
[c] J. R. Roscioli, E. G. Diken, M. A. Johnson, S. Horvath, and A. B. McCoy, J. Phys. Chem. A 110, 4943 (2006).
[d] D. T. Colbert and W. H. Miller, J. Chem. Phys. 96, 1982 (1992).