

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

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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 ( $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ ) have been of great interest for the past several years.<sup>a,b</sup> In these systems the bonded hydrogen stretch ( $\nu_2$ ), the so-called “proton-transfer” mode, as well as the in-plane ( $\nu_4$ ) and the out-of-plane ( $\nu_6$ ) bending modes have displayed unexpected intensity patterns in the experimental infrared spectra.<sup>c</sup> An example of such anomalies can be seen in the  $\nu_2$  mode of  $\text{F}^-(\text{H}_2\text{O})$ . 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  $1500\text{ cm}^{-1}$  to the red of the free OH stretch. Analysis of the first and second overtones in  $\nu_2$  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  $\nu_2$ ,  $\nu_4$ , and  $\nu_6$  modes by calculating the potential energy and dipole moment surfaces at the MP2 level of theory using aug-cc-pVTZ basis sets. The  $X^-(\text{H}_2\text{O})$  vibrational energies and wave functions are determined using one- and two-dimensional<sup>d</sup> 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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<sup>a</sup>D. D. Kemp and M. S. Gordon, *J. Phys. Chem. A* **109**, 7688 (2005).

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

<sup>c</sup>J. R. Roscioli, E. G. Diken, M. A. Johnson, S. Horvath, and A. B. McCoy, *J. Phys. Chem. A* **110**, 4943 (2006).

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