

UNDERSTANDING $X^- \cdots \text{HOCl}$ ($X=\text{Cl, Br, I}$) THROUGH VIBRATIONAL PERTURBATION THEORY

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Complexes of halide ions (Cl, Br and I) with water have provided a set of systems that allow us to explore spectral signatures of hydrogen bonding and how the frequencies and intensities map onto the strength of the hydrogen bond interactions. By substituting HOCl for HOD, we are able to further explore how the acidity of the hydrogen bonding partner is reflected in the spectroscopy. Building off of prior studies of $X^- \cdots \text{H}_2\text{O}$ ¹ it is possible to provide tentative assignments for only a subset of the features of interest. Through vibrational perturbation theory (VPT), we can obtain a more complete assignment of the vibrational spectrum of $X^- \cdots \text{HOCl}$ from 1200-4000 cm^{-1} . Applying VPT to these systems requires a flexible approach, where resonances are handled appropriately and state energies are tuned to correct for overbinding of the hydrogen to the halide ion at the MP2/aug-cc-pVTZ level of theory/basis used for this study. After including these corrections, the calculated spectra are in very good agreement with experimental spectra. This flexibility also allows for the interpretation of the origin of spectral intensity, making it possible to determine whether a transition obtains intensity through higher order terms in the expansion of the dipole moment (electrical anharmonicity), higher order terms in the expansion of the potential surface (mechanical anharmonicity), or state mixing through through couplings of nearly degenerate zero-order states. The $X^- \cdots \text{HOCl}$ systems also provide the opportunity to explore spectral implications of halogen bonding and vibrational perturbation theory is applied to the differentiation of contributions to the spectra from the halogen- and hydrogen-bonded isomers of ClHOI^- .

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