WEAK C–H···O INTERACTIONS AND H_2O INTERNAL ROTATION IN THE $HCClF_2$–H_2O AND $HCBrF_2$–H_2O DIMERS

REBECCA A. PEEBLES, SEAN A. PEEBLES, BRANDON J. BILLS, LENA F. ELMUTI, DANIEL A. OBENCHAIN, AMELIA J. SANDERS, AMANDA L. STEBER, *Department of Chemistry, Eastern Illinois University, 600 Lincoln Ave., Charleston, IL 61920*; PETER GRONER, *Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110*; BROOKS H. PATE, JUSTIN L. NEILL, MATT T. MUCKLE, *Department of Chemistry, University of Virginia, McCormick Rd., PO Box 400319, Charlottesville, VA 22904*.

The polarity of the C-H bond involved in a weak C-H···X interaction may be tuned by introducing different combinations of halogen substituents on the carbon atom. In this study, the structures of the $HCClF_2$–H_2O and $HCBrF_2$–H_2O dimers have been studied by rotational spectroscopy and theoretical methods, with the hope of observing weak C-H···O interactions. Ab initio calculations (MP2/6-311++G(2d,2p)) predict cyclic structures for both dimers, with a C-H···O and an O-H···X (X = Cl or Br) interaction present in each complex. Fourier-transform microwave spectroscopic investigations of both species have confirmed that this structural motif is present, although the experimental results display some significant differences from the theoretical predictions.

The spectra of both $HCClF_2$–H_2O and $HCBrF_2$–H_2O were doubled due to internal rotation of the water molecule within the weak complex (with the higher frequency state about three times the intensity of the lower frequency state, as expected for exchange of equivalent hydrogen nuclei). Ab initio potential energy scans have been performed to estimate the barrier to rotation of the water molecule in both dimers, and for $HCClF_2$–H_2O a global fit using ERHAM[a] has also provided an experimental determination of the energy difference between the tunneling states ($16.0(4)$ GHz) and barrier to rotation ($195(5)\ \mathrm{cm}^{-1}$). Remarkably, the more intense higher frequency transitions belong to the lower energy B internal rotation state.

[a]P. Groner, *J. Chem. Phys.*, **107**, (1997), 4483-4498.