BRIDGING THE GAP BETWEEN VAN DER WAALS AND HYDROGEN BONDING: A NEAR-IR STUDY OF THE INTERMOLECULAR MODES IN HCl DIMER

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The near IR combination band spectra of supersonically cooled $(HCL)_2$ in the 2900 cm^{-1} to 3070 cm^{-1} region have been recorded with a high resolution slit jet spectrometer. Seven vibration-rotation-tunneling (VRT) bands are observed, representing 3 (out of 4 total) intermolecular modes (van der Waals stretch v_4, geared bend v_5, and out-of-plane torsion v_6) built as combination bands on either the v_1 (free) or v_2 (bound) HCl stretches. Each of the seven combination bands are observed for both the $H^{35}Cl$-$H^{35}Cl$ and $H^{35}Cl$-$H^{37}Cl$ isotopomers. Analysis of the rotationally resolved spectra provide spectroscopic constants, intermolecular frequencies, predissociation rates, and isotopic shifts as a function of both intra- and inter-molecular excitation. The intermolecular frequencies are compared with full 6-D quantum calculations of a trial potential surface and discrepencies are discussed. Additionally, comparisons with similar studies on $(HF)_2$ and $(DF)_2$ are presented. Both tunneling rates and combination band intensities are compared between the chlorine and fluorine build dimers, illuminating dramatic differences in these seemingly similar hydrogen bonded prototypes.