SEQUENTIAL CLUSTERING OF HCl IN ARGON: NEAR INFRARED SPECTRA OF Ar_2HCl AND Ar_3HCl

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High resolution near infrared spectra of the v_{HCL}=1←0 fundamental stretch in Ar_2HCl and Ar_3HCl have been characterized using a slit-jet infrared spectrometer. Analysis of the jet cooled, rotationally resolved spectra i) permit unambigous identification of the cluster size, ii) provide vibrationally averaged geometries in the v_{HCl}=1 excited state, and iii) allow the vibrational shift of the HCl chromophore to be measured as a function of the number of Ar atoms in the complex. The equilibrium structures of the Ar_nHCl (n=1-3) clusters calculated using accurate Ar-Ar and Ar-HCl pair potentials are consistent with the vibrationally averaged structures inferred spectroscopically. The vibrational redshifts for the Ar_nHCl (n=1-3) reflect a near-linear dependence on the number of Ar atoms, which is qualitatively reproduced by simple classical calculations of the v_{HCl}=0 and 1 pairwise additive potential surfaces. Finally, predictions of the HCl matrix shifts in a relaxed fcc lattice of Ar atoms significantly overshoot the matrix value and indicate an appreciable sensitivity to non-nearest neighbors in 2nd, 3rd and higher order solvation shells.