ROVIBRATIONAL SPECTROSCOPY OF ALUMINUM CARBONYL CLUSTERS IN HELIUM NANODROPLETS

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Helium nanodroplet isolation and a tunable quantum cascade laser are used to probe the fundamental CO stretch bands of Aluminum Carbonyl complexes, Al-$(CO)_n$ ($n \leq 5$). The droplets are doped with single aluminum atoms via the resistive heating of an aluminum wetted tantalum wire. The downstream sequential pick-up of CO molecules leads to the rapid formation and cooling of Al-$(CO)_n$ clusters within the droplets. Near 1900 cm^{-1}, rotational fine structure is resolved in bands that are assigned to the CO stretch of a $^2\Pi_{1/2}$ linear Al-CO species, and the asymmetric and symmetric CO stretch vibrations of a planar C_{2v} Al-$(CO)_2$ complex in a $^2B_1$ electronic state. Bands corresponding to clusters with $n \geq 3$ lack resolved rotational fine structure; nevertheless, the small frequency shifts from the n=2 bands indicate that these clusters consist of an Al-$(CO)_2$ core with additional CO molecules attached via van-der-Waals interactions. A second n=2 band is observed near the CO stretch of Al-CO, indicating a local minimum on the n=2 potential consisting of an "unreacted" Al-CO-(CO) cluster. The linewidth of this band is $\sim$0.5 cm^{-1}, which is over 50 times broader than transitions within the Al-CO band. The additional broadening is consistent with a homogeneous mechanism corresponding to a rapid vibrational excitation induced reaction within the Al-CO-(CO) cluster to form the covalently bonded Al-$(CO)_2$ complex. For the n=1,2 complexes, CCSD(T) calculations and Natural Bond Orbital (NBO) analyses are carried out to investigate the nature of the bonding in these complexes. The NBO calculations show that both π "back" donation (from the occupied aluminum p-orbital into the π antibonding CO orbital) *and* σ donation (from CO into the empty aluminum p-orbitals) play a significant role in the bonding, analogous to transition metal carbonyl complexes. The large redshift of the CO stretch vibrations is consistent with this bonding analysis.