POTENTIAL ENERGEY SURFACE OF THE ARHCN CLUSTER DETERMINED WITH THE VAN DER WAALS BANDS OBSERVED BY MILLIMETER-WAVE SPECTROSCOPY

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Millimeter-wave absorption spectroscopy combined with a pulsed-jet expansion technique was applied to the measurement of the rovibrational transitions of the van der Waals (vdW) bending bands of the ArHCN and ArDCN clusters in the frequency region up to 300 GHz. Foundamental band (j = 1-0) together with the hot band (j = 2-1) of the vdW bending bands were observed to obtain a precise set of molecular constants, including band origins, rotational and centrifugal distortion constants, Coriolis interaction constants and hyperfine interaction constants. From these spectroscopic data, accurate term values for the j = 0 (Σ_0), j = 1 (Σ_1 and Π_1), and j = 2 (Σ_2, Π_2, and Δ_2) vdW bending substates were derived for total J up to about 15 levels for both ArHCN and ArDCN.
The determined molecular constants were compared with those derived with the potential energy surface (PES) calculated at CCSD(T) level. The CCSD(T) PES explains fairly well the observed spectroscopic constants such as the rotational and centrifugal distortion constants, and Coriolis interaction constants, but not the vdW beding band frequencies.
Experimental PES, for both ArHCN and ArDCN, was determined fitting to the observed term values. The determined PES explains rovibrational energy levels within 100 kHz for the j = 0, 1 and 2 vdW bending vibrational levels, J up to 5. Wavefuctions calculated with this PES explains also well the observed hyperfine constants.