

VAN DER WAALS BENDING BAND OF THE ArDCN CLUSTER OBSERVED BY MILLIMETER-WAVE SPECTROSCOPY COMBINED WITH A PULSED SUPERSONIC-JET TECHNIQUE

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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 ArDCN cluster in the frequency region of 182-294 GHz. Sixteen and thirty-seven rovibrational lines were observed for the $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands, respectively, split into hyperfine structure due to the nitrogen nucleus. A set of accurate molecular constants, including the band origins, rotational constants, nuclear coupling constants, and the Coriolis interaction constant between the Σ_1 and Π_1 bending substates, was determined.

The band origins for the $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ bands of ArDCN, 189.017380(7) GHz and 195.550736(12) GHz, are *larger* by 24.126585(9) and 13.566314(16) GHz than the corresponding values of ArHCN, respectively. The abnormal isotopic effect on the vibrational frequencies is attributed to the characteristic potential energy surface of ArH(D)CN, which has two minima, corresponding to the linear configuration and a much shallower minimum at the T-shaped configuration. The rotational and quadrupole coupling constants for the excited state are quite different from those of the ground state. For example, the rotational constants 1926.8863(16) and 1967.8768(9) MHz for the excited the Σ_1 and Π_1 states are significantly larger than that of the ground Σ_0 state, 1574.79316(24) MHz. It indicates the shrinkage of the bond length of the cluster by about 0.402 - 0.440 Å on the excitation of the vdW bending mode, together with the change from the linear form in the ground ($j = 0$) state to the T-shaped form in the first excited ($j = 1$) state. The determined molecular constants were compared with those calculated with the potential energy surface calculated at CCSD(T) level.