High resolution spectroscopy of Ar–CH_4 and Kr–CH_4 in the 7 μ region ($j = 1 \leftarrow 0$ transition)

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Diode laser spectra of the rare gas – spherical top van der Waals complexes Ar–CH_4 and Kr–CH_4 were measured in the wavelength region near 1310 cm^{-1} and assigned. The most prominent lines of both complexes exhibit three dense but well resolved ${}^{R}P_0$, ${}^{Q}R_0$, and ${}^{R}Q_0$ branches, correlated to the $R(0)$ transition of the triply degenerate bending vibration ν_4 of methane, CH_4. A model Hamiltonian based on Coriolis coupled states was applied for the assignment, analysis and fitting of the spectra to within the experimental accuracy of ≈ 15 MHz. The rotational B constants of the upper and lower states determined from the three allowed branches appeared to be strongly correlated. The precision in the determination of the rotational B constants of the two complexes was substantially increased by additional recording of several weak transitions in the nearly forbidden ${}^{Q}P_0$ and ${}^{R}R_0$ branches, which were fitted together with the allowed transitions. The separation between the rare gas atom and the methane molecule in the ground vibrational state was determined to be 3.999 Å and 4.094 Å for Ar–CH_4 and Kr–CH_4, respectively. The measured small values of the splitting between the K=0 and the $K = \pm 1$ levels in the vibrationally excited state (0.39 cm^{-1} and 0.67 cm^{-1} for Ar–CH_4 and Kr–CH_4, respectively), which characterizes the anisotropy of the intermolecular potential, indicated that Kr–CH_4 and Ar–CH_4 together with Ne–SiH_4 represent examples close to the free rotor limit, where the spherical top CH_4 is almost free to rotate within the complex. In comparison, the previously analyzed Ar–SiH_4 van der Waals molecule is closer to the hindered rotor limit.

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