OBSERVATION OF A LINEAR ISOMER OF THE C_3-Xe VAN DER WAALS COMPLEX

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Our emission spectra of the C_3-Xe vdW (van der Waals) complex obtained near the 2_0^{2-} band of the $\tilde{A}-\tilde{X}$ system of C_3 showed that a stable linear isomer is present at high C_3-bending vibrational levels ($v_b \geq 4$) of the ground electronic state. Ab initio calculations at the level of CCSD(T)/cc-pVTZ (effective core potential of the Xe atom) support our spectral assignments. The linear isomer lies about 250 cm $^{-1}$ above the T-shaped isomer. From the calculated potential, large amplitude vdW bending motion is expected in the high v_b levels; this explains the congested emission spectra observed from vdW bands near the 2_0^{4-} band of C_3 . Molecular orbitals at the level of HF-SCF showed that bonding with the 5p orbital of the Xe atom in a linear configuration (along the a-axis of C_3) is stabilized by mixing some high-lying π^* bonding character into one of the C-C bonds. This type of bonding is not possible in the Ar and Kr complexes because in these two complexes 3p or 4p orbitals of the rare gas atoms are used. The isomerization from the T-shaped isomer to the linear isomer probably occurs rapidly in the $\tilde{A}$ state.