

OBSERVATION OF A LINEAR ISOMER OF THE C₃-Xe VAN DER WAALS COMPLEX

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Our emission spectra of the C₃-Xe vdW (van der Waals) complex obtained near the 2₀²⁻ band of the $\tilde{A}-\tilde{X}$ system of C₃ showed that a stable linear isomer is present at high C₃-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 2₀⁴⁻ band of C₃. Molecular orbitals at the level of HF-SCF showed that bonding with the 5*p* orbital of the Xe atom in a linear configuration (along the *a*-axis of C₃) 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 3*p* or 4*p* 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.