

THE ROTATIONALLY RESOLVED ELECTRONIC SPECTRUM OF THE DIFLUOROBENZENE-N₂ VAN DER WAALS COMPLEX^a

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The rotationally resolved S₁←S₀ fluorescence excitation spectra of para-difluorobenzene (pDFB) and its N₂ complex have been observed. The high resolution spectrum of pDFB is pure b-type and spans an unusually wide energy region of over 20 cm⁻¹. The N₂ complex of pDFB exhibits two absorption bands shifted to the red of the bare molecule origin, at -27 and -25cm⁻¹. Each of these bands is a superposition of the two pure c-type spectra that result from the internal rotation of the N₂ molecule in the complex. Analyses of these bands show that the N₂ molecule lies ~ 3.59Å above the center of the ring plane in the S₀ state; this distance decreases to ~ 3.47Å in the S₁ state. The barriers to internal rotation in the two electronic states are also different. A full discussion of the factors responsible for the differences will be given.

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