THE ROTATIONALLY RESOLVED ELECTRONIC SPECTRUM OF THE DIFLUOROBENZENE-N_2 VAN DER WAALS COMPLEX[a]

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The rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra of para-difluorobenzene (pDFB) and its N_2 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 N_2 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 N_2 molecule in the complex. Analyses of these bands show that the N_2 molecule lies ~ 3.59$\AA$ above the center of the ring plane in the S_0 state; this distance decreases to ~ 3.47$\AA$ in the S_1 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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