THE ROTATIONALLY RESOLVED ELECTRONIC SPECTRUM OF THE AR-INDOLE VAN DER WAALS COMPLEX: THREE-DIMENSIONAL "AXIS-TILTING"[a]

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The rotationally resolved fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ origin band of the Ar-indole van der Waals complex has been observed. This transition is an *abc*-hybrid, with a hybrid-band ratio of approximately 15:50:35. A careful analysis of the relative intensities of the different components shows that a three-dimensional reorientation of the principal axes occurs upon electronic excitation. We use the information obtained from this analysis to determine the possible orientations of the electronic transition moment in the bare molecule. We also determine the vibrationally averaged structures of the complex in the zero point vibrational levels of both electronic states. The argon atom is found to be attached to the indole at a distance of 3.4 Å above the plane of the molecule. This distance decreases slightly (0.03 Å) on $S_1 \leftarrow S_0$ excitation.

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