ENVIRONMENTALLY INDUCED CHANGES IN THE BARRIERS TO INTERNAL MOTION [a]

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The rotationally resolved $S_1 \leftarrow S_0$ fluorescence excitation spectra of N-methyl-, 3-methyl-, and 5-methylindole and their Ar van der Waals complexes have been obtained. Analyses of these spectra show that the torsional barrier for methyl group rotation is significantly influenced by the attachment of a single Ar atom to the isolated molecule. For example, N-methylindole has $V_3(S_0) = 244$ cm^{-1} and $V_3(S_1) = 115$ cm^{-1}; upon complexation, these values change to $V_3(S_0) = 303$ cm^{-1} and $V_3(S_1) = 126$ cm^{-1}. Possible reasons for this behavior will be discussed; including (a) simple steric effects, (b) Ar atom induced changes in the electronic distribution of the parent molecule, and/or (c) changes in the nature of the motion itself.

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