

THE $S_1 \leftarrow S_0$ TRANSITION OF THE ANILINE-NITROGEN VAN DER WAALS COMPLEX REVISITED

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The LIF excitation spectra of the $S_1 \leftarrow S_0$ transition of the aniline-nitrogen van der Waals (vdW) complex have been recorded near the origin band region for a broad range of expansion conditions. They exhibit a double set of vibronic bands, involving excitation of vdW modes. The relative intensities of the two subsets are dependent upon the expansion conditions, and these subsets are assigned to the complexes with ortho- N_2 and para- N_2 respectively. The internal rotation and libration problem was solved assuming separability of the two internal rotational degrees of freedom.

Dispersed emission spectra have allowed to compare the frequencies of the vibrational modes in the S_1 and S_0 states. The assignment of the 55 cm^{-1} mode in S_1 to the first excited libration state allows to rationalize, by the concept of "stabilization by anisotropy", both the anomalously large spectral vdW shift of the $S_1 \leftarrow S_0$ transition, and the anomalously small vdW shift of the ionization potential. On the other hand, the "helicopter" motion corresponds to a nearly free internal rotation.

These assignments differ from the recently published ones [Schaefer and Pratt, *J.Chem. Phys.*115, 11147 (2001)].