ANALYSIS OF LOW FREQUENCY VIBRATIONAL PROGRESSIONS IN THE HIGH RESOLUTION ELECTRONIC SPECTRUM of 4,4'-DIMETHYLAMINOBENZONITRILE (DMABN).[a]

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Recent developments in the study of the DMABN in the gas phase[c,d] prompted us to reexamine its electronic spectrum at full rotational resolution. This examination shows that several members of the low frequency vibronic progression at +76, +113, +118, +136, +176, +190, and +193 $\mathrm{cm}^{-1}$are split into two or more components. This splitting, not reported before, is due to the varying magnitude of coupling between two internal -CH_3 rotors in the DMABN molecule in its different vibrational states. The assignment of the observed spectra was greatly facilitated by the use of genetic algorithm automated assignments.[e,f] Examination of the obtained rotational parameters leads to the determination of the geometry of the molecule in its ground and electronically excited states.
There exists a controversy in the literature on the lifetime of the excited electronic state of DMABN between various experiments. The picosecond study[g] obtained values between 1.5 ps and 24 ps, while the other works[h] yielded $\sim$5 ns. From the observed Lorentzian component of the linewidth we determined the lifetime of the excited state to be 4 ± 0.5 ns.

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