HIGH RESOLUTION ELECTRONIC SPECTRA OF METHYLPYRIMIDINES IN THE GAS PHASE. INTERMEDIATE CASE RADIATIONLESS TRANSITIONS COUPLED WITH METHYL TORSIONAL MOTION [a]

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Rotationally resolved fluorescence excitation spectra of the origin bands of the $S_1 \leftarrow S_0$ ($\pi* \leftarrow$ n) electronic transitions of 2-methylpyrimidine (2MP) and 5-methylpyrimidine (5MP) have been analyzed. Both spectra were found to contain two sets of rotational lines, one associated with the $\sigma = 0$ torsional level and the other associted with the $\sigma = \pm 1$ torsional levels of the attached methyl rotor. Almost all the lines in both spectra are inhomogeneously broadened, indicating that the molecular eigenstates have underlying unresolved structures. A singlet-triplet coupling scheme is proposed to explain the perturbations observed. The rotational structure of the $\sigma = \pm 1$ torsional states is found to be more perturbed than the rotational structure of the $\sigma = 0$ torsional state. The intensity and broadening anomalies observed in these spectra are explained in terms of the interactions with the low lying vibrational triplet (dark) states throughout an "intermediate case" intersystem crossing mechanism.

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