ABNORMAL REVERSED SPLITTINGS OF TORSIONAL SUBLEVELS INDUCED BY INVERSION-TORSION INTERACTION IN THE S\textsubscript{1} STATE OF ACETALDEHYDE

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From the study of full rotationally resolved spectrum in the system of S\textsubscript{1}-S\textsubscript{0} of acetaldehyde, abnormal reversed torsional sublevels are observed for the levels 14\textsuperscript{0}-15\textsuperscript{n}, n = 0-2 in the S\textsubscript{1} state, in which 14\textsuperscript{0+} and 14\textsuperscript{0-} denote the two inversion tunneling components of the aldehyde hydrogen out of plane bending and vibrational mode 15 for the methyl torsional motion. These abnormal splittings are attributed to be because of interaction of two large amplitude motions, the aldehyde hydrogen inversion and the methyl torsion. We use the group-theoretical formalism developed by Oda et al.\textsuperscript{a} for molecule CH\textsubscript{3}NHD to interpret these observations. This formalism derived using permutation-inversion group and extended group, treats simultaneously the methyl torsion, aldehyde hydrogen inversion and overall rotation. Fits to the rotational states of vibrational levels (14\textsuperscript{0+}15\textsuperscript{0}, 14\textsuperscript{0-}15\textsuperscript{0}), (14\textsuperscript{0+}15\textsuperscript{1}, 14\textsuperscript{0-}15\textsuperscript{1}) and (14\textsuperscript{0+}15\textsuperscript{2}, 14\textsuperscript{0-}15\textsuperscript{2}) were carried out and the rms deviations are within the experimental uncertainty except for the pair levels (14\textsuperscript{0+}15\textsuperscript{2}, 14\textsuperscript{0-}15\textsuperscript{2}) to be 0.05 cm\textsuperscript{-1}. The large deviation can be because of perturbation by the nearby state in 10\textsuperscript{1} progression.