ANALYSIS OF THE HOT BANDS OF METHYLAMINE: $3\nu_{15}\leftarrow\nu_{15}$, $4\nu_{15}\leftarrow\nu_{15}$ AND $\nu_9\leftarrow\nu_{15}$

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Methylamine is a molecule performing two large amplitude motions: CH_3 internal rotation and NH_2 inversion. These two large amplitude motions are strongly coupled and give rise to a rotation-inversion-torsion structure in the vibrational states. The rovibrational spectrum of the methylamine molecule has been extensively studied both experimentally and theoretically. The analyses of infrared bands such as inversion (ν_9) or CN stretching (ν_8) show significant perturbations from highly excited torsional states. In order to untangle the interactions in the 700 - 1200 cm^{-1} region of the methylamine spectrum, it is crucial to assign the dark states, which are the third and fourth excited torsional states ($3\nu_{15}$ and $4\nu_{15}$). These states can be experimentally observed as hot bands from the first excited torsional bands in the range 360 - 720 cm^{-1}. In the same range a hot band to the excited inversion state was discovered and since the intensities of three hot bands are similar, they must be analyzed jointly. The spectra were recorded with a resolution of 0.00125 cm^{-1} using Bruker IFS-120HR spectrometer at the University of Oulu. The accurate energy levels of the first excited torsional state, ν_{15},[1,2] were used as reference values for lower state combination differences in the assignments of the third and fourth torsional hot bands, $3\nu_{15}\leftarrow\nu_{15}$, $4\nu_{15}\leftarrow\nu_{15}$, as well as in the hot inversion-torsional band, $\nu_9\leftarrow\nu_{15}$. On the basis of the predicted energy levels for the third and fourth excited torsional states, many transitions of the hot torsional bands: $3\nu_{15}\leftarrow\nu_{15}$, $4\nu_{15}\leftarrow\nu_{15}$, not assigned previously, have been identified. Many transitions belonging to the inversion-torsion hot band, $\nu_9\leftarrow\nu_{15}$, have been assigned too. All the assignments were confirmed by the Lower State Combination Differences. Only experimental data of inversion-torsion hot band, $\nu_9\leftarrow\nu_{15}$, could be fitted to a single state model based on the group theoretical formalism of Hougen and Ohashi[3]. The transitions belonging to the hot torsional bands ($3\nu_{15}\leftarrow\nu_{15}$, $4\nu_{15}\leftarrow\nu_{15}$) require another approach like a "hybrid" Hamiltonian model[4,5], thus the analysis is still in progress.

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