THE HIGHER TORSIONAL STATES OF METHYLAMINE - PRELIMINARY ANALYSIS

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Methylamine is a molecule performing two strongly coupled large amplitude motions: CH_3 internal rotation and NH_2 inversion. The rovibrational spectrum of the methylamine molecule has been extensively studied both experimentally and theoretically. The analyses of infrared bands such as NH_2 inversion or CN stretching 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 perturbing excited torsional states ($3\nu_{15}$ and $4\nu_{15}$). Both states are located well above the top of the torsional barrier. Thus, the splittings between the lower and upper sublevels are very large (80 to 180 cm^{-1}) and only low lying sublevels of $3\nu_{15}$ or $4\nu_{15}$ will be experimentally identified. 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}, [a] [b] were used as reference values for lower state combination differences in the assignments of the third and fourth torsional hot bands, $3\nu_{15}$-ν_{15} and $4\nu_{15}$-ν_{15}. After the complete analysis in the second torsional overtone region (360-720 cm^{-1}) was performed [c], many of the remaining unassigned lines in this region could be assigned to v=3-1 and v=4-1 bands. Earlier, about 200 transitions of B, E_{1+1} and E_{1-1} symmetry for the $3\nu_{15}$ and 28 transitions of B symmetry for $4\nu_{15}$ were found [d]. On the basis of the calculated energy levels for the third and fourth excited torsional states, many transitions of the hot band v=3-1, not assigned previously, have been identified (over 1500 transitions for all symmetry species). As for v=4-1, so far, the previously assigned series were only extended to higher J values (over 100 transitions assigned of B symmetry), but the analysis is in progress. All the assignments were confirmed by the LSCD. Each set of the experimental data was fit to a single state model based on the group theoretical formalism [e].

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[d] N. Ohashi, H. Shimada, W. B. Olson, K. Kawaguchi, J. Mol. Spectrosc. 152 (1992) 298

[e] N. Ohashi and J.T. Hougen, J. Mol. Spectrosc. 121 (1987) 474