CAN THE INVERSION-VIBRATION-ROTATION PROBLEM IN THE ν_4 AND $2\nu_2$ STATES OF NH_3 BE SOLVED TO EXPERIMENTAL ACCURACY?

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The problem of coupling between a large amplitude motion state and a small amplitude vibration state remains an area of considerable interest and few conclusions in molecular physics. The ν_4 and $2\nu_2$ states of NH_3 provide an excellent opportunity to study the coupling of large and small amplitude motions in an inversion system where the quantum mechanics have been worked out in detail [a]. In spite of the well established Hamiltonian, a large body of high quality spectra remains to fit to experimental accuracy. Several recent studies have resulted in 2-10 times the infrared accuracy over restricted ranges of quantum numbers and have either been unable to fit or have completely ignored the 162 reported microwave transitions [bc]. Assessment of the perturbations details provides some insight into why previous analyses might have not completely succeeded; however, the ability of current Hamiltonian to completely model the large amplitude inversion coupled with small amplitude vibration remains to be adequately addressed. We report extensive new measurements of the rotation-inversion transitions in the ν_4 and $2\nu_2$ states, a global analysis of existing data and provide a complete assessment of the inversion-rotation-vibration Hamiltonian in NH_3.

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