MODELING THE SPECTRUM OF THE $2\nu_2$ and ν_4 STATES OF AMMONIA TO EXPERIMENTAL ACCURACY

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The vibrational spectrum of ammonia has received an enormous amount of attention due to its prevalence in hot exo-planet atmospheres and persistent challenges in assigning and modeling highly excited and often highly preturbed states, resulting from strong coupling between the large amplitude inversion and the other small amplituded vibrations. Previously, only the ground and ν_2 positions could be modeled to experimental accuracy using effective Hamiltonians.[a] However, problems persist in calculation of transition intensities especially in the “forbidden” $\Delta K = 3$ bands. Several previous attempts to analyze the $2\nu_2$ and ν_4 failed to model both the microwave and infrared transitions to experimental accuracy.[bc] We report comprehensive measurements of the pure rotational spectrum in the $2\nu_2$, ν_4 and $2\nu_2 - \nu_4$ bands. Over 180 new frequency measured transitions and several thousand infrared transitions have been assigned in the microwave spectrum, in a long path, room temperature, spectrum from SOLEIL, and in an RF discharge emission spectrum also from SOLEIL. The new data has been combined with all the previously published high resoloution data. We report a global analysis of the pure rotation in $2\nu_2$ and ν_4, the difference band $2\nu_2 - \nu_4$, the hot bands $2\nu_2 - \nu_2$ and $\nu_4 - \nu_2$, the $2\nu_2$ overtone, and the ν_4 fundamental. Experimental accuracy has been achieved in a fit of all the data with stated experimetal uncertainties. Achieving experimental accuracy required inclusion of a number of terms in the effective Hamiltonian that were neglected in previous work. These terms have also been neglected in the analysis of higher lying states suggesting that the inversion-rotation-vibration spectrum of ammonia may be far more tractable to effective Hamiltonians than previously believed.

[a] Yu, Pearson, Drouin, Sung, Pirali, Vervoet, Martin-Drumel, Endres, Shiraishi, Kobayashi, and Matsushima, *J. Chem. Phys.* **133** (2010) 174317.
[b] Cottaz, Kleiner, Tarrago, Brown, Margolis, Poynter, Pickett, Fouchet, Drossart, and Lellouch, *J. Mol. Spectrosc.* **203** (2000) 285-309.
[c] Sasada, Endo, Hirota, Poynter, and Margolis, *J. Mol. Spectrosc.* **151** (1992) 33-53.