

Electronic degeneracy in the \tilde{B}^1E'' state of partially deuterated ammonia.

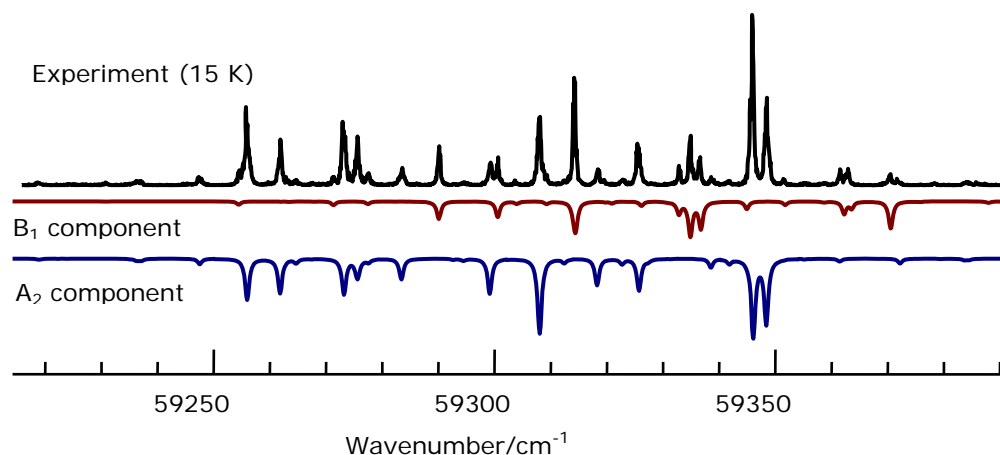
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The \tilde{B}^1E'' state of NH_3 is well known as a classic example of a degenerate electronic state with a mild Jahn-Teller effect [1], and significant extra terms are required to understand the rotational structure of this electronic transition [2]. These additional terms are well understood, and as the electronic excited state is reasonably stable, probing NH_3 and ND_3 state distributions via this state using resonance enhanced multiphoton ionisation has proved to be a productive and popular technique. In principle the same method should be applicable to the partially deuterated species, NHD_2 and NH_2D , and we have recorded REMPI spectra of both of these species to determine the required molecular constants. These spectra allow an interesting question to be addressed – the degeneracy of the electronic state must be lifted, but only by a small amount, resulting two near degenerate and possibly interacting states.

We have recently published spectra for NHD_2 [3] and will present preliminary results for NH_2D here. For both species the degeneracy is only lifted by a small amount ($\sim 35 \text{ cm}^{-1}$), and terms mixing the two electronic states must be included in the Hamiltonian to reproduce both the line positions and intensities. The terms mixing the two electronic states can be understood in terms of interactions acting within the electronic state when the degeneracy is not lifted.



[1] J. M. Allen, M. N. R. Ashfold, R. J. Stickland, C. M. Western, *Mol. Phys.*, **1991**, 74, 49.

[2] M. N. R. Ashfold, R. N. Dixon, N. Little, R. J. Stickland, C. M. Western, *J. Chem. Phys.*, **1988**, 89, 1754.

[3] C.-H. Yang, G. Sarma, A. K. Saha, D. H. Parker, C. M. Western, *Phys. Chem. Chem. Phys.*, **2013**, 15, 6390.