MARVEL analysis of the measured high-resolution spectra of $^{14}NH_3$

Phillip Coles

MARVEL [1] is an algorithm that generates effective measured molecular rotation-vibration energy levels by inverting the information contained in a uniquely defined set of experimental rotation-vibration transitions. This has in the past been used to generate lists of experimental energy levels and transitions for H_2D+, D_2H^+, HDO, H_3^+, TiO, H_2O, C_2 and $^{14}NH_3$. The reliability of the resulting energy levels depends crucially on the experimental transitions within a network of transitions - a so-called spectroscopic network - being correctly assigned. This project focuses on the application of MARVEL to $^{14}NH_3$ [2], where previous attempts to use experimental assignments as unique labels have encountered difficulties due to ambiguous quantum numbers; a problem which is exacerbated at high frequencies where dense, complicated spectra make experimental assignment difficult. Therefore, a new method of labelling transitions for the MARVEL algorithm is proposed which relies on ab initio calculations to provide these unique labels. Recent (and ongoing) improvements in the accuracy of theoretically calculated $^{14}NH_3$ line positions based on nuclear motion calculations [3] using an empirically refined *ab initio* potential energy surface [4] provides excellent grounds with which to implement this new method and thus create the best possible list of experimental energy levels.

The project begins by using new theoretical predictions to 1) validate the current best set of MARVEL energies and identify those states that are misassigned, misidentified or inaccurate; 2) where possible, further assign high energy spectral regions for which unassigned experimental data exists ([5],[6]). Once a set of reliable energy levels and transitions has been agreed upon, a consistent labelling scheme must be applied which relies on J, symmetry and block number taken from theoretical predictions. Iterations of the MARVEL algorithm will then be run, each time cleansing the database of any erroneous transitions until a complete, self-consistent set transitions and energy levels is generated. Further assignments will be made using the resulting predicted transitions.

References

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