Report: MARVEL analysis of the measured high-resolution spectra of $^{14}NH_3$
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The main objective of this project was to identify and correct those energy levels in the most recent version of the MARVEL $^{14}NH_3$ energy levels list that were either misassigned, mislabelled, or inaccurate. The ultimate aim being to generate a complete list of experimental quality energy levels that is fully compatible with the current highest level of theory. To this end, significant progress was made in the region 0-6500 cm^{-1} where, through an iterative process of matching MARVEL levels to those of theory then merging, removing, or relabelling the MARVEL states' number within the J-Symmetry block (N_{block}), 3327 states up to 6500^{-1}, J=0-15, were made fully compatible. For this purpose, we employed three theoretical energies lists: a) the variationally computed energies list BYTe; b) energies computed using the nuclear motion program TROVE and the new spectroscopic potential energy surface (we shall call NH3-2017a) generated by empirically refining the *ab initio* surface of Polyansky et al. [1]; c) the high accuracy energy levels list of Huang et al. known as HSL-pre3, taken from the SETI website [2].

By matching MARVEL levels to all three theoretical lists using J, total symmetry and N_{block} we ascribe each state to one of the following categories:

1) States that show satisfactory agreement with the matched NH3-2017a and HSL-pre3 energies.
2) States that needed to be renumbered within the J-Symmetry block.
3) States that needed to be merged. These arise from labels conflicting between experimental sources, resulting in duplicate transitions and energy levels.
4) States that were deemed inaccurate or unphysical. These were predominantly states involved in 3 or less transitions. The criteria for identifying an inaccurate or unphysical state was i) that it showed significant deviation from the corresponding NH3-2017a and HSL-pre3 energies; ii) the NH3-2017a and HSL-pre3 energies showed good agreement, e.g. residuals of less than 0.1 cm^{-1}; iii) no alternative match in the two theoretical energy lists existed; iv) multiple states from the corresponding vibrational band were included in the NH3-2017a refinement, ensuring our potential energy surface was suitably constrained along the corresponding normal mode direction.

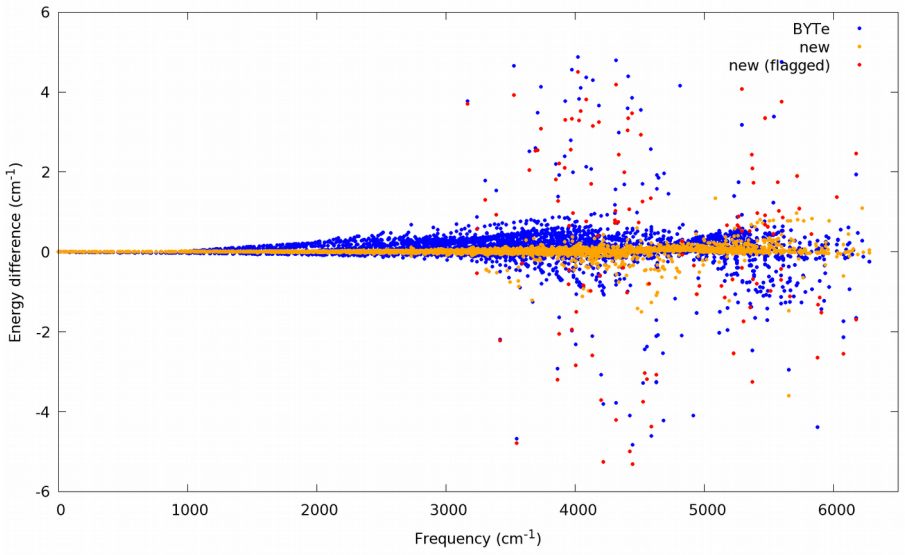

Figure 1 – Energy difference between MARVEL energies and those of NH3-2017a (orange) and BYTe (blue)

Figure 1 shows the energy difference between the original MARVEL energies list and that of BYTe (blue) and NH3-2017a (orange and red). It is clear that the BYTe energies are significantly less accurate than those of NH3-2017a, and so were not used in our comparisons. The 121 states displayed in red are those that fall into categories 2, 3 or 4 above. It should be noted that some MARVEL states that fall into category 1 (orange) still show large energy residuals, these correspond to states belonging to vibrational bands not included in the NH3-2017a refinement and so we give no guarantee of the accuracy of these bands on the NH3-2017a energies list.

Finally, we next aim to improve states above 6500 cm^{-1}. This was attempted, however, at high energies conflicting N_{block} labels between the NH3-2017a and HSL-pre3 energies lists made unambiguous labelling difficult. To resolve this we are required to repeat the refinement procedure used to generate NH3-2017a, with the inclusion of those states belonging to vibrational bands missing from the previous refinement, namely $4\nu_2$, $4\nu_2+\nu_4$, $2\nu_2+\nu_3$, $2\nu_2+\nu_4$, $2\nu_2+2\nu_4$, $2\nu_2+3\nu_4$, $2\nu_3+\nu_4^{l=0}$. It is hoped that this will resolve any conflict between our refined potential and HSL-pre3 regarding the ordering of states at high energies.

[1] O. L. Polyansky, R. I. Ovsyannikov, A. A. Kyuberis, L. Lodi, J. Tennyson, A. Yachmenev, S. Yurchenko and N. F. Zobov, J. Mol. Spec., 327 (2016) 21-30
[2] huang.seti.org, accessed 5th April 2017