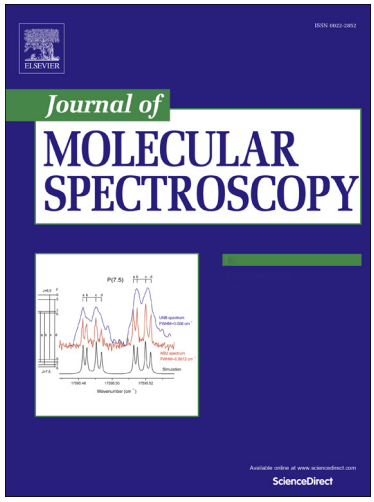

Beryllium monohydride (BeH): Where we are now, after 86 years of spectroscopy

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Beryllium monohydride (BeH): Where we are now, after 86 years of spectroscopy

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BeH is one of the most important benchmark systems for *ab initio* methods and for studying Born-Oppenheimer breakdown. However the best empirical potential and best *ab initio* potential for the ground electronic state to date give drastically different predictions in the long-range region between where the highest measurements have been made, and the dissociation energy; a region which is about $\sim$ 1000 cm^{-1} for ^{9}BeH, $\sim$ 3000 cm^{-1} for ^{9}BeD, and $\sim$ 13000 cm^{-1} for ^{9}BeT. Improved empirical potentials and Born-Oppenheimer breakdown corrections have now been built for the ground electronic states $X(1^2\Sigma^+)$ of all three isotopologues. The predicted dissociation energy for ^{9}BeH from the new empirical potential is now in agreement with the current best *ab initio* prediction in all 5 digits of the former's precision, while the previous best empirical potential was in disagreement by 74 cm^{-1}. The previous best empirical potential predicted the existence of unobserved vibrational levels for all three isotopologues, and the current best *ab initio* study also predicted the existence of all of these levels, and 7 more in total. With the exception of 2, the present empirical potential agrees with the existence of all of the *ab initio* potentials' extra levels not predicted by the earlier empirical potential. With one exception, all energy spacings between vibrational energy levels for which measurements have been made, are predicted with an agreement of better than 1 cm^{-1} between the new empirical potential and the current best *ab initio* potential, but some predictions for unobserved levels are still in great disagreement, and the equilibrium bond lengths are different by orders of magnitude.

With only 5e$^-$, BeH is the simplest neutral open shell molecule, and is therefore of paramount importance in benchmarking *ab initio* methods. The first Hartree-Fock level endeavor was in 1967 [1], and it has remained the subject of a plethora of theoretical studies since then [2–79]. It is also the second lightest neutral heteronuclear molecule after LiH, and one of the only neutral diatomics for which spectroscopic measurements on a tritium isotopologue have been performed, making it a very important benchmark system for studying the breakdown of the Born-Oppenheimer approximation [51, 74, 78, 80–82]. Due to its simplicity, BeH is expected to be present in astronomical contexts such as exoplanetary atmospheres, cool stars, and the interstellar medium [83], but in the context of astronomy, has only been found on our Sun (see [84, 85]). Finally, the extraordinarily long half-life of the halo nucleonic atom ^{11}Be makes ^{11}BeH a compelling candidate for the formation of the first halo nucleonic molecule [81].

Spectroscopic measurements on ^{9}BeH date back to 1928 [86, 87], and on ^{9}BeD date back to 1935 [88]. By 1937 there was already an octad of publications on the molecule [86–93]. Since then, higher-resolution spectra have been measured for both of these isotopologues, and also for ^{9}BeT in [10]. Various types of experiments on BeH have been performed over the years, including those described in [10, 18, 80, 94–102]. Before the present paper, the most thorough empirical analysis of ^{9}BeH, ^{9}BeD, and ^{9}BeT was that of [80], where empirical potentials were built for all three isotopologues, based on a fit to data from [10, 18, 80, 99, 102].

This state of the art 2006 empirical study left behind various mysteries which remained unsolved for the last 8 years:

1. The 2006 study predicted that the ^{9}BeH dissociation energy was $\mathfrak{D}_e = 17590 \pm 200$ cm^{-1} [80] which is higher than the value of $\mathfrak{D}_e = 17426 \pm 100$ cm^{-1} in the 1975 experimental study [95] by more than the latter's uncertainty. The most recent *ab initio* study (published in 2011) of ^{9}BeH [78] predicted its dissociation energy to be $\mathfrak{D}_e = 17702.29$ cm^{-1} which is another 112 cm^{-1} higher than the 2006 value, and is higher than the 1975 value by almost three times the latter's estimated uncertainty.

2. The 2006 analysis was unable to determine a meaningful value for the leading term u_0^{H} of the adiabatic BOB (Born-Oppenheimer breakdown) correction function, which helps define the isotopologue shifts in $\mathfrak{D}_e$ and r_e.

3. The 2006 potentials predicted the existence of 1 more vibrational level for ^{9}BeH, 3 more vibrational levels for ^{9}BeD, and 15 more vibrational levels for ^{9}BeT than have ever been observed in experiments. The 2011 *ab initio* study then predicted the same extra levels, but also 2 further levels for ^{9}BeH, 3 further levels for ^{9}BeD, and 2 further vibrational levels for ^{9}BeT (!).

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