

Abstract Submitted  
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**Ab initio study of hydrogen-halo rotation in ammonia borane<sup>1</sup>**

EVAN WELCHMAN, T. THONHAUSER, Wake Forest University — The van der Waals crystal ammonia borane  $\text{NH}_3\text{BH}_3$  is a promising hydrogen-storage material due to its large gravimetric storage density. In an isolated molecule, the H atoms reside in halos about either end of a central B–N backbone with *three-fold* rotational symmetry. However, in the solid phase at ambient temperature and pressure, experiments reveal a tetragonal unit cell with a *four-fold* rotational symmetry about the same axis, creating a geometric incompatibility. Using ab initio calculations at the DFT level (with vdW-DF to capture crucial van der Waals interactions), we elucidate this incompatibility by simulating the behavior of the hydrogen-halos and their substituent H atoms. We use Car-Parrinello molecular dynamics at several different temperatures to simulate behavior in the solid and NEB calculations to find barriers to rotation in solid and gas phase. We find that at room temperature the halos can rotate several degrees per fs and that the four-fold symmetry thus results from a time average. We further show that in the solid phase the complex network of dihydrogen bonds affects the torsional barrier for the halos, and thus their rate of rotation in the solid phase, contributing to the experimentally observed positional uncertainty.

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