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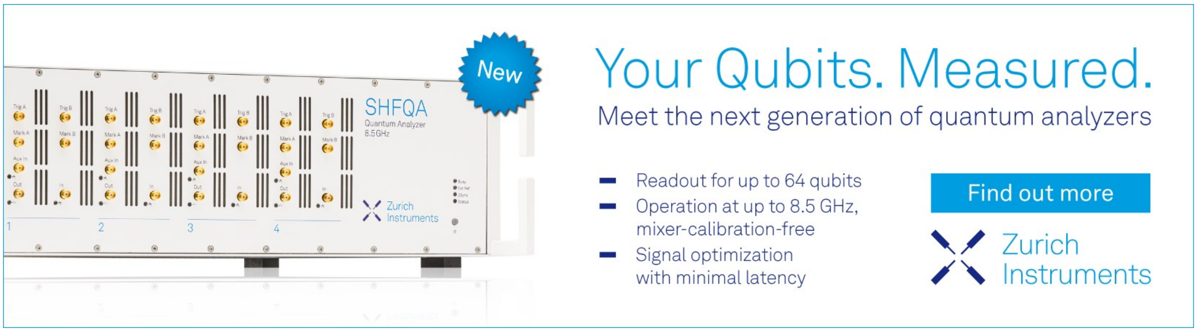
Brent R. Westbrook, E. Michael Valencia, Spencer C. Rushing, Gregory S. Tschumper, and Ryan C. Fortenberry



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Brent R. Westbrook,[a] **E. Michael Valencia, Spencer C. Rushing, Gregory S. Tschumper,**
and Ryan C. Fortenberry

AFFILIATIONS

The University of Mississippi, University, Mississippi 38677-1848, USA

[a] **Author to whom correspondence should be addressed:** bwestbr2@go.olemiss.edu

ABSTRACT

The fundamental vibrational frequency of the B–N stretch in BH_3NH_3 has eluded gas-phase experimental observation for decades. This work offers a theoretical anharmonic prediction of this mode to be 644 cm^{-1}, using a Cartesian quartic force field at the CCSD(T)-F12/cc-pVTZ-F12 level of theory. The other fundamental frequencies reported herein have a mean absolute error of only 5 cm^{-1} from the seven available gas-phase experimental frequencies, making the anharmonic vibrational frequencies and rotational constants the most accurate computational data available for BH_3NH_3 to date. The inclusion of Fermi, Coriolis, and Darling–Dennison resonances is a major source of this accuracy, with the non-resonance-corrected frequencies having a mean absolute error of 10 cm^{-1}. In particular, the inclusion of the $2\nu_6 = \nu_5$ type 1 Fermi resonance increases the B–N stretching frequency by 14 cm^{-1} compared to previous work. Ammonia borane also represents one of the largest molecules ever studied by quartic force fields, making this work an important step in extending the breadth of application for these theoretical rovibrational techniques.

I. INTRODUCTION

Spectroscopic investigation into ammonia borane stretches back to the early 1970s when Smith, Seshadri, and White reported its infrared spectrum and that of two of its deuterated isotopologs as captured in an argon matrix.[1] However, the only gas-phase investigations would not take place for nearly a decade when the work of Suenram and Thorne revealed the microwave spectrum of $^{11}BH_3NH_3$ and $^{10}BH_3NH_3$ along with some derived geometrical parameters.[2] Shortly thereafter, Thorne, Suenram, and Lovas updated this list to include a total of nine isotopologs of BH_3NH_3, including substitutions of ^{2}H, ^{10}B, and ^{15}N, but relatively little further spectroscopic data have been generated since then.[3]

The relative dearth of infrared data forced many investigations of ammonia borane to rely on the matrix data of Smith *et al.*,[1] with some assignments augmented by the SCF/6-31G(d) and MP2/6-31G(d) computations of Dillen and Verhoeven.[4] Finally, in 2012, the work of Sams *et al.* provided a combined gas-phase experimental and computational investigation of the rovibrational characteristics of BH_3NH_3.[5] Unfortunately, the B–N stretch was not detected in the experiment due to its low intensity, but the CCSD(T)/aug-cc-pVTZ harmonic frequencies combined with MP2/aug-cc-pVTZ second-order vibrational perturbation theory (VPT2) anharmonicities provide the best estimate of that stretching mode currently available at 630 cm^{-1}. Despite being the best theoretical data available, the computed values offered by Sams *et al.* are not without their limitations. Although the harmonic portions of the fundamental frequencies were computed at the CCSD(T)/aug-cc-pVTZ level, the addition of the MP2 anharmonicities cannot offer as high an accuracy as a uniform CCSD(T) treatment. This type of composite construction of the anharmonic frequencies does not allow for a robust handling of Fermi resonances at the CCSD(T) level, potentially limiting its accuracy.[6,7]

Ammonia borane's B–N stretching frequency has been suggested as an important identifier for the molecule's environment,[4,8,9] making its accurate gas-phase determination necessary for understanding how changes to its frequency are indicative of shifts in the surrounding chemical environment in applied studies. The same exquisite sensitivity that could make the B–N stretch useful also complicates experimental observation. Previous computational work[10] on the BH_3NH_3 dimer has shown that the harmonic frequency of the B–N stretch likely shifts by up to 40 cm^{-1} due to intermolecular dihydrogen bonding. Similarly, IR and Raman experiments[9,11] on solid BH_3NH_3 show even larger shifts of nearly 150 cm^{-1} from the frequency calculated by Sams *et al.* Therefore, only pure gas-phase spectra can produce the necessary vibrational frequency for the B–N stretch. As described in Ref. 5, a veritable "armamentarium" of experimental techniques have been used to investigate this molecule, but the addition of gas-phase infrared spectroscopy will provide specific information for this mode. Such is only possible if the baseline fundamental vibrational frequency can be clearly determined. Consequently, the present work seeks to provide a comprehensive anharmonic analysis at a consistent level of theory along with accuracy-boosting resonance corrections.

The state-of-the-art quantum chemical approach to calculating rovibrational spectral data for the lowest computational cost is the quartic force field (QFF). QFFs are fourth-order Taylor series expansions of the internuclear potential term in the Watson Hamiltonian.[12] When joined with coupled cluster theory at the singles, doubles, and perturbative triples level[13] within the F12 explicitly correlated construction [CCSD(T)-F12b][14,15] and a triple-ζ basis set, QFFs can typically achieve an accuracy of 5 cm^{-1}–7 cm^{-1} compared to experiment.[16–20] A limitation of the QFF methodology as previously used by our group is its reliance on symmetry internal coordinates (SICs) for the generation of the displaced geometries needed to produce the QFF. While SICs take advantage of molecular symmetry to reduce significantly the number of points that must be computed, their determination is often more art than science and can be particularly difficult for larger and more symmetric molecules, like those with C_{3v} symmetry. As such, another purpose of the present study is to demonstrate the use of Cartesian coordinates in generating the QFF displacements. Applications include molecules that would otherwise be too large or complicated to investigate via SIC-based QFFs and those where the SICs and normal coordinates are not well-aligned, requiring a broader sampling of the potential energy surface. The improvement of Cartesian QFF methodologies will allow for the faster generation of gas-phase spectra for such size-prohibitive molecules as ammonia borane.

II. COMPUTATIONAL DETAILS

All of the CCSD(T)-F12b computations performed in this study, including geometry optimizations, harmonic frequencies, and single-point energies, utilize the Molpro 2015.1 software package[21] with the cc-pVTZ-F12 basis set[16,22,23] under the frozen-core approximation and with very tight convergence criteria for all of the integrals and for the gradients in the geometry optimization (see the supplementary material for a full description of the convergence criteria). This CCSD(T)-F12b/cc-pVTZ-F12 scheme is abbreviated as F12-TZ in the following. The anharmonic vibrational frequencies and rotational constants are calculated using a Cartesian QFF methodology at this F12-TZ level. In order to map out the fourth-order Taylor series approximation of the internuclear potential energy surface, i.e., the QFF, displacements of 0.005 Å are taken along each Cartesian coordinate. These are simply vectors in the x, y, and z directions for each atom. At each displaced geometry, a single-point energy is computed and this energy is used to calculate the corresponding force constant by central finite differences. The Cartesian QFF requires a nominal total of 271 780 single-point calculations (compared to the 39 605 required for an SIC QFF), assuming every component energy of each finite difference is computed. However, saving the energy of the optimized geometry and an array of component second-derivative energies for use in the fourth-derivative finite difference calculations reduces the number of these points that actually have to be computed roughly by half because the fourth-derivative finite difference formulas are primarily composed of these energies rather than unique points. Further discussion of this technique is presented in the supplementary material.

The resulting force constants are then used by the second-order rotational perturbation theory[24] and VPT2[25,26] in the SPECTRO[27] program. Type 1 and 2 Fermi resonances and polyads, Coriolis resonances, and Darling–Dennison resonances are taken into account to further increase the accuracy of the anharmonic values.[6,7] The resonances are shown in Table S1 of the supplementary material. The anharmonic analysis was repeated for the $^{10}BH_3NH_3$ and the $BH_3^{15}NH_3$ isotopologs. These results are also shown in Tables S2 and S3 of the supplementary material, while the rest of the rotational and geometrical data is shown in Tables S4 and S5. Additional MP2,[28] CCSD,[29] and canonical CCSD(T)[13] computations were carried out to systematically examine the effects of dynamical electron correlation, basis set size, diffuse functions, and the frozen-core approximation on the optimized structures and harmonic vibrational frequencies of BH_3NH_3. The associated computational details and corresponding results are shown in Tables S6–S16 of the supplementary material. The abbreviations XZ, aXZ, and CXZ are hereafter used to describe the cc-pVXZ,[30–32] aug-cc-pVXZ,[30,33] and cc-pCVXZ[30,34] basis sets used therein. Within the CXZ computations, FC denotes that the frozen-core approximation was used, while AE indicates that all electrons were correlated.

III. RESULTS AND DISCUSSION

The substantial differences in many of the harmonic frequencies of BH_3NH_3, as shown in Table I, in going from MP2 to CCSD to CCSD(T) demonstrate the effects of the method on the

TABLE I. Harmonic vibrational frequencies (in cm^{-1}) of BH_3NH_3.

Mode	Description	MP2	CCSD	CCSD(T)		CCSD(T)-F12
		5Z	5Z	aTZ[a]	5Z	F12-TZ QFF
$\omega_1(a_1)$	Symm. N–H str.	3498	3507	3466	3476	3474
$\omega_2(a_1)$	Symm. B–H str	2486	2457	2430	2447	2445
$\omega_3(a_1)$	Symm. NH_3 def.	1329	1355	1353	1339	1340
$\omega_4(a_1)$	Symm. BH_3 def.	1213	1212	1196	1200	1199
$\omega_5(a_1)$	N–B str.	687	679	673	678	679
$\omega_6(a_2)$	Torsion	264	259	274	259	259
$\omega_7(e)$	Antisymm. N–H str.	3628	3620	3580	3592	3590
$\omega_8(e)$	Antisymm. B–H str.	2553	2512	2493	2505	2503
$\omega_9(e)$	Antisymm. NH_3 def.	1675	1692	1679	1677	1678
$\omega_{10}(e)$	Antisymm. BH_3 def.	1219	1212	1181	1202	1201
$\omega_{11}(e)$	Antisymm. BH_3 rock	1081	1085	1061	1075	1076
$\omega_{12}(e)$	Antisymm. NH_3 rock	648	654	656	646	647

[a] From Ref. 5.

frequency computations. From MP2/5Z to CCSD/5Z, the deviation is as great as 41 cm^{-1}, while that from CCSD/5Z to CCSD(T)/5Z is still 31 cm^{-1}. As shown in Tables S6–S8 of the supplementary material, moving from triple-ζ to even 6-ζ quality within a given basis set series is not as impactful. Comparing the MP2/TZ and MP2/6Z harmonic frequencies in Table S6 shows a maximum difference of only 8 cm^{-1}, with just 1 cm^{-1} between the 5Z and 6Z frequencies, suggesting that 5-ζ quality is sufficient in the other computations as well. Hence, the agreement of the CCSD(T)/5Z results with the Cartesian F12-TZ QFF values demonstrates the fortuitous performance of the substantially cheaper F12-TZ combination. The largest difference between these two datasets is 2 cm^{-1}, but most of the deviations are within 1 cm^{-1}. For ω_5 and ω_6, even CCSD/5Z produces good agreement with the CCSD(T)/5Z and F12-TZ values, and all three are within 1 cm^{-1} of each other. Such an agreement indicates at least some degree of method independence for these modes and bodes well for the reliability of the F12-TZ methodology in the anharmonic computations.

In contrast, the MP2 frequencies are typically farthest from both the CCSD(T)/5Z and F12-TZ results. The addition of the diffuse functions in the aTZ computations of Tables S6–S8 also decreases all the frequencies compared to the TZ values, introducing larger deviations than any within the *X*Z series. Moving to the larger aQZ basis set restores agreement with the *X*Z results, but neither canonical CCSD(T)/aTZ nor MP2 seems very promising on its own in light of these data. On the other hand, the effects of the frozen-core approximation seem relatively minor. The largest deviation across the three methods between the C*X*Z FC and AE results is 6 cm^{-1}, with many of the differences well inside that margin. As such, maintaining the frozen-core approximation in the F12-TZ QFF is well worth the commensurate computational savings.

Only the F12-TZ QFF approach is carried forward to the anharmonic analysis because the harmonic results suggest that it strikes a good balance between accuracy and efficiency. As shown in Table II, the anharmonic fundamental frequency of the B–N stretch, ν_5, is computed here to be 644 cm^{-1} at the F12-TZ level after the inclusion of the Fermi, Coriolis, and Darling–Dennison resonances. Whereas the value before the resonance correction of 631 cm^{-1} agrees nearly perfectly with the previous computational value[5] of 630 cm^{-1}, the inclusion of the type 1 Fermi resonance between $2\nu_6$ and ν_5 increases ν_5 by 13 cm^{-1} compared to the unperturbed value. This seemingly small but truly substantial difference indicates the importance of accounting for Fermi resonances and reflects the strength of methods that support their incorporation throughout the analysis, such as the QFF methodology conjoined with the SPECTRO program used herein.

As shown in Table II, resonance corrections do not guarantee moving closer to the individual experimental results. In the case of ν_4 and ν_{11}, the resonance-corrected F12-TZ values are actually slightly farther from the gas-phase experimental values than the uncorrected ones. However, in aggregate, the performance of the resonance-corrected F12-TZ data is substantially better than that of the other computational set. Whereas the F12-TZ frequencies have a mean absolute error (MAE) of only 5 cm^{-1} compared to the seven available gas-phase values,[5] the MAE of the CCSD(T)/aTZ harmonics augmented with MP2/aTZ anharmonicities from Ref. 5 is 24 cm^{-1}. Such performance is to be expected of F12-TZ QFFs, which typically offers accuracy within 5 cm^{-1}–7 cm^{-1} of gas-phase experiment.[16] In fact, the deviations from the experiment in all but ν_2 are less than the lower bound of 5 cm^{-1}, but the substantially larger difference of 24 cm^{-1} in ν_2 drives up the average. Regardless, the F12-TZ data represent the most accurate theoretical data available for ammonia borane.

TABLE II. Anharmonic vibrational frequencies (in cm^{-1}) of BH_3NH_3.

Mode	Matrix[a]	Gas[b]	Previous theory[c]	F12-TZ QFF[d] Pert.	F12-TZ QFF[d] Unpert.
ν_1	3337	...	3321	3333	3307
ν_2	2340	2298.861(8)	2449	2275	2338
ν_3	1301	1288.6384(3)	1297	1287	1287
ν_4	1052	1177.56(3)	1208	1174	1177
ν_5	603	...	630	644	631
ν_6	...	...	252	300	300
ν_7	3386	3417.81(6)	3410	3415	3415
ν_8	2415	2405.58(2)	2392	2401	2392
ν_9	1608	1610.62(2)	1608	1610	1622
ν_{10}	1186	...	1165	1169	1171
ν_{11}	968	1042.316(2)	1027	1047	1044
ν_{12}	...	...	648	649	649

[a] Ar-matrix infrared frequencies from Ref. 1 with reassignment of peaks from Ref. 4 by SCF and MP2/6-31G(d) computations.

[b] Gas-phase infrared frequencies from Ref. 5.

[c] CCSD(T)/aug-cc-pVTZ harmonics plus VPT2 MP2/aug-cc-pVTZ anharmonicities from Ref. 5.

[d] Modes 1, 2, 4, 5, 8, 9, 10, and 11 are affected by Fermi resonances. Unperturbed values are prior to the resonance correction.

Potential further evidence for the identification of ν_5 at 644 cm^{-1} lies in Fig. 9 of Ref. 5. In this infrared absorption spectrum of BH_3NH_3 between 550 cm^{-1} and 810 cm^{-1}, there is a clear increase in the baseline from 670 cm^{-1} to 630 cm^{-1}. The authors identified an actual peak above the noise potentially belonging to BH_2NH_2 in this region, but the presence of other peaks and the baseline elevation suggests that more may be happening in this portion of the spectrum. Most enticingly, there appear to be several unattributable peaks extending from the baseline in this region. Unfortunately, the absorbances of these fundamental frequencies are even less than that of the BH_2NH_2 peak classified as a "bump" by the authors at less than 0.004 absorbance units.[5] The low computed CCSD(T)/5Z intensity of only 12 km mol^{-1} for the B–N stretch could allow it to remain hidden in this area of the spectrum and would require a higher-resolution experiment to fully elucidate.

Also shown in Table S2 of the supplementary material is a comparison of the F12-TZ computed fundamental frequencies with the four experimental $^{10}BH_3NH_3$ frequencies obtained by Sams *et al.* The MAE for these four modes is only 3.1 cm^{-1}, suggesting that the F12-TZ QFF captures the frequency changes due to isotopic substitution very effectively. While experimental frequencies for the $BH_3{}^{15}NH_3$ isotopolog are unavailable, the F12-TZ results for that molecule are presented in Table S2 as well. Table S4 shows that both the F12-TZ and Sams *et al.* computational datasets additionally agree well with the experimental geometrical parameters, except for the F12-TZ value of the H–B–N bond angle, which appears to overshoot the experimental measurement by nearly a whole degree.

Additional rotational constants, including the first vibrationally excited principle rotational constants for the $^{10}BH_3NH_3$ and $BH_3{}^{15}NH_3$ isotopologs, are available in Tables S3 and S5 of the supplementary material.

IV. CONCLUSIONS

In conclusion, the anharmonic vibrational frequencies and rotational constants of BH_3NH_3 reported herein agree well with the available gas-phase experimental data. While previous computational results using a combined CCSD(T) and MP2 approach offered anharmonic frequencies with an average deviation from the experiment of 24 cm^{-1}, the F12-TZ QFF values in the present study achieve agreement to within 5 cm^{-1}. The inclusion of Fermi resonances in the QFF methodology further increases its accuracy, and for the B–N stretch, it is the primary difference from the previous computational result. Consequently, these represent the most accurate theoretical values currently available for BH_3NH_3, and in the case of the elusive B–N stretch, these are the only gas-phase-comparable data. While the low intensity of the B–N stretch has allowed it to elude experimental observation, it is identified here computationally to be 644 cm^{-1}, 14 cm^{-1} higher than the previous result, offering new insight into the chemical environment of this molecule. The impressive agreement of the other vibrational frequencies with the available experiment lends additional credence to the fidelity of this assignment from the purely computational value for the dark B–N stretch, as well. More generally, the success of a new Cartesian QFF methodology in describing the anharmonic rovibrational characteristics of a molecule quite complicated to examine with user-defined internal coordinates is promising for the future of QFF analysis. Additionally, Cartesian coordinates provide a more complete description of atomic movement, unconfined to specific internal coordinate schemes. This allows for the treatment of floppy systems for which SICs become ill-defined. Further improvements to the current software, such as using symmetry in the Cartesian treatment to further reduce redundant computations, will continue to extend the domain of vibrational problems that can be examined with QFFs.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional vibrational frequencies, harmonic infrared intensities, rotational constants, and equilibrium Cartesian geometries.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material. The force constants are available upon request.

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