On the Existence of BH_5

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Assisted by prior *ab initio* correlated predictions of the vibrational spectra,[1] the first experimental observation of the H_2-BH_3 complex was recently reported by Tague and Andrews (TA).[2] However, H_2-BH_3 has been calculated to have C_s symmetry,[1,3–5] following the suggestion of Kreevoy and Hutchins,[6] which requires that there be A′ and A″ bands, shifted relative to ν_3(E′) of BH_3 by about 70 and 30 cm^{-1}, that are of comparable predicted intensity;[1] yet the A″ band is not assigned. This raises several intriguing questions: (1) Does the effective BH_5 structure reflect a 3-fold or higher axis of symmetry, making the A′ and A″ bands degenerate? (2) Will higher level calculations not support the existence of BH_5? For example, the best prior calculation[1] predicts the electronic binding energy relative to H_2 and BH_3, ΔE_{el}, to be 5.4 kcal mol^{-1}, which is offset by a zero-point vibrational energy (ZPVE) difference of 4.5 kcal mol^{-1} and a basis set superposition error (BSSE) of about 1.2 kcal mol^{-1}. (3) Where should the A″ band be seen, and is it masked by other transitions? To address these issues, we report highly accurate calculations of the binding energy and the vibrational frequencies of BH_5 and BH_3, with regard to the nearly free rotation of H_2 relative to BH_3.

All calculations are performed with the ACES II program system[7,8] using MBPT(2) and CCSD(T) methods,[9] with converging correlation consistent basis sets[10] of polarized valence triple-ζ (PVTZ), augmented PVTZ (PVTZ+), and polarized valence quadruple-ζ (PVQZ) quality. For BH_5, PVTZ, PVTZ+, and PVQZ contain 100, 161, and 205 functions; the CCSD(T)/PVQZ calculations are among the largest C_s symmetry CCSD(T) calculations yet reported. Geometries of H_2, BH_3, and BH_5 are optimized at the CCSD(T)/PVTZ level, and harmonic vibrational frequencies are computed by finite differences of analytically computed gradients. The (correlated) BSSE is estimated by the counterpoise method.[11] CCSD(T) calculations with the PVTZ+ and PVQZ basis sets are made at the CCSD(T)/PVTZ geometries. The CCSD(T)/PVTZ method is a demonstrably high accuracy quantum chemical method[9] that should be suitable for describing the vibrational spectrum of H_2-BH_3. Anharmonic effects for some modes can be estimated from a CCSD(T) study of BH_3.[12]

Table 1. Contributions to the Reaction Energy for $H_2 + BH_3 \rightarrow H_2-BH_3$ (kcal mol^{-1})

method	basis	ΔE_{el}	BSSE	ΔE_{el} + BSSE	ΔZPVE	$\Delta H°$
MBPT(2)[a]	PVTZ	−7.49	2.19	−5.30	5.72[c]	0.42
MBPT(2)[a]	PVTZ+	−7.22	1.65	−5.57	5.72[c]	0.15
MBPT(2)[a]	PVQZ	−6.93	0.81	−6.12	5.72[c]	−0.40
CCSD(T)[b]	PVTZ	−5.02	0.51	−4.51	5.69[d]	1.17
CCSD(T)[b]	PVQZ	−5.68	0.16	−5.52	5.69[d]	0.17
CCSD(T)[a]	PVTZ	−7.07	2.25	−4.82	5.69[d]	0.87
CCSD(T)[a]	PVTZ+	−6.89	1.63	−5.26	5.69[d]	0.43
CCSD(T)[a]	PVQZ	−6.50	0.72	−5.79	5.69[d]	−0.10

[a] All electrons correlated. [b] Core electrons not correlated. [c] MBPT(2)/PVTZ harmonic value. [d] CCSD(T)/PVTZ harmonic value.

Table 2. Comparison of Calculated and Observed Values of High Infrared Intensity Bands of BH_3 and H_2-BH_3 (cm^{-1})[a]

		CCSD(T)/PVTZ			
		$\omega(I)$[c]	ν(anharm)[d]	ν(anharm+ matrix)[e,f]	obsd[b]
BH_3	ν_3(E′)	2721 (254)	2608	2593	2587
H_2-BH_3	ν_2(A′)	2639 (72)	2526	2511	2475
	ν_9(A″)	2694 (76)	2581	2566	?
BH_3	ν_2(A_2″)	1155 (84)	1131	1119	1129
H_2-BH_3	ν_6(A′)	1206 (35)	1182	1170	1134
	ν_7(A′)	1014 (50)	990	978	?

[a] Calculated infrared intensities (km mol^{-1}) are in parentheses. [b] Ar matrix values from ref 2; gas phase values for ν_3 and ν_2 of BH_3 are 2602 and 1141 cm^{-1}, respectively (Kawaguchi, K. *J. Chem. Phys.* **1992**, *96*, 3411). [c] The other CCSD(T)/PVTZ harmonic frequencies for BH_3 are $\omega_1(I_1)$ = 2584(0) and $\omega_4(I_4)$ = 1219(32); for BH_3-H_2 they are $\omega_1(I_1)$ = 3550(24), $\omega_3(I_3)$ = 2544(11), $\omega_4(I_4)$ = 1798(7), $\omega_5(I_5)$ = 1227(9), $\omega_8(I_8)$ = 800(14), $\omega_{10}(I_{10})$ = 1231(3); $\omega_{11}(I_{11})$ = 1051(0); and $\omega_{12}(I_{12})$ = 252(5). [d] Obtained by subtracting calculated anharmonicity corrections for BH_3 taken from ref 12. [e] Obtained by correcting for anharmonic effects and for observed BH_3 matrix effects. [f] As discussed in the text, these may be modified by uncertainties in the ω_i.

ΔE_{el}, BSSE, ZPVE, and $\Delta H°$ for the formation of H_2-BH_3 are shown in Table 1. $\Delta H°$ is very small and highly sensitive to changes in ΔE_{el}, BSSE, and ΔZPVE. The most negative CCSD(T) value obtained for ΔE_{el} + BSSE is −5.79 kcal mol^{-1} in the PVQZ basis. Going from PVTZ to PVTZ+ lowers ΔE_{el} + BSSE by 0.44 kcal mol^{-1}, so augmenting the PVQZ basis in a similar way should not lead to a value below −6.2 kcal mol^{-1}. ΔZPVE was estimated from CCSD(T)/PVTZ *harmonic* vibrational frequencies. For H_2 the calculated ZPVE is 6.30 kcal mol^{-1}, and the experimental value is 6.21 kcal mol^{-1}. The calculated harmonic ZPVE for BH_3 is 16.61 kcal mol^{-1}. From calculated anharmonic data,[12] one obtains 16.31 kcal mol^{-1}, which should be a very good estimate. Hence, the ZPVE errors for H_2 and BH_3 are very small. The errors for H_2-BH_3 are probably larger because of BSSE and larger anharmonicity in modes which are not localized BH_3 or H_2 motions. A 5% anharmonicity reduction for these modes (ω_4, ω_7, ω_8, ω_{11}, and ω_{12}) will reduce ΔZPVE by 0.35 kcal mol^{-1}. This and a basis set effect of 0.4 kcal mol^{-1} will result in $\Delta H°$ = −0.85 kcal mol^{-1}.

TA assigned bands at 2475 and 1134 cm^{-1} to H_2-BH_3 (calculations imply that these are ν_2 and ν_6). The A″ partner of ν_2, namely, ν_9, was not identified. CCSD(T)/PVTZ and experimental frequencies are given in Table 2, and isotopic shifts are given in Table 3. ω_2 of H_2-BH_3 is calculated to be red-shifted from ω_3 of BH_3 by 82 cm^{-1}, while the observed shift of matrix fundamentals is 112 cm^{-1}. Allowing for different

(1) Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 5173.
(2) Tague, T. J., Jr.; Andrews, L. *J. Am. Chem. Soc.*, in press.
(3) Hoheisel, C.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 6970.
(4) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 3438.
(5) Pepperburg, I. M.; Halgren, T. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1976**, *98*, 3442.
(6) Kreevoy, M. M.; Hutchins, J. E. C. *J. Am. Chem. Soc.* **1972**, *94*, 6371.
(7) ACES II is a quantum chemical program package especially designed for CC and MBPT energy and gradient calculations. Elements of this package are as follows: the SCF, integral transformation, correlation energy, and gradient programs written by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett; the VMOL integral and VPROPS property integral programs written by P. R. Taylor and J. Almlöf, and a modified version of the integral derivative program ABACUS written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor.
(8) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879 and references therein.
(9) Bartlett, R. J.; Stanton, J. F. Applications of Post-Hartree-Fock Methods: A Tutorial. In *Reviews in Computational Chemistry*; Boyd, D., Lipkowitz, K., Eds.; VCH Publishers: New York, 1994; Vol. 5, p 65.
(10) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007. Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
(11) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
(12) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1992**, *200*, 502.

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Table 3. Comparison of Calculated and Observed Isotopic Shifts (Relative to ^{11}B and ^{1}H Isotopomers) of High Infrared Intensity Bands of BH_3 and H_2-BH_3[a]

			$^{10}B^1H$	$^{11}B^2H$	$^{10}B^2H$
BH_3	$\nu_3(E')$	exptl	14	−634	−614
	$\omega_3(E')$	calcd	16	−696	−674
	$\nu_2(A_2'')$	exptl	11	−251	−232
	$\omega_2(A_2'')$	calcd	12	−258	−243
H_2-BH_3	$\nu_2(A')$	exptl	13	−609	−590
	$\omega_2(A')$	calcd	13	−688	−668
	"B_xH_y"	exptl	12	—	−608
	$\omega_9(A'')$	calcd	16	−677	−656
	$\nu_6(A')$	exptl	11	−251	−233
	$\omega_6(A')$	calcd	2	−335	−330
	$\omega_7(A')$	calcd	11	−236	−228

[a] Units are cm^{-1}.

anharmonicity and matrix effects for the complex, this is satisfactory agreement. ω_9 is calculated to be 55 cm^{-1} above ω_2 and 27 cm^{-1} below ω_3 of BH_3. Given the observed positions of ν_2 of H_2-BH_3 and ν_3 of BH_3, we predict ν_9 to be in the range 2530−2560 cm^{-1}. Examining the spectra of TA, a possible candidate is the "higher B_xH_y" band at 2544 cm^{-1}, whose isotopic shifts (Table 3) are close to those of ν_3 of BH_3 and in reasonable accord with calculated values for ω_9. After re-examining the spectra, Andrews concludes[13] that this band could be due to ω_9, but notes the difference in line width compared with ν_2, which may be due to the different effect of H_2 on the two motions. Alternatively, ν_9 might be masked by ν_{16} of B_2H_6 (2517 cm^{-1}), but this is less likely as the observed isotopic shifts are not consistent with those calculated.

One may also suggest that the global minimum of BH_5 is not the C_s isomer, but one with a 3-fold or higher principal axis, so that the degeneracy of ν_3 of BH_3 is not lifted, although this seems unlikely.[1] The only such viable structures are a C_{3v} end-on H_2-BH_3 complex, a D_{3h} trigonal bipyramid, or a C_{4v} square-based pyramid. In the first case, no minimum was found. In the second, the D_{3h} form is significantly higher in energy and is not a local minimum, having three imaginary frequencies. The C_{4v} form, previously considered,[1] was also found not to be a local minimum and to be higher in energy. Another factor to consider is the influence of the H_2 rotation. The small barrier to rotation (0.05 kcal mol^{-1}), means strictly that one should treat this system as a nonrigid molecule.[14] ν_2 and ν_9 will not become degenerate, but their observed values will be rotational averages.[14] To estimate the effect of H_2 rotation, we compute frequencies at three points along the minimum energy rotational coordinate, namely, twist angles of 0° (the global minimum of C_s symmetry), 45°, and 90° (C_s transition state). Relative to 0° values, the A′ and A″ modes arising from ν_3 of BH_3 respectively decrease by up to 5 cm^{-1} and increase by up to 9 cm^{-1}. These small shifts validate our rigid molecule treatment.

TA observed bands at 1129 and 1134 cm^{-1} having identical isotopic shifts. The first was assigned to $\nu_2(A_2'')$ of BH_3. Partly on the basis of the theoretical prediction of a 14 cm^{-1} blue shift,[1] the second was assigned to the corresponding band of H_2-BH_3 (ν_6). Our current high-level calculations disagree with this assignment in two ways. First, we predict a significantly larger blue shift (about 51 cm^{-1}) and, second, our $^{11}B-^{10}B$ isotopic shifts are much smaller than those of TA's 1134 cm^{-1} band (Table 3). Of the calculated normal modes of H_2-BH_3, ω_6 corresponds more closely to ω_2 of BH_3, yet it is *not* a localized BH_3 motion. It involves substantial H_2 motion as well as BH_3 motion, which is in accord with the proximity of the two molecules (about 1.4 Å). The BH_3 motion in ω_6 is along the intermolecular coordinate, and there is, consequently, significant coupling between the two motions. This is in contrast to ω_2 and ω_9 of H_2-BH_3, which involve localized BH_3 motion *perpendicular* to the intermolecular coordinate, leading to isotopic shifts close to those of free BH_3. ω_6 varies only by 1 cm^{-1} as a function of H_2 rotation.

It may be important to consider the influence of BSSE on the vibrational spectra. The primary source of BSSE in the PVTZ basis is in the description of the core electrons (Table 1). We have also performed some vibrational frequency calculations in which the core electrons are not correlated. This leads to a small "loosening" of the complex (an increase in intermolecular distance of about 0.02 Å) and small changes in positions of frequencies relative to BH_3. In particular, the shift in ω_6 is reduced to 35 cm^{-1}, but the $^{11}B-^{10}B$ isotopic shift increases only to 3 cm^{-1}, which is still far from the shift for TA's 1134 cm^{-1} band. The $\omega_2-\omega_9$ splitting is reduced from 55 to 46 cm^{-1}.

A final interesting issue is that ω_7 is predicted to have high intensity. Allowing for anharmonicity, ν_7 is likely to be in the range 940−980 cm^{-1}, but it is not observed.[13] As well as ω_6, both ω_7 and ω_8 have some character of ω_2 of BH_3, mixed in with H_2 motion, so the correlation of this mode of BH_3 with a single mode of H_2-BH_3 is an oversimplification. Indeed, the isotopic shifts of ω_7 are quite consistent with those of ν_2 of BH_3, but the normal coordinate indicates very small motion of the equivalent H atoms. ω_7 varies by up to 11 cm^{-1} as a function of H_2 rotation.

In conclusion: (1) our calculations indicate a very small enthalpy of complexation of H_2-BH_3, even at 0 K (estimated corrections imply about −0.85 kcal mol^{-1}); (2) the degeneracy of the ν_3 band of BH_3 will be lifted, and the unidentified A″ band may be the 2544 cm^{-1} band; (3) primarily because of discrepancies in isotopic shifts, we question the assignment of TA's 1134 cm^{-1} band to H_2-BH_3.

Addendum. After this paper had been reviewed, another theoretical study of BH_5 appeared.[15] While the results are in general agreement with our study, the experimental assignment of ν_6 is not questioned.

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(13) Andrews, L. Private communication.
(14) Bunker, P. R. *Molecular Symmetry and Spectroscopy*; Academic Press: New York, 1979.
(15) Schreiner, P. R.; Schaefer, H. F., III; von R. Schleyer, P *J. Chem. Phys.* **1994**, *101*, 7625.