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Infrared Spectrum of the Novel Electron-Deficient BH_4 Radical in Solid Neon

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Boron hydrides are important for understanding electron-delocalized bonding, and the textbook example diborane, B_2H_6, has been widely investigated.[1] Diborane results from simple B atom and H_2 molecule reactions, but the intermediate steps merit further examination.[2] One possible intermediate, the BH_4 radical, is interesting in its own right as another example of electron-deficient bonding. The BH_4 radical has been characterized by ESR spectroscopy, and the lone electron found to interact strongly with two equivalent H atoms.[3−5] Electronic structure calculations find a C_{2v} ground state with two long and two short B−H bonds.[4,6−9]

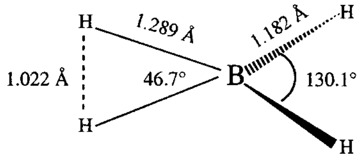
Reactions of laser-ablated metal atoms with H_2 in excess neon have proven to be a valuable source of new metal hydride molecules and complexes such as $(H_2)AuH$, $(H_2)RhH_2$, and WH_6 for matrix infrared spectroscopy.[10,11] Accordingly, we report here the first infrared spectrum of the BH_4 radical, which exhibits B−H stretching modes for short and long bonds, and a unique B−H_2 bending, H- -H stretching mode, which further characterize this novel small electron-deficient free radical.

Laser-ablated boron atoms were reacted with H_2, D_2, and HD in excess neon during condensation at 3.5 K using a Sumitomo Heavy Industries RDK-205D Cryocooler and methods described previously.[12] Natural isotopic boron ^{n}B (Aldrich, 80.4%, ^{11}B, 19.6% ^{10}B), enriched ^{10}B (Eagle-Pitcher, 93.8% ^{10}B, 6.2% ^{11}B), and enriched ^{11}B (Eagle-Pitcher, 97.5% ^{11}B, 2.5% ^{10}B) were employed as targets for laser-ablation using 10−40 mJ of 1064 nm laser energy per 10 ns pulse. Infrared spectra were recorded, samples were annealed, irradiated by a mercury arc lamp, and more spectra were recorded. Complementary density functional theory (DFT) and ab initio calculations were performed using the Gaussian 98 program,[13] B3PW91 and B3LYP density functionals and MP2 perturbation theory,[14−16] and 6-311++G(d,p) basis sets[17] to provide a consistent set of vibrational frequencies and infrared intensities for all of the boron hydride products including the mixed H,D and all-D isotopic variants. Geometries were fully optimized, and the vibrational frequencies were computed analytically from second derivatives. Natural bond orbital analysis[18] was done to determine the valence electron distribution.

Reactions of laser-ablated B with H_2 in excess neon produce spectra complementary to previous argon matrix spectra,[2] but different products are favored. Infrared spectra for ^{11}B, ^{n}B, and ^{10}B reactions are compared in Figure 1. Complete spectra will be reported and assigned in a later full paper. As before the major product is B_2H_6, and absorptions at 2608.4 cm^{-1} for ^{11}B (2623.3 cm^{-1} for ^{10}B), 2519.1 (2524.5) and 1598.0 (1602.5) cm^{-1} are obvious in the spectra. The strong features at 2186.2 (2195.8) and 2114.5 (2129.8) cm^{-1} are due to BH_4^-, which result from electron capture by BH_4 radical and are decreased 20−50% by photolysis. Sharp weak bands at 2602.5 (2616.7) and 1141.0 (1152.5) cm^{-1} are due to the reactive BH_3 species.[2]

Four sharp new absorptions at 2666.0, 2540.6, 2021.4, and 1298.4 cm^{-1} are grouped together by their 30−70% increase on photolysis in different experiments. The 2666.0 and 2021.4 cm^{-1} bands show large enough boron isotopic shifts to give 1:4 doublets with ^{n}B, which verifies that a single B atom is involved in these vibrations. Isotopic counterparts are given in Table 1. The H/D ratios 1.320, 1.346, 1.332, and 1.381 show that the former are B−H stretching modes and that the latter involves primarily hydrogen: the lack of a boron isotopic shift for the latter shows that there is no boron motion. When 1% H_2 is used instead of 4% H_2 in neon, all product bands are weaker, but B_2H_6 absorptions are reduced more than the above bands. In the ^{11}B experiment annealing to 8 K after photolysis decreased the above bands by 10% and increased the B_2H_6 bands by 10%.

Previous ESR investigations[3−5] and theoretical calculations[4,6−9] concluded that BH_4 has a C_{2v} ground state with two long B−H bonds enclosing an acute angle with a short H- -H distance and two short, normal B−H bonds enclosing an obtuse angle as illustrated below. Our structural parameters (MP2 given below) are nearly identical to those calculated previously.[4,6−9] Calculated vibrational frequencies were reported without infrared intensities.[7−9] The computed frequencies listed in Table 1 are comparable, and our calculated intensities show that four infrared absorptions might be observable: two stretching modes of the normal B−H bonds, the symmetric stretching mode of the long B−H bond pair, and the concerted in-phase symmetric bending mode. Displacement coordinates show that the latter two modes have some H- -H stretching character.



On the basis of isotopic substitution and general agreement with the frequencies and intensities computed by three different methods (Table 1), we assign the above four bands to the BH_4 radical. Infrared spectra of the HD reaction products are complicated but support this assignment. The two strongest absorptions of $(H_2)BD_2$ and $(HD)BHD$ are observed, which requires that the saddle point for exchange of inequivalent hydrogens be accessible from the reaction exothermicity, and this is in agreement with calculations.[6,8]

The two short B−H_2 stretching modes of BH_4 are slightly higher than the terminal B_2H_6 stretching modes, which is consistent with our calculation that the terminal B−H bonds in B_2H_6 are 0.005 Å longer. The one long B−H_2 stretching mode observed here for BH_4 at 2021.4 cm^{-1} is intermediate between the terminal and bridged stretching modes for B_2H_6. The most interesting absorption is the strong 1298.4 cm^{-1} fundamental, which is a concerted B−H_2 angle

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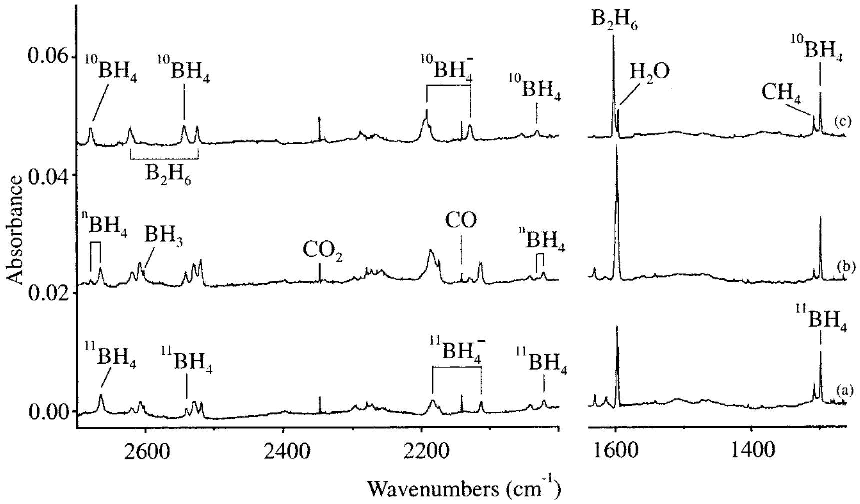

Figure 1. Infrared spectra in the 2700−1260 cm^{-1} region for laser-ablated boron and 4% H_2 reaction products in excess neon at 3.5 K recorded after deposition, 8 K annealing, and 240−700 nm photolysis. (a) ^{11}B, (b) ^{n}B, and (c) ^{10}B.

Table 1. Infrared Absorptions (cm^{-1}) in Solid Neon and Vibrational Frequencies and Infrared Intensities Calculated[a] for the BH_4 Radical

$^{10}B+D_2$	$^{11}B+D_2$	$^{10}B+H_2$	$^{11}B+H_2$	B3PW91	B3LYP	MP2
2041.1	2019.6	2680.0	2666.0[b]	2752.7 (b_2, 83)[c,d]	2750.3 (89)	2810.3 (83)
1890.9	1886.9	2543.3	2540.6[b]	2632.2 (a_1, 36)[c,d]	2633.9 (37)	2687.0 (35)
1527.9	1518.0	2030.3	2021.4[b]	2149.5 (a_1, 87)[c,e]	2112.1 (91)	2214.8 (103)
				2026.6 (b_1, 0)[c,e]	1961.1 (0)	2091.3 (0.1)
940.2	940.2	1298.4	1298.4[b]	1383.5 (a_1, 41)[c]	1339.5 (43)	1429.2 (58)
				1040.8 (b_2, 0)	1051.0 (1)	1075.8 (1)
				1004.1 (a_1, 0)	969.9 (1)	1027.5 (0)
				715.4 (b_1, 0)	743.5 (0)	869.8 (0)
				689.6 (a_2, 0)	694.2 (0)	738.4 (0)

[a] ^{11}B, H isotope; 6-311++G(d,p) basis set. [b] Integrated intensities in $^{11}B+H_2$ experiment are 0.0170, 0.0038, 0.0058, and 0.0150 au × cm^{-1}, respectively. [c] Intensities (km/mol). Frequencies calculated for ^{10}B, H isotope are 2770.1, 2639.2, 2157.8, 1383.5 cm^{-1}, respectively. [d] Short $B-H_2$ subunit. [e] Long $B-H_2$ subunit.

bending motion that involves the acute angle more than the obtuse angle. The symmetric modes with H- -H stretching character, 2021.4 and 1298.4 cm^{-1}, are low for an H- -H vibration, much lower even than in dihydrogen complexes such as $Pd(H_2)$ at 2971 cm^{-1} with 0.854 Å computed H−H bond length.[19] The NBO analysis[18] on the MP2 orbitals describes a one-electron H- -H bond with length 1.022 Å, which is very close to the one-electron bond length in free H_2^+ (MP2 value 1.050 Å) but longer than H_2 in transition metal complexes. Finally, the isostructural $(H_2)CD_2^+$ cation has a computed H- -H length of 1.091 Å.[20]

The neon matrix infrared spectrum shows that BH_4 contains short and long B−H bonds, which is in accord with the structure observed by ESR and calculated by theory.[3−9] Even though the frequencies of this electron-deficient radical are predicted reasonably accurately, the intensities do not fare as well. The a_1 mode of the long $B-H_2$ subunit is predicted to be as strong as the b_2 mode of the short $B-H_2$ subunit, but our observation is 1:3. Likewise the concerted bending mode is predicted to be half as strong as the b_2 mode, but it is in fact of comparable intensity. The latter mode is apparently the most difficult to model.

The electron-deficient BH_4 species is extremely interesting. This radical is clearly related to diborane in that both have terminal electron-pair and electron-deficient B−H bonds. The two long B−H bonds in BH_4 and the included weak H- -H bond are of appropriate length to be considered as one-electron bonds, which is substantiated by a natural bond orbital analysis of the MP2 computed molecular orbitals. However, this H- -H bond is broken when BH_2 reacts with BH_4 to form B_2H_6, and instead two bridged H−B−H bonds result.

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References

(1) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.
(2) Tague, T. J., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 4970.
(3) Symons, M. C. R.; Chen, T.; Glidewell, C. *J. Chem. Soc., Chem. Commun.* **1983**, 326.
(4) Claxton, T. A.; Chen, T.; Symons, M. C. R. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 121.
(5) Van Zee, R. J.; Williams, A. P.; Weltner, W., Jr. *J. Chem. Phys.* **1997**, *107*, 4756.
(6) Paddon-Row: M. N.; Wong, S. S. *J. Mol. Struct. (THEOCHEM)* **1988**, *180*, 353.
(7) Saxon, R. P. *J. Phys. Chem.* **1993**, *97*, 9356.
(8) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1993**, *99*, 4629.
(9) Schlegel, H. B.; Baboul, A. G.; Harris, S. J. *J. Phys. Chem.* **1996**, *100*, 9774.
(10) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2001**, *123*, 12899 ($Au+H_2$). Wang, X.; Andrews, L. *J. Phys. Chem.* **2002**, *106*, 3706 ($Rh+H_2$).
(11) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2002**, *124*, 5636 ($W+H_2$).
(12) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697.
(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S. and Pople, J. A. *Gaussian 98, Revision A.7*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(14) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
(15) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(16) (a) Mϕller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Brinkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.
(17) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.
(18) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(19) Andrews, L.; Manceron, L.; Alikhani, M. E.; Wang, X. *J. Am. Chem. Soc.* **2000**, *122*, 11011.
(20) Signorell, R.; Sommavilla, M.; Merkt, F. *Chem. Phys. Lett.* **1999**, *312*, 139 and references therein.

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