Conclusions

In summary, the microscopic structural and electronic properties of the CDW phases in a series of iron-substituted tantalum disulfide materials, $Fe_xTa_{1-x}S_2$, have been characterized with STM. For $x(\mathrm{Fe}) \leq 0.02$ the incommensurate CDW phase exhibits a regular hexagonal superlattice similar to that suggested on the basis of diffraction experiments. At the atomic level, however, these real-space STM studies show that there are also well-defined defects in this CDW structure. These defects, which are due to the iron centers in the lattice, involve a spatially localized amplitude distortion or coupled amplitude–phase distortion of the CDW. For $0.04 \leq x(\mathrm{Fe}) \leq 0.15$ the CDW superlattice exhibits large variations in the wavelength and amplitude in contrast to the hexagonal incommensurate phase suggested from diffraction studies. The origin of these differences between the STM and diffraction results has been resolved from the analysis of 2DFT power spectra of our images and real-space wavelength measurements. In addition, we have shown that these results and our previous studies of metal substitution suggest that there is a critical impurity level corresponding to one impurity/CDW maxima for substitution in the tantalum disulfide system.

Acknowledgment. We thank Jin-Lin Huang for helpful discussions. C.M.L. acknowledges support of this work by The David and Lucile Packard Foundation, the Air Force Office of Scientific Research (Grant AFOSR-90-0029), the National Science Foundation (Grant CHE-8857194), and Rohm and Haas Co.

Reactions of Boron Atoms and Clusters with Methane, Methyl Bromide, and Water under Matrix Isolation Conditions

G. H. Jeong,[1] R. Boucher, and K. J. Klabunde*

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. *Received February 13, 1989. Revised Manuscript Received November 30, 1989*

Abstract: Boron was evaporated with a pulsed XeCl excimer laser, and the vapor cocondensed on a cold window (near 10 K) with argon mixtures of CH_4, CH_3Br, and H_2O, and ^{13}C and ^2H labeled analogues. Consumption of B and B_2 was monitored by UV–vis spectroscopy, and reaction products were monitored with FT-IR. Atom insertion products H_3CBH, H_3CBBr, and HOBH were detected. Evidence was found for B_2 reactions with CH_4 and CH_3Br, suggesting the formation of dinuclear bridged hydrogen species. Larger boron clusters were detected by FT-IR, which were unreactive with CH_4 and, in one case, with water.

Boron atom chemistry has interested scientists for many years. Progress has been slow, however, due to the difficulty in producing atoms from the solid. Timms,[2] employing electron beam evaporation of boron, studied boron atom interactions with hydrogen halides and found HBX_2 (X = Cl, Br) as products, which were probably formed through a series of free radical reactions. McGlinchey, Brent, and Skell[3] reported oxidative addition reactions of boron atoms, for example with bromobenzene, $C_6H_5BBr_2$ was formed. Also, water reacted to eventually yield $B(OH)_3$ under the conditions of the experiment (codeposition at 77 K followed by warming). More recent gas-phase studies of B atom/H_2O interactions by Gole and Pace[4] indicated the formation of BO*. Sakai and Jordan,[5] using theoretical approaches, predict that the HOBH molecule should be bound by at least 90 kcal/mol with respect to B and H_2O. Further work by Sakai and Jordan[6] suggests that B–H_2O reactions should proceed with a small E_a for the insertion reaction

$$B + H_2O \rightarrow B{\cdot}OH_2 \xrightarrow{E_a = 12\ \mathrm{kcal}} HOBH \rightarrow BO^* + H_2$$

thus, HOBH should be experimentally detectable, although in the gas phase excited HOBH decomposes to BO and H_2.

Other gas-phase studies of B atoms with oxygen compounds have appeared.[7-9] Oxygen abstraction is the main reaction channel yielding excited-state BO. No direct evidence for insertion products ROBH, HOBH, or similar species has been obtained, except from our earlier study of the matrix B–CH_4 reaction, which indicated the matrix isolation of H_3CBH.[10] This work followed earlier work with Al and other metal atoms with CH_4 and CH_3Br.[11,12] The earlier work[11] attracted the attention of Lebrilla and Maier,[13] who carried out theoretical calculations on the reactions of B^+, B, B^-, C, and Al with CH_4, which predicted that very low activation energies should be encountered for the reactions of B atoms, B^-, C atoms, and Al atoms with C–H bonds. Their conclusion was that C–H activation should be a facile process if the attacking reagent has an electronic structure similar to that of a carbene: one empty orbital and one filled or partially filled orbital each of p-type symmetry.

With this background we began a more in depth study of the low-temperature reactions of B atoms/clusters with CH_4, CH_3Br, and H_2O. In our study we employed a pulsed XeCl excimer laser to evaporate boron. Since we were most interested in ground-state reactions of B atoms, we took precautions to ensure that electronically excited boron species would not live long enough to reach the reaction zone. Thus, we fashioned an apparatus where a 5-cm distance separated the boron rod and the trapping window.[10]

---

[1] Present address: Busan National University, Department of Chemistry, Busan, 609-735 Korea.

[2] Timms, P. L. *Chem. Commun.* **1968**, 258–259.

[3] McGlinchey, M.; Skell, P. S. In *Cryochemistry*; Moskovits, M., Ozin, G., Eds.; Wiley-Interscience: New York; pp 153–155. Brent, W. N. Ph.D. Thesis, Pennsylvania State University, 1974.

[4] Gole, J. L.; Pace, S. A. *J. Phys. Chem.* **1981**, *85*, 2651–2655.

[5] Sakai, S.; Jordan, K. D. *Chem. Phys. Lett.* **1986**, *130*, 103–110.

[6] Sakai, S.; Jordan, K. D. *J. Phys. Chem.* **1983**, *87*, 2293–2295.

[7] Tobacco, M. B.; Stanton, C. T.; Davidovits, P. *J. Phys. Chem.* **1986**, *90*, 2765–2768.

[8] DiGiuseppi, T. G.; Estes, R.; Davidovits, P. *J. Phys. Chem.* **1982**, *86*, 260–262.

[9] DeHaven, J.; O'Connor, M. T.; Davidovits, P. *J. Phys. Chem.* **1981**, *75*, 1746–1751.

[10] Klabunde, K. J.; Jeong, G. H. *J. Am. Chem. Soc.* **1986**, *108*, 7103–7104.

[11] Klabunde, K. J.; Tanaka, Y. *J. Am. Chem. Soc.* **1983**, *105*, 3544–3546.

[12] Parnis, J. M.; Ozin, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1699–1700.

[13] Lebrilla, C. B.; Maier, W. F. *Chem. Phys. Lett.* **1984**, *105*, 183–188.

0002-7863/90/1512-3332$02.50/0

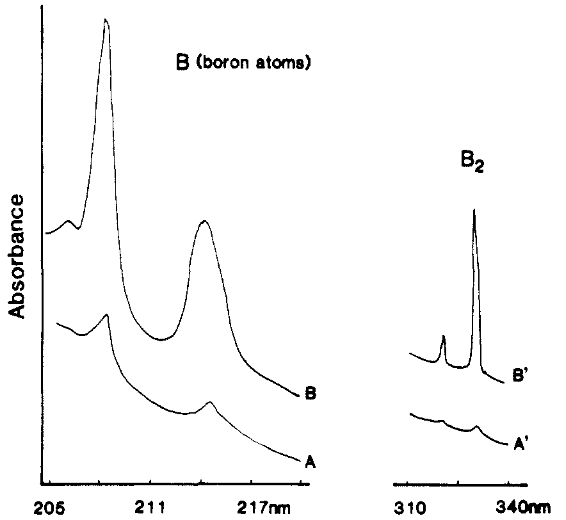


Figure 1. UV absorption spectra of B and B_2 evaporated by XeCl excimer laser (75 mJ/pulse, 10 Hz) isolated in Ar at 10 K; (A) in 5% CH_4/Ar matrix with evaporation time 10 min; (B) in pure Ar matrix evaporated 10 min more after A.

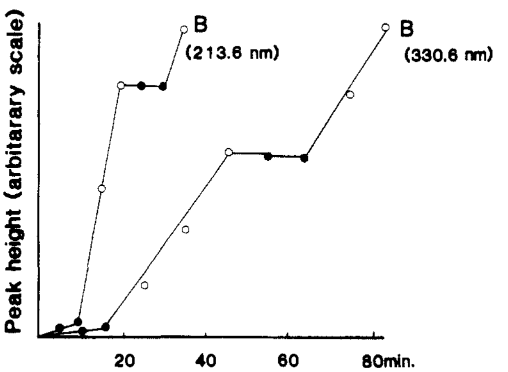


Figure 2. A plot of absorption band intensity vs condensation time of B and B_2: (○) in an Ar matrix, (●) in a 10% CH_4/Ar matrix.

Ballistic calculations indicate that the time for the B atoms to travel this distance is about 2 ms. Each laser burst is about 15-ns duration with a cycle time (time between bursts) of at least 100 ms. Thus, we believe no laser excitation of the traversing gas-phase B atoms took place. Also, any excited B atoms formed by the laser burst should decay within the 2-ms time frame, since B atoms do not have any long-lived meta-stable electronic states.[14]

Results and Discussion

Boron and Methane. Boron atoms isolated in frozen argon absorb in the UV at 213.6 and 208.0 nm.[15] Boron dimer B_2 absorbs at 330.6 and 320.6 nm. Figure 1 shows UV spectra of B and B_2 in argon and CH_4/argon mixtures. The lower spectra were obtained by codepositing boron vapor with 5% CH_4/Ar for 10 min. The upper spectra show absorptions after a 10-min deposition in pure argon under exactly the same conditions. Note that the band intensities for B atoms and B_2 are almost negligible in the presence of 5% CH_4/Ar. In pure Ar, however, these bands grew rapidly showing that much larger amounts of B atoms and B_2 were being matrix isolated. Figure 2 illustrates this in another way. We have used such matrix gas switching techniques successfully before[16,17] and believe that these data indicate that B atoms and B_2 are being consumed by CH_4.[10]

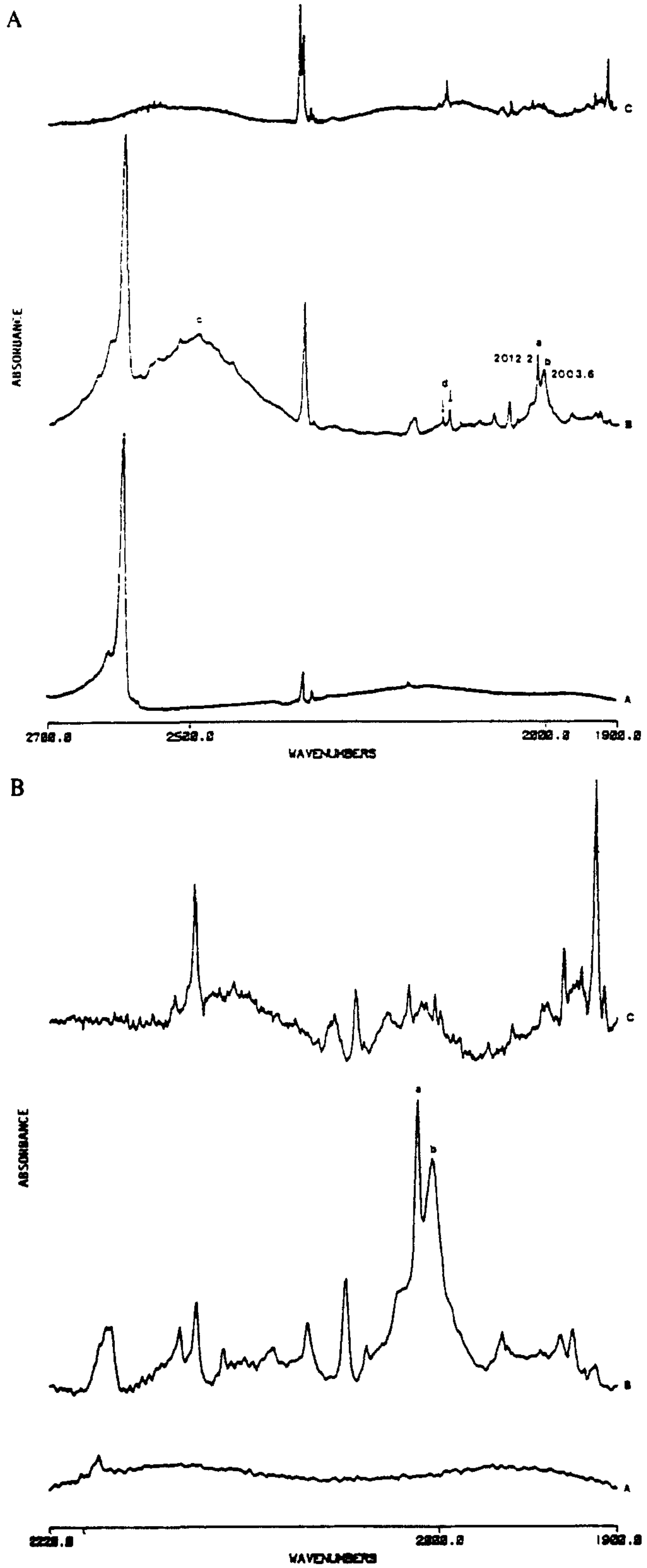


Figure 3. (A) Infrared absorption spectra of CH_4 (A), boron + CH_4 (B), and boron in argon (C) at 10 K. (B) Infrared absorption spectra of CH_4 (A), boron + CH_4 (B), and boron in argon (C). (Expanded from part A.)

When these and similar matrices were examined by FT-IR (Figures 3A-7), evidence for methane/boron vapor reaction products was obtained. Figure 3B is an expanded version of Figure 3A in the region of 2220-1900 cm^{-1}. Figure 4 was obtained by

---

[14] As far as we are aware, after a literature search, no long-lived metastable states of boron atoms are known. Helpful reports are: Bielski, A. *J. Quant. Spectrosc. Radiat. Transfer* **1975**, *15*, 463-472. Meggers, W. F.; Corliss, C. H.; Scribner, B. F. *Natl. Bur. Stand. (U.S.) Monograph 32*; U.S. Government Printing Office: Washington, DC, 1961. Lombardi, G. G.; Smith, P. L.; Parkinson, J. *Opt. Soc. Am.* **1979**, *69*, 1289-1291.

[15] Graham, W. R. M.; Weltner, W. *J. Chem. Phys.* **1976**, *65*, 1516-1521.

[16] Imizu, Y.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 3602-3605.

[17] Klabunde, K. J.; Whetten, A. *J. Am. Chem. Soc.* **1986**, *108*, 6529-6534.

Table I. FT-IR Bands and Probable Assignments for the B/CH_4 System (cm^{-1})

proposed species	ν_{B-H} terminal	ν_{B-H} bridged	ν_{C-H}	ν_{B-C}	$\delta(CH_3)$ (sym. def.)	$\delta(CH_3)$	$\rho_r(CH_3)^b$
H_3CBH	2494	2012	2939	971.0	894.0	1186	821.7
	2559	2004	2882 (sym)			1151	
	2387	2002					
$H_3{}^{13}CBH$	2545	2015	2940	962.0	885.0	1144	819.0
		2075	2878 (sym)			1108	
		2091					
D_3CBD	2150	*a*	*a*	*a*	765	813	734
						802	

[a] Obscured. [b] Rocking mode of CH_3 in BCH_3.

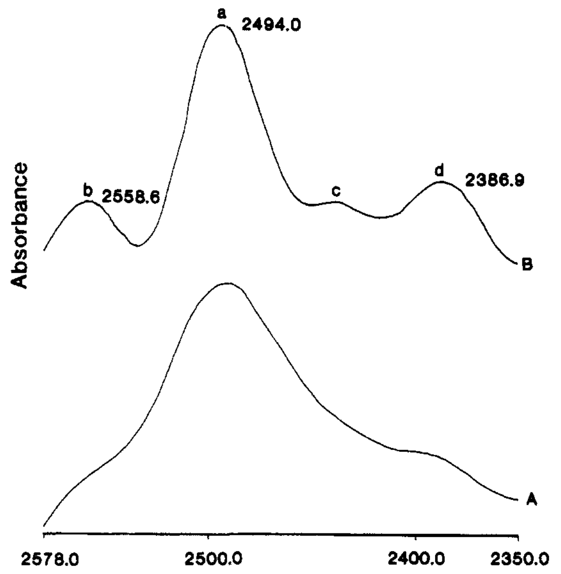


Figure 4. Partial spectrum of boron + CH_4 (A) and deconvoluted (B).

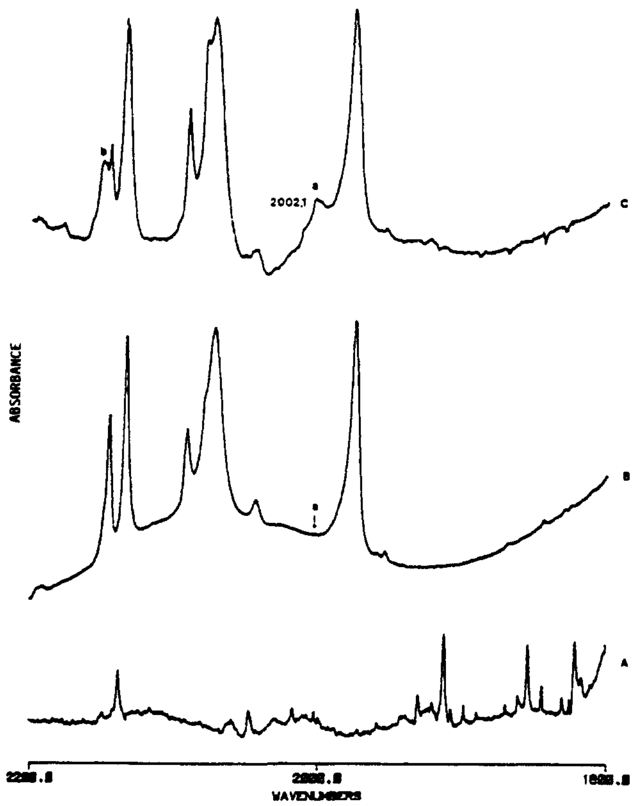


Figure 5. Infrared absorption spectra of boron in argon (A), CD_4 (B), and boron + CD_4 (C) at 10 K.

deconvolution of the broad band "c" in Figure 3A. Table I summarizes the bands observed and our proposed assignments.

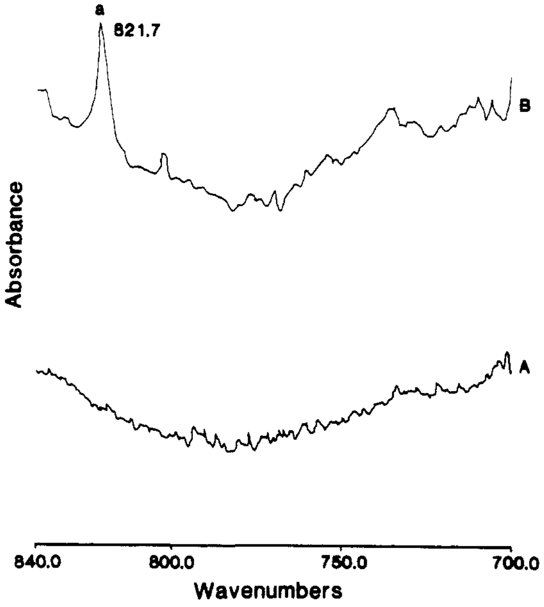


Figure 6. CH_4 (A) and boron + CH_4 (B) at 10 K.

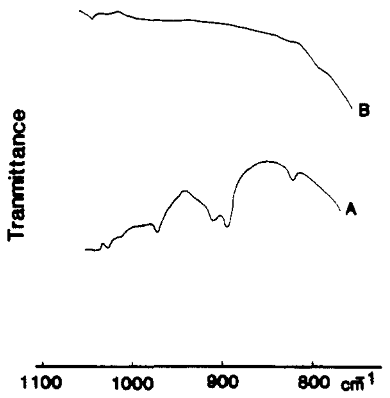


Figure 7. Partial infrared absorption spectra of boron + CH_4 (A) and CH_4 (B) at 10 K.

The most intense band appeared at 2494 cm^{-1} and was quite broad (Figure 4). Other similar bands appeared at 2559 and 2387 cm^{-1}. We believe these are due to ν_{B-H} (terminal). Stretching frequencies in this region for B–H are well established from studies of pentaboranes,[18,19] and ν_{B-H} from the B/H_2O system fall in this region (see later discussion).

Bands in the region 2000–2012 cm^{-1} could be assigned to bridged ν_{B-H}. Lehmann and co-workers[20] assigned such bands in the region 1900–2150 cm^{-1} for a series of different alkyldiboranes. Hrostowski and Pimentel[19] also assigned bridging B–H stretching at 1850–2100 cm^{-1} from studies of pentaborane.

Weak absorptions at 1186, 1151, 971, and 894 cm^{-1} were also observed, and a relatively strong one at 821.7 cm^{-1}. These could

---

(18) Grimes, R. N. *J. Organomet. Chem.* **1967**, *8*, 45–51.

(19) Hrostowski, H. J.; Pimentel, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 998–1003.

(20) Lehmann, W. J.; Shapiro, I. *Spectrochim. Acta* **1961**, *17*, 396–411.

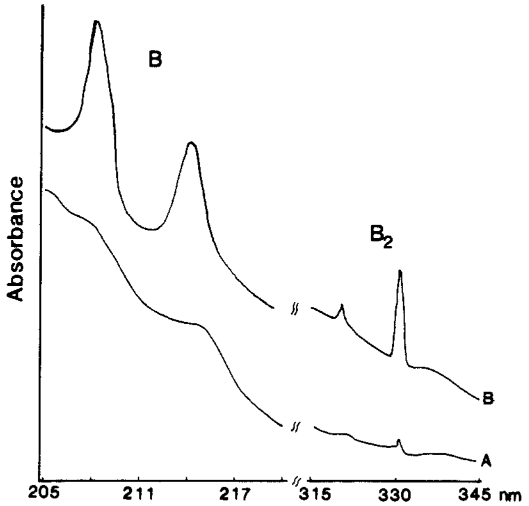


Figure 8. UV absorption spectra of B and B_2 evaporated by XeCl excimer laser (75 mJ/pulse, 10 Hz) isolated in Ar at 10 K: (A) in 5% CH_3Br/Ar matrix with evaporation time 10 min; (B) in pure Ar matrix with evaporation 10 min more after A.

Table II. FT-IR Bands and Probable Assignments for the $B/CH_3Br(CD_3Br)$ System (cm^{-1})

reactant	proposed species	ν_{B-Br}	ν_{B-C}	δ_{sym} (methyl)	δ_{asym} (methyl)
CH_3Br	H_3CBBr	812.0 800.5	1061 1037	687.4 640	1194
CD_3Br	D_3CBBr	813 801	(buried in CD_3Br bands)		859.3

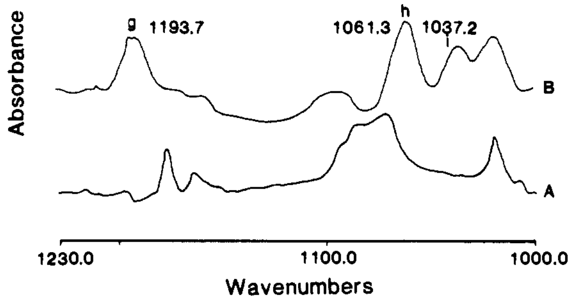


Figure 9. Infrared absorption spectra of CH_3Br (A) and boron + CH_3Br (B) at 10 K.

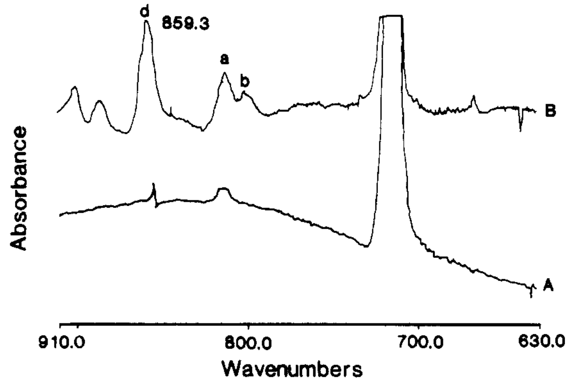


Figure 10. Infrared absorption spectra of CD_3Br (A) and boron + CD_3Br (B).

Table III. FT-IR Band and Probable Assignments for the B/H_2O System (cm^{-1})

proposed species	ν_{B-H} (terminal)	ν_{B-O}
HBOH	2573 2536	1408

be assigned to symmetric and asymmetric CH_3 bending modes.[10,11] However, since the calculated ν_{B-C} stretching frequency is 947 cm^{-1} (by assuming a bond order of 1),[21] it is possible that our 971 cm^{-1} is due to ν_{B-C}.

As a further aid in peak assignments, a series of experiments with $^{13}CH_4$ were carried out. Shifts were reproducably found as shown below:

$$CH_4/B\text{: } 1186, 1151\ 971, 894, 822\ cm^{-1}$$

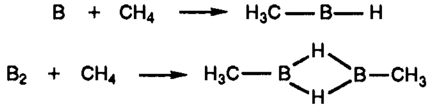
$$^{13}CH_4/B\text{: } 1144, 1108\ 962, 885, 819\ cm^{-1}$$

In addition, in the $^{13}CH_4$ matrix, ν_{C-H} bands were observable at 2940 cm^{-1} (asym) and 2878 cm^{-1} (sym), while in CH_4 these bands were at 2939 and 2882 (sym) cm^{-1}.

Isotopic shifts in CH_3Cl and $^{13}CH_3Cl$ have been reported.[22,23] Also, Ozin and co-workers[24] have calculated such shifts based on the mass of the methyl group (^{12}C vs ^{13}C). Larger shifts would suggest a stretching mode (in our case ν_{B-C}) and small shifts a CH_3 rocking mode. These data, combined with that of Becher and Bramsiepe[25] (on $(CH_3)_3B$ and $(CD_3)_3B$), and our calculated ν_{B-C} value, have allowed us to make probable band assignments, which are listed in Table I. Additional work with ^{10}B atoms reacting with CH_4 has shown the ν_{B-C} band at 990.0 cm^{-1}, the $\delta(CH_3)$ band at 902.0 cm^{-1}, and the $\rho_r(CH_3)$ band at 821.0 cm^{-1}, further confirming our assignments.

These results indicate that both B atoms and B_2 reacted with CH_4. In order to determine if one molecule of CH_4 (vs two or more) was involved in product formation, mixtures of CH_4/CD_4 were allowed to react with boron vapor. Unfortunately, CD_4 itself had interfering IR bands, and these experiments were not conclusive (see Figure 5). However, on the basis of bands we were able to see, and our earlier findings with other metals interacting with CH_4 or CH_3X, we believe that only one molecule of CH_4 is involved.

Since both B atoms and B_2 are consumed by CH_4, and since we observe both terminal and bridged ν_{B-H}, and since bands are present for CH_3 bending (and possible ν_{B-C}), we believe insertion reactions took place and these initial products were frozen and isolated in the 5% CH_4/Ar matrix:



$$B + CH_4 \longrightarrow H_3C{-}B{-}H$$

$$B_2 + CH_4 \longrightarrow H_3C{-}B(\mu\text{-}H)_2B{-}CH_3$$

Boron and Methyl Bromide. Figure 8 illustrates the UV absorption bands of B atoms and B_2 observed when CH_3Br (mixed in Ar) is codeposited and in pure Ar. It is clear that B atoms and B_2 are consumed by CH_3Br even more efficiently than by CH_4.

Figures 9 and 10 show IR absorption bands for the reaction products of boron vapor with CH_3Br (or CD_3Br), while Table II reports peak positions and possible assignments. The band "g" at 1194 cm^{-1} in Figure 9 can be assigned to the bending frequency of the CH_3 group. The ratio of δ CH_3/δ CD_3 should be about 1.4, and the band "d" at 859.3 cm^{-1} shown in Figure 10 corresponds to this assignment. Thus, the bands "g" and "d" are assigned as the bending frequencies of CH_3 and CD_3, respectively.

The bands "a" and "b" in Figure 10 were observed from both B/CH_3Br and B/CD_3Br at about the same frequency. Snelson[26] reported ν_{B-Br} at 812 cm^{-1} for the $^{11}BBr_3$ molecule in an argon matrix. Thus, it seems reasonable to assign the 812.0- and 800.5-cm^{-1} bands as ν_{B-Br}.

---

(21) Based on the force constant equation, $k = 1.67N(X_aX_b/d^2)^{3/4} + 0.30$. Reference: *Lang's Handbook of Chemistry*, 12th ed.; Dean, J. A., Ed.; McGraw Hill: New York, 1979; pp 3-11.

(22) Duncan, J. L.; Allan, A. *J. Mol. Spectrosc.* **1968**, *25*, 224-239.

(23) Jones, E. W.; Popewell, R. J. L.; Thompson, H. W. *Spectrochim. Acta* **1966**, *22*, 669-680.

(24) Parnis, J. M.; Ozin, G. A. *J. Phys. Chem.* **1989**, *93*, 1204-1214.

(25) Becher, H. J.; Bramsiepe, F. *Spectrochim. Acta* **1979**, *35A*, 53-57.

(26) Snelson, A. *High Temp. Sci.* **1972**, *4*, 318-325.

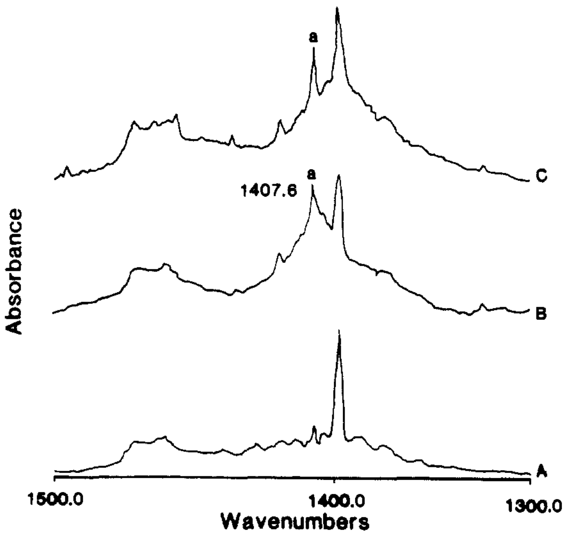


Figure 11. Infrared absorption spectra of <1% H_2O in argon (A), boron + H_2O/argon (B), and boron + D_2O/argon (C) at 10 K.

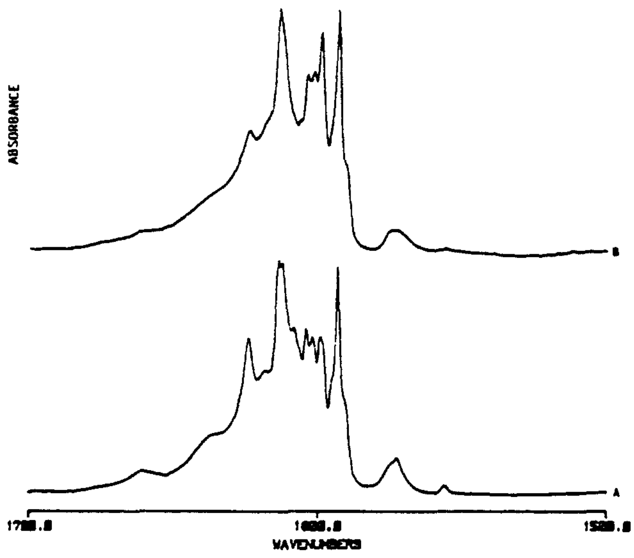


Figure 12. Partial infrared absorption spectra of H_2O/argon (A) and boron + H_2O/argon (B) at 10 K.

Lehmann and Shapiro[20] examined and correlated various methyl- and ethyldiboranes and their ^{10}B-enriched and deuterated variants. They concluded that ν_{B-C} should be in the vicinity of 970 cm^{-1}. The B atom in the expected product, H_3CBBr, has one unpaired electron, so it is possible that it might be slightly higher in frequency than 970 cm^{-1}. Thus, we believe the bands "h" and "i" at 1061 and 1037 cm^{-1} in Figure 9 are due to ν_{B-C} for H_3C-BBr and D_3C-BBr.

The bands at 687.4 and 640 cm^{-1} are probably CH_3 bending modes based on earlier reports on boron-methyl species: 675 cm^{-1} for $B(CH_3)_3$ and $(CH_3)_3BNH_3$, and 645 cm^{-1} for $(CH_3)_2BN(CH_3)_2$.[20]

We conclude that an efficient insertion reaction of B atoms (and B_2 as well) with CH_3Br took place yielding H_3CBBr.

Boron and Water. The boron/water system was also studied carefully by FT-IR. Figures 11-14 illustrate spectra recorded. Some background is necessary, however, before we analyze these spectra.

The IR spectrum of H_2O in rare gas matrices was investigated carefully by Pimentel and co-workers[27] and Milligan.[28] And, the B atom/H_2O reaction in the gas phase has been studied, as mentioned in the introduction.[4-6] Theory predicts that an adduct

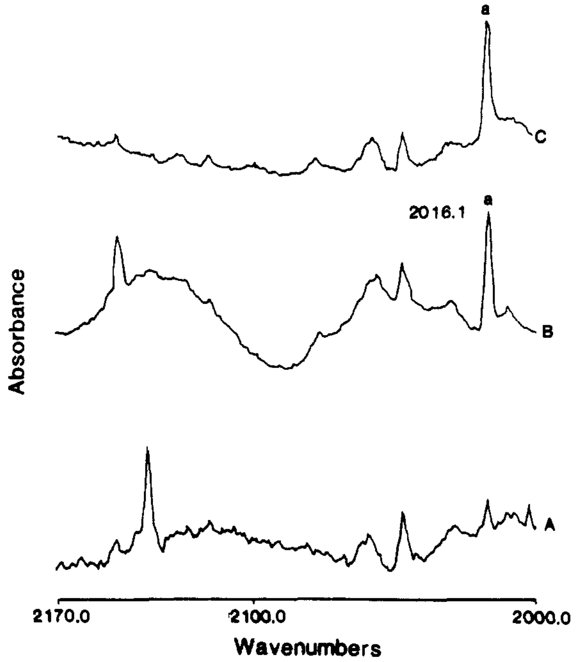


Figure 13. Partial infrared absorption spectra of boron in argon (A), boron + H_2O/argon (B), and boron + D_2O/argon (C) at 10 K.

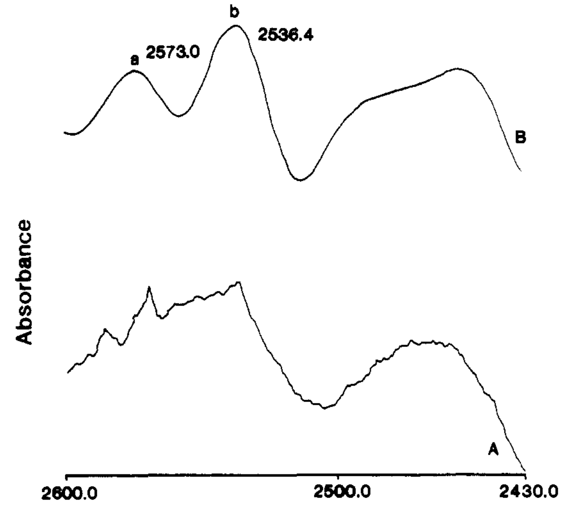


Figure 14. Partial infrared absorption spectra of boron + H_2O/argon (A) and deconvoluted (B) at 10 K.

$B-OH_2$ should lie in a small energy well, but that the insertion product lies about 90 kcal even lower, or about the same level as $BO + H_2$. Furthermore, the C_s symmetry of a $B-OH_2$ transition state means that the B atom is out of the plane of the three atoms of water, and such an arrangement should be slightly more stable than the planar counterpart.[29] Jordon and co-workers[6] report that "calculations with no symmetry constraints indicated that the transition state for this process lies only 11.9 kcal/mol above the energy of the initial reactants." The barrier for the HBOH → BO + H_2 rearrangement is well below the energy of the $B(^2P)$ + H_2O reactants, making viable the B + H_2O → *cis*-HBOH → BO + H_2 pathway for production of highly vibrationally excited BO, which was observed by Gole and Pace.[4]

Under matrix conditions then we might expect to observe adduct $B-OH_2$, insertion product HBOH, or BO + H_2. Can we determine the difference?

From ESR and theoretical studies of the $M-OH_2$ adducts, we would expect charge to be transferred from H_2O to the boron atom

---

(27) Van Thiel, B.; Becker, E. D.; Pimentel, G. *J. Chem. Phys.* **1957**, *27*, 486-490.

(28) Milligan, D. E. *J. Chem. Phys.* **1959**, *30*, 45-47.

(29) Trenary, M.; Schaefer, H. F., III; Kollman, P. A. *J. Chem. Phys.* **1978**, *68*, 4047-4050.

to obtain $B^{\delta-}–OH_2^{\delta+}$.[29,30] Since H_2O^+ exhibits a lower energy bending vibration we might expect to detect this.

Hauge, Kauffman, and Margrave[31] have reported on the Al/H_2O system and found spontaneous reaction at about 15 K while the heavier group 3A metals formed $M–OH_2$ and $M_2–OH_2$ adducts. Adduct formation caused the bending mode of H_2O to decrease by 10–21 cm^{-1}.

Finally, Lory and Porter[32] have reported ν_{B-O} values from HBO molecules trapped in solid argon. They assigned 1382 and 1398 cm^{-1} to $\nu_{^{11}B-O}$ and 1425 and 1440 cm^{-1} to $\nu_{^{10}B-O}$. Also, the Aldrich IR library assignes ν_{B-O} in the 1430–1335-cm^{-1} range.

Turning now to our results, we observed a product band at 1408 cm^{-1}. Because of its position, and because we observed it both with H_2O and D_2O, we assign this as a ν_{B-O} band.

We did not observe a shifted band for the water-bending mode near 1600 cm^{-1}, arguing against the formation of a $B–OH_2$ adduct.

In the ν_{B-H} region we observed very broad bands as shown in Figure 14A. The result of deconvolution of this band is shown in Figure 14B. Similar band shape observed with B/CH_4 is indicated. These ν_{B-H} frequencies are known for various alkylboranes[20] and pentaboranes[18,19] and are usually near 2500 cm^{-1}. As shown in Figure 14B two weak bands were observed at 2573 and 2536 cm^{-1}, and we assign these as the terminal ν_{B-H} bands.

On the basis of our results and on the Al/H_2O work of Margrave and co-workers (and their estimates of the great exothermicity for the $B + H_2O \rightarrow HBOH$ reaction),[31] we are confident that the insertion reaction took place under our matrix conditions

$$B + H_2O \rightarrow H–B–OH$$

Adduct formation $B–OH_2$ was not observed.

Boron Clusters in Argon. Throughout this work we have observed bands for boron in argon (no reactants) in the 1900–2200-cm^{-1} range. For example see Figures 3A (part C), 3B (part C), 5 (part A), and 13 (part A). These, we believe, are due to boron clusters. What their sizes or structures are remains a mystery. It is interesting that some of them remain unchanged in the presence of reactants. For example, in Figure 3B (part C), relatively strong bands are observed at about 1900 and 2150 cm^{-1}, and Figure 13 (part A) shows a persistent band at 2016 cm^{-1}. We are continuing our investigations of these interesting species.

Since B_2 is very efficiently consumed by CH_4 as well as CH_3Br and H_2O, these species, if they are boron clusters, are relatively unreactive with B_2.

Experimental Section

Vapor of boron were generated by focusing a XeCl excimer laser (Questek series 2000) beam on the target surface positioned in the vacuum chamber. A large excess of prepurified argon gas containing reactive species such as methane, methyl bromide, or water was supplied from an outside bulb. These were cocondensed on the CaF_2 window for UV–vis absorption experiments. The temperature of the window was kept at 10 K by an Air Products Displex closed-cycle helium refrigerator. The pressure of the reaction chamber was kept at about 1×10^{-5} Torr. Laser pulses continued for about 10 min for UV–vis absorption studies and for 2–3 h for infrared absorption studies.

Prepurified argon (99.995%), ultra-high-purity methane (99.73%), and high-purity methyl bromide (99.5%) were supplied by Matheson Gas Products. Argon and methane were passed through a liquid N_2 trap before being stored in the glass bulb. Methane and methyl bromide were used neat for some infrared absorption studies. For UV–vis studies, to compare the band area in solid argon compared with that in methane or methyl bromide, the reagents were mixed in argon. The concentration of reactive species in argon was 5% or 1% as desired. Water was mixed with argon both for UV–vis and infrared absorption studies. Boron pieces (99.8%) were obtained from Johnson Matthey, Inc. CD_4 (99% D) and CD_3Br (99.5% D) were supplied from ICN Biochemicals, Inc., and D_2O (99.75% D) was obtained from J. T Baker Chemical Co. Water was placed in a small tube that was connected to the main bulb through a Young valve. Before water was mixed with the argon, the water was purified to remove dissolved oxygen as follows: starting with a sample of double distilled and deionized water, a series of pumping–freezing cycles were initiated. An initial sample was placed under vacuum for 20 min. The sample was then frozen and opened to vacuum, being pumped while thawing. This freezing–thawing–pumping cycle was repeated five times for a given sample. The sample was then warmed again to room temperature and partially evaporated under vacuum to ensure complete degassing before mixing.

The UV–vis absorption spectra were taken to compare the area of absorption bands in an Ar matrix and in a reactant/Ar matrix. We used a Cary-14 spectrophotometer with a resolution of 1 nm. Reaction products were investigated by infrared absorption with a DigiLab FTS/40 Fourier transform infrared spectrometer with a resolution of 1 cm^{-1}. For infrared studies, laser-generated boron vapor was cocondensed with methane, methyl bromide, or water on a KBr window in the vacuum chamber at 10 K.

A schematic diagram of our reaction chamber has been published earlier[10] as has more detail on our matrix unit.[11,33]

Acknowledgment. The support of the National Science Foundation is acknowledged with gratitude. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(30) Kurtz, H. A.; Jordon, K. D. *J. Am. Chem. Soc.* **1980**, *102*, 1177–1178.

(31) Hauge, R. H.; Kauffman, J. W.; Margrave, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6005–6011.

(32) Lory, E. R.; Porter, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6301–6302.

(33) Tanaka, Y ; Davis, S. C.; Klabunde, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 1013–1017.