Boron cluster anions containing multiple B_{12} icosahedra

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Abstract

We report a mass spectrometric study of boron cluster anions (B_n^-, $n = 7$–55) produced by laser vaporization from two different types of boron-containing sample rods, one composed of YB_{66} and the other, pure boron. In mass spectra recorded from the YB_{66} sample, we observed a repeating intensity pattern of boron cluster anions having local maxima at $(B_{13}^-)(B_{12})_{0,2,3}$ as well as at B_{26}^-. Similar phenomena were not observed with a pure boron sample. We attribute these observations to the structural differences between the two materials, and in particular to the $(B_{12})(B_{12})_{12}$ super-icosahedral structure of crystalline YB_{66}.
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1. Introduction

In nature, boron exists in both amorphous and crystalline forms, and some of its most common crystal structures are based on icosahedral unit cells of B_{12} [1]. Boron cluster cations, B_n^+, have been studied extensively by Anderson and co-workers [2–6], who generated them by infrared laser ablation of pure boron targets. Over the size range, $n = 3$–20, he observed magic numbers at $n = 5$, 11, and 13 in their mass spectra. Anderson also conducted studies of the reactivity of boron cluster cations with H_2O and with N_2O, measuring their cross sections versus collision energy. In addition, boron cluster cations had been investigated by La Placa et al. [7], who utilized a boron nitride target in laser vaporization experiments to generate B_{2-52}^+.

Boron cluster anions, on the other hand, had only been generated as small sizes, prior to the present work. Koski and co-workers [8] produced B_{1-3}^- from gaseous boron hydrides. Middleton [9] generated high-intensity beams of B_{1-3}^- by sputtering a mixture of boron and silver powders. Also, Ishikawa et al. [10] utilized ion sputtering of boron targets to produce B_{1-3}^-. Recent work by Wang and co-workers [11] formed B_5^- by laser

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vaporization of pure boron and then explored its electronic structure by anion photoelectron spectroscopy.

Many theoretical studies have also been performed on boron clusters. Ray et al. [12] conducted calculations on neutral and cationic boron clusters over the size range, $n = 2–8$. Comparative theoretical studies of B_{13}^+, B_{13}, and B_{13}^- have been conducted by Kawai and Weare [13], Boustani [14], Ricca and Bauschlicher [15], and Fowler and Ugalde [16]. Over the past several years, Boustani et al. [17–21] have conducted an especially extensive computational research program on the geometric and electronic structures of boron clusters. In addition, Gu et al. [22] have explored the possible structures of B_{13}^+; Takeuchi et al. [23] have computed the electron affinity values of small boron clusters; Li and Jin [24] have performed comparative calculations on B_5, B_5^+, and B_5^-; Cao et al. [25] have studied the structures of B_7, B_{10}, and B_{13}; and Boldyrev and co-workers [11] have conducted calculations in support of experiments on B_5^-.

In addition to its pure crystalline forms, a variety of boron-rich crystals, such as HfB_2, LaB_6, and YB_{66}, are also known [26]. In YB_{66}, boron atoms form a $(B_{12})(B_{12})_{12}$ super-icosahedral structure, in which each vertex is occupied by a B_{12} icosahedron. This super-icosahedra structure has been well-characterized crystallographically [27–29], and discrete super-icosahedra units have been directly observed in $YB_{66}(1\,0\,0)$ crystals via scanning tunneling microscopy [30]. In order to explore fundamental properties and possible technological applications for the MB_{66} system, Becker has synthesized YB_{66} and several related materials and then conducted ion implantation studies of mass-analyzed cationic beams onto silicon surfaces. Evidence from his subsequent SIMS and depth profiling analyses of these targets pointed to the presence of B_5 aggregates, and probably to B_{11} and B_{13} clusters, embedded in the silicon.

Here, we report results from our laser vaporization/mass spectrometric study of boron cluster anions, generated from both homogeneous (pure boron) and heterogeneous (YB_{66}) boron target rods.

2. Experimental

While the boron sample rod used in this work was purchased commercially, the YB_{66} rod was provided by Ibadex, L.L.C. In both cases, boron cluster anions were generated in the same laser vaporization source. There, the second harmonic of a Nd:YAG laser (532 nm) was employed to ablate a rotating and translating rod of either pure boron or YB_{66}. The optimal laser power was only $\sim$0.2 mJ/pulse, and a small amount of helium was introduced essentially simultaneously through a pulsed valve. Higher laser powers destroyed the clusters. The resulting cluster anions were then extracted and mass analyzed by a linear, time of flight mass spectrometer. Our apparatus has been described previously [31].

3. Results and discussion

Typical mass spectra from both YB_{66} and pure boron laser vaporized sample rods are presented in Fig. 1. The top panel, Fig. 1a, shows a mass spectrum from YB_{66}, while the bottom panel, Fig. 1b, was taken by ablating a pure boron rod. Up to mass $\sim$220 amu, the two mass spectra are quite similar, both beginning with B_7^- and both displaying local maxima at B_{11}^- and B_{13}^-. As has been shown by Boustani [18], B_7 is an attractive starting size from which larger boron clusters can be built-up.

While both mass spectra are similar at lower masses, at higher masses the YB_{66} mass spectrum exhibits a completely different pattern than does the pure boron mass spectrum. There, the YB_{66} spectrum substantially repeats the main features observed in its lower mass range. Relatively persistent local maxima are seen at $(B_{13}^-)(B_{12})_{0,2,3}$, at B_{26}^-, and at B_{32}^-, and while $B_{13}^-(B_{12})_1$ is not a local maximum per se, it is likely that it is also a magic number species along with $(B_{13}^-)(B_{12})_{0,2,3}$. These patterns at higher masses do not occur in the pure boron mass spectrum. The periodic appearance of B_{12} units in the YB_{66} mass spectrum is presumably due to the ablation of relatively labile B_{12} cages from the $(B_{12})(B_{12})_{12}$ super-icosahedral structure of crystalline YB_{66}. The unusually low laser power
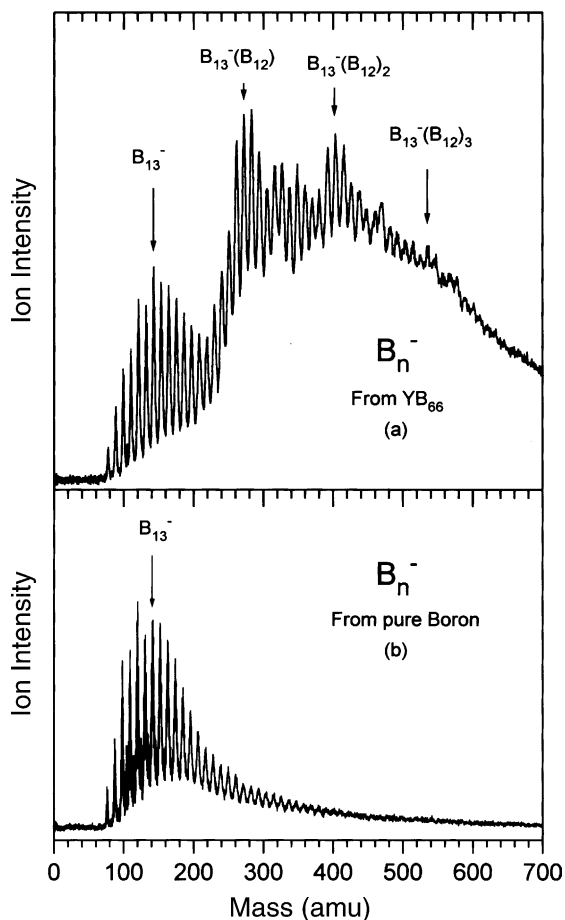
Fig. 1. Mass spectra of boron cluster anions generated by the laser vaporization of: (a) a YB_{66} rod and (b) a pure boron rod.

used in these experiments facilitated gentle desorption of material from the sample surface, minimizing the destruction of structured boron units such as B_{12} icosahedra. Interestingly, no yttrium-containing species were apparent in the YB_{66}-derived mass spectrum below $\sim$200 amu, where we would have been able to mass spectrometrically distinguish them from 'boron-only' species. Thus, the most important empirical implication of this work is that gentle laser ablation of YB_{66} appears to produce copious quantities of B_{12}.

Since the core ion in these clusters is proposed to be B_{13}^-, however, the nature of this species also deserves comment. B_{13}^- might be thought to be analogous to Al_{13}^-, the latter being a jellium-like, 40 valence electron, closed shell, magic number species. Boron, however, does not exhibit the metallic bonding found in aluminum, and such bonding is generally thought to be necessary to qualify for electronic shell model behavior. Also, B_{13}^- does not dominate the mass spectrum of boron cluster anions, as Al_{13}^- often does in the mass spectra of aluminum cluster anions. Thus, we do not expect the shell model to offer a good picture of the electronic structure of B_{13}^-.

In the negative ion mass spectra of YB_{66}, there is a prominence of the stoichiometry, $B_{13}^-(B_{12})_n$ and an abundance of B_{12} units. Even pure boron is based on icosahedral unit cells of B_{12}. Thus, there is the possibility that B_{13}^- may actually be $B^-(B_{12})$, and that $B_{13}^-(B_{12})_n$ may be $B^-(B_{12})_{n+1}$. In fact, it would be tempting to envision B_{12} as dominating this story. To test this $B^-(B_{12})$ hypothesis, we measured the anion photoelectron spectrum of B_{13}^-. The electron affinity of atomic boron is $\sim$0.3 eV [32], while the electron affinity of Al_{13} is $\sim$3.6 eV [33]. If B_{13}^- were actually $B^-(B_{12})$, its total electron binding energy (EBE) would be 0.3 eV plus some relatively small solvation energy due to the stabilizing effect of its B_{12} 'solvent'. Since B_{12} is non-polar, one would expect a stabilization contribution of only a few tenths of an electron volt to give a total EBE of well under 1 eV. Our photoelectron spectrum of B_{13}^-, however, showed signal only at its highest EBE end, with nothing significant below EBE $\sim$2.7 eV, where B_{13}^- or one of its isomers first begins to show photoelectron signal. Thus, we conclude that B_{13}^- is not $B^-(B_{12})$, and therefore that $B_{13}^-(B_{12})_n$ is not $B^-(B_{12})_{n+1}$.

So, if B_{13}^- is not a shell model species and also not $B^-(B_{12})$ either, then why are the main intensity patterns in our mass spectra built upon it? While it is speculative, we offer the following possible explanation. Both B_{13}^- and B_{11}^- display higher intensities than their immediate neighbors in both the pure boron and the YB_{66} mass spectra. This may be due to the fusion of two B_{12} units, followed by their asymmetric dissociation upon electron attachment into $B_{13}^- + B_{11}$ and $B_{11}^- + B_{13}$. This model is supported, in part, by the calculations of Boustani et al. [17], who predicted the fusion of two B_{12} units into a closed tubular B_{24} structure. The

local maxima seen at higher masses in the YB_{66} mass spectra may also be interpreted in a similar fashion. Upon laser ablation, some super-icosahedra may have been broken into smaller $(B_{12})(B_{12})_n$ fragments. Fusion of fragments or fusion of B_{12} units with fragments, followed by asymmetric dissociation upon electron attachment, could lead to $B_{13}^-(B_{12})_n$ and $B_{11}^-(B_{12})_n$. The relative prominence of B_{13}^--based species over B_{11}^--based ones in the mass spectra may be due to B_{13} having a higher electron affinity than B_{11}, as appears from photoelectron measurements to be the case. Also, for whatever reason, our photoelectron measurements (see above) indicate that B_{13}^- is a very stable species with regard to electron loss. The prominence of B_{26}^- may simply be due to an abundance of B_{13}^- and the presence of B_{13}, combining to form the complex, $B_{13}^-(B_{13})$. Also, Boustani et al. [20] have studied the structures of B_{32}, finding nanotubular forms and, to an extent, quasi-planar sheets to be more stable than hollow spherical forms. Thus, our finding that YB_{66} anion abundance (mass) spectra are dominated by $B_{13}^-(B_{12})_n$ species can be explained in terms of a fusion mechanism for forming B_{13}^- and the presence in the laser ablation plume of relatively large quantities of B_{12} cage units.

As a closing thought, one cannot help but notice several similarities between boron clusters and fullerenes. For example, aggregates of B_{12} cages, i.e., $(B_{12})_n$, within YB_{66} crystals are reminiscent of gas-phase clusters made up of multiple C_{60} cages, i.e., $(C_{60})_n$ [34]. Fullerene-based nanotubes and Boustani and Quandt's [19] prediction of quasi-planar boron sheets folding into highly stable nanotubules is another example. Still another related example is the hypothesized existence of $B_{36}N_{24}$, a cage species with a truncated icosahedral geometry analogous to C_{60} [7]. Lastly, there has been a recent report of the growth of crystalline boron nanowires [35].

Acknowledgements

References

[1] R. Naslain, in: V.I. Matkovich (Ed.), Boron and Refractory Borides, Springer, New York, 1977, p. 139.

[2] L. Hanley, J.L. Whitten, S.L. Anderson, J. Phys. Chem. 92 (1988) 5803.

[3] P.A. Hintz, S.A. Ruatta, S.L. Anderson, J. Chem. Phys. 92 (1990) 292.

[4] P.A. Hintz, M.B. Sowa, S.A. Ruatta, S.L. Anderson, J. Chem. Phys. 94 (1991) 6446.

[5] L. Hanley, S.L. Anderson, J. Chem. Phys. 89 (1988) 2848.

[6] S.A. Ruatta, P.A. Hintz, S.L. Anderson, J. Chem. Phys. 94 (1991) 2833.

[7] S.J. La Placa, P.A. Roland, J.J. Wynne, Chem. Phys. Lett. 190 (1992) 163.

[8] D.F. Munro, J.E. Ahnell, W.S. Koski, J. Phys. Chem. 72 (1968) 2682.

[9] R. Middleton, A Negative-Ion Cookbook, Department of Physics, University of Pennsylvania, 1990.

[10] J. Ishikawa, Y. Takeiri, H. Tsuji, T. Taya, T. Takagi, Nucl. Instrum. Methods 232 (1984) 186.

[11] H.-J. Zhai, L.-S. Wang, A. Alexandrova, A.I. Boldyrev, J. Chem. Phys. 117 (2002) 7917.

[12] A.K. Ray, I.A. Howard, K.M. Kanal, Phys. Rev. B 45 (1992) 14247.

[13] R. Kawai, J.H. Weare, Chem. Phys. Lett. 191 (1992) 311.

[14] I. Boustani, Chem. Phys. Lett. 233 (1995) 273.

[15] A. Ricca, C.W. Bauschlicher, J. Chem. Phys. 208 (1996) 233.

[16] J.E. Fowler, J.M. Ugalde, J. Phys. Chem. A 104 (2000) 397.

[17] I. Boustani, A. Quandt, P. Kramer, EuroPhys. Lett. 36 (1996) 583.

[18] I. Boustani, Phys. Rev. B 55 (1997) 16426.

[19] I. Boustani, A. Quandt, EuroPhys. Lett. 39 (1997) 527.

[20] I. Boustani, A. Rubio, J. Alonso, Chem. Phys. Lett. 311 (1999) 21.

[21] I. Boustani, A. Quandt, A. Rubio, J. Solid State Chem. 154 (2000) 269.

[22] F.L. Gu, X. Yang, A.-C. Tang, H. Jiao, v.R. Schleyer, J. Comput. Chem. 19 (1998) 203.

[23] T. Takeuchi, M. Yamamoto, M. Kiuchi, Nucl. Instrum. Methods B 153 (1999).

[24] Q.S. Li, H.W. Jin, J. Phys. Chem. A 106 (2002) 7042.

[25] P.-L. Cao, W. Zhao, B.-X Li, B. Song, X.-Y. Zhou, J. Phys. Condens. Matter 13 (2001) 5065.

[26] C.L. Perkins, Ph.D. Thesis, University of Illinois at Chicago, 1998.

[27] A.U. Seybolt, Trans. Am. Soc. Met. 52 (1960) 971.

[28] I. Higashi, K. Kobayashi, T. Tanaka, Y. Ishizawa, in: Proceedings of the 12th International Symposium on

Boron, Borides, and Related Compounds, Baden, Austria, 1996.

[29] J. Guenster, H. Kawanowa, T. Tanaka, R. Souda, Surf. Sci. 419 (1998) 38.

[30] C.L. Perkins, M. Trenary, T. Tanaka, Phys. Rev. Lett. 77 (1996) 4772.

[31] M. Gerhards, O.C. Thomas, J.M. Nilles, W.-J. Zheng, K.H. Bowen, J. Chem. Phys. 116 (2002) 10247.

[32] D.M. Neumark, K.R. Lykke, T. Andersen, W.C. Lineberger, Phys. Rev. A 32 (1985) 1890.

[33] X. Li, H. Wu, X.-B. Wang, L.-S. Wang, Phys. Rev. Lett. 81 (1998) 1909.

[34] W. Branz, N. Malinowski, H. Schaber, T.P. Martin, Chem. Phys. Lett. 328 (2000) 245.

[35] C.J. Otten, O.R. Lourie, M.-F. Yu, J.M. Cowley, M.J. Dyer, R.S. Ruoff, W.E. Buhro, J. Am. Chem. Soc. 124 (2002) 4564.